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Kinetic Behavior of Mn(III) Complexes of Pyrophosphate, EDTA, and Citrate

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Aqueous complexes of Mn^{3+} ion with the ligands pyrophosphate ($P_2O_7^{4-}$), EDTA ($C_{10}H_{12}O_8N_2^{4-}$, ethylenediaminotetraacetate^{4-}), or citrate (CIT^{3-}, $C_6H_5O_7^{3-}$) were prepared rapidly in solution by the general reaction: Mn(VII) + 4Mn(II)L + L→ 5Mn(III)L, where L is the ligand (in known excess). Different initial pH values of the complex solutions were obtained by prior addition of required acid, base, or buffer. Disappearance of Mn(III)L complex with time was monitored by light absorbance at appropriate wavelengths. Rates of loss for each Mn(III)L complex are found to depend on pH and the ratio $[\text{ligand}]_T/[\text{Mn}]_T$. Relative chemical time scales for Mn(III)L disappearance at neutral pH and similar ligand-to-metal ratios were manganese(III) pyrophosphate > manganese(III) citrate >> manganese(III) EDTA. The kinetic observations are interpreted as reflecting ligand hydrolysis and disproportionation in the case of pyrophosphate (a nonredox active compound), inner-sphere electron transfer from citrate to Mn^{3+}, and both outer-sphere and intramolecular electron transfer from EDTA to Mn^{3+}. In the presence of O_2, manganese(II) citrate complex is reoxidized to manganese(III) citrate. The results suggest a potential for formation of Mn(III) complexes with ligands in great excess and kinetic stabilization under certain natural water conditions (e.g., where pronounced redox gradients are present or where appreciable concentrations of superoxide, peroxide, and hydroxyl radical are produced). Similar Mn(III) behavior to that reported here might be anticipated for other ligands such as catechol and humic mattter in natural waters.

Introduction

The aim of the work reported here is to explore the rates of decomposition of complexes of manganese in the +III oxidation state as a function of the complexing ligand, the total ligand:manganese concentration ratio ($[L]_T/[Mn]_T$), and pH. Three ligands were chosen: pyrophosphate, as an example of a nonredox active ligand; EDTA, as an example of an organic ligand associated with water contamination; and citrate, as an example of a naturally occurring organic ligand expected to be found in natural waters as a consequence of biological activity.

In natural water chemistry, the oxidation states of manganese which have received the greatest attention are Mn(II) and Mn(IV). Solid phases of the composition MnO_2 have often been assumed to be common oxidation products of Mn^{2+}. However, it is now recognized that phases such as MnOOH(s) (the Mn(III) state) are often initial products upon oxidation of Mn^{2+} (*1, 2*). Mn(III) aqueous species have been recognized for some time in biochemistry and bio-inorganic chemistry (*3, 4*), electrochemistry (*5*), analytical chemistry (*6*−*8*), and soil chemistry (*9*). Until recently, little consideration was given to the possible occurrence and reactions of Mn(III) complexes in natural waters. Studies by Luther and co-workers (*10*) led to the suggestion that organic complexation of dissolved manganese might have important consequences for manganese cycling at the oxic/anoxic interface. Kostka et al. (*11*) generated manganese(III) pyrophosphate complexes by dissolution of solid Mn_2O_3 in laboratory studies and demonstrated the ability of the complex to act as a terminal electron acceptor in microbiological systems.

The oxidation−reduction energetics and kinetics of Mn(III) in aqueous solutions depend strongly on the coordination states of Mn(II) and Mn(III). Mn(III)L species can serve as both as electron acceptors (e.g., Mn(III)L + O^-_2 → Mn(II)L + O_2) and as electron donors (e.g., Mn(III)L + O_2 → MnO_2 + L) (Note: reactions not balanced with respect to charge) (*9, 12*). Mn(II) complexes (e.g., L = pyrophosphate, citrate, malate) can act as catalysts for the dismutation of superoxide, O_2^-, in vitro, with the manganese cycling between the II and III states (*13*).

Pyrophosphate complexes of Mn(II) are oxidized to manganese(III) pyrophosphate species by superoxide ion, O_2^- (*12*). At neutral pH the second-order rate constant (25 °C) is $1.68 \times 10^7\ M^{-1}\ s^{-1}$, indicating a half-reaction time ($t_{1/2}$) of about 60 ms for micromolar Mn concentrations in the presence of a 30-fold excess of pyrophosphate. Mn(II)/Mn(III) reaction kinetics involving O_2^-, H_2O_2, and OH have been incorporated in cloud chemistry models by Jacob et al. (*14*).

Manganese peroxidase enzyme (MnPase) from a white-rot basidomycete oxidizes Mn(II)L to Mn(III)L, where L is a stabilizing ligand for Mn(III) (e.g., tartrate, pyrophosphate). The Mn(III)L, in turn, can oxidize organic substrates, such as phenol (*15*).

Thermodynamic and Kinetic Background for Experiments. The aqueous Mn(III) ion, Mn^{3+}(aq), is a strong Bronsted acid. Experiments in 3 M ionic strength solutions and at very low pH yielded two hydrolysis constants for monomeric Mn^{3+} (*16*):

$$Mn^{3+} + H_2O \leftrightarrow MnOH^{2+} + H^+ \quad \log {}^*K_1 = 0.4 \pm 0.1$$

$$Mn^{3+} + 2H_2O \leftrightarrow Mn(OH)_2{}^+ + 2H^+ \quad \log {}^*\beta_2 = 0.1 \pm 0.1$$

There appears to be no information on subsequent hydrolysis equilibria.

The standard reduction potential $E°_H$, for the half reaction $Mn^{3+}(aq) + e^- = Mn^{2+}(aq)$ is approximately 1.5 V (*17*). The Mn^{3+}(aq) ion is unstable with respect to disproportionation:

$$2Mn^{3+}(aq) + 2H_2O = MnO_2(s) + Mn^{2+}(aq) + 4H^+ \quad \log K \sim 7-9$$

The value of the equilibrium constant (log $K \sim 7-9$) depends on the particular MnO_2 phase formed. For example, assuming pH = 2, $[Mn^{2+}(aq)] = 10^{-3}$ M, and $[Mn(III)]_T = 10^{-4}$

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M, we calculate that $[Mn^{3+}]$ is $\sim 8 \times 10^{-9}$ M, using the hydrolysis constants. If we assume that the solid product is δ-MnO_2, we find that the free energy of reaction (ΔG) is ~ -11 kJ mol^{-1}; disproportionation of Mn(III) is spontaneous. Experiments show that the rate of disproportionation can be slowed by low pH, high Mn(II) concentration, and low Mn(III) concentration (*17*).

