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The Kinetics and Stoichiometry of the Reaction between Manganese(III) and Hydrogen Peroxide in Acid Perchlorate Solution

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The kinetics of the reaction $2Mn(III) + H_2O_2 \rightarrow 2Mn(II) + O_2 + 2H^+$ has been studied spectrophotometrically with a stopped-flow apparatus at 25° in 1.00–3.70 *M* perchloric acid solutions of ionic strength between 2.23 and 4.90 *M*. The stoichiometry was determined by measuring the difference in the concentration of one of the reactants before and after reaction and by direct analysis of the oxygen produced. For conditions where the initial excess of peroxide was fivefold or less, the ratio of manganese(III) consumed to hydrogen peroxide consumed had the value of 1.97 ± 0.09; *i.e.*, $\Delta[Mn(III)]/\Delta[H_2O_2] = 2$, within experimental error. Deviations from this stoichiometry were observed at very high excesses of H_2O_2 by direct oxygen analysis (relative error in an individual determination = ±3%). The reciprocal of the observed second-order rate constant is dependent on $[Mn^{2+}]/[Mn(III)]_0$ and $[H_2O_2]_0/[Mn(III)]_0$. The rate is independent of ionic strength. The proposed mechanism involves the over-all rate-determining steps

$$Mn^{3+} + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mn^{2+} + H_2O_2^+ \quad (1)$$

$$MnOH^{2+} + H_2O_2 \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} Mn^{2+} + HO_2 + H_2O \quad (1')$$

where $k_1 = 7.3 \times 10^4\ M^{-1}\ sec^{-1}$ and $k_1' = 3.2 \times 10^4\ M^{-1}\ sec^{-1}$ (relative error = ±20%). The role in the mechanism of complexed Mn(III) species is discussed. The dependence of rate on $[Mn^{2+}]$ arises predominantly from the reverse of reaction 1′. The Mn^{3+} and $MnOH^{2+}$ react at similar rates with $H_2O_2^+$. Comparison of these results with those of the reactions of Co(III) and Ce(IV) indicates a relationship between reaction rate and the number of available sites in unfilled metal d orbitals. No correlation of rates with oxidation potential could be established. The observation that catalyzed decomposition of H_2O_2 occurs at high $[H_2O_2]_0$ indicates that there is a competition between Mn(III) and H_2O_2 for $H_2O_2^+$. The apparent rate of the latter reaction obtained from kinetic analysis is too high to be consistent with the measured stoichiometry and suggests the presence of complexed Mn(III) species.

Introduction

In this paper we report a study of the stoichiometry and kinetics of the rapid reaction between manganese(III) and hydrogen peroxide in aqueous perchloric acid. The stoichiometry of the reaction

$$2Mn(III) + H_2O_2 \longrightarrow 2Mn(II) + O_2 + 2H^+ \quad (I)$$

has been studied both by standard analytical methods and by direct measurement of the oxygen produced. Since the reaction is too fast to be followed by conventional kinetic methods, the rate of disappearance of Mn(III) has been followed spectrophotometrically in a stopped-flow apparatus. Manganese(III) is a strongly oxidizing species and is unstable with respect to disproportionation. Solutions of Mn(III) in perchlorate media generally produce solid hydrated MnO_2 on standing, instability increasing with increasing [Mn(III)] and decreasing acidity.[1,2]

$$2Mn(III) \rightleftharpoons Mn(IV) + Mn(II)$$
$$Mn(IV) + 2H_2O \rightleftharpoons MnO_2(s) + 4H^+$$

Complexation of Mn(III) with anions usually results in a reduction of the electrode potential of the Mn(III)–Mn(II) couple; for example, the electrode potential in the presence of EDTA is *ca.* −0.82 v,[3] while that in a perchlorate medium has been estimated[2,4] at *ca.* −1.58 v. Moreover, the presence of a number of complexed Mn(III) species in solution complicates the interpretation of kinetic data. For example, Waters and Littler[4] conclude that little information can be obtained from a study of the pH dependence of reactions of manganese(III) pyrophosphate with organic reductants because of a lack of knowledge of the nature of oxidizing species present in solution. An interesting observation regarding the magnitude of the effects of complexation on the oxidizing power of Mn(III) is that hydrogen peroxide is found as a *product* of the oxidation of oxalate by *trans*-1,2 diaminocyclohexanetetraacetatomanganate(III) at low pH.[5]

