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Reaction of Ozone with Ethene and Its Methyl- and Chlorine-Substituted Derivatives in Aqueous Solution

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Byproduct formation in ozonation processes is of interest, especially in the area of drinking water, similar to the concerns regarding the health effects of disinfection byproducts generated by chlorine and other oxidants used for that purpose. Chlorinated olefins increasingly contaminate our drinking water resources, and the byproducts formed by ozone were determined here. For a better understanding of the underlying mechanisms, some other olefins were included in this study. The rate constants of the reaction of ozone with ethene and some of its methyl- and chlorine-substituted derivatives in aqueous solution have been measured by stopped-flow (rate constants in units of dm^3 mol^{-1} s^{-1}): tetramethylethene, $>10^6$; propene, 8×10^5; ethene, 1.8×10^5; buten-3-ol, 7.9×10^4; vinyl chloride, 1.4×10^4; *trans*-1,2-dichloroethene, 6.5×10^3; 1,1-dichloropropene, 2.6×10^3; *cis*-1,2-dichloroethene, 540; 1,1-dichloroethene, 110; trichloroethene, 14. From these data, it is concluded that the rate of reaction is mainly governed by the electron density of the C═C double bond and that steric effects must be minor in comparison. In all cases, full material balances were obtained. They show that these olefins nearly exclusively follow the Criegee mechanism and cleave into a carbonyl compound and a hydroxyhydroperoxide, which in the case of a chlorine substituent in α-position rapidly loses HCl. The intermediate hydroperoxides were characterized by the kinetics of their reaction with molybdate-activated iodide ions. In unevenly substituted olefins, the substituent strongly decides on the pathway taken, e.g., propene yields formaldehyde and hydroxyethylhydroperoxide while vinyl chloride forms hydroxymethylhydroperoxide and formyl chloride (→ CO + HCl). Even with the highly substituted ethenes partial cleavage products (indicated by an asterisk) never exceed 10%. Intermediate ozonides must have a lifetime <2 ms as shown by stopped-flow conductometry. The products (yields per mole of ozone in parentheses) are the following. From ethene: formaldehyde (2.0_4) including hydroxymethylhydroperoxide (1.0_8) [→ formaldehyde + H_2O_2]; propene: formaldehyde (1.0_3), hydroxyethylhydroperoxide (0.99) [→ acetaldehyde (0.97) + H_2O_2]; vinyl chloride: HCl (1.0_5), hydroxymethylhydroperoxide (1.0_6) [→ formaldehyde (1.0_4) + H_2O_2], formic acid (0.06) [precursors: formyl chloride (0.04) and formic peracid, 0.029], CO (1.0_1) [precursor: formyl chloride (→ CO + HCl)]; *cis*- and *trans*-1,2-dichloroethene (identical yields): HCl (2.0_2), formate (1.0_1) [precursor: formic peracid (0.99); rate of hydrolysis 1.6×10^{-4} s^{-1}], CO (1.0_8) [precursor: formyl chloride], CO_2 (0.02) [precursor: formic peracid]; 1,1-dichloroethene: HCl (1.95), formaldehyde (0.96, precursor: hydroxymethylhydroperoxide (0.96) [→ formaldehyde (0.96) + H_2O_2], CO_2 (0.90) [precursor: phosgene], chloroacetic acid* (0.08), glycolic acid* (0.07), formate (0.03), dichloroacetaldehyde* (≤0.01); 1,1-dichloropropene: HCl (2.0_5), CO_2 (1.0_1) [precursor: phosgene], hydroxyethylhydroperoxide (0.88) [→ acetaldehyde (1.0_3) + H_2O_2]; trichloroethene: HCl (2.8_7), CO_2 (0.95) [precursor: phosgene], formate (0.82) [precursor: formic peracid (0.88)], CO (0.04) [precursor: chloroformic peracid), dichloroacetic acid* (0.04). Some experiments were also done with tetramethylethene: acetone (1.7_4) [the precursor of half of the acetone, 2-hydroxypropyl-2-hydroperoxide reacts too slowly with activated iodide to be quantified], 2,3-dimethyl-2,3-dihydroxybutane* **(**ca. 0.1**)**. These results show that full mineralization is not achieved.

Introduction

Ozone is widely used in drinking water and wastewater processing (for a review see ref *1*). Byproduct formation in ozonation processes is of interest, especially in the area of drinking water, similar to the concerns regarding the health effects of disinfection byproducts generated by chlorine and other oxidants used for that purpose. Our drinking water resources are increasingly contaminated with chlorinated olefins (notably tetrachloroethene, trichloroethene, *cis*-1,2-dichloroethene, and vinyl chloride), and the products formed upon their degradation by ozone was unknown. For this reason, a detailed study of the reactions of ozone with chlorinated olefins was undertaken. To put mechanistic aspects on a better footing, some other small non-chlorinated olefins were included in this study.

Being an electrophilic agent, ozone reacts fast with electron-rich olefins and aromatic compounds. Increasing chlorine substitution will hence decrease the rate constant of ozone addition to olefins (cf. Table 1), and in the case of trichloroethene and tetrachloroethene the rate constants are already so low that at the short times required in technical processes there is very little destruction. Thus for their degradation other processes, e.g., the so-called advanced oxidation processes that generate the more reactive OH radical, have to be used (for recent reviews, see refs *2* and *3*). However, the other chlorinated olefins are sufficiently reactive (cf. Table 1) to undergo efficient degradation within reasonable times (i.e., without the participation of an OH radical). Although the rate constant of the reactions of many chlorinated olefins with ozone have been determined some time ago (for a compilation of rate constants, see ref *4*), practically nothing is known about the products formed and the lifetimes of potential intermediates.