Pyrophosphate. Mn^{3+}(aq) complexes with the ligand pyrophosphate ($P_2O_7^{4-}$) have been studied by potentiometric and spectrophotometric methods. The standard reduction potential for Mn(III) in the presence of pyrophosphoric acid (the acidity constants are approximately: $pK_{a1} = 1$, $pK_{a2} = 2$, $pK_{a3} = 6$, and $pK_{a4} = 8$) has been estimated to be 1.15 V, a value from which it can be inferred that the ratio of the relevant Mn(III) and Mn(II) stability constants for pyrophosphate should be at least 10^6 (*18*). There is serious disagreement in the literature about major Mn(III) pyrophosphate species and their stability constants. One set of stability constants (*19*) leads to the conclusion that $MnHP_2O_7$-(aq) should be the major complex species at neutral pH. Based on these constants, the disproproportion reaction would then be

$$2MnHP_2O_7(aq) + 2H_2O = MnO_2(s) + MnP_2O_7^{2-} + HP_2O_7^{3-} + 5H^+ \quad \log K = -20$$

Assuming the following solution conditions, pH = 7, $Mn_T = 100\ \mu M$, $[Mn(III)]_T/[Mn(II)]_T = 10$, and $[P_2O_7]_T/Mn_T = 50$, the reaction free energy is $\Delta G \sim -82$ kJ mol^{-1}.

A different set of stability constants (*20*) indicates that $Mn(P_2O_7)_2^{5-}$ is the major complex species under neutral conditions. The disproportionation reaction would then be

$$2Mn(P_2O_7)_2^{5-} + H_2O = MnO_2(s) + MnP_2O_7^{2-} + 3HP_2O_7^{3-} + H^+ \quad \log K = -24.2$$

For the same solution conditions assumed above, ΔG is $\sim +74.7$ kJ mol^{-1}. This result implies that the manganese(III) pyrophosphate complex would be stable, not metastable, and that only at higher pH and higher Mn(III) concentrations would the disproportionation become spontaneous. The available thermodynamic data on manganese(III) pyrophosphate species are thus inconclusive, The authors have assumed that the $Mn(III)HP_2O_7$ species appears more plausible (*19*), but that $Mn(III)(P_2O_7)_{n>1}$ complexes cannot be ruled out.

In any event, it is known from spectrophotometric observations that aqueous complexes of Mn(III) with pyrophosphate do persist over long periods of time in the pH range approximately 1−7, if sufficient excess ligand is present. Slow decomposition of $Mn(III)-P_2O_7$ complexes may take place because of favorable disproportionation energetics or because of hydrolysis of the ligand (*21*): $HP_2O_7^{3-} + H_2O \rightarrow 2HPO_4^{2-} + H^+$.

EDTA. Mn(III) complexes with EDTA are metastable with respect to possible disproportionation of the III oxidation state (at higher pH) and to reduction of the III state of the metal by the reducing power of the ligand. The standard reduction potential for Mn(III)/Mn(II) in the presence of ethylenediaminetetraacetic acid (successive acidity constants described approximately by $pK_{a1} = 2$, $pK_{a2} = 3$, $pK_{a3} = 6$, and $pK_{a4} = 10$) has been determined experimentally to be 0.824 V in perchlorate medium (*22*). The stability constant for the formation reaction, $Mn^{3+}(aq) + EDTA^{4-} = Mn(EDTA)^-$, is reported to be 7.1×10^{24} in 0.20 M perchlorate medium (*22*). Titration of manganese(III) EDTA solutions over the pH range ∼3−9 indicates $pK_a \sim 5.3$ for conversion of a more-protonated (red) species to a less-protonated (yellow) species (*23*). We will denote the respective species as $MnHEDTA^0$ and $MnEDTA^-$ (but the actual states of protonation or hydroxylation are not known). For the reaction $Mn^{2+}(aq) + EDTA^{4-} = MnEDTA^{2-}$, the stability constant is $\sim 1.1 \times 10^{14}$ (*24*).

The disproportionation of $MnEDTA^-$

$$2MnEDTA^- + 2H_2O = MnO_2 + MnEDTA^{2-} + EDTA^{4-} + 4\ H^+ \quad \log K = -29$$

will be spontaneous; ΔG is ~ -10 kJ mol^{-1} for pH = 7, $Mn_T = 100\ \mu M$, $[Mn(III)]_T/[Mn(II)]_T = 10$, and $[EDTA]_T/Mn_T = 50$. For pH < 6.5, with the same metal and ligand ratios, the manganese(III) EDTA complexes become stable with respect to disproportionation, i.e., $\Delta G > 0$. Reduction of Mn(III) by EDTA species is energetically favored under a wide range of pH conditions.

The decomposition kinetics of manganese(III) EDTA complexes in the pH range 2−4.4 was studied by Schroeder and Hamm (*25*). Their work demonstrated that the rate of manganese(III) EDTA complex decomposition was pH-dependent and could be fit by a three-term rate law, representing three pathways: reduction of the Mn(III) by *excess* $HEDTA^{3-}$, reduction of Mn(III) by *internal electron transfer*, and reduction of Mn(III) by a more-protonated *excess* EDTA species, e.g, H_2EDTA^{2-}.

