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THE NATURE OF SUBSTITUTION REACTIONS IN INORGANIC CHEMISTRY

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Contribution from the Chemistry Department of Northwestern University, Evanston, Illinois

Received October 4, 1958

Substitution reactions in inorganic complexes are discussed in terms of possible dissociation and displacement mechanisms. The nature of the central atom, the nature of the ligands, the nature of the external reagent and the geometry and coordination number of the complex are discussed in terms of their effect on rates and mechanisms. An electrostatic theory is used with emphasis on corrections due to crystal field effects and incomplete screening of the nuclear charges by the outermost electrons.

Substitution reactions in inorganic chemistry include the replacement of one ligand by another in a coördination complex, or one metal ion by another. Following the terminology of Hughes and Ingold developed for organic reactions, these can be called S_N and S_E reactions, respectively. The terms mean nucleophilic and electrophilic substitution, respectively.

$$Y + M—X \longrightarrow M—Y + X \quad S_N \quad (1)$$
$$M' + M—X \longrightarrow M'—X + M \quad S_E \quad (2)$$
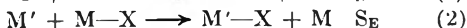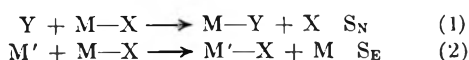
It is convenient to exclude those substitution reactions which involve changes in oxidation number. With this proviso, substitution reactions become generalized acid–base reactions in which the metal ions, or positively charged central atoms in general, play the role of the Lewis acids and the ligands are the bases. Reactions of the proton are a special subdivision of the general category.

While S_E reactions are known, as in the reaction of Hg^{2+} with $Co(NH_3)_5Cl^{2+}$, they are less important than S_N reactions. Two fundamentally different paths for the latter reaction can be visualized, the familiar S_N1 (dissociation) and S_N2 (displacement) mechanisms. In addition several other, rather restricted, mechanisms are likely in certain cases, but the greater part of the effort expended in studying substitution reactions of complexes has been concerned with trying to assign S_N1 or S_N2 labels to them. This is a perilous task at best since unequivocal evidence is hard to obtain. The strongest evidence would undoubtedly be the detection of the intermediate or reduced coördination number, M, which is characteristic of the S_N1 mechanism.

$$M—X \rightleftarrows M + X \quad (3)$$
$$M + Y \longrightarrow M—Y \quad (4)$$
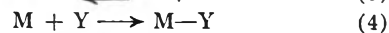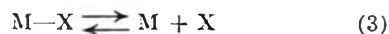
However the nature of M is generally such that it escapes detection by any direct means and subtle evidence for its presence or absence must be judged.

In spite of the difficulties, the division mentioned above has been fruitful and a general discussion of the effect that changing variables can have on the rates and mechanisms, S_N1 or S_N2, of the reactions of complexes can be given. The variables to be considered include the nature of the metal ion, the nature of the ligands, the nature of the external reagent, and the geometry and coördination number of the complex. To proceed, it is necessary to have a theory of energetics and binding in coördination compounds, so that differences in energy between the initial state and possible transition states may be at least roughly estimated. A very simple and remarkably reliable theory is the old electrostatic one with certain recent modifications.[1] This theory is usually reliable for systems containing a positively charged central ion and charged or polar ligands where π-bonding is not an important factor.

For example, the coördinate bond energy is defined as the heat of the following reaction in the vapor state

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 2.

$$ML^{m+}(g) \longrightarrow M^{m+}(g) + L(g) \qquad (5)$$
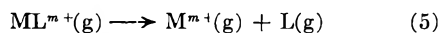
Experimentally coördinate bond energies range from about 15 kcal. per bond in a complex such as $Rb(H_2O)_6^+$ to about 500 kcal. per bond in $TiCl_4$. It is indeed remarkable that in simple cases, such as those given, a point charge electrostatic model will give theoretical bond energies in agreement with the experimental over such a wide range.[1]

In solution one can only determine differences in coördinate bond energy as one ligand is replaced by another, e.g.

$$Co(NH_3)_5Cl^{2+} + H_2O \longrightarrow Co(NH_3)_5H_2O^{3+} + Cl^- \qquad (6)$$

$$Zn(H_2O)_4^{2+} + 4NH_3 \longrightarrow Zn(NH_3)_4^{2+} + 4H_2O \qquad (7)$$

Because of the compensating effect of solvation energies, it turns out that such differences are rarely greater than 5 to 10 kcal. per bond even though the gas phase coördinate bond energies may differ by one hundred kcal. To estimate activation energies for rates of reaction in solution, one must evaluate the total electrostatic energy of the transition state in which an extra ligand has been added in the case of an S_N2 mechanism, or one ligand is partly removed in the case of an S_N1 mechanism.

While exact calculation becomes very difficult because of the irregular geometry and variable nature of the ligands, certain predictions on the basis of an electrostatic model can easily be made as to the relative tendencies toward S_N1 and S_N2 processes as the sizes and charges of the various species are changed. Table I shows these predictions. By any mechanism one may expect a slowing down of the rate as the charge of the leaving group increases and the size diminishes. This is in good agreement with what is found experimentally. Also as the size of the central ion diminishes and its charge increases, it may be expected that the rate of reaction by any mechanism will decrease. This is indeed found to be the case in general.[2] Recent work by Eigen[3] also emphasizes this point since the dependence of the rate of reaction on the size and charge for non-transition metal ions shows up very clearly in a study of very labile systems. It is also significant that rates of substitution reactions of univalent cations have not been measured as yet, rates of reaction of labile divalent cations can be measured by the special techniques used by Eigen and the slower rates of reaction of labile trivalent cations such as Fe^{3+} can be studied by more conventional techniques.[4]

An electrostatic theory using point charges, or uniformly charged spheres, cannot be taken as a complete explanation for the behavior of complex ions, however. For example, the reactivity of iron(III) complexes compared to the inertness of those of cobalt(III) must be explained as must the differences between the various transition metal ions and between the transition and non-transition ions in general.

The necessary correction comes in the crystal field theory recently applied with great success to the various physical and chemical properties of the

TABLE I

EFFECT OF CHARGES AND SIZES ON RATES OF S_N1 AND S_N2 REACTIONS

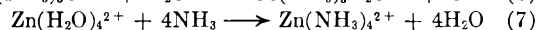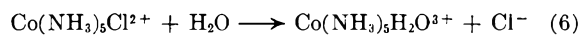|	S_N1 Rate	S_N2 Rate
Increased positive charge of central atom	Decrease	Opposing effects
Increased size of central atom	Increase	Increase
Increased negative charge of entering group	No effect	Decrease
Increased size of entering group	No effect	Decrease
Increased negative charge of leaving group	Decrease	Decrease
Increased size of leaving group	Increase	Opposing effects
Increased negative charge of other ligands	Increase	Opposing effects
Increased size of other ligands	Increase	Decrease

transition metal ions.[5] This theory has to do chiefly with the splitting in energy of the d and f orbitals of a central metal ion produced by the electrostatic field (crystal field) of the attached ligands. The most important result, for present purposes, is to show that the electrons of a central atom with an incomplete shell are not spherically distributed about the central atom. Instead the electrons will preferentially occupy the orbitals which lie furthest away from the ligands. This will lead to an increased stabilization of the complex ion over and above what a simple model based on spherical charge distributions would predict. This stabilization may conveniently be called crystal field stabilization energy (c.f.s.e.).

The great advantage of the crystal field (also called ligand field) theory is that many properties can be correlated and quantitative predictions can be made. For example, the c.f.s.e. can be calculated from measurements of the energy splittings obtained from the visible absorption spectra of complexes.

Figure 1 shows the theoretical d orbital splittings for regular complexes of various geometries. For a filled d shell all orbitals will be occupied equally and there will be no stabilization. The electron distribution will be spherically symmetrical. For incomplete shells of electrons the more stable orbitals will tend to fill first giving rise to c.f.s.e. The energy required to pair electrons in a single orbital must also be taken into account. A balance between this pairing energy and the energy differences between various orbitals will determine the electron distribution and, incidentally, the magnetic properties of the complex.

From spectral data the energy difference (known as $10Dq$) between the lower set of orbitals and the upper set in a regular octahedral complex can be found for various ligands. The order of smaller energy differences (weaker crystal fields) is $CN^- > 1,10$-phenanthroline $> NO_2^- >$ ethylenediamine $> NH_3 > SCN^- > H_2O > F^- > RCO_2^- > OH^-$

(2) Reference 1, Chapter 3.

(3) M. Eigen, Z. Elektrochem., in press; Disc. Faraday Soc., 24, 25 (1957).

(4) W. M. Smith, Proc. Chem. Soc., 207 (July, 1957); J. F. Below, R. E. Connick and C. P. Coppel, J. Am. Chem. Soc., 80, 2961 (1958).

(5) See reference 1, Chapter 2, for a resume of the contribution of various workers to this subject.

> Cl^- > Br^-. This order shows that electrostatic influence alone cannot account for the crystal field splittings. The other major factor is π-bonding (double bonding), both of the metal to ligand and of the ligand to metal type. Systems in which strong π-bonding occurs will not be adequately represented by an electrostatic model. Another complication will be covalent character in the σ-bond (single bond). However in most cases this seems to be smaller than has generally been assumed. The metal carbonyls and the organometallics will be exceptions.

For kinetic purposes we can see easily that a strongly crystal field stabilized system may be sluggish in its reactions. This is because in forming the transition state, by any mechanism, it is highly likely that a fair amount of c.f.s.e. will be lost. This effect is very large for octahedral complexes in the case of d^3, spin coupled d^6 and spin free d^8 systems. As an example, Table II gives the theoretical predictions and the experimental results for the dissociation of a series of phenanthroline complexes of various metal ions. It is assumed that an S_N1 mechanism is operating and that something resembling a square pyramid five-coördinated intermediate is formed. The theory gives the contribution to the activation energy due to crystal field effects. The experimental data give the total activation energy in cases where the rate has been measured and the statement labile where the complex reacts too rapidly for kinetic study. The data refer to the dissociation of the most highly substituted phenanthroline complex formed.

TABLE II

DISSOCIATION OF PHENANTHROLINE COMPLEXES IN WATER

Metal ion	Octa-hedral c.f.s.e.	Square pyramid c.f.s.e.	Experiment, E_a
d^5 Mn^{2+}	0.0Dq	0.0Dq	Labile
d^6 Fe^{2+}	24.0	20.0	32 kcal.[b]
d^7 Co^{2+}	9.1[a]	9.1	21 kcal.[c]
d^8 Ni^{2+}	12.0	10.0	25 kcal.[b]
d^9 Cu^{2+}	9.1[a]	9.1	Labile
d^{10} Zn^{2+}	0.0	0.0	Labile

[a] Distorted octahedron due to Jahn–Teller effect.   [b] F. Basolo, J. C. Hayes and H. Neumann, *J. Am. Chem. Soc.*, **76**, 3807 (1954).   [c] R. G. Wilkins, private communication.

Since the spectral value of Dq for phenanthroline is about 4 kcal., it is seen that there is very good agreement between the theory and the experimental observations. Thus there should be a contribution of $4Dq$ to the activation energy for iron(II) and no crystal field activation energy for cobalt(II). The difference in activation energies of 11 kcal. should then equal $4Dq$. Because of the assumption as to the transition state and because other factors can influence the rates somewhat, perfect agreement cannot be expected. The slow reaction of iron(II) is predicted only for diamagnetic complexes (spin coupled). The slowness of reactions of nickel(II) compared to Mn(II), Co(II), Zn(II), Cu(II) is what is observed for a number of complexes.[6] However the discrimination does depend

(6) Reference 1, Chapter 3.
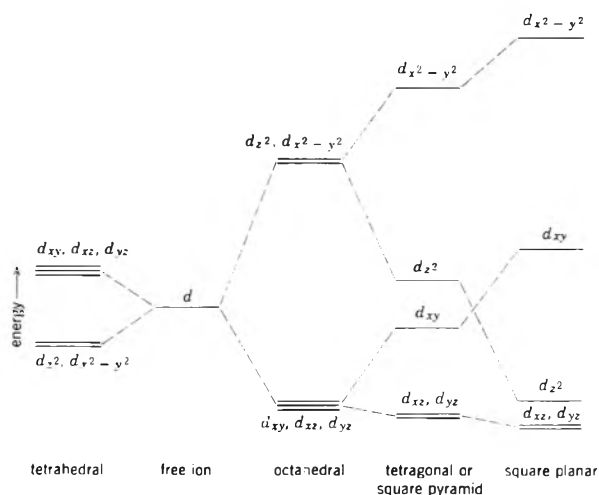
Fig. 1.—Energies of d-orbitals in complexes of various structures.

upon the crystal field strength of the ligands and would be less for ligands such as water.

Another correction must be made to the simple electrostatic theory. This has to do with the obvious fact that charge and size alone will not account for the difference in behavior of all ions even when the ligand field corrections have been applied. Thus gold(I), even though larger in size than potassium ion, forms more stable complexes, its heat of hydration is greater and its ionization potential is greater. The explanation for all of these phenomena seems to be tied up with a single obvious extension of the electrostatic theory. This is the concept of the "effective ionic charge" as opposed to the nominal charge.[7] It is well known classically that for spherical distributions of negative charge, such as the electron clouds surrounding an ion in an S state, the negative potential acting on a test charge located *within* the charge distribution is not given by q/r but is less than this. Here q is the total amount of negative charge and r is the distance of the test charge from the center of the distribution. This means that a test charge located well within the electron cloud of a cation will be subject to a positive potential q'/r where the effective charge, q', is somewhat greater than the nuclear charge minus the number of electrons.

In other words electrons far removed from the nucleus do not completely screen the positive charge of the nucleus. Particularly d electrons, which project far out, are inefficient in screening the nucleus and it is just those ions with a large number of d electrons which display the properties to be expected for an effective charge some 10 to 20% greater than the nominal positive charge. This is particularly true for the third transition series.[8]

A negative charge whether it be an electron or a ligand will be held more firmly by such an ion than by a representative ion of the same nominal charge and crystallographic radius. There is in fact an amazing linear correlation between total ionization potentials of metal ions and their heats of hydra-

(7) Reference 1, Chapter 2.
(8) D. R. Hartree, *Repts. in Prog. in Physics*, **11**, 113 (1946/1947).

tion[9] which indicates the operation of a common effect. Since ionization potentials are directly related to the average electrostatic energy of the electrons which are lost, it seems reasonable to assume that the heat of hydration, the greater part of which is due to coördination of the first layer of water molecules, is also determined by electrostatic forces.[10] In a similar way, the stability of complexes formed by metal ions will reflect the combined effects of effective charge, size and c.f.s.e. Thus a unified electrostatic theory is possible which, while an approximation, is extremely useful.

Let us consider next the effect of coördination number and geometry on the rates and mechanism of substitution reactions, starting with octahedral complexes. The well studied examples of cobalt (III) fall in this category and provide much of the data. The inertness of such systems is a consequence of high charge and small size for the central atom, and very large ligand field effects. The latter provide us immediately with some useful pieces of information. If an S_N2 mechanism operates, it will not involve attack of the incoming reagent on an octahedral edge but on an octahedral face, since the edges are where the six d electrons of the cobalt ion are concentrated. A pentagonal bipyramid seven-coördinated intermediate would involve far too much loss of c.f.s.e. Also if an S_N1 mechanism operates, the five-coördinated intermediate will not usually rearrange to a trigonal bipyramid structure since this involves considerable loss of c.f.s.e. Only in special cases (π-bonding by an electron donating ligand) will such rearrangement become likely. These arguments apply only to systems where ligand fields are important, of course.

It may also be argued that in an octahedral system, the number of groups surrounding the central atom will predispose the complex to react by a dissociation mechanism. That is, the ion becomes too crowded if seven ligands are brought close in. If one group is dissociated, however, in $Co(NH_3)_5Cl^{2+}$, for example, it is unlikely that the species $Co(NH_3)_5^{3+}$ will survive even a few molecular collisions as a square pyramid with one vacant position. Instead the first available molecule or ion that can act as a ligand will fill up the vacant spot. It is unlikely, in fact, that $Co(NH_3)_5^{3+}$ can be created without the expenditure of far more energy than is reasonably available. This creates a visualization of the mechanism of a reaction of such an ion as one in which the Co–Cl bond is lengthened to some critical distance, at which point a solvent molecule slips in to occupy the place of the chloride ion, which is then completely expelled. The assignment of an S_N1 label or an S_N2 label to such a process is not easy even conceptually.

It may be stated that the bulk of the experimental evidence on cobalt(III) and chromium(III) complexes favors an S_N1 mechanism. Referring to Table I, it is found that the effect of changing the charges and sizes of the labile ligand and the inert ligands and the effect of the external reagent is as predicted for an S_N1 mechanism. For example, in water solution it is not possible to find a reagent which appreciably accelerates the release of a labile group. An exception is hydroxide ion for which a special mechanism appears to operate (see below). It is extremely difficult to find any external reagent which will directly replace the chloride ion. This is because the ubiquitous solvent always seems to react first. Eventually, of course, a substitution reaction in which the coördinated solvent dissociates and an adjacent reagent ion takes its place will occur (the anation reaction).

The rate studies by Eigen[3] on the very fast reactions of the sulfate complexes of the divalent cations throw a great deal of light on the anation reaction. These studies are particularly important in that non-transition metal ions and transition metal ions are found to behave in the same way. The mechanism revealed by Eigen's relaxation spectrometry technique for the sulfation of a metal ion shows the prior formation of several loosely associated ion pairs. The key reaction then involves the conversion of an outer sphere complex, or ion pair, into an inner sphere complex

$$Ca(H_2O)_6^{2+}, SO_4^{2-} \rightleftharpoons CaSO_4(H_2O)_5 + H_2O \quad (8)$$

This necessity for the final reaction occurring between the metal ion and a sulfate ion in the second coördination sphere is in excellent agreement with the mechanism outlined above for cobalt complexes. Furthermore the rates depend on the hydration energies of the metal ion in such a way as to suggest that the removal or partial removal of a water molecule is the rate determining step for reaction 8. Also, and very important, the rate constant is nearly the same for a given metal ion and a variety of anions besides sulfate ion. This is strongly suggestive of an essentially S_N1 mechanism for the ion pair (an S_N1 IP mechanism).[11] Of course the over-all rate of anation would also depend upon the concentration of ion-pairs, which might vary considerably from case to case.

It would be presumptuous to believe that a single mechanism is operative for all reactions of octahedral complexes. Even in the case of cobalt(III) it is easy to see that an inert substituent X in a compound such as $Co(en)_2XCl^{2+}$ might play a dominant role in deciding the reaction mechanism. Thus an electron donating X such as NH_2, OH or Cl would favor an S_N1 mechanism, chiefly by π-bonding[12] and an electron attracting X such as NO_2 would favor an S_N2 mechanism. The latter group would operate both by increasing the positive charge on the cobalt atom, which favors a displacement mechanism according to Table I, and also by partly removing the d electrons on the cobalt which provide a powerful hindrance to the approach of an incoming reagent.

(9) "Hydration and Complex Formation of Ions in Solution," C. L. Van Panthaleon Van Eck, Thesis, Leiden, 1958.

(10) Due allowance must be made for crystal field stabilization as was pointed out by L. E. Orgel, J. Chem. Soc., 4756 (1952).

(11) A. W. Adamson, J. Am. Chem. Soc., **80**, 3183 (1958), would call reaction 8 an S_N2 IP process because the entering group exists in the activated complex. This convention does not leave any freedom for discussing the role played by the entering group. Adamson also is at variance with the usual views in stating that the solvent is not present in the transition state in an S_N1 process. It is generally assumed that the solvent is inevitably present, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 355ff.

(12) R. G. Pearson and F. Basolo, J. Am. Chem. Soc., **78**, 4878 (1956).

It may be anticipated that if the charge on the central atom is increased, then S_N2 mechanisms will become more common. This indeed seems to be the case since the octahedral complexes of platinum(IV) can be shown to react by a second-order process which seems to be a displacement mechanism,[13] e.g.

trans-Pt(en)$_2$Cl$_2^{2+}$ + NO$_2^-$ $\longrightarrow$

Pt(en)$_2$NO$_2$Cl^{2+} + Cl$^-$ (9)
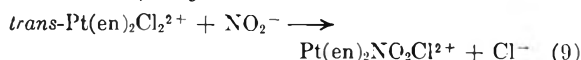
Great care to avoid photolysis and catalysis by platinum(II) must be taken in studying reactions of tetravalent platinum. The difference between the S_N2 reaction of NO$_2^-$ with Pt(en)$_2$Cl$_2^{2+}$ and the S_N1 reaction of H$_2$O with Co(en)$_2$Cl$_2^+$ is clearly shown by the effect of adding methyl groups to ethylenediamine, en, to form the tetramethylethylenediamine. The cobalt complex of this bulky amine reacts extremely rapidly with water because of steric acceleration of dissociation,[14] while the corresponding platinum complex reacts slightly more slowly with NO$_2^-$ than does the en complex.[15]

Surprisingly, hydroxide ion is not a good substitution reagent for platinum(IV) octahedral complexes. Table III shows the rate of replacement of chloride ion by hydroxide ion in trans-Pt(en)$_2$-Cl$_2^{2+}$ as a function of the hydroxide ion concentration. Since the complex ion is known to be a weak acid of pK_a equal to 10.4,[16] the initial reaction must be formation of the amido complex

$$\text{Pt(en)}_2\text{Cl}_2^{2+} + \text{OH}^- \underset{\longleftarrow}{\overset{\text{fast}}{\longrightarrow}}$$

Pt(en)(en—H)Cl$_2^+$ + H$_2$O (10)
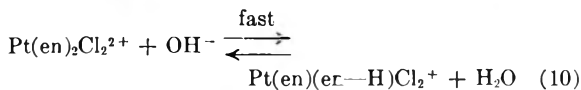
Once sufficient base has been added to make this reaction complete, the rate of reaction is independent of the concentration of hydroxide ion, except for an ionic strength effect. This is the predicted result for an S_N1 CB mechanism[11] in which the amido complex loses chloride ion by a dissociation process, and then reacts with water.

Pt(en)(en—H)Cl$_2^+$ $\longrightarrow$ Pt(en)(en—H)Cl^{2+} + Cl$^-$ (11)
Pt(en)(en—H)Cl^{2+} + H$_2$O $\longrightarrow$ Pt(en)$_2$(OH)Cl^{2+} (12)

This is the postulated mechanism for the corresponding reaction of cobalt(III) ions. The difference in the latter case is that the cobalt complexes are such weak acids ($pK_a > 15$) that complete conversion to the amido form does not occur and the rate continues to increase with increasing OH$^-$ concentration.

Turning to the square planar complexes of coordination number four, the prediction may be made that S_N2 mechanisms are much more probable than for octahedral systems because of the "vacant" positions above and below the square plane. Energetically speaking, it is quite improbable that these positions are truly vacant. Instead solvent molecules, or other molecules or ions, will certainly be in these positions as a great deal of evidence now shows. In the electrostatic theory

(13) F. Basolo, A. F. Messing, P. H. Wilks, R. G. Wilkins and R. G. Pearson, "International Symposium on Coördination Chemistry," Rome, September, 1957.

(14) R. G. Pearson, C. R. Boston and F. Basolo, J. Am. Chem. Soc., 75, 3089 (1953).

(15) M. J. G. Williams, private communication.

(16) A. A. Grinberg and K. I. Gil'dengershel, Izvest. Akad. Nauk S.S.S.R., 479 (1948).

Run	[NaOH], M	[NaClO$_4$], M	$k \times 10^2$, min.$^{-1}$
1	0.05	...	2.3
2	.05	...	2.3[a]
3	.05	0.15	3.0
4	.20	...	3.2
5	.20	0.20	4.1
6	.40	...	4.1

[a] Run 2 contained Pt(en)$_2^{2+}$ to test for possible catalysis. Some reduction to platinum(II) occurs during each run.

square complexes exist only because of strong crystal field effects, since otherwise four ligands around a central atom would arrange themselves tetrahedrally to minimize ligand repulsions. But the crystal field influence of a ligand falls off very rapidly with distance so that it is possible to have four groups close in and two groups further away, a tetragonal arrangement, and still have essentially the c.f.s.e. of a square planar complex (see Fig. 1).

The groups above and below the plane will be labile, however, and may easily be replaced by various reagents in solution. This sets the stage for the displacement of the most labile ligand in the square plane with the incoming reagent in a position to 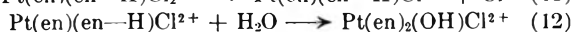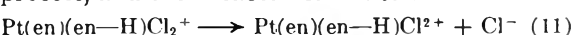help force it out. Various possibilities exist for the detailed process whereby the labile group leaves and the reagent eventually winds up in the plane.[17] Rearrangement to a trigonal bipyramid may occur, but probably only if strong π-bonding (electron accepting) groups are involved, since otherwise there is a very great loss in c.f.s.e.

It is found experimentally that a number of reagents can influence the rate of reaction of planar chloro complexes of platinum(II). The reactions are second order as expected for an S_N2 mechanism. The reagents that are effective are unsaturated ligands such as NO$_2^-$, thiourea, allyl alcohol and R$_3$P. It is of interest that these reagents are high in the "trans effect" series.[16] A number of other reagents such as Cl$^-$ and OH$^-$ are ineffective toward these platinum complexes. These reagents are low in the "trans effect" series. The good nucleophilic character of CH$_2$=CH—CH$_2$OH and the poor nucleophilic character of OH$^-$ in these cases show how dangerous it can be to make predictions as to reactivity based on experiences in organic chemistry. The d electrons of the metal ion account for the differences.

Few kinetic studies have been made on tetrahedral metal ion complexes. This is partly because tetrahedral structures have zero or small c.f.s.e's and are usually so labile that they cannot easily be studied. Tetrahedral carbon is, of course, the prototype for such systems. Here, because of the strong bonding, the rates are slow enough to measure and S_N1 and S_N2 reactions have been found. It may be expected that the larger size of the central atom in metal complexes will cause both S_N1 and S_N2 reactions to go more rapidly. It is more difficult to decide which mechanism will be preferred.

(17) Reference 1, Chapter 4.

The experimental evidence generally favors a displacement process with some evidence that the intermediate of coördination number five may be of moderate stability. This is possible either on the basis of the valence bond theory which emphasizes that empty d orbitals may be used to add a fifth group, or the electrostatic theory which states that five groups can be put around a central atom if it is large enough. However such an arrangement can be shown by calculation to be less stable than an arrangement of either four or six groups, except for special cases.

Chromium(VI), silicon(IV), sulfur(VI), phosphorus(V) and germanium(IV) are some of the tetrahedral systems for which S_N2 like reaction mechanisms have been postulated.[18] There is little information on stereochemistry, but presumably the entering group and the leaving group are 180° from each other as in the case of most reactions of carbon. In these systems, lacking d electrons, hydroxide ion again becomes a good reagent. In the case of the metal carbonyls, $Ni(CO)_4$, and related compounds, the lack of empty d orbitals and the relative weakness of the bonds will favor an S_N1 mechanism.

There is one final topic to mention in connection with the influence of the ligands on the rate of substitution reactions. This is the effect of chelation in the ligand to be substituted. It is clear that chelation will slow down the rate of reaction, since several consecutive events must occur before the ligand is removed. Thus copper(II) ammonia complexes are too labile to study, but copper(II)–ethylenediamine complexes are slow enough to measure by special methods. The dissociation of a tetradentate complex of copper(II), such as N,N'-ethylene-bis-(salicylaldimine) is very slow.

One other feature of the mechanism of reaction of polydentate ligands will cause considerable trouble in interpreting kinetic studies on such systems. If the dissociation of, say, ethylenediaminetetraacetate from a metal ion occurs in several steps, then intervention of other reagents can occur at the intermediate stages of dissociation. Hydrogen ions, or metal ions, can trap amine or carboxylate groups as they are released, and hydroxide ions, or other ligands, can fill up the vacated positions of the metal ion. The experimental results on polydentate ligands do show acceleration by many reagents. It is very difficult to distinguish between the intervention process described above, and a more direct attack of the reagent on the original complex.

Acknowledgment.—The author is grateful to Professor F. Basolo for a long and fruitful col-

(18) Reference 1, Chapter 4; O. H. Johnson and E. A. Schmall, *J. Am. Chem. Soc.*, **80**, 2931 (1958).

laboration, and to the Atomic Energy Commission for financial support.

DISCUSSION

D. H. McDANIEL.—(1) The second ionization potential of the elements (Ca–Zn) certainly represents the energy necessary to remove an electron from an atomic orbital. Does not the linear relationship between the 2nd ionization potential and the crystal field corrected heats of hydration imply the occupancy of these orbitals in the hydrates?
(2) Crystal field theory appears to represent the swing of the pendulum to the other extreme from the valence bond picture. A combination of these views appears desirable.

R. G. PEARSON.—(1) I would say that electrons are held in atoms by electrostatic forces and not by orbitals. The orbital designation is, in addition, a way of describing the angular momentum properties of the electrons.
(2) Perhaps molecular orbital theory, which combines the best features of both crystal field theory and valence bond theory, will turn out to be the most useful in the long run.

D. W. MARGERUM.—(1) The crystal field model for kinetics of tris-phen is very interesting. For tris-phen data, the crystal field model should concern transition from hexa coördination to penta-coördination since kinetics show the breaking of phen goes stepwise.
(2) I thought that for Co(II) phen complexes the slow step did not involve the tris complex but rather the mono complex, if this is so it ought not to be considered in this sequence.

R. G. PEARSON.—The data presented referred to the rate of dissociation of the tris complex. The mono complex also has been studied by R. G. Wilkins at Sheffield.

G. C. BRUMLIK.—Comment on "Hollow π Bonding"—π Bonding without simultaneous sigma bonding. (Example N_2O_4) (N to N Bond).

M. C. R. SYMONS.—Why, in view of the fact that Professor Pearson is prepared to consider π-bonding as contributing in an important manner to the way in which ligands are held to metal ions does he consider that σ-bonding is, in general, unimportant?

R. G. PEARSON.—π-bonding is, of course, primarily a delocalization method of lowering the energy and cannot be explained in terms of simple electrostatics. The σ-bond is, presumably, a mixture of ionic and covalent binding. In most complexes the covalent bonding seems to be a minor contribution. Hence a pure electrostatic model is a very good approximation.

JAMES Y. TONG.—You have shown two graphs, one showed a linear relationship between (crystal field corrected) heat of hydration and atomic number, the other a linear relationship between (crystal field corrected) heat of hydration and ionization potential. This indirectly showed a linear relationship between ionization potential and atomic number for these elements.

R. G. PEARSON.—That is correct.

D. H. BUSCH.—What are relative rates with which chloride, bromide and iodide are displaced by a common reagent from platinum(II) complexes?

R. G. PEARSON.—We do not have data to answer this question; however, Russian investigators have studied rate of halide exchange with $PtCl_4^-$ and PtI_4^-. Unfortunately they have altered two parameters through this series, the nature of the complex and the nature of the entering reagent.

THE PHOTOCHEMICAL AQUATION OF
$Cr(NH_3)_6^{+3}$ AND $Cr(NH_3)_5H_2O^{+3}$

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Studies have been made of the rate of replacement of one of the ammonia molecules in $Cr(NH_3)_6^{+3}$ by a water molecule from the solvent in the presence of light of various wave lengths. The quantum yield for the reaction is 0.32 independent of temperature, concentration, light intensity, and which of the two main ligand field bands is irradiated. Similar results are obtained for the replacement of one NH_3 in $Cr(NH_3)_5H_2O^{+3}$, except that the quantum yield is 0.25. The results are compared with photochemical experiments involving $Cr(H_2O)_6^{+3}$ and a mechanism is proposed involving reaction while the species is in its lowest spin forbidden (doublet) electronic state.

One of the principal reasons for studying the transition elements is the possibility of correlating chemical behavior with electronic configuration. Rather direct experiments for measuring such a correlation are studies of photochemical substitution reactions of transition element complex ions. Many such reactions are hastened by ultraviolet light, and it has been proposed that the mechanism involves an electron transfer from ligand to the central atom.[1] However, in addition to the electron transfer band in the ultraviolet, many transition metal complexes have weak visible absorption bands which are generally ascribed to ligand field transitions within the d subshell of the transition metal atom. It was the purpose of a previous investigation to find whether the weak, visible transitions were photochemically active.[2] The system studied was the exchange of water molecules between $Cr(H_2O)_6^{+3}$ and the solvent, and utilized O^{18} tracer. It was found that the quantum yield was very low (10^{-2} molecule reacted per quantum absorbed at $27°$); was independent of which of the three ligand field absorption bonds was irradiated; decreased strongly with decreasing temperature.

The most likely interpretation of the results of the photochemical aquation of $Cr(H_2O)_6^{+3}$ and its observed lack of fluorescence in solution seemed to be the following scheme. No matter which ligand field band is irradiated, the chromic species converts to the energetically lowest of the principal ligand field bands (spin quartet) from which it can convert further either to a lower lying spin forbidden (doublet) state, or to a high vibrational level of the ground state. To account for the temperature dependence, it was reasoned that the observed reaction resulted from the reaction of molecules while in the spin forbidden state.

Schläfer has reported the position of the doublet state for $Cr(H_2O)_6^{+3}$ as well as that for other chromium complexes.[3] For $Cr(H_2O)_6^{+3}$ the doublet lies but 7 kcal. below the lowest quartet state. Such close spacing would mean that molecules need not remain in the doublet state long enough to react before being thermally activated to the lowest quartet and thence internally converting to the ground state. This could then furnish an explanation for the quite low quantum yield observed and suggests that in the case of a chromium complex in which the spacing of the lowest doublet

and lowest quartet is wider, a larger quantum yield might be found. For $Cr(NH_3)_6^{+3}$ this spacing is over twice as great as for $Cr(H_2O)_6^{+3}$, great enough to show a separate peak in the absorption spectrum, Fig. 1. Otherwise, the spectrum is quite similar to that for $Cr(H_2O)_6^{+3}$,[2] except that the ligand field bands are shifted to shorter wave lengths so that the upper of these is covered by the electron transfer band. The spectrum of $Cr(NH_3)_5H_2O^{+3}$ also was measured and found to consist of an electron transfer band in the ultraviolet with the two ligand field bands at 3600 Å. (ϵ 29.0) and 4840 Å. (ϵ 35.0). In addition the doublet state absorption was present as a separate peak at 6600 Å. (ϵ 0.025).

The present work consists of a study of the aquation of $Cr(NH_3)_6^{+3}$ and $Cr(NH_3)_5H_2O^{+3}$ upon irradiation with light of various wave lengths and at various temperatures.

Experimental

The general procedure used involved irradiating solutions of $Cr(NH_3)_6(ClO_4)_3$ or $Cr(NH_3)_5(H_2O)(NO_3)_3 \cdot NH_4NO_3$ with sufficient $HClO_4$ added to make the solution 0.05 M in acid. Periodically a portion of the solution was removed and its spectrum measured at selected wave lengths with a Beckman DU spectrophotometer. Such measurements allowed identification of reaction products and permitted measurement of reaction rates. Identical solutions were kept in the dark at comparable temperatures and periods of time and showed no detectible aquation reaction. The irradiation set-up and actinometry procedure were essentially the same as those described previously,[2] except that in some runs the General Electric Co. AH-6 mercury arc was used.

The materials used included redistilled water, A. R. perchloric acid, $Cr(NH_3)_6(ClO_4)_3$ prepared as described previously,[4] and $Cr(NH_3)_5H_2O(NO_3)_2 \cdot NH_4NO_3$ prepared by a standard method.[5]

Results

Calculations of both the rate of reaction and the light absorbed by the species of interest were complicated by the facts that the reaction products are colored and the reaction is a stepwise one, i.e., the initial products react further. The spectra of various chromium ammines in the region used to follow reaction rates is shown in Fig. 2. The solid curves were measured by the present authors and are in reasonable agreement with literature values[6]; dashed curves are taken directly from the literature.[6] For following the rate of the first step aqua-

(1) M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **266**, 49 (1951).

(2) R. A. Plane and J. P. Hunt, *J. Am. Chem. Soc.*, **79**, 3343 (1957).

(3) H. L. Schläfer, *Z. physik. Chem.*, *Neue Folge*, **11**, 1/2, 5 (1957).

(4) A. L. Phipps and R. A. Plane, *J. Am. Chem. Soc.*, **79**, 2458 (1957).

(5) T. Moeller, "Inorganic Syntheses," Vol. V, McGraw–Hill Book Co., Inc., New York, N. Y., 1957, p. 132.

(6) R. I. Colmar and F. W. Schwartz, *J. Am. Chem. Soc.*, **54**, 3204 (1932).
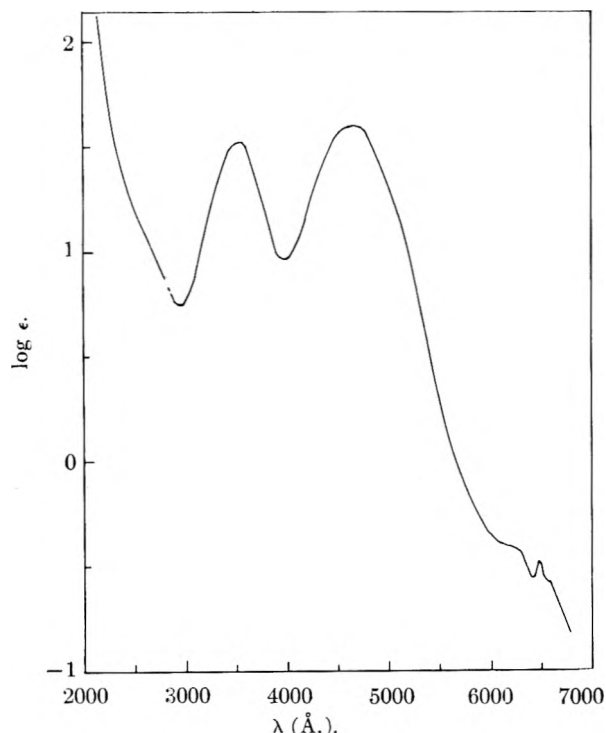
Fig. 1.—Absorption spectrum of $Cr(NH_3)_6^{+3}$.
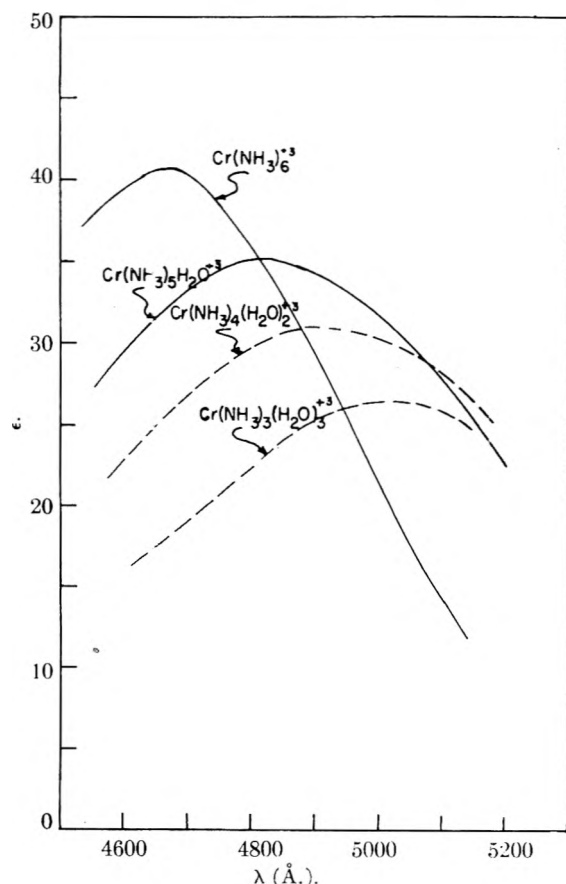
Fig. 2.—Absorption spectra of chrom ammines. (Dashed curves from ref. 6.)

tion of $Cr(NH_3)_6^{+3}$, the most useful wave length was 5040 Å., where the further aquation of $Cr(NH_3)_5H_2O^{+3}$ caused no spectral change. For

studying $Cr(NH_3)_5H_2O^{+3}$, the initial spectral change at 4700 Å. was used.

In order to correct the measured total light absorbed for that fraction absorbed by the reaction product, either a point by point analysis was made or the following simplification was introduced without detectibly affecting the results. Since the absorption spectrum of the product differs only slightly (shifted to longer wave length) from the reactant and since the light used was not monochromatic, the total light absorbed remained constant (within a few per cent.) during the course of an experiment. The light absorbed by the reactant varied, according to Beer's law, during the course of the reaction and caused the system to follow first-order kinetics for the photochemical reaction. The first-order rate combined with initial light intensity can be used to calculate quantum yields.

In Table I are summarized the data for various runs of $Cr(NH_3)_6^{+3}$ to give $Cr(NH_3)_5H_2O^{+3}$, each run representing a series of 4 to 10 points taken at various times during the single experiment. The experiments differ in chromium concentration, temperature, wave length irradiated and light intensity, but each contains $HClO_4$ at 0.05 M. The values of quantum yields reported are probably reliable to 10%.

TABLE I

QUANTUM YIELDS FOR AQUATION OF $Cr(NH_3)_6^{+3}$

Concn. [Cr-$(NH_3)_6^{+3}$]10^3	Wave length irrad., mμ	Temp., °C.	Quanta abs., M/min.	Quantum yield, molecule/ quantum
9.00	320–410	25.0	1.51×10^{-4}	0.34
9.40	320–410	25.0	5.21×10^{-5}	.38
9.39	380–600	25.0	1.49×10^{-4}	.30
9.54	320–600	25.0	5.78×10^{-3}	.29
9.44	320–600	25.0	3.50×10^{-4}	.30
7.75	320–600	25.0	2.84×10^{-3}	.31
7.90	320–600	25.0	5.25×10^{-4}	.31
0.795	320–600	25.0	7.05×10^{-5}	.36
0.769	320–600	0.0	7.40×10^{-6}	.33
7.75	320–600	37.0	2.84×10^{-3}	.31
8.09	254	25.0	5.74×10^{-5}	.49

From the results in the table, it is seen that the quantum yield is independent of light intensity, concentration of complex and temperature. In the first two experiments in the table, a blue filter was used so as to irradiate only the 3520 Å. band; in the third, a yellow filter to irradiate only the 4650 Å. band; in the next seven, both bands were irradiated. Within limits of experimental error, there seems to be no dependence of quantum yield on which absorption band is irradiated. In the last experiment, a nearly monochromatic source was used which irradiated both the highest energy one of the three ligand field bands and to some extent the charge transfer band. The quantum yield is higher by an amount which is probably outside experimental error, but may be due to the charge transfer.

For the reaction of $Cr(NH_3)_5H_2O^{+3}$, to give $Cr(NH_3)_4(H_2O)_2^{+3}$, similar results were obtained for quantum yields of aquation. Values are reported in Table II.

TABLE II

Concn.	Wave length, mμ	Temp., °C.	Quanta abs.	Quantum yield
7.87	320–600	25.0	2.16×10^{-3}	0.27
7.71	320–600	25.0	3.25×10^{-4}	.28
7.87	320–600	0.0	1.87×10^{-3}	.23
7.65	320–600	0.0	3.25×10^{-4}	.24

Qualitatively, it was observed that the aquation reaction did not stop with the formation of $Cr(NH_3)_4(H_2O)_2^{+3}$. However, at some point substitution of H_2O for NH_3 caused quantum yields to decrease markedly since even quite long irradiation failed to produce hexaquo chromium ion.

Discussion

Quantum yields for the photochemical aquation of the chrom ammines are different from those for the substitution of water in hexaquo chromic ion in two important respects. The quantum yields are larger for the ammines and do not show the strong temperature dependence observed in the case of $Cr(H_2O)_6^{+3}$. The first of these differences is to be expected if the low lying doublet state is involved in the photochemical mechanism. Since the spacing of the doublet is relatively close to the lowest quartet state for $Cr(H_2O)_6^{+3}$, thermal energy may serve to return the molecule to the quartet state from which internal conversion can take it to the ground state before chemical reaction occurs. However, in the case of the ammines, the separation is wide enough so that the doublet state will persist until the molecule is deactivated by collisions with solvent molecules.

Schläfer has suggested that the doublet state is important in the photochemical mechanism to store energy until the collision of a solvent molecule makes it available for bringing about chemical reaction. Two different considerations seem to make this mechanism unlikely. In the first place, it would demand that the energy not be conducted away by the solvent more rapidly than the time required for the chemical reaction. Judging from preliminary experiments by Albrecht[7] which measure the rotation of oriented organic molecules in rigid media during internal conversion, it seems that the energy would be conducted away from the reaction center several orders of magnitude more rapidly than reactions of this type should require.[2] Furthermore, such a mechanism could not directly account for the temperature coefficient of quantum yield observed for the $Cr(H_2O)_6^{+3}$ water exchange.

For both the photochemical aquation of the chrom ammines and the water exchange of hexaquo chromic ion, the most probable explanation seems to be that reaction occurs while the species is in the doublet state. That the species in the doublet state should be more reactive than in the ground state, is consistent with the observation that transition element complexes with an available dε orbital undergo substitution reactions more rapidly than those within which only the three dε orbitals are occupied.[8] The importance of the available orbi-

tal compared to the repulsion due to a single electron in a d γ orbital can be seen by comparing the photochemical behavior of $Cr(NH_3)_6^{+3}$ with that of $Co(NH_3)_6^{+3}$. In the latter case, despite the presence of a low-lying spin forbidden (triplet) state,[9] Adamson finds no appreciable photochemical aquation.[10]

The photochemical behavior of the chrom ammines differs from that of $Cr(H_2O)_6^{+3}$, in that the former shows no dependence of quantum yield on temperature. Even if the substitution reaction of the chromium species in the electronic doublet state has an activation energy, as seemed to be true for $Cr(H_2O)_6^{+3}$, it might not be reflected as a temperature dependent quantum yield. This would be true if the activation energy for the reaction equalled the activation energy for return to the lowest quartet state, from which internal conversion could bring about return to the ground state. Perhaps more probable is the possibility that if every molecule which entered the doublet state remained long enough for the substitution reaction to occur even at the lowest temperature measured, the quantum yield would not show temperature dependence. In this case, the lack of temperature dependence and the quantum yield of less than unity would mean that not all the molecules excited were entering the doublet state. Thus the quantum yield would indicate that only about a third of them did so. A direct test of this possibility would be afforded by measuring the quantum yield for the reaction while irradiating directly the doublet transition. Such experiments are being planned.

DISCUSSION

K. B. KRISHNAMURTY.—On the basis of your work on $Cr(H_2O)_6^{+++}$–H_2O photochemical exchange would you predict a similar situation with respect to $V(H_2O)_6^{++}$–H_2O exchange, since V^{++} is isoelectronic with Cr^{+++}?

R. A. PLANE.—It would depend on the spacing of the lowest doublet and first excited quartet state, which in turn need not be the same in the two cases. Therefore, I wouldn't want to predict.

A. W. ADAMSON.—We have been engaged in a study of the photochemical behavior of a number of Co(III) and Cr(III) complexes and find that while the latter generally undergo photo-aquation with a high and nearly wave length independent quantum yield, the former always undergo an oxidation–reduction photo-decomposition if such a reaction is at all possible thermodynamically, and with a quantum-yield generally decreasing with increasing wave length.

An additional type of example of this difference in behavior which we have found very recently concerns the complexes D–$Co(C_2O_4)_3^{-3}$ and D–$Cr(C_2O_4)_3^{-3}$. The former undergoes photo-decomposition with light between 600 and 370 mμ, with less than 1% concomitant racemization. The latter undergoes photo-racemization with high quantum yield for light in this region of wave length but no aquation or photo-decomposition.

I wonder if the speaker would comment on the manner in which he would explain photo-racemization in D–$Cr(C_2O_4)_3^{-3}$ and the lack of it with D–$Co(C_2O_4)_3^{-3}$? We have been able to explain our observation by thinking more in terms of a homolytic splitting of a metal–ligand bond as the first chemically significant stage rather than in terms of the bonding nature of the doublet state.

(7) A. C. Albrecht, Cornell University, private communication.

(8) H. Taube, *Chem. Revs.*, **50**, 69 (1952). See also F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapt. 3.

(9) C. K. Jorgenson, "Quelques Problems de Chimie Minerale," Solvay Institute, Brussels, 1956, p. 364.

(10) A. W. Adamson, *J. Am. Chem. Soc.*, **80**, 3865 (1958).

R. A. PLANE.—For the racemization, as for the aquation of the hexammines of Cr(III) and Co(III), the significant difference may lie in the nature of the lowest spin-forbidden state. In the Cr(III) doublet a $d\epsilon$ orbital can be available to enhance non-oxidation–reduction reactions which is not the case for the lowest Co(III) triplet. Incidentally, for $Cr(C_2O_4)_3{}^{-4}$, Schläfer reports the lowest doublet, the spacing for which (relative to the lowest quartet) is intermediate between that of $Cr(H_2O)_6{}^{+3}$ and $Cr(NH_3)_6{}^{+3}$; so that I would have expected a measurable quantum yield.

R. G. PEARSON.—It is proposed that in Cr^{3+} a doublet state in which two electrons are paired in a single d orbital may be reached easily. This leaves a vacant lower d orbital which may allow for easier substitution reaction, according to the suggestion of H. Taube, by a bimolecular displacement path. However, in the crystal field theory, a vacant lower d orbital allows for easier substitution reaction by either a bimolecular or unimolecular path. This is because ligands in the plane of the vacant orbital can be rearranged without excessive loss of crystal field stabilization energy.

SUBSTITUTION REACTIONS OF OXALATO COMPLEX IONS. I. OXALATE EXCHANGE REACTIONS OF THE TRIS-OXALATO-COBALT(III) AND CHROMIUM(III) COMPLEX ANIONS

BY F. D. GRAZIANO[1] AND G. M. HARRIS

Department of Chemistry, University of Buffalo, Buffalo, N. Y.

A study has been made in aqueous solution of the reactions between the ions $M(C_2O_4)_3{}^{=}$ and carbon-14-labeled $C_2O_4{}^{-}$, where M is Co^{+++} or Cr^{+++}. The exchange was followed by precipitation and radioactive assay of the free oxalate as calcium oxalate monohydrate. Ligand exchange of the cobaltiate proceeds at a rate negligible compared to that of thermal decomposition. The estimated exchange half-time is $\geqslant 130$ hours at $50°$ and pH 8, compared to 6.5 hr. for the decomposition. It is thereby confirmed that the decomposition proceeds by a mechanism not involving appreciably reversible equilibration of C_2O_4 radicals or ions. The chromiate exhibits no sign of dark thermal decomposition during several weeks at $75°$ and $4 < pH < 6$, while ligand exchange shows half-times of less than a day under similar conditions. Outside the quoted acidity limits, decomposition becomes measurable and exchange is accelerated. The rate of exchange is practically independent of (H^+) in the $4 < pH < 6$ range, but becomes first-order in (H^+) at lower pH. The reaction is first order in (complex) and partially first order in (oxalate). A mechanism consistent with cognate studies of the chromiate ion can be fitted to the data. Close analogies with the corresponding rhodiate behavior are observed.

Introduction

Reactions of the tris-oxalato complexes of the transition elements have been the subject of several kinetics investigations. Johnson[2] was the first to attempt to correlate resistance toward ligand substitution with bond-type, utilizing as his criterion the retention of optical activity. Thus, the Al(III), Mn(III) and Fe(III) complexes were classed as ionic, since resolution was impossible, while the readily resolvable Co(III) and Cr(III) analogs were stated to be covalent. Long[3] substantiated this classification in his pioneer isotopic exchange study, using carbon-11-labelled oxalate. Rapid and complete oxalate exchange occurred at room temperature with the non-resolvable complexes. The Co(III) and Cr(III) complexes, however, underwent no observable exchange (at 50 and 35°, respectively) within the short time intervals it was possible to follow the reaction with carbon-11, in spite of the fact that racemization of these compounds is extensive under similar conditions. Clearly, a simple dissociative racemization mechanism is not operative. An analogous lack of relationship between exchange and racemization exists for the complex ion $Coen_2CO_3{}^{+}$, though in this case racemization is by far the slower process.[4]

A study of cobalt electron-transfer exchange between the species $Co(C_2O_4)_3{}^{=}$ and $Co(C_2O_4)_3{}^{-4}$ has

been made by Adamson and co-workers.[5] The thermal decomposition of the former ion complicates the interpretation, but a slow exchange was observed. The mechanism proposed parallels closely that recently suggested for both thermal and photochemical decomposition reactions of the Co(III) species[6] and also provides a path for exchange of its oxalate. However, later work by Stranks and co-workers[7] supports an alternative interpretation which necessitates no appreciable back-exchange of oxalate ion into the $Co(C_2O_4)_3{}^{=}$ group, notwithstanding the measureable electron-transfer process between the Co(II) and Co(III) oxalato complexes under the reaction conditions employed.

The only other study made so far of the $Cr(C_2O_4)_3{}^{=}/C_2O_4{}^{=}$ exchange system is that of Carter, Odell and Llewellyn,[8] who found that H_2O^{18} exchanged oxygens with the Cr(III) complex much faster than exchange occurred with carbon-13-labeled oxalate ion. Further, all twelve oxygen atoms of the complex underwent exchange, suggesting a "one-ended" dissociation of oxalate ion as the initial step in this process

$$Cr(C_2O_4)_3{}^{=} + H_2O \rightleftarrows Cr(C_2O_4)_2OC_2O_3 \cdot H_2O{}^{=}$$
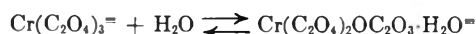
This provides a common mechanism for racemiza-

(1) Work done by F. D. Graziano as part of Ph.D. requirement of University of Buffalo, 1958. Complete report available from University Microfilms, Ann Arbor, Michigan.

(2) C. H. Johnson, *Trans. Faraday Soc.*, **28**, 845 (1932); **31**, 1612 (1935).

(3) F. A. Long, *J. Am. Chem. Soc.*, **61**, 570 (1939); **63**, 1353 (1941).

(4) J. S. Holden and G. M. Harris, *ibid.*, **77**, 1934 (1955).

(5) A. W. Adamson, H. Ogata, J. Grossman and R. Newbury, *J. Inorg. Nuclear Chem.*, **6**, 319 (1958).

(6) T. B. Copestake and N. Uri, *Proc. Roy. Soc. (London)*, **A228**, 252 (1955).

(7) W. Schneider, D. R. Stranks and F. S. Dainton, private communication from D. R. Stranks.

(8) J. H. Carter, A. L. Odell and D. R. Llewellyn, private communication from J. H. Carter.

tion, oxygen exchange and mono-aquation, each of which can be very rapid relative to oxalate exchange.

The present investigation had two purposes: (a) to confirm and supplement the findings of Long[3] relative to the oxalate exchange reaction of Co-$(C_2O_4)_3^≡$ and $Cr(C_2O_4)_3^≡$, making use of the much longer-lived isotope carbon-14, and (b) to carry out detailed kinetic studies of the exchanges, if possible, with a view toward elucidating their exact mechanisms. As will be seen, no measureable oxalate exchange takes place with the Co(III) complex notwithstanding its rapid irreversible thermal decomposition, but the kinetics of the exchange reaction of the Cr(III) species has been amenable to thorough study.

Experimental

A. Preparation, Purification and Analysis of Compounds.—Potassium tris-oxalato cobaltiate was prepared according to standard procedures[9,10] and purified by successive recrystallizations from ice-water. Cobalt was determined by the 1-nitroso-2-naphthol method[11] and oxalate by Sorensen's technique.[9] Calcd. for $K_3Co(C_2O_4)_3 \cdot 3^1/_2H_2O$: Co, 11.71; C_2O_4, 52.46. Found: Co, 11.75 ± 0.06; C_2O_4, 52.51 ± 0.03.

Potassium tris-oxalato chromate was prepared by standard methods[10] and purified in the same way as the cobaltiate. Chromium was determined by the conventional technique[12] and oxalate as before. Calcd. for $K_3Cr(C_2O_4)_3 \cdot 3H_2O$: Cr, 10.67; C_2O_4, 54.19. Found: Cr, 10.92 ± 0.10; C_2O_4, 54.81 ± 0.10.

Commercial C-14-labeled oxalic acid solution of high specific activity was diluted with A. R. grade inactive potassium oxalate solution to give a reagent of activity such that when precipitated as calcium oxalate monohydrate, the thin-sample count was approximately 600 per minute per milligram. CO_2-free water obtained from an Illcoway Research Model Ion Exchanger was used for all solutions.

B. Apparatus and Technique.—The procedure varied little from that used in similar previous studies in these laboratories.[13] Calculated volumes of standard solutions of the complex, inactive neutral or acid oxalate, and radioactive oxalate were separately brought to reaction temperature and the run commenced by mixing. Possible effects of light on both the cobaltiate and the chromiate exchange reactions were avoided by use of foil-wrapped vessels.[14] A "zero time" 2-ml. sample could be withdrawn and the free oxalate precipitated within a few minutes, utilizing a Ca-$Cl_2/NH_4Cl/NH_4OH$ mixture $N/2$ in each constituent as precipitant. After centrifugation and a double washing with water, an alcohol slurry of the calcium oxalate monohydrate was transferred to a weighed nickel-plated steel planchet and dried. When complexed oxalate activity of the cobaltiate was to be determined, the complex was decomposed by heating with alkali in the presence of precipitating agent after separation of free oxalate, and the resulting calcium oxalate, calcium carbonate and cobaltous oxalate decomposition mixture prepared for counting in the usual manner. Thin-end-window counting of solid samples was employed throughout, with corrections applied in the case of the pure calcium oxalate samples for background, self-absorption and self-scattering, as determined in separate experiments. Whenever possible, these samples were

contrived to be in the neighborhood of 0.84 mg./cm.² This corresponds to the maximum in the empirical self-absorption/self-scattering correction curve under the experimental conditions, thus tending to minimize errors in the application of the correction.[15] In absence of decomposition processes, self-buffering of the reaction solutions was provided by the oxalate–acid oxalate mixture. pH measurements were made after rapid cooling of the sample of reactant to room temperature, employing a Beckman Model G pH-meter.[16] Spectrophotometry was done on Beckman DU or DK-2 instruments. Half-times of exchange were determined from the conventional McKay plots, when applicable, and the results expressed in terms of the rate of exchange R in the usual manner,[13] neglecting possible isotope effects.

Results and Discussion

A. The Tris-oxalato-cobalt(III) Ion.—The thermal instability of this complex rendered it impossible to carry out conventional exchange studies with free oxalate ion. Preliminary experiments based on spectrophotometric determinations showed that at 50° the decomposition proceeded at the rate predicted by Copstake and Uri's results,[6] and that it was independent of the concentration of added free oxalate in the acidity range of the present study ($6 < $ pH $ < 9$). The change of pH with time of a typical reaction mixture ((complex) = 0.03505 M; (oxalate) = 0.01460 M) at 50° was followed. There was a drop in pH within the first hour from 7.0 to 6.1, then a steady rise to 8.7 at complete decomposition after many hours, corresponding to the expected pH of pure $K_2C_2O_4$ at the concentration achieved. The initial drop in pH can no doubt be ascribed to the setting up of the CO_2/H_2O equilibrium as decomposition commences. The exchange investigation was made by determining the change in activity of both complexed and uncomplexed oxalate at various stages during the thermal decomposition process. The results of such an experiment are presented in Table I.

It is clear from these data that no appreciable back exchange of oxalate ion into the complex occurs during a time interval long enough to allow extensive decomposition of the complex (about 33% in this case). The constant activity of the precipitated residual material (last column of Table I) can reasonably be ascribed to separation contamination.[17] It may therefore be concluded that the decomposition does not provide a ready path for incorporation of labeled oxalate ion into the unde-

(9) S. P. L. Sorensen, Z. anorg. Chem., **11**, 1 (1899).

(10) "Inorganic Syntheses," Vol. I, 1st Edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 37.

(11) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," 2nd Edition, John Wiley and Sons, New York, N. Y., 1953, p. 417–22.

(12) H. H. Willard, N. H. Furman and C. E. Bricker, "Elements of Quantitative Analysis," 4th Ed., D. Van Nostrand Co., New York, N. Y., 1956, p. 250–251.

(13) J. E. Boyle and G. M. Harris, J. Am. Chem. Soc., **80**, 782 (1958).

(14) Detailed studies have shown the rapid photo-decomposition of the tris-oxalato complexes of Co(III) (ref. 6) and Fe(III) (C. A. Parker, Proc. Roy. Soc. (London), **A220**, 104 (1952); **A235**, 518 (1956)).

(15) The curve has a rather flat maximum (see G. B. Cook and J. F. Duncan, "Modern Radiochemical Practice," The Clarendon Press, Oxford, England, 1952, p. 236) so that the correction is nearly constant over a range of sample thicknesses on either side of this maximum.

(16) No attempt has been made to apply temperature corrections to the pH data in the interpretation of the exchange kinetics. It has been simply assumed that the correction factors for various hydrogen ion concentrations at a given elevated temperature are roughly equal. Thus they affect only the absolute values of (H^+) at that temperature, not the relative values.

(17) It is seen that in terms of activity per milligram of the two precipitates, the contamination does not exceed 4%, nor does the total amount of this activity change appreciably from sample to sample. The figures of column 4 of the Table indicate complete retention of the oxalate activity in the free oxalate portion throughout the 7.5 hour period, within the experimental error. With the latter taken to be as great as 4%, corresponding to a maximum unobservable exchange during the period of the experiment, the oxalate exchange half-time cannot be less than about 130 hours. The half-time of decomposition under these same conditions is close to 6.5 hours.[6]

TABLE I

DETERMINATION OF ACTIVITIES OF FREE AND COMPLEXED OXALATE DURING DECOMPOSITION OF $K_2Co(C_2O_4)_3$ AT 50°

Initial conditions: (complex) = 0.03505 M; (oxalate) = 0.01460 M; pH 7.0

Time, min.	Sample wt. (mg.)		Activity, ct./min.	
	Free C_2O_4[a]	Complexed C_2O_4[b]	Cor. total free C_2O_4	Per mg. complexed C_2O_4[d]
0	3.78	34.88	822	3.9
30	4.92	...[c]	846	...[c]
60	5.40	34.30	850	3.3
90	6.06	36.03	844	2.9
120	6.66	32.91	845	2.8
180	7.81	32.77	848	2.9
240	8.80	30.39	842	2.9
300	9.74	29.41	850	3.2
360	10.59	26.89	846	2.9
420	11.36	24.65	846	3.1
450	11.76	28.68	843	3.0

[a] Pure calcium oxalate monohydrate samples. [b] Residual complex decomposition mixture samples. [c] Sample spoiled. [d] Uncorrected for self-absorption or scattering.

composed complex, in confirmation of similar findings by other workers.[7]

The mechanism proposed for the thermal decomposition[6] has as the initial rate-determining step the reaction

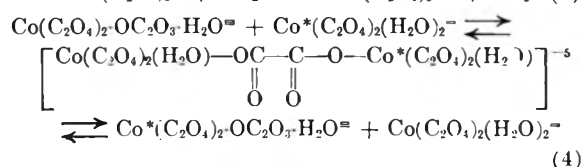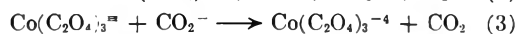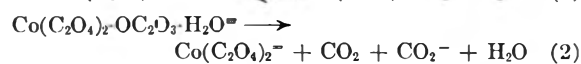$$Co(C_2H_4)_3^= + H_2O \longrightarrow HCo(C_2O_4)_2^- + C_2O_4^- + OH^-$$

This reaction would have to be essentially unidirectional to conform with our data. Stranks, et al.,[7] who based their argument on the results of a study of the radioactivity of the CO_2 liberated from the decomposing exchange system, prefer the following unidirectional initial reaction

$$Co(C_2O_4)_3^= \longrightarrow Co(C_2O_4)_2^- + CO_2 + CO_2^-$$

This reaction would be consistent with the observed non-exchange of oxalate. The reversible initial process

$$Co(C_2O_4)_3^= \rightleftarrows Co(C_2O_4)_2^- + C_2O_4^-$$

proposed by Adamson, et al.,[5] for the mechanism of cobalt electron exchange in the system Co^{60} (II) oxalate/$Co(C_2O_4)_3^=$ would be tenable only if the reverse step is slow, since rapid electron exchange between $C_2O_4^-$ and $C_2O_4^=$ is very likely. In a re-investigation of the cobalt exchange, Stranks, et al.,[7] find favor for a path involving a Co(II)/Co(III) binuclear oxalato complex intermediate. Their scheme to account for the various known reactions of the $Co(C_2O_4)_3^=$ ion is

$$Co(C_2O_4)_3^= + H_2O \rightleftarrows Co(C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^= \quad (1)$$

$$Co(C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^= \longrightarrow$$
$$Co(C_2O_4)_2^- + CO_2 + CO_2^- + H_2O \quad (2)$$

$$Co(C_2O_4)_3^= + CO_2^- \longrightarrow Co(C_2O_4)_3^{-4} + CO_2 \quad (3)$$

$$Co(C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^= + Co^*(C_2O_4)_2(H_2O)_2^- \rightleftarrows$$

$$\left[Co(C_2O_4)_2(H_2O) - OC - C - O - Co^*(C_2O_4)_2(H_2O) \atop \| \quad \| \atop O \quad O \right]^{-5}$$

$$\rightleftarrows Co^*(C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^= + Co(C_2O_4)_2(H_2O)_2^- \quad (4)$$
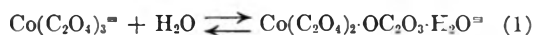
Reaction 1 is proposed by analogy with the results of Llewellyn, et al.,[8] on the chromate; it allows for rapid monoaquation, oxygen exchange and race-

mization of the cobaltiate independent of other exchange processes. Reactions 1, 2 and 3 provide the unidirectional path for the decomposition by internal electron transfer, and reactions 1 and 4 allow for the cobalt electron exchange process. Our results are consistent with this scheme, provided exchange of oxalate with the $Co(C_2O_4)_2 \cdot (H_2O)_2^-$ ion is quite slow, as seems likely in view of its relatively high stability.[7]

B. The Tris-oxalato-chromium(III) Ion.—The stability of aqueous solutions of $K_3Cr(C_2O_4)_3$ was tested in two ways. First, the change in pH on long standing at the usual reaction temperature (75°) was determined. It was found that in the range 4 < pH < 7, the acidity was constant for many hours. A slight decrease was detectable after one day, a period corresponding to several half-times of exchange for most runs. Similarly, the ultraviolet and visible spectra of the solution remained practically constant under the same conditions.

In more acidic solutions, however, appreciable changes in both pH and spectrum were observed, as illustrated in Table II.

TABLE II

CHANGE OF pH AND ABSORBANCY OF ACIDIFIED AQUEOUS SOLUTION OF $K_3Cr(C_2O_4)_3$ ON HEATING AT 75°

Time (hr.)	0	4.25	18	44	90
pH	2.5	2.7	2.7	2.7	2.7
A. (422 mμ)	0.51	0.45	0.45	0.45	0.44
A. (573 mμ)	0.40	0.35	0.35	0.35	0.34

$$(A - \log I_0/I)$$

It is apparent that an equilibrium is rapidly attained, followed by no further re-adjustments. Other experiments showed that this equilibrium state was established within an hour, and that it involved liberation of a small amount of oxalate from the complex. The significance of this will be referred to later. In any case, since the attainment of the chemical equilibrium occurred within a time which was quite short relative to the exchange half-time, measurements of the rate of exchange were not subject to corrections due to this pre-equilibration. This fact was attested to by the complete linearity of the McKay plots of runs made at low pH after a short initial period of slight curvature.

When the pH exceeded 7, another type of decomposition process commenced, which eventually involved precipitation of $Cr(OH)_3$. A thorough study of the reactions in this region has not been made, except to note the accelerating influence of high pH on the exchange rate.

Experiments were carried out at three temperatures (65, 75 and 85°) under various reactant concentration conditions. The most comprehensive set of data was obtained at 75°, and the results of the various exchange runs appear as points in Figs. 1, 2 and 3. Entirely analogous curves can be plotted from the data at 65 and 85°, which are summarized in Table III. A partial study of the effect of ionic strength[18] on the exchange has been made, as illustrated in Figs. 1 and 4.

(18) All ionic strength adjustments were made by addition of the requisite amount of A. R. sodium perchlorate.

TABLE III

RATE OF EXCHANGE IN THE $Cr(C_2O_4)_3^=/C_2^{14}O_4^=$ SYSTEM[a]

(Complex), $M \times 10^2$	(Free oxalate), $M \times 10^3$	pH (at R.T.)	R, moles l.$^{-1}$ sec.$^{-1}$
		A. Runs at 65°	
5.27	3.95	4.57	6.6×10^{-9}
5.27	3.95	1.88	7.2×10^{-8}
5.27	7.90	4.57	6.9×10^{-9}
5.27	7.90	1.86	8.2×10^{-8}
5.27	15.81	4.56	7.1×10^{-9}
5.27	15.81	1.86	10.0×10^{-8}
15.81	15.81	4.48	1.9×10^{-8}
15.81	15.81	1.92	3.0×10^{-7}
31.62	15.81	4.49	4.0×10^{-8}
31.62	15.81	1.94	5.9×10^{-7}
47.43	15.81	4.49	5.6×10^{-8}
47.43	15.81	1.98	9.0×10^{-7}
		B. Runs at 85°	
5.27	3.95	4.64	3.6×10^{-8}
5.27	3.95	1.98	2.6×10^{-7}
5.27	7.90	4.64	4.0×10^{-8}
5.27	7.90	1.95	4.1×10^{-7}
5.27	15.81	4.55	4.3×10^{-8}
5.27	15.81	1.94	7.4×10^{-7}
15.81	15.81	4.52	1.2×10^{-7}
15.81	15.81	2.04	1.5×10^{-6}
31.62	15.81	4.52	2.4×10^{-7}
31.62	15.81	2.04	3.1×10^{-6}
47.43	15.81	4.50	3.7×10^{-7}
47.43	15.81	2.07	4.7×10^{-6}

[a] Ionic strength = 0.300 in all runs.

It is apparent that the reaction is first order in (complex) under all conditions. However, the dependence of the rate in the range $2 < pH < 6$ on (free oxalate) and (H^+) is of mixed order, partially zero and partially first.[19] These data can be fitted by a rate law of the form

$$R = (complex)[k_a + k_b(oxalate) + k_c(H^+) + k_d(H^+)(oxalate)]$$

The curves shown in Figs. 1, 2 and 3 are calculated from this law, using the following "best-fit" rate-constant values

$$k_a = 1.1 \times 10^{-6} \text{ sec.}^{-1}$$
$$k_b = 1.1 \times 10^{-1} \text{ l. mol}^{-1} \text{ sec.}^{-1}$$
$$k_c = 1.8 \times 10^{-3} \text{ l. mole}^1 \text{ sec.}^{-1}$$
$$k_d = 2.6 \times 10^{-1} \text{ l.}^2 \text{ mole}^2 \text{ sec.}^{-1}$$

A mechanism of exchange which is consistent in the range $2 < pH < 4$ with this rate law is

$$Cr(C_2O_4)_3^= + H_2O \rightleftharpoons Cr(C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^= \quad K_1 \quad (1)$$

$$Cr(C_2O_4)_3^= + H_3O^+ \rightleftharpoons$$
$$Cr(C_2O_4)_2 \cdot OC_2O_3H \cdot H_2O^- \quad K_2 \quad (2)$$

$$Cr(C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^= + H_2O \rightleftharpoons$$
$$Cr(C_2O_4)_2(H_2O)_2^- + C_2O_4^- \quad k_3, k_{-3} \quad (3)$$

$$Cr(C_2O_4)_2 \cdot OC_2O_3H \cdot H_2O^- + H_2O \rightleftharpoons$$
$$Cr(C_2O_4)_2(H_2O)_2^- - HC_2O_4^- \quad k_4, k_{-4} \quad (4)$$

$$Cr(C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^= + HC_2^*O_4^- \rightleftharpoons$$
$$Cr(C_2O_4)_2 \cdot OC_2^*O_3 \cdot H_2O^= - HC_2O_4^- \quad k_5, k_{-5} \quad (5)$$

$$Cr(C_2O_4)_2 \cdot OC_2O_3H \cdot H_2O^- + HC_2^*C_4^- \rightleftharpoons$$
$$Cr(C_2O_4)_2 \cdot OC_2^*O_3H \cdot H_2O^- + HC_2O_4^- \quad k_6, k_{-6} \quad (6)$$
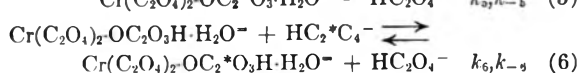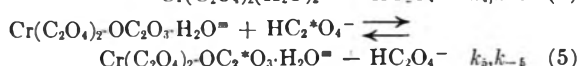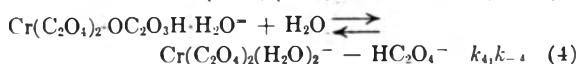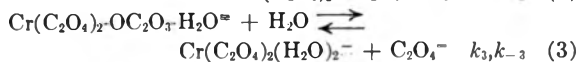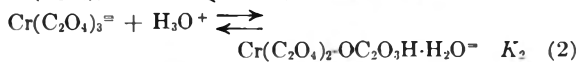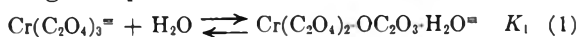
(19) The apparent acceleration of the exchange above pH 6 must be due to new processes dependent on (OH$^-$). Insufficient study of this effect has been made to warrant further discussion at this time.
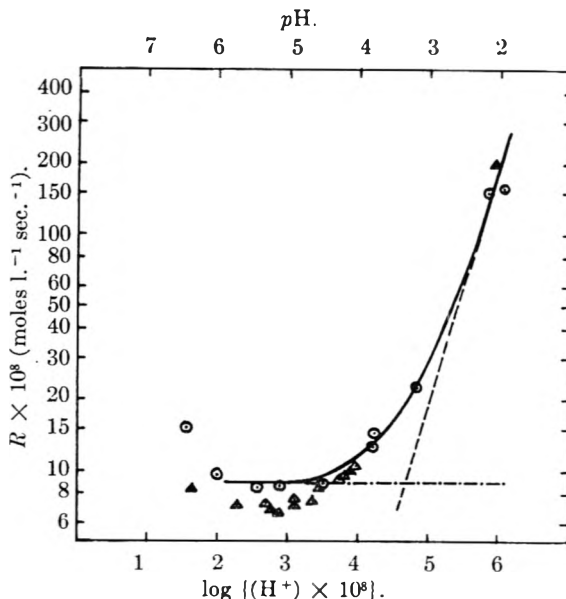
Fig. 1.—Effect of acidity on rate of exchange: (complex) = 0.03162 M; (oxalate) = 0.01581 M; temperature, 75°; – – – –, calcd. acid dependent rate ($\mu = 0.3$); –·–·–·, calcd. acid independent rate ($\mu = 0.3$); X, $\mu = 0.197$; O, $\mu = 0.300$.
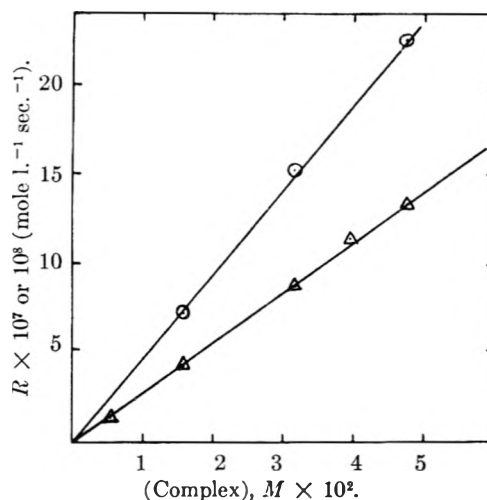
Fig. 2.—Dependence of rate of exchange on (complex); (oxalate) = 0.01581 M; temperature, 75°; $\mu = 0.300$; O, $R \times 10^7$ (pH 2.15); $\triangle$, $R \times 10^8$ (pH 4.45).

Assuming that each complex species other than $Cr(C_2O_4)_3^=$ is present in relatively small concentration,[20] and that equilibria 1 and 2 are rapidly achieved and continuously maintained, it is seen that $k_a = K_1k_3(H_2O)^2$, $k_b = K_1k_5(H_2O)$, $k_c = K_2k_4(H_2O)^2$ and $k_d = K_2k_6(H_2O)$. Reactions 1 and 2 permit the observed rapid racemization[2] and oxygen exchange[8] of the complex, and the acid catalysis of these processes.[8] Reactions 2 and 4 account for the chemical equilibration in acid solution with slight liberation of oxalate, as mentioned above. The ionic strength data of Fig. 4 enable some

(20) Support for this assumption comes from work of R. E. Hamm and R. H. Perkins (J. Am. Chem. Soc., 77, 2083 (1955)), who showed that the reaction $Cr(C_2O_4)_3(H_2O)_2^- + C_2O_4^- \rightarrow Cr(C_2O_4)_3^= + 2H_2O$ was rapid and apparently complete at 40°. The reaction is independent of (H$^+$) in the range 4.0 < pH < 9.3 and also of (oxalate). This latter feature they explain by the suggestion that chelation with water-elimination (reverse of reaction 1) is rate determining.
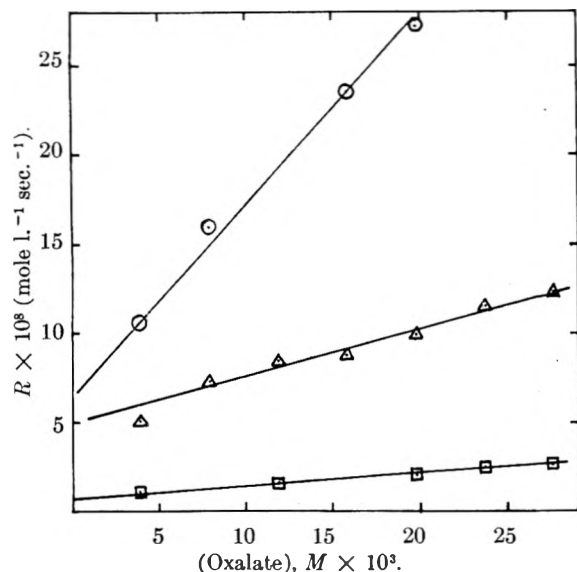
Fig. 3.—Dependence of rate of exchange on (free oxalate): (complex) = 0.00527 M; temperature, 75°; μ = 0.300; O, pH 2.15; △, pH 7.13; □, pH 4.62.
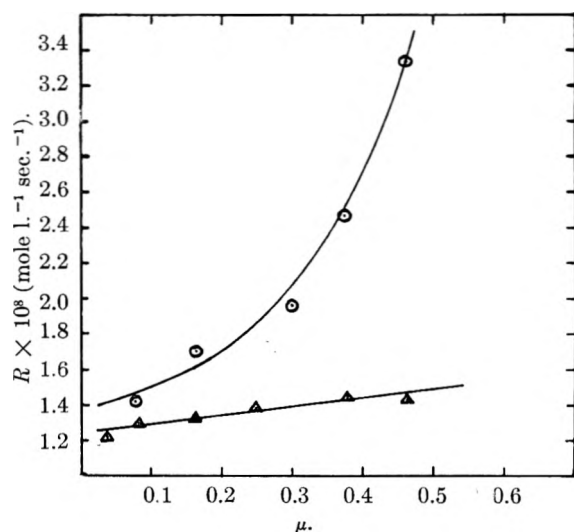
Fig. 4.—Dependence of rate of exchange on ionic strength at pH 4.2: top curve, (oxalate) = 0.01976 N; bottom curve, (oxalate) = 0.00395 M.

Fig. 5.—Variation of rate constants of exchange with ionic strength at pH 4.2: O, $k_b \times 10^5$; △, $k_a \times 10^7$.
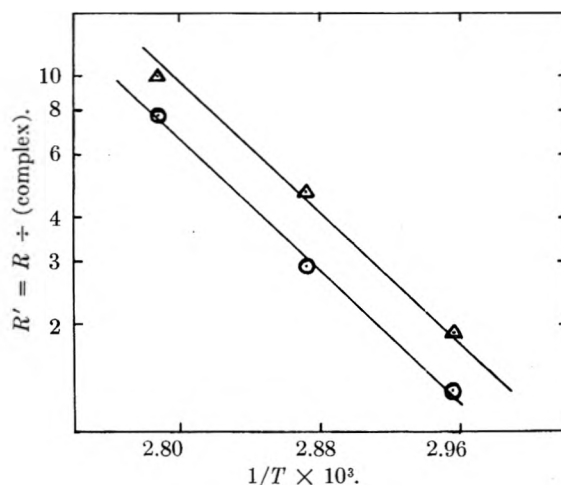
Fig. 6.—Arrhenius plot of rate data: right curve, $R' \times 10^5$ at $pH \sim 2$; left curve, $R' \times 10^6$ at $pH \sim 4.5$.

conclusions concerning the mechanism of the reaction in the middle pH range ($4 < pH < 6$). Since the (H^+) is very low in these runs, the empirical rate law is approximated by R = (complex)$[k_a + k_b(\text{oxalate})]$. The two sets of data at differing (oxalate) enable calculation of k_a and k_b at the various ionic strength levels. The logarithms of these calculated k's have been plotted *vs.* $\sqrt{\mu}$ as shown in Fig. 5. It is clear that k_a relates to an ion-molecule reaction as called for by our mechanism, since it is practically independent of μ. On the other hand, k_b is strongly dependent on μ. The slope of the curve is positive and roughly three units in magnitude, showing that the reaction is between charged species of the same sign, one of which at least must be multiply charged.[21] The

(21) Quantitative application of the Brönsted–Bjerrum theory cannot be made for large ions of diffuse charge at high ionic strength (see A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John

reactions which must be involved are (5) above and the similar process

$$\text{Cr}(C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^= + C_2{}^*O_4{}^= \rightleftarrows$$
$$\text{Cr}(C_2O_4)_2OC_2{}^*O_3 \cdot H_2O^= + C_2O_4{}^- \quad (7)$$
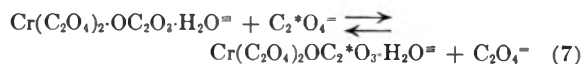
If the rates of reactions 5 and 7 are not too greatly different, the lack of dependence of the exchange rate on (H^+) is fully understandable in the range $4 < pH < 6$, since the only effect of pH change here will be to change the ratio of $HC_2O_4{}^-$ to $C_2O_4{}^=$.[22]

Wiley and Sons, Inc., New York, N. Y., Ch. 7). However, qualitative conclusions such as those drawn here undoubtedly are valid.

(22) Acceleration of the exchange rate with increasing pH takes place at pH's greater than 6, but the effect is complicated by decomposition and diol formation processes. It appears that OH^- ion-promoted reactions become prominent at this end of the pH spectrum, but the results obtained are insufficient to warrant firm conclusions.

It has been found impossible to make a complete interpretation of the temperature dependence data, since information is not available whereby room temperature pH's of oxalate buffer solutions can be translated into true hydrogen-ion concentration values at temperatures up to 35°. All the results obtained with (oxalate) = $15.81 \times 10^{-3} M$ at pH's close to 2 and 4.5 have been plotted as shown in Fig. 6. Use of the parameter $R' = R \div$ (complex) enables inclusion in one plot of data at several values of (complex), and each point on the graph is thus an average of four runs. The apparent activation energies at both pH 2 and pH 4.5 are close to 20 kcal./mole. The energy barriers for either non- or acid-catalyzed exchanges appear to be nearly identical, as might be expected from the nature of the mechanism.

The kinetics of the chromiate exchange reaction is closely analogous to that of the rhodiate,[23] the main difference being the much slower rate of the latter. Also, the $RH(C_2O_4)_3^=$ ion shows no tendency to undergo decomposition by internal electron exchange, again in agreement with the Cr(III) complex behavior and in direct contrast with that of the Co(III) analog. It is apparent that even the partially aquated $Co(C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^=$ complex is reduced readily, while neither Cr(III) and Rh(III) exhibit nearly as strong oxidizing power even in their completely aquated forms. Probably the ion $Co(C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^=$ is readily activated to the paramagnetic sp^3d^2 configuration, as has been proposed for $Co(H_2O)_6^{+++}$ to explain its rapid exchange with labeled water.[24] Such activation would be expected to facilitate greatly internal electron transfer from $C_2O_4^=$ to Co^{+++} with subsequent breakdown of the complex, since vacant 3d orbitals would occur in the activated form.[25] On the other hand, $Cr(H_2O)_6^{+++}$ is known to be resistant to water exchange,[26] inferring a rather larger excitation energy for "outer" complex formation in this case. This larger energy gap between the d^2sp^3 and sp^3d^2 configurations of Cr(III) as compared to Co(III) is to be expected, since no "forced" pairing of d electrons is necessary for the former to assume the d^2sp^3 state, as is required for Co(III). With Rh(III), the energy gap between the "inner" and "outer" complex forms would be expanded over that of Co(III) because of greater difference between 4d and 5d levels as compared to between 3d and 4d levels. One would therefore expect water

(23) D. Barton and G. M. Harris, to be published.

(24) H. Taube, et al., J. Chem. Phys., **18**, 759 (1950); J. Am. Chem. Soc., **73**, 4028 (1951).

(25) It is of interest that the ion $Coen_2C_2O_4^+$ shows *no* tendency to decompose during prolonged periods in neutral or acidic aqueous solution at 75° (S. Sheel and G. M. Harris, unpublished work). However, in basic solution, oxalate substitution (but *not* internal reduction of cobaltic ion) becomes appreciable, with direct formation of the $Coen_2 \cdot H_2O \cdot OH^{++}$ ion. The apparent inability of this ion to become excited to the reactive sp^3d^2 state is probably related to differences in basic strengths of en and OH^- as compared to $C_2O_4^=$.

(26) H. Taube, et al., J. Chem. Phys., **18**, 757 (1950); **19**, 602 (1951); THIS JOURNAL, **56**, 33 (1952); J. Am. Chem. Soc., **76**, 5960 (1954).

exchange with $Rh(H_2O)_6^{+++}$ to be slow, as has also been predicted by Taube.[27]

DISCUSSION

J. C. BAILAR, JR.—The assumption that a ring opens without loss of oxalate explains the fact that all of the oxygen atoms are exchangeable. However, the chelate effect is lost when the ring opens, and it might be expected that the oxalate would escape. (This would cause exchange of oxalate.) Racemization can take place without any loosening of the groups, but if we assume that it is due to "dissociation" (to $Cr(C_2O_4)_2OC_2O_3 \cdot OH_2^=$) we should also assume opening of a second ring to form $Cr(C_2O_4)(OC_2O_3)_2(OH_2)_2^=$. If this is so, oxalate exchange should be much faster than racemization. This is contrary to experiment. I am inclined to the belief that racemization does not depend, in this case, on the opening of the ring.

G. M. HARRIS.—It is not necessary that the singly-bonded oxalates be very much more rapidly exchangeable than chelated ones. For example, the carbonato complex $Co(NH_3)_5CO_3^+$ exchanges its carbonate at a readily measurable rate (D. R. Stranks, Trans. Faraday Soc., **51**, 505 (1955)), only a few times more rapidly than does the corresponding chelated carbonato, $Co(NH_3)_4CO_3^+$ (G. M. Harris and D. R. Stranks, ibid., **48**, 137 (1952)). The acid catalysis of the racemization of the chromioxalate ion is also most readily interpreted in terms of the ring-opening mechanism suggested.

A. W. ADAMSON.—A point of possible discrepancy between the mechanism we suggested for the thermal decomposition of $Co(C_2O_4)_3^-$ and your results is that the amount of back reaction required to explain the Co(II)/Co(III) exchange that we observed may be too high to be consistent with your finding of no oxalate exchange. Have you made any quantitative considerations of this matter?

G. M. HARRIS.—No, we have not found it possible to do so.

A. W. ADAMSON.—You mentioned an alternative possibility for explaining the Co(II)/Co(III) exchange as involving an electron transfer between $Co(OX)_3^{-4}$ and $Co(OX)_3^{-3}$ or between the diaquo forms. Such a path should lead to oxalate exchange, however, since I feel sure that the Co(II) species is quite labile. I don't therefore, see how this alternative helps.

G. M. HARRIS.—This alternative scheme is satisfactory provided oxalate exchange with the ion $Co(C_2O_4) \cdot (OH_2)_2^-$ is slow. No measurements have been made of this process, but Stranks (private communication) reports a relatively high stability constant for this species, one indication of slow exchangeability.

UNIDENTIFIED QUESTIONER.—What evidence is there for the radical ions proposed as intermediates in the mechanism of the cobaltioxalate decomposition?

R. M. NOYES.—$C_2O_4^-$ has been proposed as an intermediate in reactions such as the oxidation of oxalate by permanganate. A kinetically equivalent intermediate is $CO_2 + CO_2^-$, and this has the advantage that oxygen inhibition can be more logically explained by reaction with CO_2^- than by reaction with $C_2O_4^-$.

V. GUTMANN.—The intermediate formation of a CO_2^- radical ion has been postulated in the reaction between sodium amalgam and CO_2, which finally leads to sodium oxalate formation.

(27) H. Taube, THIS JOURNAL, **58**, 523 (1954). It is also of interest that the expected non-instantaneous exchange of water with Vaq^{++}, which is isoelectronic with $Cr^{+++}aq$, has been confirmed (K. V. Krishnamurty and A. C. Wahl, to be published).

COÖRDINATION KINETICS OF ETHYLENEDIAMINETETRAACETATE COMPLEXES*

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Kinetic studies indicate several intermediate EDTA complexes, some with decreased degree of coördination of the ligand to its central ion and others with more than one metal ion per ligand. A number of these intermediate complexes are observed in solution with ultraviolet spectrophotometry. The inertness of the EDTA exchange reactions parallels the stability of the complexes. Exchange reactions proceed by S_E2 and S_E1 paths and both are subject to acid catalysis.

The high stability, the multidentate character and the wide industrial and analytical application of the ethylenediaminetetraacetate (EDTA) complexes, has naturally led to investigations of their kinetic behavior. Many of the EDTA complexes are inert, particularly in reactions which involve the exchange of EDTA between two metal ions (electrophilic substitution). The acid dissociation of a number of complexes also proceeds at measurable rates. Those metal ions which hydrolyze and polymerize in solution such as Al(III) and Zr(IV) undergo slow formation reactions with EDTA. This frequently has been observed in titrimetric procedures for these ions. On the other hand, relatively few of the formation reactions between EDTA and a simple aquated metal ion are inert, at least not in the rate of formation of the initial complex. In most cases the displacement of the bound water molecules by the entering EDTA molecule occurs too rapidly to measure by conventional methods. Exceptions to the labile formation reactions are systems in which another metal ion has been used to greatly repress the free EDTA concentration, such as, the reaction between Cu(II) and EDTA in the presence of Zn(II). The formation rate of the Cr(III)–EDTA complex is also slow. The exchange reactions such as isotopic exchange often proceed by both S_E2 and S_E1 paths. Typically the latter involves a rate-determining acid dissociation step followed by a rapid formation step. Table I summarizes the coördination and dissociation kinetics for the 1:1 complexes. Only those systems for which definite kinetic data exist are shown in Table I. Many other EDTA reactions similar to the types discussed are believed to be rapid for ions, such as Ca(II), Mg(II), Mn(II), etc. This conclusion is drawn from rapid titrimetric end-points observed for both direct and back titrations. Complexes with high charge on the metal tend to be more inert. For the M(II) complexes, the more stable complexes tend to be more inert.

Degree of EDTA Coördination.—Recent work has established the existence of several forms of the Co(III)–EDTA complex in solution,[9] and the kinetics of the transition from Co(III)–EDTA penta-coördinated, to Co(III)–EDTA hexa-coördinated, has been measured. Similarly, the Cr(III)–EDTA complex is known to have several forms with

TABLE I

EDTA complex	pK^c	Conditions	Ref.
		(Labile complexes)	
ZnY^{--a}	16.3	Zn*(II) exchange, pH 3–11	1
FeY^{--}	14.3	Fe*(II) exchange, pH 1.5–4.7	2
CdY^{--}	16.6	Reaction with Cu(II)	3
		(Inert complexes)	
NiY^{--}	18.6	Ni*(II) exchange, pH 2–10	4
		Acid dissociation	5
PbY^{--}	18.3	Formation from ZnY^{--}	6
CuY^{--}	18.8	Formation from CdY^{--}	3
CoY^{--}	16.2	Co*(II) exchange, pH 4–7	7
FeY^{-}	25.1	Fe*(III) exchange, pH 0.5–2	2
CrY^{-}	...	Formation from Cr(III)	8
CoY^{-}	36	Formation	9
AlY^{-}	16.1	Acid dissociation	10
LnY^{-b}	...	Exchange	11
ZrY	...	Titrimetric reactions	12
ThY	23.2	Titrimetric reactions	13
IrY	...	Formation from $IrCl_6^{--}$	14

^{a} Y^{-4} refers to EDTA anion. ^{b} Ln refers to the lanthanon group. ^{c} The pK values are taken from J. Bjerrum, G. Schwarzenbach and L. E. Sillen "Stability Constants," The Chemical Society, London, 1957.

slow transitions between these forms.[8] The extent of coördination between EDTA and Cr(III) has not been determined. The ultraviolet spectra of three divalent metal ions, Ni(II), Zn(II) and Cd(II), were examined for any evidence of slow changes in the degree of their coördination to EDTA as opposed to their formation, dissociation or exchange reactions. In each case the ratio of ligand to metal ion was 1:1, and in each case the initial reactions of the aquo ion with Na_2H_2Y was

(1) A. Turco, G. Sordillo and M. Scatena, *Ricerca Sci.*, **25**, 2361 (1955).

(2) S. S. Jones and F. A. Long, THIS JOURNAL, **56**, 25 (1952).

(3) H. Ackerman and G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 485 (1952).

(4) C. M. Cook and F. A. Long, Brookhaven Conf. Dept. BNL-C-8. Chem. Conf. No. 2, 106 (1948).

(5) D. W. Margerum and J. F. G. Clarke, Jr., to be published.

(6) S. Bril, K. Bril and P. Krumholz, THIS JOURNAL, **59**, 596 (1955).

(7) F. A. Long, M. Burke and J. Backus, unpublished work.

(8) R. E. Hamm, *J. Am. Chem. Soc.*, **75**, 5670 (1953).

(9) I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958).

(10) D. W. Margerum, unpublished work.

(11) R. H. Betts, personal communication.

(12) J. S. Fritz and M. Johnson, *Anal. Chem.*, **27**, 1653 (1955).

(13) G. Schwarzenbach, "Complexometric Titrations," Interscience Publishers, New York, N. Y., 1957.

(14) W. M. MacNevin and O. H. Kriege, *Anal. Chem.*, **28**, 16 (1953).

very rapid to give a solution of approximately pH 3. Solutions of all three of these ions gave small but definite shifts in spectra on standing. These spectral shifts became larger and more rapid when the solutions were heated and then cooled. The slow spectral shifts occurred in the form of a 10 to 70% increase in absorbance in the 250–300 mμ region. These changes were not a continuation of the initial change in spectra due to the first formation of a complex. A Ni(II)–EDTA solution, which had been heated at pH 5 (causing an absorbance increase at 285 mμ), was cooled and acid was added to give pH 2.5. After a fast initial shift, a slow decrease in absorbance was noted at 285 mμ for approximately 10 minutes. This absorbance decrease is not caused by the dissociation of the complex. It is well known that all these complexes exist in an acid form, HMY^-, with a $pK_a = 3$, as well as the MY^{--} form. However, the rate of transition between these forms is very rapid. If the spectral shifts reported above were simply due to a slow change from MY^{--} to HMY^- and vice versa, then a large and slow change in pH should accompany the reaction. This is not the case. The main pH change is practically instantaneous with very slight or no additional changes on standing. These data suggest the existence of several forms of the 1:1 complex with different degrees of coördination between the EDTA and the metal ion. The observations may be explained on the basis of a hexa- and a penta-coördinated complex.

$$MY^{--} \ + \ H_2O \underset{}{\overset{slow}{\rightleftarrows}} MY(H_2O)^{--} \quad (1)$$
$$\text{(hexa)} \qquad\qquad\qquad \text{(penta)}$$

$$MY(H_2O)^{--} + H^+ \underset{}{\overset{rapid}{\rightleftarrows}} HMY(H_2O)^- \quad (2)$$
$$\text{(penta)} \qquad\qquad\qquad \text{(penta)}$$
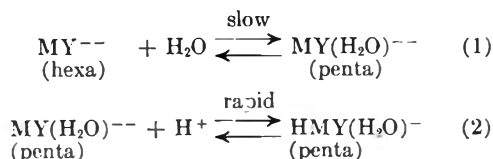
For the Ni(II)–EDTA system, failure to find the appropriate slow pH changes indicates that less than 5% of the complex is in the hexa-coördinated form in solution.