Mechanistic studies on ozone reactions have been mainly carried out in organic solvents, and very little is known about ozone reactions in aqueous solutions. The mechanism suggested by Criegee (Scheme 1) seems to be generally accepted. With olefins the electrophilic ozone first forms a π-complex that collapses into a zwitterionic σ-complex **A** (reaction 1). This primary zwitterion closes to the primary ozonide **B** (reaction 2). The primary ozonide **B** is an unstable cyclic trioxide. In organic solvents, it has often been possible to isolate Criegee ozonides **F**. To explain their formation, it has been postulated that the primary ozonide **B** cleaves an O−O bond heterolytically (reaction 3) and that this secondary zwitterion **C** decomposes into a carbonyl compound and the tertiary zwitterion **D** (reaction 4). In a nonreactive organic solvent, the carbonyl compound and the zwitterion **D** may

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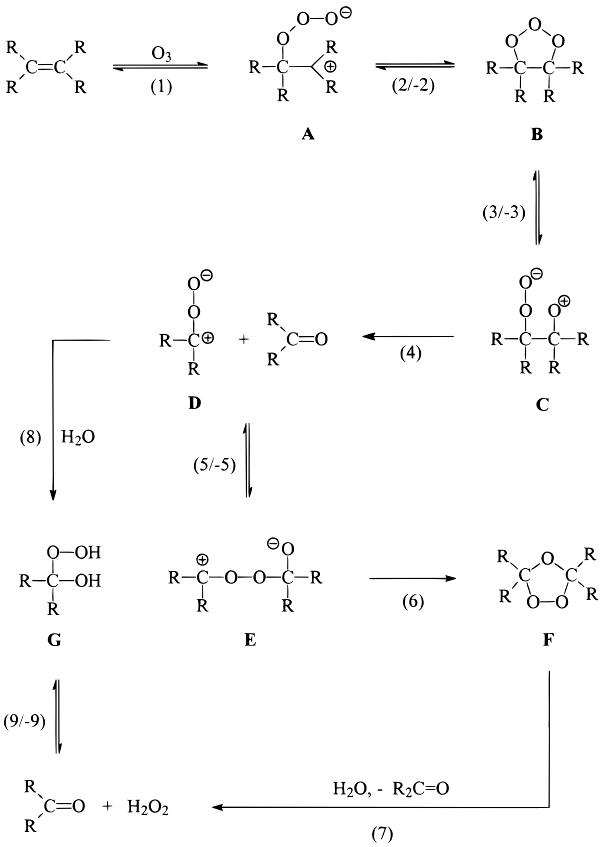
TABLE 1. Rate Constants (in Units of dm^3 mol^{-1} s^{-1}) of the Reaction of Ozone with Ethene and Its Methyl- and Chlorine-Substituted Derivatives

substrate	water	carbon tetrachloride	gas phase
tetramethylethene	$>10^6$ (this work)	2×10^5 (*7*)	6.3×10^5 (*9*)
propene	8.0×10^5 (this work)		6.4×10^3 (*10*)
ethene	1.8×10^5 (this work)	2.4×10^4 (*7*)	1.02×10^3 (*10*)
but-1-en-2-ol	7.9×10^4 (this work)		
vinyl chloride	1.4×10^4 (this work)	1.2×10^3 (*8*)	3.9 (*11*)
trans-1,2-dichloroethene	6.5×10^3 (*24*) 6.5×10^3 (this work)	590 (*8*)	150 (*12*)
1,1-dichloropropene	2.6×10^3 (this work)		
cis-1,2-dichloroethene	540 (this work)	36 (*8*)	22 (*12*)
1,1-dichloroethene	110 (*24*)	22 (*8*)	*a* (*13*)
trichloroethene	17 (*24*) 14 (this work)	3.6 (*8*)	
tetrachloroethene	<0.1 (*24*)	1 (*8*)	332 (*14*)

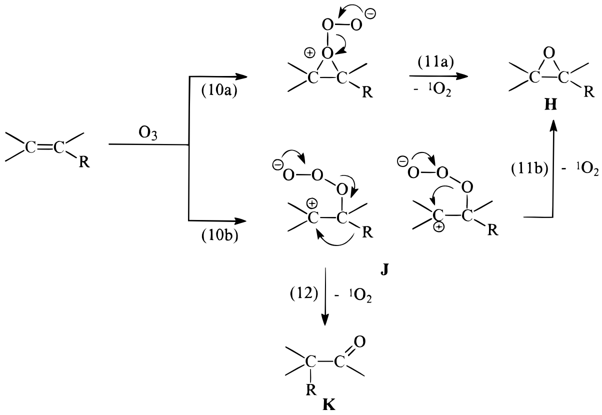
[a] The gas-phase reaction does not follow second-order kinetics.

SCHEME 1



combine to yield the Criegee ozonide via a quarterany zwitterion **E** (reactions 5 and 6) (*5*). Evidence for the zwitterion **D** has been obtained by cross-reacting it with alien carbonyl compounds. Criegee ozonides **F** can be made to react with water yielding 2 mol of carbonyl compounds and 1 mol of hydrogen peroxide (reaction 7). When water is the solvent, all four zwitterions stand a chance to react with water in competition with the other reactions. The probability for doing so will be greatest for the tertiary zwitterion **D** (reaction 8), because its addition to the carbonyl compound to yield **E** (reaction 5) is most likely much slower than reactions 2, 4, and 6, which are simple charge combination and fragmentation reactions. The hydroxyhydroperoxides **G** formed in reaction 8 are unstable in water and usually are in equilibrium with the corresponding carbonyl compounds and hydrogen peroxide (equilibrium 9).

SCHEME 2



Besides this "classical" ozonolysis, a partial oxidation of the C═C double bond (Scheme 2) is found with sterically hindered olefins that prevent an easy 1,3-cycloaddition (*6*). This can lead to the formation of epoxides and singlet oxygen (reactions 10 and 11) or a substituent shift and concomitant singlet oxygen elimination yields the corresponding carbonyl compound (reaction 12).

In the present study, we report the kinetics and the reaction products of ozone with ethene and a number of its methyl- and chlorine-substituted derivatives. It will be shown that in aqueous solutions, in contrast to the gas phase and carbon tetrachloride solutions (*7*−*14*), there is a good relationship between the rate of reaction and the electron density of the C═C double bond. In addition, whereas the material balances in the gas phase and in carbon tetrachloride solutions are poor, practically full material balances are obtained in aqueous solutions. The stopped-flow technique allows the characterization of short-lived peroxidic intermediates, and additional valuable information has been obtained with the help of a new fast conductometric detection system. The combination of kinetic and product data will allow us to draw some conclusions as to mechanistic aspects.

Experimental Section

Ethylene (Messer Griesheim), vinyl chloride (Fluka), 1,2-dichloroethene (Merck), and trichloroethene (Merck) were commercially available at a purity >98%. The mixture of cis- and *trans*-1,2-dichloroethene (Aldrich) was separated by preparative gas chromatography to a purity of >99% for both compounds. Aqueous solutions were made up in Milli-Q-filtered (Millipore) water. Reactions were carried out at natural pH, and during the course of the reaction, the solutions turned acidic. Thus, a contribution of OH radicals [induced by the (slow) reaction of ozone with OH^-] can be neglected. When gaseous olefins had to be reacted, saturated solutions were diluted if required. The solubilities in water of ethene (4.59×10^{-3} mol dm^{-3}) (*15*), propene (4.75×10^{-3} mol dm^{-3}) (*15*), and vinyl chloride (4.42×10^{-2} mol dm^{-3}) (*16*) were taken from the literature. The solubility of tetramethylethene is not yet reported. For its determination, a small amount of *tert*-butyl alcohol was added as an internal standard to its saturated solution in D_2O, and their NMR signals were integrated after accumulation overnight (Bruker, 400 MHz). The value of 8.4×10^{-4} mol dm^{-3} thus obtained is in agreement with expectations (*15*).