Citrate. A manganese(III) citrate (Mn(III)CIT) complex was utilized for Mn(III) analysis via spectrophotometry by Duke (*26*), using absorbance measurement at a peak wavelength of 430 nm. A stability constant for the complex Mn(III)CIT complex has not been reported. The acidity constants for citric acid are described approximately by $pK_{a1} = 3$, $pK_{a2} = 4$, and $pK_{a3} = 6$. By analogy with the iron(III) complex stability constant for citrate (*24*), it appears reasonable to estimate a $\log K \cong 15.0$ for the complex formation: $Mn^{3+}(aq) + CIT^{3-} = MnCIT^0$ in moderate ionic strength solutions ($\sim 10^{-3}-10^{-1}$ M). The stability constant for the $Mn(II)CIT^-$ species is reported to be approximately 5.0 at similar ionic strengths (*24*).

At neutral pH the predominant manganese species in substantial excess of citrate ligand are $Mn(III)CIT^0$ and $Mn(II)CIT^-$. The disproportionation reaction

$$2Mn(III)CIT^0 + 2H_2O = MnO_2 + Mn(II)CIT^- + CIT^{3-} + 4H^+$$

has an equilibrium constant of approximately 10^{-18}. For pH = 7, $Mn_T = 100\ \mu M$, $[Mn(III)]_T/[Mn(II)]_T = 10$, and $[CIT]_T/Mn_T = 50$, ΔG is ~ -60 kJ mol^{-1}. In neutral and alkaline solutions the decomposition of Mn(III)CIT can proceed spontaneously both by disproportionation and by reduction of Mn(III) by citrate.

Methods

Reagents. All Mn(III) complexes were synthesized using reagent grade chemicals without further purification. The ligand salts used were $Na_4P_2O_7 \cdot 10H_2O$ from Mallinckrodt, $Na_3C_6H_5O_7 \cdot 2H_2O$ from Fisher, and $Na_2C_{10}H_{14}N_2O_8 \cdot 2H_2O$ from J. T. Baker. The Mn(II) salt used was, in most cases, a $Mn(NO_3)_2$ solution (Aldrich). In cases where NO_3^- was undesirable $Mn(ClO_4)_2 \cdot 6H_2O$ (G. Frederick Smith) was used. The permanganate used was a 0.0203 M $KMnO_4$ solution (Aldrich). Commercial buffer solutions, 0.1 M *N*-tris(hydroxymethyl)-methyl-2-aminoethane sulfonic acid (TES) buffer (pH 7.5) and 0.1 M tris(hydroxymethyl)aminomethane (TRIS) buffer (pH 8.0), were used to augment pH control at low ligand concentrations (*27*).

Forming the Complexes. The Mn(III) complexes were formed using the manganous−permanganate reaction in excess ligand, as applied by Duke (*26*) for citrate, e.g.

$$4\mathrm{Mn(II)CIT}^- + \mathrm{MnO_4}^- + \mathrm{CIT}^{3-} + 8\mathrm{H}^+ \xrightarrow[\text{(excess ligand)}]{} 5\mathrm{Mn(III)CIT}^0 + 4\mathrm{H_2O}$$

A Mn(II) salt was dissolved along with the sodium salt of the ligand in distilled, deionized water. The pH was adjusted using nitric or perchloric acid plus sodium hydroxide. Equilibrium computations showed that the Mn(II) speciation in all solutions prior to $\mathrm{MnO_4}^-$ addition was essentially the Mn(II)L form. For example, in the pyrophosphate solutions the ratio $[\mathrm{Mn(II)P_2O_7}]/[\mathrm{Mn}^{2+}]$ was $>3 \times 10^3$ in all systems; in citrate solutions, the $[\mathrm{Mn(II)CIT}^-]/[\mathrm{Mn}^{2+}]$ was never less than 50 (for the smallest citrate excess). In many cases the excess ligand was used as the pH buffer; for experiments with low excess ligand an auxiliary buffer was used. The citrate ligand concentration studies used a bicarbonate buffer of 0.05 M $\mathrm{NaHCO_3}$ and nitric acid. TES or TRIS buffers were used in the $\mathrm{Mn(II)CIT}^-$ oxygenation experiments (*27*).

After the pH was adjusted, sufficient $\mathrm{MnO_4}^-$ was added rapidly to give a molar Mn(II):Mn(VII) ratio of 4:1. In general, the reaction quickly proceeded from the initial color of the permanganate to the color of the desired Mn(III) complex in a matter of a few minutes. Total manganese concentrations were typically 5×10^{-4} M, and $[\mathrm{L}]_\mathrm{T}/[\mathrm{Mn}]_\mathrm{T}$ ratios ranged from 1 to 200.

Kinetic Experiments. Decomposition reactions were carried out in polyethylene bottles or Pyrex flasks which were open to laboratory air and at laboratory temperatures, which ranged from 20 to 22 °C. However, for experiments where the effect of oxygen exclusion was to be examined, the Mn(II)−ligand solution was first prepared, adjusted to the proper pH, and then sparged with $\mathrm{N_2}$ for at least 1 h before adding permanganate to initiate Mn(III) complex formation. The reaction vessel container was then covered with Parafilm to minimize entry of air. To examine the influence of ambient laboratory light on the decomposition reactions, flasks were wrapped in foil to exclude light. Experiments on oxygenation of manganese(II) citrate solutions were conducted using either TES buffer (pH 7.5) or TRIS buffer (pH 8.0) (*27*).

Mn(III)L Measurements. Concentrations of Mn(III)L complexes were monitored spectrophotometrically by withdrawing samples periodically, filtering if necessary, and measuring absorbances at the appropriate peak wavelength using a Shimadzu UV-1201 spectrophotometer with either a 5 or 10 cm quartz cell. The wavelengths employed were 484 nm for manganese(III) pyrophosphate complex and 430 nm for Mn(III) citrate complex. In the pH range of interest, molar absorbances for the pyrophosphate and citrate complexes were found to be independent of pH. For EDTA, two distinct Mn(III) complexes, MnEDTA^- and MnHEDTA, could be followed by measuring peak absorbances at 450 nm (pH > 5.3) and 488 nm (pH < 5.3), respectively (*23*). From the measured absorbance, A, at the appropriate wavelength, the concentration, C, of Mn(III)L complex was computed. The quantity C/C_T was calculated from $A/[\mathrm{Mn}]_\mathrm{T}\epsilon_\lambda$, where $[\mathrm{Mn}]_\mathrm{T}$ is the stoichiometric concentration of the Mn(III) complex and ϵ_λ is the molar absorptivity (*27*).

