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Kinetics of the Reaction between 1,2-Diaminocyclohexanetetraacetatomanganate(III) Ion and Hydrogen Peroxide[1]

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The reaction of 1,2-diaminocyclohexanetetraacetatomanganate(III) ion (Mn^{III}CyDTA) with hydrogen peroxide was studied over the following concentration ranges: hydrogen peroxide, $(5.6-80.0) \times 10^{-3}$ M; Mn^{II}CyDTA, $(0-18.2) \times 10^{-3}$ M; hydrogen ion, 1.2×10^{-2}–1.6×10^{-4} M. The reaction was found to be second order in the manganese(III) complex, first order in hydrogen peroxide, inverse first order in hydrogen ion, and inverse first order in manganese(II) complex. A mechanism which fits these findings is

$$\text{Mn}^{III}\text{CyDTAOH}_2{}^- + \text{H}_2\text{O}_2 \overset{K}{\rightleftharpoons} \text{Mn}^{III}\text{CyDTAO}_2\text{H}^{2-} + \text{H}^+ + \text{H}_2\text{O}$$

$$\text{Mn}^{III}\text{CyDTAO}_2\text{H}^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Mn}^{II}\text{CyDTA}^{2-} + \text{HO}_2$$

$$\text{Mn}^{III}\text{CyDTAOH}_2{}^- + \text{HO}_2 \overset{k_2}{\rightarrow} \text{Mn}^{II}\text{CyDTA}^{2-} + \text{O}_2 + \text{H}^+$$
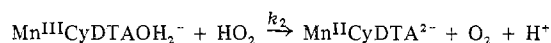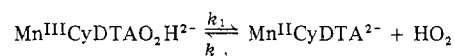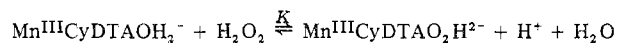
Values at 25° for $2Kk_1 k_2/k_{-1} = 2.71 \times 10^{-3}$ and $k_2/k_{-1} = 2.63$ were found and were shown to fit the experiments under all hydrogen peroxide and manganese(II) complex concentrations and under hydrogen ion concentrations from 1.0×10^{-3} to 2.5×10^{-4} M. Reasons for the variability at other hydrogen ion concentrations were proposed.

Introduction

The reactions of hydrogen peroxide with metal ions have been widely studied as shown by the extensive literature on the subject. Mechanistic studies on the oxidation of hydrogen peroxide by hydrated cations include Fe(II),[2-4] Ce(IV),[5] Co(III),[6] and Mn(III).[7,8] A peroxo complex of the cation is a likely intermediate in all these cases.[9] The earlier inference that the HO$_2$ radical is an intermediate in the oxidation of hydrogen peroxide was later established using esr measurements in the reaction between Ce(IV) and hydrogen peroxide.[10] The ferric ion catalyzed decomposition of hydrogen peroxide has been mechanistically interpreted in two ways. The older scheme, elaborated by Barb, Baxendale, George, and Hargrave[2] and more recently supported by Walling and coworkers,[3] involves as radical chain involving Fe(II), HO, and HO$_2$. The alternate path proposed by Kremer and Stein[4] and favored by a recent review[11] does not involve Fe(II) or HO but rather a series of iron–peroxide intermediate complexes.

The reaction of aqueous Mn(III) with hydrogen peroxide was studied with a stopped-flow apparatus,[7,8] with the report of somewhat contradictory results. Davies, Kirschenbaum, and Kustin[7] found the rate of the reaction to be first order in Mn(III), first order in hydrogen peroxide, and inversely dependent on Mn(II). Mechanistic interpretation of their kinetic data was complicated by the hydrolysis of the aqueous Mn(III) ion.[12] The apparent second-order rate constant was found to decrease with increasing starting hydrogen peroxide concentration. This observation was interpreted as indicating that hydrogen peroxide competes with Mn(III) for the H$_2$O$_2{}^+$ radical. Wells and Mays[8] found the rate of the reaction to be first order in Mn(III) and independent of Mn(II) and hydrogen peroxide. They also reported a rapid rise in the optical density at 470 nm suggesting the formation of a new Mn(III) species. Careful inspection of these two papers indicates that the time scales of the two investigations indicate different reactions were being studied.