Schwarzenbach[15] has proposed that the M(II) complexes are penta-coördinated with an equilibrium of the type shown in equation 2 and Fig. 1. If an additional reaction of the type in equation 1 occurred, increased temperature might well favor the stability of the hexa-coördinated form due to entropy increase in releasing water from the complex. In addition, the hexa-coördinated form might be expected to have a lower solubility (salts such as CaNiY will precipitate) than the penta-coördinated form, since it is less hydrated and less polar. It has been observed that such salts precipitate more readily when their solutions are heated.[10,16] With the exception of Co(III), it is not known whether the coördination potential of EDTA complexes in solution is utilized to the fullest extent.[17] Even in the solid state the extent of coördination is not always known. The preparation of the anhydrous compounds NaCoY and HFeY[18] has been the basis of proposing that these
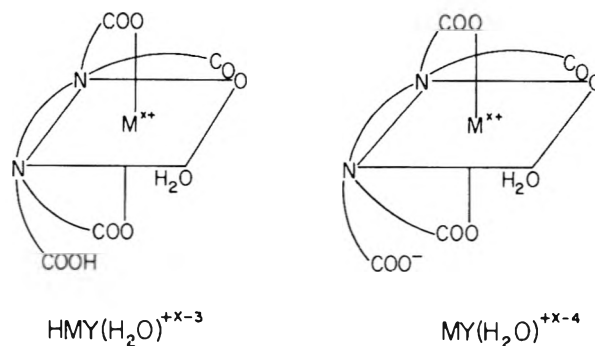
Fig. 1.—Proposed acid and ionized forms of the pentadentate EDTA complex.

compounds have hexa-coördination. The compound $Ba[CoY]_2 \cdot 4H_2O$ has been examined by Busch and Bailar[19] using infrared and they propose hexa-coördination. Recent work of Sawyer and Paulsen[20] with EDTA salts of the alkaline earths shows that infrared data support hexa-coördination for compounds like $Na_2MgY \cdot 4H_2O$, but do not prove it. They also criticize the earlier proof given for hexa-coördination of $K_2CuY \cdot 4H_2O$.[21] There is better infrared evidence for tetra-coördination, when two of the six EDTA coördinating positions are present as carboxylic acids. Examples include $H_2CuY \cdot H_2O$[21] and H_2PdY.[22] With the exception of Co(III), definite proof of hexa-coördination in the crystalline state does not exist, so it is not surprising that the degree of coördination in solution is not known. Furthermore, as was pointed out, possible effects of coördination on solubility might give different species in solution than in crystals. The acid forms of complexes in solution such as H_2PdY[23] and $HNiY^-$ have ultraviolet spectra consistent with the infrared interpretation in the crystalline state of free carboxylic acid groups. Therefore, the EDTA coördination to a metal ion probably decreases as the acidity increases.

Acid Dissociation of EDTA Complexes.—The Ni(II)–EDTA complex has been studied by direct acid dissociation[5] and by isotopic exchange.[24] These two sets of data give the dissociation rate from $10^{-5} M [H^+]$ to almost $1 M [H^+]$. The dissociation rate is first order with respect to the complex and has a complex and high order dependence on $[H^+]$. Over this acidity range there is approximately a 10^8-fold increase in the dissociation rate. At 0.7 M HCl the reaction is complete in about 30 seconds. Part of the apparent higher order dependence on $[H^+]$ is due to the formation of protonated intermediates of the complex. The following forms of the complex are shown to exist in neutral or acid solutions: NiY^{--}, $HNiY^-$, H_2NiY, H_3NiY^+. Titrimetric and spectrophotometric evidence exists for $HNiY^-$, $K_{a2} = 1.2 \times 10^{-3}$ at $\mu = 1.25$, while spectrophotometric evidence exists

(15) G. Schwarzenbach and J. Heller, Helv. Chim. Acta, 34, 567 (1951).

(16). von P. Pfeiffer and E. Schmitz, Z. anorg. Chem., 238, 247 (1949)

(17). R. G. Charles, J. Am. Chem. Soc., 76, 5854 (1954).

(18) von H. Brintzinger, H. Thiele and U. Müller, Z. anorg. allg. Chem., 251, 285 (1943).

(19) D. H. Busch and J. C. Bailar, J. Am. Chem. Soc., 75, 2574 (1953).

(20) D. T. Sawyer and P. J. Paulsen, ibid., 80, 1597 (1958).

(21) S. Kirschner, ibid., 78, 2373 (1956).

(22) D. H. Busch and J. C. Bailar, ibid., 78, 716 (1956).

(23) W. M. MacNevin and O. H. Kriege, ibid., 77, 6149 (1955).

(24) C. M. Cook, Jr., and F. A. Long, ibid., 80, 33 (1958).
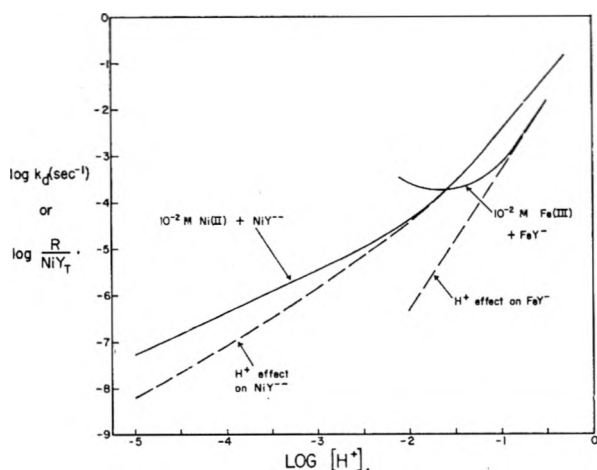
Fig. 2.—Variation of the 1st-order dissociation rate constant k_d with $[H^+]$. This is equivalent to the exchange rate constant R divided by the total complex concentration MY_T as $[M] \to C$.
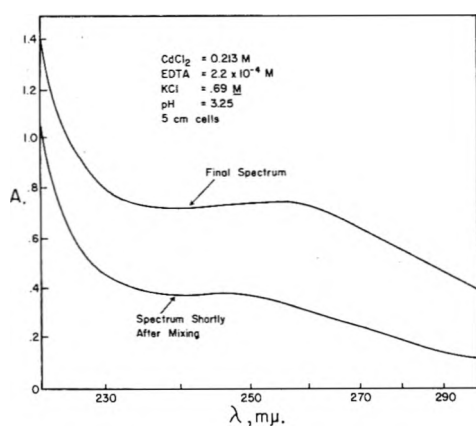
Fig. 3.—Absorption spectra indicating the formation of a polynuclear Cd(II) EDTA complex.

for H_2NiY, $K_{a1} = 0.02$ at $\mu = 1.3$, and for H_3NiY^+. The latter form begins to appear above 0.7 M HCl. Solutions sufficiently acid to have high concentrations of H_2NiY or appreciable concentrations of H_3NiY^+ undergo rapid dissociation to aquo Ni(II) and EDTA. The slow transition of what is believed to be hexa NiY^{--} to penta $HNiY^-$ has been discussed. This transition involves more than just a proton transfer as the coördination of a carboxylate group to Ni(II) must be broken to give a free carboxylic acid. It is observed with Ni(II) that this transition is much faster as the acidity increases. This suggests that equation 1 may be subject to acid catalysis, with a proton adding first to the coördinated carboxylate group. The concentration of the proposed hexa NiY^{--} is always small and therefore this effect is not apparent in the isotopic exchange data. With higher acid concentration the transition between protonated forms becomes rapid. Equilibrium is established rapidly (less than 2 seconds) between $HNiY^-$, H_2NiY and H_3NiY^+. The more protonated forms of the complex dissociate more rapidly. One more unstable intermediate, H_4NiY^{++}, must be proposed to fit these data to the acid catalysis at high acidity. Figure 2 gives a log-log plot of the first-order dissociation rate constant against acidity. At acidities below

the intersection of the exchange rate and the dissociation, the acid dissociation is calculated from the exchange data, while above this intersection it is calculated from direct spectrophotometric acid dissociation. The change in slope of this curve in the vicinity of pH 2 corresponds to the appearance of appreciable concentrations of H_2NiY. The greatly increased dissociation rate of this complex is consistent with the proposal that this form of the EDTA complex is tetracoördinated. The absence of a similar break on the pH 3–4 region is noteworthy. If the relatively stable acid intermediates exist as complexes with free carboxylic acid groups, the slow step in the dissociation must be breaking the Ni(II)–nitrogen bond. The rapid breaking of the Ni(II)–oxygen bonds may be caused by prior proton addition to the carboxylate group.

In general, the acid dissociation rate behavior of Ni(II)–EDTA is typical for the inert complexes. Similar acid dependence is observed in the dissociation rates of Fe(III), Co(II) and Al(III) complexes.

Second-order Electrophilic Substitution, S_E2.—A large body of data now exists which shows that the exchange reaction of EDTA between two metal ions does not have to proceed by dissociation but can proceed by direct interaction of the aquo ion with the EDTA complex ion. These S_E2 reactions are reported for $Ni^*(II)$ with NiY^{--}, for $Fe^*(III)$ with FeY^-, for Cu(II) with CdY^{--} and for Pb(II) with ZnY^{--}.

Figure 2 illustrates the effect that $Ni^*(II)$ has on the exchange reaction with NiY^{--}. The lower curve represents the acid dissociation reaction, while the upper curve is the combined effect of the dissociation reaction path (S_E1) and the S_E2 reaction path. Acid catalyzes the S_E2 reaction as well as the S_E1 reaction. The behavior of the Fe(III) system as reported by Jones and Long[2] is anomalous. The large increase in the S_E2 reaction is attributed to $FeOH^{++}$ formation. Actually the main Fe(III) species in solution would be the dimer $Fe_2(OH)_2^{+4}$.[25] It is difficult to see how this species can have such a large effect on the direct exchange reaction. For example, thorium(IV) does not have this effect with either FeY^{-26} or NiY^{--}.[10]

Polynuclear EDTA Complexes.—Although crystalline compounds such as $CuCdY\cdot3.5H_2O$, $CaNiY\cdot 2H_2O$, $CuZnY\cdot5.5H_2O$ and $CaMgY\cdot8H_2O$,[16] have been prepared, there is no evidence that these compounds contain two metal ions bound to one EDTA. They may be considered as ionic salts such as $Cu^{++}CdY^{--}$. No evidence has been reported heretofore for complexes in solution other than the 1:1 complexes.

Bennett and Wise[27] looked specifically for complexes of Cd(II) with CuY^{--} in aqueous solution and were unable to find any evidence of a complex. However, polynuclear EDTA complexes appear to be formed if a large excess of metal ion is used and the slow reaction of the system is allowed to proceed. When a large excess of Cd(II) is mixed with

(25) L. N. Mulay and P. W. Selwood, *ibid.*, **77**, 2693 (1955).

(26) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

(27) M. C. Bennett and W. S. Wise, *Trans. Faraday Soc.*, **52**, 696 (1956).

EDTA, the usual 1:1 complex is rapidly formed. The ultraviolet spectrum then changes very slowly as shown in Fig. 3. The final spectrum is attained on repeated heating of the solution. This type of spectral shift is more pronounced in the presence of KCl than with NaClO$_4$. This type of charge is observed only in the presence of EDTA and a 100:1 or greater ratio of Cd(II) to EDTA. The observed spectral changes are several orders of magnitude greater than the slow 1:1 shifts discussed earlier. In addition a maximum appears at 260 mμ only with the large excess of Cd(II). These facts suggest a polynuclear complex, Cd$_x$Y. The nature of this complex is now under investigation.

Zinc (II) shows a similar behavior with ZnY^{--}, but with less pronounced spectral shifts. The slowness of the formation of these complexes rules them out as the type of reaction intermediates observed in the electrophilic substitution reactions.

DISCUSSION

R. H. Betts.—What is the evidence that Th(IV) reacts slowly with EDTA?

D. W. Margerum.—Titrimetric procedures call for heating Th(IV)–EDTA solutions in order to perform direct titrations at pH 2.

R. M. Milburn.—Is there any evidence for the rapid formation of outer sphere complexes of Cr(III) and Co(III) with EDTA? One might anticipate that on addition of EDTA to Cr(III) there would be a rapid change in the ultraviolet spectrum indicative of the formation of an outer sphere complex, followed by slower changes in the visible spectrum as the waters coördinated to Cr(III) are replaced.

R. E. Hamm.—We have specifically looked for "ionpair" or "outer-sphere" complexes with Cr(III) and EDTA. The ultraviolet spectrum gives no good evidence of their existence.

T. D. Lyons.—Have you evaluated or approximated the activation energies governing the formation or dissociation of the Ni(II)–EDTA complex?

D. W. Margerum.—Not as yet. This involves several full series of acid dependent measurements.

G. I. H. Hanania.—How does one know that there is a free carboxylic acid group with the EDTA complexes?

D. W. Margerum.—In solution the evidence for a free carboxylic acid group is the assumption that the known acid forms of the complexes (proved by pH and spectral data) have their protons associated with the carboxyl group, and on the availability of another coördination position on the metal ion in the case of Co(III). The ultraviolet spectrum changes accompanying formation of the acid forms such as HNiY$^-$ are similar to the changes which EDTA itself undergoes in the formation of its acid forms. In the crystalline state the evidence is much better and I refer the question to D. Busch.

D. Busch.—In the infrared work the double-bond stretching frequency of the carbonyl function depends on the nature of the atom attached to the carboxyl group. Thus different frequencies are expected for the three possible types of carboxyl groups: complexed, anionic and acidic.

G. I. H. Hanania.—In the case of the EDTA complexes of bivalent cations, Dr. Margerum has presented an aquation equilibrium

$$MY^- \rightleftarrows MY(H_2O)^- \rightleftarrows HMY(H_2O)^-$$
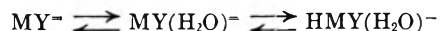
between the hexadentate ion MY$^-$ and the corresponding pentadentate ion MY(H$_2$O)$^-$ where one H$_2$O molecule occupies the sixth position and thereby frees one carboxyl ion which then picks up a proton to form the conjugate acid HMY(H$_2$O)$^-$.

One wonders, however, if this postulate is really necessary. Although pentadentate coördination of EDTA has been established in cases where the sixth position is occupied by anions, the evidence for H$_2$O is by no means unequivocal. For one thing, one expects a greater free energy of formation of the sixth bond into ligand than with H$_2$O, especially as no straining of bonds is involved. Moreover, it is questionable whether the state of the ion in dilute solution could be confidently inferred from the infrared evidence for a carboxylic acid group carried out on crystals.

The formation of one or more consecutive conjugate acid species of complex ions in dilute aqueous solution is known in other cases—such as Fe(CN)$_6^{4-}$ and Fe dipy(CN)$_4^{2-}$—where it is quite unlikely that central bonds are broken. Present views on the association of ions permit one to attribute the formation of conjugate acids of complex ions either to a general electrostatic ion pairing outside the coördination shell, or perhaps to specific bonding of H$_3$O$^+$ ions sitting on faces of the octahedron.

In any case, unless special geometrical or chemical factors require it, is it not simpler to invoke no cleavage of coordinate bonds of complex ions?

D. W. Margerum.—I have already pointed out the possible differences of the coördination in the solid state and in solution. I disagree with the statement that there is no steric strain in forming the hexa-coördinated species. Furthermore, the work of Shimi and Higginson has shown the existence of the sixth position of Co(III) occupied by water. With the MY^{--} complexes the exact nature of the acid forms is not known and the suggested electrostatic pairing is a possibility. However, some explanation is needed for the slow transition between forms of MY^{--}.

THE RATES OF ACID "HYDROLYSIS" OF THE PENTADENTATE COBALT(III) COMPLEXES OF ETHYLENEDIAMINETETRAACETIC ACID AND HYDROXYETHYLETHYLENEDIAMINETRIACETIC ACID

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The rates of acid "hydrolysis" of the bromo- and chloro-pentadentate ethylenediaminetetraacetic acid (EDTA, H_4Y) and hydroxyethylethylenediaminetriacetic acid (HETA, H_3YOH) complexes of cobalt(III) have been measured at 30, 40 and 50°. The EDTA complexes, $[Co(HY)X]^-$, convert into the hexadentate complex $[Co(Y)]^-$, while the HETA complexes $[Co(YOH)X]^-$ form $[Co(YOH)H_2O]$. The rate process is first order in starting material, pH independent over the range 1–3, and essentially independent of ionic strength, although dipositive cations exhibit an accelerating effect. These observations together with the frequency factors, which are unusually low, are interpreted in support of an S_N1 mechanism. Deviations from the first-order rate law at long reaction times are accounted for in terms of the simultaneous reaction of geometric isomers.

Introduction

Schwarzenbach[1] first prepared a series of cobalt(III) complexes in which the tetranegative anion of EDTA (Y^{4-}) behaves in a pentadentate manner. The compounds prepared by Schwarzenbach were of the general formula, $M^I[Co(HY)X]$, where X may be NO_2^-, Br^- or OH^-. The structures of these substances were subsequently confirmed by infrared spectral measurements.[2,3] The study of the complexes of platinum(II) and palladium(II) has revealed that EDTA may coördinate in a bidentate and a tetradentate manner.[4]

In those complexes cited above in which EDTA does not utilize the maximum possible number of its functional groups in coördination, the complex in question may be converted to the derivative in which the ligand exhibits its maximum polydentate behavior. Thus, the pentadentate complexes of cobalt(III) convert to the hexadentate complex while the bidentate complexes of platinum(II) convert to the tetradentate complex.

$$[Co(HY)Br]^- \longrightarrow [Co(Y)]^- + HBr \quad (1)$$
$$[Pt(H_4Y)Cl_2] \longrightarrow [Pt(H_2Y)] + 2HCl \quad (2)$$
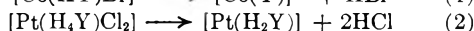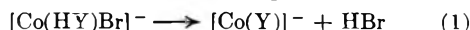
The manner in which these changes occur is of fundamental importance. Previous work[2] has revealed that the conversion of the optically active complex $[Co(HY)Br]^-$ into the related hexadentate complex $[Co(Y)]^-$ proceeds without complete racemization. The probable mechanisms of this conversion must, therefore, involve ordered processes. The three mechanisms appearing most likely are

1. Intramolecular Nucleophilic Substitution (INS).

$$[Co(HY)Br]^- \rightleftharpoons [Co(Y)Br]^= + H^+ \quad (3)$$
$$[Co(Y)Br]^= \xrightarrow{\text{slow}} [Co(Y)Br]^{=*} \quad (4)$$
$$[Co(Y)Br]^{=*} \longrightarrow [Co(Y)]^- + B^- \quad (5)$$
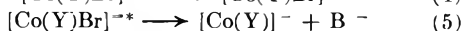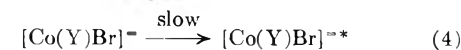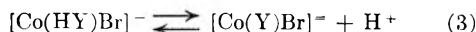
This type of mechanism would involve nucleophilic attack on the central atom by the free carboxyl group of the coördinated molecule of EDTA, producing a 7-coördinated intermediate (this is indicated by the formula $[Co(Y)Br]^{=*}$). The acid-base equilibrium preceding the rate determining

step (equation 3) indicates the pH dependence expected of this process.

2. Unimolecular Dissociation (S_N1).

$$[Co(HY)Br]^- \xrightarrow{\text{slow}} [Co(HY)]^* + Br^- \quad (6)$$
$$[Co(HY)]^* \longrightarrow [Co(Y)]^- + H^+ \quad (7)$$
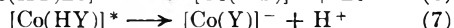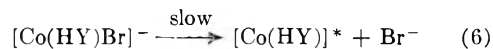
Such a unimolecular process would be agreement with the suggestions of other investigators who have discussed similar systems.[5] The intermediate would, of course, exhibit a coördination number of five.

3. Bimolecular Nucleophilic Substitution (S_N2).

$$[Co(HY)Br]^- + H_2O \xrightarrow{\text{slow}} [Co(HY)Br(H_2O)]^{-*} \quad (8)$$
$$[Co(HY)Br(H_2O)]^{-*} \longrightarrow [Co(HY)(H_2O)] + Br^- \quad (9)$$
$$[Co(HY)(H_2O)] \longrightarrow [Co(Y)]^- + H^+ + H_2O \quad (10)$$
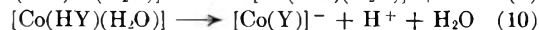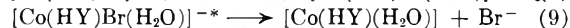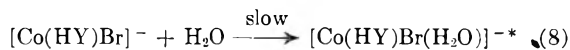
The bimolecular process would involve combination with the solvent to produce a seven-coördinated intermediate, which would then dissociate to produce the aquated complex as an additional interim product. The conversion of $[Co(HY)(H_2O)]$ into $[Co(Y)]^-$ would presumably be described by one of the mechanisms cited above.

Shimi and Higginson[6] have reported kinetic data on the conversions of $[Co(HY)(H_2O)]$, $[Co(Y)(H_2O)]^-$ and $[Co(Y)(OH)]^=$ into the hexadentate complex $[Co(Y)]^-$. It was shown that, in particular pH intervals, one of the species may be predominant in solution and that, over more limited pH ranges, individual species will dominate the rate process. In weakly acidic media, the species of primary concern is $[Co(Y)(H_2O)]^-$, while at a pH of approximately 1, the protonated species is the primary reactant, $[Co(HY)(H_2O)]$. In distinctly basic media, $pH \sim 10$, the hydroxy complex, $[Co(Y)(OH)]^=$, is of greatest importance. Shimi and Higginson have explained the pH dependence of the reactions in acidic media on the basis that the reaction

$$[Co(Y)(H_2O)]^- \longrightarrow [Co(Y)]^- + H_2O \quad (11)$$

proceeds by an intramolecular nucleophilic substitution mechanism (INS). It has been further suggested that protonation of the free carboxyl group prevents such a process, so that the reaction

(1) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

(2) D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 4574 (1953).

(3) M. L. Morris and D. H. Busch, *ibid.*, **78**, 5178 (1956).

(4) D. H. Busch and J. C. Bailar, Jr., *ibid.*, **78**, 716 (1956).

(5) F. Basolo, *Rec. Chem. Prog.*, **18**, 1 (1957); *Chem. Revs.*, **52**, 459 (1953).

(6) I. A. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958).

$$[Co(HY)(H_2O)] \longrightarrow [Co(Y)]^- + H^+ + H_2O \quad (12)$$

proceeds by a unimolecular dissociation mechanism (S_N1). The authors support their interpretations by the use of the thermodynamic part of their kinetic data. The first reaction (equation 11) is associated with an unusually large frequency factor (A), while the second reaction (equation 12) displays a frequency factor which is normal for a unimolecular process. The activation energies are identical for the two processes. It is also suggested by Shimi and Higginson that the elimination of OH^- from $[Co(Y)(OH)]^=$, or of Br^- from $[Co(Y)Br]^=$, should be entirely independent of the free carboxyl group because of the repulsion between the carboxyl group and the hydroxyl ion (or bromide ion), which would be incipiently formed in the transition state. Such a process is, therefore, expected to be unimolecular (S_N1). Further, a low value is expected for the frequency factor (A) in such reactions since the negative charge associated with the presence of the coördinated bromide must be partially concentrated on the bromide in the transition state. This should result in a transition state which is more highly solvated than is true of the normal complex and, consequently, the entropy of activation should be negative.

The investigations reported here concern the rates of "hydrolysis" of four pentadentate complexes of the class just discussed. These include $[Co(HY)Br]^-$, $[Co(HY)Cl]^-$, $[Co(YOH)Br]^-$ and $[Co(YOH)Cl]^-$, where YOH represents the trinegative anion of hydroxyethylethylenediaminetriacetic acid (structure I, hereafter denoted as

$$\begin{array}{c} HOCH_2CH_2 \\ \\ HOOCCH_2 \end{array} NCH_2CH_2N \begin{array}{c} CH_2COOH \\ \\ CH_2COOH \end{array}$$

I

HETA). The variation of these structural parameters provides significant information related to the mechanism of the processes under study.

Experimental

The cobalt(III) complexes were prepared according to the methods previously reported.[1-3] All other materials were reagent grade.

The rates of reaction were determined by a spectrophotometric method. The wave lengths chosen were 520, 540 and 600 mμ. These wave lengths provide the largest differences in absorption due to the reactants and the products. The concentrations of reactants used were approximately 0.002 molar in the majority of the experiments. The range of concentrations amenable to study by this method, using 1 cm. cells, was found to be 0.001 to 0.004 molar. The apparatus consisted of a constant temperature bath, which could be regulated to $\pm 0.02°$, a water pump, and a Beckman D.U. Spectrophotometer. During the experiments, a constant flow of water was maintained from the bath to the jacket surrounding the spectrophotometer. The temperature of the cell compartment was thermostated in this manner to $\pm 0.1°$. The cells used were Beckman–Pyrex absorption cells. Cell correction measurements were made prior to each run.

The samples of reactant were weighed on an analytical balance and placed quantitatively in calibrated 100 ml. volumetric flasks, and distilled water was added. All solutions were prepared at the temperature at which the runs were to be made. Ten ml. of a 1 M salt solution, which, in most cases, was sodium nitrate, was added and the solution was brought to a volume of 100 ml. The sample solutions were placed in the constant temperature bath. At various time intervals, aliquots of the solution were withdrawn and their optical densities were measured. The

cells containing the solutions were allowed to remain in the thermostated cell compartment and the solutions were replaced every six hours. The runs usually lasted approximately 70 hours.

The extinction coefficients of the various reactants were determined by measuring, immediately upon dilution, the optical densities of their solutions at 520, 540 and 600 mμ.

The extinction coefficients of the products were determined by adding to the solution of the reactant an amount of 0.05 M Hg(NO$_3$)$_2$ equivalent to the number of moles of the sample used. Sufficient 1 M sodium nitrate was added to make the final solution 0.1 N with respect to the total concentration of NaNO$_3$ plus Hg(NO$_3$)$_2$. Distilled water was added until a volume of 100 ml. of solution was obtained. The optical densities of these solutions were measured at 520, 540 and 600 mμ. The optical densities of these solutions were constant over a period of 12 hours. In the case of the EDTA complexes, the extinction coefficients measured in this way were checked by comparing them with the values for the pure hexadentate complex.

The concentrations of reactants and products were calculated from the spectrophotometric measurements by use of the Beer–Lambert law

$$o.d. = \epsilon_A C_A l + \epsilon_B C_B l \quad (13)$$

where ϵ_A and ϵ_B are the extinction coefficients of substances A and B, C_A and C_B are the concentrations of A and B, and l is the path length of the cell. Simultaneous solution of two such equations provides the concentrations of the reactant and product without direct use of the known total concentration of the cobalt complexes. This technique provides an effective check on the calculated concentrations at any time since they must add up to the total cobalt(III) concentration. The average difference between the calculated and measured total cobalt(III) concentration was found to be 1.7% for forty-three runs. It is, therefore, concluded that the only species present in significant concentrations at any time during the course of these experiments are the reactant and product assumed in each case.

Discussion

The rates of "hydrolysis" have been measured for the pentadentate cobalt(III) complexes of ethylenediaminetetraacetic acid, $[Co(HY)X]^-$; and hydroxyethylethylenediaminetriacetic acid, $[Co(YOH)X]^-$, where X = chloride or bromide. The majority of the data were obtained using bromoethylenediaminetetraacetatocobaltate (III), since this complex was considered to be typical of the group. The more limited number of experiments conducted with the remaining compounds were designed to provide the maximum amount of comparable information.

In any single experiment, the data clearly indicate the presence of only two cobalt-containing species which may be distinguished by the portion of the visible spectrum utilized. Substantial agreement was found between the data obtained and the first-order rate law for approximately one half-life. It was observed, in most cases, that the rate of disappearance of the reactant decreased more rapidly, thereafter, than is predicted by the first-order law. This deviation is discussed at greater length below; however, the evaluation of the initial rates in terms of the first-order law has proven quite useful and the tabulated first-order rate constants (initial rates) are collected in Table I. Comparison of the constants obtained in runs 9–10 with those reported for runs 13–14 and runs 7–8 reveals that the half-life ($0.693/k$) is independent of the initial concentration of the reactant, thus confirming the first-order dependence of the rate on the concentration of the acido-pentadentate complex.

The reaction of Na[Co(HY)Br] was studied at

TABLE I

FIRST-ORDER RATE CONSTANTS, INITIAL RATES

Compound	Run no.	Temp., °C.	Concn. 10^{+3}, mole/l.	Electrolyte	k (hr.$^{-1}$)
Na[Co(HY)Br]	1–2	30	1.997 1.991	0.1 M NaClO$_4$	0.0244
	3–4	30	2.035 2.042	.05 M NaClO$_4$ .05 M HClO$_4$	.0260
	5–6	30	1.122 2.020	.1 M HClO$_4$	.0237
	7–8	30	4.181 3.970	.1 M NaNO$_3$	.0242
	9–10	30	1.124 1.062	.1 M NaNO$_3$	.0256
	11–12	30	2.033 2.004	.1 M NaBr	.0230
	13–14	30	2.004 2.026	.1 M NaNO$_3$	.0256
	15–16	30	2.117 2.011	Dist. water	.0227
	17–18	30	1.643 1.503	0.866×10^{-3} 1.133 Na[CoY] 0.1 NaNO$_3$	.03
	43–44	30	2.017 1.997	1 M HClO$_4$	.0297
	19–20	30	2.130 2.004	0.1 M Sr(NO$_3$)$_2$	.0295
	21–22	40	2.221 2.173	.1 M NaNO$_3$	.0758
	23–24	50	1.899 1.860	.1 M NaNO$_3$	.195
Na[Co(HY)Cl]	25–26	30	2.245 2.363	.1 M NaNO$_3$	.0084
	27–28	40	1.809 2.199	.1 M NaNO$_3$	.0267
	29–30	50	1.814 2.033	.1 M NaNO$_3$	.0988
Na[Co(YOH)Cl]	31–32	30	2.056 2.335	.1 M NaNO$_3$	.0115
	33–34	40	2.214 1.694	.1 M NaNO$_3$	.0398
	35–36	50	1.971 2.030	.1 M NaNO$_3$	.112
Na[Co(YOH)Br]	37–38	30	3.261 1.870	.1 M NaNO$_3$	.0486
	39–40	40	1.228 1.819	.1 M NaNO$_3$	.146
	41–42	50	1.709 2.287	.1 M NaNO$_3$	.431

four different hydrogen ion concentrations. These were pH 3.0 (runs 1–2), 1.3 (runs 3–4), 1 (runs 5–6) and 0 (runs 43–44). The hydrogen ion concentration was adjusted with perchloric acid to avoid possible complications which might be associated with buffer solutions, such as complexing with the basic form of the buffer. The rate in distilled water (pH 3.0, as a result of the ionization of the reactant) is 0.023 hr.$^{-1}$. Those in solutions of 0.05, 0.1 and 1 N perchloric acid are 0.026, 0.024 and 0.030 hr.$^{-1}$, respectively. There appears to be little effect due to pH over the range from 1 to 3 since the variations observed in the rate are prob-

ably within the error of measurement. It is obvious that the pH dependence is not associated with the repression of the ionization of the free carboxylic acid group of the pentadentate complex since the per cent. of ionization changes from about 1 to 50% over the pH range from 1 to 3. On this basis alone, the intramolecular nucleophilic substitution mechanism may be eliminated. In 1 N perchloric acid the rate constant is approximately 30% greater than those obtained in studies at higher pH. In this case, the extinction coefficients used to give a material balance were different from those utilized in other cases. Consequently, it

appears that the reacting species differs in solutions of very low pH.

The dependence of the rate on ionic strength was tested in duplicate sets of experiments. This may be seen by comparing the experiments numbered 15–16, 1–2, and 19–20 (Table I). In proceeding from an ionic strength of approximately 10^{-3} to that of 0.1, no measurable change in rate is observed. It is therefore concluded that the effect of ionic strength on the rate is insignificant. It is, however, apparent that a more specific type of interaction may occur since the rate observed in solutions containing 0.1 M $Sr(NO_3)_2$ (ionic strength, ~ 0.3) is about 30% more rapid that those observed in the instances where uni-univalent salts were utilized as supporting electrolytes. It is also of significance that the extinction coefficients were different in the case of the solutions containing Sr^{++} from those containing only Na^+ or H_3O^+ (at $pH \geqslant 1$). On the basis of these observations and in accord with the conclusions of earlier investigators,[7] it is suggested that ion pair formation may occur between the complex ion of interest and the divalent strontium ion. The acceleration observed may reasonably be associated with ion pair formation in terms of a unimolecular dissociation process of the type discussed in the Introduction (equations 6 and 7). In such a case, the transition state would require the concentration of negative charge on the dissociating halide ion, a process which might be facilitated to a greater extent by the proximity of a highly charged positive ion than by solvation (equations 14, 15 and 16). Such an effect

$$[Co(Y)Br]^= + Sr^{++} \rightleftharpoons [Co(Y)Br\ldots Sr] \quad (14)$$
$$[Co(Y)Br\ldots Sr] \longrightarrow [Co(Y)]^{-*} + Sr^{++} + Br^- \quad (15)$$
$$[Co(Y)]^{-*} \longrightarrow [Co(Y)]^- \quad (16)$$
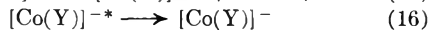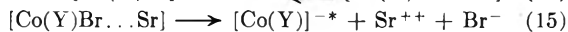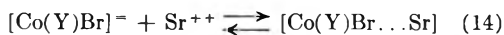
would amount to an electrophilic attack on the halide ion coördinated to the cobalt atom. It should be pointed out that the reaction utilized to prepare solutions of the products for the determination of their extinction coefficients, as described above, is more simply interpreted as such an electrophilic process. Equations similar to those numbered 14, 15 and 16 might be written in which Hg^{++} is substituted for Sr^{++}. It should also be emphasized that the reaction is quite rapid in the case of the strongly electrophilic mercuric ion. Similarly, the addition of silver ion to solutions of the acido-pentadentate cobalt(III) complexes is followed by a much more rapid precipitation of silver halide that is explainable in terms of the normal rate of release of halide ion.

In the Introduction, three possible mechanisms of reaction were discussed. These were intramolecular nucleophilic substitution (INS), unimolecular dissociation (S_N1), and a bimolecular nucleophilic substitution (S_N2) involving the solvent. Since the only mechanism postulated which involves a predictable pH dependence is the INS process, this particular mechanism may be eliminated from further consideration in the case of the complexes under study on the basis of the virtual independence of pH found in the rate measurements. An additional feature of this particular type of reaction militates against the INS mechanism. The restraint associated with the free carboxyl group, as a result of its being bound to the complexing ligand, is such that an INS displacement reaction would, of necessity, involve attack on the octahedron of the cobalt in a position adjacent to the coördinated bromide.[6] Thus, the INS mechanism would require the highly unlikely close approach of two negative entities.

As was pointed out above, Shimi and Higginson[6] have suggested that the reaction of $[Co(HY)Br]^-$ should follow a unimolecular path, producing the hexadentate complex as a primary reaction product. Corollary to this suggestion is the prediction that the frequency factor will be abnormally low and that the reaction will be associated with a negative entropy of activation. The data reported in Table II fully justify these predictions, the frequency factors varying from 10^9 to 10^{11} sec.$^{-1}$, implying negative entropies of activation. These results lend further support to the contention that the loss of bromide or chloride from the EDTA and HETA complexes proceeds by an S_N1 mechanism. As has been pointed out, the order of the reaction with respect to the reactant and the specific effect of dispositive ions also support this viewpoint.

TABLE II

ACTIVATION ENERGIES AND FREQUENCY FACTORS DERIVED FROM INITIAL RATES

Reactant	A (sec.$^{-1}$)	E_a (kcal./mole)
$[Co(HY)Br]^-$	2.4×10^9	20.3
$[Co(HY)Cl]^-$	4.0×10^{11}	24.1
$[Co(YOH)Br]^-$	2.1×10^{10}	21.2
$[Co(YOH)Cl]^-$	6.8×10^9	21.4

More direct evidence for the nature of the primary reaction product would aid greatly in the substantiation of this view. The rate data alone would not distinguish between $[Co(Y)]^-$ and $[Co(Y)(H_2O)]^-$ as the first stable product of the reaction because the rates of conversion of $[Co(Y)(H_2O)]^-$ and of $[Co(HY)(H_2O)]$ into $[Co(Y)]^-$ are approximately 1000 and 80 times as fast, respectively, as the rate of loss of bromide from the reactant, $[Co(HY)Br]^-$.[8] As a consequence, the concentration of the hydrated ion would not be great at any time during the course of an experiment. The accelerating effect of positive ions (Sr^{++}, Hg^{++}, Ag^+) is not, however, so easily explainable in terms of the S_N2 mechanism.

As a consequence of the similarity in the kinetic behavior of the complexes of hydroxyethylethylenediaminetriacetic acid to those of EDTA, a closely related mechanism must be involved. In this case, the replacement of the free carboxyl group by an ethanol group renders the formation of a hexadentate complex relatively unlikely. Therefore, it is suggested that the final product of these reactions is the aquo-pentadentate complex, $[Co(YOH)(H_2O)]$. An explanation for the relatively rapid rates of reaction of the HETA complexes (Table I) is not immediately apparent. In terms of an

(7) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 376 ff.

(8) This comparison is based on the extrapolation of the rates reported by Shimi and Higginson to 30°.

S_N1 mechanism, the greater negative ionic charge in the case of the EDTA complexes should lead to an order opposite to that observed. An INS mechanism would again predict the more rapid reaction of the complexes of EDTA. As discussed above, the INS mechanism does not operate in the case of the complex $[Co(HY)Br]^-$; however, the possibility remains that $[Co(YOH)Br]^-$ might follow such a mechanism. If this latter suggestion were valid, the kinetic behavior of the two pairs of complexes should differ materially. It would then be reasonable to expect the frequency factors to be uniformly greater for the complexes $[Co(YOH)X]^-$ than for the corresponding complexes $[Co(HY)X]^-$. The data in Table II do not support this possibility.

From Table I it is evident that the bromo complexes react more rapidly than the corresponding chloro complexes in the case of both the EDTA and the HETA derivatives. This is in agreement with the observed behavior of the halo-amine complexes of cobalt(III).[9] A very simple electrostatic model has been utilized to explain this and similar
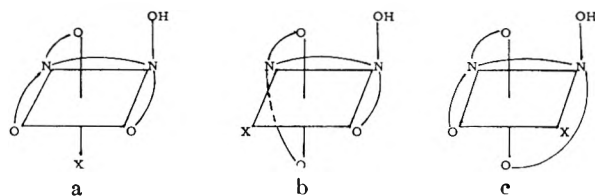
Fig. 1.—Geometric isomers of $[Co(HY)X]^-$.

trends by Basolo and Pearson.[10] It is suggested that since the coulombic attraction of the metal ion for the halide ion decreases as the size of the anion increases, the proper order for the halides should be (in order of decreasing rate of displacement) $I^- > Br^- > Cl^- > F^-$.

It should be mentioned that preliminary results have revealed a strong base acceleration of the rate processes reported here. An obvious extension of the S_N1 mechanism to include this observation appears to be lacking. The S_N1CB mechanism utilized by Basolo, Pearson, Meeker and Bergmann[11] to explain base acceleration of the hydrolysis of the halo-amine complexes of cobalt(III) must be ruled out because of the absence of ionizable protons on the donor atoms.

Despite the demonstrated first-order dependence of the rate on the concentration of the reactant, the reaction rate was observed to deviate from the first-order rate law at long times. In an attempt to account for this deviation, three models were considered. The possible existence of the following equilibrium was tested by assuming the values of the equilibrium constant required to reproduce the observed rate behavior. However the invalidity of this supposition was shown by the fact that the predicted

$$[Co(HY)Br]^- \rightleftharpoons [Co(Y)]^- + Br^- \quad (17)$$
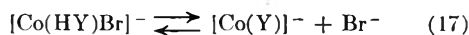
effect of excess bromide ion was not observed (compare runs 11–12 with 1–2 or 13–14). The possi-

bility that consecutive rate processes were involved, perhaps involving the intermediate formation of the aquopentadentate species or some less obvious substance, was obviated on the basis of known relative rates and on the basis of the complete material balance obtained throughout all of the experiments on the assumption that the cobalt(III) was present only as the initial reactant and the single product.

A satisfactory explanation of the deviation from the simple first-order rate law may be related to the presence of geometrical isomers. The expected geometric isomers of acido-pentadentate complexes of this structure are shown in Fig. 1. Isomer b would be expected to be of lesser stability than the other two as a consequence of the distortion of the carbon–nitrogen–carbon bond angle. It is reasonable that at least two of these isomers might be present in the materials studied. In order to treat the data, it is also necessary to assume that the isomers have identical extinction coefficients at 520, 540 and 600 mμ. A smooth curve is drawn through the experimental points for a single run in Fig. 2. It is assumed that, at long times, only the more slowly reacting isomer (B) remains and that this isomer reacts according to the first-order rate law. This asymptotic rate law is shown in Fig. 2 by the broken line. The assumed equation

$$\ln B = -k_2 t + \ln B_0 \quad (18)$$

(equation 18) may then be evaluated for the first-order rate constant, k_2, and the initial concentration of isomer B. From the equation for the rate of reaction of isomer B, the concentration of B may be calculated at any time. It is then possible to calculate the concentration of the more rapidly reacting isomer A at any time. The remaining plot in Fig. 2 indicates the agreement of the rate data for isomer A with the first-order rate law. The over-all rate law is given by equation 19.

$$\ln (C\infty - C) = \ln (A_0 e^{-k_1 t} + B_0 e^{-k_2 t}) \quad (19)$$

Figure 3 shows the agreement between the theoretical rate law and experimental points. Again, the broken line represents the asymptotic first-order process associated with the reaction of isomer B alone.

The rate constants k_1 and k_2 are shown for seven runs in Table III. Within the precision of the results both constants are independent of pH and of concentration of the starting material over the

(9) Reference 7, p. 123.

(10) Reference 7, p. 102.

(11) R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, **78**, 4878 (1956); F. Basolo, J. G. Bergmann, R. E. Meeker and R. G. Pearson, *ibid.*, **78**, 2676 (1956); R. G. Pearson, R. E. Meeker and F. Basolo, *ibid.*, **78**, 709 (1956).

TABLE III

RATES OF CONVERSION OF ISOMERIC FORMS OF $[Co(HY)Br]^-$ INTO $[Co(Y)]^-$, 30°

Run No.	$C\infty \times 10^3$	$100B_0/(A_0 + B_0)$	k_1 (hr.$^{-1}$)	k_2 (hr.$^{-1}$)	Medium
2	1.991	76.3	0.104	0.0137	0.1 M NaClO$_4$
6	2.020	65.2	.0816	.0105	.1 M HClO$_4$
8	3.870	74.7	.108	.0149	.1 M NaNO$_3$
9	1.124	69.0	.0945	.0120	.1 M NaNO$_3$
10	1.082	69.3	.0833	.0120	.1 M NaNO$_3$
13	2.044	73.9	.0869	.0121	.1 M NaNO$_3$
14	2.026	73.0	.101	.0115	.1 M NaNO$_3$
Av. values		72 ± 3	0.094 ± 0.009	0.012 ± 0.001	

limited ranges given. The rates are shown to be reproducible within about 10% of their values. The data in Table III also reveal that the percentage of isomer B initially present is reproducibly calculated with an average deviation of 3%. This is expected since all the experiments were conducted with materials prepared in a single *batch*. This, of course, would obviate the possibility of variations in the extent of isomer fractionation associated with isolation and purification. Table IV reports similar data for runs at 40 and 50°. Since these experiments were not followed for as many half-lives as was true of the runs at 30°, the average value of B_0 from the data at 30° was utilized in the calculations.

TABLE IV

RATES OF CONVERSION OF ISOMERIC FORMS OF
$[Co(HY)Br]^-$ INTO $[Co(Y)]^-$, 0.1 M NaNO$_3$

Run no.	$C_\infty \times 10^3$	$100B_0/$ $(A_0 + B_0)$	k_1 (hr.$^{-1}$)	k_2 (hr.$^{-1}$)	$T,$ °C.
21	2.173	(72)	0.328	0.0406	40
22	2.221	(72)	.292	.0384	40
		Av. values	.31	.040	
23	1.899	(72)	.597	.124	50
24	1.860	(72)	.549	.124	50
		Av. values	.57	.12	

The values of the frequency factors and activation energies are listed in Table V. Comparison of these values with those listed in Table II for the initial rate of reaction of $[Co(HY)Br]^-$ reveals that the initial rate is dominated by isomer A, as is necessitated by the model chosen. It may also be seen from Table V that the more slowly reacting material exhibits not only the greater activation energy but also the greater frequency factor. Consequently, the dominating factor in the determination of the relative rates at which the isomers react is the activation energy.

TABLE V

ACTIVATION ENERGIES AND FREQUENCY FACTORS OF THE
ISOMERIC FORMS OF $[Co(HY)Br]^-$

	A (sec.$^{-1}$)	E_A (kcal./mole)
Isomer A	6.3×10^9	20.0
Isomer B	4.0×10^{10}	22.5

Two alternate viewpoints may be adopted with regard to the isomeric composition of this compound. The substance may consist of *two* isomeric species, present in different amounts (28%, isomer A; 72%, isomer B). The relative abundances may either reflect the relative stabilities of the two isomers (assuming synthesis under equilibrium conditions) or indicate that an isomer fractionation associated with isolation and purification favors isomer B. The alternate possibility assumes that all *three* of the expected isomers are present and that two of them undergo reaction at very nearly identical rates. This point of view is in agreement with the similarity in structure of two of the isomers as compared to the third (as discussed above). It is suggested that the isomer content of the acidopentadentate EDTA and HETA complexes warrants detailed study by more direct techniques. Preliminary results of fractional crystallizations
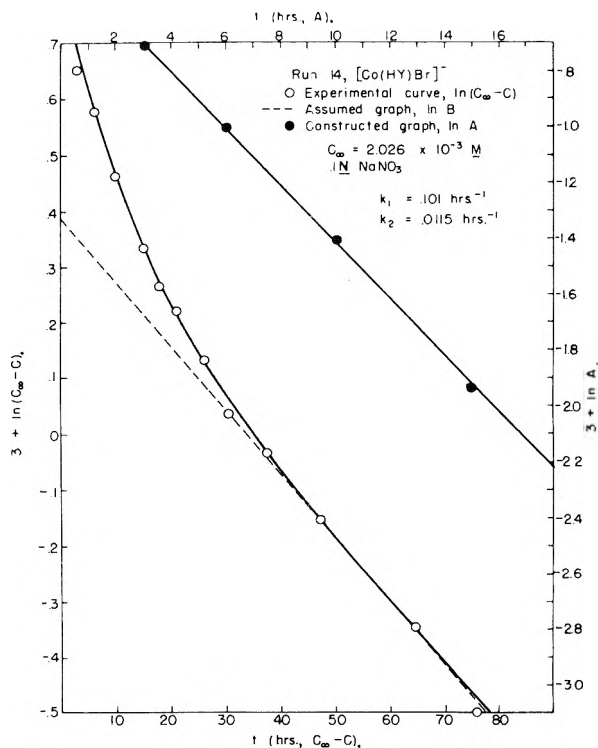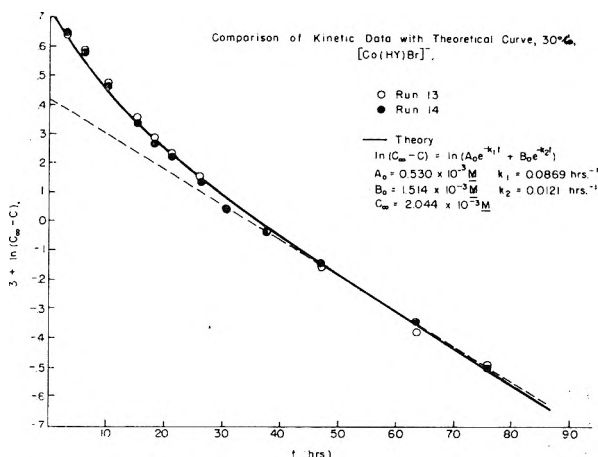

Fig. 2.

Fig. 3.—Comparison of kinetic data with theoretical curve, 30°, $[Co(HY)Br]^-$.

carried out in these laboratories indicate the existence of at least two isomers in the case of the compound $Na[Co(YOH)NO_2]$.

DISCUSSION

R. E. MEEKER.—I should like to suggest that the acceleration in alkali may result from replacement of a carboxyl group of EDTA by hydroxide ion in the coördination sphere. This hydroxo group would then accelerate the S_N1 dissociation of the bromo group through pi-bonding as described by Pearson and Basolo (*J. Am. Chem. Soc.*, **78**, 4847 (1956)). The first step probably is really the entry of solvation water into the coördination sphere when a carboxyl group lets go, followed by rapid acid–base equilibration in alkali to convert the aquo group to a hydroxo group.

Have you any evidence for or against this temporary release of a carboxyl group to give a tetradentate EDTA intermediate?

D. H. Busch.—Your suggestion is quite good and is of a nature which had not occurred to us. I do not believe that we have any strong evidence for or against this intermediate; however, the data in basic media will test your mechanism very nicely. A single factor troubles me. I fail to see why the dissociation of a carboxyl group would be

rapid, and therefore not rate determining, while the dissociation of a bromide ion is slow and rate determining (data in acid). In fact, I would expect acid acceleration rather than base acceleration if the replacement of a carboxyl group by a water molecule was the first step in the process. I suspect that protonation of the coördinated carboxyl groups might labilize them. As you recall, we did observe that a slight acid acceleration occurs in the systems studied at $pH \sim 0$; however, the reacting species was also shown to be altered. It might be $[Co(H_2Y)Br]$.

THE AQUEOUS CHEMISTRY OF INORGANIC FREE RADICALS.[1] I. THE MECHANISM OF THE PHOTOLYTIC DECOMPOSITION OF AQUEOUS PERSULFATE ION AND EVIDENCE REGARDING THE SULFATE-HYDROXYL RADICAL INTERCONVERSION EQUILIBRIUM

By Maak-Sang Tsao and W. K. Wilmarth

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, Cal.

The photolytic reaction $S_2O_8^- + H_2O \rightarrow 2HSO_4^- + \frac{1}{2}O_2$ has been studied at $32 \pm 2°$ using 2537 Å. light. At a fixed light intensity the rate is first order in persulfate ion and is essentially independent of the acidity from 0.20 N NaOH to 1.0 N HClO₄, although there is a slight increase in rate with increasing acidity, especially at low persulfate concentration and low ionic strength. Neither hydrogen ion nor sulfate ion alone influences the rate of the process (quantum yield), but the presence of both at moderate concentrations strongly inhibits the photolysis. At high values of $(H^+)(SO_4^-)$ corresponding to saturation inhibition the rate decreases not to zero, but to a value of approximately 20% of that under uninhibited conditions. Both the inhibition studies and tracer experiments using O^{18} and S^{35} suggest that the photolytic decomposition occurs through two parallel reaction paths. One of these, designated as the k_1' path, is inhibited by bisulfate ion (*i.e.*, by $(H^+)(SO_4^-)$), with the inhibition producing an induced S^{35} exchange between labeled sulfate and unlabeled persulfate. Oxygen produced in the k_1' path has the same O^{18} content as the water solvent. The other reaction path, characterized by a rate constant k_2', is not inhibited by bisulfate ion, does not induce the S^{35} exchange, and produces water with an O^{18} content which is the average of that of the solvent and the persulfate ion. By way of mechanism it has been suggested that the k_1' path generates sulfate radicals, followed by the rapid reversible equilibrium $SO_4^- + H_2O = OH + H^+ + SO_4^-$. At $(H^+)(SO_4^-) \geq 0.02$ the position of the equilibrium lies far to the left and sulfate radicals recombine to form persulfate ions, thus accounting for the bisulfate inhibition and the S^{35} exchange data. At lower $(H^+)(SO_4^-)$ hydroxyl radicals predominate and ultimately leave the system as molecular oxygen. The tentative assumption is made that HSO_5^- is initially formed in the k_2' path, but that it is destroyed rapidly, forming molecular oxygen by a radical induced chain decomposition.

Introduction

The present paper[2] deals with the possibility of generating sulfate and hydroxyl radicals by the photolysis of aqueous peroxydisulfate ion, hereafter referred to as persulfate ion. Experiments using S^{35} and O^{18} and kinetic data, all reported below, yield more detailed information about the mechanism of the photolytic decomposition of persulfate ion than has hitherto been available.[3-5] Of particular interest in this study are observations which seem to yield direct information about reaction 1, the hydroxyl–sulfate radical interconversion, a process of major interest both in its own right and in the field of radiation chemistry where aqueous sulfuric acid has most commonly been used as a solvent.

$$SO_4^- + H_2O \longrightarrow OH + H^+ + SO_4^{--} \quad (1)$$
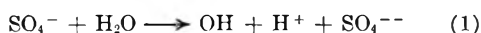
Of interest also is the implication of the present work that hydroxyl radical is not converted to its conjugate acid H_2O^+, at least in sulfuric acid solutions, although this species recently has been

postulated to explain the results of certain radiation experiments.[6]

Experimental

Materials.—The water used in the photolysis experiments and in the recrystallization of chemicals was redistilled from alkaline persulfate solution, with the steam being transported with an oxygen carrier gas through a furnace maintained at 800–900°. All chemicals were of a reagent grade and, except for the J. T. Baker 72% perchloric acid and Baker and Adamson concentrated sulfuric acid, they were recrystallized at least once before use. The water enriched in H_2O^{18} was obtained from the Stuart Oxygen Co. Before use, it was also purified by the procedure outlined above. The O^{18} content was determined by mass spectrometry, using the carbon dioxide equilibration procedure. Radioactive S^{35} was obtained from the Isotope Specialties Co., Inc., in the form of 0.17 N sulfuric acid, with a specific activity of 735 $\mu c./ml$. It was used without further purification.

The Rate of Photolysis.—Except in the quantum yield experiments, the reaction vessels were test-tubes made of No. 791 Vycor glass with a diameter of 3.5 cm. and a wall thickness of approximately 2.0 mm. During an experiment the vessels were capped with cork stoppers covered with aluminum foil, with each stopper containing a glass tube and ground joint which could be opened so that aliquots of the solution could be removed with a pipet for analysis. The source of irradiation was a 4-watt low pressure G.E. germicidal lamp (G4T4/1) equipped with a 58G827 ballast. Since 96% of the ultraviolet radiation from this lamp is of wave length 2537 Å., and since persulfate ion does not absorb appreciably at the longer wave lengths emitted by the lamp, the lamp may be considered as a monochromatic

(1) This work was supported by the Atomic Energy Commission.

(2) Later papers in this series will be concerned with the generation of these radicals by the thermal decomposition of persulfate ion.

(3) L. J. Heidt, J. B. Mann and H. R. Schneider, *J. Am. Chem. Soc.*, **70**, 3011 (1948).

(4) L. J. Heidt, *J. Chem. Phys.*, **10**, 297 (1942).

(5) R. H. Crist, *J. Am. Chem. Soc.*, **54**, 3939 (1932), and earlier papers in this series.

(6) J. Weiss, *Experientia*, **XII**, 280 (1956).

light source. In general, two experiments were performed simultaneously, with the two vessels arranged at equivalent positions approximately 8.5 cm. from the center of the lamp. Aside from preliminary experiments not reported here, the persulfate concentration was limited to the region 0.0005–0.0025 M. In the more dilute solutions there was essentially no diminution in the intensity of the light as it passed through the reaction vessel. At the maximum persulfate concentration the error arising from neglect of the internal screening may have been as large as 20%, a figure several times larger than the irreproducibility arising from variations in light intensity, aging of the lamp and analytical errors. Below 0.0005 M persulfate, errors larger than 10% would have been encountered because of inadequacies in the methods of analysis.

In each photolysis experiment 25.0 ml. of solution was used, with four or five 3.0-ml. aliquots being removed at suitable time intervals for analysis. The iodometric method of analysis yielded a separate determination of persulfate ion, HSO_5^- and hydrogen peroxide.[7]

Measurement of Quantum Yield.—The quantum yield experiments were carried out using the uranyl oxalate actinometer, with oxalic acid and uranyl oxalate concentrations at 0.005 and 0.001 M, respectively. The procedure was that described by Noyes and Leighton,[8] with the exception that the undecomposed oxalate was determined spectrophotometrically.[9] Six measurements were carried out using 0.0025 M persulfate solutions containing 0.71 M sodium perchlorate and 0.29 M perchloric acid; these are conditions which should yield the same ionic strength as that employed in the experiments presented in Fig. 1. Assuming a quantum yield of 0.65 for the uranyl oxalate actinometer, we obtain a quantum yield of 0.79 ± 0.07 for the persulfate photolysis. The accuracy of this value may be less than the reproducibility, because the solutions were not stirred during the photolysis.

S³⁵ Exchange.—The photolysis of solutions containing $H_2S^{35}O_4$ was carried out using the reaction vessels and techniques described above, with the aliquots serving for both iodometric analysis and radio-chemical analysis for S³⁵. After removal from the reaction vessel, each 3.0-ml. aliquot was added to a 15.0-ml. centrifuge cone where the sulfate ion was precipitated with excess 1.0 M BaCl₂, removed by centrifugation and discarded. To ensure complete removal of the labeled sulfate ion, a small amount of inactive sulfuric acid then was added, and the sulfate ion was again precipitated and discarded. The concentration of undecomposed persulfate now was determined iodometrically in the usual manner with only a fraction of the total solution. The remainder of the solution, now of known persulfate concentration, was added to a second 15.0-ml. centrifuge tube containing excess BaCl₂ solution and enough inactive persulfate to reduce the S³⁵ concentration to an activity convenient for handling and counting. The persulfate ion was decomposed completely by heating the sample in a water-bath and the barium sulfate which was produced was washed twice with ethanol and then transferred as a slurry to an aluminum counting disk. After drying, the surface of the precipitate was "smoothed" by applying pressure with a steel piston of the same size as the indented portion of the counting disk.[10]

Each sample contained more than 20 mg. BaSO₄/cm.², a value well above "infinite thickness," and consequently the measured activity was directly proportional to the specific activity of the sample. The S³⁵ analysis was performed using a Nuclear Chicago Corp. flow counter and a Berkeley Model 100 decimal scaler. In general, the background was approximately 200 counts/min. In a given experiment the activity of the samples varied from background activity, when the samples were removed at short times, to values as large as 3000 counts/min. at later times in the experiment. Before carrying out the exchange ex-

periments, the method of separation was tested and found to be satisfactory.

Oxygen Exchange.—In these experiments the Vycor cell was equipped with a ground joint and stopcocks so that the solutions could be evacuated to remove dissolved air before photolysis. The solvent water contained O^{18} at approximately a sevenfold enrichment; there was no appreciable dilution in a given experiment by addition of either the solid reagents or the small amount of concentrated perchloric acid. Condensation of water in the cooler regions near the top of the vessel was prevented by gentle warming of this portion of the apparatus with a nichrome heater. In a given experiment the photolysis was continued until approximately half of the persulfate had been decomposed. The oxygen was then transferred to a gas sampling tube and analyzed with a Nier type mass spectrometer. The residual solution was analyzed for persulfate in the usual manner.

Results

At the fixed light intensity employed in the present work the rate of disappearance of persulfate in any given experiment was represented by a rate constant k defined in terms of equation 2

$$-\frac{d(S_2O_8^{--})}{dt} = k(S_2O_8^{--}) \qquad (2)$$

Numerical values of k were calculated from the slope of the straight line drawn through the points in a plot of ln $(S_2O_8^{--})$ *versus* time. As the first four entries in Table I indicate, in alkaline solution at fixed ionic strength k proved to be independent of the persulfate concentration, although a slight decrease in rate might have been anticipated at the maximum concentration. At any given ionic strength k was found to increase slowly with increasing acidity, with the over-all increase being somewhat less than a factor of two. This trend is best illustrated by a comparison of experiments 4–7, but it may also be seen in experiments 8, 9 and 11 and in 3, 15 and 16. Experiments 1, 8 and 9 and

TABLE I

PHOTOLYSIS OF AQUEOUS PERSULFATE ION AT 32 ± 2°

No.	$(S_2O_8^{--})$, M	pH	μ^a	Medium	$k \times 10^5$, sec.⁻¹
1	0.0025	13.3	0.20	.2 N NaOH	5.59
2	.0005	13.3	.20	.2 N NaOH	5.30
3	.0005	13.3	.20	.2 N NaOH	5.30
4	.0010	13.3	.20	.2 N NaOH	5.60
5	.0010	6.7[b]	.20		6.42
6	.0010	3.0[b]	.20		7.21
7	.0010	0.7	.20	.2 N HClO₄	7.42
8	.0025	13.3	1.0	.2 N NaOH	4.84
9	.0025	13.3	1.0	.2 N NaOH	4.96
10	.0025	5–2.5	0.0	Unbuffered	7.10
11	.0025	5–2.5	1.0	Unbuffered	6.15
12	.0025	3.0[b]	1.0	0.1 M Na₂SO₄	5.63
13	.0025	3.0[b]	1.0	.1 M Na₂SO₄	5.66
14	.0025	0.5	1.0	.29 HClO₄	5.26 ± 0.19[c]
15	.0005	0.5	1.0	.29 HClO₄	7.00
16	.0005	0	1.0	1.0 N HClO₄	7.20
17	.0005	3.0[b]	0.2		8.43

[a] The ionic strength, defined as $\mu = \frac{1}{2} \Sigma C_i Z_i^2$, was adjusted by addition of sodium perchlorate. [b] These solutions contained phosphate buffers. [c] Based on six experiments carried out under these conditions.

10 and 11 suggest that there is a decrease in k with increasing ionic strength, an effect noted by earlier workers. The remaining experiments in the table

(7) The iodometric method of analysis will be described in detail in a paper, The Aqueous Chemistry of Inorganic Free Radicals. The Kinetics and Mechanism of the Reaction of Peroxydisulfate Ion and Bromide Ion in Aqueous Solution, to be submitted to the *J. Am. Chem. Soc.* for publication.

(8) W. A. Noyes and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, Chapter 2.

(9) J. N. Pitts, J. P. Margerum, R. P. Taylor and W. Prim, *J. Am. Chem. Soc.*, **77**, 5499 (1955).

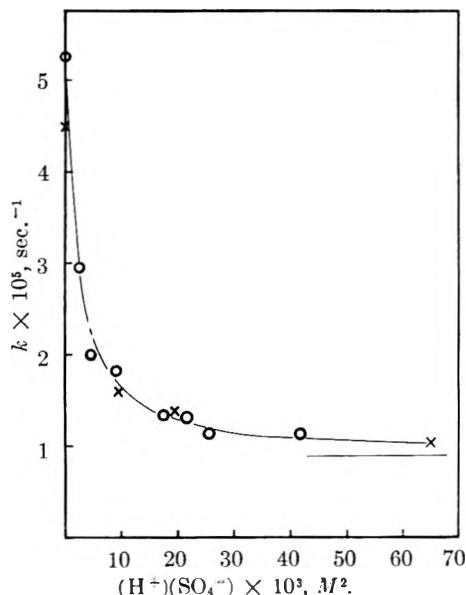(10) A. W. Adamson and R. G. Wilkins, *ibid.*, **76**, 3379 (1954).

Fig. 1.—Bisulfate inhibition at $32 \pm 2°$: $\bigcirc$, $(H^+) = 0.27 \pm 0.02$; $\times$, $(H^+) = 1.25$.

serve to show that neither hydrogen ion nor sulfate ion alone influences the rate very appreciably although, as we shall see below, the presence of both ions produces a considerable inhibition. Experiments 11, 12 and 13 show that at pH 3, 0.10 M sodium sulfate produces at most a minor decrease in rate. In experiments 15, 16 and 17 at higher acidity there is no evidence of inhibition by perchloric acid, a result reported by Heidt.[4]

The marked inhibition resulting from the presence of appreciable concentrations of both hydrogen and sulfate ions is illustrated by the data presented in Fig. 1, where we have plotted k versus the product $(H^+)(SO_4^=)$. In the majority of these experiments carried out at $\mu = 0.92 \pm 0.08$ and $(H^+) = 0.27 \pm 0.02$ only relative values of $(H^+)(SO_4^=)$ are known with any accuracy. Since the hydrogen ion concentration was constant, the data really represent only a systematic variation in sulfate ion concentration. A more extensive study of the effect of variation in hydrogen ion concentration is now under way and will be presented in a later publication. The absolute values of the quantity $(H^+)(SO_4^=)$ are rendered uncertain because of the necessity of correcting for the presence of unionized bisulfate ion, a species whose concentration was calculated by assuming rather arbitrarily that the second dissociation quotient of sulfuric acid had a value of 0.15 in the medium under consideration.[11] The remaining four experiments presented in Fig. 1 were carried out at $(H^+) = 1.25$, and $\mu = 2.0$. In view of the uncertainty regarding the effect of medium upon the extent of dissociation of bisulfate ion, the second dissociation quotient of

sulfuric acid was regarded as an adjustable parameter in these experiments; the value of 0.21 was chosen so that the points would fall on the smooth curve drawn through the data at $\mu = 0.92$. Although the four experiments confirm qualitatively the existence of bisulfate inhibition at the high acidity, the rate constants may not be of high accuracy since it was necessary to make a correction for the dark reaction using the thermal data presented below. In the extreme case the correction was as large as 40%. The major point of interest in Fig. 1 is that saturation inhibition would appear to reduce the rate not to zero but to a value of approximately 20% of that observed in the absence of appreciable concentrations of hydrogen and sulfate ions. This behavior obviously suggests that upon photo-excitation the persulfate ion decomposes by either of two parallel paths only one of which is subject to inhibition. For convenience in later discussion we will refer to the inhibition as bisulfate inhibition, although actually it is probably a coincidental feature of the system that inhibition arises at a product of hydrogen and sulfate ion concentrations which corresponds to a quite appreciable bisulfate concentration. Also it will be convenient to refer to the bisulfate inhibition reaction path as the k_1' path, to designate the bisulfate insensitive path as the k_2' path, and to define a rate constant k_0 which refers to the photolysis rate in the absence of bisulfate inhibition as $k_0 = k_1' + k_2'$. The numerical value of k_2' cannot be obtained with any certainty from Fig. 1, since an extrapolation to infinite $(H^+)(SO_4^{--})$ would be required. However, by plotting k vs. $1/(H^+)(SO_4^{--})$, as in Fig. 2, a fairly accurate value of k_2' may be obtained from only a short extrapolation to a zero value of the abscissa. The value of k_2' so obtained is indicated by the horizontal line in the lower right-hand corner of Fig. 1. The significance of the theoretical curve in Fig. 1 will be discussed below.

Earlier studies have shown that the thermal decomposition of persulfate also proceeds by two reaction paths. Both of these are kinetically first order in persulfate concentration, one is pH independent and the second, important above a pH of 3, is first order in hydrogen ion. Following the nomenclature of Kolthoff and Miller,[12] the rates of the two thermal paths may be characterized by the quantities $k_1(S_2O_8^{--})$ and $k_2(H^+)(S_2O_8^{--})$. Under the conditions employed at the higher acidity in the experiments presented in Fig. 1, calculations indicate that the k_2 path would account for more than 99% of the total thermal reaction. By following the thermal reaction for long periods of time it was possible to study the rate of this process under conditions identical with those employed in the photolysis studies. In three experiments at $T = 32.0°$, $\mu = 2.0$, $(H^+) = 1.25$ and $(H^+)(SO_4^{--})$ equal to 9.4×10^{-3}, 1.95×10^{-2} and 6.5×10^{-2}, it was established that the k_2 thermal path was not inhibited by bisulfate ion. Under these conditions k_2 was found to have the value 5.73×10^{-6} liters mole^{-1} sec.$^{-1}$.

In the experiments under consideration at (H^+)

(11) In designing these experiments it was our intention to work at variable sulfate ion concentrations, but with fixed values of $(H^+) = 0.286$ and $\mu = 1.0$. At the time it was assumed that the second dissociation constant of sulfuric acid had the value 0.38, on the basis of data presented in a paper by M. Kerker, *J. Am. Chem. Soc.*, **79**, 3664 (1957). While this value may be a good choice for pure sulfuric acid, the system considered by Kerker, the calculations and data later presented by C. F. Baes, Jr., *ibid.*, **79**, 5611 (1957), suggested that the value of 0.15 ± 0.05 might represent a better choice for a medium containing large concentration of sodium ion.

(12) I. M. Kolthoff and I. K. Miller, *ibid.*, **73**, 3055 (1951).

= 1.25, the rate constants for both the thermal and photolytic reactions were based upon the rate of disappearance of persulfate ion. However, it should be noted that quite different reaction products were produced in the two series of experiments. In the photolysis reactions only oxygen and sulfate ion were formed, whereas in the thermal reaction HSO_5^- was the predominant product. Despite this apparent difference, further experiments showed that HSO_5^- might also have been an initial, but unstable product in one or both of the paths of the photolysis reaction. This possibility was revealed by studying the photolysis of a solution which initially contained $(S_2O_8^=) = 0.0014$, $(HSO_5^-) = 0.0009$ and $(H^-) = 1.25$. In this solution the persulfate ion was photolyzed at about the expected rate, but the HSO_5^- disappeared very much more rapidly, and soon reached a concentration which was undetectably small. Calculation indicated that the quantum yield for the disappearance of HSO_5^- would greatly exceed unity, even if based upon the absorption of light by both the persulfate and HSO_5^- ion. Evidently under these photolytic conditions HSO_5^- is consumed by a quite efficient chain decomposition reaction.[13]

Previous studies have shown that there is no exchange of persulfate and S^{35} labeled sulfate under a variety of experimental conditions, including temperatures high enough to lead to decomposition of the persulfate ion.[14-17] In the experiments summarized in Table II it was found that under photolytic conditions the S^{35} exchange could readily be observed, but that the rate of exchange became appreciable only when the photolysis was inhibited by bisulfate ion. On the basis of the mechanism and equations developed in the Discussion section, it may be concluded that the rate of sulfur exchange should be characterized by a rate constant k_s defined in terms of equation 3.

$$- \ln (1 - F_B) = k_s t + \frac{k_B}{k} \ln \left(\frac{a+b}{a} - \frac{b}{a} e^{-kt} \right) \quad (3)$$

In equation 3 the various undefined symbols have the following significance: a = the total gram atoms of sulfur initially present as sulfate and bisulfate ion; b = total gram atoms of sulfur initially present as persulfate ion; $F_B = (S_B - S_{B0})/(S - S_{B0})$, where S_{B0} and S_B are the specific activity of the persulfate ion at time zero and t, respectively, and S = the specific activity which would be calculated for the persulfate ion, assuming complete isotopic equilibrium in the system.

Tracer experiments also were carried out using unlabeled persulfate ion in O^{18} enriched water. In each experiment the persulfate was photolyzed until at least half had been decomposed and the

(13) Experiments have also shown that at $T = 50°$ and $(H^+) = 0.10$, HSO_5^- also disappears rapidly in the thermal system, although it would be relatively inert at a higher acidity. The significance of these observations will be discussed in a later paper.

(14) P. C. Riesebos and A. H. W. Aten, Jr., *J. Am. Chem. Soc.*, **74**, 2440 (1952).

(15) H. Elkeles and C. Brosset, *Svensk, Kem Tidskr.*, **65**, 26 (1953).

(16) R. L. Eager and K. J. McCallum, *Can. J. Chem.*, **32**, 692 (1954).

(17) None of the studies in the literature were carried out in the pH range 2–3, where exchange may be observed, as indicated in the later sections of this paper.
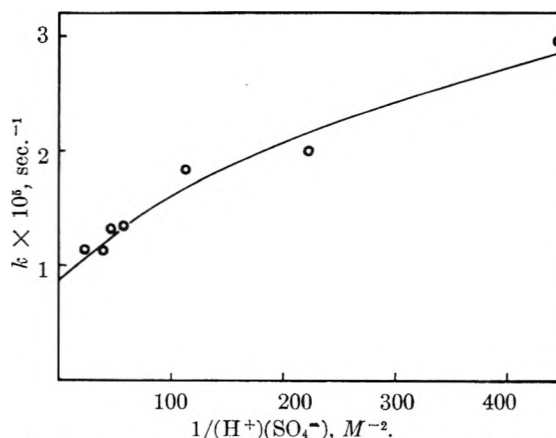

Fig. 2.—k versus $1/(H^+)(SO_4^-)$ at $(H^+) = 0.27 \pm 0.02$.

oxygen which had accumulated was then subjected to mass spectrometer analysis. In all, three such experiments were completed, and the results are listed in column four of Table III as N_{obsd}, the observed atom fraction of O^{18} in the molecular oxygen.

TABLE II

PHOTOLYTIC INDUCED EXCHANGE OF SULFATE AND PERSULFATE ION

All experiments were at $T = 32 \pm 2°$, $\mu = 1.0$ and $(S_2O_8^=) = 0.0025$

No.	$(H^+)(SO_4^-)$	Medium	$k_S \times 10^5$, sec.$^{-1}$	$k \times 10^4$, sec.$^{-1}$	$(k_S + k) \times 10^5$ sec.$^{-1}$
549	0.026	0.29 N HClO$_4$	3.93	1.08	5.01
548	.0045	.29 N HClO$_4$	3.35	2.00	5.35
550	< .0002^a	.29 N HClO$_4$	0.1	5.25	5.4
569	.0000	.20 N NaOH	<1.7 × 10^{-3}	4.94	4.94

^{a} An average value for an experiment where $(H^+)(SO_4^-)$ varied over the range 1.3×10^{-5} to 2.5×10^{-4}; the corresponding value of k_a was not determined with high accuracy.

TABLE III

THE PHOTOLYSIS OF PERSULFATE IN O^{18}-ENRICHED WATER

In all experiments $(S_2O_8^=)_0{}^a = 0.0025$, $\mu = 0.92 \pm 0.08$, $H^+ = 0.29$ and $T = 32 \pm 2°$

No.	$(H^+)(SO_4^-)$	$k \times 10^5$, sec.$^{-1}$	N^b (obsd.)	N (calcd.)
524	0.026	1.10	0.0196	0.0199
523	.0045	2.18	.0234	.0252
522	< .0002	5.00	.0293	.0283

^{a} Initial concentration. ^{b} Atom fraction of O^{18} in the O_2.
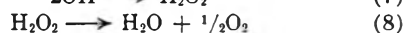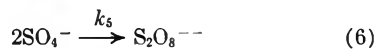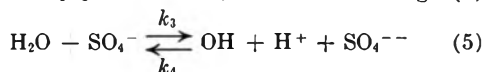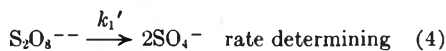
Discussion

In view of the satisfactory reproducibility and a quantum yield of less than unity, it will be assumed that in the photolysis persulfate ion is not consumed by a chain decomposition although, as we shall suggest below, chain processes may destroy a possible reaction intermediate, the HSO_5^- ion. Any reasonable interpretation of the present data would seem to require that the photolysis proceed by two parallel reaction paths. Other alternatives proposed by earlier workers are no longer tenable, since they would fail to account for the results of the S^{35} and O^{18} experiments. The mechanism to be presented below provides an explanation for not only our own data but the other data in the literature as well, with the possible

exception of Heidt's observation that perchloric acid inhibited the photolysis.[4] Even here the results may well be in agreement with our own, since the supposed perchloric acid inhibition was not present in the initial stages of the experiment and was probably caused by the reaction product sulfuric acid formed in his more concentrated persulfate solutions.

The mechanism to be proposed for the more important k_1' photolysis path involves the generation of sulfate and hydroxyl radicals and, in general, is entirely analogous to that suggested for the k_1 path of the thermal decomposition,[12] except for the mode of activating the persulfate ion. As a justification for this procedure, there is a wide variety of experimental evidence, but only a fraction of this is available in the present paper and in the chemical literature.[18] Consequently, several of the more pertinent unpublished observations will be presented in summary at this point. Perhaps most important is the observation that under appropriate conditions the k_1 thermal path induces the sulfur exchange of sulfate and persulfate ion, just as the k_1' path does.[19] Of almost equal significance is the fact that both the k_1 and k_1' reactions induce the homogeneous hydrogenation of persulfate ion, a chain reaction which is almost certainly initiated by a radical attacking the hydrogen molecule. Lastly, we note that the O^{18} tracer experiments indicate that both reactions generate molecular oxygen which originates not in the persulfate ion, but in the water solvent.

A detailed although somewhat oversimplified mechanism for the k_1' path may be presented in terms of the equations

$$S_2O_8^{--} \xrightarrow{k_1'} 2SO_4^{-} \quad \text{rate determining} \quad (4)$$

$$H_2O - SO_4^{-} \underset{k_4}{\overset{k_3}{\rightleftarrows}} OH + H^+ + SO_4^{--} \quad (5)$$

$$2SO_4^{-} \xrightarrow{k_5} S_2O_8^{--} \quad (6)$$

$$2OH \xrightarrow{k_6} H_2O_2 \quad (7)$$

$$H_2O_2 \longrightarrow H_2O + {}^1/{}_2O_2 \quad (8)$$

$$H_2O_2 + S_2O_8^{--} \longrightarrow 2H^+ + 2SO_4^{--} + O_2 \quad (9)$$
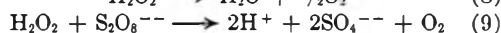
Of major importance is the assumption that the interconversion of sulfate and hydroxyl radical by reaction 5 closely approaches equilibrium, despite the very short half-lives of the radical species involved. Reaction 5 would then provide for sulfur exchange between sulfate radicals and labeled sulfate ion and for the production of labeled persulfate under conditions where reaction 6 was favored. Reactions 5 and 6 also account for the apparent inhibition of the photolysis of bisulfate ion, since at high values of $(H^+)(SO_4^{--})$ the position of the equilibrium in reaction 5 will be far to the left, sulfate radicals will predominate, and persulfate

will be regenerated by reaction 6. Conversely, low $(H^+)(SO_4^{-})$ would lead to the formation of hydroxyl radicals and to the production of hydrogen peroxide by reaction 7, except in alkaline solution, a restriction which will be discussed below.

Equations 8 and 9 do not carry mechanistic significance; they serve only to indicate that hydrogen peroxide may disappear from the system by at least two paths, only one of which involves the concurrent consumption of persulfate ion. Both of these reactions are rapid enough so that the steady-state concentration of hydrogen peroxide would be undetectably small. They proceed by rather complicated chain mechanisms which we have studied in some detail in the thermal system. It will be necessary to present certain conclusions arising from these studies if the more subtle features of the photolysis are to be appreciated, despite the fact that this brevity and absence of experimental data may make the conclusions seem rather arbitrary. The point of interest is whether hydroxyl radicals may not interact to form oxygen atoms, an exothermic process first proposed by J. Weiss[20]

$$2OH \longrightarrow H_2O + O \quad (10)$$
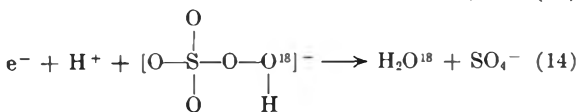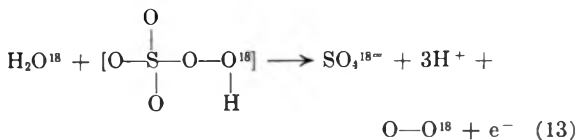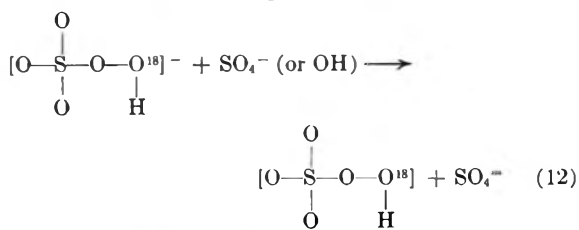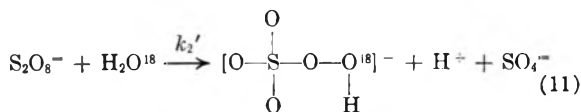$$2O \longrightarrow O_2$$
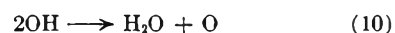
It is our conclusion that something approaching reaction 10 must occur in alkaline solution, although the actual mechanism may involve catalysis by impurities or in other ways be more complicated than equation 10 would suggest. Under these conditions, i.e., at 0.2 N alkali, the rate of disappearance of persulfate would be a true measure of the photolysis rate, with the rate increasing slightly with decreasing ionic strength, a salt effect to be expected for a reaction of the present sort. Conversely, in acid solution formation of peroxide by reaction 7 is relatively efficient, at least at low ionic strength, perhaps because of the relatively low impurity level. As the data in Table I indicate, under these conditions there is a considerable increase in the apparent rate of photolysis because of the secondary consumption of persulfate by peroxide in reaction 9.[21] This secondary decomposition is never particularly efficient, since it never reaches a value of more than 50% that calculated, assuming reactions 7 and 9 to be quantitative. At an ionic strength of unity, the conditions employed in the S^{35} and bisulfate inhibition, it is small enough so that it may be ignored in the calculations outlined below. Lastly, we note that the over-all inhibition in rate of photolysis by inert electrolyte observed by earlier workers[3-5] was caused in part by an effect on the primary process and in part by a decrease in the extent of the secondary decomposition, reaction 9.

(18) Unpublished experiments carried out in this Laboratory include kinetic studies of the reaction of persulfate with molecular hydrogen, with hydrogen peroxide, and with bromide ion.

(19) Experiments by Dr. Maak-Sang Tsao indicate that the exchange occurs only at pH of 2–3, as expected. In more alkaline solution the sulfate radical is converted to the hydroxyl radical, in more acidic solutions the acid-catalyzed thermal path predominates and produces reaction intermediates which act as efficient radical scavengers.

(20) Weiss' point of view is perhaps most clearly presented in the article by J. Weiss, Trans. Faraday Soc., 36, 856 (1940).

(21) In the thermal system where entirely analogous processes occur, it has been possible to detect the magnitude of the persulfate peroxide reaction by the diminution in rate of disappearance of persulfate caused by the addition of bromide ions. Bromide ion acts as a scavenger for hydroxyl radical, thus preventing the formation of hydrogen peroxide and its subsequent reaction with persulfate. A summary of this work may be found in the abstracts of the papers presented at the American Chemical Society meeting in San Francisco on April 13–18, 1958.

Before the exchange and inhibition experiments may be considered quantitatively, it is necessary to postulate a tentative mechanism for the k_2' photolysis path. As a guide we note that, by definition, the process is not inhibited by bisulfate ion. Also, apparently the process does not induce the sulfur exchange of sulfate and persulfate ion. Finally, and perhaps most important in influencing our choice of mechanism, there is the unusual feature that the molecular oxygen generated by this path appears to have an O^{18} content which is the average of that of the persulfate ion and the water solvent. This latter conclusion has strong experimental support. If the alternative assumption were made that the oxygen atoms in the molecular oxygen produced by the k_2' path all originated in the persulfate ion, then k_2' would have only one-half the value of 9×10^{-6} sec.$^{-1}$ obtained from the ordinate intercept of Fig. 2. While there is some scatter of the points in Fig. 2, it is very difficult to believe that the true intercept has a value half that which has been chosen, especially since any theory which we have developed would not predict an abrupt change in slope at low abscissa values.

The O^{18} data may be understood readily in terms of the formation of an unstable intermediate, the HSO_5^- ion, which has solvent labelling only on the terminal peroxide atom, and which ultimately produces molecular oxygen containing both peroxide atoms, just as hydrogen peroxide does.[22] The following mechanism is compatible with this concept. It is presented in detail, despite its tentative nature, primarily to permit a more ready visualization of the route followed by the oxygen atoms. To this end structural formulas and in some instances equations for half reactions have also been adopted.

$$S_2O_8^- + H_2O^{18} \xrightarrow{k_2'} [O-\overset{\overset{\textstyle O}{|}}{\underset{\underset{\textstyle O}{|}}{S}}-O-O^{18}]^- + H^+ + SO_4^- \quad (11)$$

$$[O-\overset{\overset{\textstyle O}{|}}{\underset{\underset{\textstyle O}{|}}{S}}-O-O^{18}]^- + SO_4^- \text{ (or OH)} \longrightarrow$$

$$[O-\overset{\overset{\textstyle O}{|}}{\underset{\underset{\textstyle O}{|}}{S}}-O-O^{18}] + SO_4^= \quad (12)$$

$$H_2O^{18} + [O-\overset{\overset{\textstyle O}{|}}{\underset{\underset{\textstyle O}{|}}{S}}-O-O^{18}] \longrightarrow SO_4^{18=} + 3H^+ +$$

$$O-O^{18} + e^- \quad (13)$$

$$e^- + H^+ + [O-\overset{\overset{\textstyle O}{|}}{\underset{\underset{\textstyle O}{|}}{S}}-O-O^{18}]^- \longrightarrow H_2O^{18} + SO_4^- \quad (14)$$

Despite the apparent complexity of reactions 12, 13 and 14, it may be noted that they constitute a chain mechanism entirely analogous to that usually postulated for the decomposition of H_2O_2, with HSO_5^-, HSO_5 and SO_4^- replacing H_2O_2, HO_2, and OH, respectively.

(22) J. P. Hunt and H. Taube, *J. Am. Chem. Soc.*, **74**, 5999 (1952).

It is now possible to attempt to calculate the rate under the conditions of bisulfate inhibition covered by the data presented in Fig. 1. Before proceeding, it should be recognized that *a priori* there is every reason to believe that HSO_5^- may be formed by combination of hydroxyl and sulfate radicals, a process not included in the simplified mechanism presented above

$$OH + SO_4^- \xrightarrow{k_7} HSO_5^- \quad (15)$$

Reaction 15 would presumably reach its maximum importance at intermediate bisulfate concentrations where hydroxyl and sulfate radicals would be present at roughly equal concentrations. The HSO_5^- arising from this source would presumably disappear rapidly in the chain process discussed above, along with that produced by the k_2' path. When reaction 15 is considered along with equation 4–8, it is possible to derive equation 16, making only the usual steady-state approximations and assuming equilibrium in reaction 5.

$$k = k_1' + k_2' - \cfrac{k_1'}{1 + \cfrac{k_6 K^2}{k_5(H^+)^2(SO_4^-)^2} + \cfrac{2k_7 K}{k_5(H^+)(SO_4^-)}}$$
$$(16)$$

Here, K is the equilibrium quotient for reaction 5, and the other constants have previously been defined as symbols over the appropriate equations. Neglect of reaction 15 would have resulted in a simplification of the last term of equation 16, the quantity which represents the decrease in rate caused by bisulfate inhibition. The simplification referred to would have been the disappearance of the quantity $2k_7K/k_5(H^+)(SO_4^-)$, a result arising from the assumption that k_7 equals zero. In this simplified form the best fit which may be made of the points in Fig. 1 is apparently somewhat outside of the limit of error of the experiment; the inhibition is not as pronounced as that required by an inverse term $(H^+)^2(SO_4^-)^2$. However, if the reasonable assumption is made that $k_7 = 2k_6 = 2k_5$, with the factor of two arising from the greater statistical probability for collision of unlike particles, the theoretical line calculated from equation 16 without simplification approaches within the limit of error of the experimental points.

As a further test of the mechanism we may now consider the quantitative features of the S^{35} exchange. Although the desired relationship may be derived algebraically, it is possible to see intuitively that the rate of the sulfur exchange should exactly equal the decrease in rate caused by bisulfate inhibition, since both phenomena are produced by the occurrence of reaction 6. In the nomenclature employed above the desired relationship may be written as $k_8 = k_0 - k$ and tested, as in the last column of Table II, by the constancy of $k_8 + k$. The derivation of the equation defining k_8 may be made readily by following the methods of Luehr, Challenger and Masters, and integrating equation 4 of their paper for the special case corresponding to our mechanism.[23]

(23) C. P. Luehr, G. E. Challenger and B. J. Masters, *ibid.*, **78**, 1314 (1956). In the notation of these authors our mechanism corresponds to the special case where $R_1(t) = 0$, $v(t) = $ constant, $R_2 = 2k_0 - k(S_2O_8^-)$, and $R_3 = 2k(S_2O_8^-)$.

Lastly, a calculation may be made of the O^{18} content of the molecular oxygen produced under various conditions. Again assuming the simplified mechanism which ignores reaction 15, in any given experiment the fraction of the oxygen coming from the k_1' path will be $(k - k_2')/k$, and the fraction from the k_2' path k_2'/k. With the atom fraction of O^{18} in the solvent and persulfate equal to 0.0307 and 0.0041, respectively, the calculated atom fraction of O^{18} in the molecular oxygen is given by equation 17

$$N_{(calcd)} = \frac{0.0307(k - k_2')}{k} + \frac{0.0174k_2'}{k} \quad (17)$$

The agreement with experiment at high and low $(H^+)(SO_4^-)$ is within the limit of error, but at an intermediate value of $(H^+)(SO_4^-)$, $N_{(calcd)}$ again deviates appreciably from experiment in the direction to be anticipated because of participation of reaction 15.

At this point some consideration should be given to the choice of formula for the sulfate radical and the possible inclusion of the H_2O^+ ion in the proposed reaction mechanism. The formula SO_4^- has been adopted since HSO_4 would almost certainly be a stronger acid than HSO_4^-, although perhaps not as strong as $HClO_4$. Assuming this formula it is then informative to note that the ratio $(H_2O^+)/(SO_4^-)$ is pH independent.

$$SO_4^- + H_2O \rightleftarrows SO_4^- + H_2O^+ \quad (18)$$
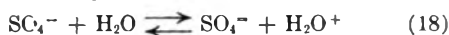
In solutions containing relatively large concentrations of both hydrogen and sulfate ion our mechanism provides an adequate explanation for the S^{35} exchange and the bisulfate inhibition only if the H_2O^+ ion is unimportant compared to the sulfate radical. Under these conditions the ratio $(H_2O^+)/(SO_4^-)$ is presumably smaller than unity, although it is possible that the H_2O^+ ion remains undetected, in part because it is kinetically inert compared to other radicals in the system. In weakly acidic solutions but still at high sulfate ion concentration, where our observations suggest that the sulfate radical is unimportant, the H_2O^+ ion must be correspondingly even less important, since the ratio of the concentrations of the two species must be constant at any given sulfate concentration. In summary, it may be concluded that in our system the H_2O^+ ion is not an important species, being unstable with respect to either the sulfate or hydroxyl radical. Unfortunately, our data do not permit any conclusion to be drawn regarding the possible presence of H_2O^+ in an acidic system not containing sulfate ion.

The present results may be of some importance in the field of radiation chemistry. In 0.8 N H_2SO_4, the aqueous medium most commonly employed, it is generally assumed that along with other products, the radiation produces the "hydroxyl radical," although it has long been recognized that "the formula might better be written $H_2SO_5^-$ or HSO_4, and it is called OH throughout this paper merely to avoid confusion."[24] Although the recognition of this complexity may be quite wide-spread, many workers have studied the competition of several species for the "hydroxyl radical" and on the basis

of their experiments have tabulated relative values of rate constants. Although the hydroxyl-sulfate radical equilibrium may be established in our system where the only competing process is bimolecular reactions of radicals, it is not evident that equilibrium would be established in the presence of high concentrations of radical scavengers. The possibility therefore exists that the relative rate constants for the different scavengers are in themselves composite quantities, representing the relative reaction rates of the scavenger with more than one radical.[25]

Very recently it has been reported that both persulfate ion and HSO_5^- are formed in the Co^{60} bombardment of 2.5 M sulfuric acid and in lesser but still detectable amounts in 0.4 M acid.[26] If our interpretation of the photolysis data is correct persulfate ion should be produced whenever $(H^+)(SO_4^-)$ exceeds a value of about 0.02. The failure to detect persulfate ion after irradiation of such dilute solutions suggests it may be destroyed immediately after formation by other irradiation products. Plans have been made to test this postulate by carrying out S^{35} experiments of the sort described above in irradiated systems.

DISCUSSION

H. TAUBE.—Does your work furnish evidence for the extent to which the association of H^+ and OH takes place?

W. K. WILMARTH.—This point was not discussed in detail in the oral presentation, but it is covered in the complete paper.

H. TAUBE.—Is it at all certain that the reaction producing the intermediate which reduces $S_2O_8^-$ is sensitive to ionic strength? Presumably an impurity in the NaClO₄ could cause the decrease in rate of formation of the intermediate.

W. K. WILMARTH.—Rather extensive kinetic experiments have been carried out in an effort to learn the mechanistic details of a seemingly simple reaction, the self-destruction of hydroxyl radicals. Despite the rather large amount of data now available, no completely satisfactory mechanism can yet be written. However, it is clear that the fate of hydroxyl radicals depends to a considerable extent upon the presence of trace impurities, as you suggest. By contrast, sulfate radicals appear to be well behaved species, in so far as their interaction with impurities is concerned.

In summary, it can be said that the production of peroxide is a reasonably efficient process if the ionic strength is low and the acidity great enough to dissolve heavy metal hydroxides. However, at pH 6 our kinetic studies should have revealed the formation of hydrogen peroxide; it does not seem to form under these conditions or in more alkaline solutions. At present, our only explanation is based on the assumption that heavy metal ions are particularly efficient

(24) A. O. Allen, *Radiation Research*, **1**, 85 (1954).

(25) In a communication to the Editor, *J. Am. Chem. Soc.*, **78**, 1768 (1956), J. T. Sworski has discussed the possible competition of hydroxyl and sulfate radicals for cerous ion and formic acid. For later work see J. T. Sworski, *Radiation Research*, **6**, 645 (1957).

(26) M. Daniels, J. Lyon and J. Weiss, *J. Chem. Soc.*, 4388 (1957).

catalysts for some process resembling reaction 10 when they are present as very low molecular weight colloids. I

would be happy to find an alternative to this admittedly not very appealing mechanism.

THE AQUEOUS CHEMISTRY OF INORGANIC FREE RADICALS.[1] II. THE PEROXYDISULFATE INDUCED EXCHANGE OF OXYGEN ATOMS BETWEEN WATER AND MOLECULAR OXYGEN AND EVIDENCE REGARDING THE ACIDITY CONSTANT OF THE HYDROXYL RADICAL

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The radical catalyzed exchange of O^{18} between water and molecular oxygen has been studied at 60°, using the thermal decomposition of persulfate ion as a means of generating the radicals. In each exchange experiment the persulfate concentration may be assumed to be constant, since the thermal decomposition was very much slower than the exchange reaction and could be ignored. The exchange process was found to proceed by a chain mechanism, with a chain length of unity being defined as exchange of two oxygen atoms for each persulfate ion which decomposed. In solutions ranging from pH 3 to 11 the chain length was approximately constant, with the value of 4.3 ± 1.5 obtained at an oxygen pressure of 0.5 atm. As the alkalinity was increased above pH 11 at the same oxygen pressure the chain length first increased rapidly, then levelled off to a value of 450 above 0.2 N alkali. In this region of maximum rate, the only condition investigated, the chain length was found to increase linearly with increasing persulfate concentration. In the proposed mechanism it has been assumed that the decomposition of persulfate generates OH and O⁻, the catalysts for the exchange, by reaction of water with sulfate radical, the initial decomposition product. In solutions more alkaline than pH 11, neutralization of hydroxyl radical occurs with increasing participation of the highly active catalyst O⁻ in the exchange reaction. The constancy in chain length in strongly alkaline region suggests that essentially complete neutralization of the hydroxyl radical has been achieved, but the interpretation here is complicated somewhat by the possible action of trace impurities in the alkali as radical scavengers.

Introduction

In recent years several studies have shown that there is a catalyzed exchange of oxygen atoms between water and molecular oxygen in systems which may reasonably be assumed to contain the hydroxyl radical or a species derived from it.[2-5] On the basis of their observation that the exchange

$$H_2O + O_2^{18} \longrightarrow H_2O^{18} + O_2 \tag{1}$$
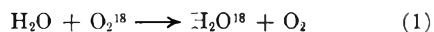
seemed to occur at an appreciable rate only in alkaline solution, Hart, Gordon and Hutchison first made the interesting suggestion that the catalysis involves not the hydroxyl radical itself, but instead its conjugate base, the O⁻ ion,[2] with the exchange proceeding through the reversible formation of the symmetrical species O_3^-.[4]

$$OH + OH^- \rightleftharpoons O^- + H_2O \tag{2}$$
$$O_2^{18} + O^- \longrightarrow O_2 + O^{18-}$$
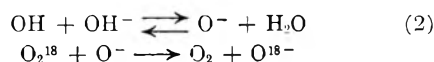
The present study of the radical catalyzed exchange of water and molecular oxygen was designed to yield more detailed information about the acidity constant of the hydroxyl radical. The thermal decomposition of persulfate ion was used as a means of generating the radicals, since the general features of the thermal decomposition mechanism seem to be well understood.[6,7] Further, its use had the added advantage that it permitted a comparison of the exchange data with

our other unpublished free radical studies using this same reagent.[8] By way of summary it can be said that although it has not been possible to obtain a quantitative measure of the acidity constant of the hydroxyl radical, it has been established fairly definitely that neutralization occurs in the region above pH 12. The acidity of the hydroxyl radical thus appears to be analogous to that of its dimer, hydrogen peroxide.