Ozone was generated from oxygen with a WEDECO SWO-70 ozonator. Solutions of the substrates were mixed with the ozone-containing water whose ozone concentration had been determined by spectrophotometry using $\epsilon(260 \text{ nm}) = 3314$ dm^3 mol^{-1} cm^{-1} (*17*).

The kinetics of the reaction of ozone with the compounds of interest were measured spectrophotometrically using a stopped-flow setup (Biologic SFM-3) equipped with a diode array system (TIDAS-16, J&M, Analytische Mess-und Regeltechnik, Aalen). In addition, some experiments were carried out using an in-house constructed conductometric detection system, similar to the one used in pulse radiolysis studies (*18*, *19*). Details of this setup will be published elsewhere.

For the product studies, the substrate concentrations were chosen ≥10 times the ozone concentration. In all cases, linear yield vs ozone concentration relationships were obtained.

Ionic products were determined by high-performance ion chromatography (HPIC, Dionex DX-100, equipped with an electrochemical suppressor, AS-9 column using $NaHCO_3$/Na_2CO_3 buffers as eluents). Carbon dioxide was also determined by HPIC as carbonate. For these measurements, the water had been freed from carbon dioxide prior to adding the substrate. The reaction with ozone was carried out in a closed vessel, and carbonate-free potassium hydroxide was added through a serum cap. After 30 min of stirring to trap gas-phase carbon dioxide, aliquots were analyzed on a AS-1 column with water as eluent (omitting the electrochemical suppressor). Carbon monoxide was identified by its IR spectrum. For quantification, the gas contained in a purgable reaction vessel was circulated past a CO detector (GWG 2502, Gesellschaft für Gerätebau, Dortmund) with the help of a peristaltic pump; the instrument was calibrated with a CO-filled 0.111 mL loop. For details see ref *20*. Formaldehyde, acetaldehyde, and acetone were determined spectrophotometrically using the Hantzsch (acetylacetone) method (*21*), 3-methylbenzthiazolin-2-one-hydrazine (*22*), and vanilline (*22*), respectively. Hydrogen peroxide and organic hydroperoxides were determined with molybdate-activated iodide (Allen's reagent) (*23*). The kinetics were followed spectrophotometrically at 350 nm by stopped flow when the reaction was too fast to monitor it by conventional UV/Vis spectrophotometry (Perkin-Elmer Lambda 16).

Results and Discussion

Kinetics of the Ozone/Olefin Reaction. The rate constants of the reaction of ozone with ethene and some of its methyl- and chlorine-substituted derivatives in aqueous solution are compiled in Table 1. For comparison, rate constants measured in carbon tetrachloride and in the gas phase are also included in this table.

Most of our data were determined using the stopped-flow technique by following the decay of the ozone absorption at 260 nm as a function of time at different substrate to ozone concentrations. To meet the conditions of pseudo-first-order kinetics, a large excess of substrate was used in these experiments. An example is shown in Figure 1.

The rate constant for the reaction of tetramethylethene with ozone is too fast to be measured by the stopped-flow technique using saturated aqueous solutions. Its solubility in water has been determined at 8.4×10^{-4} mol dm^{-3}, and thus its rate of reaction must be higher than 10^6 dm^3 mol^{-1} s^{-1}. This conclusion is supported by the data that are available for carbon tetrachloride solution (Table 1) where it reacts an order of magnitude faster than ethene.

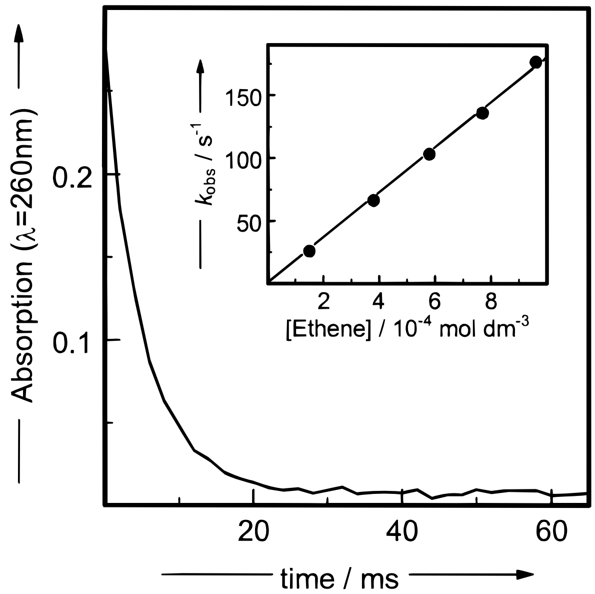


FIGURE 1. Decay of ozone as followed by its absorption at 260 nm in the presence of an excess of ethene. Inset: Observed rate of decay as a function of the ethene concentration.

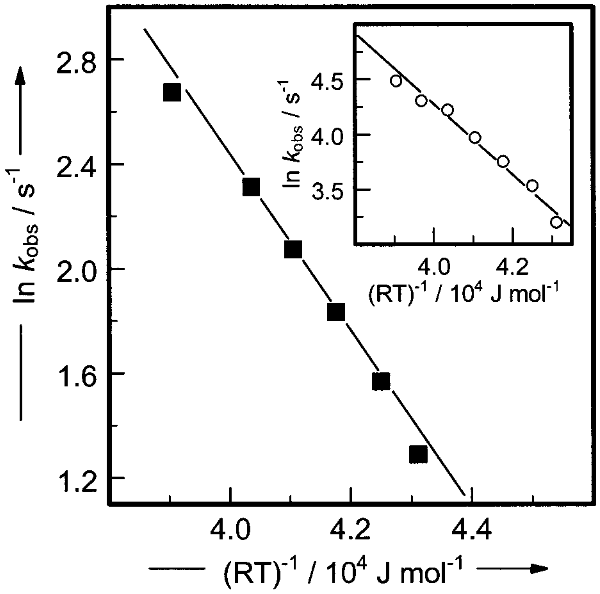


FIGURE 2. Arrhenius plot for the rate of reaction of ozone with *trans*-1,2-dichloroethene. Inset: *cis*-1,2-dichloroethene.