In contrast to the rapid reaction between aqueous Mn(III) and hydrogen peroxide, complexed Mn(III) reacts much more slowly with hydrogen peroxide. Suwyn and Hamm[13] found hydrogen peroxide as a product in the oxidation of the oxalate ion with Mn^{III}CyDTA if oxygen was present and the pH was less than 4.5. It has long been known that a small amount of hydrogen peroxide is produced in the oxidation of oxalate by permanganate.[14] Kolthoff, Meehan, and Kimura[15] studied the kinetics of the formation of hydrogen peroxide in the oxidation of oxalic acid in both the presence and absence of oxygen and Mn(II). Mn(VII), Ce(IV), and Co(III) were used as oxidants. In the presence of oxygen and Mn(II), the initial step was the formation of a Mn(III) oxalate complex regardless of which oxidant was used. An interesting observation to be made from this paper is that apparently the reaction between manganese(III) oxalate and hydrogen peroxide is too slow to be important in this system.

Because of the general interest in redox reactions of hydrogen peroxide and the marked differences between the rates

(1) Presented in part at 28th Annual Northwest Regional Meeting of the American Chemical Society, Pullman, Wash., June 1973.

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(4) M. L. Kremer and G. Stein, *Trans. Faraday Soc.*, 55, 595 (1959); M. L. Kremer, *ibid.*, 58, 702 (1962); 59, 2535 (1963).

(5) G. Czapski, B. H. J. Bielski, and N. Sutin, *J. Phys. Chem.*, 67, 201 (1963); (b) H. A. Mahlman, R. W. Matthews, and T. J. Sworski, *ibid.*, 75, 250 (1971).

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(7) G. Davies, L. J. Kirschenbaum, and K. Kustin, *Inorg. Chem.*, 7, 146 (1968).

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of reactions of complexed and uncomplexed Mn(III) with hydrogen peroxide, we were led to the study of the stoichiometry and kinetics of the reaction between Mn^{III}CyDTA and hydrogen peroxide.

Experimental Section

All solutions were prepared with deionized water which had been doubly distilled from alkaline permanganate solutions. Manganous perchlorate was obtained from G. F. Smith Chemical Co. and was recrystallized twice from hot water prior to use. Manganous perchlorate solutions were standarized by titration with standard EDTA.

The 1,2-diaminocyclohexanetetraacetic acid (CyDTA) was obtained from Geigy Chemical Corp. and was recrystallized twice from hot water and was air-dried before use. Solutions of CyDTA were standardized by titration with standard manganous solution using EBT indicator. Carbonate-free sodium hydroxide solutions were prepared from filtered portions of 50% w/w sodium hydroxide solution.

The KMnCyDTA·2.5H$_2$O was prepared as previously described.[16] The purity was checked by adding weighed amounts of the salt to an acidified potassium iodide solution and titrating the liberated iodine with standard thiosulfate solution to a starch end point. All other chemicals were reagent grade and were used without further purification. Hydrogen peroxide (30% w/v, unstabilized) was obtained from J. T. Baker Chemical Co. Stock solutions of hydrogen peroxide were prepared by diluting to *ca.* 5 × 10^{-2} M and were analyzed immediately before use with standard 0.10 M Ce(IV) solution using ferroin indicator. Sodium perchlorate was prepared by neutralizing perchloric acid with sodium carbonate and was recrystallized from hot water. A stock solution of sodium perchlorate (2.0 M used for adjusting ionic strength) was standardized by diluting the solution to about 0.1 M and passing aliquots through the hydrogen-form cation-exchange column (Dowex 50 W-X8, 100–200 mesh) followed by titrating the effluent and washings with standard 0.10 M sodium hydroxide.

Solutions of Mn^{II}CyDTA were prepared by mixing equivalent amounts of manganous perchlorate and H$_4$CyDTA. The pH was adjusted to *ca.* 5 with sodium hydroxide. The Mn concentration was determined by measurement of the absorption at 545 nm after oxidation with ammonium persulfate and potassium periodate.

Monochloroacetic acid used to prepare buffer solutions was obtained from Mallinckrodt Chemical Works. Buffer solutions were prepared by adding the proper amount of 1.0 M sodium hydroxide to weighed amounts of chloroacetic acid to give the desired pH. Sufficient 2.0 M sodium perchlorate and distilled water were added to bring the chloroacetate concentration to 0.22 M and the ionic strength to 0.25. All pH readings were taken with a Beckman research pH meter equipped with a calomel electrode filled with 4 M sodium chloride to prevent precipitation of potassium perchlorate. It was noted that aqueous solutions of chloroacetic acid and chloroacetate were unstable over a period of several months; therefore chloroacetate buffer solutions were checked before use with 1 drop of silver nitrate solution. The appearance of a slight cloudiness of this test would cause discarding of the buffer solution.