Experimental

The purification of the water and chemicals has been described elsewhere.[9] In all experiments involving alkali the sodium hydroxide was used without purification, but it was taken from the same bottle of Baker and Adamson reagent grade material, lot number J309. Because of the difficulty in obtaining reproducibility in a chain reaction of the present sort, some description should be given of the special precautions which must be employed. It is essential that only repurified water be used, both as a solvent and in recrystallizing solids. All unpurified reagents should be taken from the same reagent bottle; in a study of the hydrogenation of persulfate it was found that appreciable differences in rate were observed when the sodium hydroxide was taken from different bottles, despite the fact that the labels listed the same lot number. In another experiment in the O^{18} exchange studies, 0.3 N sodium hydroxide was prepared by partial neutralization of 1.0 N alkali using concentrated perchloric acid; the rate obtained in this experiment was only 45% of the expected value, presumably because of inhibition caused by impurities introduced in part in the alkali and in part in the perchloric acid. Finally, and most important of all, before reproducible data can be obtained it is necessary to condition the reaction vessel by carrying out a number of consecutive runs. In the present study during the conditioning period involving approximately a dozen experiments, the rate constant increased

(1) This work was supported by the Atomic Energy Commission.

(2) E. J. Hart, S. Gordon and D. A. Hutchison, J. Am. Chem. Soc., 74, 5548 (1952).

(3) E. J. Hart, S. Gordon and D. A. Hutchison, ibid., 75, 6165 (1953).

(4) O. L. Forschheimer and H. Taube, ibid., 76, 2099 (1954).

(5) H. Taube, Ann. Rev. Nuclear Sci., 6, 294 (1956).

(6) I. M. Kolthoff and I. K. Miller, J. Am. Chem. Soc., 73, 3055 (1951).

(7) Unpublished work carried out in this Laboratory.

(8) A summary of this work may be found in the Abstracts of Papers for the 131st meeting of the American Chemical Society, held in Miami, Florida, in April, 1957.

(9) Maak-Sang Tsao and W. K. Wilmarth, This Journal, 63, 346 (1959).

consistently from experiment to experiment, with the overall variation being about a factor of two.[10,11] Thereafter, the rate constants were reproducible to $\pm 15\%$, a value consistent with that obtained in the much more extensive hydrogenation studies. During the course of the experiments which are considered below, the reaction vessel was cleaned between experiments only by copious rinsing with purified water. Previous work had indicated that the use of cleaning solution or aqueous hydrofluoric acid poisoned the vessel so completely that it was necessary to repeat the conditioning cycle.

All kinetic studies were carried out at 60° in a magnetically stirred, all-glass reaction vessel.[12] The vessel had a total volume of 88.3 ml.; 50.0 ml. of solution was used in each experiment, with the residual space above the solution containing oxygen prepared by electrolysis from O^{18} enriched water obtained from the Stuart Oxygen Co. The rate of stirring was approximately 1300 r.p.m., a value which previous work has indicated was sufficient to maintain the O^{18} content of the dissolved oxygen at essentially the same concentration as that present in the gas phase. At 60° the half-life for the thermal decomposition of persulfate is 49.0 hr., a period so long that the persulfate concentration could be regarded as constant during the 1-2 hr. required for all exchange experiments except those presented in Table I. In the 1-2 hr. period the oxygen produced from the persulfate decomposition could also be ignored, since it was less than 1% of that present in the reaction vessel. The experiments presented in Table I were followed up to the half-life for the exchange reaction, a period of approximately 20 hr. Even in this longer period only a 10% error resulted from neglect of the oxygen evolution. However, a somewhat greater uncertainty may be present in the data because mass spectrometer analysis was only performed on oxygen samples taken near the beginning and end of each experiment, and the rate constant has been calculated assuming an average value of the persulfate concentration.

In any given experiment, at suitable time intervals three to five 1.2-ml. samples of oxygen were removed for mass spectrometer analysis. Although this resulted in an appreciable decrease in oxygen pressure during the course of an experiment, this procedure was acceptable since the half-life of the exchange process is pressure-independent. For purposes of tabulation it was convenient to evaluate a rate constant defined in terms of equation 3

$$\frac{1}{t} \ln (1 - F) = k(1 + V_g/V_s\lambda) \quad (3)$$

The quantity $1 - F$ may be conveniently expressed as $(N_\infty - N_t)/(N_\infty - N_0)$, where N is the mole fraction of oxygen of mass 34 and the subscripts refer to the time at which the samples were removed during a given experiment. N was calculated from r, the ratio of the mass 34 to the mass 32 peaks, obtained by mass spectrometer analysis, using the

TABLE I

RATE CONSTANTS FOR SOLUTIONS MORE ACIDIC THAN pH 11

In all experiments $T = 60°$ and the initial persulfate concentration was 0.00625 M

pH[b]	$k \times 10^4$, sec.$^{-1}$	Chain length
11	3.0	5.8
6.7	1.4	2.8
3	2.4	4.6
2-4[a]	1.7	3.4

[a] Unbuffered solution. [b] Phosphate buffer at a total concentration of 0.05 M.

formula $N = r/(1 + r)$. r_∞ was assumed to be equal to the r value for tank oxygen. Over a period of days or weeks the mass spectrometer values of r_0 and r_∞ were found to vary slightly, but there was no measurable variation of these

(10) The lack of reproducibility reported by II. Taube[3] must have arisen largely from the use of unconditioned reaction vessels.

(11) An informative account of experiments showing how the rate of a chain reaction may be influenced by the previous history of the vessel has been published by E. J. Hart and M. S. Matheson, *Disc. Faraday Soc.*, **12**, 169 (1952).

(12) W. K. Wilmarth and C. F. Baes, Jr., *J. Chem. Phys.*, **20**, 116 (1952).

quantities during the period of hours required to analyze a given series of oxygen samples. The quantity $(1 + V_g/V_s\lambda)$ in equation 3 corrects for the presence of the gas phase in the reaction vessel; k is therefore a rate constant characteristic of the solution phase. In all of the present experiments V_g, the volume of the gas phase, was 38.3 ml., and V_s, the solution volume, was 50 ml. The Ostwald coefficients λ appropriate for the various alkali concentrations were calculated, assuming the validity of the Setschenow equation and using oxygen solubility data obtained by A. F. Kapauan in this Laboratory.[13]

For the solution phase the usual symbol R may be used to represent the total rate of exchange of oxygen atoms, both labeled and unlabeled, with the statistical factor of two arising from the presence of two equivalent oxygen atoms in the oxygen molecule.

$$R = k \frac{2(O_2)(H_2O)}{2(O_2) + (H_2O)} \cong 2k(O_2) \quad (4)$$

The approximation given by the last term in equation 4 is, of course, a very good one, since the oxygen concentration is always less than 0.001 M.

The symbol C.L. may be used to represent the chain lengths; a value of unity would imply that on the average each hydroxyl radical catalyzed the exchange between a single water and oxygen molecule.

$$\text{C.L.} = \frac{k(O_2)}{k_1(S_2O_8{}^{--})} \quad (5)$$

The definition of k_1 is made in terms of equation 7 listed below.

Results

In the present work our major interest has been in the variation of rate of O^{18} exchange with pH. In Fig. 1 values of k have been plotted *versus* the hydroxide ion concentration, using a logarithmic scale for the abscissa in order to cover the important range of hydroxide ion concentrations. To obtain maximum reproducibility the experiments were carried out in a consecutive series without interruption and with each experiment requiring one day. The degree of reproducibility may be judged by the two points at 0.6 N NaOH, and also by the extent to which the points fall on a single smooth curve. To make this latter criterion a useful one the concentration of alkali was not increased continuously from one experiment to the next; instead, the order of proceeding was that indicated by the numbering of the points. Figure 1 also contains the results of the radiation studies[3] with the ordinate on the right side of the figure representing relative yield values $G(o_2)/3$ mM $O_2{}^*$, a quantity which should be comparable with our rate constants. The yield values have been decreased by the factor of the third merely to permit use of a single ordinate scale.

In addition to the data presented in Fig. 1, experiments were carried out at pH 11, 6.7 and 3 and in an unbuffered solution in the region of pH 3. The results are presented in Table I. Immediately preceding and following this consecutive series of four experiments, an exchange study was carried out in 0.3 N alkali, with the expected result indicating that poisoning of the reaction vessel had not occurred. As we have indicated, the rate of exchange in these experiments was very slow and the results may be in error by as much as 30% because of uncertainty regarding the persulfate concentration. However, the data seem to indicate

(13) At 60° the Ostwald coefficient for oxygen in 0.50 and 1.0 N NaOH was found to have the values = 0.0212 and 0.0185, respectively.

clearly that the chain length is greater than unity, a point of significance in the discussion below. Further, the comparison of the results in buffered and unbuffered solution shows that the marked decrease in rate, as compared with the alkaline solutions, does not result because of the interference of phosphate ion acting as a radical scavenger.
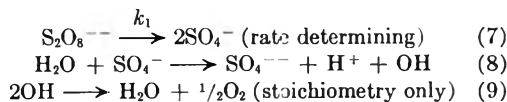
The variation of rate with persulfate concentration was studied only at 0.3 N NaOH, an alkalinity in the region where maximum exchange rates were observed. The results presented in Fig. 2 seem to indicate that the rate is first order in persulfate concentration; although the points scatter somewhat, it seems evident that the rate is definitely not dependent upon the square root of the concentration. On the basis of these data it is useful to define a rate constant k^0 which may be related to R by equation 6.

$$R = k^0(\text{S}_2\text{O}_8{}^{--})(\text{O}_2) \qquad (6)$$

As equation 5 indicates, the chain length increases linearly with the oxygen concentration. In calculating the chain lengths listed in Table I the oxygen pressure was assumed to be 0.5 atm., a value which was approximately correct. By making the same assumption the maximum chain length observed in alkaline solution was found to have a numerical value of 450.

Discussion

In this and other papers of the present series an attempt is being made to investigate the general behavior of reactive inorganic free radicals in aqueous solution. The present work is concerned with the hydroxyl radical and its conjugate base, the O⁻ ion. As a generating source for the radicals we have used the thermal decomposition of peroxydisulfate ion, a system chosen because the thermal decomposition mechanism appears to be very well understood and free from complications, at least in the range of alkalinity between pH 3 and 0.1 N alkali. Here the decomposition mechanism appears to be essentially that originally specified by Kolthoff and Miller.[6]

$$\text{S}_2\text{O}_8{}^{--} \xrightarrow{k_1} 2\text{SO}_4{}^- \text{ (rate determining)} \qquad (7)$$
$$\text{H}_2\text{O} + \text{SO}_4{}^- \longrightarrow \text{SO}_4{}^{--} + \text{H}^+ + \text{OH} \qquad (8)$$
$$2\text{OH} \longrightarrow \text{H}_2\text{O} + {}^1/_2\text{O}_2 \text{ (stoichiometry only)} \qquad (9)$$

Our unpublished work strongly confirms the general validity of this reaction sequence, although it also reveals certain hitherto unappreciated complexities which occur in weakly acidic solution, a region which is fortunately not of major interest in the present study. Further, our data indicate that there is another reaction path which becomes appreciable at about 0.5 M base and above, a region not investigated by Kolthoff and Miller. Reference will be made to this latter reaction path in the discussion below.

In the present work the major interest centers around the question whether the hydroxyl radical may be "titrated," in the sense that the pH where neutralization occurs may be determined by kinetic studies using labeled molecular oxygen as a radical detector capable of distinguishing OH and O⁻. The data presented in Fig. 1 do indeed sug-
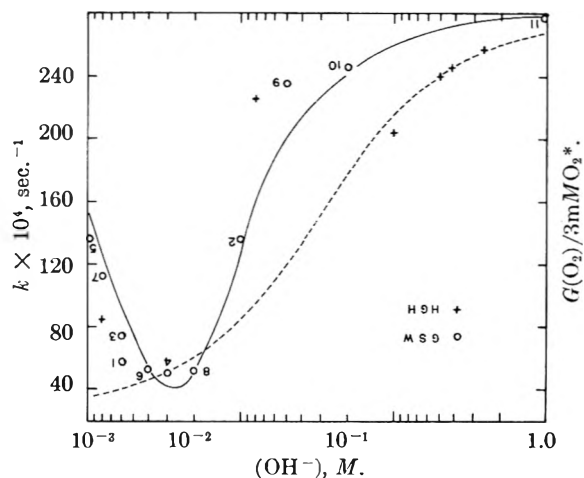

Fig. 1.—The variation in rate constant with pH: all experiments were at 60° and the persulfate concentration was 0.00625 M.
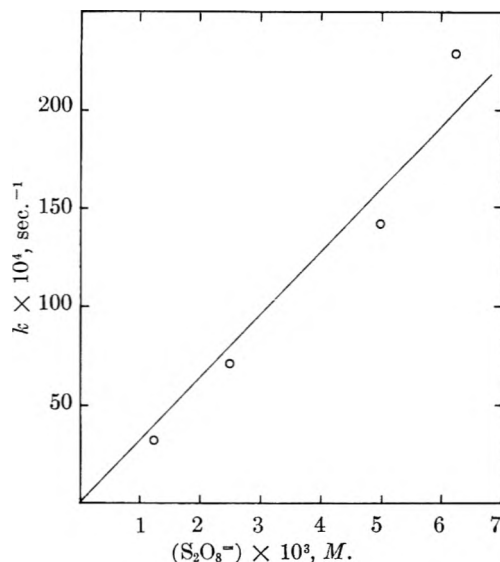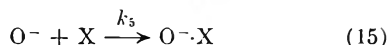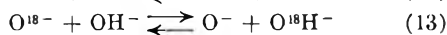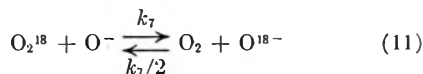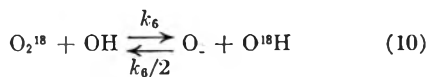

Fig. 2.—The variation in rate constant with persulfate concentration in 0.03 N alkali at 60°.

gest a titration curve, except there has been a rotation of the conventional plot of pH $versus$ ml. of alkali by 90°, followed by reflection in a mirror plane. By way of qualitative interpretation it would appear that the OH and O⁻ ions predominate, respectively, in the regions of low and high alkalinity where k becomes essentially pH independent. In the intermediate region between 0.01 and 0.2 N alkali, there is a marked variation in k caused presumably by a concurrent variation in the ratio (OH)/(O⁻). The mathematical analysis of the data, based on the mechanism now to be presented, confirms the qualitative validity of these conclusions. However, it is apparent that certain minor but poorly understood complexities prevent a completely satisfactory interpretation.

In specifying a detailed mechanism for the exchange reaction it may be assumed on the basis of previous kinetic studies that the radicals are generated by reactions 7 and 8, at a rate which is pH independent. Exchange of oxygen atoms between water and molecular oxygen would then proceed through this sequence of reactions

$$O_2{}^{18} + OH \underset{k_6/2}{\overset{k_6}{\rightleftarrows}} O_- + O^{18}H \qquad (10)$$

$$O_2{}^{18} + O^- \underset{k_7/2}{\overset{k_7}{\rightleftarrows}} O_2 + O^{18-} \qquad (11)$$

$$O^{18}H + OH^- \rightleftarrows OH + O^{18}H^- \qquad (12)$$

$$O^{18-} + OH^- \rightleftarrows O^- + O^{18}H^- \qquad (13)$$

$$OH + X \xrightarrow{k_4} OH \cdot X \qquad (14)$$

$$O^- + X \xrightarrow{k_5} O^- \cdot X \qquad (15)$$

Reactions 10 and 11 serve to account for the catalytic actions of OH and O^-, respectively; the appropriate rate constants are listed over and under the arrows, a convention also employed in equation 7. For the chain length to be greater than unity, as it is under all conditions, it is necessary that the labeled radicals exchange with water by some such processes as those given by equations 12 and 13. In the kinetic derivation it will be assumed that these latter reactions are so rapid that they maintain O^{18} equilibrium between the radicals and solvent; under these circumstances it is not necessary to specify the corresponding rate constants, and the data do not indicate whether the equations may be given mechanistic significance. Lastly, and it is at this point that the major uncertainty and oversimplification arise, the radicals, both labeled and unlabeled, are assumed to leave the system by rate determining reactions with an impurity designated as X. In all likelihood X is not a single species, but rather a mixture of trace materials present, perhaps in variable amounts under different experimental conditions. However, for the moment it will be assumed that X is present in constant amounts and in a form which is pH independent. Following reactions with the radicals, equations 14 and 15, X is to be regenerated by conversion of the radicals to water and molecular oxygen, a disproportionation reaction. The equations for these latter reactions are not required in our kinetic derivations, and they have been omitted to maintain simplicity in presentation.

A priori, reactions 14 and 15 may seem less appealing than bimolecular radical combination. However, the data seem to support the contention that O^- ions, at least, leave the system by a pseudounimolecular reaction, a process that can be formulated most reasonably in terms of interaction with impurities. Bimolecular combination of O^- ions, a process which would presumably involve solvent and yield $HO_2{}^-$, would require a half order dependence of rate upon persulfate concentration, a rate law clearly excluded by the data in Fig. 2. Independent evidence also may be cited in support of the concept that the role played by impurities cannot be ignored, especially in any solution containing commercial alkali, despite the lack of knowledge about the detailed nature of the impurity reactions.[14] The earlier work also suggests that

(14) In a study of the hydrogenation of persulfate ion, a chain reaction involving the hydroxyl radical, it was found that there was a two-fold increase in rate in alkaline solution, when the alkali employed was synthesized from distilled metallic sodium and purified water. In addition, it was found that various heavy metal ions, known

even in less alkaline solutions the impurity level is high enough so that hydroxyl radicals also disappear in impurity-catalyzed reactions, rather than by bimolecular combination. However, the information is less compelling here, and the form of reaction 14 was chosen in part to simplify the kinetic derivation.

By employing the usual steady state approximation and using only the approximations which have been mentioned explicitly, it is possible to derive equation 16.

$$k = k^0(S_2O_8{}^{--}) = \frac{2k_1}{(X)}\left[\frac{k_6 + k_7K(OH^-)}{k_4 + k_5K(OH^-)}\right](S_2O_8{}^{--}) \qquad (16)$$

The various symbols have been defined previously, except for K, the equilibrium constant for reaction 2, the neutralization of the hydroxyl radical. Equation 16 is evidently of the right general form in that at high and low alkalinity it yields limiting values of the rate constants, $k^0(\text{acid}) = 2k_1k_6/k_4(X)$ and $k^0(\text{base}) = 2k_1k_7/k_5(X)$ which are pH independent. The ratio of these limiting rate constants k_4k_7/k_5k_6 is in turn dependent upon the ratios of the rate constants for the chain carrying and chain terminating steps. In the following discussion it is convenient to use the symbol $k_{1/2}$ to represent the rate constant whose value lies midway between the limiting plateau values, *i.e.*, $k_{1/2} = [k^0(\text{acid}) + k^0(\text{base})]/2$.

In view of our emphasis upon the qualitative similarity between the present rate data and the results of a conventional acid-base titration, it is important at this point to consider just what quantitative information may be obtained in a kinetic study of the present sort, assuming the validity of the simplified theory presented above. Analogous conclusions may be reached for a variety of more complex mechanisms, although in some cases the algebraic derivations would become much more difficult or even impossible. By way of comparison, and as a means of defining the following terms, it may be noted that in an ordinary titration the hydroxide ion concentration at the midpoint, $(OH^-)_{1/2}$, equals $1/K$, the reciprocal of the neutralization constant of the acid. In the corresponding kinetic study $(OH^-)_{1/2}$ may be defined as the hydroxide ion concentration where k has reached the value $k_{1/2}$; for the data presented in Fig. 1 $k_{1/2}$ would lie in the region of 0.1 N alkali. At $(OH^-)_{1/2}$ the concentrations of OH and O^- would not in general be equal, as they are in a titration, since it can be shown that $(OH)/(O^-) = k_5/k_4$. This latter equation implies $k_4(OH)(X) = k_5(O^-)(X)$, the physical significance here being that under these conditions the two radicals are leaving the system at exactly equal rates. Finally, it may be noted that even in principle the kinetic studies do not yield a value of K, but only a product of K and k_5/k_4, where the latter ratio involves only rate constants for chain terminating reactions. For very reactive radicals, where the reaction rates become diffusion controlled, this ratio might approach unity, but in general there is no assurance that it will do so. The conclusion just drawn that K

to be present in commercial alkali, were efficient inhibitors, even in the concentration range 10^{-4}–10^{-5} M.

may not be evaluated from experimental data implies, of course, as a converse that K is not an important kinetic parameter. The most important kinetic parameter is k_4/k_5K, since it may be shown that it defines the mid-point, the relationship being $(OH^-)_{1/2} = k_4/k_5K$.

In actual fact, equation 16 does not provide a very good representation of the data, very probably because of the extreme oversimplification involved in the assumption that the concentration of X was a constant, independent of the alkali concentration. Curves calculated using equation 16 all predict the region of rapid variation of k with alkali concentration should extend over slightly more than two pH units, a situation analogous to that observed in a titration curve, whereas the actual variation of k with alkalinity is more pronounced. A curve typical of the sort which may be calculated from equation 16 is plotted as the dashed line in Fig. 1.[15]

A somewhat more satisfactory equation may be obtained by adding a term proportional to the square of the hydroxide ion concentration to the denominator of equation 16. The corresponding rate law can be derived by making the not implausible assumption that impurities arise from two different sources, with the material from each source having a somewhat different radical reactivity. One group of impurities, again designated as X, might well be present in approximately constant amounts in all experiments. These would be impurities in the chemicals other than the alkali, in the water, and especially as materials derived from the walls of the reaction vessel.[11] The second impurity source would be the alkali, with the impurity Y assumed to be present in an experiment at a concentration $(Y) = A(OH^-)$, where A is merely a proportionality constant.[14,16] The concept that there are important impurities in the sodium hydroxide gains support from the gradual decrease in exchange rate above 0.4 N alkali. However, the applicability of this evidence is somewhat uncertain, as a second thermal decomposition path begins to make its appearance in this region, and reaction intermediates so produced also might act as radical scavengers.[17] In order to utilize the equation, X is again assumed to capture radicals by reactions 14 and 15, whereas Y operates in a qualitatively similar fashion in reactions 17 and 18.

$$OH + Y \xrightarrow{k_8} OH \cdot Y \qquad (17)$$

$$O^- + Y \xrightarrow{k_9} O^- \cdot Y \qquad (18)$$
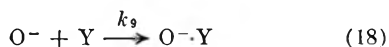
Proceeding as before, it is now possible to derive equation 19

$$k^0 = \frac{2k_1[k_5 + k_6K(OH^-)]}{k_4(X) + [k_8A + k_5K(X)](OH^-) + k_9KA(OH^-)^2} = \frac{1 + 5500(OH^-)}{3 + (OH^-) + 40(OH^-)^2} \qquad (19)$$

(15) The dashed line was calculated from the expression $k = [0.09 + 253 (OH^-)/0.03 + (OH^-)]$.

(16) Spectrographic analysis of reagent grade sodium hydroxide indicates that it contains iron, silver and lead in the concentration range 1–20 p.p.m.
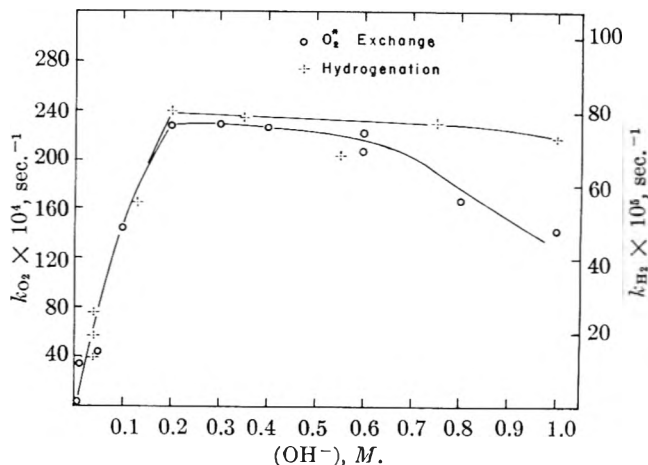

Fig. 3.—A comparison of the rate constants for the exchange reaction and for the homogeneous hydrogenation of persulfate ion. The exchange reaction was carried out at 60°, the hydrogenation at 75°.

The constants listed in the equation following the last equality sign were used to calculate the solid line in Fig. 1. Slightly different numerical values might have been chosen without greatly changing the shape of the curve or improving appreciably the agreement between theory and experiment. With the addition of another adjustable parameter the agreement between theory and experiment now begins to approach the limit of error of the data.[18] However, if point 9 is to be trusted, there is still the indication that the curve rises too slowly; more important, it fails to provide a broad enough plateau above 0.2 N alkali. In terms of theory this discrepancy is not too surprising; the mechanism still ignores such obvious complexities as a change in state of dispersion of colloidal impurities, or their possible amphoteric behavior, with increasing alkali concentration.

To the extent that it is necessary to postulate this more complex mechanism, the qualitative interpretation of Fig. 1, based on the analogy to a titration curve, may be a rather poor approximation. Physically speaking, the region of increasing rate constant would continue to imply neutralization of the hydroxyl radical. However, because of the increase in impurity concentration with increasing alkali, the upper rate plateau might now set in well before the neutralization had been completed, and consequently the mid-point would no longer have the simply physical significance pointed out above.
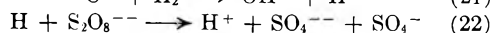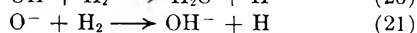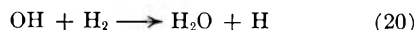
Before passing to a consideration of other matters, it is of interest to consider other explanations of the exchange data even though these seem to us less plausible than the mechanism which has been proposed. Two alternatives will be examined. In the first, most of the essential features of the above mechanism would be retained, including the concept of an equilibrium between OH and O^-.

(17) It is entirely possible that the second decomposition path is catalyzed not by the alkali, but by trace impurities present in it.

(18) The shape of the curve would not have been changed significantly if the linear term in hydroxide ion had been eliminated from the denominator of equation 19, thus reducing the number of arbitrary parameters. However, setting k_8 and k_6 equal to zero does not seem to represent a real simplification in the mechanism.

However, instead of O^- participating directly in the exchange, it might instead be a precursor of the actual catalyst. In evaluating this suggestion it can only be said that to our knowledge there is no experimental evidence that O^- (or OH) would yield a species not considered above which could act as an efficient catalyst for the exchange. The second alternative is a more radical one. It involves the concept that the increase in rate of exchange arises not from neutralization of hydroxyl radical, but instead merely a greatly enhanced steady-state concentration of the hydroxyl radical itself, presumably because the increased alkali concentration decreased the catalytic efficiency of the impurities. The reaction of the impurity with the alkali might be that of an amphoteric hydroxide, or merely a change in state of aggregation of a colloid. Again, by way of evaluation, it can only be said that the concept is not unreasonable, but that experimental support is entirely lacking. To the extent that evidence bearing on this point has been obtained in our study of hydrogenation of persulfate referred to below, the data do not seem to support this second alternative mechanism.

Despite the uncertainties involved in interpreting the physical significance of the dependence of rate upon pH there is experimental evidence that the radical neutralization concept does have some general validity, in the sense that the value for $(OH^-)_{1/2}$ is independent of the nature of the species reacting with the radicals, at least for the two reactants oxygen and hydrogen. For the hydrogenation of persulfate ion, kinetic studies indicate that the process is initiated by radicals, and terminated by impurity reactions analogous to those discussed above. The proposed chain carrying steps may be represented by equations 20, 21 and 22, with the O^- ion again being more efficient than OH in carrying the chain.

$$OH + H_2 \longrightarrow H_2O + H \qquad (20)$$
$$O^- + H_2 \longrightarrow OH^- + H \qquad (21)$$
$$H + S_2O_8^{--} \longrightarrow H^+ + SO_4^{--} + SO_4^- \qquad (22)$$

By reaction with water, equation 8, the sulfate radical would be converted to OH, thus completing the reaction sequence. The observed rate law is given by equation 23, where k has the pH dependence indicated by the data presented in Fig. 3.

$$\frac{-d(S_2O_8^{--})}{dt} = k(H_2)(S_2O_8^{--}) \qquad (23)$$

In Fig. 3 the ordinate values to the right may be used to evaluate k_{H_2}, those to the left refer to the oxygen exchange data also plotted to facilitate comparison. Within the limit of experimental error $k_{1/2}$ would seem to occur at the same hydroxide ion concentration for the two reactants, despite the considerable difference in the nature of the chain carrying reactions in the two systems. It would seem that although there is doubt about the exact validity of the equation $(OH^-)_{1/2} = k_4/k_5K$, the concepts which were discussed may be useful ones.

All of the earlier studies of the exchange reaction are in agreement with the qualitative observation that the chain length increases markedly in moderately alkaline solution. However, only the radiation studies of Hart, Gordon and Hutchison (H. G. H.) are extensive enough to justify comparison with our results.[3] Even here the data are rather sparse, since H. G. H. placed primary emphasis on nine experiments, selected because of their supposed greater reliability, and plotted in Fig. 4 of their paper. These data have been replotted in Fig. 1, using crosses to represent the experimental points, and omitting duplicate experiments. Unfortunately, only two of these experiments were carried out in the interesting region above 0.01 N alkali. It now would seem that to the extent that data are available, the results do not appear to be in disagreement with our exchange studies. However, the H. G. H. reaction mechanism and rate equations are not consistent with our observations. In their mechanism it was assumed that neutralization of OH was complete, and that the enhanced chain length in alkaline solution arose entirely from the rate influencing participation of hydroxide ion in reaction 13. That this explanation cannot be correct for the hydrogenation system is self-evident, since reaction 13 merely involves exchange of isotopically labeled oxygen atoms. Considering the close similarity of the two curves plotted in Fig. 3, it also seems unlikely that reaction 13 is rate determining in the oxygen exchange system, at least at the higher temperatures which we employed. In more acidic solution where hydroxyl radical is the predominant species its exchange with water may well be much slower, thus invalidating the assumption that reaction 12 is not rate determining. Our data are not extensive enough to yield any definite conclusion on this point.

Acknowledgment.—In the early phases of this work the mass spectrometer analyses were carried out by Mr. Robert D. Vanselow of the Department of Chemistry, University of California at Los Angeles. Later work was made possible through the use of a mass spectrometer designed and constructed under the direction of Professor Sidney W. Benson.

DISCUSSION

M. C. R. Symons.—We have found that when hydrogen peroxide is added to aqueous sodium hydroxide there is a fast build up and slow decay of a paramagnetic species which we identify as the ozonide ion, O_3^-. This based on E.S.R. studies, the spectrum obtained being identical with that for solid NaO_3 and different from that for NaO_2. It seems probable that the exchange of O^{18} described by Prof. Wilmarth proceeds via the intermediate O_3^-.

W. Wilmarth.—The suggestion that O_3^- might be an intermediate in the exchange reaction was made by O. L. Forschheimer and H. Taube,[4] and perhaps by other workers in the field. Presumably it might also be formed in the catalytic decomposition of hydrogen peroxide in alkaline solution. Recently we have had occasion to confirm the fact that a small amount of ozone is formed when the thermal decomposition of persulfate ion is carried out in solution 2.0 M and above in acid. It also seems possible that the ozone arises from free radical oxidation of O_3^- or its conjugate acid.

COÖRDINATION NUMBER CHANGES DURING OXIDATION–REDUCTION REACTIONS OF OXYANIONS. THE KINETICS OF THE ANILINE NITROSATION AND OF THE GLYCOL TELLURATE REACTION

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The rate of oxyanion reactions with reducing agents parallel the rates of oxygen exchange with water and are dependent on the acidity. No rate correlation with oxidation potential is obvious, however. These data are consistent with the postulation of a deoxygenation reaction occurring before or during the rate step. Cases where variability in coördination number of the central atom are known will be discussed as will the role of protons. Similar behavior appears where oxyanions are oxidized and when they act as catalysts for peroxide oxidations. The kinetics of two reactions have been investigated. One reaction is the aniline nitrosation. Previously unrecognized features of the kinetics will be pointed out; *e.g.*, the rate increases with buffer concentration and the order in nitrite varies between one and two. A mechanism involving the nitrosonium ion is postulated. The second is the formation of glycol complexes by tellurate ion ($H_5TeO_6^-$). The data can be interpreted as the rate-determining combination of a glycol molecule and dehydrated forms of tellurate anions. Complexing constants plus forward and reverse rate constants for several glycols will be presented.

Introduction

One of the more significant problems which faces chemists working on reaction mechanisms is whether an equilibrium combination of two reactants to produce a complex forms an intermediate on the path to the transition state or is just a storehouse for reactants. This problem has been discussed before and no general solution is available although it has been solved in a few specific cases. It is our intention to first show how this problem is important in the consideration of oxyanion reaction mechanisms, particularly those involving hydrogen peroxide, and then to discuss the work on two kinetics problems that have been studied at Brown.

Consider an oxyanion such as nitrite ion; the experimental data at hand on the structure show it is V-shaped. Nitrous acid is usually taken therefore as HONO, also V-shaped. In strongly acidic media, it probably exists as the nitrosonium ion NO^+. Yet there are other possibilities which must be considered. Nitrous acid could have a nitrogen–hydrogen bond or it could be $N(OH)_3$, although all of us rather automatically expect it to have the formula HNO_2 with an oxygen–hydrogen bond. Irrespective of what the main structure is, small amounts of other structures are possible, and may be the important ones in reaction mechanisms.

Thus the problem which one faces with oxyanions is this: what is the coördination number of the central atom in the transition state and to what species is the central atom bound? It is the proposition here that the coördination number of the central atom often changes and that the substrate species often joins in a chemical bond with the central atom during or prior to the transition state of the oxidation-reduction reaction.

The rates at which oxyanions oxidize particles like the halide ions or thiosulfate ion cover a vast range. Perchlorate, nitrate and selenate are very slow oxidants, while iodate, nitrite and selenite are rapid only in acid solution. Periodate and hypochlorite are rapid at higher pH. What data are available indicate that the rates of oxidation parallel the rates of oxygen exchange with solvent water.[1] Although there are not enough data available to see whether a linear free energy relation between rates of oxidation and rates of oxygen exchange can be made, there is certainly considerable correlation.

On the other hand, there does not seem to be any obvious relation between rates of oxidation and the oxidation potentials of the oxyanions, thus something more than the oxidizing power is involved.

Coördination Number Variability.—The central atoms of oxyanions have been found to show considerable variability in coördination number (c.n. hereafter) in their binding to oxygen. Carbon can be found in c.n. two as in carbon dioxide or c.n. three as in the normal carbonates; in the ortho-carbonates, the c.n. is four. Tetravalent sulfur is found both as sulfur dioxide with c.n. of two and as the sulfites with c.n. of three. Periodate ion can exist either as a tetrahedron or an octahedron, as can the molybdates, tungstates and probably the perrhenates and perosmates. Borates can be found in trigonal plane or tetrahedral configurations. Cationic intermediates such as NO_2^+, NO^+ and Cl^+ have been recognized in the chemistry of nitrates, nitrites and hypochlorites, respectively.[2]

There is therefore reason to believe that oxyanions in general can undergo hydration–dehydration reactions to give species with different numbers of oxygen in the coördination sphere of the central atom. There is also reason to believe that many reducing particles can replace oxygen in the coördination sphere since these particles are electron-rich and therefore are bases in the Lewis sense. In fact, there is a quantitative correlation between reducing power and strength of Lewis base.[3]

Dependence of pH.—There is another parallel between rates of oxidation and rates of water exchange which bears mentioning, and that is the strong dependence of rate on the hydrogen ion concentration. In many cases, the order in hydrogen ion concentration is two which strongly suggests a

(1) J. O. Edwards, *J. Chem. Educ.*, **31**, 270 (1954).

(2) The use of the term "cationic intermediate" for species such as NO_2^+ and Cl^+ is reasonable; however it emphasizes a factor, the charge, which is probably far less important than the availability of a binding site on the central atom. Indeed, one finds species such as $HCrO_3^+$ being postulated merely to be consistent with the terminology, whereas CrO_3 has the necessary open orbital without the need of a proton to supply a positive charge.
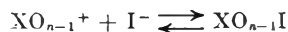
(3) J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954).

preliminary reaction of the type

$$XO_n^- + 2H^+ \rightleftharpoons XO_{n-1}^+ + H_2O$$
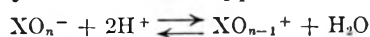
In the case of oxygen isotope exchange, the reaction can be accomplished merely by such an equilibrium. When an agent like iodide ion is being oxidized, the reaction
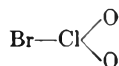
$$XO_{n-1}^+ + I^- \rightleftharpoons XO_{n-1}I$$

can occur. The species XO_{n-1} may be formed in the transition state or it may be an intermediate on the road to the transition state.

In the chlorate oxidation of bromide the observed rate law[4] is

$$R = k[ClO_3^-][Br^-][H^+]^2$$

and the postulated intermediate is

$$Br\!-\!Cl\!\!\begin{array}{c}O\\\diagdown\\O\end{array}$$

which can then decompose to give Br^+ and ClO_2^-.

Strong evidence for the existence of intermediate complexes may be found in the values of the rate constants for such reactions; in some cases the rates are so large that equilibrium constants for the intermediates must be equal to or greater than one[5] in order that the data be consistent with the collision theory. While these data do not in any sense prove what type of intermediate complex is involved, the type postulated has the advantages of being consistent with known chemical species and of providing a smooth path for transfer of two electrons from reductant to oxidant.

The oxidation of sulfite by bromate presents a mechanistic case where an oxyanion being oxidized appears to undergo a change in c.n. before electron transfer.[6] The results of both kinetic and isotope tracer studies support a mechanism of the type

$$H_2SO_3 \rightleftharpoons SO_2 + H_2O$$

$$SO_2 + HBrO_3 \rightleftharpoons \begin{array}{c}O\\ \diagup \ \ \ \diagdown \\O\end{array} S\!-\!O\!-\!Br \begin{array}{c}O\\ \diagup \\ \diagdown O\end{array} \longrightarrow \text{Products}$$
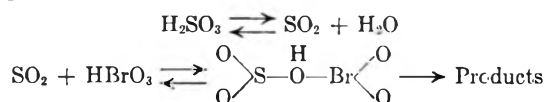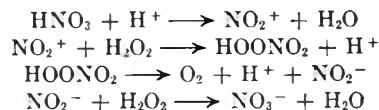
with direct oxygen atom transfer from the bromate to sulfur dioxide.

For those who wish to see a more detailed discussion of some of the problems and complexities in oxyanion reaction mechanisms, the article by Taube[7] should be consulted.

Interactions with Peroxide.—Some of the clearest examples of intermediate formation prior to the rate-determining step occur when hydrogen peroxide is present. Because of the interesting chemical properties of peroxide, it can react in many ways; four distinctly different patterns of behavior have been noted which are pertinent to the present discussion.

When the oxyanion has a high oxidation potential, oxidation of hydrogen peroxide to oxygen can be observed. Nitric acid is known to decompose peroxide and one possible mechanism involves the formation of peroxynitric acid HNO_4. There is

evidence that this peroxide does exist at low temperature,[8] although it is not stable at room temperature. This reaction could proceed through the steps

$$HNO_3 + H^+ \longrightarrow NO_2^+ + H_2O$$
$$NO_2^+ + H_2O_2 \longrightarrow HOONO_2 + H^+$$
$$HOONO_2 \longrightarrow O_2 + H^+ + NO_2^-$$
$$NO_2^- + H_2O_2 \longrightarrow NO_3^- + H_2O$$

As hydrogen peroxide is both a reducing agent and an oxidizing agent, cyclic decompositions of peroxide are also possible with other oxyanions. The kinetics of the oxidation of peroxide by iodate ion and by the hypohalites are also consistent with unstable peroxyacids as intermediates.[9] The formation and breakdown of unstable peroxychromates is well known even to students in qualitative analysis courses.

The oxidations of iodide ion and thiosulfate ion by hydrogen peroxide are not fast, however they can be made so merely by the addition of a small amount of molybdate. In view of the fact that substituted peroxides such as peroxyacetic acid and peroxymonosulfuric acid oxidize rapidly, it seems probable that the molybdate ion acts through the rapid reversible formation of a peroxymolybdate $HMoO_5^-$. It is known that replacements on molybdate are rapid. The postulated mechanism is

$$HMoO_4^- + H_2O_2 \rightleftharpoons HOOMoO_3^- + H_2O$$
$$HOOMoO_3^- + I^- \longrightarrow HOI + MoO_4^-$$
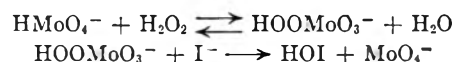
The fact that monosubstituted peroxides are rapid oxidizing agents causes another behavior pattern which is strongly indicative of intermediate formation. Nitrite,[10] selenite[11] and phenylboronate[12] ions all can be oxidized by peroxide, and in each case one of the observed rate laws has an order of two in oxyanion concentration. Taking the case of selenite as example, the mechanism

$$HSeO_3^- + HOOH \rightleftharpoons HOOSeO_2^- + H_2O$$
$$HOOSeO_2^- + SeO_3^- \longrightarrow HOSeO_3^- + SeO_3^-$$
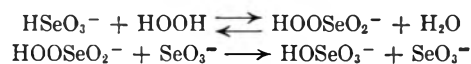
where selenite ion acts as a nucleophile in a displacement on the peroxyselenite seems reasonable. The existence of an unstable peroxynitrite plus the isotope tracer work of Taube and Anbar[10] in the oxidation of nitrite by peroxide support such a mechanism. Further support for the postulation of monosubstituted peroxides as intermediates is found in the fact that oxyanions such as molybdate, nitrite, selenite and phenylboronate ions are substitution labile, and act as catalysts, while oxyanions such as sulfate, perchlorate, phosphate and selenate which are substitution inert have not been observed to act as catalyst for peroxide reactions.

The fourth type of behavior also is strongly indicative of the formation of an intermediate peroxyanion. When sulfite ion in acid solution is oxidized by peroxide, it has been found that two of the four oxygens present in the product sulfate came

(4) J. Hirade, J. Chem. Soc. Japan, 10, 97 (1935).

(5) J. O. Edwards, Chem. Revs., 50, 455 (1952).

(6) (a) J. Halperin and H. Taube, J. Am. Chem. Soc., 74, 380 (1952); (b) F. S. Williamson and E. L. King, ibid., 79, 5397 (1957).

(7) H. Taube, Rec. Chem. Progr., 17, 25 (1956).

(8) R. Schwarz, Z. anorg. Chem., 256, 3 (1948).

(9) M. C. R. Symons, J. Chem. Soc., 5596 (1955).

(10) M. Anbar and H. Taube, J. Am. Chem. Soc, 76, 6243 (1954).

(11) F. J. Hughes and D. S. Martin, This Journal, 59, 410 (1955).

(12) H. G. Kuivila and A. G. Armour, J. Am. Chem. Soc., 79, 5659 (1957).

from the hydrogen peroxide.[13] The mechanism presumably is the rapid formation of a peroxysulfite ion followed by an intramolecular 1,2-shift of an OH^+ from oxygen to sulfur. Under certain conditions a similar behavior has been noted for the reaction of nitrite and peroxide.[10]

Diazotization of Aniline.—Nitrosation, the process by which an NO^+ group becomes attached to a molecule with a spare electron pair, is a reaction of considerable importance. The kinetics of this type of reaction have been studied often; however there is little agreement from one laboratory to the next on the mechanism. Some of the difficulties which have arisen are discussed in the papers by Anbar and Taube,[10] Hughes, Ingold and Ridd,[14] Li and Ritter,[15] Dusenberry and Powell,[16] Seel[17] and Bunton, Llewellyn and Stedman.[18] Suffice it to say here that in some cases not even the order in reactants is agreed upon by two different investigators.

In hopes of clarifying the situation somewhat, we decided in the fall of 1955 to reinvestigate the nitrosation of aniline. This reaction was chosen for several reasons: (a) the simplicity in analytical technique needed, (b) the presence of untested assumptions in the previous work, and (c) the lack of correlation of the kinetics of this reaction with isotope tracer studies.

Some weeks after submission of the abstract for this meeting, the series of papers by Hughes, Ingold and Ridd[19] came across the Atlantic. Where their results and ours are in agreement, only a brief résumé will be given here. There are some points of disagreement yet on which further work seems necessary.

Our study has been concerned with the mechanism of the aniline diazotization in buffered solutions between pH five and six. The rates, all at 0°, have been followed by coupling of the product diazonium ion with alkaline phenol and measurement of the color developed. The precision of the results obtained by this technique may be seen in Fig. 1, which also shows that the rate of reaction is not dependent on the aniline concentration. This observation, plus the fact that different anilines diazotize at the same rate, had been known. Our results of rate *versus* pH indicate that the reaction is second order in hydrogen ion concentration,[20] as had been observed previously.

The order in nitrite was found to be between one and two; also the rate was found to depend on the nature of the buffer, phthalate having a greater effect than acetate. From these results, it is apparent that only a thorough study of the rate over a range of nitrite concentrations at dif-

(13) J. Halperin and H. Taube, *J. Am. Chem. Soc.*, **74**, 380 (1952).

(14) E. D. Hughes, C. K. Ingold and J. H. Ridd, *Nature*, **166**, 642 (1950).

(15) J. C. M. Li and D. M. Ritter, *J. Am. Chem. Soc.*, **75**, 5828 (1953).

(16) J. H. Dusenberry and R. E. Powell, *ibid.*, **73**, 3266 (1951).

(17) F. Seel, *Angew. Chem.*, **68**, 272 (1956).

(18) C. A. Bunton, D. R. Llewellyn and G. Stedman, *Nature*, **175**, 83 (1955).

(19) E. D. Hughes, C. K. Ingold and J. H. Ridd, *J. Chem. Soc.*, 58, 65, 70, 77, 82, 88 (1958).

(20) The pH values for reaction mixtures were taken after mixing of the sodium nitrite with the buffer because of the small shift in pH from hydrolysis of nitrite ion.
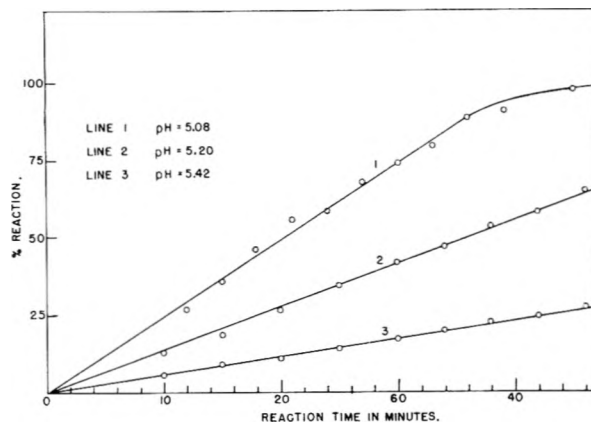
Fig. 1.—Fraction of aniline reacted as a function of time; $[C_6H_5NH_2] = 5 \times 10^{-4} M$, $[NO_2^-] = 4 \times 10^{-2} M$ and concentration of phthalate buffer $= 5 \times 10^{-2} M$.
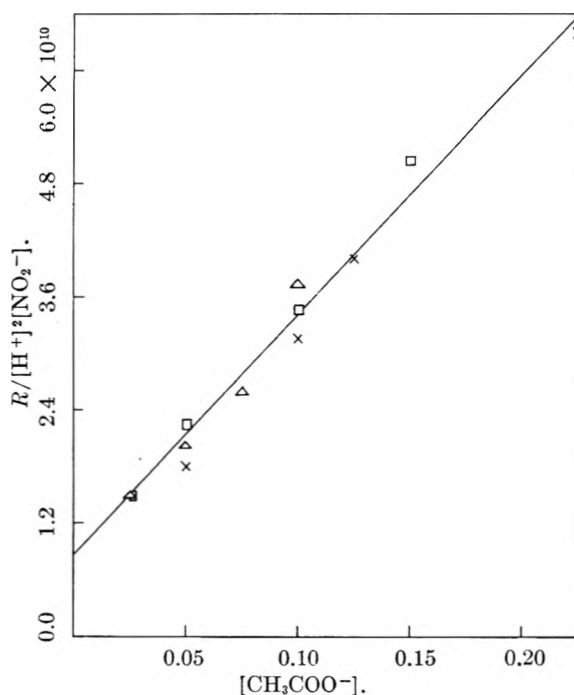

Fig. 2.—Corrected rate as a function of acetate concentration. Different symbols indicate runs on different days. Conditions comparable to those of Fig. 1.
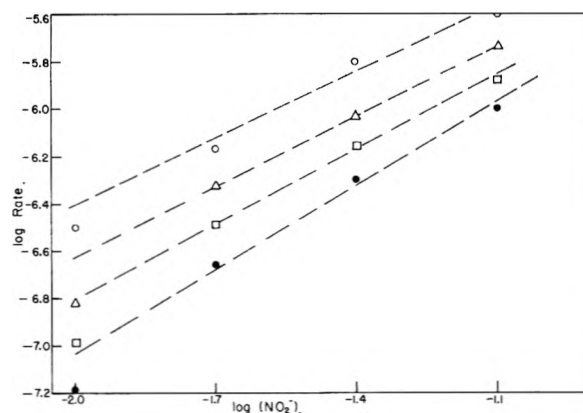

Fig. 3.—Order plot (nitrite); conditions given in Table I.

ferent buffer concentrations would allow satisfactory conclusions to be drawn. Unfortunately,

however, any variation in either nitrite or buffer concentration also changes the pH of the reaction mixture and the rate changes accordingly; for this reason all rates have to be corrected to a common pH. In Fig. 2, data are presented which show that there is a rate term zero order in buffer and another rate term which is first order in buffer concentration.

The results of one set of experiments is shown in Fig. 3, which is a log-log plot of the rate (corrected to pH 5) against nitrite concentration for four nitrite concentrations at each of four acetate concentrations. For these runs, the high precision Beckman model GS pH meter was employed in order to minimize the pH error. An increase in nitrite order as the amount of buffer decreases is clearly shown; at the highest buffer concentration, the order in nitrite is very close to one. The order in buffer concentration appears to increase as the amount of nitrite ion decreases. The numerical data for this group of experiments are shown in Table I. The dependence of rate on both nitrite and acetate concentrations is clearly apparent.

Our results agree with the most recent work[19] on the presence of a significant buffer effect and also on the fact that phthalate is more active than acetate. We cannot agree, however, that the order

Table I

Influence of Nitrite and Buffer Concentrations on Rate[a]

pH	[acetate]	[nitrite]	Rate[b] $\times 10^7$	Rate[b] $\times 10^7$
5.16	0.20	0.08	11.9	24.8
5.18	.20	.04	6.95	15.9
5.16	.20	.02	3.27	6.82
5.18	.20	.01	1.39	3.18
5.14	.10	.08	9.62	18.3
5.14	.10	.04	4.90	9.32
5.15	.10	.02	2.38	4.74
5.10	.10	.01	0.970	1.53
5.11	.05	.08	8.06	13.4
5.13	.05	.04	3.89	7.07
5.12	.05	.02	1.90	3.30
5.08	.05	.01	0.718	1.40
5.07	.025	.08	7.25	10.0
5.09	.025	.04	3.33	5.03
5.07	.025	.02	1.60	2.20
5.05	.025	.01	0.522	0.655

[a] $0°$ at $\mu = 1.0$. [b] In moles liter^{-1} sec.$^{-1}$.

in nitrite is two throughout; there is no question that this order approaches one as the concentration of buffer increases. This indicates that a dominant rate term is

$$R = k_{OAc}[NO_2^-][OAc^-][H]^{+2}$$

when acetate is the buffer. Although we have not tested the phthalate case as completely, it seems reasonable that it should have the rate term
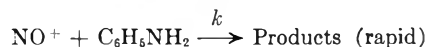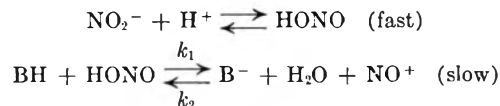
$$R = k_{phth}[NO_2^-][PhTh^-][H^+]^2$$

It is difficult to say conclusively what the rate term is for that part of the rate which does not depend on buffer concentration. After subtraction of the buffer term, the residual data appear to require two more rate terms which presumably are

$$R = k_0[NO_2^-][H^+]^2 + k_{NO_2}[NO_2^-]^2[H^+]^2$$

The dangers involved in such subtraction procedures are real; thus we wish to emphasize the tentative nature of these last two terms.

These rate terms can be interpreted as indicating that dinitrogen trioxide, nitrosonium ion, nitrosyl acetate and nitrosyl phthalate all can nitrosate aniline in a rapid step after a rate-determining formation step. A more plausible mechanism, however, is

$$NO_2^- + H^+ \rightleftharpoons HONO \quad (fast)$$

$$BH + HONO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B^- + H_2O + NO^+ \quad (slow)$$

$$NO^+ + C_6H_5NH_2 \overset{k}{\longrightarrow} Products \quad (rapid)$$

This predicts, when k_1 is the rate step, the rate law

$$R = k_1[BH][HONO] = k_1'[NO_2^-][B^-][H^+]^2$$

where B^- can be nitrite, acetate or phthalate ion or water. This mechanism can be generalized using the steady-state method if the last step is not rapid to

$$R = \frac{k_1 k_3[BH][HONO][S]}{k_2[B^-] + k_3[S]}$$

where S is the substrate being nitrosated. Depending on the nucleophilic strength of the substrate, this rate law should show different forms in different cases.

Several aspects of the nitrosation reaction are not yet clarified and further study seems appropriate. We feel that the following experiments need to be carried out: (a) a careful comparison of the rates of nitrosation of different substrates (aniline, thiosulfate ion, hydrogen peroxide, ammonia, etc.) under one set of conditions, (b) a study of the constitution of nitrous acid and nitrite ion both at various pH values and in the presence of various buffers, (c) a thorough study of the dependence of nitrosation on nature and amount of buffer, and (d) an attempt to isolate such species as Na_2HNO_3, nitrosyl acetate, etc.

Glycol Tellurate Complexes.—It has been known for some time[21] that the pH of a telluric acid solution can be decreased by the addition of a polyhydroxylic compound such as glycerol or a sugar. This was interpreted as indicating the formation of a cyclic diester in a fashion similar to those formed by borate ion and glycols. Little effort was made to measure the strengths of these complexes until a few years ago[22,23] when it was learned that the formation constants are quite large and that the glycol–tellurates are slow to form. Comparative formation constants with borate,[23] arsenite[23] and phenylboronate[24] ions showed that the ability of the four anions studied to bind a simple 1,2-diol such as propylene glycol was in the order: tellurate > phenylboronate > borate > arsenite. Fairly good linear free energy plots were found with the last three anions but formation constants

(21) F. Fouasson, Ann. Chim., 12, 594 (1948).

(22) P. J. Antikainen, Suomen Kemistilehti, B29, 14, 123, 135 (1956).

(23) (a) J. O. Edwards and A. L. Laferriere, Chemist-Analyst, 45, 12 (1956); (b) A. L. Laferriere, G. L. Roy and J. O. Edwards, J. Inorg. Nucl. Chem., 4, 106 (1957).

(24) J. Lorand, Sc.B. thesis, Brown University, 1958.

(Kc_1) for tellurate ion complexes did not correlate well as may be seen in Fig. 4. At least in part the discrepancy appears to be caused by steric effects in the octahedral tellurate complexes which are not present in the glycol complexes of the other anions; molecular models support this idea.

In order to learn more about the tellurate complexes, two paths of study have been initiated. The first is an investigation of the kinetics of the complex formation and the second is an investigation of the thermodynamics (entropy especially) of the complexing; our present discussion will be limited to the first part.

From pH data, it is apparent that the complexing is primarily with the mononegative tellurate ion. In the telluric acid–tellurate ion buffer region, the complex is formed at a measurable rate. Because of rapid protonic equilibria, the rate can be followed by the change in pH with time. Below pH 6 the rate appears to be very slow; above pH 8 equilibrium is attained almost instantaneously. This suggests that the rate depends not only on the concentration of glycol and tellurate ion, but also on the concentration of hydroxyl ion; thus we concluded that the rate law has the form

$$\frac{d[\text{complex}^-]}{dt} = \frac{k_f[\text{glycol}][\text{H}_6\text{TeO}_6{}^-]}{[\text{H}^+]} - \frac{k_r[\text{complex}^-]}{[\text{H}^+]}$$

This expression can be rearranged to give a relationship between pH and time by making certain assumptions. These assumptions have all been shown to be valid under the conditions employed and are (1) no $\text{H}_2\text{TeO}_4\text{G}$ is formed, i.e., the acid does not form a complex; (2) $[\text{H}_6\text{TeO}_6{}^-] = [\text{H}_5\text{TeO}_6{}^-]_0 - [\text{HTeO}_4\text{G}^-]$; (3) the concentrations of acid and glycol do not change significantly during the reaction.

The results obtained by rearranging the rate law are

$$-\frac{d(pH)}{dt} = \frac{k_f[\text{glycol}] + k_r}{2.3[\text{H}^+]} - \frac{\alpha k_r}{2.3Ka_1}$$

where α is the initial (denoted by a zero subscript) acid buffer ratio and is defined as

$$\alpha = \frac{[\text{H}_6\text{TeO}_6{}^-]_0}{[\text{H}_6\text{TeO}_6]_0}$$

This equation predicts that a plot of $\Delta pH/\Delta t$ versus the appropriate value of the reciprocal of the hydrogen ion concentration should be a straight line as shown in Fig. 5. By evaluating the slope and intercept of this line, values of the forward and reverse rate constants, k_f and k_r, can be calculated. These values then may be used to calculate Kc_1 which is also known from the static measurements.

As indicated in Table II, the observed values of k_f remain fairly constant with change in glycol concentration but k_r was found to vary in a fashion related to the variation of the equilibrium constant with glycol concentration. In Table III are given the results for several polyols under comparable conditions. For each series of kinetic runs, the concentration of glycol ranged from 0.1 to 1 M depending on the solubility of the polyol in the reaction mixture.

For all the runs at $\alpha = 1$, plots of $\Delta pH/\Delta t$ versus $1/[\text{H}^+]$ were fairly good lines. However when α was decreased below 0.5 the amount of
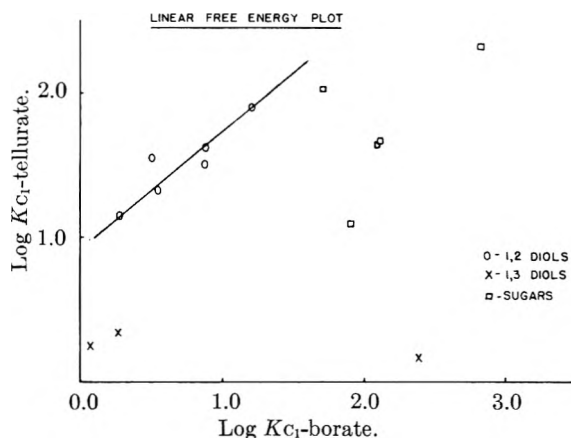

Fig. 4.—Plot of equilibrium constants for glycol tellurates against constants for glycol borate complexes.
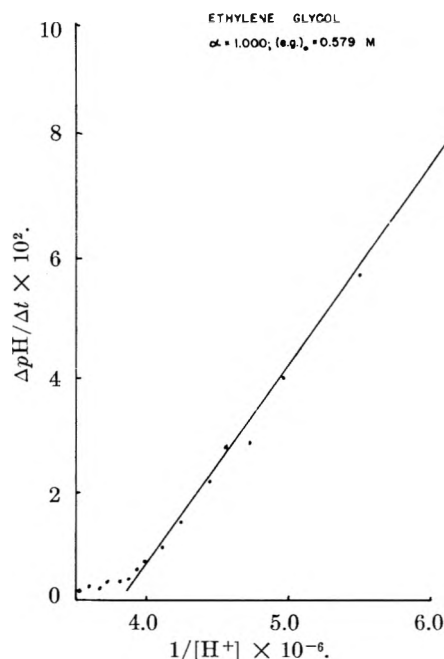

Fig. 5.—A typical rate plot; initial ethylene glycol concentration = 0.579 M, $\alpha = 1.000$, $\mu = 0.1$ and 25°.

TABLE II

VARIATION OF RATE CONSTANTS WITH PROPYLENE GLYCOL CONCENTRATION[a]

[Glycol]$_0$	k_f (min.$^{-1}$) $\times 10^8$	k_r (mole l.$^{-1}$ min.$^{-1}$) $\times 10^9$	Kc_1
1.200	6.36	7.54	8.4
0.967	6.90	7.68	9.0
.718	6.96	5.59	12.5
.710	7.00	5.51	12.7
.604	6.53	4.62	14.1
.500	6.96	4.32	16.1
.371	6.23	3.58	17.4
.231	6.54	2.38	27.5
.128	5.95	2.31	25.8

[a] At $\alpha = 1.000$, $\mu = 0.1$ and 25°.

curvature in the plots increased and also the values of k_f (as well as k_r) increased as can be seen from Table IV.

TABLE III

RATE AND FORMATION CONSTANTS FOR VARIOUS POLYOLS[a]

Glycol	Runs	k_f[c] $\times 10^8$	k_r[c] $\times 10^9$	K_{cl}[d]
Ethylene glycol	8	11.8 ± 1.0	13.5	13.9
Propylene glycol	8	6.39 ± 0.15	3.8	33.4
Glycerol	8	15.1 ± 1.3	1.9	79.6
2,3-Butanediol	7	1.42 ± 0.12	0.6	21.3
3-Methoxy-1,2-propanediol	9	6.14 ± .41	1.1	30.2
Phenyl-1,2-ethanediol	5	6.75 ± .76	0.7	42.0
1,2,4-Butanetriol	6	8.02 ± .09	1.3	42.5
L-Arabinose	3	9.32 ± .37	4.4	46.9
Fructose	10	14.5 ± 2.9	0.4	214
D-Galactose	8	8.34 ± 1.62	1.1	46.0
D-Glucose	13	11.8 ± 1.5	1.0	12.7
Mannitol	9	74.7 ± 3.8	0.5	1680
D-Mannose	6	6.03 ± 0.22	4.0	106
Pentaerythritol	4	14.0 ± 0.4	39.9	2.24
1,3-Propanediol	3	...[b]	...[b]	1.78
Polyvinyl alcohol	1	...[b]	...[b]	2.19

[a] At 25°, μ = 0.1 and α = 1.000. [b] Constants too small to be measured. [c] Values of k_f (in min.[-1]) are average values from several glycol concentrations while k_r (mole l.-min.[-1]) are extrapolated values ([glycol] = 0). [d] Equilibrium constants from static measurements extrapolated to zero glycol concentration.

TABLE IV

VARIATION OF KINETIC CONSTANTS WITH INITIAL BUFFER RATIO[a]

		Av. k_f (min.[-1]) $\times 10^8$	
α	No. runs	Ethylene glycol	Propylene glycol
1.346	7	11.7 ± 0.5	1.99 ± 0.19
1.184	8	12.0 ± 0.6	6.05 ± .25
1.000	8	11.7 ± 1.0	6.39 ± .15
1.000	8	12.0 ± 1.0	6.60 ± .32
1.000[b]	5	11.4 ± 0.2	
1.000[c]	4	12.1 ± 0.7	
0.835	8	12.6 ± 0.6	6.58 ± .44
.712	8	13.5 ± 0.2	6.71 ± .31
.712[b]	6	13.4 ± 1.2	
.680	8	14.2 ± 2.3	6.96 ± .45
.602	8	15.5 ± 0.5	7.30 ± .34
.508	8	15.2 ± 1.7	7.32 ± .35
.506[b]	6	16.4 ± 0.7	
.453	6	20.2 ± 1.6	10.26 ± .08
.403	8	15.9 ± 0.7	8.39 ± .14
.342	6	18.8 ± 1.6	10.2 ± .4
.342[b]	6	19.6 ± 0.8	
.280[b]	6	22.2 ± 1.4	
.278	8	20.9 ± 2.2	11.6 ± .1
.195	8	25.0 ± 1.6	13.7 ± .7
.146	6	30.6 ± 3.5	15.8 ± .6
.100	8	39.3 ± 2.8	19.6 ± 1.0

[a] At μ = 0.1 and 25°. [b] $[H_6TeO_6]_0$ = const. at α's = 3.12 × 10⁻³ M. [c] Doubled amount of acid buffer.

These results indicate that the expression given above for the rate law is not satisfactory over the entire range of conditions studied, particularly at higher hydrogen ion concentrations.

This variation in rate constants with α is real. In hopes of finding out the source of this variation, several related experiments have been carried out. Static determinations of the equilibrium constant over a range of values of α did not show any sig-

nificant change, thus both k_f and k_r vary in related fashion with α. It also was found that the rate constants did not depend on the amounts of buffer, thus only the ratio of initial tellurate ion to telluric acid appears to be influencing the observed rates. Also of interest is the fact that a plot of k_f against $1/\alpha$ gives a straight line as may be seen by plotting up the data in Table IV. On all such plots positive slopes and intercepts are obtained. Since the initial pH is directly related to $1/\alpha$, this led us to question the inverse hydrogen ion dependence in the rate law. We have not been able to find any more satisfactory rate law for all experiments, however; thus we feel that the rate law given is the predominant one but not the only one.

From all of the data, we have concluded that the anions $H_4TeO_6^-$ and $H_5TeO_6^-$ are both reactive, with the former being the more important. Taken together the results seem consistent with a mechanism involving reversible loss of a molecule of water by the tellurate anions to form five-coordinated species which can react with glycols to form intermediates of the type

$$\left[\begin{array}{c} HO \\ O \diagdown \vert \diagup OH \\ Te \\ O \diagup \vert \diagdown OCH_2CH_2OH \\ HO \end{array} \right]^-$$
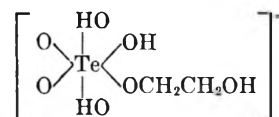
This intermediate is assumed to be in rapid equilibrium with the corresponding cyclic diester. The fact that the tellurate species have the order of reactivity

$$H_4TeO_6^- > H_5TeO_6^- >> H_6TeO_6$$

was not expected since oxyanion reactions are generally acid catalyzed. This order is similar to that found with chromium(III) complexes,[25] and presumably is related to the SN1CB class of coordination compound reactions discussed by Basolo and Pearson.[26]

Although there does not appear to be any evidence for a tetrahedral tellurate,[27] the data could also be explained by the assumption of the presence of such species.

The only diols which tellurates have been found to oxidize are the catechols.[33b] It is noteworthy that on mixing solutions of tellurate buffer with catechol the pH drops in a similar fashion as with other glycols. The rate of formation of elemental tellurium also proceeds at a rate roughly comparable to rates of complex formation. Both of these results are consistent with the slow formation of a catechol–tellurate complex prior to electron transfer.

The data on glycol–tellurates have one other significance in terms of oxidation–reduction mechanism. The discussion of the role of intermediate complexes in the oxidation of glycols by periodate ion has been heated and inconclusive. The stereochemical similarity of the octahedral periodate ion to the tellurates suggests that our results may aid in understanding the behavior of the periodate

(25) C. Postmus and E. L. King, THIS JOURNAL, 59, 1208, 1216 (1955).

(26) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 124–132.

(27) J. E. Earley and J. O. Edwards, unpublished data.

system. For example, we have found that pinacol does not complex with tellurate ion, a fact which suggests an explanation for the abnormally slow oxidation of pinacol by periodate.

Further work is being carried out on the kinetics and equilibria of the tellurate–glycol system and it is hoped that our results will be of use to those working on the periodate–glycol reaction. We wish to suggest that a study of the oxygen isotope exchange as a function of pH of tellurates and periodates be carried out in a laboratory where the necessary equipment is available. The rate of establishment of the hydration equilibrium in periodate ion also could be investigated by a spectrophotometric technique since the optical densities in the ultraviolet of the tetrahedral and octahedral forms are quite different.[28]

Experimental

Diazotization.—All runs were carried out in a fashion similar to that used previously.[14] The general procedure has been described earlier in this paper; details which follow the analytical method of Schmid and Muir[29] may be found in the M.Sc. thesis of J. R. Abbott at Brown University. Sodium nitrate was used to maintain constant ionic strength. Salts used were best grade available; no purification was attempted. Aniline was added as the perchlorate salt which was prepared here, twice recrystallized and stored in a refrigerator. Kinetic runs were carried out in flasks placed in an ice-bath.

Glycol Tellurates.—Telluric acid was prepared by oxidizing tellurium to TeO_2 with nitric acid, and then oxidizing the dioxide with potassium permanganate. The acid was purified by recrystallization from nitric acid and then by five to seven recrystallizations from water. All polyols were Eastman Kodak White Label grade except for three butanediols which were further purified by vacuum distillation. Potassium nitrate, used to maintain constant ionic strengths, and potassium hydroxide were A.C.S. grade reagents.

The kinetic runs were all carried out at $25.00 \pm 0.01°$ in

(28) (a) C. E. Crouthamel, H. V. Meek, D. S. Martin and C. V. Banks, *J. Am. Chem. Soc.*, **71**, 3031 (1949); (b) C. E. Crouthamel, A. M. Hayes and D. S. Martin, *ibid.*, **73**, 82 (1951).

(29) H. Schmid and G. Muir, *Ber.*, **70**, 421 (1937).

a glass cell which was designed to permit the reaction to be run in an atmosphere of carbon dioxide-free nitrogen. The cell which contained a magnetic stirrer, was kept at a constant temperature by circulating water through its hollow sides. All pH measurements were made using a Beckman Model GS meter, which has a reproducibility of ± 0.003 pH unit.

The procedure followed was to place water, the tellurate–telluric acid buffer and KNO_3 in the cell and measure the pH. A known amount of polyol was then added, bringing the final volume to about 110 ml. The pH measurements were made at suitable time intervals for from 30 to 90 minutes, depending upon the rate of change of pH. From six to eight runs were made with different concentrations of each polyol at any particular acid buffer ratio.

DISCUSSION

J. E. TAYLOR.—What is the evidence for the formation of the glycol tellurate complex previous to formation of the final products? That is, might not the glycol and tellurate react directly to form products and the complex serve only to inactivate the reactants?

J. O. EDWARDS.—As mentioned in the first paragraph of the paper, this is indeed the real problem. It has not been solved in the present case.

J. E. TAYLOR.—Since pinacol differs in pH *versus* rate studies (particularly in the case of the periodate glycol reaction) and therefore appears to proceed by a different mechanism, is it appropriate to extrapolate from pinacol to glycol or *vice versa*?

J. O. EDWARDS.—It may be appropriate, but extrapolation from one case to another (*e.g.*, tellurate to periodate) is a dangerous business in mechanism studies.

J. Y. TONG.—From the title of your paper I was hoping that you would discuss whether there is any relationship between reaction rates and changes in coördination number. You have shown several mechanisms in which one of the reaction steps is a "dehydration reaction" which is usually accompanied by a change in coördination number. Can you generalize that these dehydration steps are always slow?

J. O. EDWARDS.—There is certainly a correlation between rates and changes in coördination number, however it is not well defined and further study seems appropriate. The rate of a dehydration step can be very fast as in the borate case, thus no generalization is presently possible.

A REVIEW OF THE KINETICS OF THE AQUEOUS OXIDATION–REDUCTION REACTIONS OF URANIUM, NEPTUNIUM AND PLUTONIUM[1]

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The kinetics of a number of aqueous oxidation–reduction reactions of uranium, neptunium and plutonium is reviewed. The results are given in terms of the net activation processes and the thermodynamic quantities of activation. The activated complexes are formed from the hydrated reactant ions with the prior gain or loss of one or more hydrogen ions: a gain in those cases where metal–oxygen bonds are broken and a loss in those cases where such bonds are formed. It is shown that the entropies of the various activated complexes depend primarily on their charges. For the reactions considered, the evidence appears to be against electron transfer over relatively large distances. Several of the reactions were studied in D_2O to obtain evidence concerning the possible operation of hydrogen atom transfer mechanisms. It is shown that these experiments will remain inconclusive until the effect of D_2O on solvation is understood.

Introduction

This paper is not a complete review of the kinetics of the aqueous oxidation–reduction reactions of

uranium, neptunium and plutonium since it is concerned primarily with sets of similar cationic reactions in non-complexing media and with an attempt at correlating the kinetic data. Katz and Seaborg[2] have reviewed all but the most recent work on the chemistry of these elements, including the assignment of the formulas of the ions and their

TABLE I

THERMODYNAMIC QUANTITIES OF ACTIVATION AT 25°

	μ M.	ΔF^* kcal./mole	ΔH^* kcal./mole	ΔS^* cal./°mole	$S^*_{complex}$ cal./°mole	Other (H$^+$) dependences	Ref.
(1) $NpO_2^+ + NpO_2^{+2} = (*)^{+3}$	3	14	10.6	-11.7 ± 3	$- 29$	$+1$	3
(2) $Pu^{+3} + Pu^{+4} + H_2O = (*)^{+6} + H^+$	2	13.3	9.5	-13 ± 4.7	-120	0	4
(3) $Pu^{+3} + PuO_2^{+2} = (*)^{+5}$	1	16.9	4.8_2	-40.4 ± 0.6	-106	None	5
(4) $2U^{+4} + UO_2^{+2} + 2H_2O = (*)^{+6} + 4H^+$	...	25.1	32.8	$+25.8 \pm 3$	-118	None	6
(5) $NpO_2^- + NpO_2^+ + H^+ = (*)^{+3}$	1.2	24.2	17.6	-22.2 ± 0.7	$- 30$	...	7
(6) $1.5Np^{+4} + 0.5NpO_2^+ + 0.5NpO_2^{+2} + H_2O = (*)^{+4} + 2H^+ + 0.5Np^{+3}$	1.2	27.2	36.8	$+32.1 \pm 1.7$	$- 67$	...	7
or $Np^{+4} + NpO_2^{+2} + H_2O = (*)^{+4} + 2H^+$		16.0	19.9	$+13.1$	$- 67$		
(7) $Pu^{+4} + Pu^{+4} + 2H_2O = (*)^{+6} + 3H^+$	1	23.7	...	...	...	-4	8
(8) $Np^{+3} + NpO_2^+ + H^+ = (*)^{+5}$	2	15.2	5.9_3	-31.2 ± 1.8	$- 72$	None	9
(9) $U^{+4} + CeOH^{+3} = (*)^{+6} + H^+$	2	12.2	13.9	$+ 6.2 \pm 2.5$	-116	-2	10
(10) $U^{+4} + Pu^{+4} + H_2O = (*)^{+6} + 2H^+$	2	15.4	24.3	$+30.1 \pm 1.9$	-118	None	11
(11) $U^{+4} + Fe^{+3} + H_2O = (*)^{+6} + H^+$	1.02	16.8	21.4	$+15.5 \pm 1.2$	-118	-2	12
(12) $U^{+4} + Fe^{+3} + H_2O = (*)^{+5} + 2H^+$	1.02	16.0	23.6	$+25.4 \pm 2.0$	-108	-1	12
(13) $Np^{+4} + Fe^{+3} + 2H_2O = (*)^{+4} + 3H^+$	1	19.1	34.6	$+52$	$- 69$	None	13
(14) $UO_2^+ + UO_2^+ + H^+ = (*)^{+3}$	2.1	14.0	9.2	-15.9 ± 1.4	$- 30$	None	14
(15) $PuO_2^+ + PuO_2^+ + H^+ = (*)^{+3}$	1	20.8	18.8	$- 6.2 \pm 9$	$- 40$	$+2(?)$	15
(16) $Np^{+4} + NpO_2^{+2} + H_2O = (*)^{+4} + 2H^+$	2.2	19.2	24.7	$+18.4 \pm 1.0$	$- 62$	-3	16
(17) $U^{+4} + PuO_2^{+2} + H_2O = (*)^{+6} + H^+$	2	16.6	17.6	$+ 3.4 + 1.5$	$- 87$	...	17
(18) $U^{+4} + PuO_2^{+2} + H_2O = (*)^{+4} + 2H^+$	2	16.0	21.4	$+18.1 \pm 1.0$	$- 72$	...	17
(19) $V^{+3} + PuO_2^{+2} + H_2O = (*)^{+4} + H^+$	2	17.0	15.2	$- 6.0 \pm 1.7$	$- 81$	-2	18
(20) $Ti^{+3} + Pu^{+4} + H_2O = (*)^{+6} + H^+$	2	15.0	16.1	$+ 3.7 \pm 2$	-128	None	19

oxidation potentials. Although they discuss many oxidation–reduction reactions they do not attempt to correlate the kinetic results.

The kinetic information for all of the reactions under discussion is given in Table I in terms of the equations for the net activation processes and the associated thermodynamic quantities of activation. This information, together with the knowledge that all the reactions are one electron oxidation–reduction reactions, is sufficient for a complete description of the kinetics of these reactions. The equation for the net activation process is obtained from the rate law in terms of the principal species and shows the formation of the activated complex from these species without regard to the detailed mechanism. This net equation is the sum of the equation

for the formation of the activated complex in the actual rate determining step and the equations for any rapid equilibrium reactions which occur prior to the rate-determining step. For example if the mechanism is

$$A + B \rightleftharpoons C + D, \text{ rapid equilibrium}$$

$$K = \frac{(C)(D)}{(A)(B)}$$

$$C + E \xrightarrow{k} \text{ products, rate determining}$$
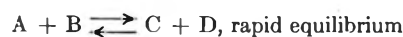
the rate law would be

$$\text{Rate} = k(C)(E) = kK \frac{(A)(B)(E)}{(D)}$$

and the net activation process would be

$$A + B + E = (*) + D$$

where the symbol (*) stands for the activated complex.

For a reaction which proceeds by more than one path, one can write a net equation for the formation of each activated complex.

For the representation of kinetic information or for the comparison of similar reactions it is immaterial whether the activation process is written in terms of the principal reactants or in terms of intermediate species formed in rapid equilibrium reactions. We have chosen to use the principal species since their concentrations are the closest to the actually measured stoichiometric quantities. In addition it is often impossible to specify a unique set of intermediates and even where this is possible their concentrations can be difficult to calculate due to inadequate knowledge of the appropriate thermodynamic quantities.

The thermodynamic quantities of activation, ΔF^*, ΔH^* and ΔS^*, were calculated from the

(2) J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," Methuen and Co., Ltd., London, 1957 (also John Wiley and Sons, Inc., New York, N. Y.).

(3) J. C. Sullivan, D. Cohen and J. C. Hindman, J. Am. Chem. Soc., 79, 3672 (1957); see also ibid., 76, 352 (1954); 77, 4964 (1955); 78, 1543 (1956).

(4) T. K. Keenan, THIS JOURNAL, 61, 1117 (1957).

(5) S. W. Rabideau and R. J. Kline, ibid., 62, 617 (1958).

(6) E. Rona, J. Am. Chem. Soc., 72, 4339 (1950).

(7) J. C. Sullivan, D. Cohen and J. C. Hindman, ibid., 76, 4275 (1954).

(8) S. W. Rabideau, ibid., 75, 798 (1953).

(9) J. C. Hindman, J. C. Sullivan and D. Cohen, ibid., 80, 1812 (1958).

(10) F. B. Baker, thesis, to be submitted to the University of New Mexico.

(11) T. W. Newton, unpublished results.

(12) R. H. Betts, Can. J. Chem., 33, 1780 (1955).

(13) J. R. Huizenga and L. B. Magnusson, J. Am. Chem. Soc., 73, 3202 (1951).

(14) H. Imai, Bull. Chem. Soc. Japan, 30, 873 (1957).

(15) S. W. Rabideau, J. Am. Chem. Soc., 79, 6350 (1957).

(16) J. C. Hindman, J. C. Sullivan and D. Cohen, ibid., 76, 3278 (1954); 79, 4029 (1957).

(17) T. W. Newton, THIS JOURNAL, 62, 943 (1958).

(18) S. W. Rabideau, ibid., 62, 414 (1958).

(19) S. W. Rabideau, unpublished results.

equations of the absolute reaction rate theory.[20] The quantity called $S^*_{complex}$ is the formal ionic entropy of the activated complex calculated from $\Delta S^{\ddagger}$ using the standard entropies of the ordinary species present. The values used for these standard entropies are given in Table II; they are based on the convention $\bar{S}^0_{H+} = 0$. The values for the actinide ions are those given by Katz and Seaborg[21] and the other values were taken from Latimer[22] or were estimated using the equation of Powell and Latimer[23] and the radius values given by Pauling.[24] It must be recognized that the use of standard entropies in solutions with ionic strengths of one or greater is merely an approximation. The equations for the net activation processes have been written with the minimum number of water molecules on the left side; this assumption is in accord with the fact that U(VI) is UO_2^{+2} rather than $U(OH)_4^{+2}$.[25]

TABLE II

ENTROPY VALUES, cal./mole

UO_2^{+2}	-17	U^{+4}	-80	$CeOH^{+3}$	(-42)
NpO_2^{+2}	-13	Np^{+4}	-84	Fe^{+3}	-70
PuO_2^{+2}	-27	Pu^{+4}	-85	V^{+3}	(-65)
UO_2^+	(-7)	U^{+3}	-34	Ti^{+3}	(-63)
NpO_2^+	-4	Np^{+3}	-37	H_2O	$+16.7$
PuO_2^+	-17	Pu^{+3}	-39		

Exchange Reactions

The accumulated data for electron exchange reactions are presented in Table I on lines 1 through 3. The NpO_2^+–NpO_2^{+2} exchange already has been studied extensively by Sullivan, Cohen and Hindman.[3] In addition to the path indicated by equation 1 in Table I there appears to be a path first power in the hydrogen ion concentration. Although the rate constant for this path was determined at $4.5°$ its temperature coefficient was not determined, so that the thermodynamic quantities of activation for this path are not available. The experimental activation energy was found to vary from 11.6 ± 0.8 kcal./mole in 0.1 M $HClO_4$ to 10.6 ± 0.8 kcal./mole in 3 M $HClO_4$. This possible variation could be due both to the change in the ionic strength and to the fact that in 3 M $HClO_4$ the hydrogen ion dependent path is relatively more important. We have assumed that the activation energy for the hydrogen ion independent path is 11.1 ± 0.8 kcal./mole for solutions with $\mu = 3$.

The rapid electron exchange reaction between Pu^{+3} and Pu^{+4} (equation 2) has been studied by Keenan.[4] His results have been recalculated in terms of the principal species by making use of Rabideau's data on the hydrolysis of Pu(IV).[26]

The values obtained for the hydrogen ion independent path were considered to be too imprecise for inclusion in the table.

Although the reaction between Pu^{+3} and PuO_2^{+2} involves a net chemical change[5] it has been listed with the electron exchange reactions since no change in metal oxygen bonding is involved.

The U(IV)–U(VI)[6] and the Np(IV)–Np(V)[7] exchange reactions are much more complicated than those discussed above since metal–oxygen bonds are involved.

For the uranium exchange, the rate law found was rate $= k[U(IV)]^2[U(VI)][H^+]^{-3}$; this reduces to rate $= k'(U^{+4})^2(UO_2^{+2})(H^+)^{-4}$ in terms of the principal species. The data support the second power dependence in U(IV) in the rather limited concentration range studied. The reaction was studied primarily in dilute chloride solutions, but it was found that the addition of $NaClO_4$ or $NaCl$ had essentially no effect on the rate. We have calculated a value for ΔF^* from the rate data at $25°$ and a pH of 0.85. This value and the reported value for the heat of activation were used to calculate the ΔS^* value given in Table I. A reinvestigation of this system in perchlorate solutions would be valuable in order to confirm the rate law and to provide rate data of precision comparable to that available for most of the other reactions discussed here.

The Np(IV)–Np(V) exchange was found to proceed by two paths according to the rate law: rate $= k_1(NpO_2^+)^2(H^+) + k_2(Np^{+4})^{1.5}(NpO_2^+)^{0.5} \times (H^+)^{-2}$. For the first term in the rate law we propose the formation of a dimer which then exchanges rapidly with Np(IV). The second term in the rate law corresponds to the net activation process given in Table I, if under the conditions of the experiment $(Np^{+3}) = (NpO_2^{+2})$. If half the equation $Np^{+4} + NpO_2^+ \rightleftarrows Np^{+3} + NpO_2^{+2}$ is subtracted from the equation for net activation process (6), the alternative activation process is obtained.

Reactions Involving Metal–Oxygen Bonds.—The remaining net activation processes given in Table I refer to reactions in which metal–oxygen bonds are formed or broken.

From entries 7–10 in Table I it can be seen that the reactions between Pu^{+4} and Pu^{+4},[8] Np^{+4} and Np^{+4} (from the reverse reaction[9]), U^{+4} and Ce^{+4},[10] and between U^{+4} and Pu^{+4},[11] have hydrogen ion dependences which are predominantly -3, -3, -2 and -2, respectively. All four reactions are first power in each of the metal ion concentrations.

Entries 11, 12 and 13 refer to reactions in which U^{+4},[12] or Np^{+4},[13] is oxidized by Fe^{+3}. Both reactions are first power in the Fe^{+3} concentration and first power in the quadrivalent ion concentration but they have different hydrogen ion dependences. The uranium reaction shows both inverse first and inverse second power dependences while the neptunium reaction shows only inverse third power dependence.

Entries 14 through 18 refer to reactions in which a quadrivalent ion is oxidized by a MO_2^{+2} ion. For reactions 14 and 15, the disproportionation of UO_2^+[14] and PuO_2^+,[15] the rates were found to be

(20) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 195-199.

(21) Reference 2, pages 172, 221 and 294. Except for UO_2^{+2} and the $+3$ ions these are not strictly standard entropy values since they are based on entropy differences determined in solutions with $\mu = 1$.

(22) W. M. Latimer, "Oxidation Potentials," 2nd Edition, Prentice-Hall, Inc., New York, N. Y., 1952.

(23) Reference 22, p. 365.

(24) L. Pauling, "The Nature of the Chemical Bond," 2nd Edition, Cornell University Press, Ithaca, N. Y., 1940, p. 350.

(25) H. W. Crandall, J. Chem. Phys. 17, 602 (1949).

(26) S. W. Rabideau, J. Am. Chem. Soc., 79, 3675 (1957).

first power in the hydrogen ion concentration; thus, the reverse reactions would be inverse third power in the hydrogen ion concentration. These reverse reactions are formally identical with the
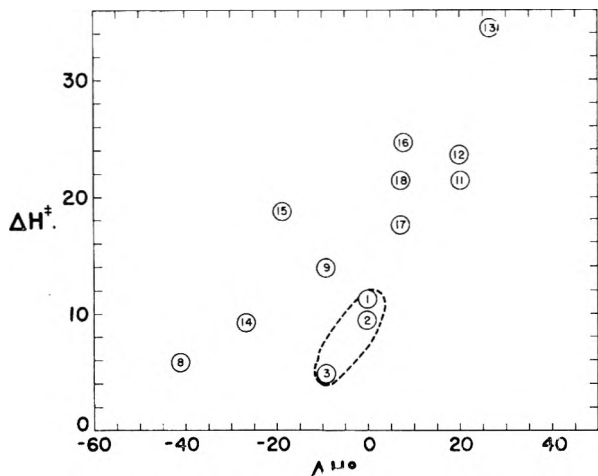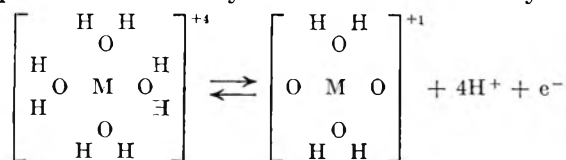

Fig. 1.—ΔH^* versus $\Delta H°$: the points for the electron exchange reactions are enclosed by the dotted line. The numbers in the circles refer to the entries in Table I.

reactions between Np^{+4} and NpO_2^{+2} [16] and between U^{+4} and PuO_2^{+2} [17] which show inverse first and inverse second power hydrogen ion dependences for the major paths in $1\ M\ HClO_4$. The values given in Table I for the UO_2^+ disproportionation reaction differ from those tabulated by Imai,[14] which apply to the apparent second-order rate constant in solutions of $\mu = 2$ and $(H^+) = 0.101_5\ M$. Also, the heat of activation has been recomputed by the method of least squares. The $U^{+4}–PuO_2^{+2}$ reaction has been shown to involve consecutive reactions and a metastable intermediate dimer.[17] It is interesting to note that equation 16 is the same as the alternate for equation 6 which applies to one of the paths of the Np(IV)–Np(V) exchange reaction. Although the two activated complexes have the same composition, exclusive of hydration, they are not the same, since the values of the thermodynamic quantities of activation are different.

Equations 19 and 20 refer to reactions in which the metal–oxygen bonds are formed in the ions VO^{+2} [18] and TiO^{+2}.[19] These reactions are similar in that each is first power in the plutonium ion concentration, first power in the V^{+3} or Ti^{+3} concentration and inverse first power in the H^+ concentration.

Hydrogen Ion Dependence.—The oxidation of a quadrivalent ion may be written schematically as

$$\begin{bmatrix} & H & H & \\ & & O & \\ H & & & H \\ & O & M & O \\ H & & & H \\ & & O & \\ & H & H & \end{bmatrix}^{+4} \rightleftarrows \begin{bmatrix} & H & H & \\ & & O & \\ O & & M & O \\ & & O & \\ & H & H & \end{bmatrix}^{+1} + 4H^+ + e^-$$

In this equation only four of the waters of hydration are shown, and it is seen that in the over-all reaction a total of four hydrogen ions must be removed from the hydration sphere of the M^{+4} ion. If the oxidizing agent is such that these are the only hydrogen ions involved, it is reasonable to expect that in the activated complex the environment of

the M will be somewhere between that of the M in M^{+4} and in MO_2^+. This means that in oxidation reactions some of the four hydrogen ions will be removed from the hydrated M^{+4} prior to the formation of the activated complex. This is in agreement with the data in Table I where hydrogen ion dependences between -1 and -4 are indicated for all of the reactions in which M^{+4} is oxidized. A similar argument applied to reduction reactions leads to the expectation of a first, or higher, power hydrogen ion dependence. This is borne out by equations 8, 14 and 15 which indicate first power hydrogen ion dependences for the reduction of NpO_2^+, UO_2^+ and PuO_2^+.

We have no explanation for the first power hydrogen ion dependence shown by the minor path for the Np(V)–Np(VI) exchange reaction.

The equations for the net activation processes given in Table I show that many formally identical reactions proceed by mechanisms with different hydrogen ion dependences. Perhaps this can be understood when we consider pairs of activated complexes which differ by just one proton. Examples of this are provided by equations 11 and 12 and by equations 17 and 18. In both examples the net activation processes leading to the lower charged activated complexes have the higher ΔH^* and ΔS^* values. This means that in both cases the process of removing one proton has positive $\Delta H°$ and $\Delta S°$ values. The sign of $\Delta F°$ for the proton removal process will determine which of the two activated complexes is the more favorable; this depends on the difference in the $\Delta H°$ and $T\Delta S°$ terms. In the two examples shown here, $\Delta F°$ is negative, but had the ΔH^* difference been slightly larger or the ΔS^* difference been slightly smaller, the other activated complex would have provided the more important path. Thus it is reasonable that for any particular reaction, the observed path (or paths) is favored over other possible ones on the basis of relatively small differences in heat and entropy terms.

Heats of Activation.—A plot of ΔH^* versus $\Delta H°$ is shown in Fig. 1. Considering only the reactions which involve metal–oxygen bonds (excluding the simple electron exchange reactions, which are encircled) it is seen that there is a general trend toward lower heats of activation as the $\Delta H°$ values become more negative. The ΔH^* values for the electron exchange reactions are noticeably lower than those of the other reactions with small $\Delta H°$ values.

Entropies of Activation.—Marcus, Zwolinski and Eyring[27] have suggested that oxidation–reduction reactions fall into two classes, one with positive entropies of activation and large heats of activation and the other with negative entropies of activation and small heats of activation. The data of Table I do not fall into two distinct classes but instead range from $\Delta H^* = 4.8$ kcal./mole and $\Delta S^* = -40$ e.u. for reaction 3 to $\Delta H^* = 34.6$ kcal./mole and $\Delta S^* = +52$ for reaction 13. However, when allowance is made for the hydrolysis equilibria involved in some of the reactions, the wide range

(27) R. J. Marcus, B. J. Zwolinski and H. Eyring, This Journal, 58, 432 (1954).

is greatly reduced. For the ions considered here, the heats and entropies of hydrolysis are roughly 10 kcal./mole and 25 e.u., respectively. Thus, for example, the kinetics of reaction 13 between Np(IV) and Fe(III) can be expressed by the activation process: $Np(OH)_2^{+2} + FeOH^{+2} = (*)^{+4}$ with ΔH^* about 5 kcal./mole and $\Delta S^{\ddagger}$ about -25 e.u.

It is interesting to note that it is impossible to estimate the sign of ΔS^* from the sign of Δz^2 for the activation process. Equations 9, 11, 12, 17 and 20 refer to processes for which both ΔS^* and Δz^2 are positive.

Reactions 2, 11 and 20 are formally identical, yet they have ΔS^* values ranging from -13 to $+15$ e.u.[28] This is significant in view of the approximate agreement among the $S^*_{complex}$ values. This indicates that an important source of the difference in the ΔS^* values lies in the differences in the entropies of the reactant ions. It would seem that the radius effect which leads to the large difference between the entropies of Fe^{+3} and Pu^{+3} is largely obscured in the activated complexes.

The most important single factor which determines the entropy of the activated complex appears to be its charge. In Table III are listed the values found for $S^*_{complex}$ for the four different charge types. Except for the value for equation 8 there is no overlap between adjacent groups. The variation within the individual groups may be due to inconsistencies in the standard entropy values as well as probably structural differences. The possibility that perchlorate ions are associated with some of the activated complexes cannot be ruled out. If such association does occur, however, it does not lower the effective charge on the activated complex by a whole unit. The values for the simple electron exchange reactions have been marked with the letter a; it is seen that the entropies of the activated complexes for these reactions are not significantly different from those for the other reactions. The high rates found for these reactions are thus due to their low heats of activation rather than to abnormally large ΔS^* values.

For equations 17 and 18, and probably for 4 and 5, intermediate dimers are involved. This means that in the activated complexes for these reactions, bonds are being formed or broken and that oxidation or reduction is not occurring by way of electron transfer over a large distance. Since the entropies of the activated complexes for these reactions are not significantly different from the entropies for the other reactions, it seems that there is no need to assume tunneling through thick barriers for any of the reactions in Table I.

The Effect of D₂O as Solvent.—For nearly all the reactions discussed in this paper, hydrogen-atom transfer mechanisms seem particularly attractive since they do not appear to involve extensive rearrangement of hydration shells before reaction
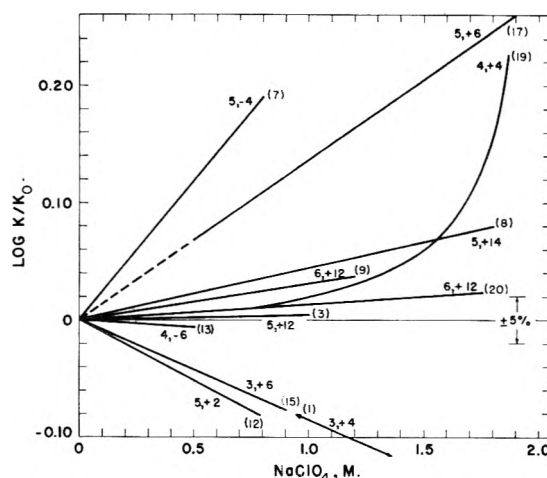

Fig. 2.—The effect of change of medium at constant ionic strength. The numbers in parentheses refer to the entries in Table I. The other numbers give the charges on the activated complexes and the Δz^2 values for the net activation processes, respectively.

can occur. Evidence for such a process has been sought by measuring the effect of D_2O as solvent on the rates of some of these reactions. The results of these experiments are shown in Table IV. The

TABLE III

ENTROPIES OF ACTIVATED COMPLEXES

Charge on the activated complex	$S^*_{complex}$ values, e.u.
+3	$-29,^a$ -30, -30, -40
+4	-67, -69, -62, -72, -81
+5	$-106,^a$ -72, -108, -87
+6	$-120,^a$ -118, -116, -118, -128

^{a} These values refer to the simple electron exchange reactions.

effect of D_2O is to slow some of the reactions and to speed others. Data for the $Cr^{+2} + Cr(NH_3)_5Cl^{+2}$ reaction[29] and the $Cl_3CH + Cl$ reaction[30] were included as examples which are known to have chlorine atom transfer and hydrogen atom transfer mechanisms respectively. The $Pu^{+4} + PuO_2^{+2}$ and the $Pu^{+3} + PuO_2^{+2}$ reactions are important since taken together they show that for the equilibrium $Pu^{+4} + PuO_2^+ \rightleftarrows Pu^{+3} + PuO_2^{+2}$ $K_H/K_D = 0.32$. This result is unexpected since water is not involved explicitly in the reaction and shows that the effect of D_2O on solvation cannot be ignored. Effects of similar magnitude are to be expected for activation processes; so that evidence for or against hydrogen atom transfer cannot be adduced from heavy water effects without the ability to predict the effect on the solvation.