In water, the rate constants are typically 1 order of magnitude higher than those measured in carbon tetrachloride (with the notable exception of tetrachloroethene). In both cases the rate of reaction largely increases with increasing electron density of the $C{=}C$ double bond, and steric effects only play a minor role. For example, the sterically hindered tetramethylethene reacts an order of magnitude faster than ethene and also faster than propene; 1,1-dichloropropene reacts about 20 times faster than 1,1-dichloroethene and about 100 times faster than trichloroethene.

In the gas phase, the trend of the rate constants is somewhat erratic. In addition, the kinetics seem not to follow second-order kinetics in all cases.

There is a considerable difference in the rate constant of *trans*-1,2-dichloroethene and *cis*-1,2-dichloroethene. The temperature dependence of their reaction with ozone has been measured between 6 and 45 °C, the upper limit being determined by degassing problems of these volatile compounds. Arrhenius plots are shown in Figure 2.

From these data an activation energy of 31 kJ mol^{-1} is calculated for *trans*-1,2-dichloroethene, but the less reactive *cis*-1,2-dichloroethene shows a very similar activation energy of 34 kJ mol^{-1}. Thus, the considerable difference in their rates of reaction must be largely due to differences in the frequency factor. A differentiation between steric and electronic effects is not possible.

In the case of chlorinated olefins, practically all the chlorine in the molecule is set free as chloride ions, i.e., HCl is formed, which results in a change in conductivity. In all cases no delayed HCl formation has been detected.

The solubility of the slowly reacting olefins (*16*), e.g., trichloroethene and 1,1-dichloroethene, is so low that at a maximum concentration the rate of ozone reaction is much slower than the resolution of the stopped-flow setup. In these cases phosgene is a potential unstable intermediate (see below), but it would hydrolyze too fast (reaction 13, $k_{13} = 9\ s^{-1}$) (*25*) to be detectable under these conditions.

$$Cl_2CO + H_2O \rightarrow CO_2 + 2\ HCl \qquad (13)$$

Vinyl chloride and *trans*-1,2-dichloroethene are sufficiently soluble, and their rate of reaction with ozone is fast enough to allow the reaction to proceed faster than the resolution of the stopped-flow setup. Yet, in both cases no HCl-releasing intermediate with a lifetime longer than 1 ms has been detected (cf. Figure 3).

According to the general Scheme 1, in these cases formyl chloride is formed (cf. reactions 19 and 23). This acyl chloride differs from the alkylated acyl chlorides that it decomposes readily into CO and HCl (reaction 14; $k_{14} = 10^4\ s^{-1}$) (*20*). Its water-induced hydrolysis (reaction 15) is too slow to compete effectively with this unimolecular decomposition and only at very high pH the OH^--induced hydrolysis (reaction 16; $k_{16} = 2.6 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$) becomes noticeable, leading to an increase of the formate yield and a concomitant drop of the CO yield (*20*).

$$HC(O)Cl \rightarrow CO + HCl \qquad (14)$$

$$HC(O)Cl + H_2O \rightarrow HC(O)OH + HCl \qquad (15)$$

$$HC(O)Cl + OH^- \rightarrow HC(O)OH + Cl^- \qquad (16)$$

In the case of *trans*-1,2-dichloroethene, the other product is the chlorohydroxymethylhydroperoxide (reaction 19). As has been found for other geminal chlorohydrines (*20*, *25*–*28*), it will lose HCl in less than a few microseconds. The fact that both reaction 14 and reaction 19 are that fast explains why the rate of ozone reaction remains the rate-limiting step with respect to the rate of HCl formation (Figure 3).

From the experiments shown in Figure 3, additional information can be derived. Of all intermediates in the Criegee mechanism, the ozonide **B** has potentially the longest lifetime (in water, reaction 5 is not expected to be able to compete with reaction 8; the long-lived ozonide **F** is hence an unlikely intermediate here). If its lifetime would exceed 1 ms, its decay would be rate limiting and hence its presence detectable by a delayed conductivity change. Since no HCl-releasing species with a lifetime longer than 1 ms was observed, it is concluded that, at least in water, such ozonides must have a considerably shorter lifetime.

Product Studies. At conversions of the substrates of less than 10%, the product yields increased linearly with the ozone dose. The products and their yields (in mole per mole of ozone) are compiled in Table 2. It can be seen from these data that in all cases a practically full material balance has been obtained. Under the conditions of the determination of the carbonyl compounds (e.g., formaldehyde by the acetylacetone method); the corresponding α-hydroxyalkylhydroperoxides (e.g., hydroxymethylhydroperoxide) are not stable, and the yields of the latter are always included in those of the former. The yields of hydroperoxides can be determined with Allen's reagent (molybdate-activated iodide ions). Since the rate of reaction is noticeably different for different hydroperoxides, they can thus be distinguished. Details are discussed in the following section.

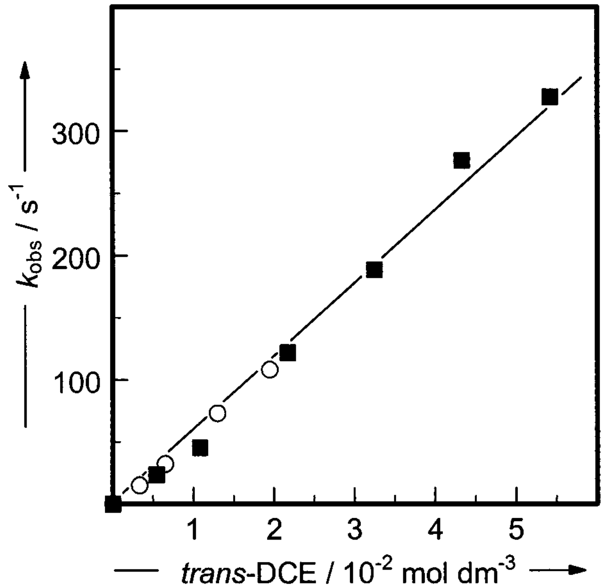


FIGURE 3. Kinetics of the reaction of *trans*-1,2-dichloroethene (*trans*-DCE) with ozone as followed by the stopped-flow technique: (○) optical measurements at 260 nm (decay of ozone), (■) conductometric measurements (HCl formation).

Determination of the Hydroperoxidic Products with Allen's Reagent. Hydroperoxides can oxidize molybdate-activated iodide ions (Allen's reagent) to iodine (detected as I_3^- at 350 nm). The kinetics of this reaction are complex. In the case of hydrogen peroxide, the rate of reaction passes through a maximum with increasing iodide concentration (*29*). Thus, in the present study a fixed final iodide concentration (0.13 mol dm^{-3}) was used for all systems investigated, and the rate of I_3^- formation has only been taken as a fingerprint for a given hydroperoxide without drawing further mechanistic conclusions.