Reaction Stoichiometry. Weighed amounts of KMn^{III}CyDTA· 2.5H$_2$O were added to known amounts of hydrogen peroxide in buffer solution. At the end of the reaction the solution was purged with purified argon to remove oxygen. The excess hydrogen peroxide was determined by titrating with thiosulfate according to the standard method.[17]

Reaction Rates. The change in absorbance at 510 nm was observed with a Cary Model 14 spectrophotometer which was fitted with a constant-temperature cell block. The temperature was monitored in both the cell block and the constant-temperature bath. The temperature could be kept within ±0.05°. Solutions containing hydrogen peroxide at a given pH and ionic strength were prepared by adding 25.0 ml of buffer solution, the proper amount of standardized hydrogen peroxide solution, and an amount of Mn^{II}CyDTA solution (when used) and diluting to 50.00 ml with distilled water. The solution was transferred to a 10.0-cm cell and thermostated to the desired temperature. A small amount of finely ground solid KMn^{III}CyDTA· 2.5H$_2$O was put in the cell, which was shaken thoroughly to dissolve the solid and which was then placed in the thermostated cell block. The time drive of the spectrophotometer was activated at the time the solid was added to the cell. The first absorbance reading was within 30 sec of the starting time. The original concentration of
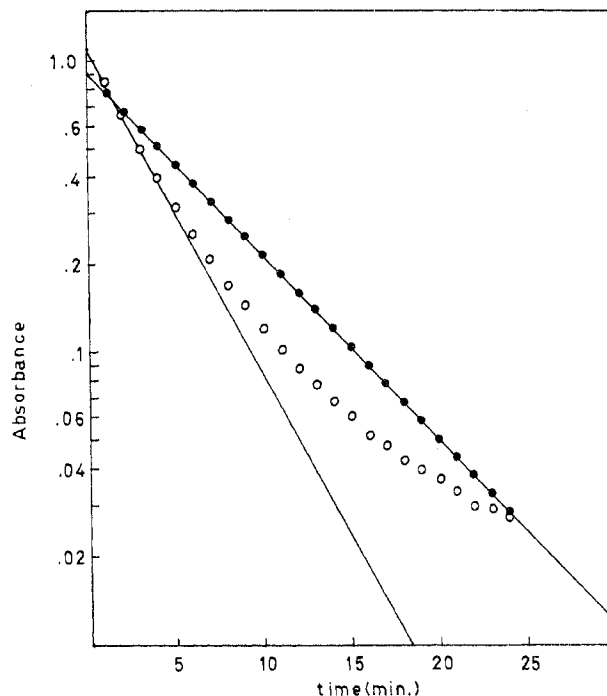
(16) R. E. Hamm and M. A. Suwyn, *Inorg. Chem.*, 6, 139 (1967).
(17) A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, Wiley, New York, N. Y., 1961, p 363.

Figure 1. Semilogarithmic plot of absorbance *vs.* time at [H$_2$O$_2$] = 0.0122 M, [buffer] = 0.22 M, and ionic strength 0.25: ●, pH 1.90; ○, pH 2.50; temperature 25.0°.

Mn^{III}CyDTA could be calculated by extrapolating the absorbance to zero time. The initial absorbance agreed well with that determined by adding weighed amounts of the solid.

For runs where Mn^{II}CyDTA was not initially present and hydrogen peroxide was in large excess the pseudo-first-order apparent rate constant was obtained from plots of ln (Abs) *vs.* time since Abs$_\infty$ = 0, where k_{app} is the negative slope of the straight-line portion at the beginning. When both Mn^{II}CyDTA and hydrogen peroxide were initially in large excess, pseudo-second-order apparent rate constants were obtained from plots of 1/Abs *vs.* time, where $k_{app} = \epsilon b\Delta(1/\text{Abs})/(\Delta t)$ ($\epsilon = 407$ cm^{-1} M^{-1}).