Possible Medium Effects.—The interpretation of the observed hydrogen ion dependences for all of the reactions discussed has been in terms of a major path with a certain hydrogen ion dependence and, where necessary, a minor path with a different

(28) E. L. King, personal communication, has emphasized that it is not meaningful to compare the ΔS^0 values for processes with different Δn values; Δn is the change in the number of moles indicated by the equation for the process. For example, if the ΔS^0 values for two processes with different Δn values are equal under one choice of standard states, in general they will be unequal under a different choice. See H. A. Bent, ibid., **60**, 123 (1956).

(29) A. E. Ogard and H. Taube, J. Am. Chem. Soc., **80**, 1084 (1958).

(30) T. W. Newton and G. K. Rollefson, J. Chem. Phys., **17**, 718 (1949).

(31) F. B. Baker and T. W. Newton, THIS JOURNAL, **61**, 381 (1957).

(32) F. R. Duke and R. C. Pinkerton, J. Am. Chem. Soc., **73**, 2361 (1951).

hydrogen ion dependence. This interpretation is based on the assumption that the substitution of

TABLE IV
EFFECT OF D₂O ON REACTION RATES

Reaction	k_H/k_D	Remarks	Ref.
$Np^*O_2^+ + NpO_2^{+2}$	1.4	0.9 for H^+ dependent path	3
$Np^{+3} + NpO_2^+$	1.25		9
$UO_2^+ + UO_2^+$	0.59		32
$PuO_2^+ + PuO_2^-$	0.85		15
$Pu^{+4} + PuO_2^+$	0.57₅		5
$Pu^{+3} + PuO_2^{+2}$	1.79		5
$Pu(III) + O_2$	1.23	SO_4^- solution	31
$Cr^{+2} + Cr(NH_3)_5Cl^{+2}$	1.3	Cl-atom transfer, 86% D₂O	29
$Cl_3CH + Cl$	4.6	H-atom transfer, gas phase, 25°	30

Na^+ or Li^+ for H^+ at constant ionic strength has an insignificant effect on the activity coefficients of the reactant ions. It has been pointed out by Kraus[33] that this assumption deserves more attention than it usually gets and that it is particularly important with respect to the reality of some of the minor paths which have been suggested by some of the hydrogen ion dependence data.

If instead of the operation of a minor path, the pertinent activity coefficients are changing at constant ionic strength, it might be expected that these changes will be similar to those for substances for which Harned's rule applies. That is, the logarithms of the individual activity coefficients would be linear in changes of medium.[34] In this circumstance plots of log k versus the salt concentration would be straight lines.

Figure 2 shows such plots for 11 reactions for which hydrogen ion dependence data are available. The apparent rate constant for the major path is designated by k, while k_0 is that rate constant in either 1 or 2 M HClO₄ depending on the total ionic strength. The numbers in parentheses refer to the equation number in Table I. It was found that for all but one of the reactions reasonably satisfactory straight lines were obtained. At first sight this makes it appear that a distinction between a medium effect and the operation of a minor path

(33) K. A. Kraus, personal communication.

(34) See for example, R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth Scientific Publications, London, 1955, Chapter 15.

would, in general, be difficult. There are, however, several reactions for which the effect is small; under the assumption that the medium effect is large, these small net effects imply an unlikely cancellation of the true medium effect and the effect of minor paths. Another argument against the operation of a large medium effect is provided by the fact that there is no correlation between the net effect and either the charge on the activated complex or Δz^2 for the net activation process. These numbers are given next to the various lines in Fig. 2. It thus appears that the usual assumption, that the activity coefficients of the positive reactant ions are but little influenced by changes in the positive ions in the medium, is quite reasonable. Where the total effect is small, however, a distinction between the operation of a minor path and a medium effect is essentially impossible.

DISCUSSION

L. POKRAS.—(1) In considering major species in polyvalent metal ion solutions, have you related your conclusions to the work of the Sillén school? After all, values of the dimerization constants of hydroxy metal ion species are quite high—of the order of 10^4, so that mononuclear species should be relatively low. (2) In regard to charge diffusion, or charge reduction mechanics for highly charged metal ions, do the "onyl" ions like UO_2^{+2}, PuO_2^{+2}, etc., differ from Fe^{+3}, etc? The latter are primarily polynuclear.

T. W. NEWTON.—(1) The relative importance of dimers depends, of course, on the total metal ion concentration. For example, the work of Hedström (*Ark. Kemi*, **6**, 1 (1953)) indicates that in Fe(III) solutions of pH 2, the dimer is the predominant hydrolyzed species only in solutions where the total Fe(III) concentration is about 5 × 10^{-3} M or greater. In the solutions used in the rate measurements under discussion, dimer or polymer complexes were relatively unimportant since the concentrations and pH's were low. (2) The work of Ahrland, Hietanen and Sillén (*Acta Chem. Scand.*, **8**, 1907 (1954)) indicates that UO_2^{+2} hydrolyzes primarily to polymers.

R. H. BETTS.—Would you give a little more detail on how you calculated the term S^* for the transition complexes in these systems?

T. W. NEWTON.—The formal entropies of the activated complexes were calculated from the net activation processes in the usual way

$$\Delta S^* = S^*_{complex} \Sigma S_{other\ ions\ on\ the\ right\ hand\ side} - \Sigma S_{reactants}$$

ELECTRON TRANSFER IN THE SYSTEM, TRIS-(1,10-PHENANTHROLINE)-COBALT(II)-TRIS-(1,10-PHENANTHROLINE)-COBALT(III)

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The rates of electron transfer in the system tris-(1,10-phenanthroline)-cobalt(II)-tris-(1,10-phenanthroline)-cobalt(III) and analogous 2,2'-bipyridine and 2,2',2''-tripyridine systems have been studied by a tracer technique. The rate laws as well as rate constants depend upon the anion present and the results are discussed in terms of ion-association. The rate is the same in D_2O as in water but decreases in acetone–water solutions with increasing acetone concentration. The latter effect is discussed in terms of the barrier tunneling model for electron transfer. The rates and energy of activation are compared to those of other cobalt systems and the results are discussed in terms of the field strength of the ligand, metal ion electron configuration and shielding or conducting nature of the ligand.

A number of electron transfer reactions have been studied in which the primary coördination spheres of the metal ion remain unaltered. These are believed to proceed by a direct electron transfer rather than by an atom transfer mechanism.

With new developments in the theory of electron transfer and in the theory of metal–ligand bonding in metal complexes it became imperative that the theories be subjected to additional experimental tests.[2]

The systems chosen for this purpose were the tris-(1,10-phenanthroline)-cobalt(II)–tris-(1,10-phenanthroline–cobalt(III) and related 2,2'-bipyridine and 2,2'2''-tripyridine systems. There are several reasons for investigating these systems. In the first place, because of the nature of the complexes, these systems would seem to require electron transfer with little possibility of atom transfer. Secondly, some work has been done on cobalt(II)–cobalt(III) systems containing ligands of weak and moderately weak ligand field strength, but no direct studies had been reported for ligands of high field strength such as 1,10-phenanthroline.[3–6] Finally it was desired to study the effect of solvent on an electron-transfer system in which little possibility of a bridge-transfer mechanism exists.

Experimental

Preparation of Compounds.—The compound [Co(phen)₃](ClO₄)₂·1H₂O was prepared by the method of Pfeiffer and Werdelmann.[7] To prepare [Co(phen)₃](ClO₄)₃·2H₂O, the product from above was refluxed for 20 min. with 10 ml. of saturated bromine water and 20 ml. of water. Five ml. of 70% HClO₄ was then added to the hot solution. This serves not only to precipitate the cobalt(III) compound but destroys any cobalt(II) remaining.

Both compounds were characterized by nitrogen and water of hydration determination and by the absorption spectra from 340–250 mμ as compared with the spectra of the ions as prepared *in situ*.

Anal. Calcd. for Co(C₁₂H₈N₂)₃(ClO₄)₂·1H₂O: N, 10.30; H₂O, 2.20. Found: N, 10.05; H₂O, 2.22. Calcd. for Co(C₁₂H₈N₂)₃(ClO₄)₃·2H₂O: N, 9.00; H₂O, 3.85. Found: N, 8.80; H₂O, 3.98.

Tris-(2,2'-bipyridine)-cobalt(III) perchlorate was prepared by the method of Ellis, Wilkins and Williams.[6] In contrast to the monohydrate reported this compound appeared to contain 3 molecules of water. The ultraviolet spectra of both the hydrated and dehydrated salts confirmed this and show that no decomposition of the compound occurred during dehydration at 156° and 5 mm. pressure. Both spectra were unchanged in 0.03 M HCl.

Anal. Calcd. for Co(C₁₀H₈N₂)₃(ClO₄)₃·3H₂O: H₂O, 6.14. Found: H₂O, 5.88.

Bis-(2,2',2''-tripyridine)-cobalt(II) perchlorate was prepared by dissolving cobaltous chloride hexahydrate (0.16 g.) and 2,2',2''-tripyridine (0.4 g.) in 5 ml. of boiled, cooled water. To this solution was added 7 ml. of NaClO₄ solution (2 to 3 g. per 10 ml.) yielding red crystals. After cooling in ice these were filtered, washed first with 75% ethanol then finally with absolute ethanol. They were dried in air; yield 53% of theoretical. Tripyridine was determined spectrophotometrically by comparing the spectrum of the complex in 4 M HCl with that of a standard solution of tripyridine in 4 M HCl.

Anal. Calcd. for Co(tripy)₂(ClO₄)₂·1H₂O: tripy, 62.9; H₂O, 2.42. Found: tripy, 63.0; H₂O, 2.16.

Bis-(2,2',2''-tripyridine)-cobalt(III) perchlorate was prepared by refluxing cobaltous chloride (0.24 g.) and tripyridine (0.5 g.) in 40 ml. of water with 22 ml. of bromine water. On the addition of 10 ml. of 70% HClO₄, yellow crystals separated. These were filtered, washed with ice-water and dried over CaCl₂.

Anal. Calcd. for Co(C₁₅H₁₁N₃)₂(ClO₄)₃·1H₂O: N, 9.98; H₂O, 2.14. Found: N, 10.03; H₂O, 2.16.

Exchange Studies.—The rate of exchange was followed by a tracer method using cobalt-60, the activity being introduced either as cobalt(II) or cobalt(III). In order to obtain the greatest precision possible, the concentration of one oxidation state was always at least twice that of the other. The activity then was introduced in the form of the oxidation state of lowest concentration.

Reaction solutions were prepared assuming additivity of volumes except in the case of the water–acetone solutions in which the volumes of acetone and water were experimentally determined to give a predetermined volume of reaction solution. The solutions were prepared to contain [Co(phen)₃]SO₄ (prepared *in situ* by mixing stock solutions of 1,10-phenanthroline and CoSO₄), excess phenanthroline (1 × 10⁻³ M to 0.85 × 10⁻³ in all runs), and buffer solution. The reaction vessels were 10-ml. volumetric flasks or 15-ml. glass stoppered test-tubes.

The reactions were started by pipetting 0.5 ml. of [Co-

(1) Based upon a portion of the thesis submitted by B. R. Baker to Northwestern University in June, 1958, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Abbott Fellow, 1955–1957.

(2) The ligand field theory of metal complexes, developed by H. Bethe, *Ann. Physik*, [5] **3**, 133 (1929) and L. E. Orgel and co-workers in numerous papers, is allied closely with the theories of electron transfer and has received consideration in this respect by L. E. Orgel, Tenth Solvay Conference, Brussels, May 1956; and F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

(3) W. B. Lewis, C. D. Coryell and J. W. Irvine, *J. Chem. Soc.*, 5386 (1949).

(4) A. W. Adamson and K. S. Vorres, *J. Inorg. Nuc. Chem.*, **3**, 206 (1956).

(5) N. A. Bonner and J. P. Hunt, *J. Am. Chem. Soc.*, **74**, 1866 (1952).

(6) The rates of electron transfer in the phenanthroline and bipyridine systems have been reported by P. Ellis, R. G. Wilkins and M. J. G. Williams, *J. Chem. Soc.*, 4456 (1957); but this was an indirect measurement, being obtained from the rate of exchange of radio-phenanthroline and radio-bipyridine with the cobalt(III) ions *via* the electron transfer with the labile cobalt(II) ions.

(7) Von P. Pfeiffer and B. Werdelmann, *Z. anorg. Chem.*, **261**, 197 (1950).

(phen)₃](ClO₄)₂ solution (approximately 1×10^{-3} M) into the reaction vessel followed by rapid stirring either by repeated inversion of the stoppered vessel or by means of a stream of nitrogen passed into the solution. Six 1-ml. aliquots were withdrawn at intervals of 2 to 5 min. and treated as described below. The solution then was allowed to warm to room temperature for a time to ensure that isotopic equilibrium had been established. Two 1-ml. infinite-time samples then were withdrawn and treated exactly as the other samples.

The experimental procedure for the 2,2'-bipyridine and 2,2',2''-tripyridine systems was similar to that of the phenanthroline system except that no excess of tripyridine could be used due to its insolubility in water. Instead a weighed quantity of [Co(tripy)₂](ClO₄)₂·1H₂O was dissolved in a measured volume of water just prior to the exchange run. The reaction was started by adding a measured volume of active [Co(tripy)₂](ClO₄)₃ solution. Under the low concentration conditions used, the cobalt(II) ion may be about 10% dissociated at equilibrium; however the dissociation of the ion is reported to be slow[8] ($t_{1/2}$ = 2.8 hr. at 15°). Thus it may be assumed that all of the cobalt(II) ion exists in the bis form.

Temperature control was provided by an ice–water mixture in a Dewar flask for the 0° runs and by an ordinary thermostated water-bath for the runs at higher temperature. All reactions were run in the dark even though there was no evidence for a light catalyzed reaction. Prior deaeration by nitrogen had no effect on the rate; however this precaution was taken for the tripyridine system because of the apparent greater ease of oxidation of Co(tripy)₂²⁺ than Co(phen)₃²⁺.

Methods of Separation.—Three methods were used for the separation of cobalt(II) from cobalt(III). In the first, an aliquot of the reaction mixture was pipetted into a mixture of 4 ml. of n-hexyl alcohol and 4 ml. of a nearly saturated solution of sodium acetate (440 g. of anhydrous sodium acetate per liter of water) at 0°. When this mixture was shaken for 35 sec. about 70–80% of the cobalt(II) was extracted from aqueous solution, or about 90% from acetone–water solution, into the alcohol phase, leaving all of the cobalt(III) in the aqueous phase. The phases were separated by centrifugation and when all the samples of a particular run had been collected the alcohol phase was withdrawn and prepared for counting. The degree of separation was reproducible as shown by the linear kinetic plots. Since exchange occurred during the separation, an attempt was made to carry out each separation in exactly the same manner so that the fraction of exchange occurring during separation was the same for each sample.

The second separation method was carried out by pipetting a reaction mixture aliquot into 1 ml. of 4 M HCl contained in a 50-ml. separatory funnel. This serves to quench the reaction due to dissociation of the cobalt(II) complex ion. The cobalt(III) ion is not affected by this treatment. To this solution was added 4 ml. of 30% NH₄SCN solution and the mixture was shaken with 15 ml. of 1:1 ether–n-hexyl alcohol solution. Extraction of Co²⁺ was about 85–90% complete and was reproducible. This procedure can be used only when the concentration of Co(phen)₃³⁺ is <10⁻⁴ M as this ion forms an insoluble thiocyanate. Comparison of the sodium acetate and ammonium thiocyanate methods show the exchange rates to be the same for each within experimental error.

The third separation procedure was used primarily for the bi- and tripyridine systems. In this procedure the cobalt(II) ion was dissociated by 4 M HCl as for the thiocyanate separation. A 1-ml. aliquot of the reaction mixture was added to 1 ml. of 4 M HCl contained in a 15-ml. centrifuge tube. One milliliter of a 1×10^{-3} M solution of cobalt(III) perchlorate solution then was added as a carrier. To this solution, 5 or 6 drops of 1 M KI₃ solution was added which precipitated salts of the type [Co(phen)₃](I₃)₃ or [Co(tripy)₂](I₃)₃. These form as red, crystalline, easily handled precipitates. They are extremely insoluble in water but very soluble in acetone. Following centrifugation the precipitates were washed with two 2-ml. portions of 0.1 M KI₃ and prepared for counting as described below.

Methods of Counting.—Three counting techniques were used. In the first, an aliquot of the aqueous phase from the sodium acetate, or ammonium thiocyanate separation was diluted with 10 cc. of water and pipetted into the jacket

surrounding the detector tube (Radiation Counter Laboratories, Mark 1, Model 71, jacketed Geiger tube, shielded with 0.5 inch of lead). The tube was connected to a model 182A scaling unit, Nuclear Instrument and Chemical Corp. The sample was counted for a total of at least 5000 counts and the appropriate background correction was made. It was shown that no coincidence corrections were necessary.

The other two techniques involved preparation of solid samples. An aliquot (0.5–1.0 ml.) of the alcohol phase from the sodium acetate separation was measured onto an aluminum counting tray containing a piece of tightly fitting filter paper. The solvent then was evaporated under a heat lamp. For counting the tray was positioned about one inch from the window of a Tracerlab Geiger tube, model TGC 2/11384, connected to the same scaling unit described above.

To count samples from the triiodide separation the precipitated cobalt(III) triiodide salt first was dissolved in 2 ml. of acetone and then transferred quantitatively to an aluminum counting tray lined with a piece of filter paper. The solvent was evaporated under a heat lamp. Preparation of a uniform sample by this procedure is difficult. For this reason the weak β-activity of the cobalt could not be measured precisely and was absorbed by an aluminum absorber leaving only the γ-radiation to be counted.

Preparation of Radioactive Solutions.—Radioactive cobalt-60 was obtained in the form of an HCl solution from the Oak Ridge National Laboratory, Union Carbide Nuclear Company. It was found to contain iron and nickel as impurities. Nickel was removed by evaporating the solution to dryness and extracting the residue with an ether solution of HCl. The cobalt is removed in such a procedure as a solution of H₂CoCl₄ along with iron. Following evaporation of the ether, iron was removed by precipitation as the hydrous oxide. The solution then was diluted to give a convenient volume of stock solution. Stock solutions prepared by further dilution of this solution, on standing, frequently led to exchange rates much greater than normal. It was found that digestion with H₂SO₄, followed by removal of the excess H₂SO₄ by repeated evaporation and ignition over a bunsen flame, led to normal rates again. Therefore all subsequent runs were made with CoSO₄ solutions prepared in this manner, the treatment with H₂SO₄ being repeated whenever necessary. This unusual behavior is possibly due to catalysis by H₂O₂ formed by radiation induced decomposition of the water.

Radioactive [Co(phen)₃](ClO₄)₃ solutions were prepared in the following manner. A 0.001 M solution of [Co(phen)₃](ClO₄)₃ (10 ml.) was heated on a steam-bath with 0.2 ml. of 0.01 M phenanthroline solution and 0.1 ml. of active CoCl₂ solution. This treatment served to convert about 90% of the active cobalt to the cobalt(III) form by electron transfer. About 0.5 ml. of 70% HClO₄ solution then was added and the solution was chilled in ice. The precipitate of [Co(phen)₃](ClO₄)₃ was washed with several portions of ice-water, the supernatant liquid being removed each time with a dropping pipet. The solid then was dissolved in 9 ml. of water, the solution passed through a sintered glass filter and its concentration determined spectrophotometrically.

Due to the greater solubility of [Co(tripy)₂](ClO₄)₃, a solution of this salt could not be prepared by the above method, therefore the following technique was used. About 0.3 ml. of active CoCl₂ was evaporated to dryness. To the residue was added 0.02 to 0.04 g. of [Co(tripy)₂](ClO₄)₃ and one or two crystals of tripyridine. About 5 ml. of ethanol then was added and the solids were dissolved by warming and dropwise addition of water. When solution was just complete about 10 ml. of ether was added which precipitated a solid, presumably a mixture of [Co(tripy)₂](ClO₄)₃ and [Co(tripy)₂](ClO₄)₂ in about a 9:1 ratio. It was assumed that isotopic equilibrium had been established. The mixture was centrifuged and the supernatant liquid removed. The solid now was washed with several portions of 1:1 ether–ethanol and finally with ether alone. The ultraviolet spectrum of an aqueous solution of the resulting solid was used to determine the concentrations of Co(tripy)₂²⁺ and Co(tripy)₂³⁺.

Reagents and Materials.—The sodium acetate was of several grades and stocks. All was recrystallized from water and dried to the anhydrous material. The n-hexyl alcohol was Eastman Kodak Co. technical grade, dried over anhydrous sodium carbonate and distilled.

(8) B. O. West, J. Chem. Soc., 578 (1954).

Acetone was purified by the method of Livingston[9] or by refluxing with crystals of KMnO₄ until a pink color persisted. The latter treatment was followed by treatment with anhydrous sodium carbonate and fractional distillation. It was stored cold and used as soon after purification as possible. Different acetone preparations, if stored not longer than several days, gave identical exchange results

Treatment of the Data.—The exchange follows the McKay equation[10]

$$-\ln\left|\frac{A_\infty - A}{A_\infty - A_0}\right| = \frac{Rt(a + b)}{ab}$$

A_∞, A_0 and A are activity at infinite, zero and time t, respectively. R is the gross rate of exchange and a and b are concentrations of the two oxidation states. The order of the reaction is determined from the equation $R = ka^\alpha b^\beta$. To obtain R, $-\ln|A_\infty - A|$ was plotted *versus* time, the slope being equal to $R(a + b)/ab$. The samples were chosen to represent the first two half-lives of the reaction. Usually individual runs gave good straight lines plotted in this manner but deviations in R from run to run were larger than expected on this basis. The probable error is felt to be about 25%.

Because of the incomplete separation, the zero-time exchange could be determined only when the activity of the alcohol phase from the sodium acetate separation (containing cobalt(II)) was measured with the activity initially in the form of cobalt(III). The fraction exchange at $t = 0$ was 0.05–0.1 in several runs.

Results

Cobalt(II), Cobalt(III) and Anion Dependences.

—The results for the determination of the dependence on cobalt(II) and cobalt(III) concentrations in KCl and KNO₃ solutions are given in

EXCHANGE RATES IN CHLORIDE SOLUTIONS—DEPENDENCE OF RATE ON Co(Phen)₃³⁺ AND Co(Phen)₃²⁺

Boric acid buffer (0.0025 M NaOH, 0.0125 M H₃BO₃), except as otherwise noted; temperature 0°, ionic strength 0.1.

Series	[Co(III)] × 10⁴	[Co(II)] × 10⁴	pH	$R \times 10^6$	k^a
A	8.00	0.57	8.8	4.11	1.8[b]
	1.00	.57	8.8	1.60	2.1[b]
	10.0	.57	8.8	6.69	0.89
	5.40	.57	8.8	3.92	1.3
	3.24	.57	8.8	3.21	1.3
	1.00	.57	8.8	1.35	1.8
				Av.	1.3[c]
B	4.3	.48	8.32	5.1	1.7
	1.90	.48	8.32	1.95	1.5
	0.95	.48	8.32	0.85	1.3
				Av.	1.5
C	0.41	3.39	8.8	1.41	1.9[d]
	.44	5.65	8.8	2.20	1.8[d]
	.44	3.39	8.8	1.69	2.2[d]
	.44	1.13	8.8	0.91	1.9[d]
				Av.	1.9
D	.52	5.65	8.32	2.20	1.8
	.52	3.39	8.32	1.22	1.3
	.52	1.13	8.32	0.90	1.6
	.52	1.13	8.32	1.01	1.8
				Av.	1.6

[a] $k = R/[\text{Co(III)}][\text{Co(II)}]^{1/2}$ where R is in units of mole/l. min. [b] [KCl] = 0.2. [c] Excluding runs in 0.2 M KCl. [d] Thiocyanate separation. All others by acetate separation.

(9) R. Livingston. *J. Am. Chem. Soc.*, **69**, 1220 (1947).
(10) H. A. C. McKay, *Nature*, **142**, 997 (1938).
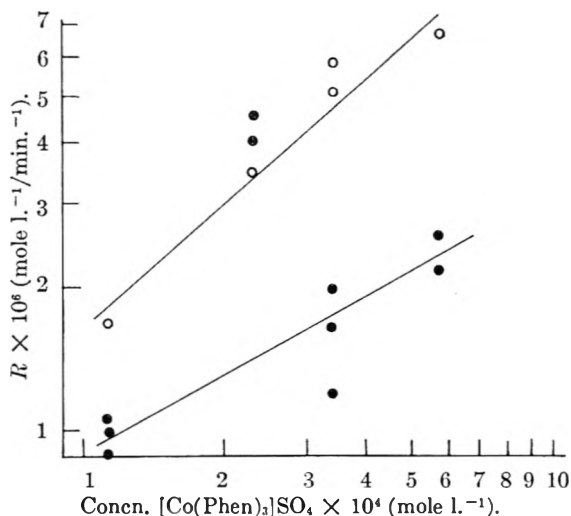
Fig. 1.—Dependence of exchange rate on cobalt(II) concentration: open circles, pH 8.3, 0.1 M KNO₃; closed circles, pH 8.3, 0.1 M KCl; hatched circles, pH 6.5, 0.1 M KNO₃. All runs at 0° and 0.52 × 10⁻⁴ M [Co(phen)₃](ClO₄)₃.
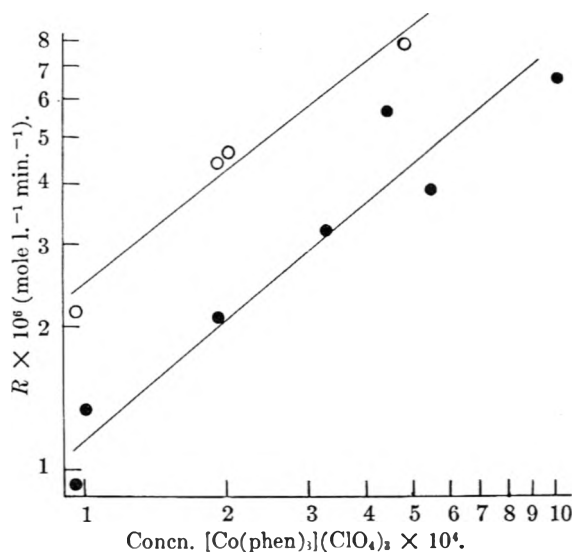

Fig. 2.—Dependence of exchange rate on cobalt(III) concentrations: open circles, 0.1 M KNO₃; closed circles, 0.1 M KCl. All runs at 0°, pH 8.3–8.8 and 0.57 × 10⁻⁴ M [Co(phen)₃](ClO₄)₂.

Tables I and II. These data are plotted in Figs. 1 and 2. Table III gives the dependence of rate on chloride and nitrate ion at constant ionic strength, and Table IV gives the results for the cobalt(II) and cobalt(III) dependence runs with no added electrolyte at three temperatures. The data for D₂O solution are shown in Table V. The results are expressed in terms of k_{H_2O}/k_{D_2O} since differences in stock solutions of active CoSO₄ exist between the two series. Run 7 was made with the same D₂O solution of active CoSO₄ used in runs 8 and 9. Since the concentration of D₂O introduced in this way is small (4% of total water) its effect was ignored. This difference in stock solutions was due to an aging of the solution as described before and, because of the effect, the results have only a relative significance. The

Table II

Exchange Rates in Nitrate Solution—Dependence of Rate on $Co(Phen)_3^{3+}$ and $Co(Phen)_3^{2+}$

Boric acid buffer; pH 8.29 except as noted; $[KNO_3] = 0.1$ M, temperature 0°, ionic strength = 0.1.

Series	$[Co(III)]$ $\times 10^4$	$[Co(II)]$ $\times 10^4$	$R \times 10^{6a}$	k (l. mole^{-1} sec.$^{-1}$)
E	0.52	5.65	6.81	3.8
	.52	5.65	16.7	9.5
	.52	3.39	5.96	5.7
	.52	3.39	5.17	5.5
	.52	2.26	3.5	5.0
	.52	1.13	1.67	4.7
	.52	2.26	4.06	5.8[b]
	.52	2.26	4.6	6.5[b]
			Av.	4.8[c]
F	4.75	0.48	6.6	4.8
	2.00	.48	3.94	6.9
	1.90	.48	3.77	6.8
	0.95	.48	1.86	6.8
			Av.	6.3

[a] R is in units of mole l.$^{-1}$ min.$^{-1}$. [b] Phosphate buffer; pH 6.50 (0.0025 M NaOH, 0.005 M KH_2PO_4). [c] Excluding runs 2, 7 and 8.

Table III

Effect of NO_3^- and Cl^- on Rate of Exchange between $Co(Phen)_3^{3+}$ and $Co(Phen)_3^{2+}$ at 0°

$[Co(III)] = 2.0 \times 10^{-4}\ M$, $[Co(II)] = 0.51 \times 10^{-4}$, ionic strength = 0.1

$[Cl^-]$	$[NO_3^-]$	$R \times 10^6$	k (l. mole^{-1} sec.$^{-1}$)	k^{1a}
	0.10	2.4	4.0	
	.10	2.5	4.1	
	.067[b]	2.0	3.3	
	.067[c]	1.7	2.7	
	.067[c]	2.1	3.5	
0.10		0.89		0.62
.10		1.1		.80
.067[d]		0.64		.45
.05[e]		0.56		.39

[a] $k^1 = R/[Co(III)][Co(II)]^{1/2}$ where R is in units of mole l.$^{-1}$ min.$^{-1}$. [b] $[Ba(NO_3)] = 0.0335\ M$. [c] $[Mg(NO_3)_2] = 0.0335\ M$. [d] $[MgCl_2] = 0.0335\ M$. [e] $[LaCl_3] = 0.0167\ M$.

Table V

Rate of Exchange in D_2O Solution

Run	Solvent	$[Co(II)]$ $\times 10^4$	$[Co(III)]$ $\times 10^4$	k (l. mole^{-1} sec.$^{-1}$)	(Av.) k_{H_2O}/k_{D_2O}
1	H_2O	4.75	0.48	1.8	
2	H_2O	4.75	.48	1.8	
3	H_2O	2.00	.48	1.5	
4	H_2O	2.00	.48	1.8	
5	H_2O	2.00	.48	2.1	
				Av. 1.8	
6	D_2O	6.66	.48	1.8	1.0
7	H_2O	1.67	.40	2.4	
8	H_2O	1.87	.40	2.6	
9	D_2O	1.87	.40	2.8	0.89

data for water–acetone solutions are shown in Table VI.[11]

Temperature Dependence.—In Fig. 3 is plotted the log k_r versus $1/T \times 10^3$ from which an activa-

(11) The values for the dielectric constant of water–acetone solutions were taken from the data of G. Akerlof, *J. Am. Chem. Soc.*, **54**, 4125 (1935).

Table IV

Rate of Exchange between $Co(Phen)_3^{3+}$ and $Co(Phen)_3^{2+}$ in Aqueous Solution with No Added Electrolyte

$[Co(III)]$ $\times 10^4$	$[Co(II)]$ $\times 10^4$	$R \times 10^6$	k (l. mole^{-1} sec.$^{-1}$)
Temp. −0°			
0.63	2.26	0.85	0.95
.63	2.26	1.04	1.2
.63	5.65	1.51	0.72
.63	7.18	1.77	0.65
.75	2.71	1.54	1.3
.59	3.39	1.26	1.0
.59	3.39	1.71	1.4
.39	3.39	0.87	1.1
5.00	0.48	1.22	0.85
2.00	.48	0.80	1.40
8.5	.48	3.00	1.23
		Av.	1.1
Temp. 4.2°			
4.75	0.48	2.50	1.8
4.75	.48	2.50	1.8
2.00	.48	0.87	1.5
2.00	.48	1.02	1.8
		Av.	1.7
Temp. 12.8°			
0.48	2.26	3.34	5.1
.48	2.26	4.49	6.9
.48	2.26	3.58	5.5
		Av.	5.8

Table VI

Rate of Exchange in Acetone–Water Solutions at 12.8°

Acetone, wt. %	Dielectric constant	k (l. mole^{-1} sec.$^{-1}$)[a,b]
0	83.0	5.1
0	83.0	6.9
0	83.0	5.5
8.1	78.6	4.6
16.5	73.3	2.5
32.8	63.0	1.3
32.8	63.0	1.8
54.1	48.6	2.0
72.7	36.2	1.7
72.7	36.2	1.6
72.7	36.2	1.8

[a] $[Co(II)] = 2.26 \times 10^{-4}\ M$ $[Co(III)] = 0.48 \times 10^{-4}$ M. [b] Reaction assumed to be first order in each ion.

Table VII

Exchange in the Systems $Co(Tripy)_2^{2+,3+}$ and $Co(bipy)_3^{2+,3+}$

System	$[Co(III)]$ $\times 10^4$	$[Co(II)]$ $\times 10^4$	$R \times 10^5$	k (l. mole^{-1} sec.$^{-1}$)[a]
Tripy	0.46	2.27	7.8	12.4
	0.46	1.72	5.66	11.9
Bipy	2.00	0.50	1.9	3.2
	2.00	.50	1.2	1.9
	2.00	.50	0.72	1.2

[a] Assumed to be second order.

tion energy of 17 ±5 kcal. mole^{-1} and an entropy of activation of +4 e.u. may be estimated.

2,2′-Bipyridine and 2,2′,2″-Tripyridine Systems. —Table VII gives the results for the exchange rates in the bipyridine and tripyridine systems at 0°,
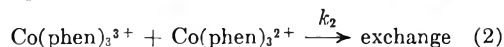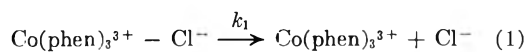
Discussion

Although the data show considerable scatter the rate seems to be dependent approximately upon the first power of each oxidation state concentration in KNO_3 solution and with no added electrolyte. However, in KCl solutions, the rate appears to be first order in cobalt(III) but approximately $^1/_2$ order in cobalt(II). These simple rate laws were used to calculate the values of k in Tables I–IV, even though they are not obeyed exactly. The data of Table II series E show that pH has no effect. The small increase in rate in the pH 6.5 buffers can be accounted for by a slightly higher salt concentration.

Specific Anion Effect.— It will be noted that for a given set of concentrations the rate R is 2 to 3 times greater for KNO_3 solutions than for KCl solutions. This is shown by Figs. 1 and 2. In view of the effects of anions on the rates of dissociation and racemization of $Fe(phen)_3^{3+}$ [12] it is not too surprising that unusual specific salt effects are also observed in the electron transfer reaction.

The behavior in chloride solution is unexpected in many ways: the rate in 0.05 M Cl^- is slower than in the absence of chloride, but additional chloride increases the rate; and the dependence on the cobalt(II) concentration is less than first order. To account for this behavior it is attractive to postulate the existence of ion-pairs between $Co(phen)_3^{3+}$ and Cl^-. Examination of models shows that the chloride ion can occupy a position quite close to the metal ion between the planes of the phenanthroline rings. In order for there to be no net free energy change during the isotope exchange, the chloride must transfer from cobalt-(III) to cobalt(II). Transfer from such a "buried" position to another similar position requires the chloride to move several ångström units. If this is energetically unfavorable because of the nature of the potential between the complex ion and the chloride ion, an inhibition of the electron transfer would be expected.

If the rate of exchange between $Co(phen)_3^{3+}$–Cl and $Co(phen)_3^{2+}$ were sufficiently slow the exchange might proceed more rapidly via the sequence of reactions

$$Co(phen)_3^{3+} - Cl^- \xrightarrow{k_1} Co(phen)_3^{3+} + Cl^- \quad (1)$$

$$Co(phen)_3^{3+} + Co(phen)_3^{2+} \xrightarrow{k_2} \text{exchange} \quad (2)$$

If the ion-pair dissociation of reaction 1 were sufficiently slow with respect to reaction 2, the fractional dependence on the cobalt(II) concentration would follow. Unfortunately the kinetic data are of insufficient precision and cover only a limited range of concentrations, therefore no attempt has been made to fit the data to such a mechanism.

It would appear difficult to explain the fractional power dependence in any other way in view of the nature of the complex ions. The ion $Co(phen)_3^{2+}$ is thermodynamically stable ($k_1k_2k_3 = 1.26 \times 10^{20}$ for the formation of the ion),[13] and the ion,

(12) J. E. Dickens, F. Basolo and H. M. Neumann, *ibid.*, **79**, 1286 (1957).

(13) J. E. Dickens, Thesis, Oxford, 1954.
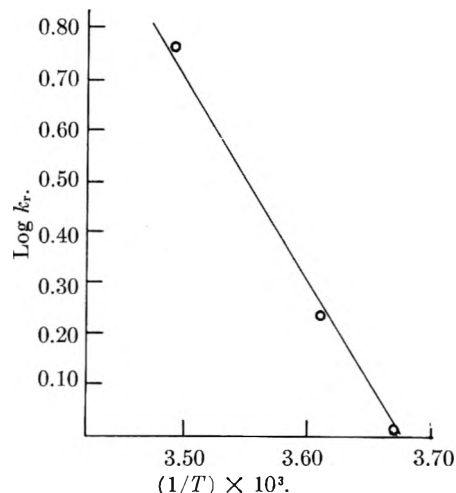
Fig. 3.—Dependence of exchange rate on temperature.
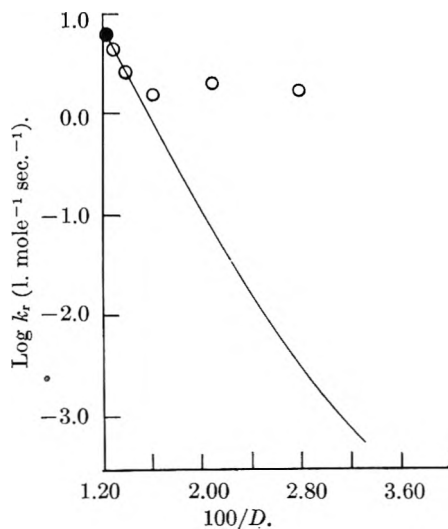
Fig. 4.—Exchange rate *versus* dielectric constant of acetone–water solutions: open circles, experimental values; closed circle, fitted value; solid curve, calculated from Marcus, Zwolinski and Eyring model; temperature, 12.8°.

$Co(phen)_3^{3+}$ is kinetically stable[6] and probably thermodynamically stable as well. Thus it seems unlikely that there would be any species other than the two tris ions $Co(phen)_3^{2+,3+}$ under the exchange conditions.

The characteristics of the proposed ion-pair require stronger binding between the ions than normally exists in ion-pairs, but the unusual geometric characteristics of the phenanthroline complexes may be responsible for this. The nitrate ion would also be expected to form ion-pairs. If it does, the nitrate ion is certainly bound less firmly than the chloride ion. Because of its size and shape the nitrate ion projects somewhat farther from the complex, and it would not have to transfer as far as the chloride ion.

It will be noted from Table III that after the initial inhibition the rate is almost first order in Cl^- concentration. This would suggest that ion-pair formation with cobalt(III) is essentially complete at $[Cl^-] = 0.05\ M$. Thereafter the increase in rate is similar to the effect caused by nitrate

ion, and this may represent a general anion catalysis.

Effect of Solvent.—From reference to Table V it is apparent that the rates in D_2O solution are the same as those in H_2O. This is expected since the effects observed in the $Fe^{2+}-Fe^{3+}$ [14] and $Np(V)-Np(VI)$ [15] systems were attributed to hydrogen atom transfer. Such a mechanism in the $Co(phen)^{2+,3+}$ system seems unlikely.

It is informative to consider the results from water–acetone solutions in terms of various theoretical models which have been suggested for electron exchange reactions. In general, the free energy of activation, $\Delta F^{\ddagger}$, is made up of three terms

$$\Delta F^{\ddagger} = \Delta F_r^{\ddagger} + \Delta F_n^{\ddagger} - RT \ln K$$

where $\Delta F_r^{\ddagger}$ is the electrostatic repulsion term; $\Delta F_n^{\ddagger}$ is the free energy associated with rearrangement of the coördination and solvation spheres; and $-RT \ln K$ is the electron tunneling probability term.

One extreme model assumes that the exchanging species are separated by several layers of solvent molecules, and the electron exchange is then treated as a barrier penetration problem. According to this model the rate should be dependent on the dielectric constant of the medium separating the exchanging species. Figure 4 illustrates the relationship between the rate constant and the dielectric constant as obtained from the experiments with water–acetone solutions. The values of log k_r are plotted as a function of $100/D$ where k_r is the specific rate constant and D is the dielectric constant. This figure also shows a comparison with the electron tunneling model of Zwolinski, Marcus and Eyring. [16] They developed equations for $\Delta F_r^{\ddagger}$ and $-RT \ln K$, but in order to calculate $\Delta F^{\ddagger}$ it is necessary to estimate $\Delta F_n^{\ddagger}$. This was done in the calculations of Fig. 3 by fitting k_r experimental, to k_r calculated, in aqueous solution, obtaining $\Delta F_n^{\ddagger} = 7.5$ kcal. mole^{-1}. The use of this constant value of $\Delta F_n^{\ddagger}$ throughout the solvent composition range is reasonably consistent with a model that postulates separation of the exchanging species by several layers of solvent molecules.

The objection may be raised that the macroscopic dielectric constant has been used in the calculation, and that, as has been suggested by Cohen, Sullivan, Amis and Hindman [17] it is the microscopic constant that should be used. If the solvation sphere has a composition different from that of the bulk of the solution the two constants will be different. If the ions are preferentially solvated by water one would expect a constant rate in solutions of high water content, and a decreasing rate in solutions of high acetone content. If the ions are preferentially solvated by acetone one would expect a decreasing rate in solutions of high water content, and a constant rate in solution

of high acetone content. Qualitatively the results correspond to the latter case. Preferential solvation by acetone is not unreasonable; examination of molecular models show that acetone can conveniently occupy "buried" positions between the phenanthroline planes. This association might be due to van der Waals forces to a large extent, and hence be similar for both cobalt(II) and cobalt(III). However, the limiting rate corresponds to a dielectric constant of about 70; and the model would then require preferential solvation by acetone which results in a microscopic dielectric constant of about 70. It appears that this model does not apply, at least over the entire solvent composition range.

A second extreme model would be one in which the ions exchange electrons while in direct contact. In this case the $-RT \ln K$ term would be assumed constant with changing solvent composition. Differences in rate would then be attributed to differences in ΔF_r^* and to differences in the free energy necessary for rearrangement of the solvation spheres; energy for rearrangement of the coördination spheres would be a constant. If the solvation rearrangement energy is the dominant requirement and if the solvation sphere has a composition and structure similar to that of the bulk of the solution, one might attempt to correlate the rate with some property related to the energy necessary to break up the solvent structure. The viscosity is one such property. The viscosity of acetone–water mixtures rises from a value of about 23 to 45 weight % acetone, and then decreases to a value of about 3 in pure acetone. By comparison, the exchange rate reached a limiting low rate at about 20% acetone. The correlation is not satisfactory, but no other property appears more promising. Preferential solvation by acetone would complicate the situation, but would be expected to lead to a limiting rate in solutions of high acetone content.

In these considerations the assumption has been made that the exchanging species were the solvated ions. There is certainly some association of $Co(phen)_3^{3+}$ with SO_4^{2-} in the solvent mixtures of low dielectric constant, even though the sulfate concentration is only 3×10^{-4} M. The limiting rate might then be a reflection of the fact that in these solvent mixtures the reaction was proceeding by the same sulfate bridge mechanism.

Effect of the Ligand.—This effect is best illustrated by reference to Table VIII.

The effect may be divided into three factors. (1) the effect of ligand on the spin multiplicity of the central metal ion; (2) effect of electron configuration of the metal on the metal–donor bond lengths; and (3) insulating or conducting nature of the ligand. When exchange can occur between two spin-free or two spin-paired configurations there will be no multiplicity restriction. This approximately corresponds, respectively, to the $Co(H_2O)_6^{2+,3+}$ and $Co(Phen)^{2+3+}$ systems. In the former the excitation of the spin-paired $Co(H_2O)^{3+}$ state to the spin free state probably requires only a small energy and in the latter case the excitation energy for formation of a spin-paired $Co(phen)_3^{2+}$ from a spin-free state is probably small. These

(14) J. Hudis and R. W. Dodson, *J. Am. Chem. Soc.*, **78**, 911 (1956).

(15) J. C. Sullivan, D. Cohen and J. C. Hindman, *ibid.*, **79**, 3672 (1957).

(16) B. T. Zwolinski, R. J. Marcus and H. Eyring, THIS JOURNAL, **58**, 432 (1954).

(17) D. Cohen, J. C. Sullivan, E. L. Amis and J. C. Hindman, *J. Am. Chem. Soc.*, **78**, 1543 (1956).

TABLE VIII

System	Ligand field strength	$r_1 - r_2$	Expected rate	$k(m.^{-1} - sec.^{-1})$	E_a	ΔS^+	Ref.
$Co(H_2O)_6^{2+,3+}$	Weak	Small	Fast	0.75 (0°)	..	..	5
$Co(en)_3^{2+,3+}$	Intermediate	Very large	Very slow	5.0×10^{-5} (25°)	14.3	−33	3
$Co(NH_3)_6^{2+,3+}$	Intermediate	Very large	Very slow	Very slow (45°)	..	..	3
$Co(EDTA)^{1-,2-}$	Intermediate	Very large	Very slow	2.1×10^{-4} (85°)	22	−17	4
$Co(phen)_3^{2+,3+}$	Strong	Large	Slow	1.1 (0°)	17	+ 4	This paper

conclusions follow from a qualitative consideration of the ligand-field theory.[2] With ligands of intermediate ligand field strength, however, there exist larger multiplicity restrictions.

The bond-distance effect is shown in Table VIII. The difference in bond-distance between the two oxidation states is given by $r_1 - r_2$. Orgel considers $r_1 - r_2$ to be due largely to the presence or absence of electrons in the d γ level of the metal ion in a cubic field.[2] These electrons will be concentrated along the bond axes and because of the repulsion exerted on the ligands, the metal–donor bond distances will be longer when d γ electrons are present than when they are absent. The larger $r_1 - r_2$, the greater must be the rearrangement to give a symmetrical transition state to allow the electron to transfer. On this basis Orgel predicted that the rate of transfer and energy of activation in the system $Co(phen)_3^{2+,3+}$ would be similar to that of chromium systems since the two systems have formal similarity in electron configuration.[19] The rate of transfer in the system $Cr(H_2O)_6^{2+,3+}$ is slower than that for $Co(phen)_3^{2+,3+}$ by a factor of at least 10^4.[20]

On the basis of the expected rearrangement requirements in the $Co(phen)^{2+,3+}$ system, the large activation energy of 17 kcal mole⁻¹ seems reasonable. However, the rate of transfer seems anomalously large and suggests the importance of the conducting nature of the conjugated ligand sphere leading to a high probability of transfer and a positive entropy of activation. This posibility has been mentioned by Ellis, Wilkins and Williams[6] and is supported to some extent by the observation of Taube.[21]

Comparison with the Data of Ellis, Williams and Wilkins.—These authors reported a value of 18.7 and 4.46 l. mole⁻¹ sec. ⁻¹ for the rate constants of the $Co(bipy)_3^{2+,3+}$ and $Co(phen)_3^{2+,3+}$ systems, respectively, at 20°. On extrapolating the data of Table IV to 20°, a value of 11.2 l. mole⁻¹ sec. ⁻¹ is obtained for k_r for the $Co(phen)_3^{2+,3+}$ system. In view of the indirect measurement of Ellis, Wilkins and Williams and the large experimental error in the present investigation, the agreement between the two sets of data is probably as good as can be expected. The somewhat better agreement previously reported[6] was based on preliminary results of the present investigation and is not reliable.

Acknowledgment.—The authors wish to acknowledge the numerous valuable discussions with

(19) The electron configurations can be written: Cr(II) ($d\epsilon^3 d\gamma^1$), Cr(III) ($d\epsilon^3 d\gamma^0$), Co(II) ($d\epsilon^5 d\gamma^1$) and Co(III) ($d\epsilon^6 d\gamma^0$). The ion $Co(phen)_3^{2+}$ is actually spin free but the excitation energy to the spin-paired state is probably small.

(20) A. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954).

(21) H. Taube, *ibid.*, **77**, 4481 (1955).

Professor R. G. Pearson regarding this investigation.

DISCUSSION

K. V. KRISHNAMURTY.—Was there any appreciable difference in induced exchange, if any, when you substituted acetone–water solvent in place of water?

B. R. BAKER.—The zero-time exchange in water was 5–10% but was not measured in acetone–water mixtures.

A. W. ADAMSON.—I certainly agree that the necessity to rearrange electric configurations must be responsible for the slowness of electron exchange with Co(II)–Co(III) system (see Proceedings of the Symposium on Coördination Chemistry, Amsterdam, 1955). It has seemed to me that the effect can be viewed equally well as an energy requirement (*e.g.*, to put the Co(II) complex into the configuration of a strong ligand field type) or as an electronic transition in the transition state which is hindered or partially forbidden by a spin or multiplicity change. A similar situation might be said to exist in the case of electronic transitions within a single complex, when the life-time of excited states (*i.e.*, the inverse of the transition probability) varies from *ca.* 0.1 sec. for the outlying doublet states to *ca.* 10^{-6} sec. for the main ligand field bands and to *ca.* 10^{-13} sec. or shorter for the near ultraviolet bands.

The Co(II)–Co(III) systems might be likened to the doublet transition in that the spin forbiddenness makes the electron transfer highly hindered, while the Fe(II)–Fe(III) systems could be compared to more normal ligand field transition whose probabilities are 10^6 times greater. (I am indebted to R. A. Plane for this analogy.)

This viewpoint can be made more general, although more qualitative, by supposing that charge transfer, insofar as it occurs adiabatically, can always be thought of as subject to quantum mechanical hindrances or degrees of forbiddenness. At one extreme, the very large difference in angular momentum between Eu⁺⁺ and Eu⁺⁺⁺ ions would lead one to suspect that electron transfer would be slow, as indeed it is. At the other extreme, however, one should also suppose that the relatively smaller variations in charge transfer rate that occur in a series of Fe(II)–Fe(III) or Co(II)–Co(III) systems may well be in part due to variations in degree of forbiddenness, and that one should not expect too close a correlation of exchange rates in such series with such ground state variables as ionic entropies, sizes, etc. I would be interested in the authors' opinion about this extension and generalization of the more specific ligand field effects which they discuss in their paper.

B. R. BAKER.—In cases where excitation of electronic levels, prior to the electron transfer, are not energetically unfavorable ($Co(H_2O)_6^{2+3+}$ and presumably $Co(Phen)_3^{2+3+}$) it is conceivable that electron transfer occurs via such an excited state as pointed out by Orgel. With intermediate field strength ligands, however, such a prior excitation seems unfavorable and exchange might occur through a spin forbidden transition. It can be suggested that the apparently anomalously low energy of activation in the $Co(en)_3^{2+3+}$ system is a reflection of this, where the spin-multiplicity restriction manifests itself through an energy independent transition probability and not through a prior excitation as postulated for the case of weak or strong field ligands.

D. H. BUSCH.—It seems that Cr(II)–Cr(III) provides an interesting case where a slow electron transfer is not associated with a change in spin multiplicity. In this case the Cr(II) should be associated with a distorted structure, on the basis of the Jahn–Teller effect, while the Cr(III) complex should be a regular octahedron. In the case of Co(II) and Co(III) both species would exist as regular octahedra (distortion due to d ϵ would be quite small).

L. I. KATZIN.—Does not sensitivity to low acetone concentration suggest effect on sensitive property of water—e.g., surface tension—or even on nature of solution of complexes with large organic groups in water?

H. N. NEUMANN.—In looking for correlations between the properties of ions of this type and properties of the solvent mixture we have been influenced by data on the rates of dissociation of $Ni(phen)_3^{2+}$, $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$ in organic–water mixtures (unpublished work of Dr. Lester Seiden). These rates show a minimum as would be expected if the behavior correlated with the viscosity. The surface tension decreases continuously on going from water to acetone, and would not lead one to expect a minimum in the rate. It seems reasonable that the rearrangement of solvent molecules would be a simpler process in the case of dissociation of a single ion than in the case of bringing two ions together, hence correlation with the dissociation data seemed more promising. It is true that the exchange re-

sults considered alone show greater similarity to the surface tension than to the viscosity.

HENRY S. FRANK.—Dr. Katzin's suggestion about surface tension may be paraphrased in more general terms by referring to the influence which non-polar groups have on water structure. For example, tetra-n-butylammonium ion affects water in such a way as to produce over 120 units of excess heat capacity beyond what can be accounted for on the basis of additivity rules. If we interpret this as an influence of the hydrophobic nature of the alkyl groups the same influence might be expected to produce a sorting tendency in mixed solvents, attracting, say, acetone, into nearest-neighbor positions, in contrast to the customary dielectric salting out effect. Something similar might happen with the tris-phenanthroline complexes, and this could account for the shape of the curve of the effect of additions of acetone.

IONIC REACTIONS IN SOLUTIONS OF CERTAIN CHLORIDES AND OXYCHLORIDES

BY V. GUTMANN

Contribution from the Institute of Inorganic and General Chemistry, The Technical University of Vienna, Austria

Ionic reactions in solutions of certain chlorides are discussed with arsenic(III) chloride and iodine monochloride as solvents and regarded as due to chloride-ion transfer reactions. Reactions in oxychlorides are discussed with nitrosyl and phosphorus oxychloride as solvents. The conclusion is reached that coördination at the oxygen atom is of importance for solvate-formation although there is ample evidence presented for the occurrence of chloride-ion transfer reactions in the solutions.

1. Introduction

Acid–base reactions in water and other protonic solutions are considered as due to proton transfer reactions

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$$
base 2   acid 1   acid 2   base 1
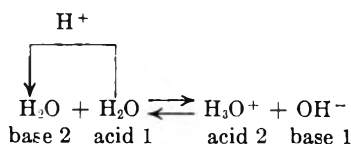
According to Brønsted and Lowry acids and bases may be defined as proton donors and proton acceptors, respectively. It is evident that other ionic transfer reactions also may take place. No protonic acids are known in liquid hydrogen fluoride as a solvent since even nitric acid serves as a base by accepting a proton from a solvent molecule[1] to form a nitracidium cation and a solvent anion

$$HNO_3 + HF \rightleftarrows H_2NO_3^+ + F^-$$
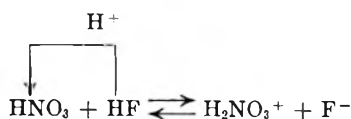
On the other hand antimony pentafluoride acts in this solvent as an acid[2] by accepting a fluoride ion from a solvent molecule, so that the concentration of solvent cations is increased

$$H_2F_2 + SbF_5 \rightleftarrows H_2F^+ + SbF_6^-$$
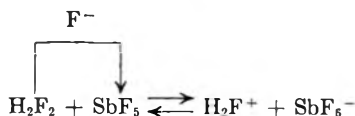
Several other fluorides soon were found to behave similarly as acids in liquid hydrogen fluoride.[3-5]

Transfer of either protons or fluoride ions is permitted by the structure of liquid hydrogen fluoride[6]

$$(HF)_n + (HF)_{m+1} \rightleftarrows [(HF)_nH]^+ + [(HF)_mF]^-$$

$$(HF)_{n+1} + (HF)_m \rightleftarrows [(HF)_nH]^+ + [(HF)_mF]^-$$
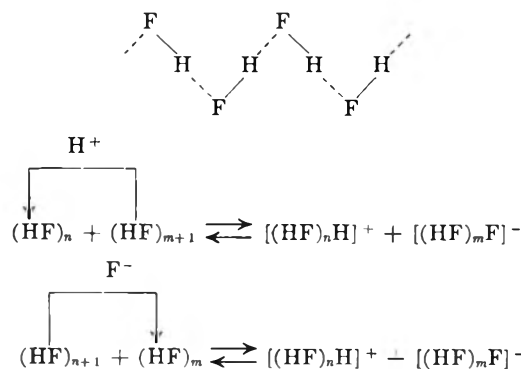
Thus an acid may be defined as a cation donor or an anion acceptor and a base as a cation acceptor or an anion donor.[7] This concept has been advanced as a method for a unified treatment of acid–base reactions in non-aqueous solvents and salt melts.[8] Ionic reactions in solutions of certain fluorides, such as bromine trifluoride,[9] also may

(1) G. Jander, "Die Chemie in wasserähnlichen Lösungsmitteln," Springer-Verlag, Berlin-Heidelberg-Göttingen, 1949.

(2) A. A. Woolf, *J. Chem. Soc.*, 3687 (1950).

(3) M. Kilpatrick and F. E. Luborsky, *J. Am. Chem. Soc.*, **76**, 5863, 5865 (1954).

(4) L. F. Audrieth and J. Kleinberg, "Non-Aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953.

(5) A. F. Clifford, H. C. Beachell and W. M. Jack, *J. Inorg. Nucl. Chem.*, **5**, 57 (1957).

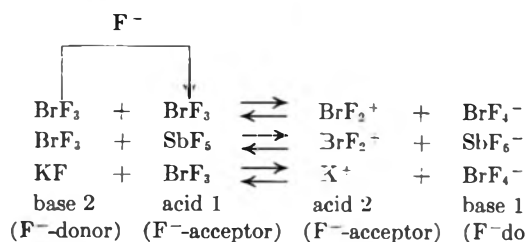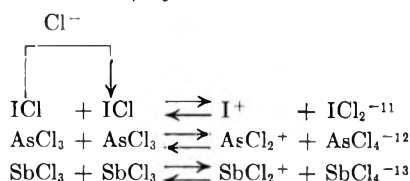(6) V. Gutmann, *Svensk. Kem. Tidsk.*, **68**, 1 (1957).

(7) V. Gutmann and I. Lindqvist, *Z. physik. Chem.*, **203**, 250 (1954).

(8) I. Lindqvist, *Acta Chem. Scand.*, **9**, 73 (1955).

be explained in terms of fluoride-ion transfer processes[6,10]

$$F^-$$

$$
\begin{array}{llllll}
BrF_3 & + & BrF_3 & \rightleftarrows & BrF_2{}^+ & + & BrF_4{}^- \\
BrF_3 & + & SbF_5 & \rightleftarrows & BrF_2{}^+ & + & SbF_6{}^- \\
KF & + & BrF_3 & \rightleftarrows & K^+ & + & BrF_4{}^- \\
\end{array}
$$

base 2   acid 1   acid 2   base 1
(F$^-$-donor) (F$^-$-acceptor) (F$^-$-acceptor) (F$^-$-donor)

2. Iodine Monochloride and Arsenic(III) Chloride as Solvents.

—Similarly chloride-ion transfer reactions have been postulated in a number of chlorine containing solvents of the type of arsenic-(III) chloride.[6–8,10] The small conductivities of the pure liquid solvents probably are due to the presence of solvent-ions, e.g.

$$Cl^-$$

$$
\begin{array}{llllll}
ICl & + & ICl & \rightleftarrows & I^+ & + & ICl_2{}^{-11} \\
AsCl_3 & + & AsCl_3 & \rightleftarrows & AsCl_2{}^+ & + & AsCl_4{}^{-12} \\
SbCl_3 & + & SbCl_3 & \rightleftarrows & SbCl_2{}^+ & + & SbCl_4{}^{-13} \\
\end{array}
$$

The existence of the solvent anions has been shown indirectly, e.g., the $ICl_2{}^-$ ion was found to be present in the solid compound $Cs^+ICl_2{}^-$,[14] which is formed by dissolution of potassium chloride in iodine monochloride and may be isolated by removal of the solvent. Compounds such as $[(CH_3)_4N][AsCl_4]$ and $KSbCl_4$ are known, but their crystals structures have not been worked out.

TABLE I

COMPOUNDS BETWEEN CHLORIDES AND IODINE MONO-
CHLORIDE OR ARSENIC(III) CHLORIDE

Chloride	ICl-compound MeCl$_n$:ICl	AsCl$_3$-compound MeCl$_n$: AsCl$_3$
Potassium chloride	1:1, KICl$_2$[14–16]	..
	1:2, KICl$_2$·ICl[16]	..
Rubidium chloride	1:1, RbICl$_2$[16]	..
Cesium chloride	1:1, CsICl$_2$[16]	..
Tetramethylammonium chloride	1:1, [(CH$_3$)$_4$N]ICl$_2$	1:1[17]
	1:3[17]	1:3[17]
Tetraethylammonium chloride	1:1, [(C$_2$H$_5$)$_4$N]ICl$_2$	1:2[17]
		2:5[17]
Aluminum chloride	1:1[18,19]	..
	1:2[18,19]	..
Phosphorus(V) chloride	1:1, PCl$_4$·ICl$_2$[20]	2:5[21]
Phosphorus oxychloride	..	1:1[17]
Antimony(V) chloride	1:2[22]	
	1:3[22]	

(9) A. A. Woolf and H. J. Eméleus, J. Chem. Soc., 2865 (1949); for a review see V. Gutmann, Angew. Chem., 62, 312 (1950).

(10) V. Gutmann, Quart. Revs., 10, 451 (1956).

(11) V. Gutmann, Z. anorg. Chem., 264, 156 (1951).

(12) V. Gutmann, ibid., 266, 331 (1951).

(13) Z. Klemensiewicz, Z. physik. Chem., 113, 28 (1924).

(14) R. W. G. Wyckoff, J. Am. Chem. Soc., 42, 1100 (1920).

(15) J. Cornog, H. W. Horrabin and R. A. Karges, ibid., 60, 429 (1938).

(16) J. Cornog and E. Bauer, ibid., 64, 2620 (1942).

(17) (a) M. Agermann, L. H. Andersson, I. Lindqvist and M. Zackrisson, Acta Chem. Scand., 12, 477 (1958); (b) I. Lindqvist, private communication.

(18) Y. A. Fialkow and K. J. Kaganskaja, J. Gen. Chem., USSR., 16, 1961 (1946).
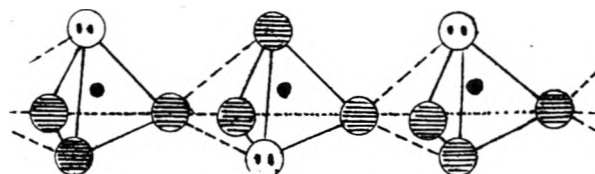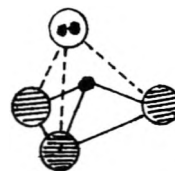
Fig. 1.—●, arsenic; ⊜, chlorine; ⊙, lone electron pair; ——, formation of the trigonal bipyramid.

The occurrence of chloride ion transfer reactions in solutions of arsenic(III) chloride has been indicated in a number of ways, e.g., by radiochlorine exchange reactions,[23] by conductometric,[12] potentiometric[24] and transport number measurements which showed high mobilities of the solvent-ions, as well as by preparative work.[12]

$$
\begin{array}{llll}
AsCl_3 & + AsCl_3 & \rightleftarrows AsCl_2{}^+ & + AsCl_4{}^- \\
(C_2H_5)_4NCl & + AsCl_3 & \rightleftarrows [(C_2H_5)_4N]^+ & + AsCl_4{}^- \\
AsCl_3 & + FeCl_3 & \rightleftarrows AsCl_2{}^+ & + FeCl_4{}^- \\
[(C_2H_5)_4N]^+ & + FeCl_4{}^- & \rightleftarrows [(C_2H_5)_4N]FeCl_4 & \\
\end{array}
$$
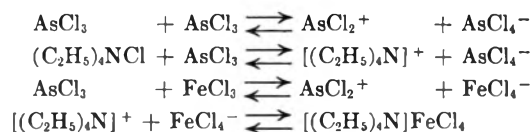
Chloride ion transfer should be possible easily without major structural changes[8] by assuming the formation of chlorine bridges in the solutions. Since the structure of the arsenic(III) chloride molecule is considered as a slightly distorted tetrahedron with one vacant position, a chlorine bridge may be erected with formation of chains containing bipyramidal AsCl$_4$ groups.[8] The tetrachloroarsenate(III) ion is isoelectronic with selenium(IV) chloride, which is expected to be structurally similar to tellurium(IV) chloride, the structure of which has been described as a trigonal bipyramid with the lone electron pair on one of the equatorial positions[25] (Fig. 1). The lone electron pair of arsenic(III) chloride, which is considered of importance in the structure, would thus remain in the equatorial plane of the trigonal bipyramid. A similar picture has been suggested recently for arsenic(III) fluoride solutions.[26]

3. Nitrosyl Chloride and Phosphorus Oxychloride as Solvents. (a) Solvates.

—The situation is somewhat different in oxygen-containing solvents such as nitrosyl chloride or phosphorus oxychloride. No compounds have been isolated which might contain solvated chloride ions, e.g.,

(19) (a) Y. A. Fialkow and K. J. Kaganskaja, ibid., 18, 289 (1948); (b) Y. A. Fialkow and O. I. Shor, ibid., 19, 1787 (1949); C. A., 44, 5672 (1950).

(20) Y. A. Fialkow and A. A. Kuzmenko, J. Gen. Chem. USSR., 19, 812, 1645 (1949).

(21) L. Kolditz, Z. anorg. Chem., 289, 118 (1957).

(22) O. Ruff, J. Zedner and L. Hecht, Ber., 48, 2068 (1915).

(23) J. Lewis and R. G. Wilkins, J. Chem. Soc., 56 (1955).

(24) L. H. Andersson and I. Lindqvist, Acta Chem. Scand., 9, 79 (1955).

(25) D. P. Stevenson and V. Schomaker, J. Am. Chem. Soc., 62, 1267 (1940).

(26) E. L. Muetterties and W. D. Phillips, ibid., 79, 3686 (1957).

$NOCl_2^-$ or $POCl_4^-$ ions, but a large number of solid compounds with acidic chlorides is known (Table II).

The existence of a nitrosonium ion is well established and a number of nitrosyl chloride compounds listed in Table II may indeed contain this ion. The structures of the solids have not, however, been worked out. The compound $PtCl_4 \cdot 2NOCl$ is isomorphous with ammonium chloroplatinate, and thus may be formulated as $(NO)_2PtCl_6$.[27] The ferric chloride compounds may be formulated as $(NO)FeCl_4$ and $(N_2O_2Cl)FeCl_4$, respectively, the latter containing the solvated nitrosonium ion,[28] which might contain either a chlorine bridge or with a higher probability an oxygen bridge

$$[|O{=}N{-}\overline{C}l{-}N{=}O|]^+ \text{ or } \left[\begin{array}{c} N \\ |O \\ N \\ |\overline{C}l \quad O| \end{array}\right]^+$$
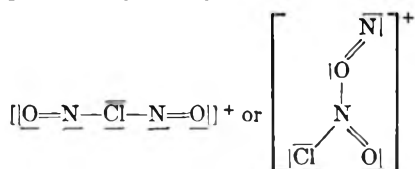
TABLE II

COMPOUNDS BETWEEN CERTAIN CHLORIDES AND NITROSYL CHLORIDE OR PHOSPHORUS OXYCHLORIDE

| | NOCl-compound | | $POCl_3$-compound | |
| | MeCl$_n$: | | MeCl$_n$: | |
Chloride	NOCl	Ref.	$POCl_4$	Ref.
Copper(II)	1:1	29, 30		
Zinc	1:1	29, 30		
Mercuric	1:1	30		
Palladium(II)	1:2	31		
Magnesium(II)	1:1	32		
Boron(III)	1:1	33	1:1	34
Gold(III)	1:1	30, 35	1:1	36
Aluminum(III)	1:1	32, 37–39	1:1	40, 41
	1:2	38, 39	1:2	41
			1:6	41
Gallium(III)	1:1	42	1:1	43, 44
			1:2	43, 44
Indium(III)	1:1	42	Not investigated	
Thallium(III)	1:1	42	Not investigated	
Arsenic(III)	1:2	45	1:1	17
Bismuth(III)	1:1	29, 37	Not investigated	
Ferric	1:1	37, 46	1:1	47
	1:2	39	2:3	47
Titanium(IV)			1:1	48
	1:2	37	1:2	48
Zirconium(IV)	1:2	49	1:1	50, 51
			1:2	50, 51
Hafnium(IV)	Not investigated		1:1	50
			1:2	50
Stannic	1:2	29, 37, 46	1:2	52
Lead(IV)	1:2	37	Not investigated	
Tellurium(IV)	Not investigated		1:1	53
Platinum(IV)	1:2	37	Not investigated	
Antimony(V)	1:1	32, 37	1:1	17, 54, 55
Niobium(V)	Not investigated		1:1	56
Tantalum(V)	Not investigated		1:1	56
Molybdenum(V)	Not investigated		1:1	57

While the presence of the nitrosonium ion in some compounds has been confirmed by Raman spectrographic investigations,[58] the existence of a discrete $POCl_2^+$ ion is, however, more doubtful, although it seems to play a predominant role in the solvated state in the solutions. The complete structure determination made on single crystals of the compound $SbCl_5 \cdot POCl_3$[59] showed the octahedral coördination of antimony as concluded from a Raman spectrographic investigation.[55] The fundamental result of the X-ray work is, however, that in the solid compound one ligand position is occupied by oxygen, thus forming an oxygen-bridge.[59] The existence of a discrete $POCl_2^+$ ion in these compounds therefore can be excluded. Coördination by the oxygen has been assumed to occur in other $POCl_3$ compounds,[60] e.g. in $AlCl_3 \cdot 6POCl_3$.[41] (Compare $AlCl_3 \cdot 6H_2O$ and $AlCl_3 \cdot 6NH_3$.)

In molten $GaCl_3 \cdot POCl_3$, however, $POCl_2^+$ ions seem to exist.[61] A solvated cation with tetrahedral coördination of phosphorus is likely to exist in phosphorus oxychloride solutions

$$\left[\begin{array}{ccc} & Cl & Cl \\ Cl{-}P{-}O{-}P{-}O \\ & Cl & Cl \end{array}\right]^+$$
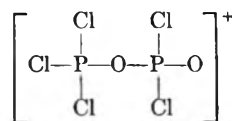
Thus the small conductivities of the pure solvents may be written

$$Cl^-$$

$$(NOCl)_n + (NOCl)_m \rightleftarrows [(NOCl)_{n-1} \cdot NO]^+ + [(NOCl)_m Cl]^-$$

(27) H. Klinkenberg, Rec. trav. chim., 56, 749 (1937); Chem. Weekblad, 35, 197 (1938).

(28) C. C. Addison and J. Lewis, Quart. Revs., 9, 124 (1955).

(29) J. J. Sudborough, J. Chem. Soc., 59, 655 (1891).

(30) J. Lewis and D. B. Sowerby, ibid., 150 (1956).

(31) J. R. Partington and A. L. Whynes, ibid., 3145 (1949).

(32) H. Gall and H. Mengdehl, Ber., 60, 86 (1927).

(33) A. Geuther, J. prakt. Chem., [2] 8, 357 (1873); A. B. Burg and M. K. Ross, J. Am. Chem. Soc., 65, 1637 (1943).

(34) G. Gustavson, Ber., 4, 975 (1871).

(35) C. C. Addison and J. Lewis, J. Chem. Soc., 2843 (1951).

(36) V. Gutmann and F. Mairinger, unpublished observation.

(37) H. Rheinbolt and R. Wasserführ, Ber., 60, 732 (1927).

(38) H. Houtgraaf and A. M. de Roos, Rec. trav. chim., 72, 963 (1953).

(39) A. B. Burg and D. E. McKenzie, J. Am. Chem. Soc., 74, 3143 (1952).

(40) W. Casselmann, Ann. Chem., 83, 257 (1852); 98, 213 (1856).

(41) W. L. Groeneveld and A. P. Zuur, Rec. trav. chim., 76, 1005 (1957).

(42) J. R. Partington and A. L. Whynes, J. Chem. Soc., 1952 (1948).

(43) N. N. Greenwood and K. Wade, ibid., 1516 (1957).

(44) N. N. Greenwood and P. G. Perkins, J. Inorg. Nucl. Chem., 4, 291 (1957).

(45) J. Lewis and D. B. Sowerby, J. Chem. Soc., 1617 (1957).

(46) W. J. van Heteren, Z. anorg. Chem., 22, 277 (1899).

(47) V. V. Danape and M. R. Rao, J. Am. Chem. Soc., 77, 6192 (1955).

(48) W. L. Groeneveld, J. W. van Spransen and H. W. Kouwenhaven, Rec. trav. chim., 72, 950 (1953).

(49) V. Gutmann and R. Himml, Z. anorg. Chem., 287, 199 (1956).

(50) E. M. Larsen, J. Howatson, A. M. Gammill and L. J. Wittenberg, J. Am. Chem. Soc., 74, 3489 (1952); I. A. Sheka and B. A. Woitowitsch, J. Inorg. Chem. (USSR), 2, 426 (1957).

(51) E. M. Larsen and L. J. Wittenberg, ibid., 77, 5850 (1955).

(52) D. S. Payne, Rec. trav. chim., 75, 620 (1956).

(53) V. Lenher, J. Am. Chem. Soc., 30, 740 (1908).

(54) R. Weber, Pogg. Ann. Chem., 132, 452 (1867).

(55) A. Maschka, V. Gutmann and R. Sponer, Monatsh. Chem., 88, 52 (1955).

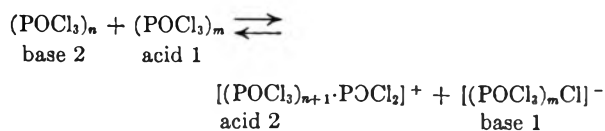(56) C. A. Nisel'son, Zhur. Neorg. Khim., 2, 816 (1957); C. A., 52, 951 (1958).

(57) A. Piutti, Gazz. chim. ital., 9, 538 (1879).

(58) H. Gerding and H. Houtgraaf, Rec. trav. chim., 72, 21 (1953).

(59) I. Lindqvist and C. I. Brändén, Acta Chem. Scand., 12, 135 (1958).

(60) W. L. Groeneveld, Rec. trav. chim., 75, 594 (1956).

$(POCl_3)_n + (POCl_3)_m \rightleftarrows$
base 2   acid 1

$[(POCl_3)_{n+1} \cdot POCl_2]^+ + [(POCl_3)_m Cl]^-$
acid 2   base 1

Accordingly radiochlorine exchange reactions between tetramethylammonium chloride and the solvents take place instantaneously in nitrosylchloride[23] and phosphorus oxychloride,[62] as well as in related solvents such as thionyl chloride,[62b,63] selenium oxychloride[62b] and to some extent even between carbonyl chloride and aluminum chloride.[64] Lewis and Sowerby[62a] have concluded that $POCl_4^-$ ions exist in solutions of phosphorus oxychloride by comparing rates of radiochlorine exchange between Et_4NCl and $POCl_3$ in phosphorus oxychloride, chloroform, nitrobenzene and acetonitrile, but no direct proof has been obtained. The T-x diagram of the system Et_4NCl–$POCl_3$ gives no indication for compound formation, but Lewis and Sowerby[62a] observed that $POCl_3$ cannot be completely removed from the solution even in a vacuum for many days. The formation of a $POCl_4^-$ ion would require for phosphorus a coordination number of 5, which seems, however, unlikely. The absence of compounds containing an $NOCl_2^-$ ion cannot be explained in the same way.

(b) **Conductivity Measurements in Phosphorus Oxychloride.**—Despite many experimental difficulties a reasonable degree of accuracy has been reached in conductivity[65] and e.m.f. measurements[66,67] in solutions of phosphorus oxychloride. The solvent showed a conductivity of $\chi = 2.10^{-8}$ [65] after complete removal of hydrogen chloride, which acts as a base in phosphorus oxychloride. In solutions of quaternary ammonium chlorides the Debye–Hückel–Onsager theory has been found applicable to very dilute solutions ($c < 5 \times 10^{-4} M$). The dissociation constants of tetraalkylammonium halides are in the order of 10^{-4}.[65]

Bromides and iodides apparently are solvolyzed to the chlorides

$Et_4NBr \rightleftarrows Et_4N^+ + Br^-$
$Br^- + POCl_3 \rightleftarrows POCl_2Br + Cl^-$
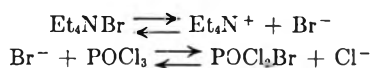
The color of the solutions (yellow for bromides and brown for iodides) thus is due probably to mixed oxyhalides of phosphorus. A spectrophotometric investigation would certainly be of interest.

Transport number measurements have shown that the solvent cation has a high transport number, as is observed in nitrosyl chloride. The ionic product of pure phosphorus oxychloride has been estimated

TABLE III

TRANSPORT NUMBERS OF SOLVENT IONS IN CHLORIDE AND OXYCHLORIDE

Solvent	Salt	Ion	Transport no.	Lit.
$SbCl_3$	KCl	Cl^-	0.9	13
$SbCl_3$	NH_4Cl	Cl^-	.9	13
$AsCl_3$	Me_4NCl	Cl^-	.9	68
$POCl_3$	Me_4NCl	Cl^-	.8	65
$POCl_3$	$SbCl_5$	$POCl_2^+$	.95	69
$NOCl$	$FeCl_3$	NO^+	.88	39

$$P \sim 6.10^{-14}(\pm 50\%)$$

in fair agreement with the results of potentiometric work.

(c) **Potentiometric Measurements.**—In phosphorus oxychloride the chloride ion may be compared with the proton in water and other protolyte systems. While the activity of the proton is considered as a measure of the acidity of the solutions, the chloride ion activity will be a measure of the basicity of solutions in phosphorus oxychloride and other chloridolyte systems. Thus a pCl-value may be defined[7,8,70]

$$pCl \equiv -\log C_{Cl^-}$$

It has not yet been possible to find a completely reversible electrode sensitive for chloride ions in phosphorus oxychloride. Silver–silver chloride electrodes, which have been used to follow reactions between acidic and basic chlorides in arsenic(III)-chloride,[24] will not work in acidic solutions of phosphorus oxychloride. Molybdenum electrodes have, however been used in solutions of thionyl chloride,[71] phosphorus oxychloride[66,67] and benzoyl chloride.[72]

A sharp change in chloride ion activity is observed near the equivalence point which shows that chloride ions are involved in the reactions.

From these measurements the order of acidities and basicities of dissolved chlorides was roughly estimated. In phosphorus oxychloride the acidity was found to decrease in the order given, with reference to tetraethylammonium chloride: $FeCl_3$, $SbCl_5$, $NbCl_5$, $TaCl_5$, $SnCl_4$, $AuCl_3$, SO_3, $ZrCl_4$, $TlCl_3$, ICl_3, $AlCl_3$, $TeCl_4$, $TiCl_4$. The basicity of chlorides was found to decrease with reference to antimony(V) chloride: Et_4NCl, pyridine, Me_4NCl, $TiCl_4$, PCl_5, $AlCl_3$.

For more precise e.m.f. measurements in highly diluted solutions of phosphorus oxychloride a calomel electrode and a chlorine electrode have been applied. From such measurements the ionic product of phosphorus oxychloride has been estimated

$$P = C_{POCl_2^+}C_{Cl^-} = 5 \times 10^{-14} (20°)$$

(d) **Color Indicators in Phosphorus Oxychloride.**—It is remarkable that color indicators, which are known to give pronounced and reversible color changes in protonic solutions at certain pH values behave similarly in non-protonic solutions such as

(61) L. A. Woodward, Proc. Chem. Soc. Meetings, Cambridge 1957, see N. N. Greenwood and I. R. Worall, *J. Inorg. Nucl. Chem.*, **6**, 34 (1958).

(62) (a) J. Lewis and D. B. Sowerby, *J. Chem. Soc.*, 336 (1957); (b) B. J. Masters, N. D. Potter, D. R. Asher and T. H. Norris, *J. Am. Chem. Soc.*, **78**, 4252 (1956).

(63) Le Roy F. Johnson and T. H. Norris, *ibid.*, **79**, 1584 (1957).

(64) J. L. Huston and C. E. Lang *J. Inorg. Nucl. Chem.*, **4**, 30 (1957).

(65) V. Gutmann and M. Baaz, *Monatsh. Chem.*, in press.

(66) V. Gutmann and F. Mairinger, *Z. anorg. allgem. Chem.*, **289**, 279 (1957).

(67) V. Gutmann and F. Mairinger, *Monatsh. Chem.*, **89**, 724 (1958).

(68) V. Gutmann and H. J. Stangl, unpublished observations.

(69) V. Gutmann and R. Himml, *Z. physik. Chem.* (n.F.), **4**, 157 (1953).

(70) V. Gutmann, *Rec. trav. chim.*, **75**, 603 (1956).

(71) H. Spandau and E. Brunneck, *Z. anorg. Chem.*, **278**, 197 (1955).

(72) V. Gutmann and H. Tannenberger, *Monatsh. Chem.*, **88**, 216 (1957).

TABLE IV

COLOR CHANGE OF CERTAIN INDICATORS IN POCl₃ AND H₂O

	In phosphorus oxychloride			In water		
Indicator	Acidic	Basic	Color change (v.)	Acidic	Basic	Color change (pH)
Thymol blue	Red	Violet	1.06–1.14	Red	Yellow	1.2–2.8
				Yellow	Blue	8.0–9.6
Phenolphthalein	Red	Colorless	0.80–1.04	Colorless	Red	8.3–10.0
Brom thymol blue	Red	Yellowish	.78–1.05	Yellow	Blue	6.0–7.6
Brom phenol red	Orange	Reddish	.78–0.95	Yellow	Red	5.2–6.8
Brom cresol purple	Red	Colorless	.76–1.02	Yellow	Purple	5.2–6.8
Thymol phthalein	Dark-red	Colorless	.73–1.03	Colorless	Blue	9.3–10.5
Brom cresol green	Wine-red	Yellowish	.70–0.79	Yellow	Blue	3.8–5.4
Brom phenol blue	Red	Yellowish	.68–0.79	Yellow	Blue	3.0–4.6
Phenol red	Orange	Red	.65–0.98	Yellow	Red	6.8–8.4

thionyl chloride[71] or phosphorus oxychloride.[66] The color of the solutions apparently depends on the pCl value and is usually different from those known for protonic solutions, but corresponds with the color change of thymol blue in highly acidic aqueous solutions.

From conductivity measurements of triethylamine in phosphorus oxychloride solutions the conclusion is reached[73] that phosphorus oxychloride is by 3 orders of magnitude more acidic toward acceptor bases, such as triethylamine than water. Therefore the colors of indicators are shifted more into the basic region. The solubilities of indicators in phosphorus oxychloride are low; hydrogen chloride seems to be produced which is soluble in the solvent. On evaporation of the solvent *in vacuo* deeply colored crystals remain, which apparently represent the ionic form of the indicators. Analyses have shown that they contain less than 2 POCl₂ groups in the molecule, probably in place of hydrogen atoms according to the reactions[74]

$$\text{Ind·H}_2 + 2\text{POCl}_3 \rightleftarrows \text{Ind·(POCl}_2)_2 + 2\text{HCl}$$
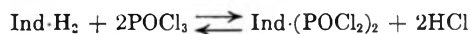
Replacement of protons by the solvent cations will enable the indicators to vary colors according to the POCl₂⁺ ion concentration of the solution. Since the POCl₂⁺ ion concentration is related to the chloride ion concentration, the color indicator may be considered a Cl⁻ ion indicator.

(e) **Spectrophotometric Investigations.**—The 10^{-2} M solution of ferric chloride in phosphorus oxychloride is reddish brown, but turns yellow on neutralization with tetraethylammonium chloride. The extinction curve of the neutralized solution shows the same maxima at 315 and 365 mμ as the ferric chloride solution in 12 M hydrochloric acid indicating the formation of FeCl₄⁻ ions by the neutralization reaction.[75]

The same effect is produced by diluting the ferric chloride solution with phosphorus oxychloride. The identity of the extinction curve with that of the neutralized solution is reached at $c = 10^{-4}$ M. Since both dilution and neutralization lead to the formation of identical complexes (probably FeCl₄ units) chloride ions seem to be present in the pure solvent.[75]

The reddish brown color of the 10^{-2} M and the deep red color of more concentrated solutions may be regarded as due to oxygen bridges between Fe-

Cl₃ and POCl₃ molecules, which in analogy to the structure of SbCl₅·POCl₃ are probably present in the solid solvates.

(f) **Mechanisms of Reactions in Phosphorus Oxychloride Solutions.**—The present experimental evidence shows definitely that (a) chloride ion transfer reactions take place in solutions of both chlorides and oxychlorides and (b) that oxygen bridges are of importance in solvate formation with oxychlorides.

We may now attempt a discussion about the mechanisms possible for the reaction of phosphorus oxychloride with an acidic chloride, such as antimony pentachloride.[76,77] These reactions are formally possible
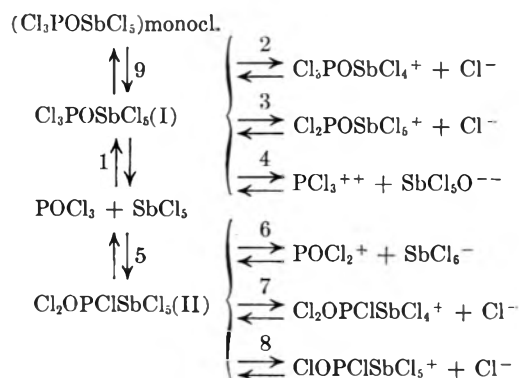
The recent structure determination of the solid POCl₃·SbCl₅ has shown that it is a coördination complex of the structure Cl₃POSbCl₅.[59] Thus reaction 1 must be possible in the solution. On the other hand, the presence of solvated POCl₂⁺ ions seems to be established particularly in more dilute solutions. Its formation by reaction 6 would require the existence of an intermediate compound formed by reaction 5, involving a chlorine bridge, while by reaction 1 a compound with an oxygen bridge is formed. With respect to the formation of compounds I and II reaction 5 is favored to reaction 1, since there are 3 chlorine to one oxygen atom in the POCl₃ molecule. On the other hand the P–O–Sb bond is energetically more stable than the P–Cl–Sb bond. Both reactions lead to an increase in coördination for Sb which is energetically favorable.

Reactions 3 and 8 are very unlikely. They in-

(73) M. Baaz and V. Gutmann, *Monhtsh. Chem.*, in press.
(74) V. Gutmann and M. Baaz, to be published elsewhere.
(75) V. Gutmann and M. Baaz, *Monatsh. Chem.*, in press.

(76) I. Lindqvist, *Acta Chem. Scand.*, **12**, 134 (1958).
(77) V. Gutmann and M. Baaz, *Z. anorg. Chem.*, in press; *Angew. Chem.*, in press.

volve the dissociation of a chloride ion from a P–Cl–bond. These bonds are however strengthened by the formation of either an oxygen or a chloride bridge.

In reactions 2 and 7 a chloride ion is dissociated from Sb. Both reactions are not extremely likely with a somewhat higher probability for reaction 2, since the P–O–Sb bond will be stronger than the P–Cl–Sb bond.

In reaction 4 the P–O bond is to be broken, which is stronger than the Sb–O bond, that would remain according to reaction 4. In addition dissociation of a 2–2 valent electrolyte in a solvent of low dielectric constant would only be possible with a higher solvation tendency, than is actually observed in POCl₃.

Reaction 6 is, however, easily possible. In the P–Cl–Sb bridge the P–Cl bond may be weaker than the Cl–Sb bond, as shown by the fact that $SbCl_5$ is a stronger acid than $POCl_3$ or PCl_5. The electrostatic contribution of the bond will allow the dissociation to $POCl_2^+$ and $SbCl_6^-$ ions as univalent electrolytes of similar ionic size are dissociated in phosphorus oxychloride. This reaction will be favored by the solvation of the $POCl_2^+$-ion

$$POCl_2^+ + POCl_3 \rightleftarrows [POCl_3 \cdot POCl_2]^+$$

The potentiometric measurements show that the chloride ion activity in the $SbCl_5$ solution is very small as compared with that of the pure solvent. Therefore reaction 2, which would lead to an in-crease in chloride ion activity cannot be of any importance.

Thus the order of the probabilities of the reactions leading to the formation of ions will be as follows: $6 \gg 2 > 7 > 4$ and $6 + 7 \gg 2 + 4$.

The reactions following reaction 5 are therefore more likely than the reactions following reaction 1.

It is very likely that due to solvation processes reaction 6 is more probable than 5 so that the actual competition in solution will occur between reaction 6 and 1 (since $2 + 3 + 4 \ll \ll 1$). According to the conditions the equilibrium system will be shifted by the precipitation of the energetically favorable solid phase.

It is to be hoped that further aspects may be opened up by spectrophotometric and conductometric investigations, as well as by studies of magnetic resonance spectra of the solutions.

DISCUSSION

I. LINDQVIST.—Called upon to comment upon this lecture, I will only add that the structure of $SbCl_5 \cdot POCl_3$ showing oxygen association (first suggested by Groenveld), has led us to study association compounds of $SbCl_5$ and sulfoxides or sulfones as well. The association compound with $(CH_3)_2SO$ is even stable in air for a rather large time. We also have determined the structure of $SeOCl_2 \cdot 2C_6H_5N$ which has an octahedral coördination around Se with two N in trans position and two Cl atoms in trans position. The sixth corner is formally occupied by the inert electron pair. The Se–Cl distances are larger than in $SeOCl_2$ and the Se–N bond distances are as large as 2.2–2.3 Å. The chemical bonds will be discussed after refinement of the structure.

ISOTOPIC EXCHANGE REACTIONS IN LIQUID SULFUR DIOXIDE AND RELATED NON-AQUEOUS SYSTEMS[1]

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Results of isotopic exchange experiments suggest the desirability of a modification of the formal solvent systems interpretation of the chemistry of liquid sulfur dioxide. While sulfite exchanges readily with the solvent, thionyl halides show no significant exchange, indicating the non-formation of thionyl ions. Further experiments indicate rather ions of the type SOX^+ from thionyl halides. Sulfur trioxide exchanges oxygen readily but sulfur scarcely at all with the solvent. A mobility of oxide ions in acidic or basic solutions is inferred. Ionic halides catalyze the thionyl halide–sulfur dioxide exchange, apparently *via* basic halide catalysis, mobile halide ions here being indicated. Acid chlorides also show catalysis, though much less strongly, a different mechanism being involved. Acid and basic chlorides mutually inhibit each other's catalytic effect through formation of non-catalytic complex ions. The solvent concentrated sulfuric acid exchanges radiosulfur with sulfur dioxide only at high temperature. Rate measurements suggest some common features with the liquid sulfur dioxide system, particularly with regard to the sluggish S^*O_2–SO_3 exchange. The results emphasize the utility of the Lewis interpretation for understanding acid–base phenomena in sulfur dioxide solutions.

Following Walden's pioneering work,[2] a thorough study of chemical phenomena in the solvent liquid sulfur dioxide by Jander and co-workers[3] has yielded a broad basis for an understanding of the system. More recently isotopic tracers have provided a novel, revealing technique for further study and their use is leading to considerable clarification of details of reactions, particularly of the acid–base type. The present paper offers a summary and critical appraisal of the more impor-tant results of this tracer work, including both experiments in liquid sulfur dioxide itself and also some pertinent appearing work in certain related systems.

Acids and Bases in Liquid Sulfur Dioxide.— In interpreting his results Jander paid particular attention to the nature of acids and bases in this system, framing his ideas in terms of the solvent systems theory[4] of such entities. Thus the solvent was thought of as undergoing self-ionization to give small concentrations of thionyl and sulfite ions

$$2SO_2 \rightleftarrows SO^{++} + SO_3^{=} \qquad (1)$$
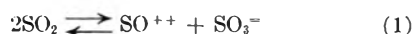
(1) Oregon State College, Research Paper No. 344, School of Science, Department of Chemistry.

(2) P. Walden and M. Centnerszwer, *Z. anorg. Chem.*, **30**, 145 (1902).

(3) G. Jander, "Die Chemie in Wasserähnlichen Lösungsmitteln," Springer-Verlag, Berlin, 1949, pp. 209–307.

(4) H. P. Cady and H. M. Elsey, *J. Chem. Ed.*, **5**, 1425 (1928).

Thionyl compounds and sulfites are here, respectively, acids and bases, hypothetically ionizing to some extent according to such equilibria as the following to give "characteristic" cations and anions

$$SOCl_2 \rightleftarrows SO^{++} + 2Cl^- \qquad (2)$$

$$(Me_4N)_2SO_3 \rightleftarrows 2Me_4N^+ + SO_3^- \qquad (3)$$
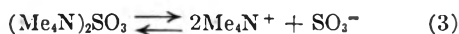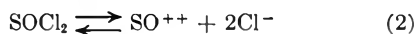
Reactions involving acids, bases and salts (e.g., neutralization or metathesis) were thought of as occurring ionically analogously to corresponding aqueous processes.

Although such an interpretation is consistent with the types of chemical processes observed, it is not, as Bateman Hughes and Ingold[5] indicated, a necessary consequence. Sulfur dioxide has a dielectric constant of 14.1 (20°)[6] as compared to 80.4 (20°)[7] for water and thionyl chloride gives in it only a feebly conducting solution.[8] Bateman and co-workers pointed out the inherent improbability of the occurrence of the double ionization shown by equation 2, emphasizing the greater likelihood of a process yielding SOCl+ ions

$$SOCl_2 \rightleftarrows SOCl^+ + Cl^- \qquad (4)$$
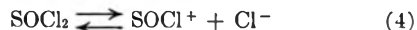
Radioactive tracers provide means for testing the validity of the solvent systems equilibria 1, 2 and 3. If these are important, a relatively rapid exchange should follow the labeling either of solvent or solute (acid or base) with an isotopic tracer (radiosulfur or oxygen-18). Such experiments, involving thionyl chloride and thionyl bromide solutes, have been done in our laboratory[9,10] (sulfur labeled) and by Grigg and Lauder[11] (oxygen labeled). The sulfur exchange experiments, sometimes lasting up to four months, have been run at room temperature and, in the case of thionyl chloride, from 0 to 61°. There was never a suggestion of any significant exchange rate, minimum half-times of half a year or more being estimated for thionyl chloride even at 61°. (The data also suggest for thionyl bromide a possible approximate half-time of about two years.)

These results clearly imply equilibrium 1 or equilibrium 2 cannot be operative. It further seems reasonably certain that equilibrium 2 can be discarded; any thionyl ion, SO++, so formed would surely exchange rapidly with the solvent, if not via equilibrium 1, then by pulling an oxide ion off a solvent molecule. This follows from the mobility of oxide ions deduced from the experiments described below. Thus the solvent systems picture of the production from thionyl halide acids of cations characteristic of the solvent cannot be supported. Most probably any important ionization of these compounds must be in accordance with equilibrium 4.

(5) L. C. Bateman, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 243 (1944).

(6) A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," Natl. Bur. Standards, Circ. 514, 1951, p. 4.

(7) Reference 6, p. 1.

(8) Reference 3, p. 237.

(9) R. E. Johnson, T. H. Norris and J. L. Huston, J. Am. Chem. Soc., 73, 3052 (1951).

(10) B. J. Masters and T. H. Norris, ibid., 77, 1346 (1955).

(11) E. C. M. Grigg and I. Lauder, Trans. Faraday Soc., 46, 1039 (1950).

Supplementary to the thionyl halide experiments, the radiosulfur exchange between the soluble base tetramethylammonium pyrosulfite (normal sulfites cannot be isolated from liquid sulfur dioxide[12]) and the solvent sulfur dioxide has been studied.[9] The exchange was followed by observing the sulfur acitivity (both sulfurs together) of the solid recovered from labeled solvent. Experiments at ca. −75° showed essentially complete exchange in 20 minutes, in sharp contrast to the results described above. The exchange could, of course, occur via equilibrium 1, but results observed in the study of the sulfur dioxide–sulfur trioxide exchange reaction[14] suggest the concentration of sulfite ions from this equilibrium to be quite small in sulfur dioxide. Hence a more likely mechanism seems to be a direct oxide ion transfer from sulfite ions to sulfur dioxide molecules.

$$SO_3^- + S^*O_2 \rightleftarrows SO_2 + S^*O_3^- \qquad (5)$$

This implies in basic sulfur dioxide solutions a mobility of oxide ions analogous to the mobility of aqueous protons, a type of acid–base process not envisioned in the solvent systems picture.