According to the general Scheme 1, the symmetrically substituted olefins can yield only one kind of hydroperoxide and the corresponding carbonyl compound (reactions 17–19).

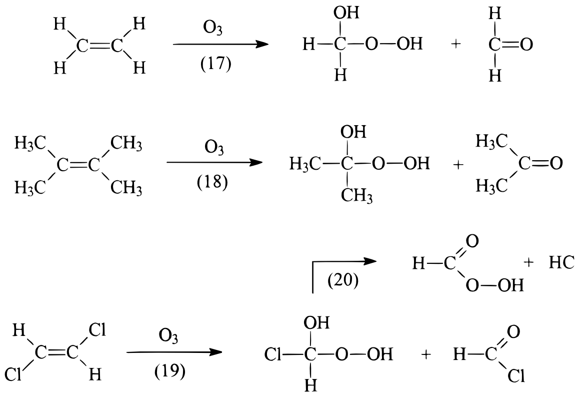
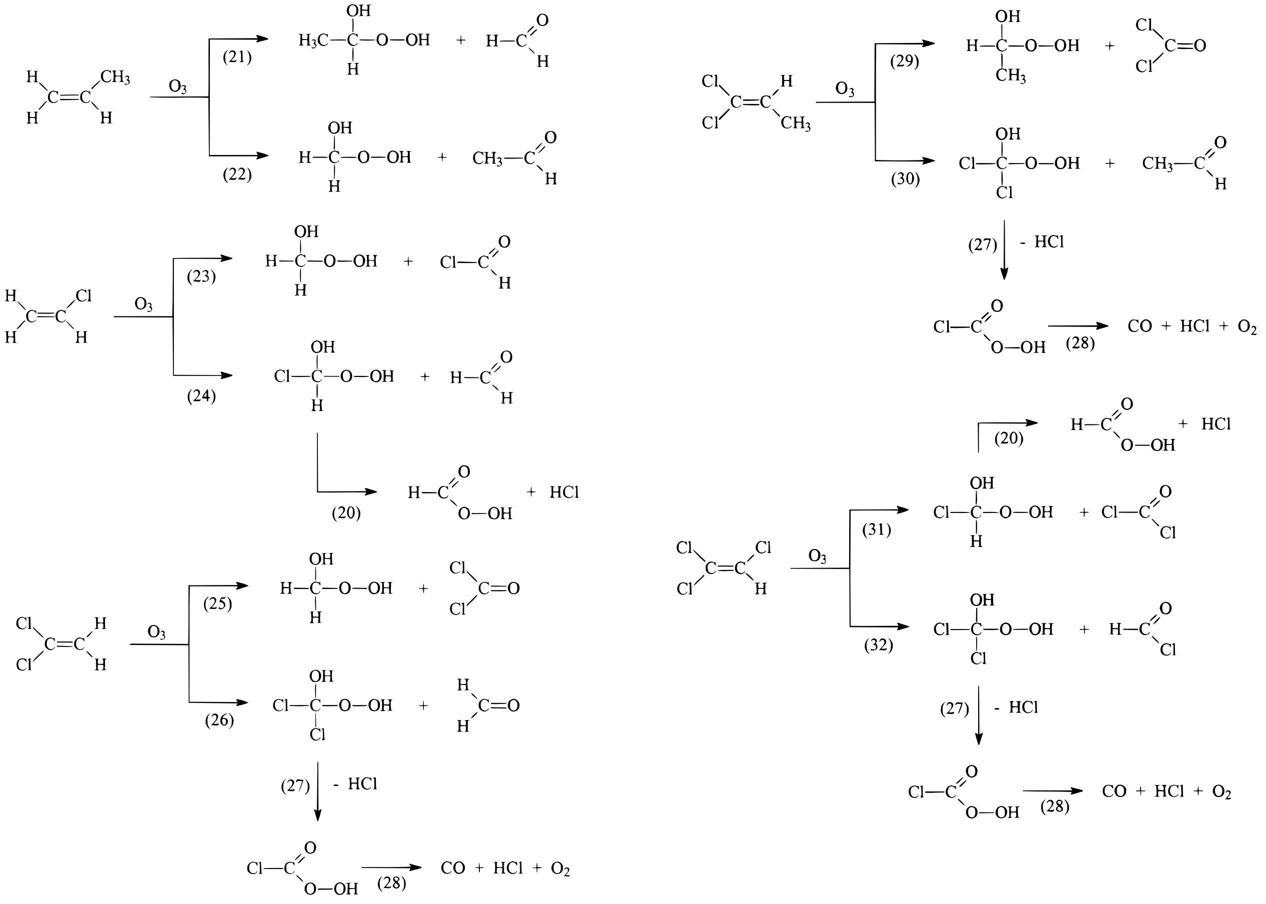


TABLE 2. Products and Their Yields (per Mole of Ozone) in the Ozonolysis of Ethene and Some of Its Methyl- and Chlorine-Substituted Derivatives[a]

product	ethene	propene	Me$_4$Ethen	Cl-ethene	1,1-Cl$_2$-ethene	1,2-Cl$_2$-ethene	Cl$_3$-ethene	1,1-Cl$_2$-propene
HCl				1.05	1.95	2.02	2.87	2.05
HC(O)OH				0.06	0.03	1.01	0.82	
HC(O)OOH				0.02*		0.98*	0.88*	
HOCH$_2$COOH					0.07***			
CO				1.01		1.08	0.04	
CO$_2$					0.90	0.02	0.95	1.01
CH$_2$O	2.04	1.03			0.96			
H$_3$CCHO		0.97						1.03
(CH$_3$)$_2$CO			1.74					
HOCH$_2$OOH	1.08**			1.06**	0.96**			
CH$_3$CH(OH)OOH		0.99**						0.98**
(CH$_3$)$_2$C(OH)OOH			****					
Cl$_2$CHCHO					<0.01***			
ClCH$_2$C(O)OH					0.08***			
Cl$_2$CHC(O)OH							0.04***	
[(CH$_3$)$_2$C(OH)]$_2$			≈0.1***					

[a] (*) Precursor of formic acid. (**) Precursor of aldehydes. (***) Product of partial cleavage reaction. (****) The reaction with Allen's reagent is too slow for its determination.