The reaction was studied over the following concentration ranges: hydrogen peroxide, (5.6–80.0) × 10^{-3} M; Mn^{II}CyDTA, (0–18.2) × 10^{-3} M; H$^+$, 1.2 × 10^{-2}–1.6 × 10^{-4} M; initial Mn^{III}CyDTA, (1.8–6.0) × 10^{-4} M. The variation of Mn^{III}CyDTA concentration was restricted by formation of O$_2$ bubbles on the cell windows at higher concentrations. Therefore most runs were done in 10-cm cells to minimize the problem.

Results

Stoichiometry. The stoichiometry was investigated at pH 3.0 and 5.7. At pH 5.7 the reaction is rapid and is complete in less than 30 sec, while at pH 3.0 the reaction requires 45–60 min. The stoichiometry was found to be the same at both hydrogen ion concentrations with [Mn^{III}CyDTA]/[H$_2$O$_2$] = 2.06 ± 0.03. The presence of initial Mn^{II}CyDTA had no effect on the stoichiometry nor could any evidence be found for Mn^{II}CyDTA catalysis of the decomposition of hydrogen peroxide at 25°. These results agree with the overall reaction

2Mn^{III}CyDTA(H$_2$O)$^-$ + H$_2$O$_2$ → 2Mn^{II}CyDTA^{2-} + O$_2$ + 2H$^+$ + H$_2$O
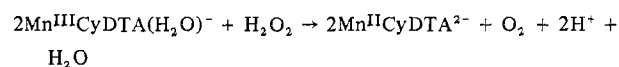
Kinetics. The rate of the reaction was found to be first order with respect to hydrogen peroxide in all data that were taken, since plots of both pseudo-first- and pseudo-second-order rate constants *vs.* starting hydrogen peroxide concentration were linear with zero intercepts.

When Mn^{II}CyDTA was not initially present, the rate of the reaction was first order in Mn^{III}CyDTA as shown by plots of ln (Abs) *vs.* time as shown in Figure 1. At pH values less

than 2.1 the plots were linear over the complete reaction, while at pH values greater than 2.1, the plots became non-linear during the latter parts of the reaction, showing earlier and greater nonlinearity with higher pH values. The pseudo-first-order apparent rate constant derived from the linear portion of the plots was inversely dependent on the hydrogen ion concentration as shown in Figure 2.

When $[Mn^{II}CyDTA]_0 \gg [Mn^{III}CyDTA]_0$, plots of 1/Abs *vs.* time were linear over the complete reaction indicating the rate of the reaction to be second order in $Mn^{III}CyDTA$. The pseudo-second-order rate constant was found to be independent of the starting $Mn^{III}CyDTA$ concentration. The data in Table I show the pseudo-second-order apparent rate constant to be proportional to the hydrogen peroxide concentration and inversely dependent on both $Mn^{II}CyDTA$ and H^+. At pH values less than 3.0 and greater than 3.6, the apparent rate constant shows a complex dependence on the hydrogen ion concentration as shown by Figure 2.

With no initial $Mn^{II}CyDTA$ present the experimental rate law has the form

$$-\frac{d[Mn^{III}CyDTA]}{dt} = \frac{k'[Mn^{III}CyDTA][H_2O_2]}{[H^+]} \quad (1)$$

From the data shown in Figure 2, k' can be calculated to be $(8.7 \pm 0.3) \times 10^{-4}$ sec^{-1}.

Under conditions where $[Mn^{II}CyDTA]_0 \gg [Mn^{III}CyDTA]_0$, the experimental rate law has the form

$$-\frac{d[Mn^{III}CyDTA]}{dt} = \frac{k''[Mn^{III}CyDTA]^2[H_2O_2]}{[H^+][Mn^{II}CyDTA]} \quad (2)$$
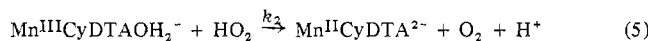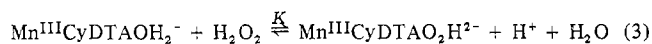
A plot of the pseudo-second-order rate constant *vs.* $[H_2O_2]$ (data in Table I) at constant $[Mn^{II}CyDTA]$ and $[H^+]$ gave a straight line which had zero intercept within experimental error and allowed the calculation of $k'' = (2.61 \pm 0.03) \times 10^{-3}$ sec^{-1}. This rate constant can also be calculated from a plot of 1/(pseudo-second-order rate constant) *vs.* $[Mn^{II}CyDTA]$ (data in Table I), at constant $[H^+]$ and $[H_2O_2]$, giving a value of $(2.73 \pm 0.05) \times 10^{-3}$ sec^{-1}.