Results and Discussion

Kinetic observations revealed that the method of forming Mn(III)L complexes yielded some variations in the initial conditions for some kinetic runs. It was found that the initial C/C_T was sometimes less than unity (loss of expected Mn(III)L product) and sometimes greater than unity (unreacted Mn(VII) or precipitation of light-absorbing or light-scattering particles). For example, at a $[\mathrm{P_2O_7}]_\mathrm{T}/[\mathrm{Mn}]_\mathrm{T}$ ratio of 10 and pH 7.8, rapid formation of particles was seen, indicative of disproportionation of the forming complex. Oxide particle formation was also noted in manganese(III) citrate experiments for $[\mathrm{CIT}]_\mathrm{T}/[\mathrm{Mn}]_\mathrm{T}$ ratios below 50. Direct reduction of permanganate by excess EDTA, yielding an manganese(III) EDTA complex, has been studied kinetically by Bose et al. (*28*). On the basis of their rate law for $\mathrm{HEDTA}^{3-} + \mathrm{MnO_4}^-$, we estimate that at pH 5 and with an excess [EDTA] ratio of 60:1, the half-reaction time for the direct reduction would be about 1 min. This competing reaction for $\mathrm{MnO_4}^-$ would cause initial C/C_T values to be on the low side at neutral and alkaline pH, and on the low side the greater the excess EDTA concentration. This is what was observed. The effect is not so great as to interfere with observing the time course of the reaction. Direct reaction with citrate would be very slow, based on kinetic data (*29*).

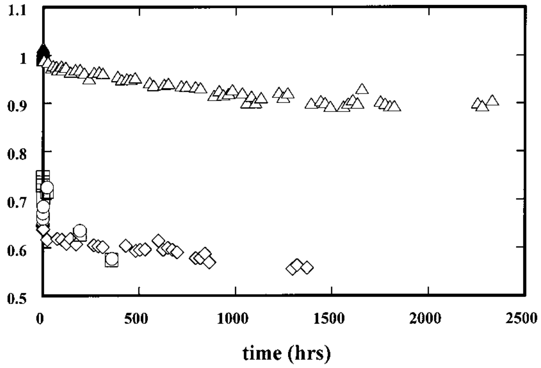

FIGURE 1. Disappearance of manganese(III) pyrophosphate species with time. C/C_T equal to actual concentration divided by predicted [Mn(III)L]. The pH's are (□) 6.94, (△) 7.33, (○) 8.04, and (◇) 8.98. Excess ligand served as a pH buffer. Total Mn was 0.5 mM and total $\mathrm{P_2O_7}$ was 25 mM (20−22 °C).

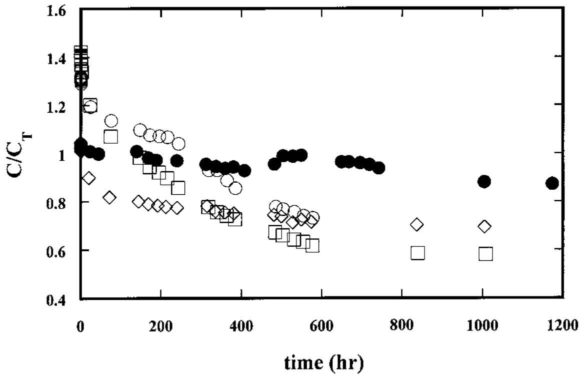

FIGURE 2. Disappearance of manganese(III) pyrophosphate species with time. C/C_T equal to actual concentration divided by predicted [Mn(III)L]. Four different ligand concentrations are shown: (○) 12.5 mM, (●) 25 mM, (□) 50 mM, and (◇) 100 mM. Values above 1.0 are due to either unreacted $\mathrm{MnO_4}^-$ or solids formation. Excess ligand acted as pH buffer. Total Mn was 0.5 mM and the pH was 7.8 (20−22 °C).

Manganese(III) Pyrophosphate. Manganese(III) pyrophosphate complexes in the pH range 7−9 and at pyrophosphate:manganese mole ratios of 25 or greater decompose very slowly, with half-lives ranging from approximately 25 to 530 days (first-order rate constants from about 3×10^{-7} to 1.5×10^{-8} s^{-1}). Figure 1 shows typical results for C/C_T = [manganese(III) pyrophosphate]/$[\mathrm{Mn_T}]$ vs time based on absorbance measurements at 484 nm. First-order fits of the data in Figure 1 ($r^2 > 0.85$) were used to estimate the half-lives. The ligand:Mn ratio is 50. Kinetic stabilization is greatest at pH 7.3 ($t_{1/2}$ = 532 days). Figure 2 shows kinetic measurements of manganese(III) pyrophosphate loss for various ligand:Mn ratios (25−200) at a pH of 7.8. Kinetic

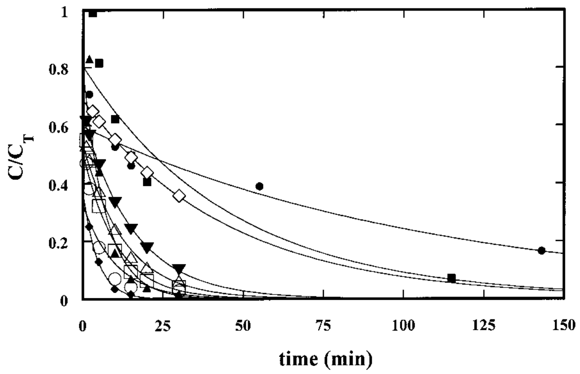

FIGURE 3. Disappearance of manganese(III) EDTA species with time. C/C_T equal to actual concentration divided by predicted [Mn(III)L]. The pH's are (●) 3.6, (■) 4.1, (▲) 5.2, (◆) 6.0, (○) 6.5, (□) 6.9, (△) 7.3, (▼) 7.7, (◇) 9.5. Excess EDTA served as a pH buffer. Total Mn was 0.5 mM and total EDTA was 25 mM (20–22 °C). At pH 3.6, $k_1 = 1.7 \times 10^{-4}$ s^{-1}; at pH 5.2, $k_1 = 3.4 \times 10^{-3}$ s^{-1}; at pH 6.9, $k_1 = 2.1 \times 10^{-3}$ s^{-1}; at pH 7.7, $k_1 = 1.08 \times 10^{-3}$ s^{-1}; and at pH 9.5, $k_1 = 3.8 \times 10^{-4}$ s^{-1}.