SCHEME 3



In the unsymmetrically substituted ones, two different sets may be formed. The various possibilities are depicted in the reactions shown in Scheme 3.

According to these reactions, five different hydroperoxides are expected (the asterisk indicates the symmetric olefins that can only yield one kind): hydroxymethylhydroperoxide (from ethene*, propene, vinyl chloride, and 1,1-dichloroethene), 1-hydroxyethylhydroperoxide (from propene and 1,1-dichloropropene), 2-hydroxy-2-propylhydroperoxide (from tetramethylethene*), formic peracid (vinyl chloride, 1,2-dichloroethene*, and trichloroethene), and chloroformic peracid (1,1-dichloropropene and trichloroethene). The latter hydroperoxide is believed to be very short-lived and, if formed, not detectable under our conditions. Its hydroperoxidic function may be quite acidic due to the neighboring electron-withdrawing group, and reaction 28 may proceed from the chloroperoxoformate ion by O$_2$ and chloride ion loss.

In Figure 4 the kinetics of the reaction of the hydroxymethylhydroperoxide (obtained from the ozonolysis from vinyl chloride) is shown. In the inset of this figure the corresponding kinetics of hydrogen peroxide are displayed. It can be seen that the hydroxymethylhydroperoxide reacts 2 orders of magnitude more slowly than hydrogen peroxide.

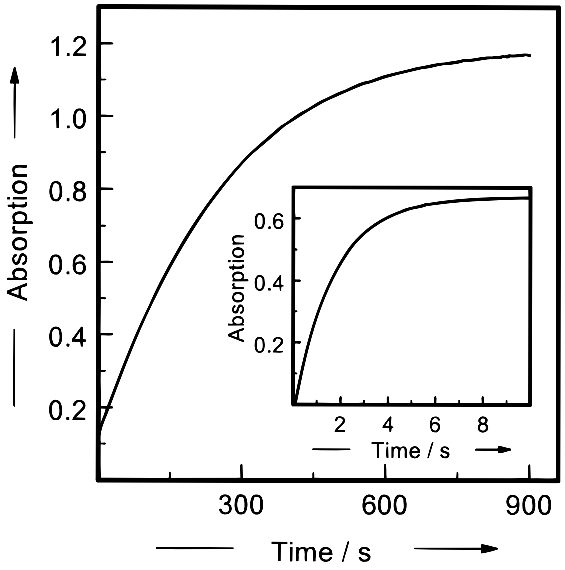


FIGURE 4. Kinetics of the reaction of the hydroxymethyl hydroperoxide (generated in the reaction of vinyl chloride with ozone) with Allen's reagent as followed by the buildup of the absorption of I_3^- at 350 nm. Inset: Kinetics of the reaction with hydrogen peroxide.

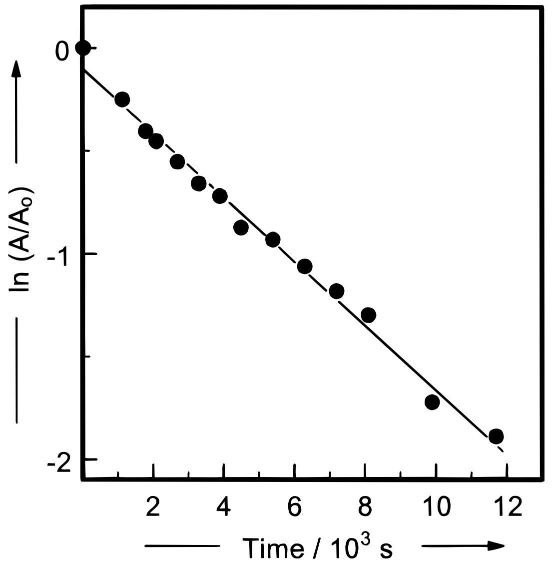


FIGURE 5. Kinetics of the hydrolysis of formic peracid into formate and hydrogen peroxide. The reaction has been followed by the contributions of the fast (formic peracid) and slow (hydrogen peroxide) reactions with Allen's reagent. $A_0 = I_3^-$ absorption of the fast buildup at time zero, A = absorption at time t (see text).

TABLE 3. Rate Constants of the Reaction of Various Hydroperoxides with Allen's Reagent (Iodide Concentration 0.13 mol dm^{-3})

hydroperoxide	k_{obs} (s^{-1})
HCOOOH	218
H_2O_2	0.27
$HOCH_2OOH$	3.4×10^{-3}
$CH_3CH(OH)OOH$	5×10^{-2}
$(CH_3)_2C(OH)OOH$	$\approx 2 \times 10^{-5}$

Authentic hydroxymethylhydroperoxide was prepared by reacting hydrogen peroxide with an excess of formaldehyde, and the same kinetics as those shown in Figure 4 were obtained.

The organic hydroperoxides that are formed in the present systems react with considerably different rate constants, and from their compilation in Table 3 it can be seen that it is even possible to decide by a kinetic analysis whether in unsymmetrically substituted olefins two different hydroperoxides are formed. For example, vinyl chloride may yield hydroxymethylhydroperoxide (reaction 23) and/or formic peracid (reactions 24 and 20). The formation of the latter to any major extent can be excluded from the kinetic trace shown in Figure 4. When the reaction is followed by stopped flow, the yield of performic acid is determined at 2%. The offset in Figure 4 could indicate a higher yield, but the intercept results not only from the contribution of performic acid but also from the reaction that has occurred during the time when the reagents were manually mixed outside the spectrophotometer.

In aqueous solution, hydroxymethylhydroperoxide is in equilibrium with formaldehyde and hydrogen peroxide (equilibrium 33).

$$HOCH_2OOH \rightleftharpoons CH_2O + H_2O_2 \qquad (33/-33)$$

For the stability constant of equilibrium 33, values of $K_{33} = 1.27 \times 10^4$ dm^3 mol^{-1} (*30*) and $K_{33} = 160$ dm^3 mol^{-1} (*31*) have been reported. Under our conditions, after 24 h the major part of the hydroxymethyl hydroperoxide was still present. This agrees with the reported value for $k_{33} = 1.5 \times 10^{-6}$ s^{-1} (*30*).

The reaction of the 2-hydroxy-2-propyl hydroperoxide (from the reaction of H_2O_2 with acetone or the ozonolysis of tetramethylethene) with Allen's reagent is too slow to be followed up to completion, and the value of the rate constant given in Table 3 has been obtained by fitting data of the formation of I_3^- to a pseudo-first-order rate law. Due to these uncertainties, its yield in the ozonolysis of tetramethylethene cannot be quantified by this method, and hence its value is missing in Table 2.