This last conclusion prompts inquiry into other conditions under which oxide ion mobility may occur and raises the question of how generally acid–base processes in this medium can be described in terms of such a process.

First of all, one may note that, in a generalized sense, basic solutions include those containing dissolved basic halides; catalysis studies in such systems (see below) indicate here too a mobility, though a significantly slower one, of oxide ions. That this mobility is probably not limited to basic solutions, however, is shown by the results observed in the sulfur dioxide–sulfur trioxide exchange system (see below) which suggest that sulfur dioxide acts as a base toward the strong acid sulfur trioxide, yielding to it an oxide ion in some such equilibrium as

$$SO_2 + SO_3 \rightleftarrows SO^{++} + SO_4^- \qquad (6)$$
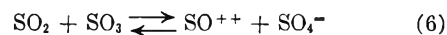
In interesting contrast to the sulfur trioxide situation is the observation of Grigg and Lauder,[11] who found no exchange of oxygen-18 between thionyl chloride and sulfur dioxide even after nine days. Such a result has implications beyond the invalidating of equilibrium 2, for it shows that thionyl chloride, unlike sulfur trioxide, cannot act as an oxide ion acceptor from sulfur dioxide

$$SO_2 + SOCl_2 \rightleftarrows SO^{++} + SO_2Cl_2^- \qquad (7)$$
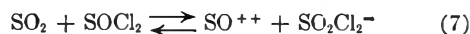
This result may perhaps be "explained" as due to thionyl chloride being a weaker acid than sulfur trioxide, with a consequent lesser tendency to pull an oxide off the base sulfur dioxide. Nor is the result surprising since equation 7 actually appears to represent an even less probable equilibrium than equation 2, being essentially the equivalent of the

(12) The unsymmetrical structure[13] of pyrosulfite ion, O₃S-SO₂⁻, makes its use in this experiment equivalent to the use of normal sulfite.

(13) W. H. Zachariasen, Phys. Rev., 40, 923 (1932); I. Lindqvist and M. Mörtsell, Acta Cryst., 10, 406 (1957). We are indebted to Dr. V. Gutmann for bringing the latter structure determination to our attention.

(14) J. L. Huston, J. Am. Chem. Soc., 73, 3049 (1951).

latter with both chlorides lodging on a single sulfur dioxide molecule. A much more likely ionic interaction between thionyl chloride and sulfur dioxide, as shown by further exchange experiments to be described, would consist of a *chloride* ion transfer

$$SO_2 + SOCl_2 \rightleftharpoons SO_2Cl^- + SOCl^+ \qquad (8)$$
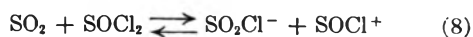
Equilibrium 8 has the advantage over (7) of producing singly rather than doubly-charged ions. The foregoing suggests the value of studying the oxygen exchange between thionyl chloride and sulfur dioxide at significantly higher temperatures, with a view to finding conditions under which measurable exchange rates might be observed. A similar comparative study involving sulfur tracer also would be inviting.

Finally, what of the mobility of oxide ions in pure liquid sulfur dioxide?[15] The non-occurrence of equilibrium 7 as an oxygen exchange pathway renders dubious the probability of rapid oxygen exchange *via* the somewhat analogous equilibrium 1. The basic halide catalysis experiments described below provide further rather strong evidence to the same effect. Such considerations, though not entirely conclusive, appear to imply that oxide ion mobility in the pure liquid probably is not rapid.

Thus we find mobile oxide ions in sufficiently acidic or basic but not neutral solutions, and it appears that many acid–base processes in this solvent can be described in terms of these transfer processes. On the other hand, as further experiments to be described show, acid–base phenomena are not limited to processes of this type and it appears that in general an outlook of broader scope is indicated.

The Ionization of Thionyl Halides in Liquid Sulfur Dioxide.—In view of the unimportance of equilibrium 2 type ionizations for thionyl halides in sulfur dioxide solutions, it becomes worthwhile to try to verify the occurrence of the alternative production of SOX^+ ions (equilibrium 4). Radiochlorine exchange experiments have therefore been done between tetramethylammonium chloride and thionyl chloride dissolved together in sulfur dioxide solution.[16] An ionization according to equilibrium 4 should lead to a rapid exchange with the ionic tetramethylammonium chloride. Rapid exchange is in fact observed, complete even in five minutes at $-20°$, for a maximum estimated half-time of about one minute. Thus, while thionyl chloride does not give thionyl ions, SO^{++}, it does probably engage in *some* ionic process involving chloride ions. This *could* be an ionic dissociation in accordance with equilibrium 4, but exchange might also occur *via* an association equilibrium

$$SOCl_2 + Cl^- \rightleftharpoons SOCl_3^- \qquad (9)$$

In an effort to distinguish between dissociation and association, the radiosulfur exchange has been studied between thionyl chloride and thionyl bromide dissolved together in sulfur dioxide.[17]

The sulfur exchange would, of course, actually be effected by an interchange of halides between the two thionyl compounds. In these solutions, containing no halide salts, no association equilibrium could occur (except possibly by virtue of dissociation-produced halide ions). A rapid exchange, therefore (assuming this to imply an ionic process) would indicate the reality of dissociation to SOX^+ for either one or both of the thionyl halides (unstable SOClBr serving as intermediate). The experiments do in fact indicate the exchange to be rapid and complete, even at $-50°$ with either thionyl halide in excess, maximum half-times of 2 to 5 minutes being estimated. This exchange could occur either *via* a simple dissociation of the equilibrium 4 type or alternatively *via* direct halide transfer, *e.g.*

$$SOCl_2 + SOBr_2 \rightleftharpoons SOCl^+ + SOBr_2Cl^- \qquad (10)$$

In either case the production of SOX^+ ions by at least one of the thionyl halides is definitely established. It seems reasonable to assume such production by both.

Experiments in Thionyl Halide Solvents.—As natural accompaniments to the exchange experiments in liquid sulfur dioxide solution, experiments have been done in thionyl chloride (and also in one case in thionyl bromide). These are of particular value relative to the experimental investigation by Spandau and Brunneck[18] of thionyl chloride's properties as an ionizing solvent. In their first paper, Spandau and Brunneck propose a self-ionization scheme for the solvent involving production of doubly charged thionyl ions, along the lines of equilibrium 2; in their second, only the production of $SOCl^+$ ions (as in equilibrium 4) is indicated.

The radiosulfur exchange between sulfur dioxide and thionyl chloride has been studied in excess thionyl chloride by Muxart[19] and in our laboratory.[9] Negligible exchange occurs at room temperature (estimated minimum half-time, over six years) or even at $66°$, just as in sulfur dioxide. Clearly, one may disregard any possible self-dissociation to SO^{++} ions (equilibrium 2), any significant ionization presumably yielding $SOCl^+$ ions (equilibrium 4). Another point: Spandau and Brunneck account for the conductance of a dilute solution of sulfur dioxide in thionyl chloride in terms of the ionization equilibrium (wherein one of the $SOCl^+$ ions is derived from SO_2)

$$2SO_2 + SOCl_2 = (SOCl)_2SO_3 \rightleftharpoons 2SOCl^+ + SO_3^- \qquad (11)$$
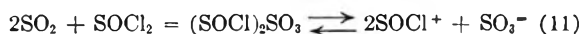
The occurrence of such a reversible equilibrium would lead to a ready exchange of radiosulfur between sulfur dioxide and the solvent and so cannot be supported. The conductance of sulfur dioxide-containing solutions must be otherwise explained. As a reasonable possibility we again suggest the simple transfer of a chloride ion from thionyl chloride to sulfur dioxide (equilibrium 8), a process rendered plausible by the results observed in the halide catalysis studies.

(15) Huston has attempted to test for this phenomenon by oxygen-18 self exchange experiments in the liquid, but a rapid heterogeneously catalyzed exchange of the gas phase reaction renders such experiments difficult: J. L. Huston, THIS JOURNAL, **63**, 389 (1959).

(16) B. J. Masters, N. D. Potter, D. R. Asher and T. H. Norris, *J. Am. Chem. Soc.*, **78**, 4252 (1956).

(17) L. F. Johnson, Jr., and T. H. Norris, *ibid.*, **79**, 1584 (1957).

(18) H. Spandau and E. Brunneck, *Z. anorg. allgem. Chem.*, **270**, 201 (1952); **278**, 197 (1955).

(19) R. Muxart, *Compt. rend.*, **231**, 1489 (1950).

Radiochlorine exchange experiments have also been done in thionyl chloride solutions.[16] The exchange is rapid and complete at 0° between the solvent and both tetramethylammonium chloride and antimony trichloride, respectively. These experiments appear to support the ionization of thionyl chloride to $SOCl^+$ (equilibrium 4). While the tetramethylammonium chloride result could be ascribed either to an association or a dissociation equilibrium it seems more plausible to think of antimony trichloride achieving exchange as an acceptor of chloride ions formed via equilibrium 4 rather than as a chloride ion donor as in equilibrium 9.

This last conclusion is further supported by the study of the radiosulfur exchange between thionyl chloride and thionyl bromide, done in mixtures of the two liquids (no sulfur dioxide).[17] The exchange is rapid and complete at ca. −20° in excess of either thionyl halide. Thus, here as in sulfur dioxide solution, the formation of SOX^+ ions from at least one of the thionyl halides seems indicated.

In contrast to the above, and also to the rapid exchange in sulfur dioxide solution, the radiosulfur exchange between the two thionyl halides appears to be measurable at −50°.[17] Single experiments, both showing incomplete exchange, gave estimated half-times of ca. 3 minutes in excess thionyl chloride and ca. 80 minutes in excess thionyl bromide. Although this result somewhat clouds the above conclusions regarding thionyl halide ionization, it seems reasonable to believe that ionization mechanisms may still be involved. It is tempting to try to relate the lower exchange rates in thionyl halide as compared to sulfur dioxide solutions to a lower rate of ionic dissociation in the former with their lower dielectric constants (SO_2, 14.1; $SOCl_2$, 9.25; $SOBr_2$, 9.06; all at 20°).[6] The decrease in dielectric constant from sulfur dioxide is, however, not great and probably does not in itself suffice to account entirely for the lower exchange rates, a point further emphasized by the definite difference in rates observed in the two thionyl halides despite their quite similar dielectric constants.

The observation of measurable sulfur exchange rates at −50° invites further investigation. It would be interesting to study the exchange of acidic and basic chlorides (e.g., $SbCl_3$ and Me_4NCl) with solvent thionyl chloride at −50° to look for a measurable chlorine exchange rate, and if such is found, to compare it with the sulfur exchange rate between the two thionyl halides. One might hope that kinetics work in these systems would provide information on such now obscure points as, for example, whether the Me_4NCl–$SOCl_2$ exchange goes via an association or dissociation (of thionyl chloride) equilibrium. Furthermore, the results would probably be illuminating relative to the acid–base catalysis experiments in these systems.

Acid–Base Catalysis in Sulfur Dioxide.—In contrast to the negligibly slow rate described above, the thionyl halide–sulfur dioxide radiosulfur exchange is found to be strongly catalyzed by alkali and quaternary ammonium halides,[20,21] potassium

chloride (saturated) for example giving with thionyl bromide a half-time of about 15 hours at 25°. The process consists of a homogeneous basic catalysis by halide ions.

The thionyl bromide exchange, studied in detail with tetramethylammonium bromide, gives a rate law, Rate = $k(Me_4NBr)$, where k = 4.17 × $10^6 e^{-13,200/RT}$ sec.$^{-1}$. The inferred mechanism involves a preliminary equilibrium addition of bromide to SO_2, serving to promote oxide ion transfer to another SO_2 molecule in the rate-determining step

$$S^*O_2 + Br^- \rightleftarrows S^*O_2Br^- \qquad \text{fast} \quad (12)$$

$$S^*O_2Br^- + SO_2 \rightleftarrows S^*OBr^+ + SO_3^- \quad \text{slow} \quad (13)$$

$$SOBr_2 \rightleftarrows SOBr^+ + Br^- \qquad \text{fast} \quad (14)$$
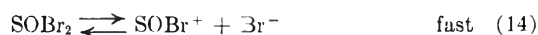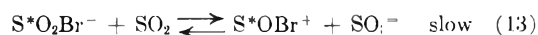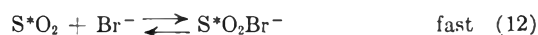
In this mechanism the bromide ion concentration represents total bromide, presumably largely ion pairs, no indication being found for any possible catalytic distinction between these and free ions.[22] Equation 13 is analogous to the rapid oxide ion transfer process 5, but is slower possibly because it leads to cation–anion pair creation, in contrast to simple charge transfer in (5). These results, showing the rapid mobility of bromide ions, indicate that acid–base phenomena in sulfur dioxide are not limited to oxide ion mobility alone. They also, incidentally, imply that oxide ion transfer between sulfur dioxide molecules in the absence of bromide ions must be negligibly slow. Thus further evidence is provided against the rapidity in pure sulfur dioxide of equilibrium 1.

The thionyl chloride–sulfur dioxide exchange differs from the above in rate law and mechanism, giving Rate = k_3(catalyst)($SOCl_2$)(SO_2). With tetramethylammonium chloride catalyst in sulfur dioxide solution k_3 = 1.08 × $10^7 e^{-14,700/RT}$ l.^{2} mole^{-2} sec.$^{-1}$. The inferred mechanism is

$$S^*O_2 + Cl^- \rightleftarrows S^*O_2Cl^- \qquad \text{fast, } K \ll 1 \quad (15)$$

$$S^*O_2Cl^- + SOCl_2 \rightleftarrows S^*OCl_2 + SO_2Cl^- \quad \text{slow} \quad (16)$$
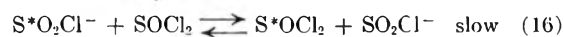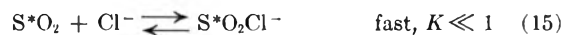
Here the slow, rate-determining step involves the simultaneous interchange of chloride and oxide, presumably via a binuclear-type activated complex, having a chlorine and an oxygen bridge between sulfurs. A simple oxide ion transfer leading to the improbable species $SO_2Cl_2^=$, seems less likely.

This mechanism appears to apply throughout the solvent range from excess sulfur dioxide to excess thionyl chloride, although about a threefold increase in k_3 occurs in the latter solutions (21.7 vs. 6.25 × 10^{-2} l.^{2} mole^{-2} hr.$^{-1}$ at 0°). The k_3 variation with solvent is scarcely unexpected, but its exact explanation is not immediately obvious. Quite possibly it may be related primarily to a shift in equilibrium 15 (the K value for which is included in k_3), the formation of SO_2Cl^- being favored in excess thionyl chloride.

Here, as with thionyl bromide, "chloride ion" represents total chloride, irrespective of form (e.g., ion pairs or free ions) no distinction in catalytic activity being apparent. That ion pairs probably dominate in the solution, despite its con-

(20) R. H. Herber, T. H. Norris and J. L. Huston, J. Am. Chem. Soc., **76**, 2015 (1954).

(21) B. J. Masters and T. H. Norris, ibid., **77**, 1346 (1955).

(22) A similar phenomenon was found in the chloride catalysis of the thionyl chloride–dibutyl sulfite reaction: P. D. Bartlett and H. F. Herbrandson, ibid., **74**, 5971 (1952).

ductivity, appears probable, however, from the observation that tetramethylammonium chloride gives k_3 values about twice those with rubidium chloride (6.25 vs. 3.02 × 10^{-2} l.^{2} mole^{-2}hr.$^{-1}$ at 0°). A similar effect was observed with the corresponding bromide catalysts in the thionyl bromide exchange ($k = 0.37$ vs. 0.21 hr.$^{-1}$ at 0°). It seems reasonable that the larger quaternary ammonium cation would favor the transfer of halide ions to sulfur dioxide molecules, the rate difference being derived from shifts in equilibria 12 and 15. The observation in the thionyl chloride exchange of the same activation energies with both catalysts, but different pre-exponential terms (10.8 vs. 5.31 × 10^6 l.^{2} mole^{-2} sec.$^{-1}$) may point in this direction. Further work in this area would be desirable.

The thionyl chloride exchange goes at about seven times the rate of the thionyl bromide exchange at comparable concentrations, despite a higher apparent activation energy (14.7 vs. 13.2 kcal./mole), the pre-exponential term being considerably larger (463 vs. 4.17 × 10^6 sec.$^{-1}$ with tetramethylammonium halide catalysts, both values calculated from $k_1 = \text{Rate}/(\text{catalyst})$). The interpretation of this rate change must be correlated with the change in mechanism, and the situation here is still somewhat uncertain. It seems possible that a greater basicity for chloride than bromide ion would shift equilibrium 15 to the right relative to (12), but this would not explain the mechanism change. Possibly the binuclear activated complex has a higher probability of formation with chlorine rather than bromine in the bridge. Then its more ready formation with thionyl chloride would lead to a sufficiently greater exchange rate by this pathway to dominate the equation 13 type pathway, yielding the observed mechanism change.

Acid catalysis of the thionyl chloride–sulfur dioxide exchange is also found to occur, antimony pentachloride[23] and aluminum chloride[21,23] giving, respectively, at comparable concentrations, about 1 and 0.1% the rates shown by tetramethylammonium chloride. The antimony pentachloride catalysis apparently involves a rapid equilibrium formation of an antimony pentachloride–thionyl chloride complex, followed by a rate-determining reaction of complex with sulfur dioxide molecules. The equilibrium and rate constants involved seem to be essentially constant over the entire solvent range from excess sulfur dioxide to excess thionyl chloride, the constancy possibly being attributable to the absence of ions from the mechanism. The complex, consistent with both Jander's[24] and Spandau and Brunneck's[18] views, presumably involves the formation of hexachloroantimonate by coördination to the antimony of one chloride from thionyl chloride. This suggests for the activated complex the coördination of a sulfur dioxide molecule (through sulfur) to an adjacent chloride in octahedral hexachloroantimonate. This then puts the two sulfurs in a reasonable position to form between themselves just such a double chlorine–oxygen bridge as was postulated for the basic chloride-catalyzed activated complex.

The complexity of such an activated complex might account for the lower rate here observed as compared to the basic catalysis. Although the activation energy is actually slightly lower than in the later case, the entropy of activation is found to have a very much larger negative value, seemingly consistent with such an interpretation.

Exchange catalysis by aluminum chloride has been only most cursorily examined. Nothing is known of the rate law or mechanism, but if this should prove the same as for antimony pentachloride, it is possibly conceivable that the ten-fold lower exchange rate might be accounted for in terms of geometrical factors in the activated complex: tetrahedral vs. octahedral coördination for the metal ion and shorter Al–Cl than Sb–Cl bond lengths.

The observation of catalysis by both acidic and basic chlorides, together with the reported formation of a variety of hexachloroantimonate and tetrachloroaluminate complexes in sulfur dioxide[25,26] invites experiments in mixtures of such catalysts. Possibly one might expect to find a minimum catalysis at stoichiometric ratios corresponding to the composition of the complexes, i.e., in "neutral" solutions. In recent experiments[23] this expectation has been realized, both $AlCl_3$–Me_4NCl and $SbCl_5$–Me_4NCl mixtures showing for the $SOCl_2$–SO_2 exchange a minimum catalysis at 1:1 ratios. The complexes appear to be but little dissociated and to show scarcely any catalytic activity. Besides confirming the formation of complexes in these solutions, these experiments serve nicely to corroborate the acid–base interpretation of catalysis in this system here presented.

These catalysis experiments show the broadness of scope of acid–base processes in sulfur dioxide, transcending the types envisioned in such a picture as that of the solvent systems theory. Treatment in terms of generalized acid–base theory[27] is evidently indicated in such a situation.

Oxidation–Reduction Exchange Reactions.—1. Various exchange reactions between compounds containing sulfur in different oxidation states bear on those already discussed. In particular both oxygen-18 and radiosulfur exchange have been studied between sulfur dioxide and sulfur trioxide in the liquid phase. Nakata[28] reported the former to be fast at room temperature in excess trioxide, while Huston[14] found the latter negligibly slow at room temperature in excess of either component, giving only ~1.6% exchange in 26 days at 132° (excess trioxide). Nakata, explaining his results, had proposed the reversible formation of the symmetrical[29] dithionate ion, $S_2O_6^=$, from trioxide and sulfite ion, derived from sulfur dioxide ionization

(23) D. E. Burge and T. H. Norris, ibid., in press.

(24) Reference 3, pp. 299 ff.

(25) Jander reported that either aluminum chloride or antimony pentachloride greatly increases the solubility of potassium chloride, the latter giving a solution of good conductivity (ref. 3, p. 300).

(26) Nitrosyl, acetyl and benzoyl chlorides give with antimony pentachloride strongly conducting solutions. Benzoyl chloride plus aluminum chloride gives no increase in conductance, but a complex appears to be formed. F. Seel, Z. anorg. Chem., **252**, 24 (1943); F. Seel and H. Bauer, Z. Naturforsch., **2b**, 397 (1947).

(27) G. N. Lewis, J. Franklin Inst., **226**, 293 (1938).

(28) S. Nakata, J. Chem. Soc. Japan, **64**, 635 (1943). Also J. L. Huston, ref. 15.

(29) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, 1945, p. 304.

via equilibrium 1. Lack of sulfur exchange excludes this possibility, rather indicating the previously mentioned direct oxide ion transfer which gives oxygen but not sulfur exchange

$$SO_2 + SO_3 \rightleftharpoons SO^{++} + SO_4^{-} \qquad (6)^{30}$$
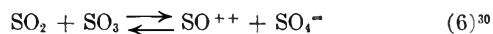
This equilibrium finds the weaker acid acting as base toward the stronger acid. One may note that, in contrast, for sulfur exchange to occur, an oxygen bridge would be required in the activated complex with the strong acid trioxide acting as base toward the weaker acid dioxide. Possibly the slowness of this exchange may at least qualitatively and in part be related to reluctance toward such complex formation.

2. In analogy to the above, the sulfur exchange between thionyl chloride and sulfuryl chloride (excess) has also been found negligibly slow.[17] It seems likely that the same explanation may here too be applied, exchange requiring an oxygen bridge furnished by the stronger acid playing base toward the weaker. It would be of interest to find whether chlorine or oxygen exchange between these compounds might, in contrast, be rapid, occurring *via* an acid–base pathway analogous to (6). The situation here is somewhat uncertain, however, since such a process gives the resulting anion a coordination number of five. Radiochlorine experiments of this sort are currently being commenced in this Laboratory.

3. Two further relevant experiments by Muxart[19] should be mentioned briefly. In these it was shown that sulfur exchanged negligibly slowly between sulfur dichloride and sulfur dioxide even at 50°, but between sulfur dichloride and thionyl chloride a measurable rate did occur (45% exchange in 2 hours at 60°; essentially complete in 2 hours at 89°). While the first result is scarcely surprising (exchange would require a fourfold chlorine, oxygen bridge!), it is interesting to find the second somewhat faster than the processes described in the preceding two paragraphs, an oxygen bridge, as Muxart indicated,[31] obviously being here too involved, with the (presumably) stronger acid acting as base. The fact that the exchange is measurably slow, however is still qualitatively consistent with the idea of a certain reluctance toward formation of such an activated complex.

4. Finally it seems appropriate to refer to exchange results in the solvent concentrated sulfuric acid, a material of interest both because of its high acidity and high dielectric constant (101, 25°, 100% acid[33]), contrasting sharply with that of other solvents here discussed. In analogy to the sulfur dioxide–sulfur trioxide exchange, the radio-

sulfur exchange between sulfur dioxide and the acid has been found to go only at high temperature, an approximate half-time of about 7.5 hours at 211° being indicated, with an activation energy of about 29 kcal./mole.[34] Further study of this exchange in this Laboratory[35] covering the acid range 85–98% appears to suggest that the primary rate-determining step may possibly involve a bimolecular reaction between bisulfate ions and sulfur dioxide molecules.[36]

While the research is not yet entirely complete and certain unsolved difficulties relative to this interpretation remain, it is interesting to observe certain points of similarity here to other systems discussed in this paper. In particular the postulated rate-determining step suggests a binuclear bridge activated complex formed by two bisulfate oxygens coördinated to a sulfur dioxide. Possibly the dominance of such an activated complex involving bisulfate rather than sulfuric acid molecules may be related, at least in part, to the latter's being clearly the weaker base of the two. On the other hand the fact that bisulfate ion itself is not a strong base provides, as in the SO_2–SO_3 exchange, an explanation for the slowness of the exchange. The validity of this interpretation, finally, is given added support by quantitative comparison of exchange rates in these two cases, sulfur trioxide, an even weaker base than sulfuric acid, presumably being even more reluctant toward activated complex formation. Estimated half-times for the SO_2–SO_3 and SO_2–H_2SO_4 exchanges are, respectively, ~1100 days (132°)[14] and 20.5 days (137°).[34]

Conclusions.—A number of exchange reaction systems have been discussed, involving exchange between pairs of compounds, each with sulfur as the central atom. These have included both pairs with sulfur in the same and in different oxidation states. Although the focus has been elucidation of the nature of reactions in liquid sulfur dioxide, this discussion has led to consideration of reactions in other sulfur-containing solvents. The available data, treated in a unified manner, make a significant contribution toward our understanding of the general characteristics of reactions in sulfur dioxide solutions.

While extensive generalization seems scarcely warranted as yet, it is interesting to note the use, implicitly or explicitly, of generalized acid–base considerations (in the Lewis[27] sense) throughout the discussion. Furthermore the very fact of its seeming appropriate to include, along with the sulfur dioxide results, a discussion of exchange experiments in other media, emphasizes the general desirability of avoiding reaction interpretations too narrowly restrictive in terms of any one solvent. In at least one case, we have found the same reaction occurring with apparently the same mechanism and rate in sulfur dioxide and thionyl chloride. While there is nothing new in such an occurrence, its observation here does further illustrate the inherent advantages of seeking generalizations which transcend particular solvents.

(30) Jander proposed this type of equilibrium (indicating the formation of the actually, in excess trioxide, more probable pyrosulfate anion) in explanation of the observation of conductance in this type of solution: G. Jander, *Naturwissenschaften*, **26**, 795 (1938).

(31) In this connection it is interesting to note the demonstration of oxygen bridge mechanisms in two other closely related reactions studied by Muxart[19] and Muxart, Daudel and Boscardin,[32] viz.

$$SO_3HCl + SCl_2 \longrightarrow SOCl_2 + SO_2 + HCl, \text{ and}$$
$$SO_3 + SCl_2 \longrightarrow SOCl_2 + SO_2$$
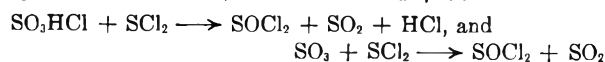
(32) R. Muxart, P. Daudel and B. Boscardin, *J. chim. phys.*, **46** 466 (1949).

(33) R. J. Gillespie and R. H. Cole, *Trans. Faraday Soc.*, **52**, 1325 (1956).

(34) T. H. Norris, *J. Am. Chem. Soc.*, **72**, 1220 (1950).

(35) T. H. Norris, B. J. Masters and P. E. Doherty, to be published.

(36) Sulfur dioxide has been shown to exist as SO_2 molecules in 100% sulfuric acid: V. Gold and F. L. Tye, *J. Chem. Soc.*, 2932 (1950).

Some of the described experiments suggest that certain acid–base processes in liquid sulfur dioxide, in which the solvent itself is directly involved, can best be understood in terms of an oxide ion mobility. This concept has its usefulness, like Gutmann and Lindqvist's[37] more general one of "ionotropy" covering similar processes in a variety of solvents; such ideas have an advantage in some cases just because of their limited applicability, in contrast to the greater generality of the Lewis theory, which is, in a sense, a source of weakness as Gutmann and Lindqvist have pointed out. Nonetheless this limited applicability must be recognized. The persistence of the same reaction as the medium is continuously changed from one solvent to another, or the smooth merging of acid–base processes such as complex ion formation in which no solvent ions are directly involved with those in which such ions are involved—such processes demand an interpretation of acid–base phenomena of greater generality. The utility of the Lewis concept has been nicely illustrated by the described experiments and it seems clearly to offer the most satisfactory picture for the general interpretation of acid-base processes in solutions of this type.

Acknowledgment.—This research has been supported by the U. S. Atomic Energy Commission under Contract AT(45-1)-244.

(37) V. Gutmann and I. Lindqvist, Z. physik. Chem. (Leipzig), **203**, 250 (1954).

DISCUSSION

V. GUTMANN.—Have you ever attempted to isolate a compound which might contain the SO_2Cl^- ion? e.g., as Seel has shown that KSO_2F can be isolated from SO_2 solutions?

T. H. NORRIS.—Our observations on this point suggest that at best such a compound would have a quite low stability. In the tetramethylammonium chloride catalyst experiments, for example, evaporation at room temperature (in high vacuum) of all volatile material (sulfur dioxide plus thionyl chloride) readily yields a dry residue containing no sulfur and analyzing closely the same as the original catalyst. Tetramethylammonium bromide similarly recovered from sulfur dioxide, incidentally, also shows no sulfur retention. (In the latter case, with thionyl bromide also present the situation becomes more complex, but that is another story.) The apparent instability of the chlorine and bromine as compared to the fluorine–containing compounds harmonizes with Seel's observations and is in a general way consistent with our supposition that the equilibrium $SO_2 + Cl^- \rightleftarrows SO_2Cl^-$ lies well to the left, so that one might expect a certain difficulty in isolating a SO_2Cl^- ion-containing compound.

JAMES Y. TONG.—In the catalyzed sulfur exchange between $SOCl_2$ and SO_2 where you have observed different rates in $SOCl_2$ and in SO_2, have you tried expressing the concentrations in other units?

T. H. NORRIS.—Yes, we have, but the results do not really seem much more satisfactory than with our units. It is true that with concentrations expressed as mole fractions the difference between the rates in $SOCl_2$ and SO_2 is appreciably decreased, but a significant difference still remains, and the data taken as a whole do not look much better, the rate constants in excess SO_2 for example appearing to be somewhat less constant and showing a decreasing trend with increasing $SOCl_2$ concentration.

EXCHANGE REACTIONS IN CERTAIN ACIDIC SOLVENTS

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Isotopic exchange experiments with several acid chloride liquids have supported the validity of the application to these solvents of the solvent systems formulation of acids and bases. This formulation, however, is inapplicable to phosgene, which must be dealt with in Lewis terminology. Work on phosgene has touched on the role of hydrogen halides as Friedel–Crafts promoters and led to a current investigation of the systems aluminum chloride–hydrogen chloride, and aluminum chloride–hydrogen chloride–phosgene. Self-exchange experiments with sulfur dioxide have appeared to confirm the lability of oxide ions in the pure liquid, but must be interpreted with care. Oxide ion lability between sulfur dioxide and sulfur trioxide has been confirmed, and work has been extended to the systems carbon dioxide–sulfuric acid and sulfur dioxide–sulfuric acid, where it appears that each gas can act toward sulfuric acid either as a Lewis acid or Lewis base, depending on the strength of the sulfuric acid.

Introduction

There is no dearth of systems for classification of substances as acids and bases; to the five available a few years ago[1] has been added at least one more, the "Ionotropy" concept[2] of Gutmann and Lindqvist, (which may be considered a refinement of the formulation of solvent systems). To the present author this is by no means a bad situation. The venerable concept of acidity and basicity is a matter of classifying certain chemically active substances into two categories, in such fashion that the members of each category have a greater tendency to react with those of the other than with themselves. Obviously, the requisite definitions can be stated in several ways, to give formulations of greater or lesser generality. The function of theory is to correlate facts and ideas and to assist in the planning of experimentation. The great generality of the Lewis formulation of acids and bases[3] can be a weakness as well as a strength in such planning, while the greater specificity of such a formulation as that of solvent systems is here of value. This paper will review and present some tracer experiments with one acid chloride (phosgene) and some with sulfuric acid, which contradict the solvent systems point of view, and require application of Lewis' formulation. There is also a growing body of data from tracer experiments in other acid chlo-

(1a) W. F. Luder and S. Zuffanti, "The Electronic Theory of Acids and Bases," John Wiley and Sons, New York, N. Y., 1946.

(1b) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1952.

(2) V. Gutmann and I. Lindqvist, Z. physik. Chem., **203**, 250 (1954).

(3) (a) G. N. Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Company, New York, 1923. p. 142. Two brief paragraphs contain his own formulation, along with partial or complete anticipation of three others. (b) G. N. Lewis, J. Franklin Inst., **226**, 293 (1938).

rides which are in accord with the theory of solvent systems.

Acid Chlorides

The theory of solvent systems or of "Ionotropy" imply ionic mobility in solvents and a number of recent tracer experiments with several acid chlorides have yielded results in accord. Thus, complete exchange between solvent and solute in the time needed to perform each experiment was observed for ionic chlorides in nitrosyl chloride[4]; "acidic" chlorides (ferric chloride and antimony pentachloride)[5] in nitrosyl chloride; ionic chlorides and one "acidic" chloride (antimony trichloride) in thionyl chloride[6]; ionic chlorides in phosphorous oxychloride[5,6]; ionic chlorides in arsenic trichloride; and ionic chlorides and one "acidic" chloride (ferric chloride) in selenium oxychloride. None of these proves the existence of a self-ionization in the pure solvent, but each is consistent with such a process: one of the postulates of the solvent systems and "Ionotropy" formulations.

With the rapidity of these exchange processes established, it is possible to study them in solvents and obtain real kinetic data. Exchange of chloride ion with phosphorous oxychloride takes place at a measurable rate[7] in chloroform, nitrobenzene and acetonitrile, with the rate proportional to $[Cl^-][POCl_3]$.

A very recent paper[8] reports on the exchange, in acetonitrile, of chloride ion with the compounds $[PCl_4][PF_6]$, $[PCl_4]F$ and $[PCl_4][PCl_6]$, the latter being PCl_5 totally ionized by acetonitrile ($\epsilon = 38.8$, 20°). The ion PCl_6^- exchanges with immeasurable speed, but the ion PCl_4^+ goes at measurable rates in all three cases, even with PCl_6^- present. The authors present reasonable explanations of these interesting results.

Phosgene.—It is a curious fact that the solvent which provided the first substantial experimental foundation for the solvent systems formulation should be the one where tracer experiments[9] (from this Laboratory) have shown that this formulation cannot apply. Although Cady and Elsey[10] are often cited as being primarily responsible for the origination of this theory, their ideas were based mostly on ammonia (the Brønsted–Lowry formulation was shortly to make such ideas superflous) and only a very little material on one non-protonic system: namely, that thionyl chloride and cesium sulfite undergo metathesis in sulfur dioxide solution.

Germann's total body of work on solutions of aluminum chloride in phosgene[11] is substantial, and shows that these solutions are obviously "acidic." They conduct electricity better than the pure sol-

vent, with evolution of carbon monoxide and chlorine. They dissolve metals with evolution of carbon monoxide, and they dissolve such ionic chlorides as sodium chloride, calcium chloride, etc. (which are insoluble in phosgene). Considering that the Lewis formulation was not well known at the time and, indeed, had been treated rather cursorily by Lewis himself[3a] (and expanded only much later[3b]), it was natural for Germann to think that a cation, analogous to hydronium ion, must be the active agent in these solutions. He postulated[12] the ionizations

$$COCl_2 \rightleftarrows CO^{++} + 2Cl^-$$

$$COCl_2 + Al_2Cl_6 \rightleftarrows CO^{++} + Al_2Cl_8^=$$
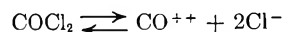
Aluminum chloride thus makes phosgene "acidic" by increasing the concentration of the active agent CO^{++}, which is capable of reacting with "solvo bases"

$$[CO^{++}][Al_2Cl_8^=] + CaCl_2 \longrightarrow$$
$$[Ca^{++}][Al_2Cl_8^=] + COCl_2$$
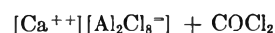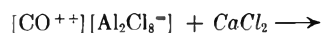
to give solutions of "solvo salts." His set of definitions[13] is more formal than that of Cady and Elsey, but not essentially different.

The tracer experiments[9] which strongly indicate the applicability of the Lewis formulation to this system, and the total inapplicability of the solvent systems formulation may be summarized. Although aluminum chloride is readily soluble in phosgene, there is no evidence for strong acid–base interaction of the two. (1) A compound was obtained, of composition $COCl_2 \cdot AlCl_3$. The phosgene was easily distilled off *in vacuo* and it was shown that the chlorines of the two parts were nonequivalent. (2) Chloride exchange between solute and solvent, expected to be fast, was slow. (3) Most importantly, when aluminum chloride solutions dissolved ionic chlorides, the ionic chloride went directly to the aluminum chloride without mediation by the solvent, and found its way to the solvent only by slow exchange, and, incidentally, without catalysis of solute–solvent exchange. Probably we should next study the effect of adding *small* amounts of ionic chlorides; something like catalysis might be possible here.

Why is phosgene different from the other acid chlorides? Its dielectric constant (4.34, 22°) is the lowest of the lot, and it will be of considerable interest to bring aluminum chloride and phosgene together in a solvent of higher value, e.g., acetonitrile or nitromethane. Aluminum chloride, like phosphorus pentachloride, is a chameleon, ionic in the solid state, covalent in liquid or gas,[14] and if induced to ionize, might exchange more readily with phosgene. It should also be possible to bring phosgene into homogeneous contact with ionic chlorides, which are insoluble in the pure liquid.

Hydrogen Chloride.—Considerable pains were taken, during this work, to assure that the phosgene was free of hydrogen chloride, for fear of exchange catalysis by the latter. Initial experiments, wherein hydrogen chloride deliberately was

(4) J. Lewis and R. G. Wilkins, *J. Chem. Soc.*, 56 (1955).

(5) J. Lewis and D. B. Sowerby, *ibid.*, 1617 (1957).

(6) B. J. Masters, N. D. Potter, D. R. Asher and T. H. Norris, *J. Am. Chem. Soc.*, **78**, 4252 (1956).

(7) J. Lewis and D. B. Sowerby, *J. Chem. Soc.*, 336 (1957).

(8) L. Kolditz and D. Hass, *Z. anorg. allgem. Chem.*, **294**, 191 (1958).

(9) (a) J. L. Huston, *J. Inorg. Nucl. Chem.*, **2**, 128 (1956); (b) J. L. Huston and C. E. Lang, *ibid.*, **4**, 30 (1957).

(10) H. P. Cady and H. M. Elsey, *Science*, **66**, 27 (1927); *J. Chem. Educ.*, **5**, 1425 (1928).

(11) A. F. O. Germann and D. M. Birosel, THIS JOURNAL, **29**, 1468 (1925), et ante.

(12) A. F. O. Germann, *Science*, **61**, 70 (1925).

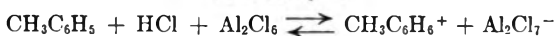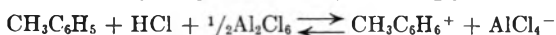(13) A. F. O. Germann, *J. Am. Chem. Soc.*, **47**, 2461 (1925).

(14) For example, N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford, 1950, p. 423 ($AlCl_3$), p. 754 (PCl_5).

added to the aluminum chloride–phosgene system, showed rather a suppression (ref. 9b, p. 37) of the rate of chloride exchange between these two. However, work previously unpublished has since shown that at mole ratios of hydrogen chloride/aluminum chloride of less than 0.5 the rate of exchange is enhanced, peaking to about 40% increment at mole ratios of less than 0.1. This initial enhancement probably is due to introduction of ions into the solution (see equation below) by hydrogen chloride, the resultant "Ionic Strength" effect on the rate of exchange being greater, at low mole ratios, than the tendency of hydrogen chloride to "neutralize" the acidity of aluminum chloride. Similar effects have been observed before.[9]

At the same time an immeasurably fast exchange is taking place between hydrogen chloride and aluminum chloride. We[9b] suggested that a reversible equlibrium such as

$$^1/_2Al_2Cl_6 + HCl + COCl_2 \rightleftarrows HCOCl_2{}^+ + AlCl_4{}^-$$
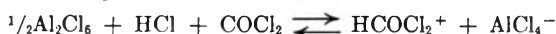
is taking place, where the very strong Lewis acid, aluminum chloride, is forcing hydrogen chloride to donate a proton to phosgene, though phosgene would normally hardly be classed as a good Brönsted "base." This fits in nicely with the observation by Brown and Pearsall[15] that aluminum chloride, insoluble in toluene, goes into solution in the presence of hydrogen chloride, seemingly as

$$CH_3C_6H_5 + HCl + {}^1/_2Al_2Cl_6 \rightleftarrows CH_3C_6H_6{}^+ + AlCl_4{}^-$$

$$CH_3C_6H_5 + HCl + Al_2Cl_6 \rightleftarrows CH_3C_6H_6{}^+ + Al_2Cl_7{}^-$$

These authors suggest that such reactions explain the well known ability of hydrogen halides to promote the action of aluminum halides as Friedel–Crafts catalysts, by getting the aluminum halide into solution and furnishing a polar medium in which ionic intermediates can dissolve and react, this in spite of the well established[16] inability of hydrogen chloride and aluminum chloride to form a compound of any great stability.

There appeared here an opportunity to use tracer techniques to obtain information on the Friedel–Crafts reaction and simultaneously to look for a technique for putting the strengths of Lewis acids into relative order—and such a technique is badly needed—to determine whatever exchange might occur homogeneously between liquid hydrogen chloride and solute aluminum chloride; then to study the effect of adding such compounds as phosgene, stannic chloride, arsenic trichloride, etc. (The exchange has been studied heterogeneously,[16] but a hydrogen chloride molecule polarized on an ionic surface is, of course, much different from one in solution.) The experiments appeared feasible, Richardson and Benson[16a] having reported a solubility (Raoult's law) of 3.8 mole % for aluminum chloride in hydrogen chloride liquid, at Dry Ice temperature.

Unfortunately, when such an experiment was set up, the radioactive aluminum chloride failed to dissolve. Direct solubility determinations,[17] shak-

ing for periods up to 72 hours, indicate a much lower solubility, by a factor of 10^{-3}. It is not possible satisfactorily to account for the discrepancy, except that the tank gas used by Richardson and Benson may have contained enough organic material, e.g., chlorobenzene, to permit a sizable solubility. It may still be possible to do the tracer experiments, by using aluminum chloride of very high specific activity.

Sulfur Dioxide

Several years ago we[18] suggested a mobility of oxide ions in liquid sulfur dioxide, essentially the self-ionization of solvent systems. This was based in part [cf. the preceding paper of this Symposium) on the observation by Nakata[19] of exchange of labeled oxygen between sulfur dioxide and sulfur trioxide in the liquid state (sulfur trioxide in excess). Examination of Nakata's paper showed an unsatisfactory situation, in that the time of his shortest run was one hour and his oxygen was only slightly labeled with O^{18} (30 λ water equivalent).

Through the kindness of Professor Taube of the University of Chicago, confirmatory experiments were undertaken, doing direct mass spectrometry of sulfur dioxide samples. Duplicate experiments were performed at 20° with sulfur dioxide and sulfur trioxide present in about equal molar ratio and also with a trioxide–dioxide ratio of approximately 2. One experiment was performed at 0° under the latter condition. In all cases exchange was complete within the time necessary to conduct the experiments, and it can be stated that the half-time for exchange is, at 20°, less than 0.25 minute and, at 0°, is less than 0.75 minute. No experiments were performed with excess sulfur dioxide because of rapidly developing memory effects in the mass spectrometer. Considering that we are having second thoughts on oxide ion mobility in liquid sulfur dioxide, it would be well to perform such experiments in this less acidic medium.

The only way to look for self-ionization in a pure liquid is to look for isotopic self-exchange

$$SO^{18}O^{16} + SO^{18}O^{16} \rightleftarrows 2SO^{16}O^{18}$$
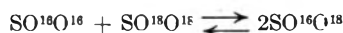
A sample of heavily enriched oxygen furnished by Professor O. C. Nier[20] of the University of Minnesota was converted to sulfur dioxide and these self-exchange experiments undertaken. Any sample of liquid sulfur dioxide must necessarily be in contact with gaseous sulfur dioxide, the latter at room temperature. Since sulfur dioxide has a vapor pressure of slightly less than 1 cm. at Dry Ice temperature, experiments were done on gaseous sulfur dioxide at room temperature, and, actually, at a slightly higher pressure (1.7 cm.). The runs were done in glass apparatus, in such fashion that two samples of sulfur dioxide at comparatively high pressure, one labeled and one unlabeled, could be admitted to a mixing chamber by

(15) H. C. Brown and H. Pearsall, J. Am. Chem. Soc., **73**, 4681 (1951).

(16) (a) R. L. Richardson and S. W. Benson, ibid., **73**, 5096 (1951); (b) M. Blau, W. T. Carnall and J. E. Willard, ibid., **74**, 5762 (1952).

(17) D. M. Sharp, private communication.

(18) R. E. Johnson, T. H. Norris and J. L. Huston, J. Am. Chem. Soc., **74**, 4985 (1952).

(19) S. Nakata, J. Chem. Soc., Japan, **64**, 635 (1943).

(20) The separation of the oxygen isotopes was made possible by a grant to Professor A. O. Nier made by the Committee on Growth of the National Research Council, acting for the American Cancer Society.

break-off tips; thence after a few seconds *via* a stopcock to a mass spectrometer.

These runs were made as commercial samples on a Consolidated 21—103 mass spectrometer. The operation of this instrument, fortunately, involves the expansion of the sample into a large ballast bulb (4 l.) whence it passes through a pinhole into the analyzing chamber of the mass spectrometer. The self-exchange proved to be heterogenous on glass, having at room temperature a half-time of 6 ± 1 sec. when $S/V = 3.7$ and a half-time of 2 ± 0.5 sec. when $S/V = 12.65$. It was possible to mix samples and, after a few seconds, pass them into the ballast bulb where, because of the low S/V ratio, the exchange process was effectively "frozen."

It was thus established that oxide ion mobility can indeed exist in sulfur dioxide condensed on the surface of Pyrex glass, and for a time it seemed that the question of mobility in pure liquid had been satisfactorily answered. But considering (see below) that sulfur dioxide exchanges oxygens at a measurable rate with the strong Lewis acid, sulfur trioxide (in fuming sulfuric acid), it is probably best to think of ionic mobility in the pure liquid as *potential*, capable of manifestation when ionic substances are dissolved in the liquid or when molecules are condensed on the highly polarizing surface of glass. The question remains moot.[21]

Liquid Oxygen

A sample of liquid oxygen, containing ordinary oxygen and heavily labeled oxygen, was kept 7.5 days at liquid nitrogen temperature. Samples were withdrawn at intervals (Toepler pump) and showed no appreciable self-exchange, 0–5%. This illustrates the well-known non-equivalence of bonds in the O_4 molecule, and shows they do not flip around, at least at liquid nitrogen temperature.

Sulfuric Acid

If, instead of using pure sulfur trioxide as a device for pulling oxide ions off sulfur dioxide, we use sulfuric acid solutions measurable rates of exchange can be obtained,[22] faster in either the water or fuming region than at 100% sulfuric acid. Approximate half-times are as given (25°, *ca.* 90-fold molar excess sulfuric acid): 100% H_2SO_4, 42 hr.; $H_2O/H_2SO_4 = 0.50$, 16 min.; $SO_3/H_2SO_4 = 0.25$, 35 min.; $SO_3/H_2SO_4 = 0.49$, 20 min. So sulfur dioxide is being attacked as a Lewis base in the fuming region and is operating as a Lewis acid in the water region; it will not be at all surprising if the minimum rate turns out to be exactly at 100% sulfuric acid. Any ionic process for exchange between sulfur dioxide and sulfuric acid requires the latter to act as a base.

More remarkably it appears from preliminary results that much the same situation obtains between sulfuric acid and carbon dioxide, crude half-

times, uncorrected for the fact that most of the carbon dioxide is in the gaseous phase, are as shown (132°, *ca.* 90-fold molar excess sulfuric acid): 100% H_2SO_4, 40 days; $H_2O/H_2SO_4 = 0.50$, 1.1 day; $H_2O/H_2SO_4 = 1.0$, < 13 hr.; $SO_3/H_2SO_4 = 0.49$, 42 days. Although the rate is not notably greater in the fuming region than at 100% acid, it is notable that it exists at all. Surely the carbon dioxide is being attacked as a Lewis base, by the strong acid, sulfur trioxide.

We seem to have here systems where the "relativistic" character of the Lewis formulation make that formulation uniquely applicable. A substance is not simply an acid or a base, but acidic or basic dependent on its chemical environment. The "relativistic" nature of his theory was recognized by Lewis in his original formulation. "Some of these substances which we have set down as acid are obviously basic as well; the sulfur atom in sulfur trioxide is acid, but the oxygen atoms in sulfur trioxide may act in a basic manner."

Another aspect of the Lewis formulation, its great generality, makes it especially applicable to the tracer experiments thus far done with liquid phosgene.

Experimental

Hydrogen chloride was generated from sulfuric acid and sodium chloride. It was passed through anhydrous calcium sulfate and distilled from Dry Ice to liquid nitrogen. Sulfur dioxide was generated from sulfuric acid and sodium sulfite, and treated similarly. Labeled carbon dioxide and sulfur dioxide were obtained by exchange with O^{18}-labeled water, removed after the water had been frozen with Dry Ice, and again similarly purified.

Heavily labeled sulfur dioxide was obtained by burning elementary sulfur in Professor Nier's oxygen and purified by several distillations from Dry Ice to liquid nitrogen. Mercury was shaken in the gas to assure freedom from trioxide.

Sulfur dioxide–trioxide runs were made in all-glass apparatus, with appropriate use of ampules, seals and breaks. They were separated in spirals chilled with Dry Ice. Sulfur dioxide and sulfuric acid runs were done in a bath at 25°, with magnetic stirring for the longer term ones (100% acid) and manual agitation for the short term runs. Carbon dioxide runs were made in refluxing vapor of chlorobenzene (132°) the whole apparatus being subjected to gentle rocking. Other techniques have been described previously.

One hundred per cent. sulfuric acid was prepared by titrating ordinary acid into fuming acid contained in a closed system, a procedure similar to that of Gillespie,[23] taking its freezing point to within 0.05° of his value (10.38°). Other manipulations were done in a dry box, with provision for continuous circulation of air through a cold trap or barium oxide. The strength of fuming acid ($H_2SO_4 \cdot 0.49H_2O$) was determined by titration and measurement of density, using a calibrated ultramicro (100 λ) pipet and a microbalance.

DISCUSSION

H. H. HYMAN.—Aside from general chemical considerations, is there any definite evidence that oxide ion transfer in the SO_2-SO_3 system doesn't involve an SO_3 transfer to SO_2 to yield SO_2^{++} + SO_3^{-}.

J. L. HUSTON.—No, and I suppose it does happen to some small extent.

(21) It is interesting to note that the self-exchange took place from a background of 40 to 50%, the magnitude of the background being substantially unaffected by the intensity of the ionizing current and, therefore probably independent of anything happening in the analyzing chamber. Graham's Law of Effusion is derived from a picture of molecules hitting a pinhole and passing into a vacuum; it appears here that almost 50% of the sulfur dioxide molecules passing into the vacuum had been adsorbed on the surface of the gold foil.

(22) Experiments performed by Mr. Thomas M. Spittler, S.J.

(23) R. J. Gillespie, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2473 (1950).

TETRAHEDRAL NiCl4⁻ ION IN CRYSTALS AND IN FUSED SALTS. SPECTROPHOTOMETRIC STUDY OF CHLORO COMPLEXES OF NICKEL(II) IN FUSED SALTS[1,2]

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Received October 4, 1958

The absorption spectra of Ni(II) isomorphously substituted for Zn(II) in crystals of Cs_2ZnCl_4 and of $NiCl_2$ dissolved in fused pyridinium chloride, LiCl, CsCl, Cs_2ZnCl_4 and $LiNO_3$–KNO_3 eutectic have been obtained. The spectra show that Ni(II) is present as the tetrahedral $NiCl_4^-$ ion in fused pyridinium chloride, CsCl and Cs_2ZnCl_4. Spectral changes observed in fused LiCl were interpreted as arising from tetragonal distortion of the $NiCl_4^-$ ion due to the large effective crystalline field in this solvent. Addition of chloride ion to solutions of Ni(II) in $LiNO_3$–KNO_3 eutectic results in the formation of chloro complexes of Ni(II).

A number of studies have been concerned with chloro complexes of bivalent metal ions in pure chloride melts and in nitrate melts to which excess chloride ion was added.[3] The nature and stability of the complexes was investigated chiefly by means of conductivity,[4,5] cryoscopic[6-8] and solubility[9] measurements. None of these studies, however, can be rigorously interpreted from a structural point of view.

It has been shown recently that studies of the visible absorption spectra of transition metal ions in fused salts can give detailed structural information about the nature of the ionic species in melts.[10,11] The present investigation extends this earlier work on chloro complexes of cobalt[11] and uranium[12] to nickel dissolved in chloride and nitrate melts.

Experimental

Details of spectrophotometric measurements on fused salt solutions up to temperatures of 850° have been given in other publications.[12-14] A Beckman Model DU spectrophotometer was modified for high temperature operation by replacing the usual cell compartment with a water cooled compartment containing an electrically heated #310 stainless steel block machined to accommodate two 1 cm. square optical cells. In order to eliminate interference from black body radiation, the normal positions of light housing and phototube compartment were reversed so that light from the source passed first through the sample, then through the monochromator before finally striking the phototube. With this arrangement, some resolution was lost because of the altered distance between light source and slit. The decrease in resolution did not however affect the resolution of the relatively broad band spectra characteristic of most transition metal ions at these temperatures.

Absorption spectra of $NiCl_2$ (prepared by dehydrating $NiCl_2 \cdot 6H_2O$ in a stream of HCl gas) dissolved in $LiNO_3$–KNO_3 eutectic, pyridinium chloride, LiCl, CsCl and Cs_2ZnCl_4 were obtained. The $LiNO_3$–KNO_3 eutectic was prepared by drying reagent grade chemicals in an oven at 110°, melting them together in the proper proportions and passing dry N_2 through the melt for one hour to remove traces of moisture. Pyridinium chloride was prepared by two distillations of Eastman's Practical grade material. Reagent grade LiCl and reagent grade CsCl were dehydrated by melting the salts in fused silica tubes and bubbling dry HCl gas through the melts for 0.5 hour. The salt Cs_2ZnCl_4 was prepared by slow evaporation of a 6 *M* HCl solution containing stoichiometric amounts of CsCl and $ZnCl_2$. The colorless crystals, after separation from the mother liquor, were washed with absolute ethyl alcohol, acetone and carbon tetrachloride. The dried material then was melted in a fused silica tube and dry HCl gas bubbled through the melt to remove the last traces of water vapor.

The optical absorption cells were filled on a vacuum line and sealed off under vacuum. Two cells were prepared in every case: one, the blank cell, contained the fused salt solvent alone; the other, the sample cell, contained in addition an appropriate amount of dissolved $NiCl_2$.

Absorption spectra were measured in the range 350–1200 mμ.

Solid solutions of Cs_2NiCl_4 in Cs_2ZnCl_4 were prepared by dissolving stoichiometric amounts of CsCl and $NiCl_2$ in molten Cs_2ZnCl_4. The molten salt solution was then allowed to cool giving a blue colored solid. Absorption spectra of the solid were measured on a Cary Spectrophotometer using the KBr pellet technique which has previously been employed by us for similar measurements on uranium compounds.[15]

Analyses for Ni were carried out gravimetrically after dissolving the salts in water.

Molar extinction coefficients were calculated using the following density values for the fused salt solutions:

Solvent	Density, g./cm.³	Temp., °C.
$LiNO_3$–KNO_3 eutectic	1.94	160
Pyridinium chloride	1.14	160
LiCl	1.5	700
CsCl	2.8	700
Cs_2ZnCl_4	2.46	650

Results and Discussion

A. Absorption Spectra of Ni(II) in Chloride Melts.

The absorption spectrum of $NiCl_2$ dissolved in molten pyridinium chloride at 160° is shown in Fig. 1A. The spectrum at this temperature consists of two bands with maxima at 655 and 705 mμ, respectively. It is of interest to see what can be learned about the nature of the ionic species responsible for this spectrum.

(1) Part of a paper "Reaction Mechanisms in Fused Salts" presented at the Symposium on Mechanisms of Inorganic Reactions in Solution, Northwestern University, July 7–10, 1958.

(2) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(3) G. J. Ganz, C. Solomons and H. J. Gardner, *Chem. Revs.*, **58**, 461 (1958).

(4) H. Bloom and E. Heymann, *Proc. Phys. Soc. (London)*, **A188**, 392 (1947).

(5) M. F. R. Mulcahy and E. Heymann, This Journal, **47**, 485 (1943).

(6) E. Kordes, W. Bergman and W. Vogel, *Z. Elektrochem.*, **55**, 600 (1951).

(7) G. Petit and C. Bourlong, *Compt. rend.*, **237**, 457 (1953).

(8) E. R. Van Artsdalen, This Journal, **60**, 176 (1956).

(9) F. H. Duke and M. L. Iverson, *ibid.*, **62**, 417 (1958).

(10) D. M. Gruen, *Nature*, **178**, 1181 (1956).

(11) D. M. Gruen, *J. Inorg. Nucl. Chem.*, **4**, 74 (1957).

(12) D. M. Gruen and R. L. McBeth, *ibid.* (in press).

(13) D. M. Gruen, P. Graf and S. Fried, Proceedings of the XVIth International Congress of Pure and Applied Chemistry, Paris, July, 1957.

(14) D. M. Gruen, P. Graf, S. Fried and R. L. McBeth, Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Geneva, September, 1958.
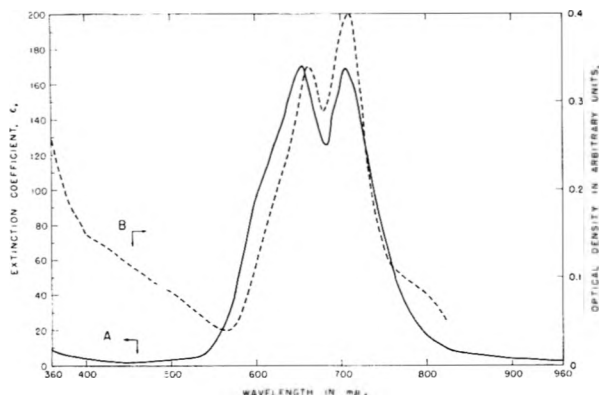
(15) D. M. Gruen and M. Fred, *J. Am. Chem. Soc.*, **76**, 3850 (1954).

Fig. 1.—A, absorption spectrum of NiCl₂ dissolved in pyridinium chloride at 160°; B, absorption spectrum of solid solution of ≈25% Cs₂NiCl₄ in Cs₂ZnCl₄ at room temperature in KBr disk.
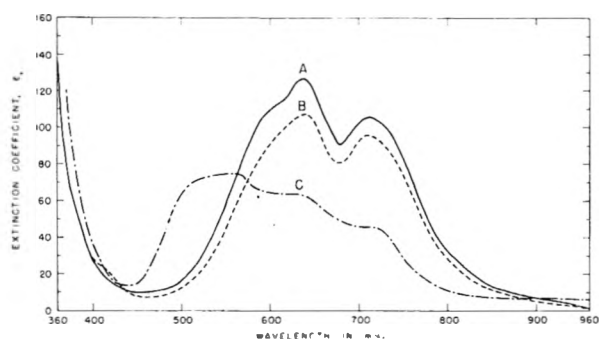

Fig. 2.—Absorption spectra of Ni(II) in fused chlorides: A, Cs₂ZnCl₄ at 650°; B, CsCl at 700°; C, LiCl at 700°.

There has been a good deal of discussion in recent years about the coördination chemistry of Ni-(II) and particularly about the absorption spectra of Ni(II) in compounds and in solutions.[16,17] It is generally agreed that Ni(II) can exist in either the hexa-coördinated or tetra-coördinated form; tetra-coördinated Ni(II) in turn is found in either the planar or tetrahedral configurations.

We speculated that the "blue" spectrum shown in Fig. 1A is due to tetrahedral $NiCl_4^=$ ions present in the melt and set about to find experimental evidence for this supposition. The approach was the same as that employed in the study of Co(II).[11] In that case, the compound Cs_2CoCl_4 was well known and the identity of its spectrum with that of a solution of Co(II) in pyridinium chloride showed the presence of $CoCl_4^=$ in the melt.

The isomorphous compounds of the type Cs_2-MCl_4 with M = Co, Cu and Zn have been prepared and have been found to be isostructural with K_2-SO_4.[18] In these compounds, the bivalent metal ions are tetrahedrally surrounded by four chloride ions in a slightly distorted tetrahedral arrangement. The pure double salt Cs_2NiCl_4 on the other hand appears to be unstable[19] and has not been reported. Indeed, no compounds of tetrahedral Ni(II) con-

(16) J. S. Griffith and L. E. Orgel, Quart. Rev., 11, 381 (1957).

(17) W. E. Moffitt and C. J. Ballhausen, Ann. Rev. Phys. Chem., 7, (1956).

(18) B. Brehler, Z. Krist., 109, 1 (1957); M. A. Porai-Kochitz, Kristallografiya, 1, 293 (1956); L. Helmholz and R. F. Kruh, J. Am. Chem. Soc., 74, 1176 (1952).

(19) Indirect evidence for this instability is to be found in the observations of F. M. Hornyak, ibid., 79, 5435 (1957).

sisting entirely of inorganic constituents appear to have been reported—the tetrahedral configuration being notoriously unstable for this transition metal ion.[16,17] (The compound $CsNiCl_3$ is known but its structure, though not yet determined, is probably like $CsCuCl_3$ where the transition metal ion is surrounded by four chloride ions in a square planar arrangement.[20,21]) We have now found that one can replace Zn(II) isomorphously by Ni(II) as explained in the Experimental section thus stabilizing the tetrahedral configuration. These solid solutions were examined crystallographically and found to be isomorphous with pure Cs_2ZnCl_4. Solid solutions containing ≈25% Ni were prepared in this way and were preserved without special precautions for months, their deep blue color persisting throughout this time. With Ni(II), then, the Cs_2ZnCl_4 host lattice acts to "induce" the tetrahedral configuration so that now the complete series of $MCl_4^=$ ions (Co, Ni, Cu, Zn) is known to occur in crystals.[22]

The absorption spectrum taken at room temperature of a solid solution of $Cs_2Zn(Ni)Cl_4$ containing about 25 mole % Ni is shown in Fig. 1B. The very close similarity of this spectrum with the melt spectrum (Fig. 1A) leaves little doubt that the *tetrahedral $NiCl_4^=$ ion is present in solutions of $NiCl_2$ in fused pyridinium chloride*.

NOTE ADDED IN PROOF.—Dr. A. Liehr of Bell Telephone Laboratories suggests in a private communication that the two peaks at 655 mμ (15,300 cm.⁻¹) and 705 mμ (14,200 cm.⁻¹) are due to transitions from the $^3T_1$ ($^3T_{1g}$, t_{2g}^2) ground state to the spin-orbit split states of ^3P, that is $^3P_2$ (Γ_3, Γ_5) at ~14,250 cm.⁻¹ and $^3P_1$ (Γ_4) at ~14,550 cm.⁻¹ plus $^3P_0$ (Γ_1) at ~14,800 cm.⁻¹. These energy values are for a Dq of approximately 200 cm.⁻¹. Dr. Liehr further suggests that a spin-allowed transition should be found at ~5000 cm.⁻¹. This has not yet been looked for.

It was of interest to inquire into the temperature stability of the $NiCl_4^=$ ion. Pyridinium chloride is not well suited for this purpose since it decomposes above 200°. The solvents Cs_2ZnCl_4 and pure CsCl were chosen instead. The spectra of Ni(II) in these solvents are shown in Fig. 2A and 2B. It can be seen that these spectra are quite similar to the solid spectrum (Fig. 1B) pointing to the presence of $NiCl_4^=$ ions even in these high temperature melts. However, it is clear that the similarity with the solid spectrum (Fig. 1B) is not as complete as in the case of the pyridinium chloride solvent. It will be worthwhile to discuss the differences in the spectra in greater detail.

The half-widths of the absorption bands of the Ni(II) spectra in fused Cs_2ZnCl_4 and CsCl at ≈1000°K. are considerably larger than those of the pyridinium chloride solution at 460°K. or of the solid at 300°K. Temperature broadening of spectra is of course a quite general phenomenon. However, in the case of transition metal ions, such temperature broadening would be expected to be most pronounced on the long wave length side of the absorption bands due to thermal popula-

(20) A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, England, 1950, p. 303.

(21) H. Remy and F. Meyer, Verh. dt. Chem. Ges., 77, 679 (1944).

(22) It would be interesting to look for other examples of configuration inductivity. Thus it might be possible to stabilize tetrahedral $FeCl_4^=$ in the Cs_2ZnCl_4 host lattice or planar $CoCl_4^=$ by incorporation into the Cs_2PtCl_4 host lattice.

tion of ligand field levels with increasing temperature. Comparison of Fig. 1 with Fig. 2 shows that the absorption intensity in the long wave length region of the spectrum has actually decreased in going to higher temperatures.

The magnitude of this effect which can be looked upon as a shift of the spectrum to shorter wave lengths is almost the same and quite small in both the Cs_2ZnCl_4 and the pure CsCl melts. By comparison, there is a very marked shift of the spectrum toward shorter wave lengths in fused LiCl (Fig. 2C). In this solvent, the Ni(II) spectrum bears very little resemblance to the spectra shown in Fig. 1.

In the solid, the tetrahedral configuration of the $NiCl_4^=$ ion is "frozen in," and in the pyridinium chloride melt there appears to be very little distortion from tetrahedral symmetry. The shift of the absorption spectrum to shorter wave lengths which already makes itself felt in fused CsCl and is so extremely pronounced in fused LiCl could be due to distortion of the $NiCl_4^=$ ion from tetrahedral symmetry.

Recent theoretical studies on the electronic configuration of Ni(II) have made it clear that the energy levels of the $3d^8$ configuration are very dependent on the metal ion–ligand distances.[23–25] Ballhausen and Liehr[25] define a "tetragonality parameter" which is directly dependent on the effective crystalline field seen by the Ni(II) ion. They find that the larger the effective crystalline field, the larger is the numerical value of this parameter.

Applied to our situation, their theory predicts that the larger the effective crystalline field, the larger would be the resultant distortion from tetrahedral symmetry.

The effective crystalline field which the Ni(II) ion sees in the melt is due, in first approximation, to the surrounding chloride ions. In the LiCl melt, the chloride ions form a quasi-lattice in which presumably there is anion–anion contact.[26] In the CsCl melt, on the other hand, one calculates the Cl–Cl distances to be larger by about 15% than in LiCl on the basis of molar volume data.[26,27] One may picture the Ni(II) ion as situated in a cage of chloride ions, the cage being smaller in the LiCl than in the CsCl melt. Thus, a mechanism is provided for increasing the "effective crystalline field" acting on Ni(II) in the LiCl melt *versus* the CsCl melt and for the tetragonal deformation to be more pronounced in the former than in the latter solvent.

On this picture, the Ni(II) spectrum in fused LiCl arises from a strongly tetragonally deformed $NiCl_4^=$ species while the spectrum in fused CsCl is due to a weakly deformed (very closely tetrahedral) $NiCl_4^=$ species.

An additional important factor causing the tetrag-

onal distortion of the $NiCl_4^=$ ion in LiCl melts is due to the ability of the small Li^+ ion to neutralize very effectively the electrostatic repulsion between the chlorides of the $NiCl_4^=$ complex ion, thus making the tetragonally deformed configuration energetically more favorable.

In CsCl and pyridinium chloride melts, on the other hand, the repulsion between the chlorides of the $NiCl_4^=$ ion is the dominant factor so that especially in the latter solvent where the very large pyridinium ion has difficulty in neutralizing the electrostatic repulsion one observes spectra characteristic of very nearly tetrahedral $NiCl_4^=$.

It is premature to assess the relative importance of the various factors that have been discussed. However, it should be pointed out that effects similar to those observed in the case of Ni(II) solutions will in all probability be found in many other kinds of fused salt solutions. Their exact interpretation undoubtedly will contribute in a fundamental way to our understanding not only of fused salt systems but also of the coördination chemistry of transition metal ions.

An interesting study of the temperature dependence of the Ni(II) spectrum in LiCl–KCl eutectic was published recently by Boston and Smith.[28] These workers observed that the spectra in the LiCl–KCl solvent shifted toward longer wave lengths with increasing temperatures and they interpreted their results as due to the presence of at least two light absorbing species.

The spectral changes observed by Boston and Smith[28] as a function of temperature and those observed by us in fused CsCl and fused LiCl complement one another. Indeed, their 540° spectrum is similar to the CsCl spectrum taken at 700° and their 364° spectrum resembles the LiCl spectrum taken at 700°. With increasing temperature of the LiCl–KCl melt, the equilibrium internuclear Cl–Cl distances would be expected to increase. Expansion of the melt itself will lead to larger Cl–Cl distances. Volume expansion results in a decrease in the density of the melt by $\approx 1\%$ in going from 350–550°.[26] More importantly, one would expect the Cl–Cl distances of the $NiCl_4^=$ complex to increase with temperature since the molecule will be in higher vibrational modes. As a result, the effective crystalline field seen by the Ni(II) ion can be expected to decrease and the $NiCl_4^=$ ion to assume a more nearly tetrahedral symmetry with increasing temperature.

In addition, because of the increased vibrational amplitudes of the chlorides in $NiCl_4^=$ with increasing temperature, the resultant increase in electrostatic repulsion would be an additional factor favoring tetrahedral symmetry.

The spectral changes observed by Boston and Smith[28] when interpreted on the basis of the above discussion can therefore be associated with a change from tetragonally distorted to tetrahedral $NiCl_4^=$ with increasing temperature.

B. Some Remarks about Non-ideality in Fused Salt Solutions.—The Temkin model[29] for fused salts when statistically interpreted corresponds to

(23) H. Hartmann and H. Fischer-Wasels, *Z. physik. Chem.*, **4**, 297 (1955).

(24) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958).

(25) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81**, 538 (1959).

(26) E. R. Van Artsdalen and L. S. Yaffe, THIS JOURNAL, **59**, 118 (1955).

(27) J. W. Johnson, P. A. Agron and M. A. Bredig, *J. Am. Chem. Soc.*, **77**, 2734 (1955).

(28) C. R. Boston and G. P. Smith, THIS JOURNAL, **62**, 409 (1958).

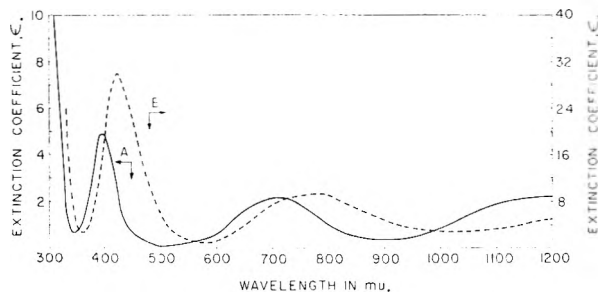(29) M. Temkin, *Acta Phys. Chem., U.R.S.S.*, **20**, 411 (1945).

Fig. 3.—Absorption spectra of Ni(II) in: A, 1 M HClO$_4$ at room temperature; B, LiNO$_3$–KNO$_3$ eutectic at 160°.
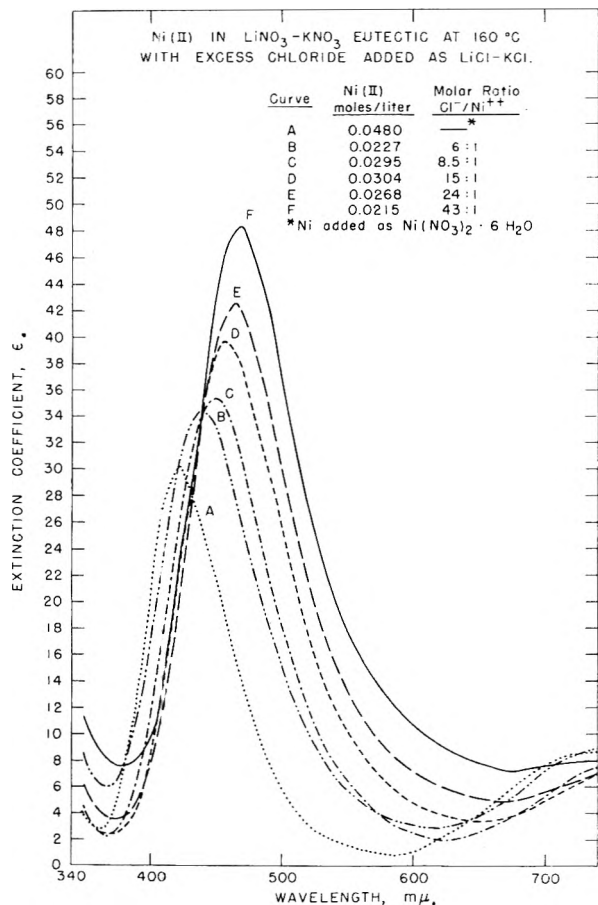

Fig. 4.—Absorption spectra of Ni(II) in LiNO$_3$–KNO$_3$ eutectic at 160° with increasing amount of LiCl–KCl added.

an ionic mixture in which the anions are randomly distributed among themselves and similarly the cations. Deviations from this ideal model can arise from restrictions in mixing which need not be a result of complex ion formation.[30]

However, the non-ideal behavior of bivalent metal halides in alkali halide or alkaline earth halide solutions can be discussed in a meaningful way on the basis of complex ion formation.

In a revealing series of studies, Lantratov and Alabyshev[31] investigated activities of bivalent metal chlorides dissolved in alkali and alkaline earth metal chlorides. One can come to two fairly

general conclusions on the basis of their work: (1) for the same solvent, the smaller the size and the higher the charge of the solute cation, the greater will be the deviations from ideality of the solute cations; (2) for the same solute, the smaller the size and the higher the charge of the solvent cation, the less will be the deviations from ideality of the solute cations.

The second conclusion is the one having the greatest bearing on the present work. We would like to suggest that the changes observed in the spectrum of Ni(II) in going from CsCl solvent to LiCl solvent are associated with a change in the activity coefficient of Ni(II), the activity coefficient being closer to unity in the LiCl solvent than in the CsCl solvent.[32]

The picture of the NiCl$_4^=$ complex developed in the previous section can shed light on the thermodynamic behavior of bivalent metal chlorides in alkali halide solvents. According to this picture, Ni(II) is present in the form of tetrahedral NiCl$_4^=$ ions in dilute solutions of CsCl. The Cl–Cl distances in the NiCl$_4^=$ tetrahedra are probably very close to 3.6 ± 0.1 Å. or about twice the ionic radius of the chloride ion. This supposition is supported by the X-ray investigation of Helmholz and Kruh who found the Cl–Cl distance of CuCl$_4^=$ tetrahedra in solid Cs$_2$CuCl$_4$ to be between 3.50 and 3.70 Å. The Cl–Cl distance in solid CsCl on the other hand is 4.11 Å. This distance can be expected to be diminished by a few per cent. in the melt. The crux of the argument, however, is that the Cl–Cl distances of the tetrahedral NiCl$_4^=$ complex in the melt are much shorter than the Cl–Cl distances of the bulk CsCl melt. The four chlorides about the Ni(II) are therefore quite distinct from the chloride ions making up the rest of the melt since they are so closely associated with the bivalent metal ions. One can therefore speak about NiCl$_4^=$ complex ions, and it is not surprising that the activity coefficient of Ni(II) is low.

If one now regards dilute solutions of Ni(II) in LiCl, a somewhat different picture emerges. Complex NiCl$_4^=$ ions are still present, albeit somewhat tetragonally deformed. However, since in the LiCl melt one can presume that there is anion–anion contact, the Cl–Cl distances associated with the NiCl$_4^=$ complexes and those associated with the bulk melt will be very closely similar. Therefore the association of chloride with Ni(II) must be regarded as being somewhat weakened in the LiCl compared with the CsCl melt. It is more difficult to distinguish in this case between chloride ions associated with Ni(II) and chloride ions belonging to the bulk of the LiCl melt. Qualitatively, the effects described will tend to make solutions of Ni(II) (and probably solutions of many other bivalent metal chlorides) in LiCl correspond more closely to the ideal Temkin model than would similar solutions in CsCl. As a result, deviations from ideality will tend to be less pronounced in the

(30) H. Flood, T. Forland and K. Grjotheim, Z. anorg. Chem., **276**, 289 (1954).

(31) M. F. Lantratov and A. F. Alabyshev, J. Appl. Chem., U.R.-S.S., **26**, 235, 321 (1953); **27**, 685 (1954).

(32) The activity coefficients of Ni(II) in LiCl–KCl eutectic have been measured by R. D. Walker and D. E. Danley and found to be of the order of 0.1 for dilute Ni(II) solutions ("Activities of NiCl$_2$ from E. M. F. Measurements in LiCl–KCl Eutectic," presented at the July, 1957, Molten Salt Symposium at Oak Ridge National Laboratory).

former than in the latter solvent. An interesting consequence of this point of view is that the free energies of formation of pure liquid bivalent metal halides can be expected to be more closely similar to free energies of formation of the same halides measured in fused LiCl than in fused CsCl.

This discussion could be extended along similar lines to include qualitatively all of the observations summarized above under conclusions (1) and (2). It is hoped that detailed considerations of this sort can form the subject of a future paper.

C. Solutions in LiNO₃-KNO₃ Eutectic.—It was shown in Section A that Ni(II) is tetra-coordinated in chloride melts. It was of interest to see whether coördination numbers other than four would occur, for example, in oxygen containing fused salt solvents. In earlier work it had become apparent that the absorption spectra of many transition metal ions in the LiNO₃-KNO₃ eutectic solvent are similar to their aqueous solution spectra.[11] Since it is generally agreed that the bivalent transition metal ions are hexa-coördinated in aqueous solution, the similarity of their spectra in water and in LiNO₃-KNO₃ suggested that the coördination of these ions with oxygen would be similar in the two media.

The absorption spectra of Ni(II) solutions in 1 M HClO₄ at 25° and in LiNO₃-KNO₃ eutectic at 160° are shown in Fig. 3A and 3B, respectively. It can be seen that the ultraviolet absorption band which peaks at 395 mμ with a molar extinction coefficient of 5 in 1 M HClO₄ is shifted to 422 mμ and has a molar extinction coefficient of 30 in the LiNO₃-KNO₃ eutectic. The infrared absorption band peaking at 710 mμ in 1 M HClO₄ (ϵ, 2.2) has been shifted to 775 mμ (ϵ, 11). The half-widths of these bands are larger by about 30% in the nitrate eutectic as compared with water while the absorption intensity has been increased by a factor of about 7 in the fused salt compared with the aqueous solution.

It is perhaps surprising that the similarity of the spectra in water and in the nitrate melt is so pronounced. The Ni(II) spectrum in the region shown in Fig. 3A and B is due to transitions between ligand field levels produced by Stark splitting of the ground state derived from the 3d⁸ configuration.[16,17] The energy differences between these levels will be determined in first approximation by the magnitude of the effective crystalline field seen by the Ni(II) ion. The fact that the two bands of the Ni(II) spectrum occur at almost the same wave lengths in the two solvents suggests that the effective crystalline field is of about the same strength whether it arises from the oxygens of the water dipoles or the oxygens of the nitrate ion.

A possible model for Ni(II) in the nitrate melt places the ion in the center of four nitrate groups tetrahedrally arranged about it. Since the nitrate groups are planar, the twelve oxygens belonging to the nitrate groups can then occupy positions equidistant from the central metal ion in a cubic array. The twelve oxygens of the nitrate groups in cubic array about Ni(II) would have to give rise to an effective electric field of about the same intensity as that produced by the six oxygens of the water molecule octahedrally surrounding the ion in its hydration sphere. Detailed calculations are of course required to test this or any alternative model.
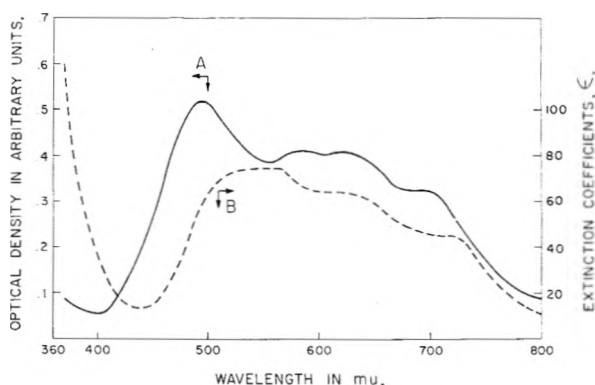
Fig. 5.—Absorption spectra of Ni(II) in: A, LiNO₃-KNO₃ eutectic at 232° saturated with LiCl-KCl ($\approx$5 M in Cl⁻); B, LiCl at 700°.

Changes had previously been observed in the absorption spectrum of Co(II) in LiNO₃-KNO₃ eutectic on addition of chloride ion. These changes were interpreted as due to the successive replacement of nitrate groups by chloride ion resulting at high chloride ion concentration in the formation of the tetrahedral CoCl₄⁻ ion.[11] Similar phenomena have now been observed in the case of Ni(II).

Absorption spectra of Ni(II) in LiNO₃-KNO₃ eutectic to which varying amounts of chloride ion were added are shown in Fig. 4. The shift of the 422 mμ band to longer wave lengths is interpreted as due to the stepwise formation of chloro complexes of Ni(II). The detailed interpretation of these results in terms of stability constants is not yet complete but it was thought to be of interest to show qualitatively the behavior of this system.

At 160°, the formation of appreciable concentrations of the fully complexed NiCl₄⁻ species is limited by the solubility of LiCl-KCl in the nitrate melt. At a temperature of 230°, the chloride solubility is sufficiently increased (about 5 M) so that the NiCl₄⁻ spectrum is indeed observed (Fig. 5A). The similarity of the NiCl₄⁻ spectra in the LiNO₃-KNO₃ eutectic with added chloride and in pure LiCl is evident on comparing Fig. 5A with Fig. 5B.

HOMOGENEOUS CATALYTIC ACTIVATION OF MOLECULAR HYDROGEN BY METAL IONS AND COMPLEXES[1]

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Certain metal ions and complexes, notably those of copper, silver and mercury, have been found to react homogeneously with molecular hydrogen in solution, or to catalyze homogeneously the reactions between hydrogen and other dissolved substrates. Such reactions have been studied in a variety of solvents including water, amines, carboxylic acids and hydrocarbons. Because of their greater simplicity, both from the chemical and the kinetic standpoint, it has been possible to obtain a much clearer understanding of the nature and function of the catalytic species in these systems, than in systems involving heterogeneous hydrogenation catalysts. The path of splitting of hydrogen, as deduced from kinetic and thermodynamic considerations and from isotopic exchange studies, may be either heterolytic or homolytic, depending on the nature of the catalytic species, its valence state and its environment (state of complexing, solvent, etc.). Some metal ions (*e.g.*, Cu^+ or Ag^+) may activate hydrogen by either path and in such cases the path involving heterolytic splitting is favored when the metal ion is surrounded by basic ligands or solvent molecules which can act as proton acceptors. Catalytic activity in these systems appears to be linked primarily to electronic, rather than to geometric factors. Particularly pronounced catalytic activity is exhibited by "bi-functional" complexes in which electron-accepting and proton-accepting sites are both present. Some aspects of heterogeneous and enzymic catalysis, and of catalytic poisoning, also may be interpreted in the light of these considerations.

It is now well recognized that even under relatively mild conditions, molecular hydrogen can undergo many reactions homogeneously in solution. This recognition is, however, of fairly recent origin and can be traced to Calvin's[2] discovery in 1938 that at temperatures of about 100°, hydrogen reduces cupric acetate or benzoquinone homogeneously in quinoline solution, in the presence of dissolved cuprous acetate. The latter functions as a true homogeneous catalyst for these, as well as for reactions of hydrogen, *e.g.*, parahydrogen conversion. Subsequently, and particularly since 1953, many other systems in which hydrogen undergoes homogeneous reactions, have been discovered and studied.[3] Most of these involve metal ions or complexes as reactants or catalysts. In this paper, the mechanisms by which these species "activate" or split hydrogen are examined, with a view to finding a common basis for their activity and to interpreting the dependence of this activity on electron configuration, ligands and solvent. An attempt also is made to relate the catalytic properties of these relatively simple species to those of the more conventional heterogeneous hydrogenation catalysts.

Metal Ions in Aqueous Solution.—Among the species which activate hydrogen are a number of simple metal ions, *e.g.*, Cu^{++}, Ag^+, Hg^{++} and Hg_2^{++} and the oxyanion MnO_4^-. In aqueous solution these ions are reduced homogeneously by hydrogen at temperatures below 100° to compounds of lower valence or to the metallic state. Cu^{++} and Ag^+ also catalyze exchange of hydrogen with water and the hydrogenation of dissolved substrates such as oxygen or dichromate which do not react with hydrogen in the absence of a catalyst.

These reactions can be divided, on the basis of

their kinetics and mechanisms, into two classes, depending on whether one or two metal ions participate, together with a hydrogen molecule, in the rate-determining step. It seems likely that the hydrogen undergoes heterolytic splitting in reactions of the first type and homolytic splitting in those of the second type. This is illustrated by the following equations which are believed to represent the rate-determining steps in some of the homogeneous hydrogenation reactions which have been observed in aqueous solution. In each case the measured activation energy (kcal.) is also given.

<div align="center">Class I Reactions</div>

$$Cu^{++} + H_2 \longrightarrow CuH^+ + H^+ \ (E = 27) \quad (1)$$

$$Ag^+ + H_2 \longrightarrow AgH + H^+ \ (E = 24) \quad (2)$$

$$Hg^{++} + H_2 \longrightarrow HgH^+ + H^+ \ (E = 18) \quad (3)$$

$$MnO_4^- + H_2 \longrightarrow HMnO_4^- + H^+ \ (E = 15) \quad (4)$$

<div align="center">Class II Reactions</div>

$$2Ag^+ + H_2 \longrightarrow 2AgH^+ \ (E = 15) \quad (5)$$

$$Hg_2^{++} + H_2 \longrightarrow 2HgH^+ \ (E = 20) \quad (6)$$

$$Ag^+ + MnO_4^- + H_2 \longrightarrow$$
$$AgH^+ + HMnO_4^- \ (E = 9) \quad (7)$$
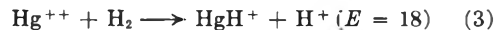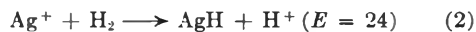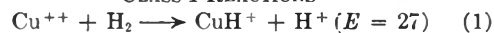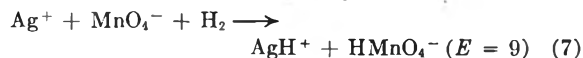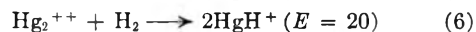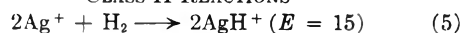
The corresponding entropies of activation are all in the "normal" range, *i.e.*, of the order of -10 e.u. for the bimolecular reactions and -25 e.u. for the two termolecular ones.

The mechanisms proposed for the splitting of hydrogen by Cu^{++} and Ag^+ have been adequately substantiated. For some of the other reactions there is some uncertainty about the configurations of the intermediates[4] and the proposed representations are based on analogy and on indirect kinetic and thermodynamic evidence.[3b,c] Most of these intermediates are unstable and either undergo back-reaction to regenerate hydrogen or take part in some further reactions in which the metal ion itself, or some other dissolved substrate, is reduced.

It is noteworthy that Ag^+ can split hydrogen either heterolytically or homolytically. The latter

(1) Support of this project through grants from the Research Corporation, the National Research Council of Canada, and Imperial Oil Limited, is gratefully acknowledged.

(2) M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938); *J. Am. Chem. Soc.*, **61**, 2230 (1939).

(3) Much of the historical background and experimental work pertinent to the discussion in this paper is reviewed in (a) S. W. Weller and G. A. Mills, *Advances in Catalysis*, **8**, 163 (1956); (b) J. Halpern. *ibid.*, **9**, 302 (1957); *Quart. Revs. (London)*, **10**, 463 (1956); (c) A. H. Webster and J. Halpern, This Journal, **61**, 1239, 1245 (1957).

(4) For example, $HgH^+(aq)$ is probably unstable with respect to $Hg(aq)$ and $H^+(aq)$ but its formation as the initial product of the splitting of H_2 by both Hg^{++} and Hg_2^{++}, as shown, is favored on mechanistic grounds. Similar considerations apply to the Mn(V) and Mn(VI) intermediates in equations 4 and 7, respectively.

path is termolecular but is favored relative to the alternative bimolecular path, particularly at low temperatures because of its lower activation energy (15 *vs.* 24 kcal.). Similarly the Ag^+-catalyzed reduction of MnO_4^- by H_2, involving a termolecular rate-determining step (eq. 7) competes with the bimolecular uncatalyzed reduction (eq. 4) because of its lower activation energy (9 *vs.* 15. kcal).

A number of other metal ions including Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, Tl^{3+}, Ce^{4+}, UO_2^{2+}, VO_3^- and CrO_4^{2-} have been tested, in this Laboratory, for catalytic activity in aqueous solution, in most cases at temperatures up to 150° and found to be inactive. No autocatalysis due to Cu^+ was noted[5] during the reduction of aqueous solution of cupric perchlorate or sulfate by hydrogen, indicating that the activity of Cu^+, if any, is small compared with that of Cu^{++}. This is of interest in view of the pronounced catalytic activity which cuprous salts display in certain organic media.[2,6,7] Similarly, no autocatalysis due to MnO_4^- was noted in the reduction of MnO_4^- basic solutions.[8] Pd^{++} also appears to activate hydrogen in aqueous solution, although attempts to study this system quantitatively were unsuccessful because of the tendency for traces of metallic palladium, a powerful heterogeneous catalyst, to form; however, catalytic activity has been demonstrated[9] for the complex, $PdCl_4^-$.

Effects of Complexing.—The rates of activation of hydrogen by metal ions are greatly influenced by complexing as shown by Table I, in which the reactivities of a number of complexes of copper-(II),[10] mercury(II)[11] and silver(I)[3c] are compared with those of the corresponding aqua-ions.

The reactions being considered in this comparison all belong to Class I and involve the heterolytic splitting of hydrogen in the rate-determining step. A plausible representation of the transition state in such a reaction, for a complex MX_n^{Z+}, is

$$X_{(n-1)}-M\overset{Z^+}{\underset{\underset{H-\!-\!H^+}{|\quad|}}{\cdots}}X$$
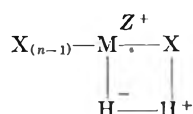
where X is a ligand molecule or ion (a water molecule in the case of the aqua ion) originally coördinated to the metal. Formation of the transition state thus involves heterolytic stretching of the M–X and H–H bonds and incipient formation of covalent M–H and X–H bonds. The reactivity of the complex should thus depend directly on the strengths of the M–H and X–H bonds and inversely on the strength of the M–X bond, all of which vary with the nature of X. Most of the

(5) E. R. Macgregor and J. Halpern, *Trans. Met. Soc. A.I.M.E.*, **212**, 244 (1958).

(6) (a) S. Weller and G. A. Mills, *J. Am. Chem. Soc.*, **75**, 769 (1953); (b) L. W. Wright and S. Weller, *ibid.*, **76**, 3345 (1954); (c) M. Calvin and W. K. Wilmarth, *ibid.*, **78**, 1301 (1955); (d) W. K. Wilmarth and M. Barsh, *ibid.*, **75**, 2237 (1953); **78**, 1305 (1935).

(7) A. J. Chalk and J. Halpern, unpublished.

(8) A. H. Webster and J. Halpern, *Trans. Faraday Soc.*, **53**, 51 (1957).

(9) P. E. Potter and J. Halpern, unpublished.

(10) E. Peters and J. Halpern, *Can. J. Chem.*, **34**, 554 (1956).

(11) G. J. Korinek and J. Halpern, *ibid.*, **34**, 1372 (1956); THIS JOURNAL, **60**, 285 (1956).

TABLE I

EFFECT OF COMPLEXING ON ACTIVITY

Complex[a]	"Mean" formation constant[b]	Relative activity
$CuBu_2$	. . .	150
$CuPr_2$	. . .	150
$CuAc_2$	30	120
$CuSO_4$	100	6.5
$CuCl_4^-$	~1	2.5
Cu^{++}	. . .	1
$CuGl_2$	5×10^7	<0.5
$Cu(en)_2$	1×10^{10}	0.1
$HgSO_4$	22	1.8
Hg^{++}	. . .	1
$HgAc_2$	1.6×10^4	4×10^{-2}
$HgBr_2$	. . .	4×10^{-2}
$HgCl_4^-$	6×10^3	3.2×10^{-3}
$HgCl_2$	4×10^6	2.5×10^{-3}
$HgBr_2$	3.5×10^7	1.7×10^{-3}
$Hg(en)_2^{++}$	5.1×10^{11}	1×10^{-3}
$AgAc$	~3	80
$Ag(en)_2^+$	7×10^3	25
Ag^+	. . .	1
$Ag(CN)_2^-$	2.4×10^9	Inactive

[a] Ligand designations: Bu^- = butyrate; Pr^- = propionate; Ac^- = acetate; Gl^- = glycinate; en = ethylenediamine. [b] $\sqrt[n]{K_n}$ where $K_n = [MX_n]/[M][X]^n$.

effects in Table I can be explained in terms of these concepts.

Thus the low reactivities of the ethylenediamine and glycine complexes of Cu^{++} relative to that of the aqua-ion, are attributed to strong metal–ligand bonding, reflected in the large formation constants (Table I) of these complexes. Excessive electron displacement from the ligand to the metal ion, in very stable complexes such as these, probably also contributes to a lowering of reactivity by weakening the M–H bond. The implication of this, expressed in the language of the valence bond theory, is that the unfilled orbitals of the metal ion, needed for bonding with hydrogen, are less available because of their participation in covalent bonding with the ligands. In terms of the ligand field theory, this effect can be correspondingly ascribed to promotion of these orbitals, due to the high ligand field intensity in these complexes.

In complexes with relatively weak metal–ligand bonding, *i.e.*, those with small formation constants, these effects should be small and the main influence of the ligand on reactivity should be that arising from variation in the strength of the X–H bond. This implies that the reactivities of "weak" complexes should increase with the basicity of the ligands. The enhancement of the activity of the cupric ion by complexing with a number of anions, which follows the same order as their basicities, *i.e.*, $H_2O < Cl^- < SO_4^- < $ acetate < propionate, butyrate, is in accord with this.

In general, the effects of complexing on the reactivites of the mercuric and silver ions, are susceptible to similar interpretations although it should be noted that the order of activity of the various complexes differs for the three metal ions. Thus, the chloride and acetate complexes of the mercuric ion, which are much more stable than the corresponding cupric complexes, are less reactive than the

aqua-ion, while the relatively unstable sulfate complex is more reactive. In the case of silver, the acetate and ethylenediamine complexes are more reactive than the uncomplexed ion, while the very stable cyanide complex is inactive. It should be noted that the enhanced activity of the former two complexes is associated with the path in which hydrogen is split heterolytically. Since this path involves release of a proton, it is favored to a greater extent than the homolytic path when the water molecules adjacent to the metal ion are replaced by more basic ligands.

It is of interest that, although the reactivities of $HgCl_2$ and $HgAc_2$ are much lower than that of the uncomplexed Hg^{++} ion, further complexing with Cl^- or Ac^- results in a slight increase in reactivity. Thus the reactivity of $HgCl_4^=$, while still much lower than that of Hg^{++}, is about 30% higher than that of $HgCl_3$; the corresponding effects for the acetate and propionate complexes are much greater.[11] This behavior, at least for the chloride system, is consistent with the general interpretation of the effects of complexing, suggested earlier, in view of the marked decrease (Table I) in the mean formation constants in going from $HgCl_3$ to the higher complexes.[12]

The addition of basic anions such as Ac^-, $CO_3^=$ and OH^- has been found[11] to increase, in the order listed, the rate at which $Hg(en)_2^{++}$ reacts with H_2. These effects were observed under conditions of complete complexing of the mercuric ion with ethylenediamine, and are unlikely to arise through replacement of ethylenediamine by the added anions. A possible explanation of the effect of OH^- (which was also observed[1c] for the ethylenediamine complex of Ag^+) is an acid–base equilibrium of the type

$$(-Hg-NH_2R)^{++} + OH^- \rightleftharpoons$$
$$(-Hg-NHR)^+ + H_2O \quad (8)$$
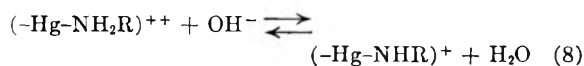
which has been recognized[13] for other ammine and ethylenediamine complexes, e.g., $Co(NH_3)_6^{3+}$, $Au(en)_2^{3+}$, $Pt(NH_3)_5Cl^{3+}$. The enhanced reactivity of the resulting complex is attributed to replacement of ethylenediamine (NH_2R) by a more basic ligand ($-NHR$). Alternatively the enhanced reactivity could be due to formation of an ion-pair complex of the type, $Hg(en)_2^{++} \cdot X^-$ in which the anion replaces an outer-sphere water molecule.