stabilization is maximum at a ligand:Mn ratio of 50. At lower $[P_2O_7]_T/[Mn]_T$ values, i.e., less that ~10, the decomposition half-life decreases to only 5 h at pH 7.8. For pH > 9, disproportionation of the complex and precipitation of oxide particles begins to occur rapidly. The following paths for loss of manganese(III) pyrophosphate complex are proposed:

hydrolysis

$$\mathrm{Mn(III)HP_2O_7 + H_2O \rightarrow Mn(III)HPO_4^{+} + HPO_4^{2-} + H^{+}}$$

disproportionation 1

$$\mathrm{2Mn(III)HPO_4^{+} + H_2O \rightarrow MnO_2 + MnHPO_4 + HPO_4^{2-} + 4H^{+}}$$

disproportionation 2

$$\mathrm{2Mn(III)HP_2O_7(aq) + 2H_2O \rightarrow MnO_2(s) + Mn(II)P_2O_7^{2-} + HP_2O_7^{3-} + 5H^{+}}$$

The rate constant for pyrophosphate hydrolysis at pH 8.3 in sterilized Lake Mendota water was reported to be about 1×10^{-6} s^{-1} (*21*). The corresponding half-life ($t_{1/2}$ ~ 190 h) is comparable to the half-lives of manganese(III) pyrophosphate complex at a $[P_2O_7]_T/[Mn]_T$ ratio of 100:1. However, the available data do not clearly distinguish between the contribution of the hydrolysis and disproportionation reactions to the loss of manganese(III) pyrophosphate complex.

Manganese(III) EDTA. *Influence of pH.* Decomposition of manganese(III) EDTA complexes was observed over the pH range from 3.6 to 9.5 with $[EDTA]_T/[Mn]_T = 50$ ($[EDTA]_T$ = 25 mM and $[Mn]_T$ = 0.5 mM). It was found that manganese(III) EDTA complexes decompose rather rapidly in solution and that the rate depends on pH. Figure 3 shows concentrations of manganese(III) EDTA complexes vs time at different fixed pH values and a constant *excess* EDTA of 24.5 mM. Initial manganese(III) EDTA concentrations (1–2 min after adding MnO_4^- to a Mn^{2+} and EDTA solution) are observed to vary with pH and ligand concentration. As explained above, there are several reactions that compete with formation of the manganese(III) EDTA complexes by the method used or could result in the loss of the complex (*23, 28*). Manganese(III) EDTA complexes show the most rapid decomposition in the pH interval 5–6, as shown in Figure 4, which presents half-lives vs pH. First-order rate constants, k_1, were fit to the data in Figure 3 (r^2 > 0.85).

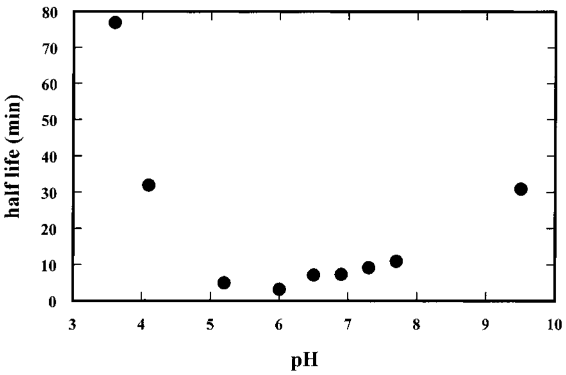

FIGURE 4. Half-life of the manganese(III) EDTA complex versus pH. Total Mn was 0.5 mM and total EDTA was 25 mM (20–22 °C).

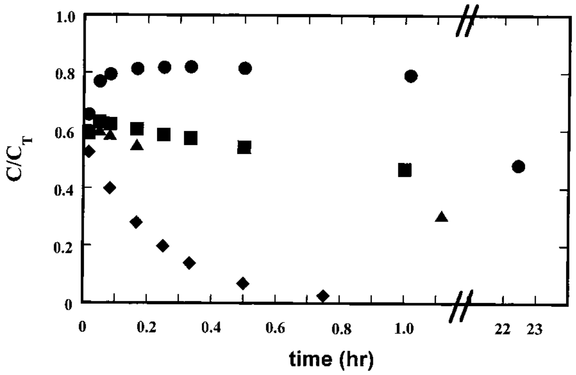

FIGURE 5. Disappearance of manganese(III) EDTA species with time at pH 6.8. C/C_T equal to actual concentration divided by predicted [Mn(III)L]. Ligand concentrations are (●) 0.5 mM, (■) 2.5 mM, (▲) 5 mM, and (◆) 25 mM. TES was used as an additional pH buffer. Total Mn was 0.5 mM (20–22 °C).

Because the solutions were open to air, the rate constants must be regarded as describing *net* loss of manganese(III) EDTA. However, previous work by Bilinski and Morgan (*30*) showed that excess EDTA *inhibited* Mn(II) oxygenation, notwithstanding the greater stability of Mn(III) complexes over Mn(II) complexes with EDTA. Further, the results of Zang and van Eldik (*31*) for Fe(II)–EDTA solutions showed that oxygenation was enhanced only in solutions of pH < 4. We interpret these observations as showing that the structural aspects of Mn(II)L complexes may govern oxygenation kinetics and that relative stability of the III and II states is not the only relevant factor.

The first-order rate constants for decomposition of the species MnHEDTA and $MnEDTA^-$ were found to have a fractional order dependence on $[H^+]$ (~$[H^+]^{-1/2}$ and ~$[H^+]^{1/3}$, respectively) which suggests contributions of more than one pathway for loss of the manganese(III) EDTA complexes, as observed earlier by Schroeder and Hamm under acidic conditions (*25*).