Least-squares treatment of the data in Table II gave $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the pseudo-second-order reaction as 7.27 ± 0.22 kcal/mol and -45.9 ± 0.8 eu and for the pseudo-first-order rate constant as 14.7 ± 0.3 kcal/mol and -22.9 ± 0.9 eu.

Both the pseudo-first- and pseudo-second-order rate constants decreased slightly with increasing ionic strength when other variables were held constant.

Discussion

A mechanism that is consistent with the experimental data is

$$Mn^{III}CyDTAOH_2^- + H_2O_2 \overset{K}{\rightleftharpoons} Mn^{III}CyDTAO_2H^{2-} + H^+ + H_2O \quad (3)$$

$$Mn^{III}CyDTAO_2H^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mn^{II}CyDTA^{2-} + HO_2 \quad (4)$$

$$Mn^{III}CyDTAOH_2^- + HO_2 \overset{k_2}{\rightarrow} Mn^{II}CyDTA^{2-} + O_2 + H^+ \quad (5)$$

Assuming a steady-state approximation for the HO_2 radical, one can derive the rate law

$$-\frac{d[Mn^{III}CyDTA]}{dt} = \frac{2Kk_1k_2[Mn^{III}CyDTA]^2[H_2O_2]}{k_{-1}[H^+][Mn^{II}CyDTA] + k_2[H^+][Mn^{III}CyDTA]} \quad (6)$$

Under conditions of initial $[Mn^{II}CyDTA] = 0$, eq 6 reduces to
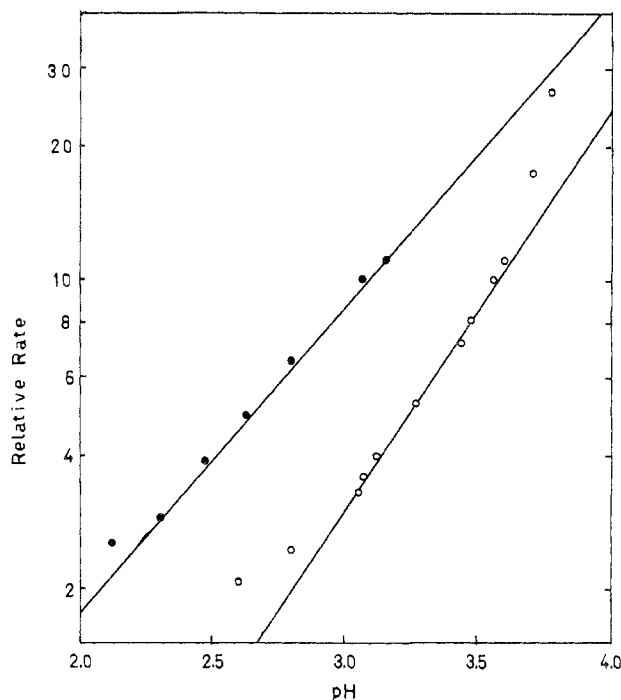
Figure 2. Semilogarithmic plot of relative rate *vs.* pH at $[H_2O_2] = 0.0111\ M$, $[Mn^{II}CyDTA] = 0.00997\ M$, [buffer] = 0.22 M, ionic strength 0.25, and 25.0°: ●, $(k_{app}/[H_2O_2]) \times 10$; ○, k_{app}.

Table I. Experimental and Calculated Rates of Reaction between $Mn^{III}CyDTA$ and Hydrogen Peroxide at 25°, Ionic Strength 0.25, and 0.22 M Monochloroacetate Buffer[a]

$10^3 \times$ $[H_2O_2]$,[b] M	k_{app}		$10^3 \times$ $[H_2O_2]$,[b] M	k_{app}	
	Exptl	Calcd		Exptl	Calcd
5.60	1.79	1.77	39.8	13.0	12.6
11.2	3.51	3.55	59.8	19.0	18.9
19.9	6.20	6.30	79.7	25.7	25.2
22.4	7.04	7.09			

$10^3 \times$ $[Mn^{II}Cy-DTA]$,[c] M	k_{app}		$10^3 \times$ $[Mn^{II}Cy-DTA]$,[c] M	k_{app}	
	Exptl	Calcd		Exptl	Calcd
3.64	8.39	8.12	12.6	2.59	2.58
5.47	5.87	5.64	18.2	1.86	1.81
9.11	3.51	3.52			

	k_{app}			k_{app}	
pH[d]	Exptl	Calcd	pH[d]	Exptl	Calcd
3.05	3.27	3.28	3.44	7.18	8.02
3.15	3.97	4.17	3.47	8.18	8.75
3.27	5.17	5.42	3.60	12.1	11.6