The observation[11] that the activity of Hg_2^{++} is only about one-tenth that of Hg^{++} can be interpreted by considering Hg_2^{++} as a complex of Hg^{++} containing a covalently bonded Hg atom as a ligand. The low activity of this complex is then consistent with its high formation constant ($[Hg_2^{++}]/[Hg^{-+}][Hg] \simeq 2 \times 10^8$).

Effects of Solvent.—At temperatures above 120°, both cupric and cuprous heptanoates have been found[7] to activate hydrogen by heterolytic splitting, i.e.

$$CuHp_2 + H_2 \longrightarrow (CuH)Hp + HHp \quad (9)$$

and

$$CuHp + H_2 \longrightarrow CuH + HHp \quad (10)$$
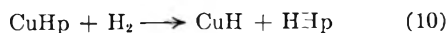
in non-polar media such as diphenyl, octadecane and heptanoic acid. The activation energies for these reactions, measured in the latter solvent (the rates in all three solvents were similar) are 30 and 21 kcal./mole, respectively. The activity of $CuHp_2$ in these solvents is much lower than that of cupric carboxylate salts in aqueous solution. This behavior probably is related to the requirement, noted earlier, for stretching of the metal–ligand bond in the transition state; in view of the charge separation involved, this would require more energy in a non-polar medium. Furthermore, the magnitude of this medium effect should depend inversely on the charge of the metal ion; in line with this it is found that the ratio of the reactivities of cuprous salts to those of the corresponding cupric salts, increases markedly in going from aqueous solution to non-polar media.

Cuprous acetate and other cuprous salts have also been found[1,6] to activate hydrogen in quinoline solution, but no activity could be detected for the corresponding cupric salts. The rate law is second order in the cuprous salt and the splitting of hydrogen, like that in the analogous "low temperature" path of activation of hydrogen in aqueous solution (eq. 5) is probably homolytic, giving CuH^+ as an intermediate. The reason for the difference in mechanism between quinoline and the "inert" solvents is not clear. In addition to the acetate, other cuprous salts including the salicylaldehyde, stearate and benzoate are active in quinoline solution, while the nitrobenzoate, nitrosalicylaldehyde and the complexes of certain Schiff bases are inactive. The general trend appears to be for the catalytic activity to increase with the basicity of the anion. This has been attributed[6c] to a decrease in the energy required to promote electrons from the full 3d shell to empty upper orbitals.

It has been found that hydrogen is split heterolytically by silver acetate in pyridine[14,15] and by silver heptanoate in heptanoic acid.[7] The activation energies for these reactions are 13–16 and 19 kcal./mole compared with 24 kcal. for the corresponding reaction (eq. 2) in aqueous solution. These differences are attributable, in part at least, to differences in the basicities of the ligands in these complexes.

Electron Configuration and Reactivity.—The ability to activate hydrogen in solution appears to be restricted to a relatively small group of species. It is therefore natural to inquire whether these possess some property in common, to which their catalytic activity is related. If such a common basis for catalytic activity exists it is clearly not to be found in a single mechanism for the hydrogen activation process. Thus there is ample evidence that hydrogen can be activated in solution both by homolytic and heterolytic splitting and that superficially similar catalysts, or even a given catalyst (e.g. Ag^+ or Cu^+) under different conditions or in different solvents can split hydrogen by different mechanisms.

(12) B. Lindgren, A. Johnson and L. G. Sillén, Acta Chem. Scand., 1, 461 (1947).

(13) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 386.

(14) L. W. Wright, S. Weller and G. A. Mills, This Journal, 59, 1060 (1955).

(15) W. K. Wilmarth and A. F. Kapauan, J. Am. Chem. Soc., 78, 1308 (1956).

A comparison of the electron configurations of the various catalytic species shows more promise. Thus it can be seen from Table II that all the metal ions which react with hydrogen in solution have outer electron configurations corresponding to nearly filled or just filled d-shells (d^8 − d^{10}); ions with electron configurations outside this range apparently are inactive.

TABLE II

ELECTRON CONFIGURATIONS OF CATALYTIC IONS

Metal ion	Outer electron configuration	"Isoelectronic" metal
Cu^{++}	$3d^9$	Co
Cu^+	$3d^{10}$	Ni
Pd^{++}	$4d^8$	Ru
Ag^+	$4d^{10}$	Pd
Hg^{++}	$5d^{10}$	Pt

Some insight into the significance of this can be derived from an inquiry into the causes of the inertness of hydrogen. This property is a consequence of the high dissociation energy (*ca.* 103 kcal.) and the closed-shell electron configuration of the molecule which result in strong repulsion forces when it approaches to within reacting distance of another electronically-saturated species (one in which the low-lying orbitals are filled). The activated complex in such a reaction generally contains more electrons than can be accommodated in low energy orbitals and consequently some electrons must be promoted to anti-bonding orbitals; this is reflected in a high activation energy. An essential requirement governing the ability of a species to "activate" electronically-saturated molecules such as hydrogen should thus be the presence of suitable unfilled-low-lying orbitals which can accept "unwanted" electrons, thus permitting reaction to proceed through a path of low activation energy. An interpretation of catalytic activity along these lines has been suggested previously by Eyring and Smith.[16]

The presence of low-lying orbitals capable of accepting electrons should be reflected in a high electron affinity and this property would thus be expected to characterize all those species which activate hydrogen homogeneously. This is borne out by the data in Table III which lists the total "electron-affinities" (as measured by the sum of the first and second ionization potentials of the corresponding atoms[17]) of a number of divalent metal ions. It is seen that the electron affinity increases along each transition series (because of increasing nuclear charge), passing through a maximum value for an ion with a filled or nearly filled d-shell. In each period the highest electron affinity is associated with the catalytically active ions.

A closer examination of the relationships just considered suggests that the optimum configuration for catalytic activity is achieved when the d-shell is filled or nearly filled but when the ion has, or can make available by electron promotion, an empty d-orbital. In the case of ions with d^{10} configurations this involves promotion of electrons to higher orbitals and accordingly it would be expected

that the reactivity of the ion should depend inversely on the energy of separation of the d- and s-levels. For an atom or ion of given electron configuration this separation increases with nuclear charge; accordingly it is not surprising to find that while Cu^+ and Hg^{++} are active, the more highly charged isoelectronic ions, Zn^{++} and Tl^{+++}, are inactive. Furthermore, the fact that the separation of d- and s-levels decreases with increasing quantum number helps to explain why $Hg^{++}(5d^{10})$ is active, while $Cd^{++}(4d^{10})$ and $Zn^{++}(3d^{10})$ are inactive.

The same principles can account for the catalytic activity of other types of metal complexes including $Co_2(CO)_8$[18] and $Co(CN)_5^{\equiv}$[19] which also activate hydrogen in aqueous solution. Thus, $Co_2(CO)_8$ with 34 electrons in the combined "outer shells" of the two cobalt atoms and $Co(CN)_5^{\equiv}$ with 17 "outer" electrons are each just short, by two and one electrons, respectively, of a "closed-shell" configuration. Similarly, the high reactivity of MnO_4^- is in line with its high electron affinity; on the other hand, the isoelectronic $CrO_4^{\equiv}$ ion, in which the gap between the highest occupied and lowest unoccupied orbitals is considerably larger,[20] is inactive.

Relation to Heterogeneous Catalysis.—The concepts developed above appear to have some validity also in relation to heterogeneous catalysis, particularly by metals. In line with this, there is much evidence to support the view that the ability of metals to chemisorb hydrogen readily and to function as efficient hydrogenation catalysts is related to the presence of an unfilled (but not too empty) d-band.[21] Thus, it is only the transition metals which chemisorb hydrogen rapidly below room temperature and it is also these metals, particularly those belonging to group VIII of the periodic table, which are the most active hydrogenation catalysts. Moderate activity above room temperature is exhibited by copper, silver and gold, the elements immediately succeeding the transition groups, and this can be attributed to the ease of d-s promotion and consequent creation of d-band vacancies in these metals. Most other elements are inactive even at higher temperatures.

Some features of the dependence of catalytic activity of metals on electron configuration are strikingly similar to that which has already been described for metal ions. This is emphasized by Table II which shows that while most of the metals whose ions activate hydrogen homogeneously (*e.g.*, Cu, Ag, Hg) are not themselves catalytically active, the elements whose atoms are isoelectronic (*i.e.* have the same number of outer electrons) with these ions are among the best metallic catalysts (Ni, Co, Pd, Pt, etc.). This suggests an important link, through electron configuration, between catalysis in homogeneous and heterogeneous systems. The interpretation proposed earlier for metal ions, namely, that catalytic activity is as-

(16) H. Eyring and R. P. Smith, THIS JOURNAL, **56**, 972 (1952).

(17) A similar pattern is obtained if the hydration energies of the ions are subtracted, to give the corresponding electron-affinities in solution.

(18) I. Wender, H. W. Sternberg and M. Orchin in "Catalysis," Vol. 5, P. H. Emmett, ed., Reinhold Publ. Corp., New York, N. Y., 1943, p. 73.

(19) G. A. Mills, S. Weller and A. Wheeler, THIS JOURNAL, **63**, 403 (1959).

(20) A. Carrington, D. Schonland and M. C. R. Symons, *J. Chem. Soc.*, 659 (1957).

(21) B. M. W. Trapnell, *Quart. Revs. (London)*, **8**, 404 (1954).

TABLE III

Two-electron Affinities $(E)^a$ of Divalent Metal Ions and Work Functions (ϕ) of "Isoelectronic" Metals[b]

Outer electron configuration	d^0	d^5	d^6	d^7	d^8	d^9	d^{10}	$d^{10}s$	$d^{10}s^2$
Ion	Ca^{++}	Mn^{++}	Fe^{++}	Co^{++}	Ni^{++}	Cu^{++}	Zn^{++}	Ga^{++}	Ge^{++}
E	18.0	23.1	24.3	25.2	25.8	27.9	27.4	26.5	24.1
Metal	..	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
ϕ	..	4.1	4.4	4.0	4.6	4.3	4.9	4.5	4.3
Ion	Sr^{++}	Tc^{++}	Ru^{++}	Rh^{++}	Pd^{++}	Ag^{++}	Cd^{++}	In^{++}	Sn^{++}
E	16.7	..	(24)	(26)	27.9	29.0	25.9	24.7	21.9
Metal	..	Nb	Mo	Te	Ru	Rh	Pd	Ag	Cd
ϕ	..	3.8	4.2	..	4.5	4.7	5.0	4.7	4.0
Ion	Ba^{++}	Re^{++}	Os^{++}	Ir^{++}	Pt^{++}	Au^{++}	Hg^{++}	Tl^{++}	Pb^{++}
E	15.2	(21)	(24)	(25)	(27)	29.2	29.2	26.4	22.4
Metal	..	Ta	W	Re	Os	Ir	Pt	Au	Hg
ϕ	..	4.1	4.5	5.0	4.6	4.6	5.4	4.7	4.5

[a] E = exothermicity of the process: $M^{++}(g) + 2e \rightarrow M(g)$. [b] All values are from Landolt–Börnstein, "Atom- und Molekularphysik," and are given in electron-volts. Values in parentheses are of uncertain accuracy.

sociated with high electron affinities, also appears to be applicable to metallic catalysts and provides at least a partial explanation for this link. Thus it may be seen from Table III that the electron affinities (measured by the work-functions) of metals follow a pattern somewhat similar to that of the "isoelectronic" ions, the maximum in each period occurring just prior to the filling of the d-band and being associated with the d^{10} groups of metals (Ni, Pd, and Pt) which generally exhibit the most pronounced catalytic activity.

Attention should also be drawn to the very close link between the well-recognized poisoning of metallic catalysts by adsorption of electron-donating substances such as sulfur compounds[22] and the examples in Table I of "poisoning" of metal ion catalysts through complexing.

Bi-functional Catalysts.—Most of the catalysts which have been found to activate hydrogen homogeneously can be regarded as "bi-functional," *i.e.*, their action involves two essential functional groups. In those catalysts which split hydrogen homolytically, both of these are usually metal atoms or ions. On the other hand, the catalysts which split hydrogen heterolytically are usually comprised of a metal ion and a base which exert concerted action on the molecule during the activation process, splitting it by a "push–pull" mechanism. In such cases the two functional groups contribute, to some degree independently, to determining the activity of the catalyst. Thus the Cu^{++} ion, a good electron and hydride acceptor, activates hydrogen even when coupled with a relatively weak base such as water. At the other extreme, a very strong base such as OH^- or NH_2^-, appears to be able to activate hydrogen even in the absence of a metal ion, the role of the hydride acceptor being assumed by an H_2O or NH_3 molecule.[23] However, greatly enhanced activity can be achieved with a catalyst such as cupric acetate, in which a metal ion possessing good electron- and hydride-accepting properties is coupled with a relatively strong base. This emphasizes a very im-

portant general principle in catalysis, with wide applications both in the understanding of catalytic phenomena and in the preparation of more powerful and selective catalysts.

It appears, however, that this principle cannot be exploited very effectively in relatively simple species, such as ordinary metal complexes. Thus metal ions such as Cu^{++} and Hg^{++} in aqueous solution cannot be coupled, simply by complexing, with very strong bases either because (as in the case of OH^-) of solubility restrictions, or because catalytic activity is destroyed by metal–ligand interaction. To be effective, the two functional groups must be so disposed that they can interact simultaneously with a hydrogen molecule, but at the same time are prevented from interacting with (neutralizing) each other. This involves anchoring the groups to some "rigid" framework such as a surface or a suitable molecule.

An interesting model system of this type, in which 2-hydroxypyridine acts as a bifunctional catalyst for the mutarotation of tetramethylglucose has been described by Swain and Brown.[24] This principle also appears to have wide applicability to enzymes, including the hydrogen-activating enzyme *hydrogenase*,[25] and has been invoked to account for the pH-dependence of enzyme activity and for the high catalytic activity and specificity of enzymes relative to ordinary catalysts.[26,27]

DISCUSSION

R. G. Pearson.—What is your explanation for the nonreactivity of Ni^{++} as compared to Pd^{++}? Could electronegativity differences account for the difference in this case and in that of Hg^{++} compared to Cd^{++} and Zn^{++}?

J. Halpern.—Qualitatively, these differences appear to conform to the pattern of electron affinities in Table III, *i.e.*, Pd^{++} and Hg^{++} have higher electron affinities than Ni^{++} and Cd^{++} (or Zn^{++}), respectively. However, a

(22) E. B. Maxted, *Advances in Catalysis*, **3**, 129 (1951).

(23) W. K. Wilmarth, J. C. Dayton and J. M. Flournoy, *J. Am. Chem. Soc.*, **75**, 4549 (1953); W. K. Wilmarth and J. C. Dayton, *ibid.*, **75**, 4553 (1953).

(24) C. G. Swain and J. F. Brown, Jr., *J. Am. Chem. Soc.*, **74**, 2538 (1952).

(25) D. Rittenberg, *Proc. Int. Conf. Enzyme Chem.*, Tokyo, 1957.

(26) K. J. Laidler, *Disc. Faraday Soc.*, **20**, 83 (1955); "Introduction to the Chemistry of the Enzymes," McGraw–Hill Book Co., Inc., New York, N. Y., 1954, pp. 17, 154.

(27) J. B. Wilson, in "The Mechanism of Enzyme Action," W. D. McElroy and B. Glass, eds., John Hopkins Press, Baltimore, Md., 1954, p. 642; *Disc. Faraday Soc.*, **20**, 119 (1955).

quantitative account of differences in reactivity in terms of this or any other single parameter, is unlikely.

R. L. BOHON.—Does the change in catalytic activity due to ligand variation result from change in the activation energy alone, or does the entropy term also vary?

J. HALPERN.—In aqueous solution the activation energies for the reactions of Cu^{-+} and $CuAc_2$ with H_2 are 26.6 and 24.2 kcal., respectively; the corresponding entropies of activation are -10 and -7 e.u. The 120-fold increase in activity is thus reflected predominantly in the activation energy. This appears to be the case also for other ligand and solvent effects.

H. FREISER.—Can the enhancement of the activity of $Hg(en)_2^{++}$ by OH^- be explained by a mechanism involving direct stabilization of the proton by OH^-, e.g., $(en)_2Hg^{++}\ldots$ $H\ldots.H\ldots.OH^- \rightarrow (en)_2HgH^+ + HOH$? Furthermore, can the effect of CO_3^- be attributed simply to the accompanying pH increase?

J. HALPERN.—A mechanism of this type seems plausible and could arise through an ion-pair complex, $Hg(en)^{++}.X^-$, of the type considered. The effect of CO_3^- is much larger than would be expected simply from the accompanying increase in OH^- and must involve CO_3^- explicitly.

H. B. JONASSEN.—Do any of the copper(II) carboxylates give rise to dimeric species?

J. HALPERN.—This does not occur in aqueous solution but is probably appreciable in some of the non-polar solvents that have been used. However, even in these systems there is no suggestion of a link between dimer formation and catalytic activity. In the case of copper(I) heptanoate it appears that the dimer which forms in non-polar solvents is catalytically inactive while the monomer is active.

R. E. MEEKER.—What is the order of reactivity of cupric dicarboxylate complexes?

J. HALPERN.—The maleate complex is about 30 times as reactive, and the succinate and fumarate complexes about 60 times as reactive, as the uncomplexed cupric ion.

D. W. MARGERUM.—Is there any chelate effect observed in the catalytic activity of the complex ions? For example, would $Cu(NH_4)_4^{++}$ behave much differently from $Cu(en)_2^{++}$.

J. HALPERN.—We have no data for $Cu(NH_3)_4^{++}$. However, a chelate effect may be reflected in our observations that the activities of the cupric succinate and maleate complexes, which may have chelate structures, are only about half those of the acetate and fumarate, respectively.

CATALYTIC ACTIVATION OF MOLECULAR HYDROGEN BY COBALT CYANIDE SOLUTIONS

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Aqueous potassium cobaltous(II) cyanide solutions were investigated by studying their reduction, D_2–H_2O exchange, paramagnetic properties and ultraviolet absorption. For freshly prepared solutions of a few tenths molar at 0–25° and one atmosphere hydrogen pressure, reduction to cobalt^I cyanide occurs rapidly (e.g., $\tau_{1/2} = 1$ minute). On standing the Co^I solutions become progressively less reducible, largely losing reducibility within a period of an hour. Fresh solutions have a paramagnetism which corresponds to one electron for each Co^{II} ion, but they lose this paramagnetism at a rate paralleling loss of reducibility. This "aging" process is believed due to dimerization. Reduced solutions (Co^I) and aged, non-reducible Co^{II} solutions both catalyze D_2–H_2O exchange. Exchange is relatively rapid, although slower than reduction. The kinetics of both reduction and exchange show a large primary salt effect. Species such as $Co(CN)_5^{3-}$ are believed capable of activating hydrogen by reactions (c). Probably other cobalt species are also capable of activating hydrogen in this complex system.

Introduction

The powerful influence of coördination on cobalt chemistry has long been famous. For instance, trivalent cobalt ion is one of the strongest oxidizing agents known. It decomposes water with liberation of oxygen and formation of divalent cobaltous ion. However, when ligands such as cyanide ion are present which form covalent bonds, such coordination so stabilizes trivalent cobalt that now cobaltous ion attacks water with liberation of hydrogen. When an oxidizing agent more suitable than water is present, it is reduced by the cobaltous cyanide solution. Molecular oxygen, for example, is reduced by cobalt cyanide solutions to form hydrogen peroxide.

Cobaltous cyanide solutions have other interesting properties. When prepared in basic solution, for example by adding KCN to $CoCl_2$ so that the precipitate of $Co(CN)_2$ is redissolved at CN/Co of $\gtrless 5$, these solutions are relatively stable and liberate H_2 very slowly. As Iguchi[1] discovered, when potassium cobaltous cyanide solutions are exposed to an atmosphere of H_2, they are reducible, absorbing an amount of hydrogen corresponding to the

reduction of $Co^{II} \rightarrow Co^I$. Winfield has studied this system recently[2,3] seeking to determine the species activating H_2 particularly when solid cobalt cyanide is present. Simultaneously we have been investigating the homogeneous solution.[4]

Our investigation was inspired by the report[5] that when an acidified potassium cobaltous cyanide solution liberated H_2 in the presence of D_2, there was observed formation of HD. Ogg considered that HD formation was due to presence of atomic hydrogen and that cobalt species were not active catalytically.

One previous paper by Farkas and Farkas[6] had shown that the hydrogen liberated from water possessed an equilibrium amount of deuterium.

Recent attempts to interpret the catalytic properties of transition metals have placed an increasing

(1) M. Iguchi, *J. Chem. Soc. (Japan)*, **63**, 634 (1942).

(2) J. Bayston, N. K. King and M. E. Winfield, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1957, p. 312.
(3) M. E. Winfield, *Rev. Pure. Appl. Chem. (Australia)*, **5**, 217 (1955).
(4) G. A. Mills, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1957, p. 376.
(5) R. A. Ogg, Jr., Abstracts 123rd Meeting of Am. Chem. Soc. Los Angeles, 1953, p. 24-P.
(6) A. Farkas and L. Farkas, *J. Chem. Phys.*, **2**, 468 (1934).

emphasis on the electronic structure of individual metal ions in the surface. Theoretical and practical problems associated with investigation of solid surfaces have led us to study solutions of metal ion complexes, with the expectation that general principles will be obtained which apply to heterogeneous as well as homogeneous catalysis.[7,8] Our experiments on potassium cobaltous cyanide solutions have included (1) measurements of kinetics of reduction of Co[II] cyanide solutions, (2) measurement of exchange between D_2 and aqueous cobalt cyanide, (3) paramagnetic measurement of solutions and (4) spectral determinations as a function of solution concentrations, temperature and time of solution aging. This last variable, namely, time after solution preparation, has been occasioned by the discovery that there is an interesting aging process for freshly prepared solutions. When 0.1–0.4 M cobaltous cyanide solutions are reduced to Co[I] by molecular hydrogen, the reaction is very rapid, with a half time of the order of one minute at 25°. However, these solutions progressively become less reducible and after one-half to two hours at this temperature, they can absorb only very little hydrogen. On the other hand, they are still able to *activate* hydrogen as shown by their ability to catalyze D_2–H_2O exchange. Winfield, working only at low temperatures and concentrations, has not reported such an aging process.

Experimental

In almost all instances the cobalt solutions were 0.1 to 0.4 molar. They were made freshly from cobalt chloride by adding an appropriate amount of KCN solution. In most instances the CN/Co ratio was either 5 or 6. Clear solutions were used in all experiments, the initial precipitate being dissolved readily at CN/Co of 5.

The hydrogen absorption apparatus was similar to that previously described,[9] except that a high speed stirring apparatus, rather than a shaking apparatus, was used to obtain better liquid–gas contact. Stirring was accomplished with a Lew magnetic stirrer equipped with a Teflon paddle; the stirring speed was normally 1300–1400 r.p.m. Even with this device, however, the absorption of hydrogen under some conditions was so rapid (*e.g.*, $\tau^{1/2} < 1$ minute) as to be diffusion limited. One of the ground joints of the 300 ml., three neck reaction flask was fitted with a small, bent tube. Cobalt chloride solution of the desired amount and concentration was placed in this tube; 40–100 ml. of potassium cyanide solution was placed in the reaction flask. After the reagents were in place, the flask was evacuated; by rotating the bent tube through 180° the cobalt chloride solution was then dumped into the flask, either under vacuum or in the presence of hydrogen at atmospheric pressure. Hydrogen uptake was followed on a gas buret kept at constant pressure of one atmosphere.

The deuterium–water exchange experiments were carried out with the same apparatus. Pure deuterium was introduced into the evacuated flask to a pressure of one atmosphere. Small gas samples were taken at intervals during the run by means of a special "dip tube," which extended into the middle of the gas space in the flask. The gas samples were led through a drying tube containing Drierite and analyzed for deuterium content by a thermal conductivity gauge, or, in some cases, by mass spectrometer. The decrease in atom per cent. deuterium of the gas phase was taken as the measure of extent of reaction.

In order to minimize diffusional limitations during the hydrogen uptake experiments and some of the faster exchange experiments, the extent of gas–liquid interface was

(7) S. W. Weller and G. A. Mills, "Advances in Catalysis," Vol. VIII, Academic Press, Inc., New York, N. Y., 1956, p. 163.

(8) J. Halpern, *Quart. Rev.*, **10**, 463 (1956).

(9) S. Weller and G. A. Mills, *J. Am. Chem. Soc.*, **75**, 769 (1953).

increased by adding a foaming agent. Du Pont BCO was very effective for this purpose.

Magnetic susceptibility measurements were made with a Gouy balance having a permanent magnet of 1960 gauss field strength and a semi-micro balance of 0.01 mg. sensitivity. A sample tube, divided in the center and with end openings covered by rubber serum bottle caps, was used to permit differential measurements. The solutions of cobalt cyanide complex were made up under nitrogen, and they were transferred to the top portion of the sample tube without exposure to air by the use of a specially modified hypodermic syringe. Measurements were made only at 25°. The apparatus was calibrated with solutions of nickel chloride and ferrous ammonium sulfate. Molar susceptibilities were obtained by the equation

$$\gamma_M = 214 \times 10^{-6} \frac{\Delta W \text{ (mg.)}}{M \text{ (moles/l.)}}$$

where Δw is the apparent weight change when the magnetic field is applied, and effective magnetic moments were calculated by the equation

$$\mu_{eff} = 2.83 \sqrt{\chi_M T}$$

Results

Reduction of Cobaltous Solutions.—The rate and amount of deuterium absorbed at 25° by freshly prepared solutions of potassium cobaltous cyanide are shown in Fig. 1 and Table I. The reaction is very rapid at 25° and absorption is completed in about two minutes. The deuterium absorbed corresponds to about three-fourths of that calculated to reduce the cobalt present from the divalent to the monovalent state. If the experiments are conducted at 0° and with 2 N NaOH present, the amount of sorption corresponds to 90% of theoretical (Table I). The last column of Table I shows the half-time for deuterium–water exchange by these solutions after the absorption is completed. These results are discussed in the next section.

TABLE I

EFFECT OF COBALT CONCENTRATION ON DEUTERIUM ABSORPTION AND EXCHANGE

(6:1 CN$^-$/Co^{++}, fresh solutions, 40 ml. liquid)

Temp., °C.	NaOH concn., M	Co, mmoles	D₂ absorbed, mmoles Theor.	Obsd.	$\tau^{1/2}$ for exchange, min.
25	0	4	2	1.52	~1000
		8	4	3.31	69
		12	6	4.62	24
		16	8	5.41	7.7
0	2	4	2	1.88	310
		6	3	2.79	104
		12	6	5.55	21

The amount of absorption is decreased if the potassium cobaltous cyanide solution is allowed to stand *in vacuo* before reduction is begun. The results are shown in Table II and Fig. 2. Evidently even when "fresh" solutions are used there is sufficient aging to bring about less than stoichiometric reduction, as is evident in the experiments quoted above. Change of reducibility of solutions was measured after aging various lengths of time. After 60 minutes at 0° the solution absorbed an amount of hydrogen corresponding to only 60% of theoretical, while at 25° after the same time only 30% of theoretical was observed, Table II and Fig. 2.

In these experiments, carried out at a cobalt concentration of 0.2 M, there was no evidence of

TABLE II

EFFECT OF AGING TIME ON HYDROGEN ABSORPTION

(5:1 CN$^-$/Co^{++}, 40 ml. liquid, 8 millimoles Co)

Aging temp., °C.	Aging time, min.	Temp. of H$_2$ abs., °C.	H$_2$ absorbed, mmoles
0	0	0	3.52
0	10	0	3.23
0	20	0	2.93
0	60	0	2.49
25	0	25	2.93
25	10	25	2.56
25	20	25	1.81
25	60	25	1.23

hydrogen evolution even after one hour of standing *in vacuo* at 25°. At a cobalt concentration of 0.4 *M*, however, there is a slow evolution of hydrogen at 25°.

The aging phenomenon is affected by the chemical composition of the solution, for example by the OH$^-$ concentration, but the rate of loss of reducibility will not be developed here on a quantitative basis.

We have not observed any ability to absorb hydrogen by solutions of Co^{III} cyanide complexes, whether freshly prepared or not. Such solutions appear to be inactive for catalyzing deuterium–water exchange.

Deuterium Exchange.—The rate of reduction by deuterium is about equal to that experienced with hydrogen. However, when the Co(II) solution is reduced with deuterium, the rapid reduction is followed by a much slower exchange reaction between D$_2$(g) and H$_2$O(l). The reduction is essentially complete in less than five minutes, even at 0°. By contrast, the "half-times" ($\tau_{1/2}$) for exchange are frequently many times greater. Typical values shown in the last column of Table I, vary from several minutes to many hours, depending on conditions. Figure 3 illustrates the comparison of absorption and exchange rates for a run at 0° with 0.15 *N* cobalt. The half-time for exchange exceeded that for absorption by several hundred-fold.

The effect of aging (prior to reduction) on the exchange rate also was studied. Table III contains the results of several comparisons of exchange activity, expressed as $\tau_{1/2}$, between an unaged solution and a solution aged one hour prior to reduction. Aging, when done, was carried out at 25°. D$_2$ absorption and D$_2$–H$_2$O exchange were at 25 or 0°, as indicated in Table III. The first pair of runs in the table, for solutions containing no added alkali, shows that the aged solution was as active for exchange at 25° as was the unaged solution. At 0° the same result was obtained (second pair of runs), although the slow rates make the results less accurate. The addition of NaOH to the 2 *N* level increased greatly the exchange rates at 0° for both aged and unaged solutions (*e.g.*, 55 *vs.* 350 min., and 220 *vs.* 350 min. for $\tau_{1/2}$). In this case, however, the effect was greater for the unaged solution, which was four times as active as the aged solution (55 *vs.* 220 min. for $\tau_{1/2}$).

Even in the case of no added alkali, the exchange rate does fall off somewhat with long aging times. In one experiment at 25° (0.1 *M* Co, CN/Co = 6), the exchange rate after the solution had been un-
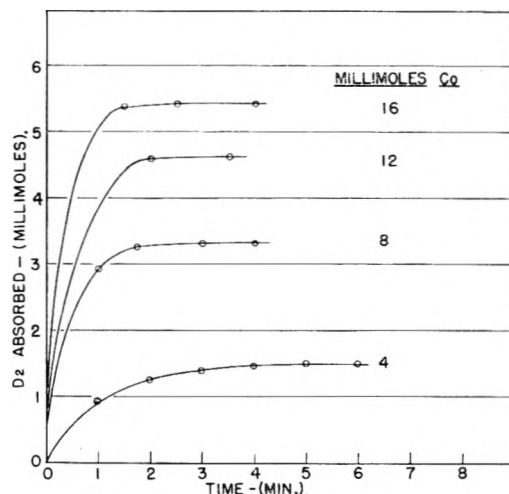
Fig. 1.—Absorption of D$_2$ at 25° by fresh potassium cobaltous cyanide solutions.
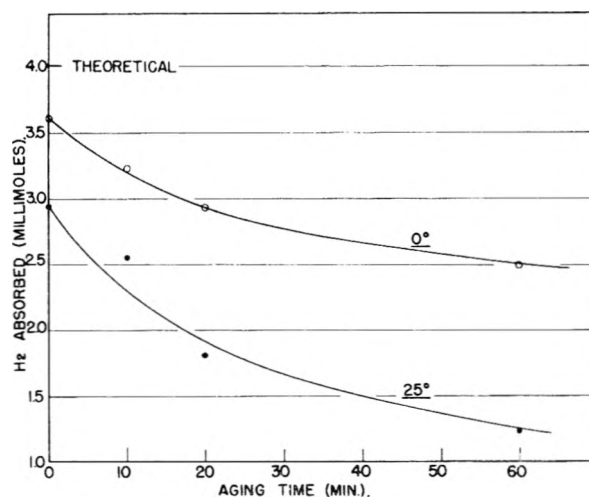
Fig. 2.—Effect of aging time on hydrogen absorption (8 millimoles Co, CN/Co = 5, 40 ml. solution).

TABLE III

EFFECT OF AGING ON EXCHANGE ACTIVITY

(8 millimoles Co, CN/Co = 6, 40 ml. solution)

NaOH concn., *M*	Aging time at 25°, min.	D$_2$ Absorption T, °C.	Mmoles	D$_2$–H$_2$O Exchange T, °C.	$\tau_{1/2}$, min.
0	0	25	3.27	25	69
0	60	25	0.65	25	69
0	0	0	3.51	0	~350
0	60	25	1.31	0	~350
2	0	0	3.84	0	55
2	60	25	0.41	0	220

der vacuum for 3 hours was 85% of that of the unaged solution, and after 16 hours of aging the rate had decreased to 60% of the unaged value.

Of particular interest is the influence of added alkali on the isotopic distribution in the gas phase during deuterium–water exchange. The effect is shown in Table IV for exchange experiments at 0 and 25°; the gas samples were analyzed by mass spectrometer. Addition of alkali results not only in an increased rate but also in an increase of the H$_2$/HD ratio. Comparison of the second and third experiments in Table IV (0°, 2 *M* NaOH *vs.*
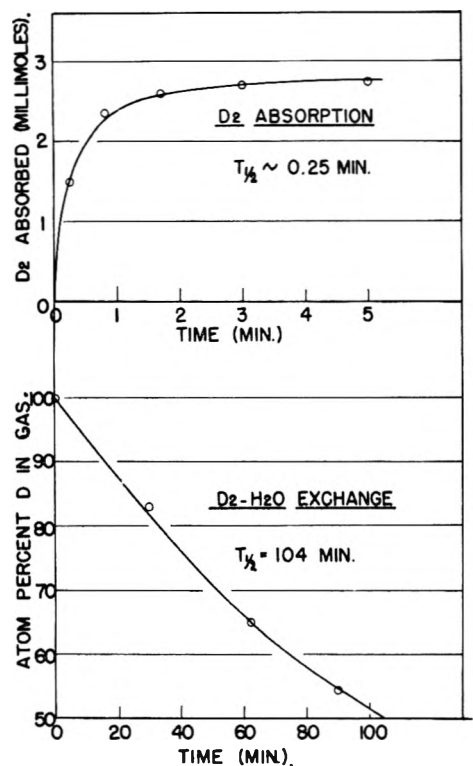
Fig. 3.—Comparison of D_2 absorption and D_2–H_2O exchange; 40 ml. solution, CN^-/Co^{++} = 6, 6 millimoles Co^{++}, 2 N NaOH, 0°.

25°, no NaOH) gives the striking result that even when the over-all exchange rates are comparable in magnitude, the sample with alkali shows a much higher H_2/HD ratio.

TABLE IV
EFFECT OF ALKALI ON ISOTOPE DISTRIBUTION DURING EXCHANGE
(8 millimoles Co. $\overset{.}{C}N/Co$ = 6, 40 ml. solution, no aging)

NaOH concn., M	Exch. T, °C.	Sample taken after, min.	D₂ Vol. %	HD Vol. %	H₂ Vol. %
0	0	80	77.2	13.7	9.1
2	0	67	43.5	2.4	54.1
0	25	60	44.2	31.5	24.3
2	25	60	5.8	0.7	93.5

Salt Effect in Reduction and Exchange.—Determination of the rate law is an important aid in establishing the identity of the species reacting in the rate-determining step. It was desirable, therefore, to find the dependence of the reduction and exchange rates on the cobalt concentration. Iguchi[1] had already shown, however, that at fixed cobalt concentration the reduction rate was greatly increased by the addition of KOH or of KCl. He observed, for example, that addition of KCl to the level of M/3 increased the initial rate of hydrogen absorption (i.e., uptake in first five minutes) by a factor of almost three.

We have confirmed and extended Iguchi's results on hydrogen absorption, and, in addition, we have found a salt effect of comparable magnitude in the deuterium–water exchange reaction. The data for hydrogen absorption at 25° (by fresh solutions) are given in Table V and for exchange at 25°

TABLE V
SALT EFFECT FOR HYDROGEN ABSORPTION, 25°

CoCl₂	KCN	Compd.	Concn.	μ[a]	k, min.⁻¹
0.0261	0.157			0.235	0.20
.0261	.159			.235	.20
.0261	.148			.226	.16
.0261	.261			.339	.32
.0522	.313			.469	.83
.0174	.104			.157	.11
.0783	.470			.704	1.43
.0261	.470			.548	0.71
.0131	.470			.508	.56
.0131	.261			.300	.18
.0131	.157			.196	.10
.0522	.470			.626	1.00
.0131	.348			.387	0.33
.0348	.348	NaOH	0.696	.800	1.11
.0348	.348			.452	.63
.0348	.348			.452	.63
.0522	1.044			1.200	2.00
.0348	0.348	KCl	.870	1.321	1.67
.0261	0.157	KCl	.870	1.105	1.67
.0261	1.028			1.105	1.67
.0522	0.313	KCl	.609	1.079	1.67
.0261	.157	Na₂SO₄	.287	1.096	0.53
.0261	.157	BaCl₂	.287	1.096	1.43

^{a} $\mu \equiv \frac{1}{2}\{6[Co] + [CN] + [K] + \sum\limits_{\substack{added \\ ions}} C_i Z_i^2\}$.

TABLE VI
SALT EFFECT FOR DEUTERIUM–WATER EXCHANGE, 25°

CoCl₂	KCN	Compd.	Concn.	μ[a]	k,[b] min.⁻¹
0.100	0.600			0.80	0.007
.200	1.200			1.60	.098
.300	1.800			2.40	.278
.091	0.546	KCl	0.91	1.64	.046
.091	.546	KCl	1.82	2.55	.322
.091	.546	KCl	0.45	1.18	.031
.091	.546			0.73	.015
.200	1.200	NaOH	2.00	3.60	.322
.300	1.800	NaOH	2.00	4.40	.500

^{a} $\mu \equiv \frac{1}{2}\{6[Co] + [CN] + [K] + \sum\limits_{\substack{added \\ ions}} C_i Z_i\}$. ^{b} The gas: liquid ratio was varied in some of these experiments. To make all the results comparable, the observed values of k were multiplied by V_{gas}/V_{liquid}, i. e., $k = k_{obs}(V_{gas}/V_{liquid})$.

(by reduced, fresh solutions) in Table VI. In these tables the ionic strength, μ, was calculated on the assumption that all the cobalt was present as a trivalent, pentacyano complex.[10] Although this is probably true for the fresh solutions of cobalt(II), it probably is not the case for reduced solutions, and for these the tabulated values of μ probably deviate from the true ionic strength. In any single run, both the reduction and the exchange reactions behaved as first-order reactions. Therefore, the reaction rates were expressed in terms of the apparent first-order rate constant, k, given in the final column of Tables V and VI. For both reactions the first-order rate constant increases as the cobalt concentration is increased. However, to a first approximation the same increase is obtained if the

(10) A. W. Adamson, ibid., **73**, 5710 (1951).

Fig. 4.—Salt effect for hydrogen absorption, 25°.
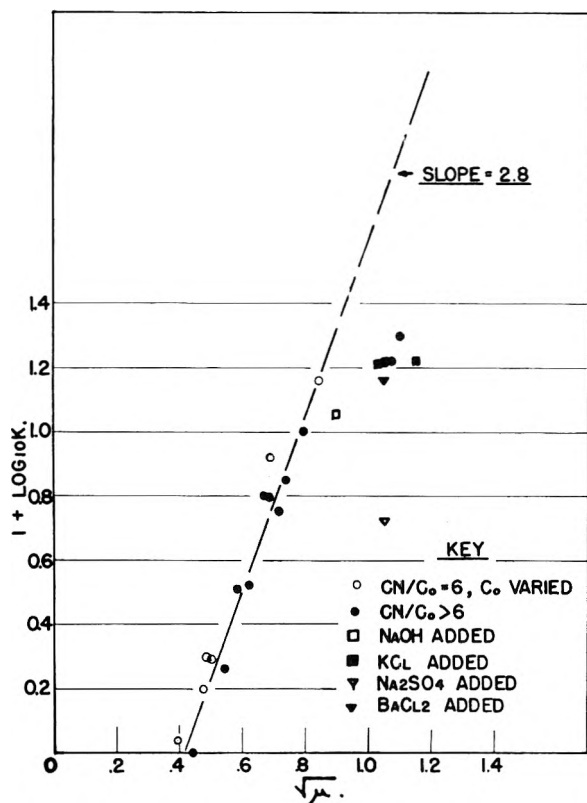
Fig. 5.—Salt effect for deuterium–water exchange, 25°.

cobalt concentration is held constant and a salt such as KCl is added to give the same ionic strength. This is brought out in Figs. 4 and 5, in which log k is plotted against $\sqrt{\mu}$ for the two reactions. For the hydrogen absorption, $CoCl_2$, KCN, NaOH, KCl and $BaCl_2$ are of approximately equal effectiveness if compared at the same ionic strength; Na_2SO_4 is less effective. Although fewer, and more scattered, data are available for the exchange reaction, here also change of cobalt concentration is no more significant than change of, say, KCl concentration for the same ionic strength. It may be noted in Figs. 4 and 5 that although the relationship between log k and $\sqrt{\mu}$ is not linear, the data can be fitted by a straight line over much of the range studied.

Magnetic Measurements.—Measurements of magnetic susceptibility were made, at a fixed CN/Co ratio of 6, as a function of (a) time of standing after preparation of the cyanide complex, (b) cobalt concentration from 0.02 to 0.4 M, and (c) pre-reduction by hydrogen.

The susceptibilities of solutions 0.02 and 0.05 M in cobalt did not change in a few hours of standing under nitrogen. Solutions of concentration 0.1 M, or higher, however, showed a rapid decrease in susceptibility on standing. The drop in susceptibility, as measured by the apparent weight change (Δw) when the field is applied, is illustrated in Fig. 6 for 0.1 and 0.2 M solutions. This "magnetic aging" closely parallels the loss in ability to absorb hydrogen with increased standing time. In the case of the 0.1 M solution, the extrapolated value for zero time of standing corresponds, within considerable limits of error, to the susceptibility expected for one unpaired electron per Co ($\Delta w = 0.59$ mg. $\approx \chi_M = 1260 \times 10^{-6}$), in agreement with Adamson's result.[10] Solid $K_3Co(CN)_5$, by contrast, is diamagnetic.[10] Solutions 0.4 M in Co aged even more rapidly; the molar susceptibility after 10 minutes standing time was less than 10% of the theoretical value for one unpaired electron.
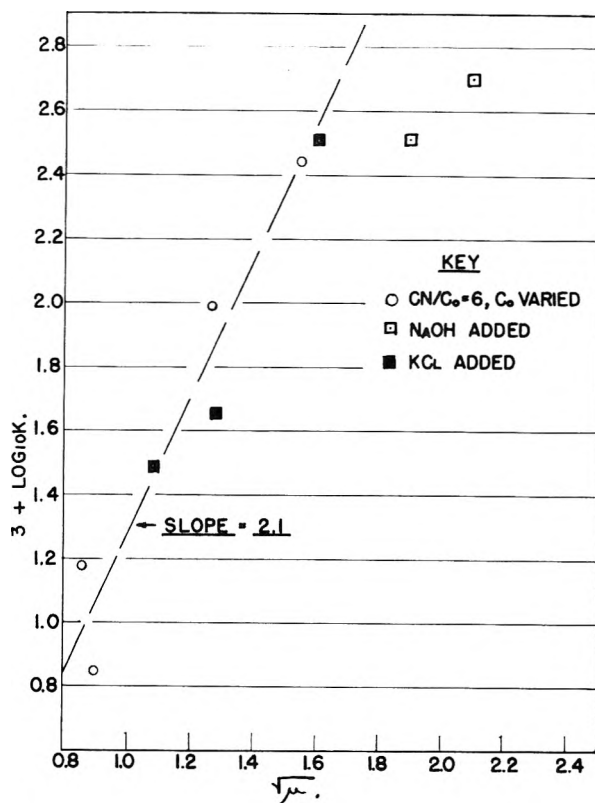
As Fig. 6 indicates, the magnetic susceptibility for the more concentrated solutions appeared to approach a limiting low value after several hours. The effective magnetic moments calculated from these limiting values, and designated as "equilibrium" moments, are shown in Table VII as a function of cobalt concentration. Within experimental error the values for the 0.02 and 0.05 M solutions correspond to that expected for one unpaired electron per cobalt (1.73 Bohr magnetons), while the "equilibrium" moments for high concentrations correspond to only about 0.05 unpaired electron per cobalt.

TABLE VII

"EQUILIBRIUM" MAGNETIC MOMENTS OF UNREDUCED AND REDUCED SOLUTIONS

Co concn., M	Aging time, hr.	"Equil." μ_{eff}	H_2 abs., % of theor.	μ_{eff}
0.02	1	1.82		
.05	1	1.62		
.1	6	0.90	82	0.85
.2	3	.58	84	0.60
.4	2	.28	44	0.39

The effective moments also were determined for solutions which were reduced in hydrogen at 25° prior to measurement. These moments, which did *not* change with time of standing, are also shown in
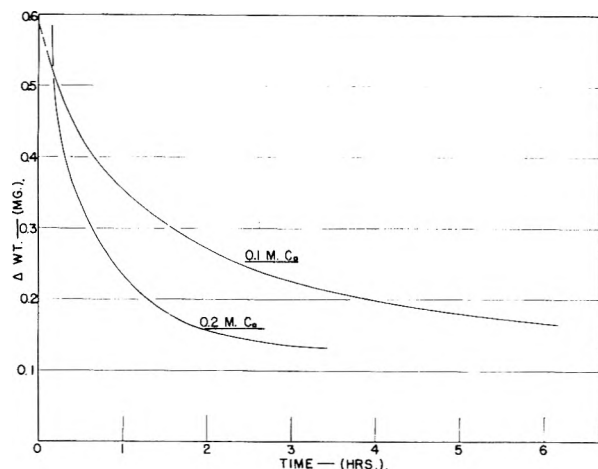
Fig. 6.—Magnetic aging of cobalt(II) cyanide complexes, 25°.

Table VII. Included in Table VII are the amounts of hydrogen absorbed during the pre-reductions, expressed as per cent. of the amount needed for stoichiometric reduction, assuming one hydrogen molecule reduces two cobalt ions. It is clear that the reduced solutions have low effective moments, generally comparable with those of the aged, unreduced solutions.

Absorption Spectra.—The ultraviolet and visible spectra of solutions were surveyed under various conditions, particularly with respect to changes during the aging process.[11] First, in agreement with the results of Smith, Kleinberg and Griswold,[11a] all solutions of Co^{III} examined were found to have an absorption peak at about 380 mμ. By contrast, fresh Co^{II} cyanide solutions and reduced fresh solutions (Co^I) are relatively transparent in this region. Moreover, aged Co^{II} solutions are even more transparent here than the fresh solutions. This implies that the aging process does not involve the disproportionation 2Co^{II} → Co^I — Co^{III}, unless the Co^{III} species so formed is one, as yet unknown, that does not absorb at 380 mμ.

Discussion

One of the most remarkable features of the reduction process is the rapidity with which it occurs. The rate is so great at high ionic strength that even with high-speed stirring, mass transfer of hydrogen from the gas to the solution probably is somewhat limiting. This is the most active homogeneous system so far reported for the catalysis of molecular hydrogen.

The exchange reactions offer remarkable evidence for the catalytic properties of potassium cobalt cyanide solutions, even when activity is not observed by reduction experiments. It is noteworthy that both reduced (Co^I) and aged Co^{II} solutions show catalytic exchange and, in some cases at least, equal activity to bring about exchange.

(11) L. C. Smith J. Kleinberg and E. Griswold, *ibid.*, **75**, 449 (1953).

(11a) A more detailed study of the spectra was carried out by Prof. Milton Wadsworth in the Houdry Laboratories. This study confirmed that the chemical system is very complex and that the rate of the aging process depends on the presence of added ions such as OH$^-$ or CN$^-$. It is hoped to complete this study and present these results at a later date.

While exchange is slower than reduction, it is still relatively rapid, and the homogeneous cobalt system offers interesting D$_2$–H$_2$O exchange possibilities.

The effect of alkali on the isotope distribution during exchange (Table IV) may be understood in terms of the relative rates of exchange and gas–liquid equilibration. Kloosterziel, *et al.*,[12] have discussed the dependence of hydrogen isotope exchange of hydrocarbons upon the relative rates of exchange and desorption. If the isotope effect on rates is ignored, the exchange reaction may be represented by the simplified scheme

$$\begin{array}{ccc} D_2(g) & HD(g) & H_2(g) \\ k_1 \downarrow \uparrow k_1^1 & k_1 \downarrow \uparrow k_1^1 & k_1 \downarrow \uparrow k_1^1 \\ [Co \cdot D_2] \xrightarrow[k_2]{H_2O} & [Co \cdot HD] \xrightarrow[k_2]{H_2O} & [Co \cdot H_2] \end{array}$$
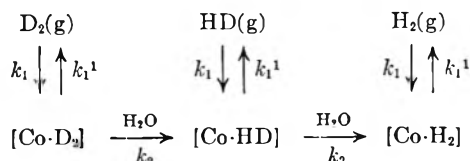
where [Co·D$_2$], for example, represents whatever complex is formed in solution between deuterium and the active cobalt species. The reverse exchange reaction may be neglected because of the large excess of water. For this reason, if the rate at which the "activated" deuterium exchanges with water is very fast compared with the rate at which the complex is formed and is dissociated (*i.e.*, $k_2 \gg k_1, k_1^1$), most of the exchanged product will appear in the gas phase as H$_2$; this is the case with added alkali. In the absence of alkali the exchange rate is lower than with alkali, and the rates of formation–dissociation and of exchange with water are more nearly comparable. It is not known whether salts such as KCl also cause a similar change in isomer distribution, since these experiments were carried out by the thermal conductivity method.

The existence of a major salt effect is surprising, since work on other homogeneous systems which activate hydrogen indicated that the slow step there involved molecular hydrogen (a neutral molecule) as a reactant. The magnitude of the salt effect is great; addition of 2 N KCl, for example, can increase the rate of the exchange reaction by more than twenty-fold. Iguchi's results on hydrogen absorption imply a somewhat smaller salt effect than we observed. However, it is probable that his absorption rates are partially mass-transfer-limited, particularly at higher ionic strengths.

The fact that so many anions (OH$^-$, CN$^-$, Cl$^-$) have about the same effect on rate makes it unlikely that the salt effect is caused by a change in composition of the cobalt complex ion, *e.g.*, by a shift from a pentacyano ion to, say, a mixed cyanochloro one which might be more active. If composition changes are ruled out, however, it becomes necessary to interpret the observed salt effect in terms of the theories normally advanced for such cases.[13] According to theory, an effect of this magnitude implies that at least two of the species reacting in the rate-determining step are

(12) G. Dallinga, H. Kloosterziel and H. Bolder "Characteristics of Hydrogen Isotope Exchange Reactions of Hydrocarbons," Abstracts 133rd Meeting of A.C.S., San Francisco, Cal., 1958, p. 13-I.

(13) E. S. Amis, "Kinetics of Chemical Change in Solution," Chaps. IV and VIII, The Macmillan Co., New York, N. Y., 1949.

ionic; the fact that the rate increases with increasing salt concentration implies that these ions are of the same sign. The equation normally used for a primary salt effect in a reaction between two ions of charge Z_1 and Z_2 is

$$\log k/k_0 = 1.0 Z_1 Z_2 \sqrt{\mu} \qquad (1)$$

where k_0 is the rate constant at infinite dilution. The dotted straight lines shown in Figs. 4 and 5 correspond to values for the product (Z_1Z_2) of 2.8 and 2.1, respectively. Taken at face value, this result implies that the rate-determining step is neither (1) a bimolecular reaction of a cobalt complex ion with molecular hydrogen, since hydrogen is neutral, nor (2) reaction involving two highly-charged cobalt ions, since this would result in high values of (Z_1Z_2). However, a termolecular reaction involving molecular hydrogen and two similarly charged ions would be consistent with the observed salt effect. Actually, the high ionic strengths studied and the complexity of the cobalt species make it very difficult to draw quantitative conclusions on the basis of the simple theory of salt effects. It may be recalled that the inversion of sucrose, which also involves reaction of an ion with an uncharged molecule, shows a large salt effect.[14,15] It is clear, in any case, that any attempt to establish the dependence of the rate on cobalt concentration must take the salt effect into consideration; otherwise the apparent order of the reaction will be erroneously high.

As mentioned earlier, lack of complete correspondence between H_2 uptake and $Co^{II} \to Co^I$ stoichiometry seems due to the aging process, whereby loss of reducibility is experienced. Indeed, this aging process is one of the most significant phenomena investigated. In addition to the data given above, certain other observations were noted. For instance, at low Co^{II} concentration when aging at or below 25° no gas evolution occurred. Also, the amount of oxygen absorbed at 25° is the same for fresh solution as for a solution aged one hour. Furthermore, titration with potassium ferricyanide (which converts Co^{II} to Co^{III}) is the same after one hour aging under nitrogen as for fresh solution. These experiments show that the aging does not consist of the reaction of $Co^{II} + H_2O \to Co^{III} + \frac{1}{2} H_2 + OH^-$.

In our experiments pH increases somewhat during aging, in agreement with Winfield.[16] However, Winfield[2] did not observe loss of reducibility due, evidently, to the dilute solutions he employed and the low temperature, which so slowed down aging in his experiments that it was not observed.

Hume and Kolthoff[17] have pointed out that thermodynamic values are, unfortunately, not reliably established for cobalt cyanide complexes. One can only speculate, on the basis of their observed behavior, as to the relative stability of the various species. This scheme seems to be internally consistent

(14) C. F. Kautz and A. L. Robinson, *J. Am. Chem. Soc.*, **50**, 1022 (1928).

(15) E. S. Amis and G. Jaffé, *J. Chem. Phys.*, **10**, 598 (1942).

(16) N. Kelso King and M. E. Winfield, *J. Am. Chem. Soc.*, **80**, 2060 (1958).

(17) D. N. Hume and I. M. Kolthoff, *ibid.*, **71**, 867 (1949).
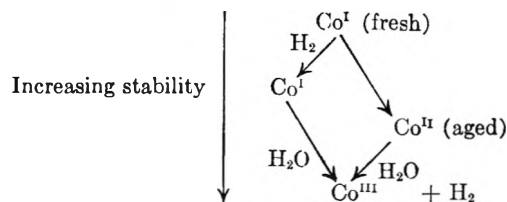
This scheme indicates that Co^{II} (fresh) is unstable toward both reduction and aging. Co^{II} (aged) is not reducible by hydrogen and is therefore indicated as more stable than Co^I. Although Co^I is unstable with respect to oxidation by water to give Co^{III}, it is nevertheless formed, for kinetic reasons, when Co^{II} (fresh) is exposed to hydrogen. Co^{III} is the most stable form.

The electronic structure of the species indicated above as Co^I, Co^{II}, Co^{III} in the following complexes, and their analogs with ligands other than CN^-, are probably the most important to be considered
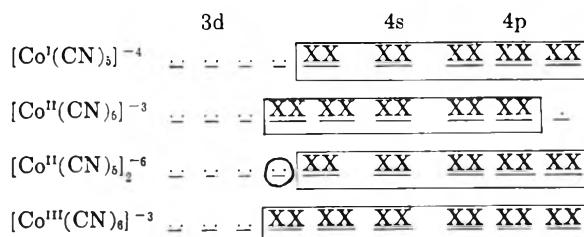
(The boxes represent filled orbitals used in forming covalent bonds with ligands.)

Of these complexes only the monomeric Co^{II} has an unpaired electron and is paramagnetic. The dimeric Co^{II} species, presumably present in solid potassium cobaltous cyanide,[10] is diamagnetic because the odd electrons become paired in the formation of a cobalt–cobalt bond, encircled in the diagram. Although five cyanide ligands are indicated for the Co^I and Co^{II} complexes, it may be noted that no change in magnetism would result either from a different number of cyanide ligands or from substitution of other groups, such as OH^- or Cl^-, which supply electron pairs. The loss of paramagnetism on aging is, therefore, not attributable to a change in number or identity of these ligands. Two possibilities for the "magnetic aging" process are suggested by these considerations

disproportionation $2Co^{II} \longrightarrow Co^I + Co^{III}$ (1)

dimerization $2Co^{II} \longrightarrow (Co^{II})_2$ (2)
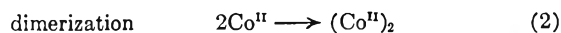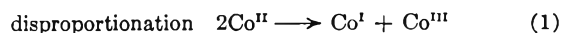
As pointed out above, the spectroscopic evidence indicates that Co^{III} is probably absent in aged solutions. On this basis dimerization is believed to be the more probable reaction. It is interesting to note that Rasmussen and Bjerrum[18] have reported that solutions of certain Co^{III} complex ions undergo an aging process in which polynuclear complexes are formed.

It is instructive to consider the structure of the systems which activate deuterium, namely, cobalt II cyanide, fresh or aged, as well as cobalt^I cyanide. The reaction

(18) S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 735 (1955).

$$2[\text{Co}^{\text{II}}(\text{CN})_5]^{3-} + \text{H}_2 \longrightarrow 2[\text{Co}^{\text{II}}(\text{CN})_5\text{H}]^{3-} \longrightarrow$$
$$2[\text{Co}^{\text{I}}(\text{CN})_5]^{4-} + 2\text{H}^+ \quad (a)$$
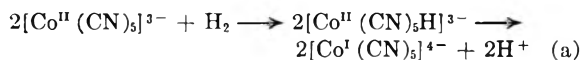
represents a plausible mechanism in which a homolytic scission of the hydrogen occurs. For the aged solution (i.e., Co_2^{II} dimer) a small reversible dissociation would provide for deuterium activation and exchange, with the dimer remaining unreduced because of extra stability gained by Co–Co bond formation. The activity of Co^{I} also might be due to some equilibrium amount of Co^{II} present in the reduced system. This scheme does not, of course, explain the equal exchange activities which may be exhibited by Co^{I} and aged Co^{II} solutions.

Other possibilities exist, for instance

$$[\text{Co}^{\text{II}}(\text{CN})_5]^{3-} + \text{H}_2 \longrightarrow [\text{Co}^{\text{II}}(\text{CN})_5\text{H}_2]^{3-} \quad (b)$$

$$[\text{Co}(\text{CN})_5\text{H}_2]^{3-} + [\text{Co}^{\text{II}}(\text{CN})_5]^{3-} \longrightarrow$$
$$2[\text{Co}^{\text{I}}(\text{CN})_5]^{4-} + 2\text{H}^+$$

$$[\text{Co}^{\text{II}}(\text{CN})_5]^{3-} + \text{H:H} + \text{X}^- \longrightarrow$$
$$[\text{Co}^{\text{II}}(\text{CN})_5\text{:H}]^{4-} + \text{H}^+\text{X}^- \quad (c)$$

$$[\text{Co}^{\text{II}}(\text{CN})_5\text{:H}]^{4-} + [\text{Co}^{\text{II}}(\text{CH})_5]^{3-} \longrightarrow$$
$$2[\text{Co}^{\text{I}}(\text{CN})_5]^{3-} + \text{H}^+$$
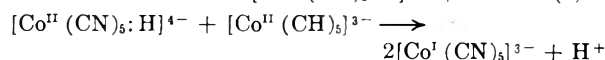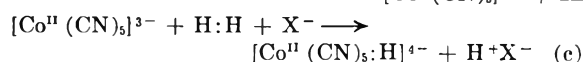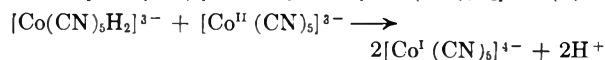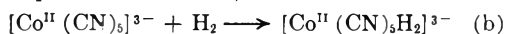
Equation c represents a heterolytic scission of the hydrogen molecule. Other examples of heterolytic scission by action of a monomer metal ion, aided by an anion acting to pull off a proton, are now well established.[8] Since such reactions are known and since equation c is consistent with the observed salt effect, this reaction is favored as representing the reduction reaction.

When this work was begun, it was hoped to establish a clear, unique definition of a cobalt cyanide complex with a specific electronic structure capable of reacting catalytically with hydrogen. Such a situation has appeared to be established with certain other metal ions. However, it seems most reasonable to suggest that while the $\text{Co}^{\text{II}}(\text{CN})_5$ structure discussed above is catalytically active, in this system there are also other species with catalytic properties. The complexity of the system has made unique conclusions difficult; on the other hand, this system has been revealed to have even more interesting properties as illustrated by the exchange and aging characteristics observed.

Finally, it seems worth while to mention the general similarity which appears to us to exist between such metal–organic catalysts and metals and metal oxides. For example, cobalt metal is largely covalent, each atom surrounded in the solid by 8 or 12 neighbors and using about 6 electrons per atom for bonding. It may be similar, therefore, to cobalt cyanides from a catalytic standpoint. While metals have characteristics best defined for certain purposes in physicists' terms, yet it may be best for catalytic purposes to return to chemical considerations. This can be particularly true in dealing with a surface at which there are chemisorbed molecules and where it is the relatively localized condition which determines the chemical-catalytic properties. Previous considerations of metals by Beeck, Boudart, Dowden and others have provided some understanding of the chemical reasons for maxima of catalytic activity according to position in the periodic table. While the goal is distant, it appears possible to establish what electronic levels are needed for catalytic activity, and to create and modify these levels by varying the coördinating environment. We believe these considerations will ultimately apply generally for metals, salts, or metal–organic complexes.

DISCUSSION

A. W. ADAMSON.—I would like to point out that air oxidation of Co(CN)_5^{-3} does not give $\text{Co(CN)}_5\text{H}_2\text{O}^{-2}$, but rather a binuclear complex, as shown by Wilmarth and Haim in our department. The $\text{Co(CN)}_5\text{H}_2\text{O}^{-2}$ species has a different spectrum from that of the result of air oxidation. The peak is around 350 mμ, not at 380 mμ. I feel that the possibility of disproportionation needs further examination.

S. WELLER.—This unpublished result is certainly pertinent to the question of disproportionation. It will be very interesting to examine the data of Wilmarth and Haim when they appear.

R. M. NOYES.—D_2 exchanges to HD unless strong alkali is present, when the gas returned is H_2. This implies the intermediate XD formed from D_2 can react with solvent to form HD but can somehow in presence of alkali be converted to XH and then react with solvent to give H_2. Is this consistent with a heterolytic split leaving an H^- on the cobalt?

S. WELLER.—The interpretation given for the effect of alkali on isotope distribution was based on general kinetic considerations and is independent of the detailed mechanism of exchange. As far as the detailed mechanism is concerned, I see no reason why a hypothetical intermediate with D^- on the cobalt (resulting from a heterolytic split of D_2) should not exchange with water to give H^- on the cobalt.

H. C. DEHM.—Winfield has reported recently that it appears that we have a cation effect operating here rather than a salt effect. In particular he reports unusual enhancement by cesium ion. Would you care to comment on this?

S. WELLER.—The recent publication by King and Winfield (J. Am. Chem. Soc., 80, 2060 (1958)) is concerned with H_2 evolution in the heterogeneous region (CN/Co = 4) rather than H_2 absorption in the homogeneous region (CN/Co = 5). The salt effect is similar to ours in being large, but a much greater cation specificity apparently obtains in the H_2 evolution reaction than in H_2 absorption.

H. TAUBE.—How do you understand the observation that the rate of hydrogen exchange is independent of time of aging?

S. WELLER.—The exchange activities of reduced, unaged solutions and of aged solutions are not, in fact, identical (cf. runs with OH$^-$ added or with long aging times). Nevertheless it is difficult to explain the similarity of rates of reduced solutions (Co^{I}) and aged solutions (Co_2^{II}?) without assuming that several Co species have activity for exchange, some of them coincidentally being comparable in magnitude.

W. K. WILMARTH.—Your mechanism does not seem to provide a path for the formation of methylamine, a reaction product reported by Iguchi. Do you have reason to believe that methylamine is not formed in the reaction?

S. WELLER.—We have not checked Iguchi's claim that methylamine is formed. However, it is difficult to see why the limiting hydrogen absorption should be one hydrogen atom per cobalt if the hydrogen were used in reducing cyanide to methylamine.

BINUCLEAR COMPLEXES AS CATALYSTS[1]

By Hans B. Jonassen and V. V. Ramanujam[2]

Contribution from the Richardson Chemical Laboratory of Tulane University, New Orleans, La.

Received October 4, 1958

It has been shown that when nickel(II) ion reacts with tris-(2-aminoethyl)-amine (abbrev. tren) in basic solution, the complex ion $[Ni_2tren_2(OH_3)]^+$ is formed in which there are OH^- ion bridges between two coördinated nickel ions. This complex has been shown to be a catalyst for the decomposition of H_2O_2. The concept of binuclear singly bridged complexes as catalysts is applied to organic free radical and ionic reactions in homogeneous and heterogeneous systems.

In recent years the mechanism of aqueous oxidation–reduction reactions has been of great interest to many investigators.[3] However, the data obtained do not clearly indicate whether such processes are brought about by an electron transfer or atom transfer.[4] Much evidence has been accumulated[5,6] that bridging anions which would reduce the coulombic repulsion between the two cations[7] will greatly facilitate electron transfer reactions, and orders of electron transfer have been determined such as Br^-, $N_3^- > Cl^- > OH^- > F^- > NCS^- > H_2O$ for the system $Cr(II) \rightarrow Cr(III)$.[8]

It recently has been observed in these laboratories that in basic solution tris-(2-aminoethyl)-amine (abbrev. tren) forms binuclear complexes with the cobalt(II) ion where the fifth position of each cobalt(II) is occupied by an hydroxo group and another hydroxo group bridges the sixth position of two cobalt(II) ions. This complex was found to decompose H_2O_2 catalytically.[9]

Although this process seems to be similar to that found for iron polyamine complexes[10] it involves a binuclear complex with a peroxidic intermediate[11] which might rock in and out about the
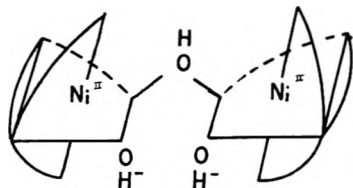
bridging group. Such rocking might increase the rate of peroxide bridge breaking.[12] However, in a binuclear complex the over-all mechanism could also be similar to that given by Basolo and Pearson[13] for the H_2O_2 decomposition by cobalt(II) ions involving in this case electron transfer through the hydroxyl bridge.

(1) Presented in part at the University of Illinois, May 8, 1956.

(2) Abstracted in part from the Ph.D. Dissertation submitted by V. V. Ramanujam to the Tulane University, 1958.

(3) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 303–308.

(4) B. J. Zwolinski, R. J. Marcus and H. Eyring, *Chem. Revs.*, **55**, 157 (1955).

(5) H. Taube, *J. Am. Chem. Soc.*, **77**, 4481 (1955).

(6) A. E. Ogard and H. Taube, *ibid.*, **80**, 1084 (1958).

(7) W. F. Libby, This Journal, **56**, 863 (1952).

(8) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958).

(9) H. B. Jonassen and G. Strickland, *ibid.*, **80**, 312 (1958).

(10) J. H. Wang, *ibid.*, **77**, 4716 (1955).

(11) E. L. King, "Catalysis," Vol. II, Ed. P. H. Emmett, Reinhold Publ. Corp., New York, N. Y., 1955, p. 438–445.

(12) R. C. Jarnagin and J. H. Wang, *J. Am. Chem. Soc.*, **80**, 786 (1958).

(13) Ref. 3, p. 324.

Triethylenetetramine (trien) the isomer of tren on the other hand was found to be oxidized irreversibly to cobalt(III) when treated with H_2O_2. It was postulated that this occurred because the hydroxo groups attached themselves in octahedral *trans* positions.

Attempts to substantiate this by magnetic susceptibility measurements proved unsuccessful since both the trien and tren complexes showed a moment corresponding to one unpaired electron.

It was therefore decided to investigate the complexes of these two tetramines with nickel(II) ion in basic solution. Spectrophotometric, conductometric and potentiometric titrations (Figs. 1–3) with the two isomeric amines again indicated that in the 1:1 tren nickel(II) complex a *cis* configuration for the two remaining positions in the octahedron is obtained. Breaks in the curve for three OH^- for two Ni(II) furthermore indicate that the $[Ni(II)_2tren_2(OH)_3]^{+1}$ ion is formed containing a hydroxo bridge
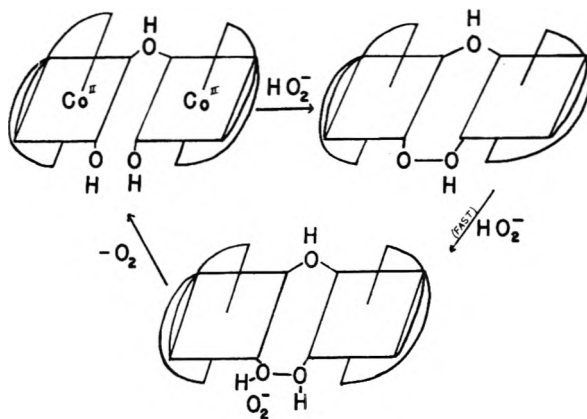
The 1:1 trien–nickel complex on the other hand added two OH^- ions to give the complex [Nitrien-$(OH)_2]^0$. This precipitates after 6 OH^- equivalents have been added to the nickel(II) trien·4HCl mixture.

Some very interesting and important results are obtained from the magnetic susceptibility titration. As a mixture of trien·4HCl and an equivalent amount of Ni(II) ions is titrated with OH^- ions the magnetic susceptibility decreases and at the point of neutralization of the four hydrogen ions the [Nitrien]$^{2+}$ complex ion is found to be diamagnetic. The trien molecule occupies now the four positions in the same plane with the d_{z^2} orbital filled with two paired electrons to give the structure

Fig. 1.—Conductometric titration of nickel perchlorate and trien·4HCl with NaOH (———) and nickel perchlorate and tren·3HCl with NaOH (———).
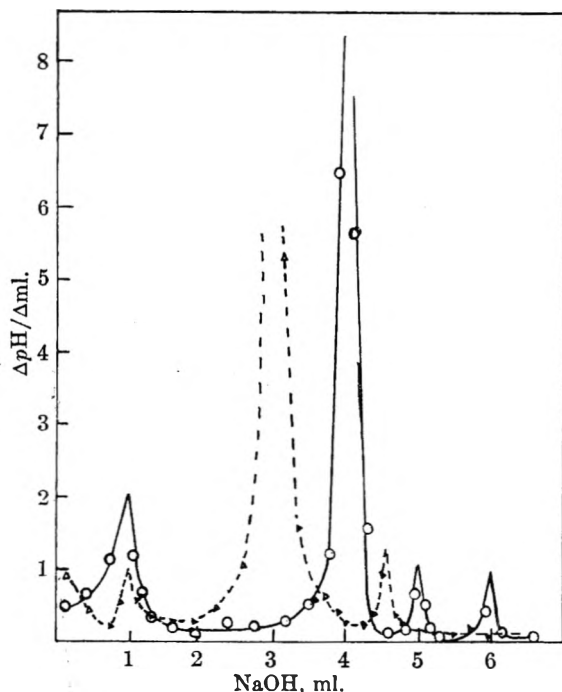
Fig. 2.—Potentiometric titration of nickel perchlorate and trien·4HCl with sodium hydroxide (———) and nickel perchlorate and tren·3HCl with sodium hydroxide (———).

with the splitting of the d levels typical for square coplanar complexes

$$E \quad \begin{array}{l} -d_{x^2-y^2} \\ -d_{z^2} \\ -d_{xy} \\ = d_{yz},\ d_{xz} \end{array}$$
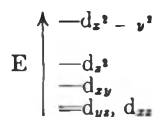
As further OH^- ions are added, the H_2O is displaced by OH^- in the fifth and sixth coördination positions. Due to the decrease in the ability[14] to split the d levels for OH^- ion compared to H_2O, the splitting of the d level reverts to d and d and the magnetic susceptibility of the *trans* bishydroxo complex increases reaching that expected for two unpaired electrons occupying the d_{z^2} and $d_{x^2-y^2}$ levels in a typical sp^3d^2 octahedral complex with d^8 configuration.

On the other hand, for the tren complex, Fig. 4 shows that at the point of neutralization of the 3 HCl, the complex is paramagnetic with two unpaired electrons, in the d_{z^2} and $d_{x^2-y^2}$ orbitals giving an sp^3 type bonding with the amino nitrogen atoms of tren leaving the H_2O molecules in the octahedral *cis* positions.
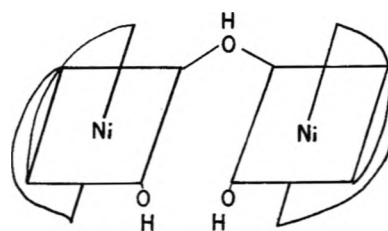
As further hydroxide ions are added the paramagnetic susceptibility decreases reaching diamagnetism at 1.5 OH^- ion added.

The stereospecificity of the tertiary nitrogen in tren requires that the electron pairing in this case would have to occur in the $d_{x^2-y^2}$ orbital to give the *cis* configuration shown below
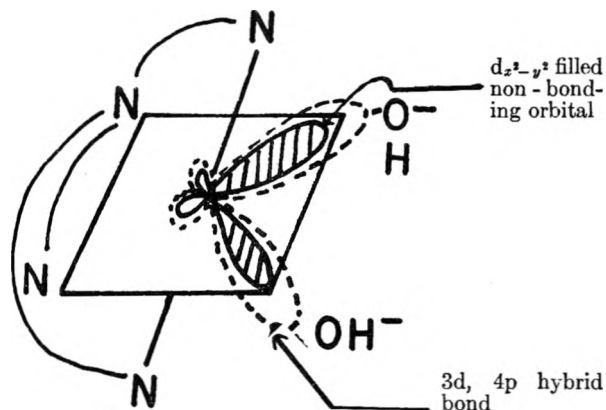
This would then produce repulsion toward the first OH^- ion entering the fifth position by the filled $d_{x^2-y^2}$ orbital and repulsion for the sixth position would be still greater. However, by bridging the sixth OH^- ion the charge and the repulsion would be decreased and a skewed octahedron with dsp^3 hybridization would be formed.

Addition of further hydroxide ion would further

(14) L. E. Orgel, *J. Chem. Phys.*, **23**, 1819 (1955).

decrease the ligand field and lead to the normal weak field splitting for d^8 octahedral system with outer orbital sp^3d^2 configuration.

The skewed octahedron with bonding in the $d_{z^2 - y^2}$ orbital direction would lead for the nickel-(II) ion to excited states which would allow the type of electron transfer mentioned by Basolo and Pearson[15] for the cobalt(II)–cobalt(III) transfer.

Such a system seems to exist for both the nickel-(II) tren and cobalt(II) tren complexes in their catalytic behavior for decomposition of H_2O_2 shown by the hydroxo bridged complexes in solution.

Since the repulsion (and the bond distance) is greater for the doubly occupied $d_{z^2 - y^2}$ orbital the Ni(II) complex should be less effective as a catalyst through the formation of a peroxidic intermediate than the cobalt(II) complex which contains a singly occupied $d_{z^2 - y^2}$ orbital. This was found to be true, the relative rate constants being 0.17 min.$^{-1}$ for the cobalt complex (catalyst concentration $2.5 \times 10^{-4}\ M$) and 0.042 min.$^{-1}$ for the nickel complex (catalyst concentration $6.6 \times 10^{-4}\ M$) at 25°.

Since some of these polydentate amine metal complexes are known to be catalysts in the free radical polymerization of butadiene and styrene in basic solution it was of interest to determine the possible existence of binuclear complexes with a single hydroxo bridge in these systems.

One of these catalyst systems contains equivalent quantities of iron(II) ions and Na_3EDTA to which zinc sulfoxylate has been added to reduce the iron(III) ion formed back to the iron(II).

Conductometric titration of the iron(II) EDTA system (Fig. 5) shows a break in the curve after the addition of one half equivalent of OH^- ions. Breaks at this same point also were observed in spectrophotometric titrations.

In view of the findings with the nickel(II) and cobalt(II) complexes the formation of one single hydroxo bridge is postulated linking two Fe complexes.

If it is assumed that the third carboxyl group hydrolyses[16] and does not coördinate this hydrolysis produces one hydroxide ion which can coördinate in the fifth position. The tertiary nitrogen has then the same stereospecific requirement as that in tren and the binuclear complex shown above should be present when one additional half equivalent hydroxide ion is added.

This complex should then initiate the polymerization by allowing cumene hydroperoxide for example to bridge between the two iron(II) ions as shown above for the Co(II) tren complex.

Liberation of the cumene free radical would leave the peroxy free radical attached and permit the transfer of one electron from the metal ion. The bridged peroxide would then decompose and oxidized metal ion would be reduced by the sulfoxylate.

This explanation would be in line with the data reported by Jones and Long[17] and the discussion of

(15) Ref. 3, p. 308, 321.

(16) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice–Hall, New York, N. Y., 1952.

(17) S. S. Jones and F. A. Long, THIS JOURNAL, 56, 25 (1952).
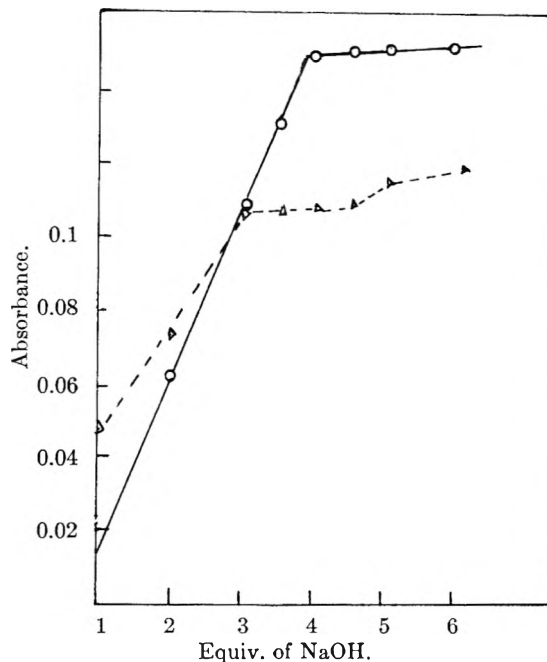
Fig. 3.—Spectrophotometric titration of nickel perchlorate and trien·4HCl with NaOH (————, 910 mμ) and nickel perchlorate and tren·3HCl with NaOH (————, 570 mμ).
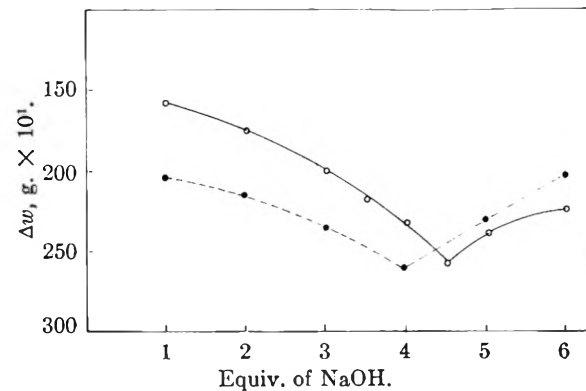
Fig. 4.—Magnetic titration of nickel perchlorate and trien·4HCl with sodium hydroxide (————) and nickel perchlorate and tren·3HCl with sodium hydroxide (————).

Reynolds and Lumry.[18] It is well known that these catalyst systems develop very intense colors; such highly intense colors have been attributed to bridged complexes of mixed valence[19] in line with the above argument.

This concept of bridged binuclear metal complexes is analogous to the concept of coenzyme systems so successfully applied in the field of biochemical reactions.

It also can be applied to many organic reactions in which bridging by electron rich groups should produce a path for electron transfer in non-polar or slightly polar media.

This concept can be helpful especially in reactions which are postulated to occur by ionic mechanisms. One of the most fruitful approaches is the application of bridging binuclear complexes as catalyst to polymerization reactions.

In a recent patent (U. S. 2,587,141) it was

(18) W. L. Reynolds and R. Lumry, J. Chem. Phys., 23, 2560 (1955).

(19) C. L. Brown, R. P. Craig and N. Davidson, J. Am. Chem. Soc., 73, 1946 (1951).

stated that for the polymerization of propylene to give its tetramer the effective catalyst was not BF_3 alone nor the BF_3 etherate but a mixture of the two: BF_3 etherate a slight excess of BF_3. Using the typical δ^+ δ^- shift the active catalyst can be pictured as
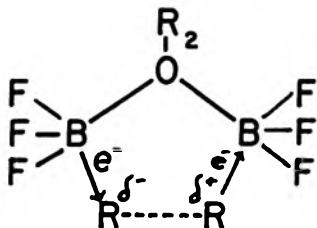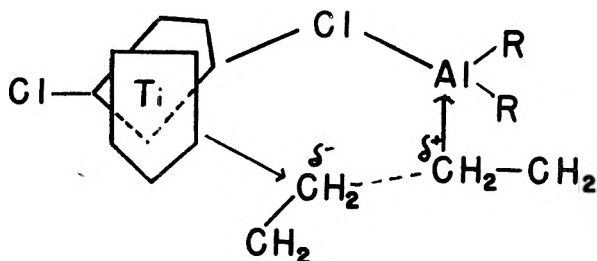

where the OR_2 group acts as the bridging unit.

A similar binuclear complex $BF_3 \cdot OH_2BF_3$ is also postulated as being the active intermediate in the isomerization of butenes.[20] This electron transfer mechanism can be applied to the aluminum isopropoxide catalyst used for polymerization of propylene oxide.[21] This is especially effective when combined with $ZnCl_2$. Postulating a binuclear bridged complex the following structure with the usual δ^+ δ^- shift should be obtained
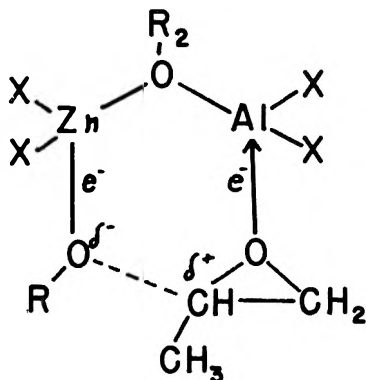
Price's own mechanism is in line with this except that he postulates a mononuclear catalyst intermediate. In a catalyst system of two different metal ions, they certainly would favor ionic bridged structures as electron transfer agents.[22]

The recently reported catalytic action of freshly prepared $(C_5H_5)_2TiCl \cdot Al(C_2H_5)_2Cl$ in ethylene polymerization[23,24] can be explained similarly by a binuclear singly bridging chloride complex especi-

ally since the binuclear doubly bridged complex of the above is not a catalyst.[25] Preliminary results in these laboratories[26] also indicated the existence of a dimer of n-butyllithium in the presence of very dilute but equivalent concentration of benzene in hexane or heptane. The heterogeneous phase which has been observed by Tobolsky[27] is not present under these conditions. A dimer possibly loosely linked to benzene would be bridged through the alkyl group and a δ^+ δ^- shift would be possible as indicated below. Such interaction with isoprene chelated to one lithium would allow cis 1,4-addition. The heterogeneous phase is no doubt important in its ability to produce an increase in isoprene concentration.

A somewhat similar mechanism also could be postulated for the heterogeneous polymerization of olefin in the Ziegler system. The chloride ion in the titanium halide lattice would be the bridging ion between the Ti^{III} and Al^{III} ions through which electron transfer should occur to give δ^+ δ^- shift in the olefin.

An extensive program attempting to determine orders of electron transfer for these various bridged metal ion systems in non-polar or slightly polar media is under way in these laboratories.

Experimental

1. Preparation of the Pure Amine Hydrochlorides.—A mixture of the amine containing approximately 70% trien and 30% tren, obtained from the Carbide and Carbon Chemical Corporation was treated in cold ethanolic solution at 5° with concentrated hydrochloric acid. Tren·3HCl precipitated out first as white crystals. This was collected in several fractions and the last fractions rejected. The hydrochloride was purified by dissolving in water and precipitating with ethanol. This process was repeated thrice.

Trien began to precipitate out later from the mixed amine as its hydrochloride, a cream-colored material. This was also collected in several fractions and the earlier ones rejected. Trien·4HCl was purified in the same way as tren hydrochloride.

The salts were analyzed for their chloride content mercurimetrically as a check on their purity. A purity of 99.8% was recorded in each case.

Conductometric Titrations.—Conductometric titrations were performed using an assembly consisting of a Leeds and Northrup No. 7651 Student Potentiometer, Leeds, and Northrup No. 4775 Decade Resistance box, Heathkit Oscilloscope, Heath Kit Audiogenerator and vertical dipping platinized platinum electrodes. The cell used was a 250-ml. Berzelius type beaker closed with a rubber stopper carrying the electrode assembly, inlet and outlet tubes for nitrogen and the buret. The nitrogen outlet was closed by a Bunsen valve. A magnetic stirrer was employed for stirring. All titrations were performed under nitrogen.

Potentiometric Titrations.—Potentiometric titrations were made with a Beckman Model G pH meter (National Instruments Co., Pasadena), using glass and calomel electrodes. The same arrangement as used in the conductometric titrations was employed to keep out oxygen.

Spectrophotometric Measurements.—A Beckman Model B Spectrophotometer (National Instruments Co., Pasadena) was used. Matched standard 1-cm. Corex cells were employed.

Magnetic Measurements.—Measurements of changes in magnetic susceptibility were made using the Gouy method. The apparatus was constructed and calibrated using a Cinaudagraph type permanent magnet (field strength 4768 gauss) and a Christian Becker semi-micro analytical balance. The balance was equipped with an optical system by

(20) J. M. Clayton and A. M. Eastman, ibid., **79**, 536 (1957).

(21) C. C. Price, 15th National Organic Chemistry Symposium, Rochester, 1957.

(22) Ref. 3, p. 362.

(23) G. Natta, P. Pino, G. Mazzanti and H. Gianinini, J. Am. Chem. Soc., **79**, 2975 (1957).

(24) D. S. Breslow and N. R. Newberg, ibid., **79**, 5072 (1957).

(25) G. Natta, P. Carradini and G. W. Bassi, ibid., **80**, 755 (1958).

(26) J. H. Sutter, unpublished results.

(27) H. Marita and A. V. Tobolsky, J. Am. Chem. Soc., **79**, 5853 (1958).

which fractional weights below 100 mg. could be directly read on a scale. The balance had a sensitivity of 0.02 mg.

A Pyrex, tube, about 15 cm. long, closed flat at one end was used to contain the solutions. The average cross-sectional area was measured by weighing the mercury filling a measured height in the tube.

Description of the Method Used in Filling up the Tube.—Exactly one milliliter of the metal salt solution was transferred into the tube described above, followed by exactly one ml. of the amine hydrochloride solution. The tube was then closed with a rubber serum cap and two hypodermic needles, a long one extending to the bottom and a short one, staying near the top, were introduced. The long needle served as the inlet and the short one, the outlet. Nitrogen was bubbled through for about ten minutes, and a small syringe attached to the outlet needle. The air in the syringe was displaced by nitrogen, and a measured volume of sodium hydroxide placed in it. The escaping nitrogen now bubbled through the sodium hydroxide solution. After about five minutes the solution was forced into the tube, pulling up the longer tube momentarily to prevent back-suction. Water was then placed in the syringe and forced into the tube. This washed the sodium hydroxide completely into the tube. The amount of water was so regulated that the total volume was exactly four milliliters. The tube was then suspended below the left pan of the balance and weighed in the magnetic field and in the absence of it. The same was repeated with the dry empty tube with the rubber cap and the apparent change in weight subtracted from the weight change shown by the sample. The changes in weight (Δw) were plotted against the volume of sodium hydroxide. The moments were calculated for the points where a sharp change in slope occurred.

DISCUSSION

S. Weller.—In connection with the Li-catalyzed polymerization of isoprene, would you care to comment on the reasons for the difference in behavior of Na and Li?

H. B. Jonassen.—The difference seems to lie in the greater covalent character of the lithium bond.

C. F. Gibbs.—Professor Tobolsky, as indicated in your slide, has postulated a heterogeneous reaction for the stereospecific initiation of isoprene polymerization. Do you feel that a surface is involved?

H. B. Jonassen.—Yes, there seems to be no question of heterogeneity—this would be important in increasing the concentration near the binuclear singly bridged complex acting as the initiator.

B. E. Douglas.—What structure of the cis-dihydroxy or cis-diaquo Ni complex of trien do you feel accounts for the diamagnetic behavior? I would not expect the difference in field strength of water and hydroxide ion to be great enough to account for this. Decreased splitting of the $d\gamma$ and $d\epsilon$ should not be great enough to account for this and both of the higher energy orbitals should be affected approximately equally for a cis octahedral structure. It seems to me that a trans configuration or a 4- or 5-coordinate structure would be required to account for the diamagnetism.

H. B. Jonassen.—Yes, a trans configuration is postulated for trien, but a 5-coordinated structure would explain these data, but it would necessitate the removal also of a proton from an NH_2 of the amine, this would give a possibility of bridging by the RNH^-. However, such a removal of a proton from NH_2 has not been found to occur under these conditions.

For the tren complex, however, the $d_{z^2-y^2}$ level was lowered by the approaching OH^- ion with corresponding increase of d_{z^2} level this would give lowering of susceptibility and also the formation of a skewed octahedral structure. The sharing of the (-1) charge of the OH^- ion by two Ni(II) would increase the splitting tendency of the bridging OH^- ion vs. the monodentate OH^- ion to give the structure

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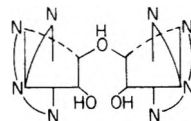
THE FERRIMYOGLOBIN CATALYZED OXIDATION OF FERROCYANIDE ION BY HYDROGEN PEROXIDE

By Philip George and D. H. Irvine

Department of Chemistry, University of Pennsylvania, Philadelphia, Pa.

A mechanism for the ferrimyoglobin-catalyzed oxidation of ferrocyanide ion by H_2O_2, in which catalysis proceeds by a sequence of reactions involving changes in the oxidation state of the hemoprotein (III → IV → III), is shown to be in good agreement with the experimental data. The reduction step has been investigated in some detail. The reaction shows first-order kinetics when excess ferrocyanide is used, but the first-order constants are not directly proportional to the hydrogen ion concentration. These features are explained by assuming two reduction paths, one involving ferrocyanide ion and the conjugate acid species of the higher oxidation state of ferrimyoglobin, the other involving the conjugate acid of the ferrocyanide ion and the conjugate base species of the higher oxidation state. The general features of catalysis by ferrimyoglobin, peroxidase and catalase, are compared.

It has long been known that ferrimyoglobin is a poor catalyst for the oxidation of reducing agents by peroxides, whereas both ferriperoxidase and ferricatalase, hemoproteins having the same prosthetic group as ferrimyoglobin, are very efficient catalysts for the oxidation of aromatic amines, phenols, etc., on the one hand, and aliphatic alcohols on the other. The intermediate compounds formed in the catalytic reactions of ferriperoxidase and ferricatalase were at one time regarded as "enzyme substrate" complexes according to the Michaelis-

Menten theory of enzyme action,[1-3] and, by analogy, the red compound formed when ferrimyoglobin reacts with H_2O_2 was described similarly.[4]

In previous papers[5-11] we showed conclusively

(1) B. Chance, *Arch. Biochem.*, **21**, 416 (1949).

(2) B. Chance, *ibid.*, **22**, 224 (1949).

(3) B. Chance, *J. Biol. Chem.*, **179**, 1331 (1949).

(4) D. Keilin and E. F. Hartree, *Proc. Roy. Soc. (London)*, **117B**, 1 (1935).

(5) P. George and D. H. Irvine, *Biochem. J. (London)*, **52**, 511 (1952).

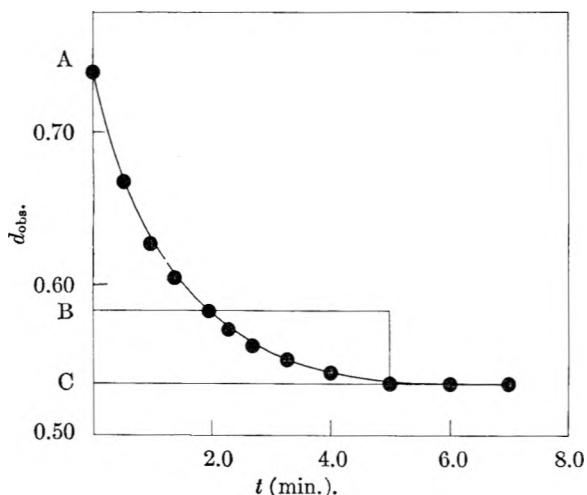(6) P. George and D. H. Irvine, *ibid.*, **55**, 230 (1953).

Fig. 1.—Plot of optical density against time in stationary state experiment: $T = 18°$, $I = 0.05$, pH 8.4, $H_2O_2 = 6.16 \times 10^{-5}$ M, $Fe_{Mb}^{III} = 5.10 \times 10^{-6}$ M, $Fe(CN)_6^{4-} = 5.0 \times 10^{-4}$ M.

that these intermediates are not enzyme substrate complexes but higher oxidation states of the parent hemoprotein. In the case of ferrimyoglobin only one stable intermediate is obtained, having iron in the oxidation state +4, while in the case of peroxidase and catalase two intermediates are formed with iron in the oxidation states +5 and +4, respectively. A detailed study of the ferrimyoglobin–H_2O_2 reaction[5] showed that a transient oxidizing entity also was produced along with the stable red compound. This entity has many of the properties of the OH radical, and the chemistry of the ferrimyoglobin–H_2O_2 reaction can be satisfactorily accounted for on the assumption that it is formed according to the equation

$$Fe_{Mb}^{III}(H_2O) + H_2O_2 \longrightarrow Fe_{Mb}^{IV} + OH + etc. \quad (1)$$
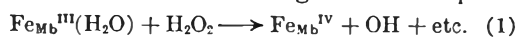
where $Fe_{Mb}^{III}(H_2O)$ denotes ferrimyoglobin and Fe_{Mb}^{IV} its higher oxidation state. On this basis there is formal similarity to the first step in the reaction between ferrous ion and hydrogen peroxide when it is written in the form

$$Fe^{2+}_{aq} + H_2O_2 \longrightarrow Fe^{3+}_{aq} + OH + OH^- \quad (2)$$
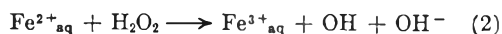
However, an alternative mechanism of the ferrimyoglobin–H_2O_2 reaction, which involves an initial two-equivalent oxidation giving a compound with iron in the +5 oxidation state followed by rapid reduction of the latter to the stable +4 state, would account equally well for the experimental observations. There is indeed some evidence from the energetics of the reaction[12] that a mechanism of this type may be more probable. This mechanism would suggest a formal similarity between the ferrimyoglobin–H_2O_2 reaction and the reactions of peroxidase and catalase with peroxides, and would imply that the different catalytic behavior of these hemoproteins is one of degree rather than kind, possibly brought about by the higher oxidation states having different chemical structures. It seemed desirable therefore to make

(7) P. George and D. H. Irvine, *Biochem. J.*, **58**, 188 (1954).

(8) P. George and D. H. Irvine, *ibid.*, **60**, 596 (1955).

(9) P. George, *ibid.*, **54**, 267 (1953); **55**, 220 (1953).

(10) P. George, *J. Biol. Chem.*, **201**, 413 (1953).

(11) P. George, *Science*, **117**, 220 (1953).

a detailed study of the catalytic action of ferrimyoglobin, and we report in this paper the results obtained with ferrocyanide ion as the reducing agent.

Experimental

Ferrimyoglobin used in these experiments was prepared and purified according to the method described in an earlier paper.[5]

The hydrogen peroxide was pure 97% w./w., free from inhibitors. It was kindly supplied by Laporte Chemicals Ltd. A stock solution of the peroxide was standardized before use against a standard solution of A.R. potassium permanganate and then diluted to give the desired concentration.

Potassium ferrocyanide was A.R. grade $K_4Fe(CN)_6 \cdot 3H_2O$. It was used without further purification.

Conductivity water was used in all the experiments.

Measurements of optical density were made on a Unicam Quartz spectrophotometer adapted for work at constant temperature. Reactions were followed at 409.5 mμ, the wave length maximum of ferrimyoglobin in the Soret region.

pH measurements were carried out on a Cambridge pH meter.