Influence of $[EDTA]_T$. At pH 6.8, the total concentration of EDTA was varied from 0.5 to 25 mM. Rates of manganese(III) EDTA complex loss at pH 6.8 were observed to increase with increasing $[EDTA]_T/[Mn]_T$ ratio, as shown in Figure 5. For a stoichiometric ratio of unity (no *excess* EDTA) the manganese(III) EDTA complex decomposes rather slowly, with a half-life of ~1 day. With increasing excess ligand levels, the half-lives decrease progressively, e.g., at a 5-fold excess, $t_{1/2}$ ~ 140 min; at a 10-fold excess, $t_{1/2}$ ~70 min; at a 50-fold excess, $t_{1/2}$ ~ 10 min. Regression of log k_{obs} vs log $[EDTA]_{excess}$ shows that k_{obs} varies as $[EDTA]_{excess}^{1.06}$, i.e., the rate of manganese(III) EDTA complex decomposition is essentially proportional to $[EDTA]_{excess}$ at constant pH. The direct relationship between excess EDTA concentration and rate of decomposition of the Mn(III)EDTA complex supports the conclusion that reduction of manganese(III) $EDTA^-$ by $EDTA^{4-}$ or $HEDTA^{3-}$, depending on pH, is a dominant path for decomposition at pH ≥ 6, even though disproportionation is also energetically favorable. For pH ≤ 6, thermodynamic calculations indicate that disproportionation is not spontaneous; reduction of MnEDTA species by $HEDTA^{3-}$ ligand is the available path. A rate law of the form $R = k'[HEDTA^{3-}]_{excess}\,[Mn(III)EDTA] + k''[Mn(III)EDTA]$ would be consistent with the kinetic observations. The kinetic results which we obtained at lower pH can be compared with those reported by Schroeder and Hamm (*25*). Using their three-term rate law and substituting the appropriate concentration values for our experiment at pH 5.2 (Figure 3), the *calculated* k_1 is $3.5 \times 10^{-3}\ s^{-1}$. Our *observed* k_1 is $3.4 \times 10^{-3}\ s^{-1}$.

The results for the pH range > 6 and with varying excess EDTA are also consistent with earlier kinetic results at pH < 5 (*25*). A two-term rate law would describe

(i) electron transfer to the complex from a reactive free EDTA species, e.g.

$$Mn(III)EDTA^- + HEDTA^{3-} \rightarrow Mn(II)EDTA^{2-} + HEDTA^{\bullet}$$

(ii) intramolecular electron transfer between bound EDTA and Mn(III), e.g

$$Mn(III)C_{10}H_{12}O_8\,N_2^- \rightarrow Mn(II)\,C_{10}H_{12}O_8\,N_2^{\bullet -}$$

followed by hydrogen atom abstraction

$$Mn(II)C_{10}H_{12}O_8\,N_2^{\bullet -} + C_{10}H_{12}N_2O_8^{4-} \rightarrow Mn(II)H_{13}N_2O_8^- + C_{10}H_{11}N_2O_8^{\bullet 4-}$$

Influence of Ionic Strength. Experiments at higher ionic strengths, 0.5 and 5 M $NaClO_4$, were made to see if there was a substantial effect on the decomposition rate for Mn(III)-$ETDA^-$. At pH 8 and with a 50-fold excess of EDTA, ionic strengths of 0.5 and ~5 M resulted in fitted first-order rate constants of 1.3×10^{-4} and $1.4 \times 10^{- \ -4}\ s^{-1}$, respectively. These results are approximately a factor of 2–3 less than those observed at lower ionic strength (~0.08 M, resulting from 25 mM Na_2H_2EDTA with pH adjustment to ~8).

Influence of Light. Experiments were made to assess the influence of light on $Mn(III)EDTA^-$ decomposition in the alkaline region (pH 8.8, 25 mM total EDTA). Identical reaction flasks were set up, with one in normal laboratory light as usual and the other wrapped in foil and stored in the dark. Comparison of the kinetic data for the two experiments showed no observed light influence on the decomposition on these conditions. Experiments on manganese(III) HEDTA decomposition kinetics under acidic pH conditions (*25*) also showed no influence of ordinary laboratory light.

Manganese(III) Citrate. Concentrations of Mn(III)CIT changing over time were observed as a function of pH, with a Mn_T concentration of 1 mM and a $[CIT]_T$ concentration of 200 mM. The experimental flasks were open to the atmosphere, and so contained dissolved O_2 at 0.1–0.2 mM concentrations. It was observed that absorbance by Mn(III)CIT (at 430 nm) first decreased and then increased over long time periods, as shown in Figure 6a,b. Figure 6a shows concentration profiles over a period of more than 100 days; Figure 6b focuses on the first few days. Over long times, the higher pH solutions were restored to the initial absorbance values for Mn(III)CIT. Evidently, $Mn(II)CIT^-$, or a similar species, can be reoxidized to Mn(III)CIT by O_2. Similar behavior was qualitatively described by Milad et al. (*32*). The early time concentration profiles in Figure 6b were fit to first-order kinetics, including only those measurements which represented *decreasing* absorbance. The first-order rate constants for early net loss of Mn(III)CIT in the presence of oxygen decrease with pH, from approximately $1.5 \times 10^{-5}\ s^{-1}$ at pH 6 to approximately $3 \times 10^{-6}\ s^{-1}$ at pH 9, i.e., half-lives from ~0.5 days to ~2.5 days. (These values are lower bounds for the actual disappearance rates.) The empirically observed pH dependence shows the rate varying approximately as $[H^+]^{0.3}$.