As can be seen from Table 3, the rate of the Allen's reaction of formic peracid and of hydrogen peroxide differ by nearly 3 orders of magnitude. This allows us to follow the kinetics of the hydrolysis of formic peracid (reaction 33) by measuring the ratio of the fast and the slow part of the buildup as a function of time.

$$HC(O)OOH + H_2O \rightarrow HC(O)OH + H_2O_2 \qquad (34)$$

$$HC(O)OOH \rightarrow CO_2 + H_2O \qquad (35)$$

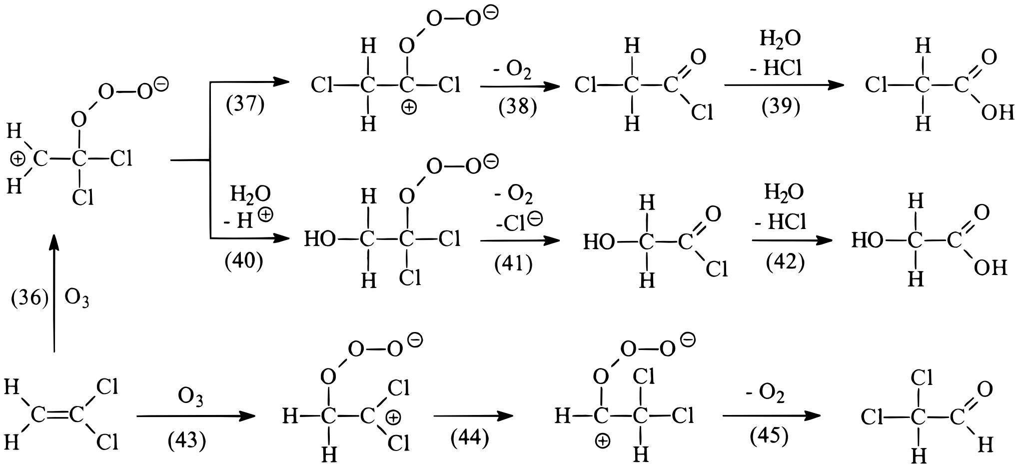
The hydrolysis is of first-order kinetics, and from the slope of the straight line in Figure 5, a rate constant of $k_{34} = 1.6 \times 10^{-4}$ s^{-1} is obtained. Compared to the rate of the hydrolysis of formic peracid, the hydrolysis of acetic peracid ($k = 3.5 \times 10^{-5}$ s^{-1}) (*32*) is considerably slower. This is understood if water addition to the electrophilic carbon determines the rate of reaction.

It has been noted that the total hydroperoxide yield does not remain fully constant over the whole decay of the formic peracid, and it is envisaged that reaction 35 may occur in competition to a small extent. This is supported by the fact that in the ozonolysis of *cis*- and *trans*-1,2-dichloroethene carbon dioxide is formed in a yield of about 2% (Table 2).

The Criegee Mechanism and Partial Cleavage. In all cases, the formation of the major products can be explained on the basis of the Criegee mechanism (Scheme 1). With ethene itself and with its low-substituted derivatives (propene, vinyl chloride, and 1,2-dichloroethene), no products of a partial cleavage have been detected. Since in these cases the material balance is very good, not much material seems to have escaped our attention. *Cis*- and *trans*-1,2-dichloroethene yield an identical product distribution. For this reason, no separate columns are given in Table 2.

In the case of ethene, 2 mol of formaldehyde are formed, because the hydroxymethylhydroperoxide decomposes into

SCHEME 4



formaldehyde and hydrogen peroxide under the conditions of the Hantzsch reaction. The yield of hydroxyhydroperoxide is half of that of the total yield of formaldehyde. For putting up similar material balance considerations in the cases of vinyl chloride and *cis*- and *trans*-1,2-dichloroethene, one has to keep in mind that the formyl chloride decomposes mainly into CO and HCl (only a few percent hydrolyze yielding formic acid), i.e., that the CO yield is a measure for the formyl chloride yield in these systems.

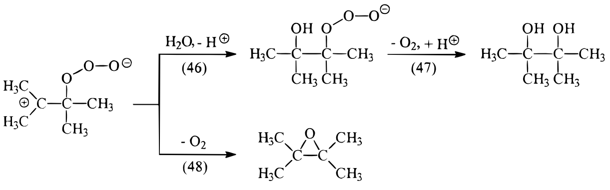
Unsymmetrically substituted olefins provide an interesting mechanistic aspect since they may yield two different carbonyl compound and two different hydroperoxides. From an analysis of the final products, a distinction would not be possible because the hydroperoxides decompose into the carbonyl compounds and hydrogen peroxide. However, the very different kinetics of the reactions of the hydroperoxides with Allen's reagent allows us to differentiate between the various hydroperoxides. It has been found that in the case of propene practically only the hydroxyethylhydroperoxide is formed, i.e., reaction 21 strongly dominates over reaction 22. A similarly strongly directing effect of the substituent, but now in the other direction, is found in the case of vinyl chloride. Here practically only the hydroxymethylhydroperoxide is formed (reaction 23), and the competing reaction 24 that would yield formic peracid amounts to about 2% only.

In the case of 1,1-dichloroethene, hydroxymethylhydroperoxide is the only hydroperoxide (reaction 25), while 1,1-dichloropropene yields only hydroxyethylhydroperoxide (reaction 29). The other potentially competing reactions (reactions 26 and 30, respectively) are not followed. This conclusion is based on the fact that in a stopped-flow experiment no rapidly reacting peracid is detected. This would not be a sufficient condition for the exclusion of reaction 30, since the chloroformic peracid could rapidly decompose (reaction 28). Since no CO is formed, pathway 30 can indeed be neglected.

Trichloroethene shows a strong dominance in the formation of formic peracid (reaction 31 followed by reaction 20), and the route to chloroformic peracid (reaction 32 followed by reactions 27 and 28) has only a small contribution as judged from the CO yield. On the basis of the formic peracid and CO yields (cf. Table 2), the branching ratio for reaction 31 over reaction 32 is 22:1. Thus the selectivity is quite high. These results seem to be best explained by a fast equilibrium between the ozonide **B** and the zwitterion **C** (equilibrium 3 in Scheme 1; in unsymmetrically substituted olefins two different zwitterions may be formed), and that the final product distribution is determined by the rate of reaction 4 which will be slow when a methyl group stabilizes the positive charge by electron donation and fast in the case of chlorine substituents that further withdraw electron density.