Results

If to a mixture of ferrimyoglobin and ferrocyanide ion, the latter present in large excess, H_2O_2 is added such that its concentration is about ten times that of the ferrimyoglobin concentration and the reaction followed spectrophotometrically, then it is found that the optical density of the solution at first decreases, consistent with the disappearance of ferrimyoglobin and the formation of its higher oxidation state, but eventually becomes constant, and remains so for some minutes even though an appreciable fraction of the original ferrimyoglobin is still present in the system (Fig. 1). At this stage, then, ferrimyoglobin is being regenerated in the system at the same rate at which it is being oxidized, *i.e.*, it is acting as a catalyst for the oxidation of ferrocyanide ion by H_2O_2.

On the basis of equation 1 and the known fact that one mole of ferrocyanide ion reduces one mole of the higher oxidation state,[5] we would propose that in this system these reactions occur

$$Fe_{Mb}^{III} + H_2O_2 \xrightarrow{k_P} Fe_{Mb}^{IV} + OH + etc. \quad (3)$$

$$OH + Fe(CN)_6^{4-} \xrightarrow{fast} Fe(CN)_6^{3-} + OH^- \quad (4)$$

$$Fe_{Mb}^{IV} + Fe(CN)_6^{4-} \xrightarrow{k_F} Fe(CN)_6^{3-} + Fe_{Mb}^{III} \quad (5)$$
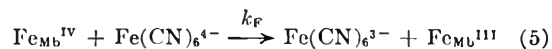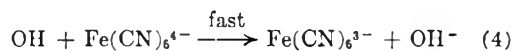
There is evidence that radical consumption of $Fe(CN)_6^{4-}$ must occur, either according to reaction 4 or, in a similar manner, by reaction with a second radical produced by the reaction of OH with organic substrate, since when an equimolar concentration of H_2O_2 is added to an equimolar mixture of ferrimyoglobin and ferrocyanide the higher oxidation state is obtained in almost the same yield as in the absence of ferrocyanide.[5] The alternative mechanism in which Fe_{Mb}^{V} is produced in the first step in the above reaction sequence would give identical results, since Fe_{Mb}^{V} in its reduction to Fe_{Mb}^{IV} would provide the oxidizing equivalent needed to oxidize $Fe(CN)_6^{4-}$ according to (4).

It is shown easily that from the above that in the stationary state

$$[Fe_{Mb}^{III}]_s/[Fe_{Mb}^{IV}]_s = k_F [Fe(CN)_6^{4-}]_s/k_P[H_2O_2]_s \quad (6)$$

where subscript "s" refers to concentrations in the

stationary state. Moreover, if the concentrations of $Fe(CN)_6^{4-}$ and H_2O_2 are both large with respect to the ferrimyoglobin concentration the initial disappearance of ferrimyoglobin should follow first-order kinetics, the first-order constant of the reaction being given by the equation

$$k_{obs} = k_p[H_2O_2] + k_r[Fe(CN)_6^{4-}] \qquad (7)$$

For a quantitative check of the proposed mechanism a knowledge of the kinetics of reactions 3 and 5 is essential. The results of our studies of reaction 3 have been reported elsewhere.[12] We now present data on reaction 5.

The Kinetics of the Ferrocyanide Reduction of the Higher Oxidation State of Ferrimyoglobin.— The addition of excess ferrocyanide ion to the higher oxidation state of ferrimyoglobin gave first-order kinetics, as might have been anticipated from the known 1:1 stoichiometry of the reaction. However, the first-order constants obtained with different concentrations of ferrocyanide did not vary directly with the latter, as can be seen from Fig. 2. A similar, though less pronounced, behavior also was observed with iodide ion as the reducing agent, but the effect was absent if phenol was used (Figs. 3 and 4). Under the pH conditions of the experiment (8.0–9.0) the phenol was present almost entirely in its conjugate acid form, and the absence of this effect with phenol suggested that the behavior was characteristic of the negatively-charged reducing agents.

The rate of the reduction by ferrocyanide also was found to be directly proportional to the hydrogen ion concentration (Fig. 5). Preliminary experiments indicated that the rate of reduction by iodide and phenol, under conditions where the latter was present almost entirely as its conjugate acid, was also dependent on the hydrogen ion concentration. It is not yet known, however, whether in these cases the same direct proportionality holds and further experiments are being conducted along these lines.

The data in Fig. 2 are fitted very well by the equation

$$k_{obs} = \frac{a[F]}{b + [F]} + c[F] \qquad (8)$$

where k_{obs} is the observed first-order constant, [F] the concentration of ferrocyanide, and a, b, c are constants having, respectively, the values 3.4×10^{-3}, 1.5×10^{-5}, 4.55 at 18° and pH 8.4, and 6.3×10^{-3}, 1.25×10^{-5}, 6.6 at 25° and the same pH. Thus, using equation 8, k_{obs} at ferrocyanide concentrations of 1.5×10^{-4} M and 2.0×10^{-3} M was calculated to be 3.82×10^{-3} sec.$^{-1}$ and 7.95×10^{-3} sec.$^{-1}$. The observed values were $(3.57 \pm 0.16) \times 10^{-3}$ sec.$^{-1}$ and $(8.06 \pm 0.38) \times 10^{-3}$ sec.$^{-1}$.

A mechanism which would be consistent with all the above features involves the assumption that the reduction occurs through two paths in which both the higher oxidation state and its conjugate acid as well as ferrocyanide and its conjugate acid are reacting species. There is substantial evidence that the higher oxidation state of ferrimyoglobin has a ferryl ion type of structure.[8] We may therefore denote it by the symbol $Fe_{Mb}C$ and its conjugate acid

(12) P. George and D. H. Irvine. *J. Coll. Science*, **11**, 327 (1956).
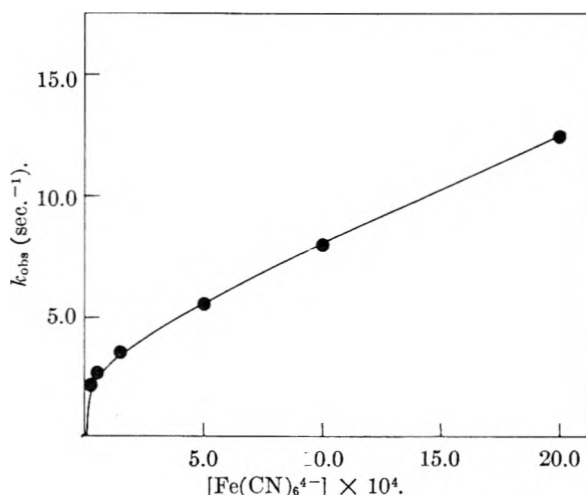
Fig. 2.—Variation of the observed first-order constant with $Fe(CN)_6^{4-}$ concentration for the reduction of the higher oxidation state of ferrimyoglobin by ferrocyanide: $T = 18°$, $I = 0.05$; pH 8.4.
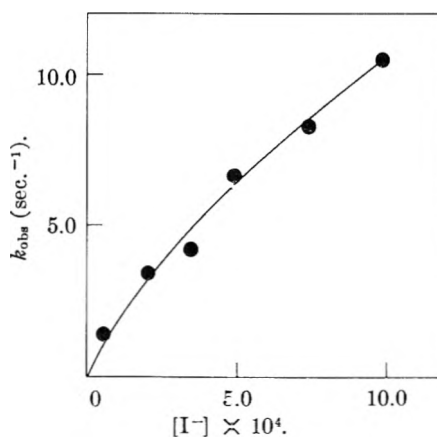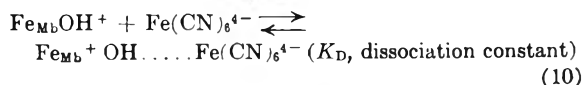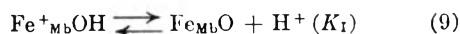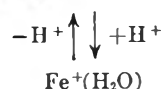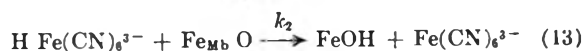

Fig. 3.—Variation of the observed first-order constant with iodide concentration for the reduction of the higher oxidation state of ferrimyoglobin by iodide ion: $T = 18°$, $I = 0.05$; pH 6.05.

by $Fe^+_{Mb}OH$, since in ferrimyoglobin the iron atom carries one net positive charge (*i.e.*, $Fe^+_{Mb}(H_2O)$). The reduction of the higher oxidation state of ferrimyoglobin by ferrocyanide is then assumed to take place according to this sequence of reactions

Path 1:

$$Fe^+_{Mb}OH \rightleftharpoons Fe_{Mb}O + H^+ \quad (K_I) \qquad (9)$$

$$Fe_{Mb}OH^+ + Fe(CN)_6^{4-} \rightleftharpoons$$
$$Fe_{Mb}^+ OH \ldots \ldots Fe(CN)_6^{4-} \ (K_D, \text{ dissociation constant}) \qquad (10)$$

$$Fe_{Mb}^+ OH \ldots \ldots Fe(CN)_6^{4-} \xrightarrow{k_1} Fe_{Mb} OH + Fe(CN)_6^{3-} \qquad (11)$$

$$-H^+ \uparrow \downarrow +H^+$$

$$Fe^+ (H_2O)$$

Path 2:

$$H Fe(CN)_6^{3-} \rightleftharpoons Fe(CN)_6^{4-} + H^+ \quad (K_F) \qquad (12)$$

$$H Fe(CN)_6^{3-} + Fe_{Mb} O \xrightarrow{k_2} FeOH + Fe(CN)_6^{3-} \qquad (13)$$

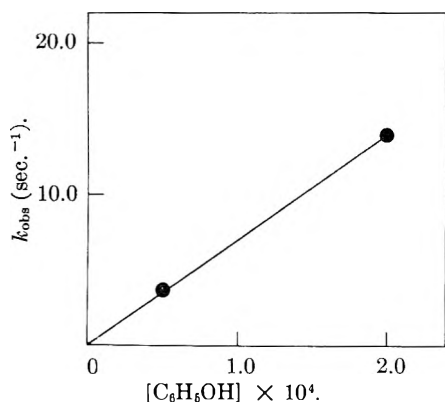$$-H^+ \uparrow \downarrow +H^+$$

$$Fe^+(H_2O)$$
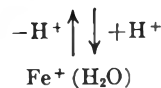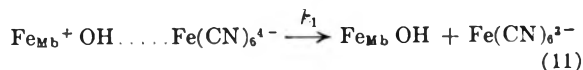
Fig. 4.—Variation of the observed first-order constant with phenol concentration for the reduction of the higher oxidation state of ferrimyoglobin by phenol: $T = 20.2°$, $I = 0.05$, pH 8.4.
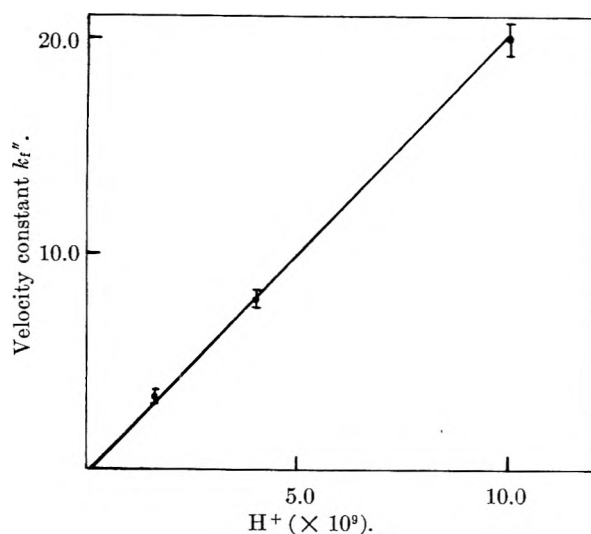

Fig. 5.—The effect of hydrogen ion concentration on the rate of reduction of the higher oxidation state by ferrocyanide: $T = 18°$, $I = 0.05$, $Fe_{Mb}^{IV} = 5.0 \times 10^{-6}$ M $Fe(CN)_6^{4-} = 1.0 \times 10^{-3}$ M; $k_f'' = k_{1st\ order}/[Fe(CN)_6^{4-}]$.
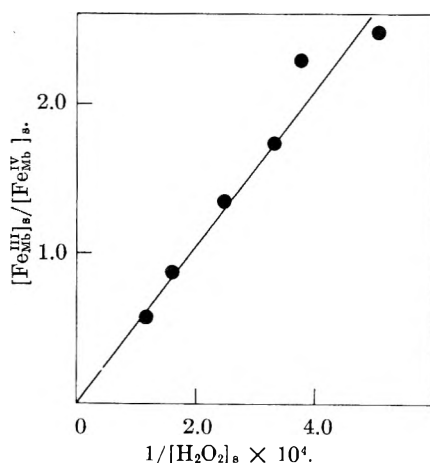

Fig. 6.—Stationary state experiments, plot of $1/[H_2O_2]$ against $[Fe_{Mb}^{III}]_s/[Fe_{Mb}^{IV}]_s$: $T = 18°$, $I = 0.05$, pH 8.40, $Fe_{Mb}^{III} = 5.0 \times 10^{-6}$ M, $Fe(CN)_6^{4-} = 1.0 \times 10^{-3}$ M.

From this sequence of reactions k_{obs} is given by the expression

$$k_{obs} = \frac{k_1[F]}{K_D + [F]} \times \frac{[H]}{K_I + [H]} + k_2 \frac{[F][H]}{K_F + [H]} \quad (14)$$

For K_I and $K_F \gg H$ this expression reduces to

$$K_{obs} = \frac{k_1[F][H]}{K_I(K_D + [F])} + \frac{k_2[F][H]}{K_F} \quad (15)$$

which at constant [H] is of the same form as (8). A comparison of (8) and (15) gives $K_D = 1.5 \times 10^{-5}$ and 1.25×10^{-5}, $k_1[H]/K_I = 3.4 \times 10^{-3}$, and 6.3×10^{-3}; $k_2[H]/K_F = 4.55$ and 6.6 at $18°$ and $25°$, respectively. Further discussion of the significance of these values must however be deferred until more experimental data on the system are acquired.

The Catalytic Oxidation of Ferrocyanide Ion by H_2O_2.—Irrespective of the detailed mechanism of the reduction a quantitative check on the catalytic scheme (equations 3–5) is possible as long as k_p and k_F (*i.e.*, $k_{obs}/[F]$) appropriate to the conditions of the experiments are known. Tables I and II, and Fig. 6 summarize the results of experiments in which (a) the ferrocyanide ion concentration was varied while the concentrations of H_2O_2 and ferrimyoglobin were kept constant, (b) ferrimyoglobin concentration was varied while the concentrations of H_2O_2 and ferrocyanide were kept constant, (c) the H_2O_2 concentration was varied while ferrimyoglobin and ferrocyanide concentrations were kept constant. The results in Table I show good agreement between the observed ratio $[Fe_{Mb}^{III}]_s/[Fe_{Mb}^{IV}]_s$, obtained spectrophotometrically, and that calculated from equation 6. In the calculation the initial concentration of ferrocyanide, being very large with respect to ferrimyoglobin, was assumed to remain constant, but a slight correction was made for the amount of H_2O_2 used up in at-

TABLE I

STATIONARY STATE EXPERIMENTS

$[H_2O_2]$ kept constant $(6.16 \times 10^{-5}\ M)$, $[Fe(CN)_6^{4-}]$ varied, $[Fe_{Mb}^{III}] = 5.10 \times 10^{-6}\ M$

$[Fe(CN)_6^{4-}]$	$\frac{[Fe_{Mb}^{III}]_s}{[Fe_{Mb}^{III}]_s}$	$\frac{k_f[Fe(CN)_6^{4-}]}{k_p[H_2O_2]_s}$ (calcd.)	k_{obs} $\times 10^2$ sec.$^{-1}$	$\frac{k_f Fe(CN)_6^{4-} + k_p[H_2O_2]}{(\times 10^2)}$ (calcd.)
2.0×10^{-3}	1.54	1.68 ± 0.16	2.18 ± 0.08	2.06 ± 0.09
1.0×10^{-3}	1.07	$1.10 \pm .10$	$1.54 \pm .06$	$1.62 \pm .07$
5.0×10^{-4}	0.81	$0.77 \pm .08$	$1.27 \pm .04$	$1.37 \pm .06$
2.67×10^{-4}	.70	$.60 \pm .06$	$1.15 \pm .04$	$1.23 \pm .05$
1.50×10^{-4}	.50	$.49 \pm .05$	$1.11 \pm .04$	$1.17 \pm .05$

TABLE II

STATIONARY STATE EXPERIMENTS

$[H_2O_2]$ constant $(6.16 \times 10^{-5}\ M)$; $Fe(CN)_6^{-4}$ constant $(1.0 \times 10^{-3}\ M)$

$[Fe_{Mb}^{III}]$	$\frac{[Fe_{Mb}^{III}]_s}{[Fe_{Mb}^{IV}]_s}$
2.90×10^{-6}	1.06
4.35×10^{-6}	1.07
5.10×10^{-6}	1.07

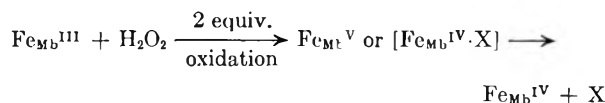taining the stationary state. This was calculated from the rate equation

$$\frac{d[H_2O_2]}{dt} = k_p[Fe^{III}_{Mb}][H_2O_2]$$

where Fe_{Mb}^{III}, the average concentration of ferrimyoglobin reacting during the time taken to attain the stationary state, was estimated graphically. Varying the ferrimyoglobin concentration, as in Table II, should not alter substantially the ratio $[Fe_{Mb}^{III}]_s/[Fe_{Mb}^{IV}]_s$ since, under the conditions, the concentra-

tion of ferrocyanide remains almost constant and the concentration of H_2O_2 does not change by more than 10%. Calculation shows that in the range of ferrimyoglobin concentration used in the experiments the ratio $[Fe_{Mb}^{III}]_s/[Fe_{Mb}^{IV}]_s$ lies within the limits 1.00 and 1.10. The values in Table II are in good agreement with these calculated values. Finally, according to equation 6 a plot of $1/[H_2O_2]_s$ against the ratio $[Fe_{Mb}^{III}]_s/[Fe_{Mb}^{IV}]_s$ ought to be linear with a slope equal to $k_F[Fe(CN)_6^{4-}]/k_p$. The linear plot in Fig. 6 has a slope of 5.5×10^{-5} which is in satisfactory agreement with the value of 6.1×10^{-5} calculated using the appropriate values of k_F, k_p and $[Fe(CN)_6^{4-}]$.

Discussion

The ferrimyoglobin-catalyzed oxidation of ferrocyanide ion by hydrogen peroxide has been shown to proceed by a sequence of reactions in which the hemoprotein undergoes changes in its oxidation state from III → IV → III. It has been reported in the literature[13] that in the ferrihemoglobin-catalyzed oxidation of certain polyphenols oxyhemoglobin is formed, and, in view of the close similarity between ferrihemoglobin and ferrimyoglobin in other reactions, it may be assumed that ferrimyoglobin would behave similarly. This observation can be fitted into a general picture of catalysis by these two hemoproteins somewhat similar to that proposed for peroxidase and catalase,[14] viz.

$$Fe_{Mb}^{III} + H_2O_2 \xrightarrow[\text{oxidation}]{\text{2 equiv.}} Fe_{Mb}^{V} \text{ or } [Fe_{Mb}^{IV} \cdot X] \longrightarrow$$

$$Fe_{Mb}^{IV} + X$$

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(13) D. Keilin and E. F. Hartree, *Nature (London)*, **173**, 720 (1954).

(14) P. George, *Biochem. J. (London)*, **52**, XIX (1952).

$$Fe_{Mb}^{IV} + AH_2 \longrightarrow [Fe_{Mb}^{III} \cdot AH]$$

1 equiv. reduction path | 2 equiv. reduction path

$$Fe_{Mb}^{III} + AH \qquad Fe_{Mb}^{II} + A$$
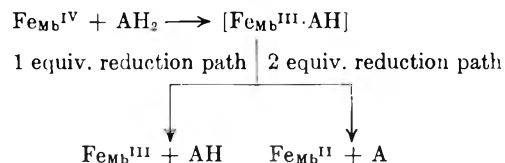
The mechanism would also account for the observation by Keilin and Hartree[15] that oxyhemoglobin is formed when a large excess of H_2O_2 is added to ferrihemoglobin. In this case H_2O_2 acts both as an oxidizing and reducing agent, the oxyhemoglobin being produced according to the two-equivalent reduction path shown in the above scheme.

The formal similarity between the ferrimyoglobin catalysis and that of peroxidase and catalase can be further illustrated. According to reports in the literature[16] ferrocatalase is obtained when H_2O_2 is added to a mixture of ferricatalase and azide or hydroxylamine. It is only under these conditions that ferrocatalase is obtained readily and it is believed[13] that under these conditions it is stabilized as the Fe_{cat}^{II}·NO complex. We would suggest that under these conditions the catalase cycle at the Fe^{IV} stage proceeds in a similar manner proposed for ferrimyoglobin above, the ferrocatalase being produced by the two-equivalent reduction path and stabilized by the NO produced in the oxidation–reduction reaction. These reaction mechanisms would imply a formal similarity in the catalytic behavior of the four hemoproteins through the utilization of various oxidation states of the prosthetic group, the differences being brought about by different structures of the higher oxidation states.

(15) D. Keilin and E. F. Hartree, *Nature (London)*, **166**, 513 (1950).

(16) D. Keilin and E. F. Hartree, *Biochem. J. (London)*, **39**, 148 (1945).

MOLTEN SALT THERMOCELLS

By Benson R. Sundheim and Joseph Rosenstreich

Contribution from Department of Chemistry, New York University, Washington Square, New York 3, N. Y.

The determination of the thermopotential of the thermocell $Ag/AgNO_3/Ag$ is described. The contributions to the thermopotential are analyzed. Some speculations on the significance of the results are presented.

A particularly simple form of the thermocell occurs when a temperature gradient is established between two identical, reversible electrodes immersed in a one-component molten salt. The properties of such a "molten salt/metal thermocouple" are intimately connected with the processes of thermal and electrical conductivity in the molten salt and with the electrode process.

Although galvanic cells involving temperature gradients have been the subject of a number of recent publications,[1] little attention has been paid to

the molten salt thermocell.[2,3] The pioneering study of Poincare includes approximate values for thermopotentials in the $Ag/AgNO_3/Ag$ system. Holtan gives very brief reports[3b] in the form of graphs from which the Thomsen coefficients in the $AgNO_3$ and $AgCl$ systems can be estimated.

In the present study the thermopotential of the $Ag/AgNO_3/Ag$ system is carefully determined. The equation for the thermopotential is presented in a form well suited for molten salts and is used to interpret the results. Finally some speculations

(1) E. g., (a) H. J. V. Tyrrel and G. L. Hollis, *Trans. Faraday Soc.*, **45**, 411 (1949); and others of this series; (b) R. Haase, *Erg. exacte Naturwiss.*, **26**, 56 (1952); *Trans. Faraday Soc.*, 724 (1953); This Journal, **11**, 379 (1957); **13**, 21 (1957); (c) C. Moreau and G. Lepoutre, *J. chim. phys.*, **52**, 498, 765 (1955); (d) H. Holtan, P. Mazur and S. R. deGroot, *Physica*, **19**, 1109 (1953).

(2) (a) L. Poincare, *Ann. chim. phys.*, [6] **21**, 289 (1890); (b) K. Hirota, *Science (Japan)*, **13**, 13 (1943); (c) D. Markov, *Doklady Akad. Nauk, SSR*, **108**, 115 (1956).

(3) (a) H. Holtan, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **57B**, 138, 592 (1954); (b) *Tids. Hsemi. Bergvesent. Met.*, **12**, 5 (1952); (c) Thesis, Utrecht (1953); (d) ref. 1d.
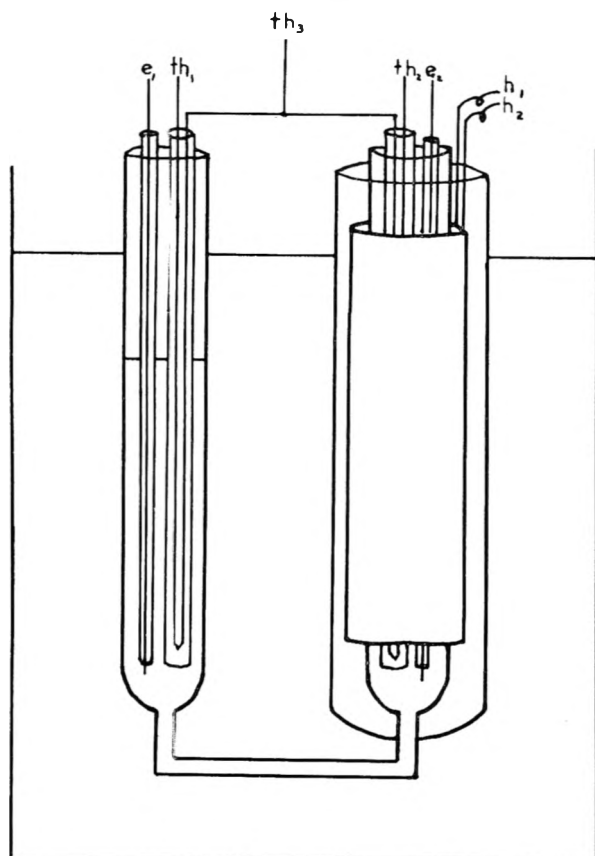
Fig. 1.

about the significance of thermopotentials are presented. In a later paper the extension of experiment and theory to multicomponent systems will be made.

I. Experimental

The thermopotentials were measured in a Pyrex U-tube (Fig. 1). One arm of the cell was fitted with a heating coil made of nichrome wire cemented onto an aluminum sleeve with Sauereisen cement, a Pyrex sleeve protecting the heater from the bath and forming an air-bath around that arm of the U-tube. The entire cell was immersed in a molten salt bath contained in a large pot melting furnace. This thermostat was fitted with a stirrer, thermoregulator and heater and maintained the outside of the cell to within 0.05° of a selected temperature.

The electrodes were fine silver wires sealed through a piece of 6 mm. Pyrex tubing, the protruding wire being wrapped around the tip. Thermocouple junctions were mounted in the electrode compartments; the junctions where the silver wires were joined to copper were immersed in an ice-bath. The thermocouples were connected so as to measure the difference in temperature between the electrodes and the difference in temperature between one electrode and an ice-bath. All potentials were measured to the nearest microvolt. The AgNO$_3$ was analytical grade and was used without further purification.

After the cell was filled with AgNO$_3$, the electrodes and thermocouples inserted and the cell brought to operating temperature, it was usually found that the potential difference between the electrodes was not zero when the temperature difference vanished. This residual e.m.f. of a few tens of microvolts was not affected by aging the electrodes in the salt.

As soon as the heater was energized the temperature of one arm of the cell began to rise; the steady state was achieved in approximately 30 minutes. Then about ten pairs of cell e.m.f. and thermocouple e.m.f. measurements were made at intervals of three minutes. These readings were acceptable only if there was no evidence of systematic

drift. The voltage applied to the heater was then changed and a new set of measurements made after the new steady state was achieved. Three different settings of increasing temperature difference were used, followed by another three in the direction of decreasing temperature difference so that changes in the system with time would be detected. No such changes ever were found. The experiment was performed at four different bath temperatures so that the thermoelectric power could be determined from 230 to 375°. The measurements in each range were repeated to establish an index of precision.

The data collected in a typical experiment are shown in Fig. 2. Each point on the graph represents the average of at least ten points. Each such set of points was fitted to a straight line by the method of least squares. The slopes of these lines are the thermoelectric powers and are reported in Table I. Although there is no experimentally significant curvature in the data from any single run, the entire set shows a slight but distinct trend with temperature. The coefficient $d(\Delta\phi/\Delta T)dT$ apparently changes from positive to negative as the temperature increases; its absolute magnitude is less than 10^{-6} volt/deg.[2] The magnitude of the thermoelectric power (-344μ volts/deg. at 305°) may be compared with that for the corresponding aqueous solution[1a] (-500 to -1100μ volts/deg. at 25° depending upon the concentration) or with that for the iron constantan thermocouple (55.5 μ volts/deg.).

II. Discussion

It is generally agreed[1] that the potential of a cell of this type may be represented as the sum of several terms

$$\Delta\phi = \Delta\phi_{med.} + \Delta\phi_{het.} + \Delta\phi_{metal} \quad (1)$$

The notation used here is explained in Fig. 3.[4]

The form of these is well understood but requires some further comment in the case of the molten salt. A derivation of an expression for the potential of a thermocell in the general case of an electrolytic solution was given by Holtan, Mazur and de Groot[1d] (cf. also 1b) as their equation 41

TABLE I

T, °C.	$\Delta\phi/\Delta T \times 10^4$
240.0	3.30
264.1	3.47
284.4	3.52
307.6	3.44

$$F\Delta\phi_T = \sum_k (t_k/c_k) \sum_j [(\partial\mu_k/\partial c_j)\Delta c_j]\cdot F \quad (2)$$

$$- \sum_k (t_k/z_k)Q_k^{xx}\Delta T/T - (Q_{el}^{xx}\Delta T/T)$$

$$- \Delta S\Delta T + \sum_j (\partial\Lambda/\partial c_j)\Delta c_j/\sum_k \nu_k z_k$$

Specializing to the case of a one component molten salt in which the same forward and reverse reactions occur at the two electrodes, (2) becomes

$$F\Delta\phi = -[(t_1/z_1)Q_1^{xx} + (t_2/z_2)Q_2^{xx} + Q_{el}^{xx}]\Delta T/T \quad (3)$$

In this notation F is the Faraday, t_1, z_1 and Q_1^{xx} the transference numbers, algebraic valences and reduced heats of transfer of the species (1 for cation 2 for the anion and el. for the electron within the electrode). The mass-average velocity is chosen as reference for the various fluxes and transference numbers. The Q_1^{xx} are related to the usual heats of transport, Q_1^x by the equation[5]

(1) The sign convention used here is that adopted by deGroot and others. A positive value for $\Delta\phi/\Delta T$ means that the hotter of the two electrodes becomes positive. The reverse convention is often used for metallic thermocouples.

$$Q_i^{xx} = Q_i^x - h_i = T(S_i^x - S_i) \qquad (4)$$

Here h_k is the partial enthalpy, S_i the partial entropy and S_i^x the entropy of transport of species i. The Q_i^{xx} are the quantities which arise most naturally when the heat flow does not contain the convective flow of enthalpy.[6] The term ΔS in (3) is the change in entropy due to the heterogeneous electrode reaction when one Faraday of positive electricity passes through the cell from the colder to the hotter electrode. Consequently it will always contain the single ion entropy of the species to which the electrode is reversible and the entropy of an electron within the electrode. In the particular case of the $Ag/AgNO_3$ cell

$$\Delta S = S_{Ag^+} + S_{el} - S_{Ag}$$

and the expression for the thermopotential may be written

$$F\Delta\phi = -[t_{Ag^+}Q_{Ag^+}^{xx} - t_{NO_3^-}Q_{NO_3}^{xx} + Q_{el}^{xx}]\Delta T/T \qquad (5)$$
$$+ [S_{Ag} - S_{Ag^+} - S_{el}]\Delta T$$
$$= t_{Ag^+}[Q_{Ag^+}^{xx} + Q_{NO_3}^{xx}]\Delta T/T - Q_{el}^{xx}\,\Delta T/T +$$
$$[S_{Ag^+} - S_{el}]\Delta T$$
$$= [-t_{Ag^+}S_{Ag^+}^x + t_{NO_3^-}S_{NO_3}^x]\Delta T -$$
$$[S_{el}^x + S_{Ag} - t_{NO_3^-}S_{AgNO_3}]\Delta T$$

In the last we have used $t_1 + t_2 = 1$ together with (4). Adopting the definition $(t_{Ag^+}S_{Ag^+}^x - t_{NO_3^-}S_{NO_3^-}^x) = \hat{S}_{AgNO_3}$ we obtain finally

$$F\frac{\Delta\phi}{\Delta T} = -\hat{S}_{AgNO_3} - S_{el}^x + S_{Ag} - t_{NO_3^-}S_{AgNO_3} \qquad (6)$$

The first two terms are entropies of transfer and the last two ordinary "thermostatic" entropies.

It is clear that in any such thermocell the single ion thermodynamic quantities connected with the electrode process will always combine with the single ion thermodynamic quantities involved in the homogeneous thermopotential so that the result will be free of these quantities. Only the entropies of transport involve single ion quantities.

The various terms of (6) may be evaluated as follows.

The entropy of silver metal at 500°K. is 13.35 e.u.[7] The entropy of $AgNO_3$ has been measured up to 25° by Pitzer, et al.[8] An extrapolation of their heat capacity data leads to an approximate value of 49.14 ± 1 e.u. at 500°K. We adopt the expression for S_{el}^x from Sommerfeld[9]

$$S_{el}^x = (2/3)S_{el}(1 - l'_r/l) \qquad (7)$$

By use of a third law integration of the Thomsen heat, Temkin and Khorosin[10] found l'_r/l for Ag to be 0.26 at room temperature. We assume that it is only weakly temperature dependent. The entropy of the electrons in the metal, S_{el}, is taken as that of a Fermi gas of the appropriate density[11]

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(6) J. Kirkwood and B. Crawford, Jr., *J. Phys. Chem.*, **56**, 1048 (1952).

(7) L. Quill, "Chemistry and Metallurgy of Miscellaneous Materials," McGraw-Hill Book Co., New York, N. Y., 1950.

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(9) G. Lepoutre, Dissertation, Yale University, 1953.

(10) M. Temkin and Khorosin, *J. Phys. Chem. U.R.S.S.*, **26**, 500 (1902).

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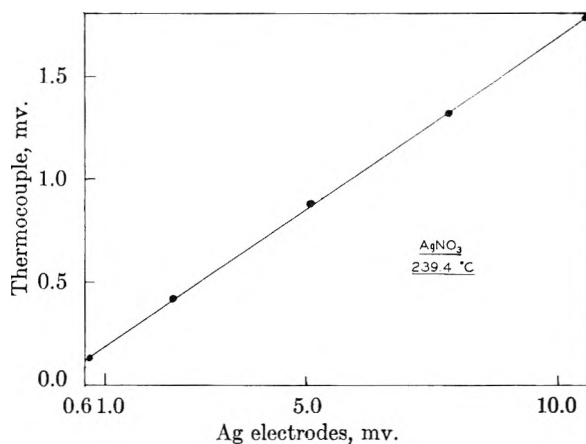
Fig. 2.
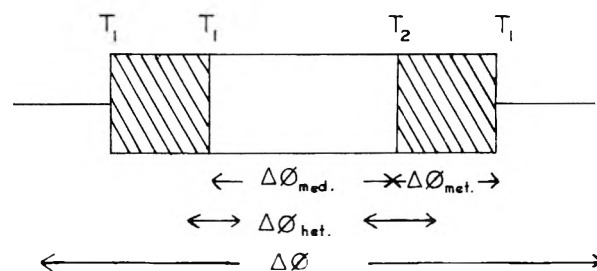
Fig. 3.

$$S_{el} = 4\pi^2 m k^2 T(\pi v/3N)^{2/3}/h^2 \qquad (8)$$

The value computed for S_{el}^x in this way is 0.03 e.u. at 500°K. Combining these values with the experimental thermopotential (6) becomes

$$-7.93 \text{ e.u.} = 13.35 - 0.635 \times 49.14 - \hat{S}_{AgNO_3} - 0.03 \qquad (9)$$

$$\hat{S}_{AgNO_3} = -9.95 \text{ e.u.}$$

We have assigned the value 0.635 to the transference number of the nitrate ion in molten $AgNO_3$. It is the value which is appropriate when the mass-average velocity serves as reference.[12]

Thomsen's second relation[5] can be used to calculate the Peltier heat π, from the thermoelectric power $\Delta\phi/\Delta T$

$$\pi = -T\Delta\phi/\Delta T$$
$$= 4.57 \text{ kcal./Faraday at } 305°$$

This relationship is obtained readily by examining the rate of production of entropy at the electrode/medium interfaces during an isothermal electrolysis. The Peltier heat is the heat absorbed (or evolved) when one Faraday of charge is passed through the cell, temperature gradients being eliminated by the use of an external thermostat. In the present case the sign indicates that the heat is absorbed at the cathode and evolved at the anode during electrolysis.

The expression (9) may be presented in the form

$$\hat{S}_{AgNO_3} = t_+ S_{Ag^+} - t_- S_{NO_3^-} + \hat{Q}_{AgNO_3}/T$$

where

$$\hat{Q}_{AgNO_3} = t_+ Q_{Ag^+}^{xx} - t_- Q_{NO_3^-}^{xx}$$

The symbols $\hat{S}_{AgNO_3}$ and $\hat{Q}_{AgNO_3}^{xx}$ denote the entropy and reduced heat of electrochemical trans-

(12) B. Sundheim, This Journal, **60**, 138 (1956).

port. $S^*_{AgNO_3}$ ($= S^*_{Ag^+} + S^*_{NO_3^-}$) and $Q^{**}_{AgNO_3}$ ($= Q^{**}_{Ag^+} + Q^{**}_{NO_3^-}$) would be the entropy and reduced heat of transport as they are used in theories of thermal diffusion.

Further progress cannot be made without the aid of highly speculative postulates. No meaningful operational definition of single ion entropies exists. The source of the difficulty is the fact that the process of electrical conduction through the ionic medium (the term involving $\hat{Q}_{AgNO_3}$) and the electrode reactions (the term in the single ion entropies) cannot be made to occur independently although they can be made to occur at different places. Many years ago Wagner[13] suggested that the single ion entropies in a 1:1 electrolyte be split equally between the two ionic species. Some slight justification for this assumption may be found in the fact that the long range electrostatic forces are more or less symmetrical in their effect on the quasi-lattice of the molten electrolyte. If we adopt this hypothesis tentatively we are led to a value of -1.66 kcal. for $\hat{Q}_{AgNO_3}$. This quantity denotes the heat carried from one electrode to the other per Faraday by the conduction process in the salt. (The reference plane taken here is that used for the transference numbers, i.e., the mass average velocity of the ions as defined by a porous plug.)

Discussion of the quantities of transport is made difficult by the fact that the connection between these quantities and the mechanisms of electrical and thermal conductivities is not well understood. With this in mind, we now address ourselves to the question of what kind of mechanistic information is obtainable from the data?

The fundamental source of the thermoelectric effect, the carrying of heat along with electricity and vice versa, is that the transport mechanisms of heat and electricity are inextricably coupled. In the case of metals this interaction is very direct, the diffusion of electrons being the transport agent in both cases and the coupling is expressed in the Franz–Wiedeman law[14] as well as in the thermoelectric powers.

In the molten salt case the coupling is less obvious—the flow of electricity takes place by the physical transport of charged ionic species, whereas the flow of heat takes place by two different types of mechanisms. On the one hand the drift of particles with a higher average kinetic energy to regions with lower average kinetic energy is the direct

mechanism. In condensed phases there is also a significant contribution to the heat current due to molecular interaction. Under this heading is included the so-called "potential transport" whereby ions transfer potential energy and work via long range forces.[15,16] Thus, if we picture a representative ion in a molten salt, the remaining ions are coupled to it by coulombic attraction and repulsion and experience a fluctuating force corresponding to the movements of this ion. Since the coulombic forces have a long range, this mechanism of transport is quite important in an ionic fluid. The electrical force is directly linked only to that part of the heat flow which is carried by direct migration.

Some insight into the heat of transport may be obtained if it is considered to arise in the following way.[17] The application of the external electrical field causes a displacement of the ions with respect to their ionic atmospheres, potential energy being initially absorbed in this process. The relaxation and consequent release of this potential energy occur a slight distance in the direction of motion of the ion. If this effect is considered to be more or less the same for the displacement of ions of either sign from their quasi-lattices then the net effect would be a transfer in the direction of the motion of the ion with the largest transference number. The Wagner hypothesis can thus be extended by assuming that the Q_i^{**} are equal. The value for the ionic heat of transport so calculated is 7.1 kcal./equivalent for either ion. The reason for the resultant net value of -1.66 kcal./Faraday is then seen as the result of the fact that the transference number of the anion is larger than that of the cation.

The mechanisms underlying the thermoelectric phenomena are those of the conduction of heat and electricity and of the electron transfer step at the electrode. The inadequacy of our understanding of these processes in so simple a case as a metal in contact with a one component fluid electrolyte presents a sharp challenge to theoretical electrochemistry.

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(14) G. Wiedemann and R. Franz *ibid.*, **89**, 497 (1953).

(15) J. Irving and J. Kirkwood, *J. Chem. Phys.*, **18**, 817 (1950). These authors give an expression for the heat of transport in terms of equilibrium molecular distribution functions and their perturbations. Unfortunately it involves quantities which cannot be evaluated in our present state of knowledge.
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THE REVERSING PULSE TECHNIQUE IN ELECTRIC BIREFRINGENCE

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Equations for the birefringence of a macromolecular solution in a rapidly reversed electric field are derived. The equations are plotted for various values of the electrical parameters of the molecule and the advantage of the reversing pulse method for determining these parameters is discussed. The effect of a time dependent polarizability and of polydispersity is considered. A more quantitative interpretation of O'Konski, *et al.'s* experimental data is made.

Introduction

The reversing pulse technique in electric birefringence, first introduced by O'Konski,[1] is an improved method for obtaining information about the electrical properties of macromolecules. An electric field is applied to a solution and the birefringence is measured in the usual manner,[2] then the electric field is rapidly reversed in sign. Qualitatively we can say that if there is no change in birefringence on field reversal, then the orienting torque on the molecules must be entirely due to a fast induced dipole moment. A change in birefringence, however, indicates either some permanent dipole or slow induced dipole contribution to the orienting torque. More quantitative conclusions cannot be made until equations relating molecular parameters to the observed birefringence are available.

These equations are derived in the present paper. They are presented graphically for various values of the molecular parameters. Direct comparison with experiment will thus give the desired quantitative description of the permanent and induced dipole moments of the molecules. These electrical properties in principle can be determined from the curves for the rise of the birefringence.[3,4] However, as will be seen from the figures the reversing pulse method is more accurate and convenient.

Theory

The derivation of the equations will only be sketched here as the formalism has been described before in a paper[4] which we shall refer to as I. The model used will be discussed in more detail, polydispersity will be considered, and some errors in I will be corrected. A more logical notation will be used.

A solution of non-interacting rigid macromolecules in an electric field will be considered. The non-interaction implies that the solutions are so dilute that the macroscopic properties of the solution, such as refractive index, dielectric constant, etc., are essentially those of the solvent. The magnitude of the field, E, will be such that the potential energy of a molecule in the field will be less than kT. This means that only terms up to E^2 need to be considered in the angular distribution function of the molecule.

The molecule is assumed to have roughly cylindrical symmetry (two rotary diffusion coefficients must be equal), but it need not be specified further.

This does not necessarily imply an ellipsoid of revolution. A rod, a flat disk, a string of beads, a cylinder with square cross section, etc., are included. This assumption is less stringent than that used in flow birefringence theories. The orienting torque in flow birefringence is hydrodynamic and only a few simple shapes have been treated theoretically. In the present experiment the orienting torque is electrical and is not dependent explicitly on the shape of the molecule. To relate the rotary diffusion coefficients to molecular dimensions, a specific model must be chosen, however.

Consideration of the completely general, arbitrary shape with three unequal rotary diffusion coefficients would be extremely difficult. This is the unsymmetric top problem; it does not have a solution in closed form.

The cylindrically symmetrical shape of the molecule imposes its symmetry on the polarizability. Both the electronic polarizability and the polarizability due to mobile protons on the surface of the protein[5] or to the ion atmosphere[1,2] should have the same symmetry as the molecule.

We, therefore, characterize a macromolecule by a rotary diffusion tensor with principal values $\Theta_{11} = \Theta_{22}$ and Θ_{33}. The rotary diffusion coefficient for rotation about the symmetry axis is Θ_{33}. The polarizability tensor is specified by $\alpha_{11} = \alpha_{22}$ and α_{33} along these same principal axes. The permanent dipole vector of the molecule has a completely arbitrary direction; it is specified by its components (μ_1, μ_2, μ_3) along the previously chosen axes.

All three above parameters (Θ, α, μ) will depend on the solvent. The rotary diffusion coefficient Θ is inversely proportional to the viscosity of the solvent.[6] The polarizability α is actually the polarizability increment of the solute, the difference in polarizability between solute and solvent. It is convenient to discuss α in two parts: α_E (electrical polarizability) and α_o (optical polarizability). The value of α_o simply depends on the shape of the molecule and the differences in refractive index of solvent (n) and those of the solute $(n_1 = n_2, n_3)$. This relation for ellipsoids of revolution may be found in I. The value of α_E may have various contributions. The electronic and atomic polarizability may be characterized by dielectric constants $(\epsilon_1 = \epsilon_2, \epsilon_3)$ and analogous equations for α_0 used. However, for a mobile ion contribution to the polarizability, general equations relating number and mobility of ions, and particle shape to

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(5) J. G. Kirkwood and J. B. Shumaker, *Proc. Natl. Acad. Sci.*, **38**, 855 (1952).

(6) This is not necessarily true for mixed solvents.

α_E are not yet available. Relations among the apparent dipole moment in solution, μ', the ideal, vacuum dipole moment μ, and the solvent properties are quite complex. We will ignore the problem by using the definition

$$\mu E_r = \mu' E$$

where E_r is the generally unknown, effective orienting field on the molecule and E is the measured, external field. Our subsequent equations will be written in terms of μ'. For simple, generally unrealistic models such as spheres[7] or ellipsoids[4] with point dipoles at their centers, equations for μ/μ' are available. These models are particularly inappropriate for large molecules whose dipole moments are primarily due to charges distributed over the periphery of the molecule. For example, inside a protein molecule with a conducting coating[8] the electric field would approach zero (a perfect conductor in an electric field has an inner field identically equal to zero) and produce no orienting torque on a point dipole inside. Molecules with a net charge introduce no difficulty as it is well known that the torque is equal to that on a molecule with a neutralizing charge at the center of drag.[5,9]

We have not discussed any orienting mechanism involving the conductivity of the solvent. These effects are complicated and will be omitted. Their inclusion would not change the form of our equations.

Equations.—The electric pulse and resulting birefringence are considered in three regions: I, rise; II, reverse and III, decay. The rise and decay curves were first derived by Benoit[3]; his model was extended in I. To obtain the birefringence, Δn, one must find the general angular distribution function $f(\theta, \chi, t)$ as defined in I.[10] Then for each region the appropriate conditions must be applied. These are: I, $f_I(t_I = 0) = 0$, $E = E$; II, $f_{II}(t_{II} = 0) = f_I(t_I \to \infty)$, $E = -E$; III, $f_{III}(t_{III} = 0) =$ any f, $E = 0$. Multiplying f by an optical factor which is the same for all regions, one obtains Δn.

At equilibrium in a static electric field

$$\Delta n_e = Ag(p_3 - p_1 + q) \qquad (1)$$

$A = 2\pi c E^2 / 15 n \rho$
Δn_e = equilibrium birefringence in electric field
c = concentration in g./ml.
$g = (\alpha_{0,33} - \alpha_{0,11})/v$
$\alpha_{0,33} - \alpha_{0,11}$ = anistropy of optical polarizability
v = volume of solute particle
E = field strength in e.s.u. volt/cm.
n = refractive index of solution
ρ = density of solute
$p_3 = (\mu'_3/kT)^2$
$p_1 = [(\mu'_1)^2 + (\mu'_2)^2]/2(kT)^2$
$q = (\alpha_{E,33} - \alpha_{E,11})/kT$
μ' = effective dipole moment
k = Boltzmann's constant
T = absolute temperature

The dynamic birefringence curves are much more useful when one normalizes them by dividing by Δn_e. Therefore, they will be presented thus

(7) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).
(8) C. T. O'Konski, *J. Chem. Phys.*, **23**, 1559 (1955).
(9) K. J. Mysels, *ibid.*, **21**, 201 (1953).
(10) The second plus in eq. 4 of I, which defines f, should be a minus.

I. **Rise**
(a) $5\Theta_{11} \neq \Theta_{33}$

$\Delta \equiv \Delta n/\Delta n_e = 1 - [3p_3/2(p_3 - p_1 + q)]e^{-2\Theta_{11}t}$
$+ [6\Theta_{11}/(5\Theta_{11} - \Theta_{33})][p_1/(p_3 - p_1 + q)]e^{-(\Theta_{11}+\Theta_{33})t}$
$+ [p_3/2 + p_1 - q - 6\Theta_{11}p_1/(5\Theta_{11} - \Theta_{33})][1/(p_3 - p_1 + q)]e^{-6\Theta_{11}t}$ (2)

(b) $5\Theta_{11} = \Theta_{33}$
$\Delta = 1 - [3p_3/2(p_3 - p_1 + q)]e^{-2\Theta_{11}t}$
$+ [(p_3/2 + p_1 - q + 6p_1\Theta_{11}t)/(p_3 - p_1 + q)]e^{-6\Theta_{11}t}$ (3)

II. **Reverse**
(a) $5\Theta_{11} \neq \Theta_{33}$
$\Delta = 1 - [3p_3/(p_3 - p_1 + q)]e^{-2\Theta_{11}t}$
$+ [12\Theta_{11}/(5\Theta_{11} - \Theta_{33})][p_1/(p_3 - p_1 + q)]e^{-(\Theta_{11}+\Theta_{33})t}$
$+ [3p_3 - 12\Theta_{11}p_1/(5\Theta_{11} - \Theta_{33})][1/(p_3 - p_1 + q)e^{-6\Theta_{11}t}$ (4)

(b) $5\Theta_{11} = \Theta_{33}$
$\Delta = 1 - [3p_3/(p_3 - p_1 + q)]e^{-2\Theta_{11}t}$
$[(3p_3 + 12p_1\Theta_{11}t)/(p_3 - p_1 + q)]e^{-6\Theta_{11}t}$ (5)

III. **Decay**

$$\Delta = e^{-6\Theta_{11}t} \qquad (6)$$

The previous equations are for the simplest case: a monodisperse system with fast induced dipole effects.

If there are slow induced dipole effects, the equations must be modified. A polarizability due to mobile ions which redistribute themselves over the surface of the molecule in a time of the same order of magnitude as $1/\Theta$ would cause these effects. The previous equations can be modified by adding the following terms: IA and IIA, rise and reverse (add to eq. 2, 3, 4, or 5)

(a) $6\Theta_{11}\tau_3 \neq 1$; $6\Theta_{11}\tau_1 \neq 1$
$- [6\Theta_{11}\tau_3 q_{i,33}/(6\Theta_{11}\tau_3 - 1)(p_3 - p_1 + q)]e^{-t/\tau_3}$
$+ [6\Theta_{11}\tau_1 q_{i,11}/(6\Theta_{11}\tau_1 - 1)(p_3 - p_1 + q)]e^{-t/\tau_1}$
$+ [6\Theta_{11}\tau_3 q_{i,33}/(6\Theta_{11}\tau_3 - 1)$
$- 6\Theta_{11}\tau_1 q_{i,11}/(6\Theta_{11}\tau_1 - 1)][1/p_3 - p_1 + q]e^{-6\Theta_{11}t}$ (7)

(b) $6\Theta_{11}\tau_3 = 1$; $6\Theta_{11}\tau_1 = 1$
$- [6\Theta_{11}t(q_{i,33} - q_{i,11})/(p_3 - p_1 + q)]e^{-6\Theta_{11}t}$ (8)
$q_{i,jj} = \alpha^i_{E,jj}/kT \; j = 1 \text{ or } 3$
$\alpha_{E,jj} = \alpha^e_{E,jj} + \alpha^i_{E,jj}(1 - e^{-t/\tau_j})$
$q = q_e + q_{i,33} - q_{i,11}$

$\alpha_{E,33}$; $\alpha_{E,11}$ = ionic components of the electrical polarizability along the symmetry and transverse axes, respectively
τ_3, τ_1 = relaxation times for these components
q_e, α_{eE} = electronic or atomic contributions.

If there is an ionic polarizability with a relaxation time short compared to the time of rotation of the molecule, then eq. 2-5 are correct as they stand.

The influence of polydispersity will be discussed in the succeeding section.

Results

The general equations in the preceding section are more useful if one considers special cases. If either $\Theta_{33} = \Theta_{11}$ or $\Theta_{33} \gg \Theta_{11}$, the equations are simplified considerably. The previous equations can be written as

1B. Rise $\Theta_{33} \gg \Theta_{11}$ or $\Theta_{33} = \Theta_{11}$
$\Delta = 1 - (3/2)\beta/(\beta + 1)e^{-2\Theta_{11}t}$
$+ (1/2)(\beta - 2)/(\beta + 1)e^{-6\Theta_{11}t}$ (9)

IIB. Reverse $\Theta_{33} \gg \Theta_{11}$ or $\Theta_{33} = \Theta_{11}$
$\Delta = 1 + [3\beta/(\beta + 1)][e^{-6\Theta_{11}t} - e^{-2\Theta_{11}t}]$ (10)

If $\Theta_{33} = \Theta_{11}$, then $\beta = \beta_0 = (p_3 - p_1)/q$
If $\Theta_{33} \gg \Theta_{11}$, then $\beta = \beta_p = p_3/(q - p_1)$

To use with eq. 9 and 10, eq. 1 can be written in the form

$$\Delta n_e = Ag(\beta_0 + 1)q \qquad (11)$$

$$\text{or} \quad \Delta n_e = Ag(\beta_p + 1)(q - p_1) \qquad (12)$$

Eq. 9 and 10 are plotted in Figs. 1,2 for various values of β. The rise curves have been given before by Benoit[3]; however, the advantage of the reversing pulse method is immediately apparent from the figures. The reversing pulse birefringence is much more sensitive to β than the rise, particularly for positive values of β. For example, a β of 0.1 would cause an easily apparent 10% dip in the birefringence on reversing the field, but would give a rise curve practically indistinguishable from $\beta = 0$.

As seen from the figures the position and magnitude of the various minima and maxima give a quick measure of the molecular parameters. The appropriate equations, obtained from the derivatives of eq. 9 and 10 for the time t_m at the extremum and the value of $\Delta(\Delta_m)$ at this time are

IC. Rise $\Theta_{33} \gg \Theta_{11}$ or $\Theta_{33} = \Theta_{11}$

$$t_m = \frac{\ln[(\beta - 2)/\beta]}{4\Theta_{11}} \qquad (13)$$

$$\Delta_m = 1 - \beta^{3/2}/(\beta + 1)(\beta - 2)^{1/2} \qquad (14)$$

IIC. Reverse $\Theta_{33} \gg \Theta_{11}$ or $\Theta_{33} = \Theta_{11}$

$$t_m = (\ln 3)/4\Theta_{11} \qquad (15)$$

$$\Theta_{11} = 0.2747/t_m \qquad (16)$$

$$\Delta_m = 1 - 2\beta/\sqrt{3}(\beta + 1) \qquad (17)$$

$$\beta = \frac{1 - \Delta_m}{0.1547 + \Delta_m} \qquad (18)$$

Eq. 13 shows that for the rise curve t_m depends on both β and Θ, and that there are no maxima or minima for positive values of β. For the reverse curve, however, t_m is independent of β. Therefore, both Θ_{11} (eq. 16) and β (eq. 18) can be obtained conveniently and rapidly. More accurate values can, of course, be obtained from a lengthy complete analysis of the reverse and decay curves.

Values of t_m and Δ_m cannot be obtained explicitly from the general equations with an arbitrary value of Θ_{33}. These values would depend on both rotary diffusion coefficients and all electrical parameters. However, special cases are again of interest. If $p_1 = 0$, then $\beta_0 = \beta_p = p_3/q$, and independent of the ratio Θ_{33}/Θ_{11} eq. 9 and 10 can be used instead of eq. 2–5. If $q = 0$, then the birefringence will depend on the ratios Θ_{33}/Θ_{11} and p_3/p_1. Figure 3 shows the results for one value of p_3/p_1 and five values of Θ_{33}/Θ_{11}. We notice that in general we have to know the ratio of the rotary diffusion coefficients before we can interpret the rise and reverse curves.

If there are slow induced dipole terms, many new combinations of effects become possible. We shall consider the case where a slow polarizability along the symmetry axis is the only important orienting factor. Figure 4 gives the results for four values of $6\Theta_{11}\tau_3$. Equations 2, 4, 7 and 8 were used with $p_1 = p_3 = q_e = q_{i,11} = 0$. It is apparent that a slow induced dipole can give results qualitatively like a permanent dipole. The shapes of the birefringence curves, however, are different.

For the reverse curve t_m and Δ_m are given by

IID. Reverse (only $q_{i,33}$ important)

(a) $6\Theta_{11}\tau_3 \neq 1$

$$t_m = \frac{\tau_3 \ln 6\Theta_{11}\tau_3}{(6\Theta_{11}\tau_3 - 1)} \qquad (19)$$
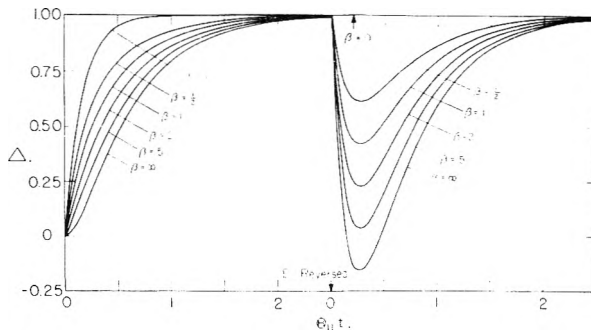
Fig. 1.—The rise and reverse birefringence plotted vs. $\Theta_{11}t$ for various positive values of β. If the rotary diffusion coefficients are equal, $\Theta_{33} = \Theta_{11}$, then $\beta = \beta_0 = (p_3 - p_1)/q$. If $\Theta_{33} \gg \Theta_{11}$, then $\beta = \beta_p = p_3/(q - p_1)$.
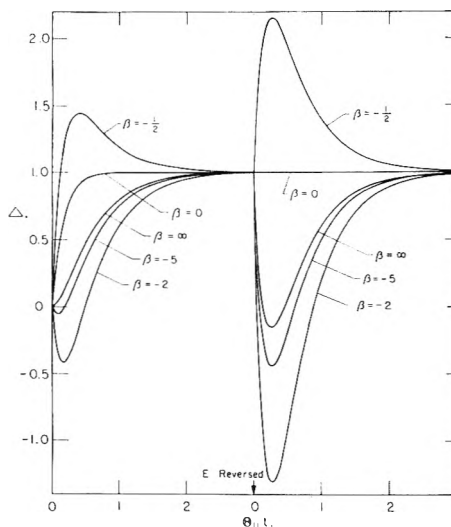
Fig. 2.—The rise and reverse birefringence plotted vs. $\Theta_{11}t$ for various negative values of β. The ratio Θ_{33}/Θ_{11} equals 1 or ∞.

$$\Delta_m = 1 - (6\Theta_{11}\tau_3)^{1/(1 - 6\Theta_{11}\tau_3)} \qquad (20)$$

(b) $6\Theta_{11}\tau_3 = 1$

$$t_m = 1/6\Theta_{11} \qquad (21)$$

$$\Delta_m = (1 - 1/e) \qquad (22)$$

Figure 4 and eq. 19–22 will be useful if, for a monodisperse system with $\theta_{33} \gg \theta_{11}$ or $\theta_{33} = \theta_{11}$, θ_{11} obtained from the minimum in the reverse curve does not agree with θ_{11} obtained from the decay curve. A non-zero value of τ_3 thus indicated, its magnitude could be estimated by direct comparison with Fig. 4.

Polydispersity.—All the previous equations have referred to monodisperse systems. Unfortunately these systems are very hard to find in macromolecular chemistry. For a polydisperse system the analysis of birefringence curves becomes difficult. We will consider the case where $\Theta_{33} \gg \Theta_{11}$ and the polydispersity is mainly in the length of similar molecules. Good examples are such systems as synthetic polypeptides or some TMV samples. For these molecules all $\rho_i = \rho$ and $g_i = g$. We will not include slow induced dipole effects. The equations now become

$$\Delta n_e = \sum_i \Delta n_{e,i} \qquad (23)$$
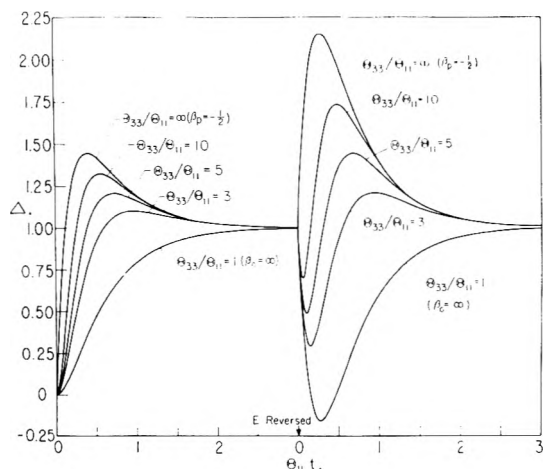
$$\Delta n_{e,i} = Agc_i(p_3 - p_1 + q)_i \qquad (24)$$

Fig. 3.—The rise and reverse birefringence plotted *vs.* $\Theta_{11}t$ for $q = 0$, $p_3/p_1 = 1/2$, and various values of Θ_{33}/Θ_{11}.
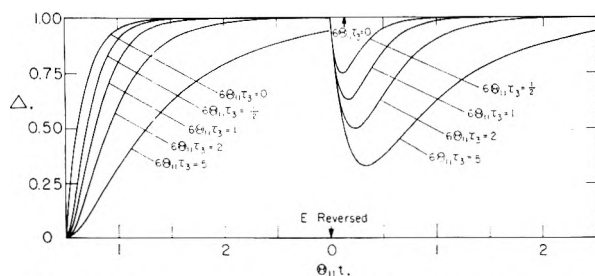

Fig. 4.—The rise and reverse birefringence plotted *vs.* $\Theta_{11}t$ for a time dependent polarizability along the symmetry axis of the molecule and no other orienting factors. The value of τ_3 characterizes the relaxation time of the polarizability.

Rise, reverse, or decay

$$\Delta n = \sum_i \Delta n_{e,i} \Delta_i \qquad (25)$$

$$\Delta_i = \begin{cases} \text{eq. 9 for rise} \\ \text{eq. 10 for reverse} \\ \text{eq. 6 for decay} \end{cases}$$

From eq. 23 and 24 it follows that the equilibrium birefringence for a polydisperse system gives a weight average value of the electrical parameters.

$$\langle p_3 - p_1 + q \rangle = \frac{\sum_i w_i (p_3 - p_1 + q)_i}{\sum_i w_i} \qquad (26)$$

$$w_i = \text{weight of component } i$$

Analysis of the reverse curve can be made by an approximate method. We can write the polydisperse reverse equation as[11]

IIE. Reverse

$$\Delta = \frac{\Delta n}{\sum_i \Delta n_{e,i}} = 1 + \frac{3 \sum_i c_i p_{3,i} [e^{-6\Theta_i t} - e^{-2\Theta_i t}]}{\sum_i c_i (p_3 - p_1 + q)_i} \qquad (27)$$

If we assume that this equation can be approximated by one with the same form as the monodisperse curve (eq. 10), *i.e.*, we substitute $\langle \Theta \rangle$ for Θ in eq. 10, we can obtain an average rotary diffusion coefficient $\langle \Theta \rangle$ from the equation for the extremum time.

(11) The subscript 11 has been dropped from the equations in this section for simplicity.

$$t_m = (\ln 3)/4 \langle \Theta \rangle \qquad (28)$$

The value of $\langle \Theta \rangle$ is a complicated average of the Θ_i involving the electrical properties of the molecules. If t_m is substituted into eq. 27 we obtain the value Δ at the extremum.

$$\Delta_m = 1 - \frac{3 \sum_i c_i p_{3i} B_i}{\sum_i c_i (p_3 - p_1 + q)_i} \qquad (29)$$

$$B_i = (3)^{-\Theta_i/2\langle \Theta \rangle} [1 - (3)^{-\Theta_i/\langle \Theta \rangle}] \qquad (30)$$

Calculation shows that when $0.5 < (\Theta_i/\langle \Theta \rangle) < 2$ then $0.3 < B_i < 0.38$ while for $\Theta_i/\langle \Theta \rangle$ outside these limits B_i falls rapidly to zero. Equation 27 can therefore be approximated by

$$\frac{\sum_i c_i p_{3,i}}{\sum_i c_i (p_3 - p_1 + q)_i} = (\sqrt{3}/2)(1 - \Delta_m) \qquad (31)$$

This equation is analogous to eq. 17 and 18 for a monodisperse system. Using eq. 31 and 26 one can therefore get a weight average p_3 for molecules with rotary diffusion coefficients within a factor of 2 of $\langle \Theta \rangle$. It should be emphasized that this treatment of the polydisperse reverse curve is only applicable if it has a shape similar to a monodisperse curve. If the experimental reverse curve has two minima for example then the previous discussion is not valid.

Information about the distributions (as distinct from averages) in polydisperse systems can be obtained from a method not involving a reverse pulse. This is the non-equilibrium pulse method. The birefringence is measured using pulses which are not long enough to allow the equilibrium orientation to be attained. The equation for the decay curves which result will be

$$\Delta n(T) = \sum_i \Delta n_{e,i} \Delta(T)_{i,\text{rise}} e^{-6\Theta_i t} \qquad (32)$$

where T is the pulse length. As $T \to \infty$, $\Delta(T) \to 1$ and the equation will reduce to eq. 25. The decay curves can be analyzed for 2 or 3 Θ_i and $\Delta n_{e,i}\Delta_{i,\text{rise}}$ in the usual manner.[12]

As the equation for $\Delta_{i,\text{rise}}(T)$ is eq. 9 with T substituted for t, a plot of $\Delta_{i,\text{rise}}$ *vs.* $\Theta_i T$ will give a value of β_i. Therefore using this method, values of β_i and Θ_i are obtainable for as many components as can be found in the decay curves.

Application.—There are two reports in the literature that one can analyze using these equations.

The common strain of tobacco mosaic virus shows no transient on field reversal and the sign of the electrical birefringence is the same as that of the flow birefringence.[1] The original authors therefore concluded that the permanent dipole orientation is negligible. They proposed that the orientation was due to a polarizable ion atmosphere with a relaxation time of order of magnitude 5×10^{-7} sec. In our notation this means $q \gg (p_3$ and $p_1)$ and $\tau_3 \cong 5 \times 10^{-7}$ sec.

Using the present equations we can make the following statements. Assuming that a 2% change

(12) C. T. O'Konski and A. J. Haltner, *J. Am. Chem. Soc.*, **78**, 3604 (1956).

in birefringence on field reversal would be noticeable, eq. 17 gives $-0.02 < \beta_p < 0.02$. The sign of the birefringence shows that $\beta_p \equiv p_3/(q - p_1)$ is positive so we need not consider the left side of the inequality. We can then conclude that $p_3 < 0.02 (q - p_1)$ and that $q > p_1$. No further knowledge of the relative magnitude of q and p_1 can be gained from these data. If we do assume, however, that p_3 and p_1 are negligible we can use eq. 19 and Fig. 4 to obtain $\tau_3 < 0.02/6\Theta_{11}$. As Θ_{11} was found to be[1,12] 333 sec.$^{-1}$, the relaxation time τ_3 must be less than 10^{-5} sec. We, therefore, have found upper limits for p_3 and τ_3 which agree with the previous workers; however, we cannot show that p_1 is negligible.

The Holmes Rib Grass strain of tobacco mosaic virus shows a large transient on reversing the field; the decay curve yields two rotary diffusion coefficients,[13] $\Theta_1 = 480$ sec.$^{-1}$ and $\Theta_2 = 200$ sec.$^{-1}$ The minimum in the reverse curve is characterized by values of[14] $t_m \cong 10^{-3}$ sec. and $\Delta_m \cong 0.1$. The minimum could be caused in principle either by a permanent dipole or by a slow induced dipole moment. We can rule out the slow induced dipole moment as its relaxation time τ_3, which mainly depends on the size and shape of the molecule, should be roughly equal to that of the common strain of the virus. We can then use eq. 28 and 31 to obtain $\langle \Theta \rangle \cong 280$ sec.$^{-1}$ and $\sum_i c_i p_{3,i} / \sum_i c_i \, (p_3 - p_1 + q)_1 \cong 0.8$. The value of $\langle \Theta \rangle$ from the minimum is consistent with the values of Θ_i from the decay curve; this lends confidence to the conclusion that for this strain the primary orientation is through a permanent dipole moment along the symmetry axis.

Discussion

The equations presented here can be used to obtain a great deal of information about macromolecules from dynamic electric birefringence

measurements. For each system a different set of equations will be useful, so no further discussion of special cases will be given.

We should like to point out that in I[4] no distinction of $5\Theta_{11} = \Theta_{33}$ was made; that is, I, eq. 12 applies only to $5\Theta_{11} \neq \Theta_{33}$. Furthermore, the induced dipole effect was treated incorrectly. In the present paper the equations (eq. 7 and 8) for a slow induced dipole effect were derived by solving the diffusion equation with a time dependent polarizability for the angular orientation function f. In the earlier work the time dependence had been put into the induced dipole term in the final birefringence equation. This procedure is not correct.[15] The proper equation to replace I, eq. 18, if a slow polarizability along the symmetry axis is the only important orienting factor, is

$$\Delta = 1 - e^{-6\Theta_{11}t} + [6\Theta_{11}\tau_3/(6\Theta_{11}\tau_3 - 1)][e^{-6\Theta_{11}t} - e^{-t/\tau_3}]$$

The notation used here, although different from I and Benoit's paper, is consistent with more recent work[16]; we believe it to be more logical. The subscript 3 (instead of 1) is most commonly used to designate symmetry axes. Use of double subscripts for tensor quantities and single subscripts for vector quantities is also widespread. Finally to keep our axis designation, yet to have a simple symbol for the optical polarizability per unit volume we have used g for this quantity instead of the very common $(g_1 - g_2)$.[17] This new symbol can also serve as a reminder that $g_1 - g_2$ refers specifically to ellipsoids of revolution while other shapes are included in the present equations.

Acknowledgment.—We wish to thank Prof. C. T. O'Konski and Dr. R. M. Pytkowicz for suggesting this problem. They and Mr. W. H. Orttung also provided many helpful discussions and suggestions.

(13) C. T. O'Konski and R. M. Pytkowicz, J. Am. Chem. Soc., **79**, 4815 (1957).

(14) R. M. Pytkowicz, Ph.D. Thesis, University of California, 1957.

(15) We wish to thank Prof. C. T. O'Konski for drawing this to our attention.

(16) I. Tinoco, Jr., and W. G. Hammerle, This Journal, **60**, 1619 (1956).

(17) A. Peterlin and H. A. Stuart, "Hand und Jahrbuch der Chemischen Physik," Vol. 8, Sect. 1B, Leipzig, 1943.

GAS CHROMATOGRAPHY WITH HYDROGEN AND DEUTERIUM[1]

By Carl O. Thomas[2] and Hilton A. Smith

Contribution from the Department of Chemistry, University of Tennessee, Knoxville, Tennessee

Partial resolution of the components of a hydrogen–deuterium mixture was obtained by gas-elution chromatography. The fixed phase was palladium deposited on quartz and the carrier gas was argon. The separation of the two components was less than that which might be expected from a comparison of the elution peaks for pure hydrogen and for pure deuterium. Thus, the partition coefficient for either component of the mixture is not independent of the presence of the other component. This conclusion was further verified by the fact that following a series of runs with hydrogen it was necessary to "condition" the column by several runs with deuterium before a reproducible value for the retention volume of deuterium could be obtained. The experimental results reported by Glueckauf and Kitt in which a sample of very pure deuterium was obtained by the displacement and by the frontal techniques was verified.

Martin and Synge[3] suggested that the chromatographic technique might be applicable to the separation of isotopes; however, there have been only a

few attempts to apply the method to isotope separations. Glueckauf, Barker and Kitt[4] reported the enrichment of lithium isotopes by ion-exchange chromatography and of neon isotopes by adsorption chromatography at low temperatures. Com-

(3) A. J. P. Martin and R. L. M. Synge, Biochem. J., **35**, 1358 (1941).

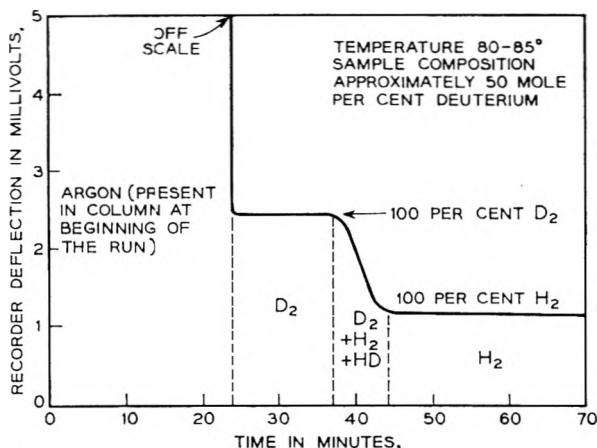(4) E. Glueckauf, K. H. Barker and G. P. Kitt, Disc. Faraday Soc., **7**, 199 (1949).

Fig. 1.—Recorder trace for separation of deuterium from hydrogen by displacement chromatography.
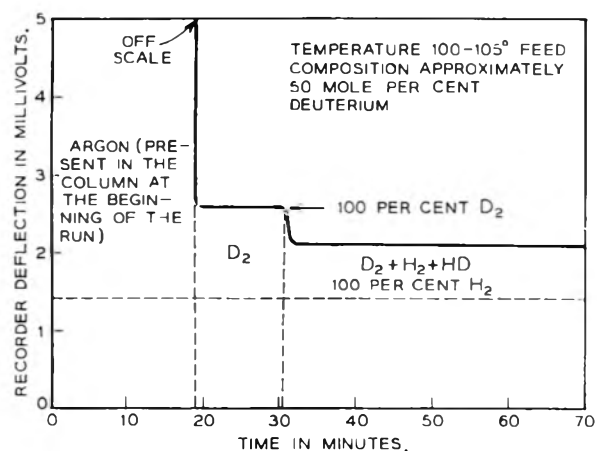

Fig. 2.—Recorder trace for separation of deuterium from hydrogen by break-through chromatography.
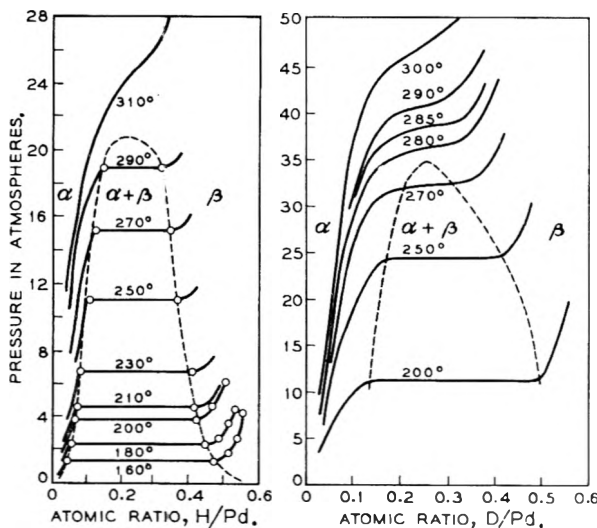

Fig. 3.—Distribution isotherms for the hydrogen–palladium and the deuterium–palladium systems.

plete separation was not accomplished. Spedding, Powell and Svec[5] described a method for separating nitrogen isotopes by ion exchange. Glueckauf and Kitt[6] reported the preparation of very pure sam-

(5) F. H. Spedding, J. E. Powell and H. J. Svec, *J. Am. Chem. Soc.*, **77**, 1393 (1955).

ples of deuterium by displacement and by frontal techniques in a column containing palladium on asbestos as the fixed phase. Their results were verified and the investigation was extended to include elution chromatography of hydrogen and deuterium.

Experimental

Apparatus.—The apparatus consisted of a column fashioned from a single piece of copper tubing 43-ft. in length and with an inside diameter of $^7/_{32}$ in. After the column was packed it was folded several times until its over-all length was approximately 5 feet. It was then placed in an electrically heated glass tubing jacket which was insulated with ordinary pipe insulation.

The column packing consisted of 7 g. of palladium metal deposited on 40–60 mesh flint quartz. To prepare the packing a slurry of the quartz in a solution of palladium chloride was evaporated to dryness. The mixture was then packed into the column and the salt reduced to the metal by sweeping the column with hydrogen at 150°.

The carrier gas was argon which could be introduced directly into the column or could be by-passed through a small sample cell of known volume. A multiple-section mercury manometer, capable of indicating pressures to 60 p.s.i.g. was used to measure input pressures. The output pressure was that of the atmosphere. Gas flow rates were monitored by means of calibrated capillary orifices. Flow rate data used in calculations were obtained by means of a soap-film meter attached at the output side of the system.[7]

To prepare hydrogen–deuterium samples of known size and composition, the sample cell was first evacuated. Hydrogen and deuterium gas were then admitted successively and after each addition of gas the pressure in the cell was measured by means of a mercury manometer. The argon carrier gas then was diverted to sweep the entire sample into and through the column.

The detector was a symmetrical double-cell katharometer with thermistor sensing elements. The body of the katharometer was machined from a large piece of solid brass which had sufficient heat capacity to eliminate thermal transients. The average temperature of the katharometer was kept below 30° by means of a copper cooling coil which was soldered directly to the brass block. Without this cooling coil heat conduction from the column caused overheating of the katharometer. No additional temperature regulation was necessary.

The effluent gas from the column was passed through the measuring side of the katharometer, while the reference side was connected to the argon supply through a capillary leak and a needle valve.

The record of a run was obtained by means of a Wheatstone bridge circuit and a potentiometer recorder.

Materials.—The argon carrier gas was obtained from The Matheson Company and from the Welding Gas Products Company. No difference in operation was observed as a result of changing the source of the argon. Ordinary commercial tank hydrogen was obtained from the National Cylinder Gas Company. Deuterium, reported to be 99.5% pure, was obtained from the Stuart Oxygen Company. Nitrogen, which was sometimes used as an internal marker for the hydrogen and the deuterium samples, was obtained from the National Cylinder Gas Company. All gases were used without further purification.

The flint quartz was obtained from Whittaker, Clark and Daniels, Inc.

A matched pair of mounted thermistors, manufactured by the Victory Engineering Corporation, was used in the katharometer.

Results and Discussion

Displacement and Break-through Experiments.— Glueckauf and Kitt[6] reported the separation of hydrogen and deuterium by displacement chromatography in a column containing palladium supported

(6) E. Glueckauf and G. P. Kitt in D. H. Desty, "Vapor Phase Chromatography," Butterworths Scientific Publications, London, 1957, p. 422.

(7) A. I. M. Keulemans, "Gas Chromatography," Reinhold Publ. Corp., New York, N. Y., 1957, p. 56.

on asbestos as the fixed phase. They also performed some experiments using the break-through technique, which is analogous to classical chromatographic frontal analysis. For the work discussed in this report, some separations were performed by both methods in order to obtain general information on the characteristics of the column and to obtain data for a direct comparison of the results with those of Glueckauf and Kitt.

Figure 1 illustrates the results of a typical displacement run. The recorder reading for 100% deuterium concentration was determined by passing hydrogen through the reference side of the cell, and deuterium through the sensing side of the cell. Hydrogen was used both as the carrier and as the reference gas.

For break-through experiments hydrogen and deuterium were fed simultaneously to the column until the feed composition appeared in the effluent. The feed composition, an approximately equimolar mixture of hydrogen and deuterium, was determined by the relative flow rates of the two gas streams through calibrated capillary orifices. Figure 2 shows a typical recorder trace for a break-through experiment. Hydrogen was used as the reference gas.

Prior to each type of run the column was swept with argon until essentially no hydrogen remained in the column. The data presented in Figs. 1 and 2 are in agreement with the results reported by Glueckauf and Kitt.

Distribution Isotherms and Column Desorption Experiments.—The distribution coefficient, k, is defined by equation 1

$$k = \frac{\text{concn. of solute in the fixed phase}}{\text{concn. of solute in the mobile phase}} \quad (1)$$

For a linear distribution isotherm k is a constant equal to the slope of the isotherm. A linear distribution isotherm is usually more desirable than either type of non-linear isotherm for elution chromatography since symmetrical peaks are produced and separations are obtained more easily.

Typical distribution isotherms for the hydrogen–palladium[8] and the deuterium–palladium[9] systems are shown in Fig. 3. It can be seen that these isotherms exhibit the characteristics of both types of non-linear isotherms. The data points for these isotherms represent equilibrium conditions. Gillespie and Hall[10] were able to accelerate the attainment of equilibrium by the use of a 360° heat treatment prior to each measurement. Nace and Aston[11] used an extremely finely divided palladium black, but still found that two to six hours was required to reach pressure equilibrium after the addition of an increment of hydrogen to the system at room temperature.

In a chromatographic column the equivalent of hundreds of equilibrations may occur in a relatively short time. It is evident therefore that the isotherms shown in Fig. 3 may possibly be quite

(8) H. Bruning and A. Sieverts, *Z. physik. Chem. (Leipzig)*, **A163**, 432 (1933).

(9) L. J. Gillespie and W. R. Dowrs, *J. Am. Chem. Soc.*, **61**, 2501 (1939).

(10) L. J. Gillespie and F. P. Hall, *ibid.*, **48**, 1207 (1926).

(11) D. M. Nace and J. G. Aston, *ibid.*, **79**, 3619 (1957).
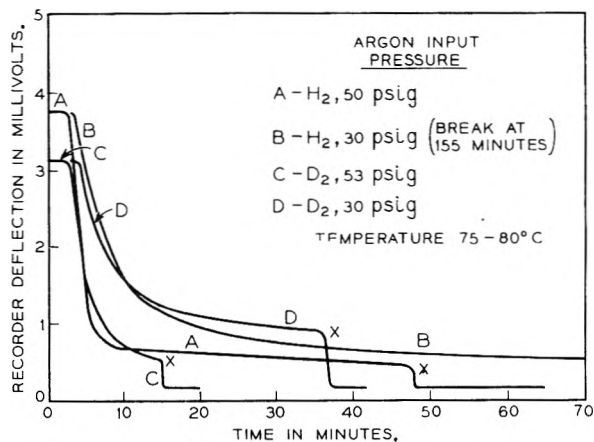
Fig. 4.—Column desorption curves for hydrogen and deuterium at 75–80°.
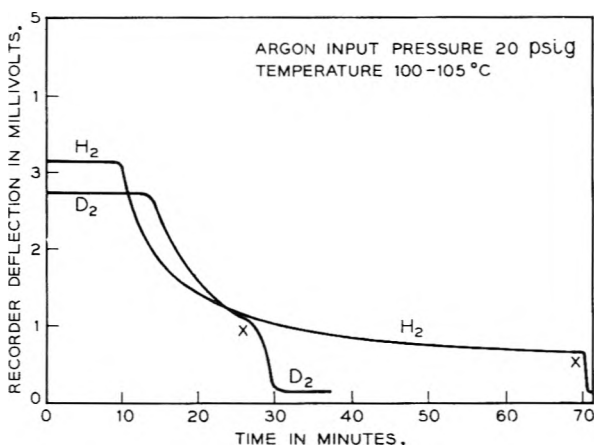
Fig. 5.—Column desorption curves for hydrogen and deuterium at 100–105°.
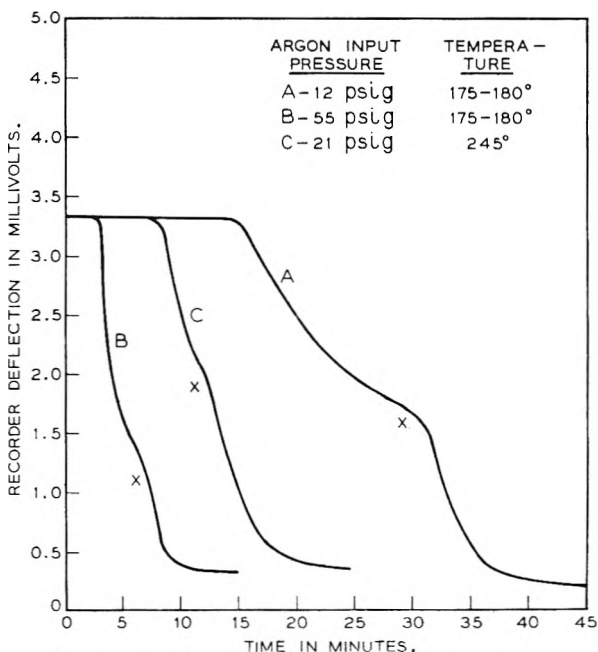

Fig. 6.—Column desorption curves for hydrogen at 175–180° and at 245°.

different from the effective distribution isotherms which are applicable to a chromatographic column containing palladium as the fixed phase.
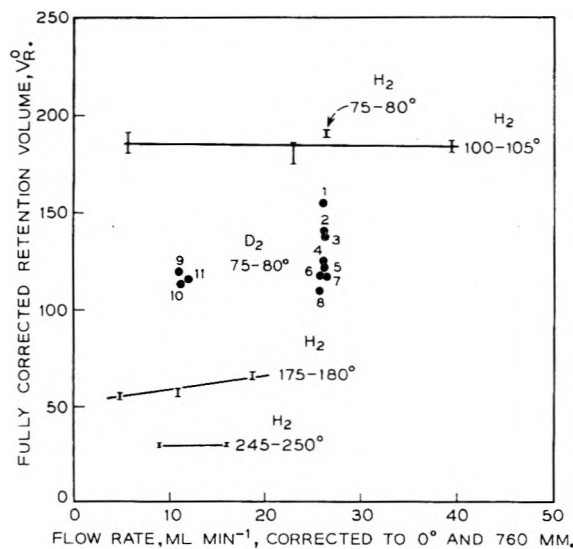
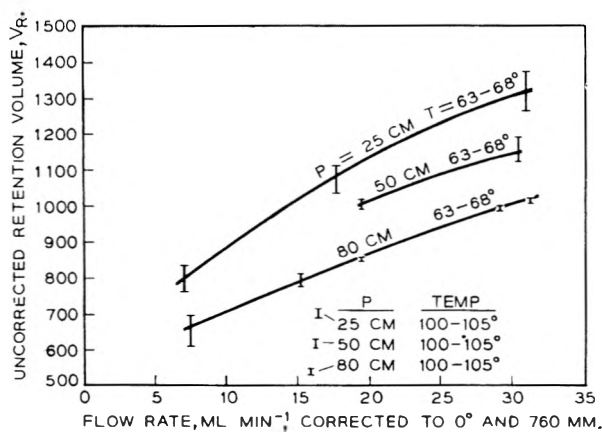Fig. 7.—Fully corrected retention volumes for hydrogen and for deuterium.

Fig. 8.—Effect of sample size upon uncorrected retention volume for hydrogen.

The following desorption experiments were performed in an attempt to obtain information regarding the nature of the effective distribution isotherms and to determine whether the column operated as an adsorption column or as a partition column with the hydrogen gas actually dissolved in the palladium metal.

Hydrogen was injected continuously at a constant pressure into the column. Argon was used as the reference gas. After a time the katharometer recorder indicated the break-through of hydrogen. At this point the mobile phase in the column was hydrogen. The column was then swept with the argon carrier until the recorder trace showed that the gas leaving the column was essentially pure argon. Similar experiments were performed with deuterium. The hydrogen and the deuterium samples were injected at a constant input pressure of 10 p.s.i.g. The flow rate during the desorption portion of the run was fixed by the argon input pressure.

A typical set of column desorption curves for hydrogen and for deuterium are shown in Figs. 6, 7 and 8. There are two distinct portions of these curves which are separated by the breaks at points X. On either side of X the tailing is characteristic

of a distribution isotherm which is concave toward the axis of the mobile phase. The equilibrium distribution isotherms for the hydrogen–palladium and for the deuterium–palladium systems have two regions of concavity toward the pressure axis. It therefore appears possible that the steps which are present in the desorption curves may correspond to the transition between the α-phase and the β-phase. The upper portion of the curves would correspond to desorption from the β-phase and the lower portion would correspond to desorption from the α-phase.

If the above interpretation is correct, it follows that in the column the rate of diffusion of hydrogen and deuterium within the metal is sufficiently rapid for the α- and β-phase solutions to form. Hence the metal acts as a solvent for the gas, and the column may be considered as a partition column. If the rate of diffusion within the palladium metal were too slow for H–Pd and D–Pd solutions to form, the desorption curves should not show the breaks at points X. The rapidity of the solution process is probably a result of the very finely divided state of the palladium metal in the column. If the metal were assumed to have formed a smooth coating of uniform thickness on the quartz particles, it can be shown that this coating would be only some 20 molecules thick. It appears more probable that the reduction process at a temperature of only 150° may have formed a very finely divided powder which would also have a large surface development.

The Retention Volume.—Littlewood, Phillips and Price[12] have defined a fully corrected retention volume, V_R^0

$$V_R^0 = \frac{3}{2}(t_s - t_i)F\left[\frac{(P/P_0)^2 - 1}{(P/P_0)^3 - 1}\right] \qquad (2)$$

where t_s and t_i are, respectively, the retention times of the sample and of a gas not retarded by the column packing, F is the volume flow rate at the column exit, and P/P_0 is the input/output pressure ratio.

The retention volumes of hydrogen and of deuterium were determined using a sample-cell volume of 1.32 ml. The sample size was varied by varying the sample pressure in the cell. Each sample contained nitrogen at a partial pressure of approximately 3 cm. The nitrogen provided a marker so that fully corrected retention volumes could be calculated. Flow rates were corrected to 0° and 760 mm. after correcting for the vapor pressure of water in the soap-film flow meter.

Figure 7 illustrates the effect of temperature and of flow rate upon the corrected retention volume. For correction to the column temperature the value of V_R^0 must be multiplied by $T/273$, where T is the column temperature indicated in the figure. The sample pressure was 80 cm. for these runs. Horizontal lines indicate the range of flow rate values and vertical lines indicate the precision of the retention volume measurement.

The retention volume for a given set of conditions is dependent upon the previous history of the column. The numbered data points in Fig. 7 for the retention volume of deuterium at 75–80° indi-

(12) A. B. Littlewood, C. S. G. Phillips and D. T. Price, *J. Chem. Soc.*, 1480 (1955).
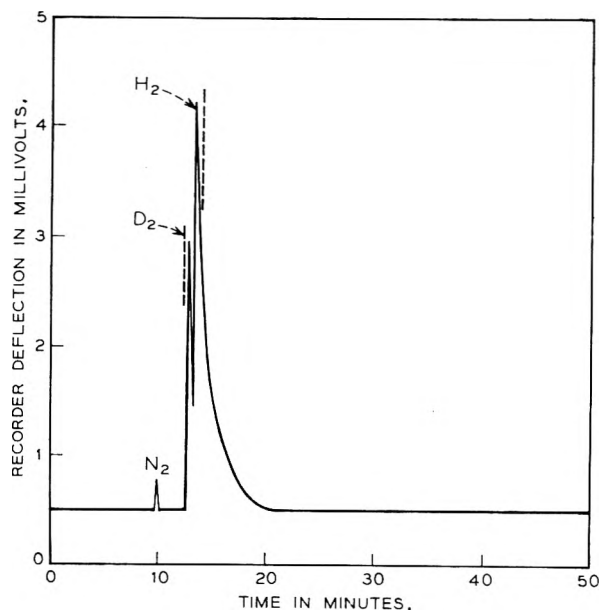
Fig. 9.—Partial separation of deuterium from hydrogen by elution chromatography with palladium as the fixed phase.

cate the sequence of the experiments which followed a series of experiments with hydrogen. The elapsed time for each experiment was approximately 45 minutes. In order to obtain reasonably reproducible values of the retention volume, it was necessary to "condition" the column by sweeping several hydrogen or deuterium samples through it and to maintain a fixed time interval between runs.

Figure 8 illustrates the effect of sample size upon the retention volume. The sample size was 1.32 ml. at the pressures and temperaturs indicated in the figure. These values could not be corrected since the data were obtained early in the investigation before the input pressure manometer was installed and before arrangements were made for introducing nitrogen markers. Thus the retention volumes shown in Fig. 8 are simply the product of the retention time, measured from the start of the runs to the leading edge of the elution peaks, and the corrected flow rate. Nevertheless the effect of sample size is shown.

Elution Chromatography of Hydrogen Isotopes.— The distribution coefficient, k, was defined by equation 1. The separation factor α for two components of a sample is defined as the ratio of the distribution coefficients for the two components. In ideal elution chromatography, two components will be separated if the value of α is different from unity and if the column contains a sufficient number of theoretical plates. An additional condition for ideal chromatography is that the value of the distribution coefficient for a component must be unaffected by the presence of other sample components.

The equilibrium separation factor in the hydrogen–deuterium–palladium system has been shown to be different from unity. The difference in the retention volumes for hydrogen and deuterium in a palladium packed column, which are given for a typical set of conditions in Fig. 7 shows that the non-equilibrium separation factor also is different from unity. Additional evidence is the separa-

tion of hydrogen and deuterium by the breakthrough and the displacement techniques, which was reported by Glueckauf and Kitt[6] and confirmed in the present work.

Although hydrogen and deuterium elution peaks exhibit tailing, which makes separation more difficult by the elution technique, an attempt was made to separate at least partially the two isotopes by elution chromatography using argon as the carrier gas.

Experimentally it is difficult to isolate the contribution of each parameter to the observed separation. For example at constant temperature the flow rate and the input–output pressure ratio are interdependent. In order to circumvent the necessity for evaluating the contribution of each parameter, a factorial-design experiment was conducted to cover the range of the pertinent variables. Figure 9 illustrates the best separation obtained in this factorial experiment. The conditions under which this curve was obtained were

Column length	43 feet
Palladium content	7 g.
Sample size	4.37 ml. at 100 cm.
Temperature	175–180°
Input pressure	50 p.s.i.g.
Gas flow rate	60 ml. min.$^{-1}$

The dotted lines in the figure indicate the average location of hydrogen and of deuterium peaks for pure samples run under the same conditions. It can be seen that the distribution isotherms for hydrogen and for deuterium are not independent of each other and that the separation is not as large as would be expected from the properties of the peaks for the pure samples. Additional evidence for this conclusion already has been discussed in connection with Fig. 5.

The temperature could be varied between approximately 150 and 190° before the peaks merged. At lower temperatures the peaks were too broad to distinguish any resolution which might have occurred. At higher temperatures the peaks were sharp, but no resolution was distinguishable, probably because the separation factor decreases with increasing temperature.

The Separation Factor.—Figure 10 shows the relationship between the separation factor and the temperature. Glueckauf and Kitt[6] obtained an expression for the temperature dependence of the separation factor

$$\log \alpha = 215/T - 0.47$$

where T is the temperature in degrees Kelvin. The data obtained in the present work give an expression

$$\log \alpha = 222/T - 0.51$$

The temperature coefficients in both cases are similar to that observed by Gillespie and Downs,[13] but the absolute values are different.

James and Phillips[14] have shown how the distribution isotherm and consequently the partition coefficient may be determined by the chromatographic displacement technique. The method is applicable only for systems which exhibit isotherms

(13) L. J. Gillespie and W. R. Downs, *J. Am. Chem. Soc.*, **61**, 2496 (1939).

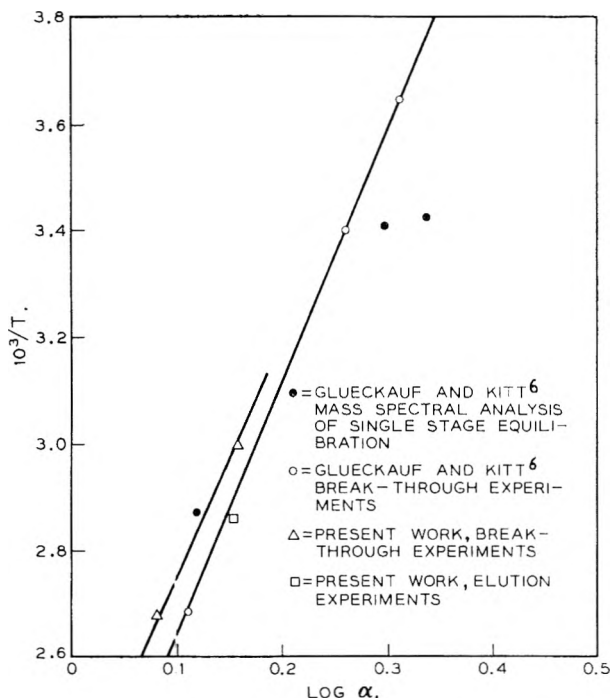(14) D. H. James and C. S. G. Phillips, *J. Chem. Soc.*, 1066 (1954).