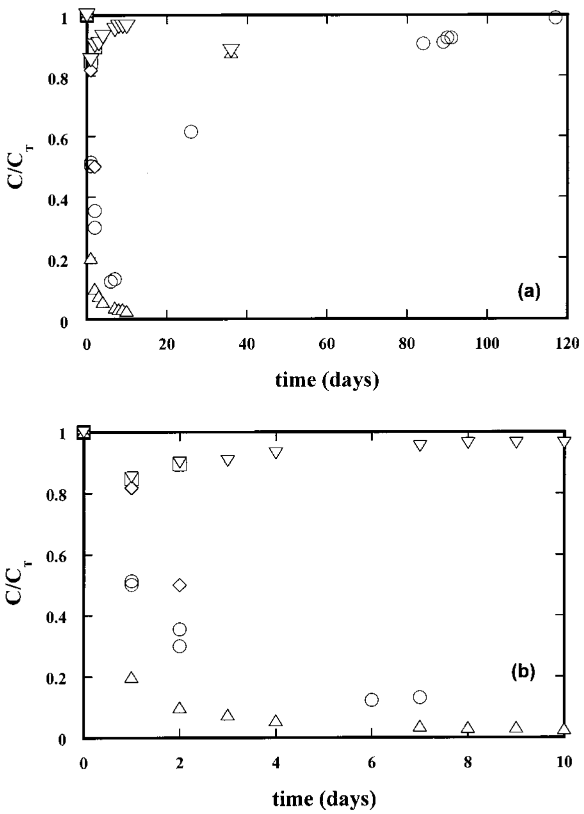

FIGURE 6. Disappearance of Mn(III)CIT species with time. C/C_T equal to actual concentration divided by predicted [Mn(III)L]. The pH's are (△) 6.1, (○) 6.8, (◇) 8.5, (▽) 9.2, and (□) 9.8. Total Mn was 1 mM and total citrate was 200 mM. All solutions were open to the atmosphere. Excess ligand was used as the pH buffer. Part (a) 0–120 d. Part (b) 0–10 d (20–22 °C).

Influence of Oxygen. Experiments were made to observe the behavior of the Mn–citrate system in the *absence* of O_2. Solutions were sparged with N_2 for an extended period and then covered with paraffin seals. No restoration of absorbance by Mn(III)CIT was seen in those solutions from which O_2 had been removed (Figure 7). With O_2 *present* (Figure 7) data for pH 9.2 show that Mn(III)CIT is restored to its initial concentration in about 3 days; longer term observations for the same experiments (not presented) showed that after about 5 days the pH 6.8 system reached a minimum in Mn(III)CIT concentration, and then Mn(III)CIT increased toward its original concentration with a characteristic time of about 60 days.

Confirmation of Mn(II)CIT oxidation by O_2 was sought through separate experiments in which 0.5 mM Mn(II) salt was dissolved in a 50-fold excess of sodium citrate solution and the pH set by the use of either 0.1 M TES buffer (pH 7.5) or 0.1 M TRIS buffer (pH 8.0). (Equilibrium computations showed that the initial solution speciation for Mn(II) in these systems was dominated by $Mn(II)CIT^-$. At pH 8.5, the ratio $[Mn(II)CIT^-]/[Mn(II)TRIS]$ is approximately 2×10^3.) Solutions were open to the atmosphere. Absorbance at 430 nm was monitored periodically for about 1 month. Figure 8 shows that Mn(III)CIT concentrations increased rather steadily with time. The reaction at pH 8.0 appears to be

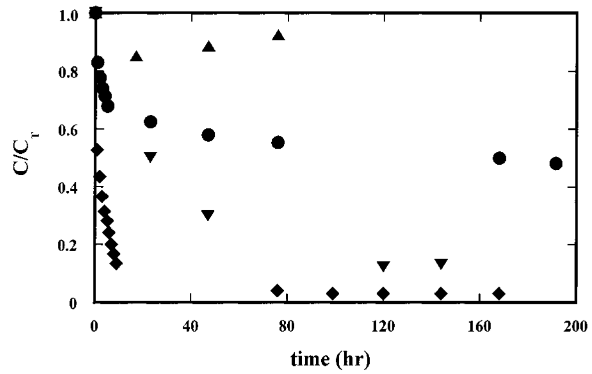

FIGURE 7. Influence of O_2 on disappearance of Mn(III)CIT species with time. *C*/*C*$_T$ equal to actual concentration divided by predicted [Mn(III)L]. Conditions: ●s represent pH 9.1 with oxygen absent. ▲s represent pH 9.2 with oxygen present. ◆s represent pH 7.4 with oxygen absent. ▼s represent pH 6.8 with oxygen present. Total Mn is 0.5 mM and total citrate is 25 mM. Oxygen absent samples were sparged with N_2 for an hour before an experiment began, and samples for measurement were kept in a Parafilm sealed spectrophotometric cell (20−22 °C).

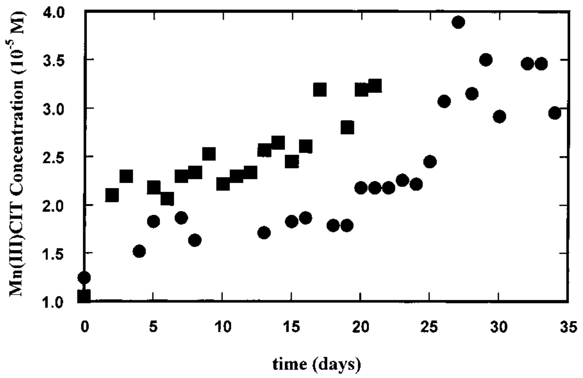

FIGURE 8. Formation of Mn(III)CIT in Mn(II)CIT solutions open to the atmosphere. The pH's are (■) for pH 8 (TRIS buffer); (●) pH 7.5. Total Mn is 0.5 mM and total citrate is 25 mM (20−22 °C).

slightly more rapid than at pH 7.5. The Mn(II) oxidized to Mn(III) is approximately 10% of the inital concentration in 30 days. (By comparison, Mn(II) in bicarbonate solution at pH 8 would require on the order of 300 days for 10% oxygenation (*33*).) At least in part, these observations tend to support the suggestion by Luther et al. (*34*) that organic complexes of manganese might play a role in manganese cycling in natural waters. Although more experimental work is needed to provide details of mechanism and rates, the following reactions, illustrated by citrate, may prove relevant in Mn(II)/Mn(III) cycling:

$$\mathrm{Mn}^{2+} + \mathrm{C_6H_5O_7}^{3-} \rightarrow \mathrm{Mn(II)C_6H_5O_7}^{-} \quad \text{(complexation)}$$

$$\mathrm{Mn(II)C_6H_5O_7}^{-} + \mathrm{O_2} \rightarrow \mathrm{Mn(III)C_6H_5O_7} + \mathrm{O_2}^{\bullet -} \quad \text{(oxygenation)}$$

$$\mathrm{Mn(III)C_6H_5O_7} \rightarrow \mathrm{Mn}^{2+} + \mathrm{C_6H_5O_7}^{\bullet 2-} \quad \text{(reduction)}$$

Further reaction of radical species could lead to decarboxylation and possibly oxidation of Mn(II) by superoxide. An overall consequence of the sequence of Mn(III) reduction, Mn(II) complexation, and MnCIT^- oxygenation would be catalytic degradation of citrate.