Partial cleavage has been observed only with tetramethylethene, 1,1-dichloroethene, and trichloroethene. In all cases the importance of the partial cleavage pathway is below 10%. Chloroacetic acid and some dichloroacetaldehyde as well as glycolic acid are formed from 1,1-dichloroethene, and dichloroacetic acid is formed from trichloroethene. It is clear that the formation of the chlorinated acetic acids requires a chlorine shift. With 1,1-dichloroethene, two primary zwitterions **A** can be formed, one where the positive charge is at the methylene group (reaction 36) and the other where the positive charge is at the dichloromethylene group (reaction 43, see Scheme 4). In the latter the charge is less stabilized, although its formation seems to be more likely for steric reasons. In ionic processes, charge stabilization often determines the reaction pathway. In competition with the ring-closing reaction (cf. reaction 2 in Scheme 1), the zwitterion formed in reaction 36 may undergo a chlorine shift (reaction 37) or react with water (reaction 40). Both reactions will be followed by a loss of O_2 (reactions 38 and 41). In reaction 41, a geminal chlorohydrine anion will be formed that rapidly loses a chloride ion (see above), thereby yielding hydroxyacetyl chloride which subsequently hydrolyze into glycolic acid (reaction 42). In reaction 38, chloroacetyl chloride is formed. Its subsequent hydrolysis (reaction 39) proceeds with a rate constant of $k_{39} = 5.5\ s^{-1}$ (Dowideit and von Sonntag, to be published). A minor product in this system is dichloroacetaldehyde, which may be formed by a hydride shift according to reaction 44 which is again followed by O_2 loss (reaction 45).

The formation of dichloroacetic acid from trichloroethene will be analogous to that depicted above for the formation of chloroacetic acid from 1,1-dichloroethene. In tetramethylethene a major product is 2,3-dimethyl-2,3-dihydroxybutane. A reaction analogous to reaction 40 explains its formation (reactions 46 and 47).



Epoxides such as ethylene oxide and its tetramethyl derivative are stable in neutral aqueous solutions (cf. refs *33* and *34*; ethylene oxide hydrolyses in water of pH 5.7 with a half-life of 1.1 month; H.-P. Schuchmann and C. von Sonntag, unpublished results), and hence the observed glycol cannot have the epoxide as precursor. Thus in water, ionic processes prevent epoxide formation (reaction 47) that dominate the partial cleavage pathway in nonaqueous solution (Scheme 2).

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Literature Cited

(1) Glaze, W. H. *Environ. Health Perspect.* **1986**, *69*, 151−157.
(2) von Sonntag, C. *J. Water Supply Res. Technol.—Aqua* **1996**, *45*, 84−91.
(3) von Sonntag, C.; Mark, G.; Mertens, R.; Schuchmann, M. N.; Schuchmann, H.-P. *J. Water Supply Res. Technol.—Aqua* **1993**, *42*, 201−211.
(4) Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027−1284.
(5) Bailey, P. S. *Ozonation in Organic Chemistry. Vol. I. Olefinic Compounds*; Academic Press: New York, 1978.
(6) Bailey, P. S.; Lane, A. G. *J. Am. Chem. Soc.* **1967**, *89*, 4473−4479.
(7) Williamson, D. G.; Cvetanovic, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 3668−3672.
(8) Williamson, D. G.; Cvetanovic, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 4248−4252.
(9) Huie, R. E.; Herron, J. T. *Int. J. Chem. Kinet.* **1974**, *7*, 165−181.
(10) Herron, J. T.; Huie, R. E. *J. Phys. Chem.* **1974**, *78*, 2085−2088.
(11) Sanhueza, E.; Hisatsune, I. C.; Heicklen, J. *Chem. Rev.* **1976**, *76*, 801−826.
(12) Blume, C. W.; Hisatsune, I. C.; Heicklen, J. *Int. J. Chem. Kinet.* **1976**, *8*, 235−258.
(13) Hull, L. A.; Hisatsune, I. C.; Heicklen, J. *Can. J. Chem.* **1973**, *51*, 1504−1510.
(14) Mathias, E.; Sanhueza, E.; Hisatsune, I. C.; Heicklen, J. *Can. J. Chem.* **1974**, *52*, 3852−3862.
(15) Okouchi, S.; Saegusa, H.; Nojima, O. *Environ. Int.* **1992**, *18*, 249−261.
(16) Horvath, A. L. *Halogenated Hydrocarbons: Solubility-Miscibility with Water*; Marcel Dekker: New York, 1982.
(17) Forni, L.; Bahnemann, D.; Hart, E. J. *J. Phys. Chem.* **1982**, *86*, 255−259.
(18) Bothe, E.; Janata, E. *Radiat. Phys. Chem.* **1994**, *44*, 455−458.
(19) von Sonntag, C.; Schuchmann, H.-P. *Methods Enzymol.* **1994**, *233*, 3−20.
(20) Dowideit, P.; Mertens, R.; von Sonntag, C. *J. Am. Chem. Soc.* **1996**, *118*, 11288−11292.
(21) Nash, T. *Biochem. J.* **1953**, *55*, 416−421.
(22) Kakac, B.; Vejdelek, Z. J. *Handbuch der photometrischen Analyse, Vol 1*; Verlag Chemie: Weinheim, 1974.
(23) Allen, A. O.; Hochanadel, C. J.; Ghormley, J. A.; Davis, T. W. *J. Phys. Chem.* **1952**, *56*, 575−586.
(24) Hoigne, J.; Bader, H. *Water Res.* **1983**, *17*, 173−183.
(25) Mertens, R.; von Sonntag, C.; Lind, J.; Merenyi, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1259−1261.
(26) Köster, R.; Asmus, K.-D. *Z. Naturforsch.* **1971**, *26B*, 1108−1116.
(27) Latif, N.; O’Neill, P.; Schulte-Frohlinde, D.; Steenken, S. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 468−471.
(28) Mertens, R.; von Sonntag, C. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2181−2185.
(29) Merga, G.; Schuchmann, H.-P.; Rao, B. S. M.; von Sonntag, C. *J. Chem. Soc., Perkin Trans. 2* **1996**, 551−556.
(30) Bothe, E.; Schulte-Frohlinde, D. *Z. Naturforsch.* **1980**, *35B*, 1035−1039.
(31) Zhou, X.; Lee, Y. *J. Phys. Chem.* **1992**, *96*, 265−272.
(32) Uher, G.; Gilbert, E.; Eberle, S. H. *Vom Wasser* **1991**, *76*, 225−234.
(33) Pritchard, J. G.; Siddiqui, I. A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 452−457.
(34) Lamaty, G.; Maloq, R.; Selve, C.; Sivade, A.; Wylde, J. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1119−1124.

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