Fig. 10.—Temperature dependence of deuterium–hydrogen separation factor in a chromatographic column with palladium as the fixed phase.

concave toward the pressure axis. For this type of isotherm the partition coefficient may vary along the length of the column as a function of pressure. Thus for exactness the method should be restricted to the limiting case where the ratio of the input–output pressures approaches unity.

The number of theoretical plates in the column is not involved in the calculation of the partition coefficient from displacement data. Thus the only advantage to increasing the length of the column beyond that required to establish the zones is to increase the size of the sample which may be handled.

In like manner the break-through technique is suitable only for the study of systems involving distribution isotherms which are concave toward the pressure axis; however, with the break-through technique the retention time becomes larger as the column length is increased. Thus the break-through technique offers an advantage over the normal equilibration technique for the determination of partition coefficients. The detector sensitivity is not involved in the calculation of k from break-through data. In addition there is no necessity for direct analysis of the composition of the fixed phase.

Anderson,[15] and Porter, Deal and Stross[16] have discussed methods for the determination of the partition coefficient from elution chromatographic data. Although the calculation is strictly valid only for a system involving linear isotherms, it was used to calculate the partition coefficient and thus the separation factor at one temperature as is shown in Fig. 10. Considering the assumptions which are necessary in the calculation, the agreement with the single-stage equilibrium measurement at approximately the same temperature is good.

It should be pointed out that the break-through experiments were carried out with mixed hydrogen and deuterium samples while the separation factor calculated from elution data was based on separate runs with hydrogen and with deuterium, and that a number of runs were made with each before a reproducible value of V^0_R was obtained. This fact probably accounts for the higher value of the separation factor obtained from elution data as compared with that obtained from the break-through data, and also for the better agreement between the values obtained from the break-through experiment and the single stage equilibration.

Conclusions

The partial separation of hydrogen isotopes by displacement, break-through, and elution chromatographic techniques has been accomplished. Complete separation of the isotopes was not accomplished by any of the techniques. All three methods involve batch operation and are therefore not particularly well suited for preparative processes without further modification. Since, however, the separation factor has been shown conclusively to be different from unity, continuous separation of the isotopes might possibly be accomplished by a technique similar to the hypersorption process.[17,18] A very recent communication[19] indicates that elution peaks for hydrogen (H_2) and deuterium (D_2) gas are sufficiently separated when an alumina column at 77.4°K. is used so that separation may be possible under these circumstances; however, the presence of HD in the gas may cause difficulty. When palladium is employed in the column, an equilibrium between H_2, D_2 and HD is maintained, so that the HD is converted into the pure isotopes as the H_2 and D_2 become separated in the column.

(15) J. R. Anderson, *J. Am. Chem. Soc.*, **78**, 5692 (1956).

(16) P. E. Porter, C. H. Deal and F. H. Stross, *ibid.*, **78**, 2999 (1956).

(17) C. L. Mantell, "Adsorption," 2nd ed., McGraw–Hill Book Co., Inc., New York, N. Y., 1951, Chapter 16.

(18) M. Freund, P. Benedek and L. Szepesy in D. H. Desty, "Vapour Phase Chromatography," Butterworths Scientific Publications, London, 1957.

(19) W. R. Moore and H. R. Ward, *J. Am. Chem. Soc.*, **80**, 2909 (1958).

HETEROGENEOUS FLASH INITIATION OF THERMAL REACTIONS[1]

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Heterogeneous flash initiation is a widely applicable technique for initiating thermal reactions. The only requirements are: (1) a very intense light source, in our case a flash lamp which produces light pulses of several milliseconds duration, and (2) a finely divided light-absorbing material (particles, filaments or foils) suspended in (3) a reasonably transparent poor thermal conductor. The radiant flux (near ultraviolet, visible and near infrared) is mainly converted to heat at the absorbing surface, causing local temperature rises which depend on the incident light intensity and the rate of energy dissipation. For materials of smallest dimension near 10 μ these temperature rises approach 2000° in condensed phase insulators and 5000° *in vacuo* or low pressure gases for the experimental conditions used. Calculated temperature rises agree with experiment. Thermal reactions have been initiated at solid surfaces surrounded by a vacuum, gases, liquids and transparent polymers, resulting in vaporization, melting, pyrolysis, explosion and other rapid reactions. Because of the short initiation times required, flash heating should find application analogous to flash photolysis and shock tube techniques for producing labile intermediate species in rapid reaction studies.

Introduction

Earlier work by the authors[2] has shown that tiny dark particles suspended in a transparent polymeric matrix can be heated to very high temperatures by black-body absorption of intense flashes of light. During this heating, the temperature of the matrix rises sharply, and pyrolysis occurs. Here we shall show that this flash heating is a rather general phenomenon which may be used to initiate many thermal reactions at temperatures and on a time scale not easily attainable by other means. The requirements for such initiations are simply (1) a very intense light source, in our case a capacitor-discharge flash lamp, (2) a finely divided dark material in the form of particles, filaments or foils suspended in (3) a fairly transparent poor thermal conductor. The thermal reactions may occur in the insulating matrix, as in the case of the polymer pyrolysis, or may involve the finely divided material, or some combination of the two.

We have used the technique to obtain intense rapid heating at solid surfaces surrounded by vacuum, gases, liquids and transparent polymers. In some cases we have explosively evaporated tungsten powders and wires *in vacuo* with subsequent deposition of heavy films, an indication that instantaneous temperatures approaching several thousand degrees centigrade are readily obtainable in our flash times of several milliseconds.[2b] It is thus possible to initiate flash pyrolyses, carbon formation, explosions, evaporations, meltings and other thermal processes in systems without discrete photochemical absorption in a manner somewhat parallel to the flash photolysis technique[3] which has been applied successfully to the preparation of labile molecules for kinetic spectroscopy[4] or rapid mass spectrometry.[5] In gases, the method produces effects similar to shock tube pyrolyses[6] but with a considerably larger instantaneous volume of labile intermediates, which should simplify kinetic measurements and end-product analyses.

Procedure.—The system for irradiating the samples is shown schematically in Fig. 1. We used spiral flash lamps[7] very similar to Christie and Porter's Type III.[8] The lamps were made of fused silica and filled with xenon at about 70 mm. pressure. In order to obtain maximum incident flux, the lamp was surrounded by an aluminum cylinder coated inside with magnesium oxide. This type of flash lamp emits very nearly a flat continuum extending from the near ultraviolet through the visible into the near infrared region of the spectrum.[9] The lamp output between 2000 and 4000 Å. was shown by uranyl oxalate actinometry[8,10] to be 10^{19}–10^{20} quanta flash^{-1} cm.$^{-2}$ for flashes of several milliseconds duration,[2b] depending on the capacitance used.

The lamp was powered by a commercial photographic capacitor bank and power supply[11] capable of charging to 4 kv. capacitances of 36 to 1296 μF., variable in 36 μF. steps. The materials to be irradiated were enclosed in No. 7740 chemical Pyrex tubes of $^1/_2$ in. diameter, which were flashed while suspended along the spiral axis of the lamp.

Experimental Results

In this section we shall describe a number of experiments which indicate the applicability of heterogeneous flash initiation to thermal processes. We shall discuss them according to the phase of the insulating matrix. All flash energies E have been calculated from $E = ^1/_2CV^2$, where C is the capacitance and V is the charging voltage (always 4 kv.).

Solid-Vacuum Experiments.—The simplest thermal reaction was the evaporation of a finely divided dark-colored material suspended *in vacuo*. With one flash at 5184 j. we evaporated sieved Ag, C, Cr, Mo, Ni, W and Zn of particle diameter below 100 μ suspended on the walls of an evacuated Pyrex tube. The lower boiling metals, such as Zn and Ag completely gasify at the lower energies of 2592 j./flash, laying down heavy, smooth mirrors, while the higher boiling metals such as Mo and W, are more difficult to evaporate in powder form and require about 10,000 j./flash for heavy depositions of metal. Tungsten wire of 7.5 μ diameter, when tangled into a wool and suspended in an evacuated $^1/_2$ in. diameter Pyrex tube, evaporated somewhat at 2592 j./flash and explosively at 5184 j./flash. Amorphous and graphitic carbon powders ($<100~\mu$ diameter) also evaporated quite easily on flashing at 5184 j./flash with deposition of heavy mirrors of carbon, and considerable internal crazing inside the Pyrex tube in which it was suspended. (The crazing is quite common in these experiments, occurring at the higher energies per flash with many materials; it never has caused shattering or leakage of the tubes, however.)

(1) Presented before the American Chemical Society, Chicago, September, 1958.

(2) (a) J. L. Lundberg and L. S. Nelson, *Nature*, **179**, 367 (1957); (b) J. L. Lundberg, L. S. Nelson and M. Y. Hellman, "Proc. Third Conference on Carbon," Buffalo, N. Y., 1957, in press.

(3) G. Porter, *Proc. Roy. Soc. (London)*, **A200**, 284 (1950); G. Herzberg and D. A. Ramsay, *J. Chem. Phys.*, **20**, 347 (1952); R. Marshall and N. Davidson, *ibid.*, **21**, 659 (1953).

(4) R. G. W. Norrish and B. A. Thrush, *Quart. Rev. (London)*, **10**, 149 (1956).

(5) G. B. Kistiakowsky and P. H. Kydd, *J. Am. Chem. Soc.*, **79**, 4825 (1957).

(6) E. F. Greene, R. L. Taylor and W. L. Patterson, Jr., THIS JOURNAL, **62**, 238 (1958).

(7) Prepared by the General Electric Co., Lamp Division, Cleveland, Ohio.

(8) M. I. Christie and G. Porter, *Proc. Roy. Soc. (London)*, **A212**, 390 (1952).

(9) M. I. Christie and G. Porter, *ibid.*, **A212**, 398 (1952).

(10) G. S. Forbes and L. J. Heidt, *J. Am. Chem. Soc.*, **56**, 2363 (1934).

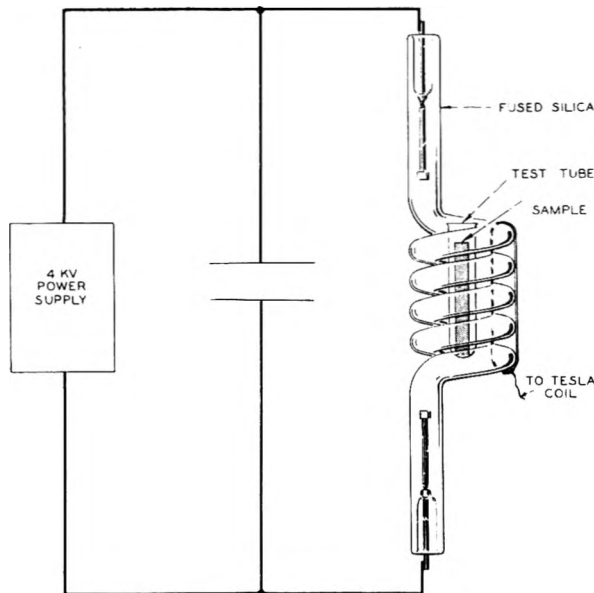(11) Obtained from the Edgerton, Germeshausen and Grier Corp., Boston, Mass.

Fig. 1.—Circuit and lamp for flash heating.

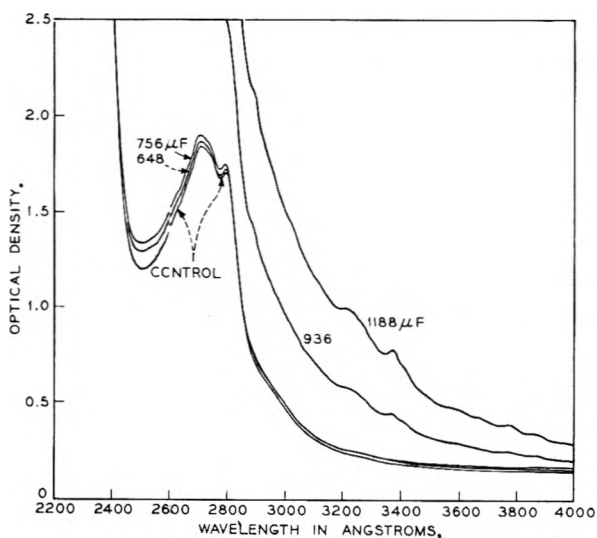Fig. 2.—Absorption spectra of mineral oil samples after one flash with various capacitances charged to 4 kv.

Foils of Ni and Perminvar (5–10 μ thick) suspended *in vacuo* melt when flashed at lower energies ($\sim$2000 j./flash) and evaporate rapidly at higher energies ($\sim$5000 j./flash). At intermediate energies etching occurs, and microscopic structure becomes apparent on the surface of the metal.

When the finely divided material is of organic nature, various thermal reactions can be initiated in the flash. An exploratory joint experiment with the Bureau of Mines on the flash heating of powdered coals sealed off in Pyrex tubes has shown some interesting pyrolytic results.[12] The hydrocarbons formed were of four carbon atoms or less, and in very different distribution than observed in conventional pyrolyses. In addition, C_2H_2, methylacetylene, CS_2 and HCN were observed. Obviously this is a pyrolytic technique requiring more investigation.

Solid–Gas Experiments.—By the technique of flash heating, we have decomposed gaseous CH_4 (Phillips Research Grade) by suspending 25 m. of 7.5 μ diameter black W wire as a loose wool in a $1/2$ in. diameter Pyrex tube filled with 285 mm. of the gas. With one flash at 2592 j. carbon was deposited, and, as shown by gas chromatography on a silica gel column. H_2, C_2H_6, C_2H_4 and C_2H_2 were formed. A control sample of CH_4 flashed without the wire showed no change. By comparison of the chromatographic peak areas

with known mixtures, it was found that 3 micromoles of H_2 was formed per meter of wire. Assuming that for every mole of H_2 produced, one-half mole of CH_4 was decomposed, at the pressure used a cylinder of CH_4 at least 0.36 mm. in diameter was pyrolyzed. This means that the wire influences about 400 times its own volume in the gas phase.

Since methane does not absorb radiation in the visible or near ultraviolet, this is an example of heterogeneous "sensitization" which has been used to convert a short pulse of predominantly visible radiation into chemical energy, somewhat like the action of homogeneous photochemical sensitizers.

We also have initiated explosions in the non-absorbing systems CH_4–O_2 and H_2–O_2. Metallic initiators such as W and Mo could not be used, because of a rapid oxidation of the metal in preference to the explosion. However glass wool evidently absorbs sufficiently over the wave length range of the flash to rise to the temperature for initiation of the explosion, although only at the highest flash energy (10,386 j./flash). In $1/2$ in. diameter Pyrex tubes, loose 5 mg. skeins of ordinary laboratory grade Pyrex wool ($\sim$8 μ fiber diameter) were closed off with 100 mm. of stoichiometric mixtures of CH_4 or H_2 and O_2. One flash triggered the explosion, the occurrence of which was detected by condensing the products in liquid nitrogen. After the flash, some of the more densely packed glass fibers were fused into coarser fibrous networks.

Solid–Liquid Experiments.—We have flash pyrolyzed a commercial mineral oil containing suspended sieved Mo of diameter below 74 μ, C of diameter below 36 μ or W wool of 7.5 μ diameter. The oil was placed in a $1/2$ in. diameter Pyrex tube with 0.03% by weight of the finely divided material. Above a threshold flash near 7500 j. the mineral oil turned an inky black (as compared to a grey cast before flashing in the case of the two powders), effervesced a small amount, and exhibited a bluish fluorescence when excited by 3661 Å. mercury radiation. Electron micrographs of the new carbon particles showed chain-like aggregates of spherical particles approximately 100 Å. in diameter. Below the threshold energy, no change in the suspension could be detected visually. Outgassing to a residual pressure of 10^{-5} mm. had no effect on these experiments.

A series of mineral oil samples pyrolyzed with carbon particles by flashing at different energies was filtered overnight in air through a fine filter paper. Absorption spectra of each clear filtrate were recorded spectrophotometrically, in 10 mm. thickness as shown in Fig. 2. The lower curves marked 756 and 864 μF. are very nearly coincident with a control mineral oil sample which had been mixed with the sieved carbon, allowed to stand in contact with the carbon as long as the other samples, but filtered without flashing.

The absorbance curves shown in Fig. 2 are quite similar to curves obtained from mineral oils which have undergone high-field electrical degradation.[13] The absorbance increase in this case is thought to result from formation of large unsaturated molecules.

In comparison, no degradation of the type seen above could be found in purified liquid *n*-octadecane suspensions of the same materials, even with repeated flashes of the highest energies. This probably is due to cooling by microscopic vaporization even though no bubbles were visible to the eye several seconds after the flash. Phase changes in the matrix which occur below its decomposition temperature will very likely prevent pyrolysis by this technique.

The case of flashing 0.03% by weight of zinc powder ($<$100 μ diameter) suspended in the mineral oil used above is interesting. There was a noticeable darkening in color of the suspension with one flash at 10368 j./flash but the change in color was due only to deposition of a more finely divided zinc, and not to degradation products. Neither carbon nor fluorescence was observed. Evidently the zinc evaporated inside the structure of the liquid and then reprecipitated in finer form. The boiling point of zinc is 907°, and for such an evaporation and condensation process to occur, instantaneous local temperatures approaching this must have been reached, yet no degradation occurred. We also have observed this behavior when flashing zinc dust incorporated in polyethylene. Much zinc vaporized from the polymer, but no degradation of the polymer was de-

(12) Personal communication from Dr. M. D. Schlesinger.

(13) H. Basseches and D. A. McLean, *Ind. Eng. Chem.*, **47**, 1782 (1955).

tected. This may be due to a free radical quenching by the zinc vapor, similar to the Paneth mirror removal reaction.[14]

Solid–Solid Experiments.—The heterogeneous flash initiation of thermal reactions was first found accidentally when exposing polymers to intense light of a flash lamp in an attempt to decrease exposure times in studying photodegradation of polymers.[2a] Consequently, polymer–solid systems have been studied in some detail. We have shown that dark particles smaller than 90 μ in diameter embedded in polymers, become sufficiently hot, when flashed at our highest energy, 10,368 j., that gases, fluorescent materials and carbon are formed by decomposition of the polymer around the hot particles.[2]

We have extended this study by flashing black tungsten wire embedded in polyethylene. Such wire 130 μ or less in diameter is heated sufficiently, when flashed, to pyrolyze the surrounding polymer. Wires have the obvious advantage of handling ease as compared to sieved particles. Moreover, air-borne particles are difficult to exclude from the polymer while either sieved particles or wires are being embedded in the polymer. When the polymer is flashed, the pyrolyses around intentionally and accidentally added particles are indistinguishable. Since degradation around a wire is limited to a thin carbonaceous, fluorescent cylinder surrounding the wire, little doubt as to source of degradation exists. When wires are embedded in a polymer sample to form a coördinate grid system, microphotography under white or ultraviolet light before and after flashing allows unique identification of reactive sites. It was easily demonstrated that pyrolysis occurs around particulate impurities and the wires of the grid, but not around occasional fluorescent impurity centers initially trapped in some commercial polymer specimens.

The gases formed by the flash pyrolysis of polyethylene are what might be expected from hydrocarbons heated in the absence of air. By collecting the pyrolysis gases with a Toepler pump and bulb system, the total number of moles of volatiles per gram of polyethylene was found to be nearly proportional to the square of the number of flashes (Fig. 3). A study of the volatiles from the flash pyrolysis of polyethylenes has been reported recently by Nelson and Kuebler.[15]

Attempts to separate the fluorescent materials formed in the flash pyrolysis of polyethylene from the matrix polymer have been unsuccessful. Thus no detailed study of these materials has been possible as yet. The fluorescence spectrum of a flashed polyethylene was measured using a xenon-mercury arc as an exciting source and a ratio-recording spectrophotometer with a fluorescence attachment. A broad, featureless emission extending from 3500 to 5600 Å., was observed.

Discussion

We have explained these experiments by the black-body absorption of the polychromatic light pulse and its conversion to heat at the surface of a finely divided material. The instantaneous temperature reached will depend on the incident intensity and the rate of dissipation of the thermal energy from the surface region by reradiation, heating of the absorber and matrix, and heats of chemical reaction or phase change. We have shown,[2b] if heats of reaction and phase change are neglected,

$$(T - T_0)_{\text{sph}} = \cfrac{\alpha_1 F}{\dfrac{\rho_1 c_{p_1} r}{3} + \dfrac{K_2 \Delta t}{r} + \alpha_1 \sigma \Delta t (T^2 + T_0^2)(T + T_0)} \quad (1)$$

that where $(T - T_0)_{\text{sph}}$ is the temperature rise of a spherical particle of radius r, emissivity α_1, density ρ_1 and heat capacity c_{p_1} irradiated with a radiant flux of F of duration Δt where the particle is embedded in a transparent matrix of thermal conductivity K_2 and σ is the Stefan–Boltzmann radiation constant. A maximum temperature rise at radius

(14) F. A. Paneth and W. Hofeditz, *Chem. Ber.*, **62B**, 1335 (1929).

(15) L. S. Nelson and N. A. Kuebler, American Chemical Society, Chicago, September, 1958.
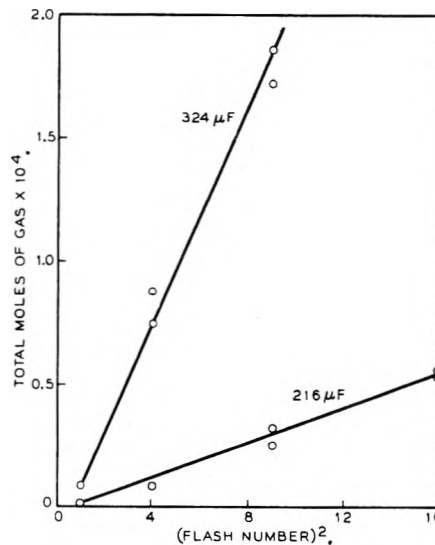
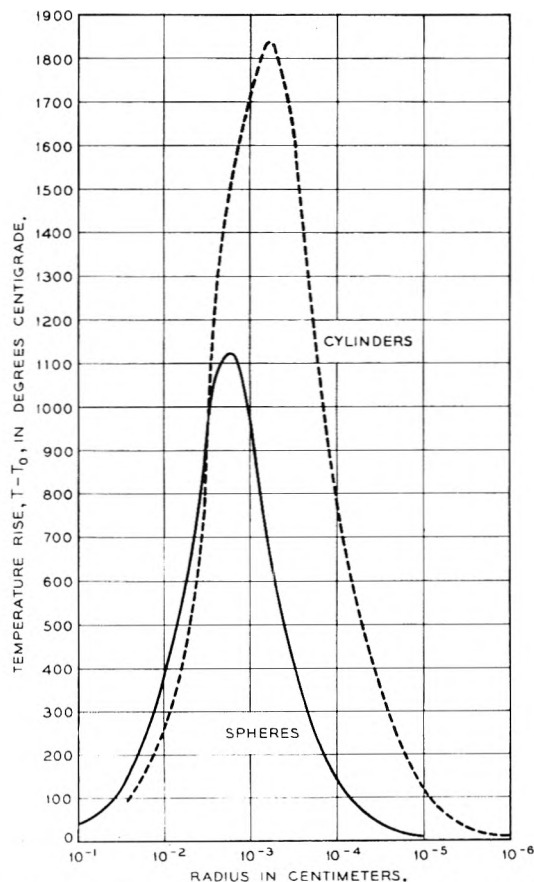Fig. 3.—Total gas produced per gram of flash pyrolyzed polyethylene.

Fig. 4.—Calculated temperature rises of carbon spheres and cylinders suspended in liquid hydrocarbon matrix.

$$r_{(T - T_2)\text{max, sph}} = \left[\frac{3 \Delta t K_2}{\rho_1 c_{p_1}} \right]^{1/2} \quad (2)$$

was predicted[2] from equation 1.

By completely analogous reasoning

$$(T - T_0)_{\text{cyl}} = \cfrac{\alpha_1 F}{\dfrac{\rho_1 c_{p_1} r}{2} + \dfrac{K_2 \Delta t}{r \ln r_1/r} + \alpha_1 \sigma \Delta t (T^2 + T_0^2)(T + T_0)} \quad (3)$$

and

$$r_{(T - T_3)\text{max. cyl}} = \left(\frac{2\Delta t K_2}{\rho_1 c_{p_1}} \left[\frac{\ln r_1/r - 1}{(\ln r_1/r)^2} \right] \right)^{1/2} \quad (4)$$

for an infinite cylindrical absorber of radius r suspended along the axis of a cylindrical transparent insulator of radius r_1.

Inserting the values $F = 1.32$ cal. cm.$^{-2}$ flash^{-1}, $\Delta t = 2.5 \times 10^{-3}$ sec., $K_2 = 4.0 \times 10^{-4}$ cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$, $\sigma = 1.36 \times 10^{-12}$ cal. sec. deg.$^{-4}$, $\rho_1 = 2.25$ g. cm^{-3}, $c_{p_1} = 0.45$ cal. g.$^{-1}$ deg.$^{-1}$, $\alpha_1 = 0.997$, $r_1 = 0.05$ cm. and $T_0 = 298°K$. we obtain the bell-shaped curves shown in Fig. 4 for temperature rises of spheres and cylinders of carbon embedded in a matrix with the thermal conductivity of a liquid hydrocarbon. If, the matrix is a gas at low pressure, the lower thermal conductivity causes the temperature to approach $5000°$[2b] at radii below 10^{-4} cm. These are the temperatures necessary to vaporize the carbon and tungsten mentioned earlier. The temperature rises in gases are seen to be in the same range as those produced by shock tubes.[6]

Note from equations 1 and 3 that temperature rise increases with increasing flux F, and with decreasing flash time Δt. We have not studied these variables independently as yet, because in our circuit both depend on capacitance per flash, our only circuit variable. Our several millisecond flash times are rather long compared to other flash circuits[16–18] so that probably we have not reached the highest temperatures possible.

Recently flash photolysis[3] has been used extensively to initiate rapid photochemical reactions, including some which are essentially pyrolyses.[19–21] The short reaction times and the vigor of the reactions produced by heterogeneous flash heating

suggest that it might be used as an alternate method for initiating rapid reactions, but with the important differences outlined below.

(1) There is only slight dependence of blackbody absorption on wave length. In the usual flash photolyses, often only the ultraviolet tail of the flash emission is used for excitation because many of the molecules of interest absorb only in the blue or ultraviolet regions of the spectrum. The flash lamp output,[9] however, extends from the ultraviolet into the near infrared wave length regions. With the heterogeneous heating technique, much more of the flash lamp output can be converted into chemical excitation.

(2) There is a threshold flash energy for the pyrolytic excitation (Fig. 2) which is not seen in true photochemical reactions, except perhaps with very short flash times, or unless part of the discretely absorbed radiation is converted to heat in the secondary reactions, which could add an intensity-dependent pyrolysis to the original photolysis.

(3) The pyrolytic process does not depend on the wave length of absorption of the reagents. This permits initiation in weakly or non-absorbing systems, and, if kinetic spectroscopic measurements are to be made on the reaction intermediates, it is possible to select parent reagents whose spectra do not interfere with those of the labile species. It is also likely that the flash heating technique will permit study of intermediates which do not occur in photochemical reactions.

(4) The flash heating technique has a hot, very reactive surface present. Such a heterogeneous energy transfer medium will complicate many reactions, just as with homogeneous sensitizers.[20–21] This may be a serious disadvantage in some cases, but perhaps of great interest in the study of surface-labile species interactions.

(16) J. H. Callomon and D. A. Ramsay, *Can. J. Phys.*, **35**, 129 (1957).

(17) S. Claesson and L. Lindqvist, *Arkiv Kemi*, **12**, 1 (1958).

(18) H. Fischer, *J. Opt. Soc. Am.*, **47**, 981 (1957).

(19) K. Knox, R. G. W. Norrish and G. Porter, *J. Chem. Soc.*, 1477 (1952).

(20) R. G. W. Norrish and G. Porter, *Proc. Roy. Soc. (London)*, **A210**, 439 (1952).

(21) R. G. W. Norrish, G. Porter and B. A. Thrush, *ibid.*, **A227**, 423 (1955).

NOTES

ADSORPTION CHARACTERISTICS OF HOMOIONIC BENTONITES

By W. H. Slabaugh

Contribution from the Department of Chemistry, Oregon State College, Corvallis, Oregon

A number of investigators[1–5] have examined the

adsorption and desorption of water vapor by clay materials. The present work is an attempt to point out further the importance of the exchangeable cation on these adsorption characteristics, and to propose a two step process in the adsorption of water vapor.

Experimental

Materials.—Homoionic bentonites were prepared in an ion-exchange column in a manner described previously.[6]

(1) S. B. Hendricks, R. A. Nelson and L. T. Alexander, *J. Am. Chem. Soc.*, **62**, 1457 (1940).

(2) R. W. Mooney, A. G. Kienan and L. A. Wood, *ibid.*, **74**, 1371 (1952).

(3) A. C. Zettlemoyer, G. J. Young and J. J. Chessick, THIS JOURNAL, **59**, 962 (1955).

(4) J. R. Goates and C. V. Hatch, *Soil Sci.*, **75**, 275 (1953); **77**, 313 (1954).

(5) H. D. Orchestron, *ibid.*, **76**, 453 (1953).

(6) W. H. Slabaugh, THIS JOURNAL, **59**, 1022 (1955).

The bentonite was a Wyoming type, supplied by the Baroid Division of the National Lead Company.

This study was based primarily upon the performance of ordinary freeze-dried clays, with an occasional reference to oven-dried clays which usually showed quite similar behavior, particularly with the univalent cation types. There was an obvious advantage in studying the freeze-dried samples because of their rapid response to vapor pressure changes, particularly upon out-gassing, where oven-dried clays showed a tendency to "explode" when vapor was drawn off rapidly. Equilibration time was usually about one hour on adsorption and three or more hours on desorption.

Apparatus.—An eight-place gravimetric adsorption device, employing Cu–Be alloy springs thermostated at 30.0 ± 0.1°, was used to observe the adsorption behavior of eight samples concurrently. There was an over-all accuracy of measurement, accounting for temperature control, spring drift, and indeterminate sources of error, of no more than 0.4% error in the weight measurements.

Results and Discussion

In all, adsorption characteristics of fourteen homoionic clays were examined by observing their interaction with water vapor at three temperatures. These clays fell into three groups, those similar to sodium bentonite (Fig. 1), those similar to calcium bentonite (Fig. 2), and those that produced a smooth, conventional S-shaped isotherm. The first group—sodium, potassium and magnesium clays—adsorb water vapor in two distinct steps. For example, sodium bentonite over the temperature range 14 to 37.5° adsorbed water vapor linearly up to 28 mg. per gram of clay. At this point the slope of the isotherm changed abruptly, and water vapor was further adsorbed linearly. The desorption of water vapor from the monovalent cation clays was far from reversible, as noted in the desorption curve at 14° in Fig. 1.

Calcium bentonite was unique and alone in the second group. The three adsorption isotherms for calcium bentonite in Fig. 2 show that, even though some kind of phase change or discontinuity appears at lower temperatures, there is apparently smooth adsorption at the highest temperature (37.5°). Call[7] discovered a similar two-stage process in the swelling of calcium bentonite that was freeze-dried, the two stages corresponding to two different 001 spacings of the lattice. In another study, to be reported in a later paper, there is evidence that at about 31° there is a notable change in the surface behavior of calcium bentonite. Consequently, it is not surprising to observe a change in the shape of the adsorption isotherm at temperatures above this transition point.

A third group of clays showed S-shaped adsorption isotherms similar to the calcium bentonite curve at 37°. These include H, Li, Sn, Ba, Zn, Cd, Fe and Ni bentonites, and none of them show any obvious indication of discontinuities up to 0.8 relative vapor pressure.

In spite of the lack of discontinuities in many of these isotherms, many of them, upon analysis through the BET equation, reveal two distinct values for V_m, the volume of water vapor required to form a monolayer. Following the concept of Dole[8] the two values for V_m, as derived from the two slopes and the two corresponding intercepts for the two legs of each curve shown in Fig. 3, are con-

(7) F. Call, *Nature*, **172**, 126 (1953).

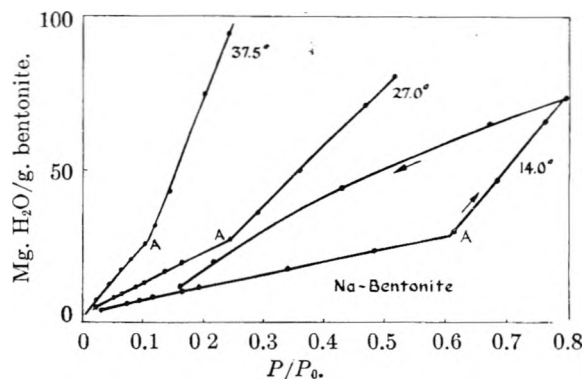(8) M. Dole, *J. Chem. Phys.*, **16**, 20 (1948).

Fig. 1.—Adsorption isotherms of sodium bentonite at three different temperatures.
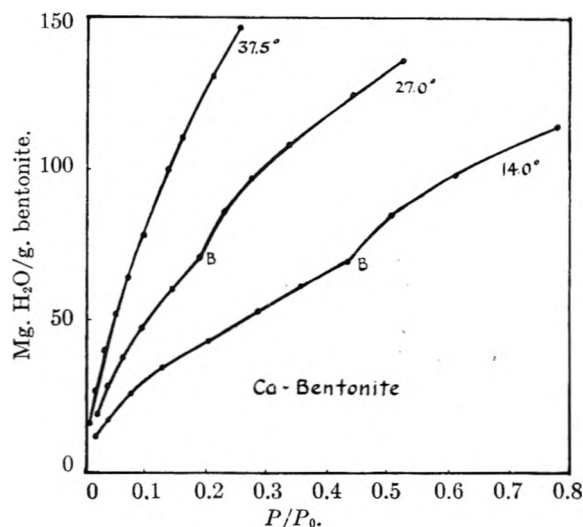

Fig. 2.—Adsorption isotherms of calcium bentonite at three different temperatures.
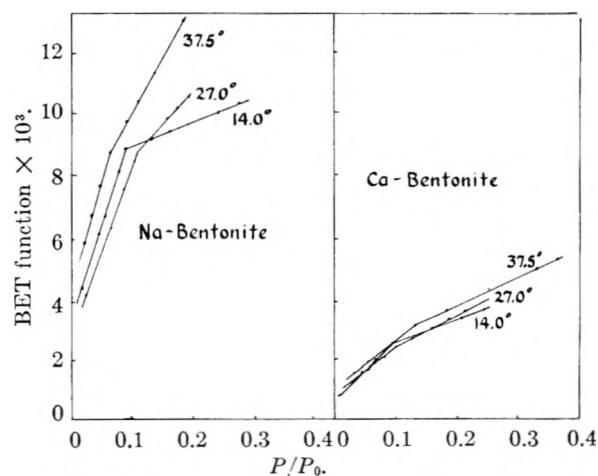

Fig. 3.—BET plots for water vapor on sodium and calcium bentonite at three different temperatures.

sidered to be two groups of molecules adsorbed at unique energies. For instance, at 27.0° the first value of V_m for sodium bentonite gives an area of 86 m.²/g. and the second value of V_m corresponds to 188 m.²/g. For calcium bentonite the areas are 299 m.²/g. and 462 m.²/g. for its two V_m values. Occasionally, the BET plots gave relationships from which only one V_m value could be determined.
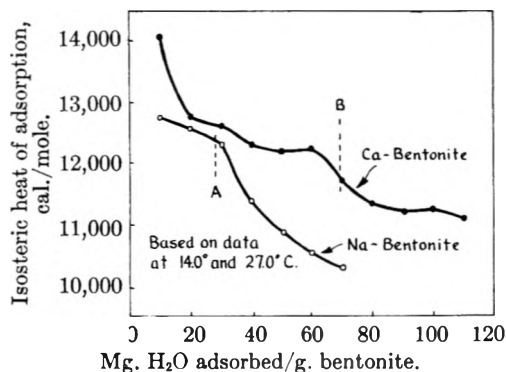
Fig. 4.—Isosteric heats of adsorption of water vapor by sodium and calcium bentonites.

Ordinarily, isosteric heats are calculated from a pair of reversible isotherms at two temperatures. In this instance, however, there was hysteresis in the adsorption–desorption process, particularly with the monoionic clays, and the isosteric heats obtained in this manner may not be strictly valid. In spite of this, isosteric heats of adsorption, calculated from data collected at 14.0 and 27.0° for the adsorption process, not only agree well with the heats of adsorption derived from heat of immersion studies,[3] but they further agree with the proposal that there is a discontinuity in the adsorption process. Figure 4 summarizes the isosteric heats for sodium and calcium bentonite, with points A and B corresponding to the discontinuities A and B in Figs. 1 and 2 for sodium and calcium bentonite, respectively. Table I lists the isosteric heats at the two V_m values obtained from BET plots. These conclusions are further substantiated by the fact that similar calculations on the desorption isotherms give almost the same results.

TABLE I

ISOSTERIC HEATS OF ADSORPTION CORRESPONDING TO THE TWO VALUES OF V_m DERIVED FROM BET PLOTS, IN KCAL. PER MOLE OF ADSORBED WATER, AND BET AREAS WITH ARGON

Cation type clay	ΔH_1	ΔH_2	Area. m.²/g.
Li	14.0	. .	22.4
Na (oven-dried)	12.5	10.0	10.3
Na (freeze-dried)	11.4	10.6	13.9
K	11.1	10.0	29.6
H	12.9	11.3	
Mg	15.6	12.5	
Ca	14.6	11.0	
Ba	14.9	12.6	
Sn	13.8	12.4	
Zn	15.1	11.6	
Cd	13.0	11.9	21.0
Cn	16.4	13.5	33.6
Fe	12.8	. .	26.4
Ni	9.8	. .	35.0

PYRIDINE CATALYSIS OF THE OXIDATION OF ISOPROPYL ALCOHOL BY CHROMIC ACID

BY F. H. WESTHEIMER AND Y. W. CHANG

Contribution from the Mallinckrodt Laboratories of Harvard University Cambridge, Mass.

Received September 9, 1958

In 1951, Holloway, Cohen and Westheimer[1] re-

ported that the chromic acid oxidation of isopropyl alcohol is slightly but significantly catalyzed by pyridine. The reaction was carried out in aqueous solution at 25° with a pyridine–pyridinium ion buffer and about $0.005 M$ (H^+). Recently[2] Roček and Krupička have repeated this work and find that the catalysis by pyridine is less than that previously[1] reported, and in fact is too small to be of importance. When we use the exact experimental conditions described by the respective authors, we can (at least approximately) repeat both sets of data. However, a reconsideration of these experimental conditions shows that, in conformity with Roček and Krupička's claim, the catalysis by pyridine is very small.

Roček and Krupička added crystalline pyridinium perchlorate to their solution of alcohol, perchloric acid and chromic acid. We have confirmed that their procedure is satisfactory. In the earlier experiments,[1] however, the acidities of the solutions containing sodium perchlorate on the one hand and pyridinium perchlorate on the other were matched by adjusting the solutions until a spectrophotometric determination of indicator color was the same for the two solutions. This method involved the assumption that, at constant ionic strength, the effects of the two salts (sodium and pyridinium perchlorates) on the activity coefficients of the dye were the same. Reinvestigation has shown that this assumption is not correct.

Experimental

Materials.—Thymolsulfonphthalein (Eastman Kodak) of m.p. 212–214° (with dec.) showed only a single spot in paper chromatography.[3] 4-Chloro-2,6-dinitrophenol[4] was

TABLE I

SALT EFFECT ON THYMOLSULFONPHTHALEIN

Indicator, 3.45×10^{-5} molar, $T = 25°$.

	HClO₄. M	$pH^{a,b}$	$d_{446m\mu}{}^a$
Indicator alone	0.00473	2.36	0.227
NaClO₄, 0.195 M	.00473	2.35	.224
PyHClO₄, 0.195 M	.00473	2.33	.192
PyHClO₄, 0.195 M	.00608	2.22	.223
N-MePyClO₄, 0.195 M	.00473	2.35	.186
N-MePyClO₄, 0.195 M	.00629	2.24	.224

a Average of three measurements. *b* Measured with a glass electrode and a Beckman model G pH meter.

TABLE II

SALT EFFECT ON 4-CHLORO-2,6-DINITROPHENOL

Indicator, 5.22×10^{-5} molar, $T = 25°$

	HClO₄. M	$pH^{a,b}$	$d_{446m\mu}{}^a$
Indicator alone	0.00473	2.36	0.081
NaClO₄, 0.195 M	.00473	2.36	.086
PyHClO₄, 0.195 M	.00473	2.35	.104
	.00625	2.19	.086
N-MePyClO₄, 0.195 M	.00473	2.37	.108
	.00702	2.18	.087

a Average of three measurements. *b* Measured with a glass electrode and a Beckman model G pH meter.

purified by recrystallization of the potassium salt, and then of the phenol; m.p. 81–82°. Merck reagent grade per-

(1) F. Holloway, M. Cohen and F. H. Westheimer, *J. Am. Chem. Soc.*, **73**, 65 (1951).

(2) J. Roček and J. Krupička, *Coll. Czech. Chem. Communications*, in press; J. Roček, private communication.

(3) G. T. Franglen, *Nature*, **175**, 134 (1955).

(4) M. Dubois, *Z. Chem.*, **10**, 206 (1867).

TABLE III

RATES OF CHROMIC ACID OXIDATION OF ISOPROPYL ALCOHOL AT 25°

HClO₄ (mole/l.)	NaClO₄ (mole/l.)	PyHClO₄ (mole/l.)	N-MePyClO₄ (mole/l.)	pH^a	$d_{545}{}^b$	k, l./mole min.⁻¹ × 10⁴
0.0053	0.195			2.34	0.233	0.83
.0055	.195			2.34	.235	0.91ᶜ
.0053		0.195ᵈ		2.22	.239	1.54ᶜ
.0055		.195ᵉ		2.33	.197	1.04ᶜ
.0055			0.195	2.35	.190	0.90ᶜ
.0046	.195					0.591¹
.0046		.190ᵈ				1.22¹
.0046	.16					0.72²
.0046		.16ᵉ				0.87²

ᵃ Measured with a glass electrode and a Beckman model G pH meter. ᵇ Thymolsulfonphthalein. ᶜ Average of two measurements. ᵈ By matching. ᵉ Crystalline pyridinium perchlorate.

chloric acid was standardized and used without further purification; Mallinckrodt analytical reagent chromic acid was twice recrystallized from water. Merck reagent grade pyridine was dried over BaO, distilled from KMnO₄ and fractionated; the fraction boiling at 115–116° was used.

Pyridinium perchlorate, recrystallized from water and dried under high vacuum at room temperature, melted at 284–286°. *Anal.* Calcd. for C₅H₆O₄NCl: C, 33.43; H, 3.37; Cl, 19.73. Found: C, 33.42; H, 3.47; Cl, 19.69.

N-Methylpyridinium perchlorate was prepared from the calculated amounts of silver perchlorate and N-methylpyridinium iodide.⁵ The salt, recrystallized from aqueous methanol, melted at 135–136°. *Anal.* Calcd. for C₆H₈O₄NCl: C, 37.21; H, 4.16. Found: C, 37.60; H, 4.21.

Indicator Characteristics.—Thymolsulfonphthalein (3.45 × 10⁻⁵ M) gave an optical density of 1.305 at 545 mμ in 12 N hydrochloric acid, 1.338 in 6 N acid and 1.329 in 2 N acid, at 25°. Since these values are closely the same, the value of 1.33 was chosen. The optical density of the indicator solution at pH 4 or 6.85 was 0.051. A series of measurements with 0.002 to 0.05 M hydrochloric acid established the indicator constant (extrapolated to infinite dilution) as 0.025. The full color of 4-chloro-2,6-dinitrophenol (5.22 × 10⁻⁵ M, at 25°) is obtained in 0.02 N alkali at 446 mμ; the optical density is 0.384. In 0.5 N HCl the optical density is zero. pH Measurements were made with a Beckman model G pH meter.

Salt Effects.—The salt effects upon the indicators are shown in Tables I and II.

Rates of Oxidation.—The rates of oxidation of isopropyl alcohol in the presence of perchloric acid and sodium perchlorate, pyridinium perchlorate or N-methylpyridinium perchlorate are shown in Table III. The rates are compared under conditions where the acidities of the three systems are the same as measured by glass electrode, and also under conditions where the colors of the indicator (thymolsulfonphthalein) have been matched.

Discussion

Both pyridinium perchlorate and N-methylpyridinium perchlorate lower the activity of the acid form of thymolsulfonphthalein and of dinitrophenol more than sodium perchlorate does, so that the assumption (implicit in the work of Holloway, Cohen and Westheimer) that there is no specific salt effect, was in error.

Under the experimental conditions shown in Table III, and using the technique of matching indicator colors to control acidity, the rates are not far from those reported earlier. However when the acidity is controlled by glass electrode measurements, the rate of chromic acid oxidation is only about 15% faster, in the presence of pyridinium perchlorate, than in the presence of N-methylpyridinium perchlorate or sodium perchlorate. These findings are in agreement with those of Roček and Krupička. Most of the error (and perhaps all of it)

(5) E. D. Bergmann, F. E. Crane, Jr., and R. M. Fuoss, *J. Am. Chem. Soc.*, **74**, 5979 (1952).

arose from the method of measuring acidity. The implication of these facts for the mechanism of the oxidation of isopropyl alcohol will be considered in later publications.

INTERACTION OF IMIDAZOLE WITH COBALT(II)

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Studies on the interaction of imidazole with Cu,ᴵᴵ Zn,ᴵᴵ Cdᴵᴵ and Niᴵᴵ have been made by earlier workers.²⁻⁴ The present note describes the interaction of imidazole with Co.ᴵᴵ

Experimental

Potentiometric measurements were made with a Beckman general purpose glass electrode in conjunction with a precision potentiometer and an electrometer null-detector incorporating an Osram electrometer tube ET1. A Beckman saturated calomel half-cell was used as reference electrode. The over-all accuracy of measurements was expected to be within ±0.01 pH unit.

Measurements on freshly prepared mixtures of imidazole nitrate, NaOH and cobaltous nitrate were made in an air-conditioned room maintained at 25.0 ± 0.5°. An ice-water bath was used for measurements at 2.0 ± 0.5°.⁵ In general, the experimental procedure described by Edsall and co-workers² was followed.

Analytical grade reagents were used throughout. A stock solution of cobalt nitrate was standardized gravimetrically as cobaltinitroso-β-naphthol.⁶ Imidazole was an Eastman Kodak Co. product used after prolonged drying over P₂O₅. All measurements were made in a nitrate medium of 0.15 ionic strength.

The procedure for the evaluation of successive formation constants was as described by Li and co-workers for the system: Niᴵᴵ-imidazole.⁴ The Scatchard function $Q(=\bar{v}/(N - \bar{v})(I_m))$, where $\bar{v}$ is the average number of imidazole molecules bound per metal ion, (I_m) the equilibrium con-

(1) Indian Institute of Technology, Worli, Bombay 18.

(2) J. T. Edsall, G. Felsenfeld, D. S. Goodman and F. R. N. Gurd, *J. Am. Chem. Soc.*, **76**, 3054 (1954).

(3) C. Tanford and M. L. Wagner, *ibid.*, **75**, 434 (1953).

(4) N. C. Li, T. L. Chu, C. T. Fujii and J. M. White, *ibid.*, **77**, 859 (1955).

(5) The glass electrode was first introduced into the solution. After the temperature had become reasonably constant, the tip of the calomel electrode was then introduced into the solution and the reading taken after ten minutes. No significant error was introduced even when readings were taken after longer periods.

(6) F. J. Welcher, "Organic Analytical Reagents," Vol. III, D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 303.

Table I

pk': $25.0 \pm 0.5° = 7.10 \pm 0.01$; $2.0 \pm 0.5° = 7.60 \pm 0.01$; total imidazole concentration $= 0.1200\ M$; total Co^{II} concentration $= 0.0103M$.

(NaOH)	2° pH	25°	(Hm+)	(Im) 2°	25°	$\bar{v}$ 2°	25°	log Q 2°	25°
0.00187	4.93	4.67	0.11813	0.00025	0.00040	0.157	0.143	2.04	1.78
.00374	5.28	5.03	.11626	.00055	.00099	.31	.27	1.99	1.69
.00748	5.70	5.41	.11252	.00140	.00226	.59	.51	1.89	1.61
.0150	6.15	5.82	.1050	.0036	.0055	1.10	.92	1.79	1.52
.0214	6.40	6.07	.0986	.0061	.0091	1.48	1.19	1.73	1.44
.0357	6.81	6.42	.0843	.0135	.0174	2.15	1.77	1.62	1.38
.0536	7.21	6.77	.0664	.0266	.0310	2.61	2.19	1.47	1.27
.0750	7.59	7.14	.0450	.0439	.0486	3.02	2.56	1.36	1.18

centration of basic imidazole and N the coördination number of the metal ion) was evaluated on the assumption of $N = 6$ for Co^{II}.

Results

The relevant titration data are listed in Table I. The pK' values of 7.10 and 7.60 for the dissociation of imidazolium ion at 25 and 2°, respectively, are in general accord with those reported by earlier workers, although the value of 7.60 at 2° is somewhat larger than expected from the value of 7.50 at 4.5° reported by Edsall and co-workers.[2] Plots of log Q vs. $\bar{v}$ suggest a linear decrease of log Q with $\bar{v}$. In this connection, it is of interest to note that the slopes of log Q vs. $\bar{v}$ curves for Co^{II}–imidazole and Ni^{II}–imidazole[4] systems are of the same order and, consequently, that the intrinsic affinity of these metal ions for imidazole decreases in much the same manner with successive associations.

The successive formation constants are listed in Table II. The corresponding constants for the interaction of ammonia with Co^{II} in $2/M$ ammonium nitrate at 30° are also listed in Table II for comparison.[7] In view of uncertainties in the extrapolation of log Q vs. $\bar{v}$ curves to $\bar{v} = 6$, it is indeed doubtful whether the constants k_4–k_6, may have any significance. As such, only the first three formation constants, k_1–k_3, are listed in Table II. For all practical purposes, however, only the first two formation constants are important and these are expected to be accurate to within $\pm$ 0.05 logarithmic units.

As log Q vs. $\bar{v}$ curves for the two temperatures studied have been found to be parallel to each other, it may be concluded that the standard heat of reaction, $\Delta H°$, for successive associations is of the same order. In so far as the present data indicate, this value is $- 2.2$ kcal. per mole.

Certain aspects of the effect of prolonged exposure to oxygen on Co^{II}-imidazole systems, as evidenced by spectrophotometric, magnetic and infrared absorption studies will be presented in a separate communication.

Table II

	Imidazole 25°	2°	Ammonia 30°
log k_1	2.49	2.80	2.11
log k_2	1.88	2.18	1.63
log k_3	1.35	1.64	1.05

(7) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution." Haase & Son, Copenhagen, 1941.

HYDROLYTIC BEHAVIOR OF METAL IONS. IX. ULTRACENTRIFUGATION OF Sn(IV) IN ACIDIC CHLORIDE AND PERCHLORATE SOLUTIONS[1]

By James S. Johnson and Kurt A. Kraus

Contribution from the Oak Ridge National Laboratory, Chemistry Division, Oak Ridge, Tenn.

In earlier papers,[1,2] we have shown by equilibrium ultracentrifugation that relatively stable low molecular weight polymeric species form during the hydrolysis of some metal ions. We have now extended our studies to the easily hydrolyzable (very acidic) Sn(IV),[3-6] whose mechanism of hydrolysis seems to deviate considerably from this pattern.

Experimental

Centrifugations were carried out with a Spinco Model E Ultracentrifuge with 30 mm. cells. The schlieren optical system was used. Experimental techniques have been described earlier.[2]

Solutions were prepared from $SnCl_4\cdot5H_2O$, the composition of which was checked by tin analysis. Tin(IV) perchlorate solutions were prepared in two ways. In one, $SnCl_4\cdot5H_2O$ was dissolved in $HClO_4$, and chloride was precipitated by addition of an equivalent amount of $AgClO_4$. In the second, $HClO_4$ was added to solutions of Na_2SnO_3. A precipitate, which was formed on first addition of acid, redissolved to give a clear solution.

All chemicals were C.P. or reagent grade.

Results

Tin(IV) solutions in $HClO_4$, prepared by either of the methods described above, were found to be unstable against precipitation during the time necessary for attainment of centrifugation equilibrium. Although the solutions were initially clear, turbidity developed over a period of days, and precipitate was deposited, even from 6 M $HClO_4$. A rough estimate for the material remaining in 3 M $HClO_4$ solution after several days centrifugation

(1) Work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, operated by the Union Carbide Corporation, Oak Ridge, Tennessee. Previous paper of series: R. W. Holmberg, K. A. Kraus and J. S. Johnson, to J. Am. Chem. Soc., 78, 5506 (1958).

(2) (a) J. S. Johnson, K. A. Kraus and R. W. Holmberg, ibid., 78, 26 (1956); (b) J. S. Johnson and K. A. Kraus, ibid., 78, 3937 (1956); (c) R. W. Holmberg, K. A. Kraus and J. S. Johnson, ibid., 78, 5506 (1956).

(3) G. E. Collins and J. K. Wood, J. Chem. Soc., 121, 441 (1922).

(4) N. K. Kulrestha, A. K. Dey and S. Ghosh, Kolloid-Z., 141, 106 (1955).

(5) J. Guéron, Compt. rend., 197, 247 (1933).

(6) D. A. Everest and J. H. Harrison, J. Chem. Soc., 1439 (1957).

placed the degree of polymerization above 100. These solutions were initially 0.05 and 0.1 M in Sn(IV), and were prepared by the method involving precipitation of chloride with $AgClO_4$.

Stable Sn(IV) solutions can be prepared in the presence of HCl provided a sufficient excess of hydrochloric acid is added; presumably tin is then complexed to the species $SnCl_6^=$.[7] Solutions prepared with 1 M HCl in excess of the component $SnCl_4$ (0.05 M) remained apparently stable for over two years; with 0.5 M excess HCl, precipitation occurred over a period of a year, though during the time necessary for equilibrium ultracentrifugation, the solution was stable (see below); for 0.2 M and less excess HCl, turbidity developed in less than a week.

We have carried out centrifugations of solutions 0.05 M in Sn(IV) and 1.2, 0.7, 0.4, 0.3 and 0.2 M HCl in excess of the component $Sn(OH)_4$. Enough NaCl was added to make the total supporting electrolyte concentration equal to $ca.$ 1 M. The results were computed[8] as apparent degrees of polymerization N_e of $SnCl_4$ on the assumption that the charge per monomer unit z' is zero, although the actual species in solution are not known. Other plausible choices of species and charge per monomeric unit do not affect the computed values of N_e sufficiently to alter the principal conclusions. Volumes of $SnCl_4$ were computed from literature values of densities.[9]

The results of the centrifugations are summarized in Fig. 1 as plots of N_e $vs.$ concentration of HCl in excess of the component $Sn(OH)_4$. Since the acidic solutions were all $ca.$ 0.05 M in Sn(IV), the concentration of HCl in excess of the component $SnCl_4$ may be obtained by subtracting 0.2 from the values of M HCl on the abscissa. The apparent degree of polymerization appears to be unity at high HCl and rises abruptly for M HCl less than 0.7. In M HCl < 0.7, turbidity developed and precipitation occurred during the centrifugation, and the values plotted in Fig. 1 are rough estimates of N_e for the material remaining in solution at the termination of centrifugation. There is no evidence for stable low molecular weight polymers intermediate between monomers and large aggregates.

For the sake of completeness, the figure includes results on centrifugations in basic solutions presented in detail elsewhere.[10] Here also, in the presence of a large excess of base, N_e seems to be unity, with a slight increase in polymerization at the composition Na_2SnO_3. In the presence of less base than corresponds to this composition, polymerization (and rapid precipitation) occurs. Figure 1 also includes results of diffusion measurements by Jander and co-workers.[11] These are plotted as $k/(D\eta)^2$ where D is the diffusion coefficient and η is viscosity. The constant $k = \frac{1}{8}$

Fig. 1.—Polymerization of Sn(IV). Excess acid and base are computed for component $Sn(OH)_4$: —+—, ultracentrifugation (~0.05 M Sn(IV) unless specified); —O—, diffusion coefficient measurements (0.05 M Sn(IV)) presented as function roughly proportional to degree of polymerization and normalized to match centrifugation results in monomer region. (Jander, Busch and Aden, $Z.$ $anorg.$ $allgem.$ $Chem.$, **177**, 345 (1929).)

was introduced to match ultracentrifugation and diffusion measurements in the monomer region. Agreement between the two studies is good.

Acknowledgment.—The authors are indebted to Miss Neva Harrison for technical assistance.

REVERSIBLE SPECTRAL CHANGES IN RETINENE SOLUTIONS FOLLOWING FLASH ILLUMINATION[1,2]

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In the course of our investigations of the spectroscopy and photochemistry of the visual pigments we have applied the technique of flash photolysis[3] to the study of retinene (vitamin A aldehyde) and its p-toluidine complex.

Experimental

Apparatus.—Two types of apparatus were used in these experiments, hereafter referred to as the flash spectrographic apparatus and the flash kinetic apparatus. In the flash spectrographic apparatus the flash source was a two-turn helical quartz tube filled with xenon gas (200 mm.) having duraluminum electrodes, and mounted inside a magnesium oxide-coated tubular reflector. The tube operated at 4000 volts and approximately 400 joules. At the center of the flash tube, mounted in the optical path, was a 50 mm. cylindrical cell containing a degassed solution of retinene. Along the optical path were mounted, in turn, a small spectral flash tube (General Electric FT-230) operating at approximately 30 joules, a condensing lens, the cell containing retinene solution, a baffle system to minimize scattered light, a filter, and finally a cylindrical lens to focus the light beam onto the slit of a Bausch and Lomb

(7) See, $e.g.$, L. A. Woodward and L. E. Anderson, $J.$ $Chem.$ $Soc.$, 1284 (1957).

(8) J. S. Johnson, K. A. Kraus and G. Scatchard, This Journal, **58**, 1034 (1954).

(9) A. Heydweiller, $Z.$ $anorg.$ $allgem.$ $Chem.$, **116**, 42 (1921).

(10) J. S. Johnson and K. A. Kraus, $J.$ $Am.$ $Chem.$ $Soc.$, in press.

(11) G. Jander, F. Busch and T. Aden $Z.$ $anorg.$ $allgem.$ $Chem.$, **177**, 345 (1929).

(3) G. Porter, $Proc.$ $Roy.$ $Soc.$ $(London)$, **A200**, 284 (1950).
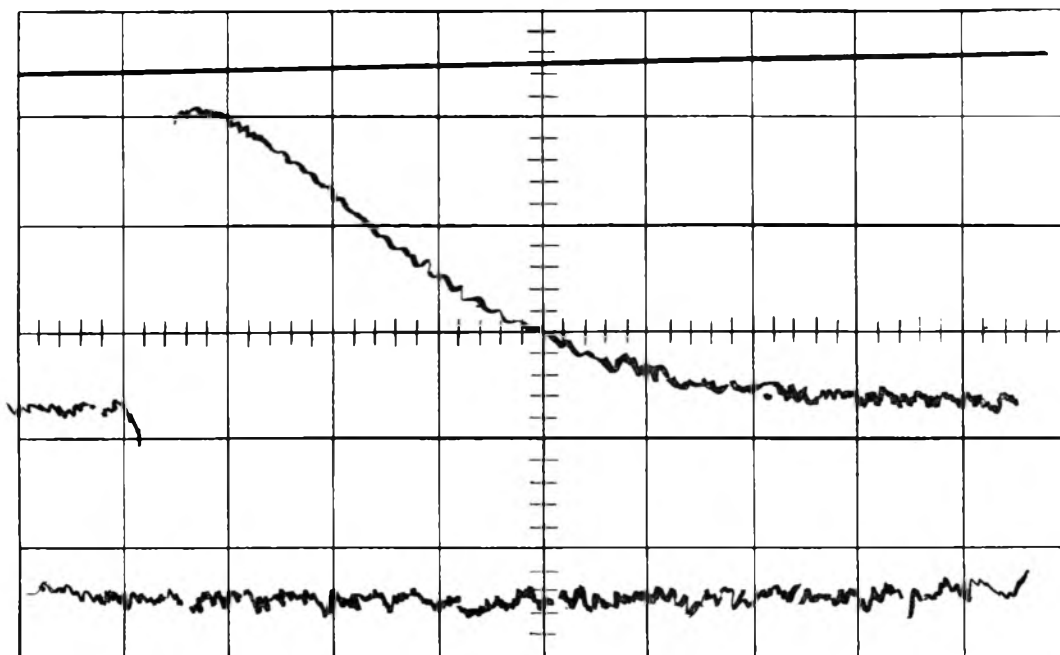
Fig. 1.—Oscillogram showing formation and decay of the triplet state of *trans*-retinene, 4.0 × 10⁻⁵ M in tetrahydrofuran; ordinate, % transmission at 4400 Å.; abscissa, time (one large division is 10 microseconds).
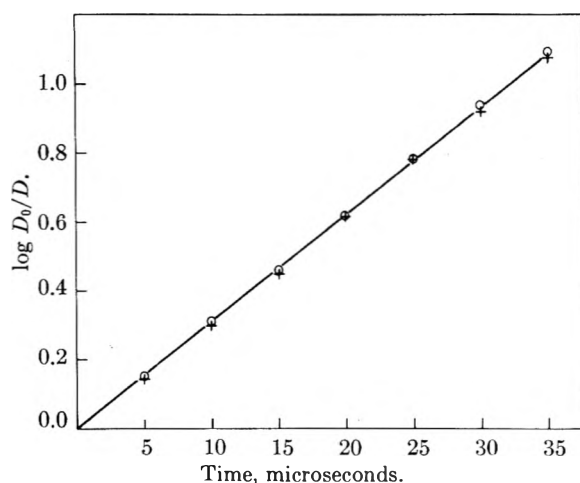

Fig. 2.—Decay kinetics of the triplet state of *trans*-retinene in tetrahydrofuran; λ 4500 Å. ○, 4.0 × 10⁻⁵ M; +, 4.0 × 10⁻⁶ M; k = 7.2 × 10⁻⁴ sec.⁻¹.
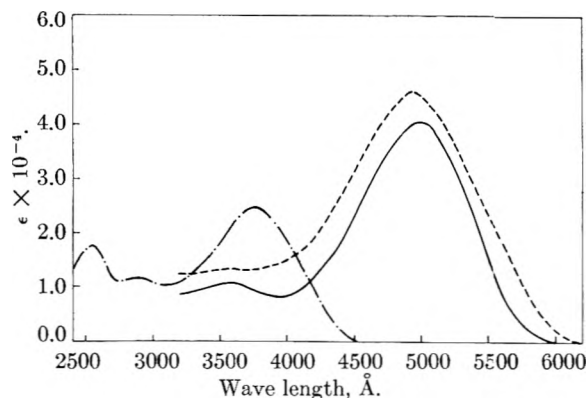
Fig. 3.—Absorption spectra: ——, rhodopsin in aqueous digitonin solution; ——, *p*-toluidine complex of *trans*-retinene in tetrahydrofuran (0.25 M HCl); ———, neo-retinene b in ethanol.

Medium Quartz Spectrograph.⁴ By using a pulse generator (Grass Instrument Model S-4) and appropriate triggering circuits it was possible to trigger first the photolytic flash and after a measurable delay, the spectral flash. To correct for scattered light entering the optical path the ground state spectrum was taken by firing the spectral flash before the photolytic flash.

The flash kinetic apparatus used in these experiments was the same as used and described by Linschitz and Sarkanen.⁵ It differed from the flash spectrographic apparatus in that it employed a steady, intense zirconium arc point source in place of the spectral flash, and a large aperture Bausch and Lomb Grating Monochromator replaced the spectrograph. Spectral changes at various wave lengths were detected by a multiplier-phototube whose response was displayed as a single sweep oscillogram on an oscilloscope (Tektronix, Model 535).

Materials.—*trans*-Retinene, kindly donated to us by C. D. Robeson of Distillation Products Industries, was used without further purification. Methylcyclohexane and tetrahydrofuran were purified by fractional distillation over sodium. *p*-Toluidine was twice recrystallized from water.

Procedure.—A reservoir attached to the photolysis cell was filled with solution to a predetermined volume. Excess solvent was added and the system closed by a ground joint and stopcock. The solution was degassed and the excess solvent removed by distillation on a high vacuum system.

Absorption spectra of the solutions before and after flashing were measured on a Cary Recording Spectrophotometer, Model 11, using a special adapter to position the photolysis cell.

Calculations.—Rate data from oscillograms (Fig. 2) were enlarged and the percentage transmission (ordinate) was converted to absorbance. In Fig. 3, D_0 is the difference in absorbance between an arbitrary zero time on the decay curve (Fig. 2), taken after the completion of the flash, and the final absorbance at the completion of the decay. D is the corresponding difference in absorbance between any time t after zero time and the final absorbance.

Rate Data.—Decay kinetics of the species produced by flash illumination were obtained by calibrating each oscillogram as follows: A cell containing solvent only was flashed with the shutter to the steady scanning arc closed. This furnished a zero transmission base line together with a

(4) Loaned to us by Professor Nathan Ginsberg, Department of Physics, Syracuse University.

(5) H. Linschitz and K. Sarkanen, *J. Am. Chem. Soc.*, **80**, 4826 (1958).

scattered time profile of the flash (Fig. 1, uppermost trace). The shutter then was opened and a single sweep taken without flashing to obtain the 100% transmission line (lowest trace). The solvent cell then was replaced by an identical cell containing solution and the solution flashed with the shutter to the scanning arc open.

Results and Discussion

A series of flash spectrograms of solutions of *trans*-retinene in methylcyclohexane was taken at various time intervals following flash illumination. A spectrogram taken ten microseconds after flashing showed pronounced bleaching of the ground state absorption peak at 3700 Å. accompanied by a marked increase in absorption in the region of 4400 Å. At 100 microseconds after flashing the spectrum was identical to that of the ground state. Apparently flash illumination of *trans*-retinene produces a new species absorbing at 4400 Å. which rapidly reverts to the ground state in times of the order of ten microseconds. In air saturated solutions these effects are barely detectable indicating that oxygen markedly quenches the new species.

The decay kinetics of this new species were followed on the flash kinetic apparatus and a typical oscillogram is shown in Fig. 1. Rate data obtained from the oscillograms are shown in Fig. 2. The linearity of the log D_0/D vs. time plot shows that the decay is first order up to ground state retinene concentrations as high as 4.0×10^{-5} M.

Reasonable consideration of the structure of retinene, the decay kinetics and the excitation energies involved essentially rule out ionized or free radical fragments as the new species. The fact that it has a rather long lifetime ($t_{1/2} = 9.9 \times 10^{-6}$ second) and is markedly quenched by oxygen suggest that the new species is the lowest triplet state of retinene showing a triplet–triplet absorption peak at 4400 Å. This behavior is in essential agreement with the results obtained in the flash illumination of anthracene[6] and chlorophyll[5] although the first-order rate constants for the triplet decay in these cases are considerably smaller.

If the new species is indeed a triplet it is not likely that it is populated by direct internal conversion (intersystem crossing) from the π-π excited singlet state as is the case with anthracene,[5] since reasonable estimates of the total yield of actinic light from the flash and the extent of population of the long-lived state are inconsistent with the relatively short maximum (radiative) lifetime ($\sim 2 \times 10^{-9}$ second) of the π-π excited singlet state and the lower limit of 10^{-7} second imposed on the radiationless transition between states of different multiplicity in hydrocarbons.[7]

In retinene where the conjugation includes an oxygen atom there is the possibility that an n-π singlet state lies at somewhat lower energies than the π-π singlet.[8] Under these conditions internal conversion can occur rapidly ($\sim 10^{-12}$ second) from the π-π to the n-π singlet. The radiative lifetime of an n-π singlet is sufficiently long (10^{-5} to 10^{-7} second) to permit appreciable population of a lower lying n-π triplet state through intersys-

tem crossing. That this appears to be the mechanism for triplet population in the case of retinene is substantiated by the fact that in the flash illumination of the corresponding alcohol, vitamin A, where no n-π states are possible, no long-lived states are evident.

Retinene readily forms protonated Schiff base complexes with amines[9] showing a marked red shift in the absorption spectrum due to the introduction of charge resonance into the conjugated system. The visual pigment, rhodopsin, is believed to be just such a complex between neo-retinene b and the protein, opsin.[10]

The *p*-toluidine complex of *trans*-retinene has an absorption spectrum very similar to rhodopsin (Fig. 3). When oxygen free solutions of this complex in tetrahydrofuran (0.25 M in HCl) were flash illuminated, neither transient nor irreversible spectral changes could be detected. This was not an unexpected result since no n-π transition is possible in the protonated complex and hence no long-lived triplet state is likely to be populated.

To the extent that the protonated *p*-toluidine complex is representative of rhodopsin the above results are consistent with two of the mechanisms proposed for the primary photochemical process in the bleaching of rhodopsin: namely, photoisomerization[11] and photoionization.[12]

(9) S. Ball, F. P. Collins, P. D. Dalvi and R. A. Morton, *Biochem. J.*, **45**, 304 (1949).

(10) R. A. Morton and G. A. J. Pitt, *ibid.*, **59**, 128 (1955).

(11) R. Hubbard and C. C. St. George, *J. Gen. Physiol.*, **41**, 524 (1958).

(12) C. Reid, "Excited States in Chemistry and Biology," Academic Press, New York, N. Y., 1957, p. 161.

(13) Developed and constructed with the help of AEC support (Syracuse University Contract No. AT(30-1)-820).

DIFFUSION EFFECTS IN THE TRANSPIRATION METHOD OF VAPOR PRESSURE MEASUREMENT[1]

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An important technique for the determination of vapor pressures is the one variously known as the transpiration or transportation method. In essence, the measurement consists of passing a stream of an inert gas over the sample of interest at a known rate which is slow enough to achieve saturation of this "carrier" gas with the vapor. The vapor from the sample is then condensed at some point downstream and the vapor pressure is calculated from the amount of the sample material collected in a known time period. The application of the method to studies of vapor pressures of inorganic compounds at elevated temperature has

(6) G. Porter and M. Windsor, *Disc. Faraday Soc.*, **17**, 183 (1954).

(7) One of us (EWA) is indebted to Professor Michael Kasha for an enlightening discussion on radiationless transitions.

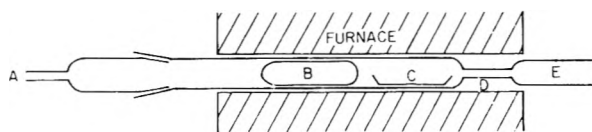(8) J. R. Platt, *J. Opt. Soc. Amer.*, **43**, 252 (1953).
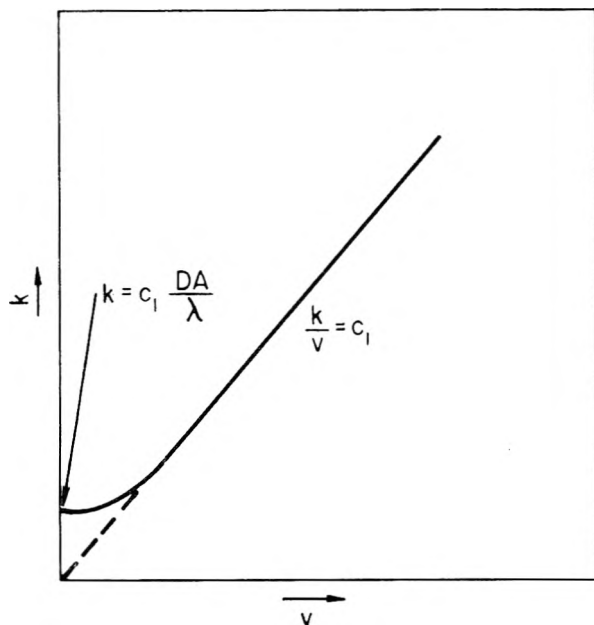
Fig. 1.—Transpiration apparatus.

Fig. 2.—Variation of vapor transport with gas flow rate.

been discussed in recent reviews.[2] In the following paragraphs we wish to present a means of examining certain aspects of the method for the purpose of designing experiments and interpreting results.

A typical experimental arrangement is shown schematically in Fig. 1. The carrier gas is introduced at A, flows around a heat shield B, into an essentially isothermal region in the neighborhood of the sample-containing boat C. The vapor-laden gas then passes through a capillary constriction D and into the condensing region E.

The flow of vapor through the capillary may be thought of as the sum of a slug-flow term and a diffusion term so that the mass of the vapor passing any point along the tube in unit time is given by

$$k = A \left(Vc - D \frac{dc}{dx} \right)$$

where A is the cross-sectional area of the capillary, V is the linear velocity of the gas mixture through the capillary, x is the distance along the capillary measured from left to right in Fig. 1 and is taken as zero at the exit end, c is the vapor density at any point and D is the interdiffusion coefficient for the carrier gas and the vapor. At steady state, k must be constant over the length of the capillary if no condensation occurs in this region, so we may solve the differential equation simply to obtain the result

$$c = \frac{k}{VA} + B \exp \left(\frac{V}{D} x \right)$$

where B is a constant of integration and we have

assumed that there is no temperature or total pressure gradient along the capillary and that D is independent of concentration. This solution of the differential equation yields a form of the concentration gradient different from that assumed by Lepore and Van Wazer[3] in their treatment, the results of which have been widely used in examining data obtained by this technique. We believe that our result will be more useful in discussing the method. Evaluating B for a capillary of length λ and assuming, for the present, that the vapor is condensed immediately as it leaves the capillary region (i.e., $c = 0$ at $x = 0$), we have

$$c_1 = \frac{k}{VA} \left[1 - \exp\left(- \frac{V\lambda}{D} \right) \right]$$

where c_1 is the vapor density at the inlet end of the capillary (i.e., at $x = -\lambda$). Replacing V by the gas flow rate in volume units v, and assuming the vapor behaves as an ideal gas, we have

$$V = \frac{v}{A}$$

and

$$p_1 = \frac{c_1}{M} RT = \frac{k}{v} \frac{RT}{M} \left[1 - \exp\left(- \frac{v\lambda}{DA} \right) \right] \quad (1)$$

where p_1 and T are the pressure and absolute temperature of the vapor at $x = -\lambda$, R is the gas constant and M is the molecular weight of the vapor. (Corrections for deviations from the ideal gas law have been discussed by Gerry and Gillespie.[4]) Thus, if we determine k as a function of v with a given experimental arrangement, and T and p_1 are constant, we will obtain a curve of the form shown in Fig. 2. For large v, diffusion effects are negligible and

$$p_1 = \frac{k}{v} \frac{RT}{M} \quad (2)$$

This is essentially the expression which has generally been used to interpret transpiration measurements. At $v = 0$, only the diffusion flow is observed and

$$p_1 = \frac{k}{D} \frac{\lambda}{A} \frac{RT}{M} \quad (3)$$

In the derivation of equation 1 we have assumed that the vapor concentration is zero at the exit end of the capillary and that the capillary is at a uniform temperature. In an actual experiment, condensation will generally not occur until a point is reached some distance downstream from the capillary, hence, $c > 0$ at $x = 0$. This fact can be corrected for by employing an effective length which is obtained by adding to the actual length of the capillary the quantity $(A/A')\lambda'$ where A' and λ' are the cross-sectional area of the exit tube and the distance from the end of the capillary to the point of condensation, respectively. In many cases, $A' \gg A$ and $\lambda' \cong \lambda$, so that the correction may be neglected. The temperature gradient in the capillary is actually maintained near zero in most instances to prevent condensation in this

(2) See, for example, O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," 2nd ed., John Wiley and Sons, Inc., New York, 1956, p. 151.

(3) J. V. Lepore and J. R. Van Wazer, "A Discussion of the Transpiration Method for Determining Vapor Pressure," MDDC-1188, U. S. Atomic Energy Commission.

(4) H. T. Gerry and L. J. Gillespie, Phys. Rev., 40, 269 (1932).

region and plugging of the passage, but there is a temperature gradient over part of the length λ'. Since this is generally in a large-diameter region of the tube, the equivalent capillary length of this region is small, and the assumption that the temperature is constant to the point of condensation should not lead to serious errors.

If the transpiration experiment is properly designed, it should always be possible to use the simple equation 2 to interpret the results. The equations derived above may be used as a guide to proper design, since D may be estimated by methods outlined by Dushman[5] and the dimensions of the capillary and the flow rates to be studied may then be chosen in such a way that the term $\exp(-v\lambda/DA)$ in equation 1 is negligible compared to unity. It should be noted that the diffusion correction vanishes as the flow rate is increased and that, as a result, the extrapolation of the k/v line passes through the origin, not through the zero-flow point on the k axis.

At high flow rates, the measured values of k will fall below the curve in Fig. 2 because saturation will not be achieved, and these points must be neglected in analyzing the results. Even if no straight-line relationship can be achieved because of failure to reach saturation at flow rates where diffusion is negligible, it is possible to solve for the vapor pressure provided only that data can be obtained at two significantly different flow rates where saturation is achieved. For instance, results from a zero flow rate experiment may be used to calculate the product p_1D from equation 3, and the answer used, together with one other result satisfying equation 1, to eliminate D and determine p_1. When saturation is not achieved, p_1 will be a function of the sample surface area. This fact may be used as a test for saturation.

The calculation of p_1 from the experimental data requires knowledge of the molecular weight M of the vapor species. In favorable instances, the assumed value may be checked in the following way: once the quantity c_1 has been calculated, equation 1 or 3 may be solved for D, the interdiffusion coefficient for the carrier gas and the vapor. By methods outlined by Dushman,[5] one may then calculate rough values of D for various possible species and compare them to the measured value. A selection of the appropriate species will be possible if the candidates differ sufficiently in D.

(5) S. Dushman, "Scientific Foundations of Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 74.

THE SEPARATION OF MIXTURES OF ORDINARY AND HEAVY WATER BY ZONE REFINING[1]

BY HILTON A. SMITH AND CARL O. THOMAS

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The freezing point of pure heavy water (D_2O)

is 3.8° higher than that of ordinary water.[2,3] This difference in the freezing points has been the basis for a number of attempts to separate the two isotopic forms by fractional crystallization. Although many of the early measurements were inconclusive, Eucken and Schafer[3] were able to confirm experimentally the theoretically predicted temperature change which occurred during the process of freezing a mixture of light and heavy water. Weston[4] rechecked the theoretical calculations which indicate that the heavy isotope should concentrate in the solid phase. Smith and Posey[5] recently measured the concentration difference between the solid and liquid phases of an H_2O–D_2O mixture under equilibrium conditions. Their work shows conclusively that fractional crystallization of a mixture of ordinary and of heavy water produces some isotope separation, with the heavy isotope concentrating in the solid phase. However, the separation factor is much too small, only 1.0211, and the required freezing rate is too slow for a batch process to give useful separation of the isotopic forms of water. Posey[6] performed some exploratory experiments to investigate the applicability of the zone-refining technique. The work discussed in the present report was performed in order to determine whether or not the zone-refining technique would be useful for the separation of heavy water from ordinary water, and to obtain a comparison between the observed and theoretically predicted extent of separation.

Experimental

Apparatus.—The zone-refining apparatus consisted of a spiral of Tygon tubing wound onto a 1.5-inch diameter cylinder of wire mesh. The Tygon tubing was filled with a mixture of H_2O and D_2O in approximately equimolar amounts and was plugged at each end with a Pyrex stopper. The spiral was mounted with its axis horizontal and with about one-half of each turn submerged in the refrigerated brine-bath which was operated at −10°. In order to provide a constant seed for freezing, the end of the tubing at which the zones originated was folded inside of the spiral and remained frozen throughout a run. The spiral geometry allowed 40 evenly spaced zones to move simultaneously through the sample.

At the beginning of a run the entire sample was frozen by packing Dry Ice around it. The bath was covered with a sheet of plywood in which was cut a 1-inch wide slot. The slot was located immediately above and ran the length of the spiral. A heater, placed above the slot, maintained a temperature of 35–40° at the exposed surface of the spiral. Under these operating conditions, each frozen zone moved almost to the top of a turn before it was completely melted. Freezing occurred within the first 0.5 inch after the tubing re-entered the bath. The melted zone occupied a length of about 1.5 inches, or about 25% of each circumference.

The cylinder was rotated by a geared-down Telechron motor, which gave an operating speed of 0.75 revolution per hour, or a linear speed of 4.1 inches per hour.

Water Samples.—The heavy water, which was reported

(2) A. Eucken and K. Schafer, *Z. anorg. allgem. Chem.*, **225**, 319 (1935).

(3) A. Eucken and K. Schafer, *Nachr. Ges. Wiss. Gottingen, Math. physik Klasse, Fachgruppe III*, (N.S.), **1**, 109 (1935).

(4) Ralph E. Weston, Jr., *Geochim. et Cosmochim. Acta*, **8**, 281 (1955).

(5) John C. Posey and Hilton A. Smith, *J. Am. Chem. Soc.*, **79**, 555 (1957).

(6) John C. Posey, Doctoral Dissertation, The University of Tennessee, Knoxville, Tennessee, 1955.
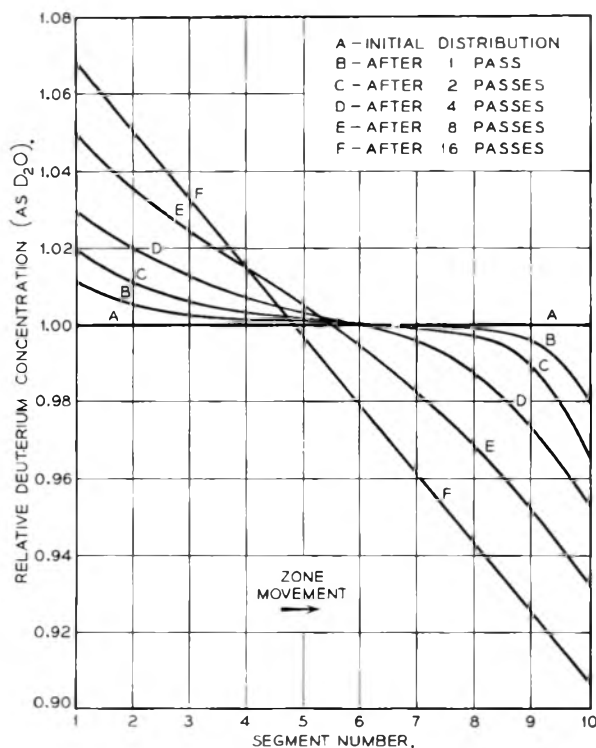
Fig. 1.—Theoretical concentration profiles for zone refining of a mixture of light and heavy water.
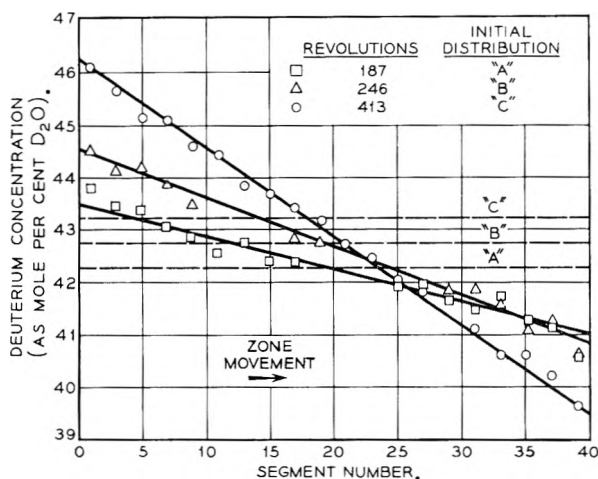

Fig. 2.—Experimental concentration profiles for zone refining of a mixture of light and heavy waters.

to be 99.8% pure, was supplied in sealed Pyrex ampoules by the Stuart Oxygen Company and was used without further processing. Ordinary distilled water was obtained from the general laboratory supply and was redistilled before use.

Analytical Method.—At the completion of each run, the entire water sample was frozen in the Tygon tubing by the addition of Dry Ice to the refrigerated bath. The tubing was cut into segments, each one turn in length, for the isolation of samples along the length of the tubing. Each segment contained approximately 0.5 ml. of water. The samples were totally distilled in order to remove possible salt contamination. The compositions of the water samples were determined by the falling-drop method of Combs, Googin and Smith.[7] Analytical standards were prepared from the water samples described above.

(7) R. L. Combs, J. M. Googin and Hilton A. Smith, THIS JOURNAL, **58**, 100 (1954).

Calculations and Results

Birman's matrix method[8] was used for the development of a mathematical analysis to describe zone refining in the H_2O–D_2O system, since it includes the boundary conditions and since it allows numerical solution of the equations by algebraic methods.

In order to simplify further the calculations, several assumptions regarding the zone-refining process were made. (1) All molten zones pass through the entire length of the sample. (2) The diffusion rate in the solid is negligible. (3) Diffusion in the liquid is rapid and complete. (4) The *segregation coefficient* k is constant, and is defined by equation 1, where C_S is the D_2O concentration in the

$$k = C_S/C_L \qquad (1)$$

solid freezing in equilibrium with the liquid, and where C_L is the D_2O concentration in the liquid.

If k is greater than unity, the solute concentrates in the solid phase, which produces a net movement of solute along the sample in a direction opposite to the motion of the liquid zones. It should be pointed out that Smith and Posey calculated the *equilibrium separation factor* α by use of equation 2, as for a Rayleigh distillation, where

$$\alpha \log\left[\frac{H_L + H_S}{H_L}\right] = \log\left[\frac{D_L + D_S}{D_L}\right] \qquad (2)$$

H and D are the total number of moles as H_2O and as D_2O, and where L and S subscripts refer to the liquid and the solid phases, respectively. The matrix solution of the zone-refining process requires the use of the *segregation coefficient* k if prohibitive complexity is to be avoided. When α is small, as is true in the present case, and for an idealized equilibrium process, the value of α can be used when k is specified in the matrix with small error and with great simplification of the calculations.

A simple zone-refining process in an H_2O–D_2O system was evaluated numerically for the following conditions. (1) Only one molten zone is present in the sample at a time. (2) The length of the molten zone is 20% of the total sample length. (3) The value of 1.02 for the *equilibrium separation factor*, found by Smith and Posey, is used for the *segregation coefficient*.

The first two conditions were selected because they require the manipulation of only a 10 × 10 matrix. For a matrix of this size the calculations can be done manually in a reasonable length of time. The third condition was selected in order to evaluate the maximum separation which might be expected.

The theoretical concentration profiles are shown in Fig. 1. An initially uniformly distributed unit concentration was assumed.

Experimental concentration profiles are shown in Fig. 2. Horizontal lines indicate the initial concentration profiles. Straight lines were fitted to the data points by the least-squares method in which the squares of the ordinate differences were minimized. Zone movement was in the direction of the higher segment numbers. Thus the heavy isotope concentrated in a direction opposite to that

(8) Joseph L. Birman, *J. Appl. Phys.*, **26**, 1195 (1955).

of the zone movement, which is in agreement with the theoretical predictions. However, the maximum concentration difference obtained experimentally was much less than that predicted by the theory.

Discussion

The conditions for the numerical evaluation of the theoretical separation were selected in order to limit the matrix size and the volume of the calculations. These conditions imply that ten discrete fractional crystallizations occur as the molten zone moves through the length of the sample. A larger matrix would more accurately represent the true conditions in the process and would also result in a larger theoretical separation of the isotopes.

The effects of the isotopic equilibrium

$$H_2O + D_2O \rightleftharpoons 2HDO$$
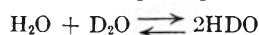
on the calculations were avoided by basing all the analytical data upon standards prepared from pure (99.8%) D_2O and pure H_2O. Thus the experimental concentration profiles do not imply that the deuterium is bound as D_2O or as HDO, and the value of the equilibrium separation factor used in the matrix calculations likewise avoids this implication.

The interface at which freezing occurs is moving into a liquid film which has a lower deuterium concentration than that calculated for the liquid zone as a whole. Adequate stirring of the liquid zone increases the effective separation factor. Smith and Posey found that vigorous agitation and a slow freezing rate were necessary in order to approach the value of α for an equilibrium process. For non-equilibrium conditions they found values of α as low as 1.0007. The absence of agitation in the zone-refining apparatus probably contributed significantly to the great quantitative difference between the theoretical and the experimental concentration profiles. In the spiral apparatus the freezing-interface was in a vertical portion of the tubing. Because of the temperature gradient immediately above the freezing interface there was the possibility that a density inversion in the liquid would contribute a mixing effect and thus improve the observed separation. However, the separation does not appear to have been significantly improved by this arrangement. Possibly ultrasonic techniques might be applied in order to agitate the liquid zone.

The zone-refining process for the separation of heavy water from ordinary water is so slow at present that its application may be limited to theoretical studies or to the procurement of ultra-pure samples of D_2O or of H_2O.

PREPARATION AND PROPERTIES OF THE SYSTEMS LnFexCr1-xO3 AND LaFexCo1-xO3

By Aaron Wold[2] and William Croft[3]

Contribution from the Departments of Chemistry, Lincoln Laboratory,[1] Lexington, Mass., and Radio Corporation of America, Needham Heights, Mass.

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Recent papers[4,5] have indicated that certain rare earth-transition metal oxides possess perovskite-type structures which are ideal for the study of indirect magnetic exchange mechanisms. The perovskite cell contains cations which occupy the B sites and are arranged in a simple-cubic array with an oxygen ion at the center of the edges of the cube. The systems presented in this paper were studied in order to determine whether an ordering takes place on the B sites of rare earth–iron–chromium, lanthanum–iron–cobalt oxides. It was expected[6] that in lanthanum–iron–chromium oxide, an ordering of the cations on the B sites into alternate (111) planes would result in an overlap of the oxygen p orbitals with empty chromium e_g orbitals on one side, half filled iron e_g orbitals on the other. It is believed that such a configuration would result in a ferromagnetic Fe–O–Cr interaction. Ordering in alternate (111) planes of diamagnetic Co^{+3} in lanthanum–iron–cobalt oxides would produce a different number of Fe^{+3} ions in the various (111) planes. Since the Fe–O–Fe interaction is antiferromagnetic, this would produce a measurable ferrimagnetic moment. However, no magnetic moments were observed for these systems at liquid helium temperature. It is therefore concluded that the transition metal ions occupy the B sites in a random fashion.

Experimental

Samples of $LnCr_xFe_{1-x}O_3$ (Ln = La, Nd, Sm, Y) were prepared by treating the rare earth oxide with varying molar mixtures of iron(III) oxide and chromium(III) oxide in air for 96 hours. The samples were reground several times during the heating period. Lanthanum–iron–cobalt oxides, $LaCo_xFe_{1-x}O_3$ were prepared by heating lanthanum oxide with varying molar mixtures of iron(III) oxide and cobalt(II) carbonate at 1100° in air for 96 hours and at 1300° for 18 hours. Standard analytical techniques were used to determine the amount of rare earth, iron, chromium and cobalt present in these compounds. The rare earth–iron–chromium oxides were fused with sodium peroxide and the chromium, present as chromate, was extracted with hot water. The rare earth and iron hydroxides, formed by the fusion, were dissolved in hydrochloric acid and the iron and cobalt were separated from lanthanum by precipitation of the latter with ammonium oxalate.

The saturation magnetization at 4°K. was measured by Menyuk and Dwight using a modified vibrating-coil mag-

TABLE I

CELL DIMENSIONS OF THE SYSTEMS LnFexCr(1-x)O3

Composition	a_0	b_0	c_0	Volume (Å.³)
LaFeO₃	5.548	5.557	7.851	242.05
LaCrO₃	5.480	5.507	7.758	234.12
NdFeO₃	5.456	5.585	7.761	236.5
NdCrO₃	5.411	5.471	7.702	228.0
SmFeO₃	5.393	5.595	7.714	232.76
SmCrO₃	5.367	5.496	7.649	225.63
YFeO₃	5.278	5.584	7.603	224.07
YCrO₃	5.245	5.518	7.540	218.22

(1) The research in this document was supported by the Army, Navy and Air Force under contract with the Massachusetts Institute of Technology.

(2) Staff Member, Lincoln Laboratory, Lexington, Massachusetts.

(3) Semi-Conductor and Materials Division, Radio Corporation of America, Needham Heights, Massachusetts.

(4) J. B. Goodenough, *Phys. Rev.*, **100**, 564 (1955).

(5) A. Wold, R. J. Arnott and J. B. Goodenough, *J. Appl. Phys.*, **29**, 387 (1958).

(6) J. B. Goodenough, private communication.

TABLE II
CELL DIMENSIONS OF THE SYSTEM $LaFe_zCo_{1-z}O_3$

Orthorhombic phase

Composition	Prepared at 1100°			Prepared at 1300°		
	a_0	b_0	c_0	a_0	b_0	c_0
					Orthorhombic	
$LaFeO_3$	5.548^a	5.557^a	7.851^a	5.548^a	5.557^a	7.851^a
$LaCo_{0.1}Fe_{0.9}O_3$	5.540	5.554	7.844	...	...	...
$LaCo_{0.2}Fe_{0.8}O_3$	5.542	5.546	7.839	...	...	...
Both Phases						
$LaCo_{0.25}Fe_{0.75}O_3$	...	...	...	...	...	...
$LaCo_{0.5}Fe_{0.5}O_3$	...	...	...	5.472	5.497	7.761
					Rhombohedral	
$LaCo_{0.55}Fe_{0.45}O_3$	...	...	...	5.483		13.196
$LaCo_{0.6}Fe_{0.4}O_3$	...	...	...	...		...
Hexagonal (rhombohedral) phase						
$LaCo_{0.65}Fe_{0.35}O_3$	5.469		13.167	...		...
$LaCo_{0.75}Fe_{0.25}$	5.466		13.138	...		...
$LaCo_{0.9}Fe_{0.1}O_3$	5.446		13.104	...		...
$LaCoO_3$	5.424		13.068	5.449		13.098

^{a} The third decimal place of all lattice constants is less significant because the peaks in the back reflection region of the X-ray patterns are broad.

netometer recently described by Dwight, Menyuk and Smith.[7] No appreciable moment was observed for these compounds at liquid helium temperature in a magnetic field of 10,000 oe. The lattice symmetry and lattice constants were calculated from spectrometer traces taken with a Philips Norelco Diffractometer, using $K\alpha$ iron radiation. The results of chemical and crystallographic analysis are summarized in Tables I and II.

Discussion

In order for a net ferromagnetism to result from a Fe–O–Cr interaction in the rare earth–iron–chromium oxides or for ferrimagnetism to result from the antiferromagnetic Fe–O–Fe interaction in lanthanum–iron–cobalt oxide, it is necessary that there be a preferential ordering on alternate (111) planes of the perovskite lattice of the cobalt or chromium atoms and the iron atoms. Since no magnetic moments were observed at liquid helium temperature, it is concluded that the transition metal ions occupy the B sites in a random fashion.

X-Ray diffraction measurements (Table I) have established the solid solubility between $LaFeO_3$ and $LaCrO_3$, between $NdFeO_3$ and $NdCrO_3$ between $SmFeO_3$ and $SmCrO_3$ and between $YFeO_3$ and $YCrO_3$. The end member, $LnFeO_3$ and $LnCrO_3$, are orthorhombic; their space group is $D_{2h}(16)$ Pbnm and there are four formula weight per unit

(7) K. Dwight, N. Menyuk and D. Smith, *J. Appl. Phys.*, **29**, 491 (1958).

cell. In all cases the substitution of Cr^{+3} for Fe^{+3} results in a decrease of the unit cell volume. The compounds obey Vegard's rule between each pair, and the unit cell volumes decrease with a corresponding decrease of the rare earth ionic radius.

The system $LaCo_xFe_{1-x}O_3$ (Table II) prepared at 1100° possessed orthorhombic symmetry from $LaFeO_3$ to $LaCo_{0.2}Fe_{0.8}O_3$. A small decrease in the cell volume was observed upon substitution of cobalt for iron. Between $LaCo_{0.25}Fe_{0.75}O_3$ and $LaCo_{0.6}Fe_{0.4}O_3$ both an orthorhombic and a rhombohedral phase were present. Pure lanthanum cobalt oxide and compositions to $LaCo_{0.65}Fe_{0.35}O_3$ were rhombohedral. Samples of the system $LaCo_x$-$Fe_{1-x}O_3$ prepared at 1300° showed orthorhombic symmetry from $LaFeO_3$ to $LaCo_{0.5}Fe_{0.5}O_3$ and was rhombohedral from $LaCo_{0.55}Fe_{0.45}O_3$ to pure $LaCoO_3$. The small increase of the unit cell size of $LaCoO_3$, noted in Table II, is caused by the formation of several per cent. of Co^{+2} in the sample heated to 1300°.

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