Influence of $[\mathrm{CIT}]_\mathrm{T}$. Experiments at pH 6.0 (in 0.01 M $NaHCO_3$ solutions acidified with HNO_3) revealed only a slight influence of total citrate concentration on the rate of loss of the Mn(III) complex, as long as the $[\mathrm{CIT}]_\mathrm{T}/\mathrm{Mn}_\mathrm{T}$ ratio was at least 5. (At lower ratios the complex was more difficult to form initially, with a yield of about 50%, a result of a rapid disproportionation reaction.) The $\mathrm{Mn(III)CIT}^0$ decomposition was about 60% faster at $[\mathrm{CIT}]_\mathrm{T}/\mathrm{Mn}_\mathrm{T} = 2$ than at $[\mathrm{CIT}]_\mathrm{T}/\mathrm{Mn}_\mathrm{T} \geq 5$). For total stoichiometric ratios ranging from 5 through 50, initial rates of $\mathrm{Mn(III)CIT}^0$ disappearance varied only from 9.2×10^{-6} to 7.8×10^{-6} s^{-1}. These experiments did not exclude O_2. Thus, over the period from 3 to 20 days the disappearance of the Mn(III) complex was reversed, the reoxidation rate increasing with excess ligand concentration. The absence of a strong influence of $[\mathrm{CIT}]_\mathrm{T}$ (thus *excess* ligand) on rates of Mn(III)CIT decomposition is consistent with an intramolecular transfer of electrons from citrate to Mn(III) as the principal reaction mechanism.

With a large excess of citrate, no precipitates of manganese oxide or manganous carbonate were formed. These systems remained homogeneous with time. However, with smaller excesses of citrate, disproportionation and resulting precipitation of MnO_2 (verified by a redox dye, leucocrystal violet) or $MnCO_3$ (judged by characteristic color) occurred after reaction times of 2−12 days, the shorter times being associated with lower excesses of citrate. For reaction times beyond the point at which solids formation was observed, no fits of the data were attempted.

Concluding Remarks

This exploratory study of the kinetics of decomposition of Mn(III) complexes indicates that ligands such as pyrophosphate, EDTA, and citrate can lend a *kinetic stabilization* to Mn(III) over a range of pH and ligand:manganese ratios. The three ligands investigated differ significantly from one another with respect to their stabilizing power. The mechanisms are fundamentally different between redox active ligands such as EDTA and redox inactive ligands such as pyrophosphate. Similar redox active kinetic behavior can be anticipated for other ligands known to form stable Mn(III) species, e.g., tartrate, catechol, and salicylate (*5, 15*). For redox active ligands such as EDTA, with a dominant outer sphere reduction path, the speciation of the excess ligand will be influenced not only by pH but also by other cations capable of complexing the ligand. By contrast, Mn(III)L complexes undergoing intramolecular redox reaction may be less influenced by other complexing cations. A redox inactive ligand such as pyrophosphate decomposes by two paths: hydrolysis of the ligand and disproportionation at low excess ligand. These differences in ligand behavior account for observed differences in effects of ligand concentration on stabilization of Mn(III)L species.

It should prove of interest to examine Mn(III)/Mn(II) reactions under conditions resembling those of natural waters, in particular focusing on lower manganese concentrations, e.g., micromolar to nanomolar and with other ligands than those examined here. Although the experiments reported here involved formation of Mn(III)L complexes by two particular processes, the 4Mn(II) + 5L + Mn(VII) reaction and the $\mathrm{Mn(II)} + \mathrm{CIT}^{3-} + \mathrm{O_2}$ reaction, one can envision other processes for Mn(III)L formation, e.g., $\mathrm{MnO_2} + \mathrm{L'} \rightarrow \mathrm{Mn(III)L'} + ...$ where L′ is a reducing ligand in excess, such as EDTA or citrate; and $\mathrm{MnOOH} + \mathrm{L} \rightarrow \mathrm{Mn(III)L}$, dissolution of a Mn(III) solid by either a redox inactive or redox active ligand (*27*).

The significant findings of this research are summarized as follows:

(1) Disappearance *rates* of Mn(III) complexes in substantial ligand excess and at neutral pH are in the order EDTA >> CIT > P_2O_7. The respective half-reaction *time scales* are $\sim 5 \times 10^2$ s for EDTA, $\sim 1 \times 10^5$ s for CIT, and $\sim 5 \times 10^6$ s for P_2O_7.

(2) Observed pH dependences for rates of Mn(III)L disappearance are complex. In the case of EDTA parallel paths of external and internal electron transfer indicate multiple term rate laws (*25*), reflecting different protonated species of reactants. For EDTA, the rate of disappearance of the Mn(III) complex decreases with increasing pH over the range 6−8; a similar trend is observed for citrate; decomposition rates for manganese(III) pyrophosphate show only a slight pH dependence between pH 7 and 9.

(3) In the alkaline pH region, typical laboratory light does not influence the rate of reaction of manganese(III) EDTA species.

(4) Mn(II) oxygenation, $\mathrm{Mn(II)} + \mathrm{O_2} \rightarrow \mathrm{Mn(III)}$, is accelerated in the presence of excess citrate in the pH range 7−9.

(5) An outer sphere electron-transfer process between Mn(III)EDTA$^-$ and excess HEDTA^{3-} is supported by direct dependence of the decomposition rate on excess ligand concentration.

(6) A predominant intramolecular electron-transfer process for the Mn(III)CIT^0 species is consistent with the observed weak influence of excess CIT^{3-} concentration on rate.

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