[a] Each experimental rate is the average of at least two runs. The values used for calculated k_{app} were $k'' = 2.71 \times 10^{-3}$ and $k_2/k_{-1} = 2.69$. [b] $[H^+] = 8.87 \times 10^{-4}\ M$; $[Mn^{II}CyDTA] = 0.00911\ M$. [c] $[H^+] = 8.87 \times 10^{-4}\ M$; $[H_2O_2] = 0.011\ M$. [d] $[H_2O_2] = 0.0111\ M$; $[Mn^{II}CyDTA] = 0.00997\ M$.

Table II. Pseudo-First- and Pseudo-Second Order Rate Constants as a Function of Temperature[a]

Temp, °C	10^3k_{app}, pseudo 1st order	k_{app}, pseudo 2nd order	Temp, °C	10^3k_{app}, pseudo 1st order	k_{app}, pseudo 2nd order
39.4		10.7	20.1	15.4	5.13
34.6		9.12	16.4	10.6	4.53
25.0	22.9	5.83	12.1	7.43	3.41

[a] For all of these runs pH is 3.00 and $[H_2O_2] = 0.0231\ M$; for the second-order rate constants $[Mn^{II}CyDTA] = 0.00997\ M$.

eq 1 where $k' = 2Kk_1$, and when Mn^{II}CyDTA has some relatively high initial value, where one can assume that [Mn^{II}CyDTA] $\gg (k_2/k_{-1})$[Mn^{III}CyDTA], eq 6 reduces to eq 2 and $k'' = 2Kk_1k_2/k_{-1}$, so that $k_2/k_{-1} = k''/k'$.

If eq 6 is the complete rate law for the reaction, then one should be able to fit the data for a complete kinetic run where the initial concentration of Mn^{II}CyDTA is zero. To test this, the following substitutions were made in eq 6: $2Kk_1k_2[\text{H}_2\text{O}_2]/k_{-1}[\text{H}^+] = a$, $k_2/k_{-1} = b$, [Mn^{III}CyDTA]$_0 = A_0$, and [Mn^{III}CyDTA]$_t = x$, giving

$$-\frac{dx}{dt} = \frac{ax^2}{(A_0 - x) + bx} \tag{7}$$

Rearranging, integrating and evaluating at $t = 0$ where $x = A_0$, gives

$$\frac{A_0}{x} + (1 - b) \ln \frac{x}{A_0} = at + 1 \tag{8}$$

A computer program was written to evaluate a and b from eq 8 by the method of least squares. Under conditions of [H$_2$O$_2$]$_0$ = 0.0116 M, pH 3.00, and 25°, the following values were calculated based on three separate runs: $2Kk_1k_2/k_{-1} = (2.71 \pm 0.07) \times 10^{-3}$ sec^{-1} and $k_2/k_{-1} = 2.69 \pm 0.06$ (dimensionless). The calculated values of the pseudo-second-order apparent rate constants in Table I are based on these values. The value of k' calculated from these values is slightly higher than the one determined directly from the initial slopes of the experiments run with no initial Mn^{II}CyDTA, probably because of the difficulty in determining the initial slopes.

The Mn^{III}CyDTA ion has been reported to be seven-coordinate in aqueous solution with CyDTA acting as a hexadentate ligand and a water molecule occupying a seventh coordination site.[16] Recently the same interpretation has been made for Mn^{III}CyDTAOH$_2^-$ in methanol.[18] According to the proposed mechanism, hydrogen peroxide replaces the water molecule in a fast preequilibrium step to form a Mn^{III}CyDTA-peroxo complex. No spectral evidence could be obtained for the existence of such a species. The reason for not detecting such an intermediate could be that the equilibrium constant, K, was so small that a negligible change in the absorbance resulted, or that the ϵ's of the two complexes were not sufficiently different. If the assumption is made that the spectrum for Mn^{III}CyDTAO$_2$H^{2-} is similar to that of Mn^{III}CyDTAOH^{2-},[16] then at least 5% of the total Mn(III) concentration would have to be in the peroxo complex to observe any spectral change. From this assumption one can estimate an upper limit for $K \approx 5 \times 10^{-3}$ and thus $k_1 \approx 0.1$ sec^{-1}.

The pH dependence of the pseudo-second-order apparent rate constant plotted in Figure 2 shows deviations from straight-line values at pH values less than 3.0 and greater than 3.6. From the stability constants given by Anderegg[19] for Mn^{II}CyDTA it can be calculated that a significant fraction of the manganese would exist as free Mn^{2+} at pH values below 3.0, thus indicating that deviation would be expected. At pH values greater than 3.6 appreciable amounts of the HO$_2$ radical would be expected to disassociate[20]

$$\text{HO}_2 \rightleftharpoons \text{H}^+ + \text{O}_2^- \qquad \text{p}K = 4.8$$
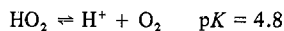
In light of recent work reported by Rabani, Klug-Roth, and Lilie,[21] who found that cupric ions were reduced more rapidly by O$_2^-$ than by HO$_2$ it would be expected that a similar thing would occur with the manganese(III) complex.

A preequilibrium step involving H$^+$ is necessary to explain the inverse dependence on hydrogen ion in eq 1. An alternate mechanism that would avoid proposing a peroxo complex and gives an identical rate law would be

$$\text{H}_2\text{O}_2 \underset{}{\overset{K_a}{\rightleftharpoons}} \text{H}^+ + \text{HO}_2^- \qquad K_a = 5.4 \times 10^{-12} \text{ 22} \tag{9}$$

$$\text{Mn}^{III}\text{CyDTAOH}_2^- + \text{HO}_2^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{Mn}^{II}\text{CyDTA}^{2-} + \text{HO}_2 \tag{10}$$

$$\text{Mn}^{III}\text{CyDTAOH}_2^- + \text{HO}_2 \overset{k_4}{\rightarrow} \text{Mn}^{II}\text{CyDTA}^{2-} + \text{O}_2 + \text{H}^+ \tag{11}$$

Since both mechanisms give the same rate law, one cannot distinguish between the two on kinetic grounds. But if this is the correct mechanism, then $2K_ak_3 = k' \approx 1 \times 10^{-3}$ sec^{-1} and $k_3 \approx 1 \times 10^8 M^{-1}$ sec^{-1}; which seems unreasonably large when compared with other rapid reactions involving the Mn(III) ion.[23] Since this value does not exceed diffusion control, this mechanism cannot be completely ruled out.

The distinction between an inner-sphere mechanism as suggested by eq 3-5 or an outer-sphere one as suggested by eq 9-11 is difficult to make in the absence of spectral evidence because of the lability of both the Mn(II) and Mn(III) ions. Since the reported rate constants for oxidations by Mn^{III}CyDTA and Mn^{III}EDTA are much smaller than the rate constant for water exchange, an inner-sphere mechanism cannot be ruled out.

In the present case the inner-sphere mechanism seems more reasonable since metal ion–peroxo complexes are widely known.[24] Further support for this mechanism comes from a recent study by Meisel, Czapski, and Samuni[25] on the complexation of several metal ions (Th(IV), U(VI), Zr(IV), Ti(IV)) by HO$_2$. They found that HO$_2$ complexed metal ions in a rapid, reversible equilibrium.

For the oxidation of all species that have been studied with Mn(III)$_{aq}$ and Mn^{III}CyDTA or Mn^{III}EDTA the reaction is several orders of magnitude faster with the aquomanganese. This situation was also found for the oxidation of azide where the Mn^{III}EDTA(N$_3$)$^{2-}$ complex was formed and isolated.[26] Davies has recently presented a thorough discussion of this problem for the Mn$^{III}_{aq}$ ion.[23] The reaction of the manganese(III) complex with hydrogen peroxide is believed to be so slow because of the formation of the intermediate complex or, expressed another way, the fact that both Mn^{II}CyDTA and Mn^{III}CyDTA compete to react with the HO$_2$ radical.

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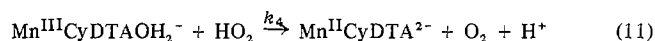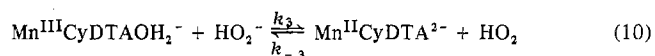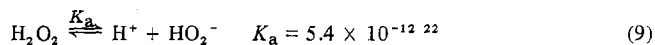
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