In 1963, Rosseinsky[1] showed that it is possible to prepare moderately stable solutions of Mn(III) in high concentrations of perchloric acid. Stabilization with regard to disproportionation is achieved with a large excess of Mn(II). In the presence of a 25-fold excess of the latter ion, solutions of Mn(III) with $[Mn(III)]_0 \leq 10^{-3}\ M$ are reasonably stable with $[HClO_4]$ as low as 1.5 *M*.[1] By employing an ionic strength of 4 *M*, adjusted by addition of Mn(II), Wells and Davies[6] reduced the lower limit of the experimental acidity range to 0.10 *M* $HClO_4$ and were thereby able to show that the predominant equilibrium in freshly prepared solutions of Mn(III) is represented by

$$Mn^{3+} \underset{}{\overset{K_H}{\rightleftharpoons}} MnOH^{2+} + H^+$$

(1) D. R. Rosseinsky, *J. Chem. Soc.*, 1181 (1963).
(2) H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964).
(3) R. E. Hamm and M. A. Suwyn, *Inorg. Chem.*, **6**, 139 (1967).
(4) W. A. Waters and J. S. Littler in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, pp 185–241.
(5) M. A. Suwyn and R. E. Hamm, *Inorg. Chem.*, **6**, 142 (1967).
(6) C. F. Wells and G. Davies, *Nature*, **205**, 692 (1965).

in the temperature range 1–35°. Thus, the proportions of the two predominant Mn(III) species in solution can be calculated over wide acidity ranges using the experimentally determined value of the acid dissociation constant of the ion Mn^{3+}. This constant has an unusually high value (0.93 M at 25°) compared with those of other trivalent cations of the first transition series.[7]

Hydrogen peroxide, on the other hand, is a very weak acid,[8] and exists entirely as molecular H_2O_2 at the acid concentrations where Mn(III) can be produced (see Table I). Acidity dependences of reaction rates in the present study can then be interpreted in terms of shifts in the acid dissociation equilibrium, which is very rapidly established.[9] The kinetics of reactions of H_2O_2 with oxidizing and reducing substrates have been widely studied.[10] Mechanistic examinations of the reactions of H_2O_2 with metal ions include studies of Ce(IV) (in 0.80 M H_2SO_4),[11] Co(III),[12] Fe(II),[13a] and Fe(III).[13b] The earlier inference that HO_2 radical is an intermediate in the oxidation of H_2O_2 was later established using epr measurements in the reaction between Ce(IV) and hydrogen peroxide.[14] Recently, many direct determinations of the rate constants of free-radical reactions, including those of HO_2, have been carried out by pulse radiolysis.[15,16]

TABLE I

EQUILIBRIUM DATA AT 25°

Reaction	Medium	Constant
$H_3O_2^+ \rightleftharpoons H^+ + H_2O_2$	1 M perchlorate	$\sim 10^3$ [a]
$H_2O_2 \rightleftharpoons H^+ + HO_2^-$	1 M perchlorate	5.4×10^{-12} M [a]
$HO_2^- \rightleftharpoons H^+ + O_2^{2-}$	1 M perchlorate	Extremely small [a]
$H_2O_2^+ \rightleftharpoons H^+ + HO_2$	Acidic	*Ca.* 10^{-1} M [b]
$HO_2 \rightleftharpoons H^+ + O_2^-$	10^{-2} M perchlorate	$(3.5 \pm 2) \times 10^{-5}$ M [c]

[a] See ref 8, in particular ref 49E therein. [b] B. H. J. Bielski and A. O. Allen, "Proceedings of the Second Tihany Symposium on Radiation Chemistry," Akademiai Kiado, Budapest, 1967, p 81. Earlier work (H. Taube, *J. Am. Chem. Soc.*, **64**, 2468 (1942)), also supports this assignment. [c] G. Czapski and L. M. Dorfman, *J. Phys. Chem.*, **68**, 1169 (1964); *cf.* E. J. Hart, *Ann. Rev. Nucl. Sci.*, **15**, 125 (1965).

Equilibrium data for H_2O_2 and HO_2 relevant to this study have been collected in Table I. The values of the acid dissociation constants for $H_3O_2^+$, H_2O_2, and HO_2 are of such magnitude as to preclude their inclusion in the present scheme.

Experimental Section

Reagents.—All solutions were prepared from commercially available distilled water. Further purification of this water by distillation from alkaline permanganate followed by another stage of distillation had no detectable effect on the kinetic or stoichiometric results. All other chemicals were reagent grade. Perchloric acid (Baker and Adamson) was standardized, after dilution to *ca.* 0.1 M, by titration with standard 0.10 M NaOH, using phenol red as indicator. Sodium perchlorate solution (4.00 M, used for the adjustment of ionic strength μ) was prepared by the neutralization of perchloric acid with anhydrous Na_2CO_3 (Fisher Scientific Co.). Barium perchlorate was likewise prepared using $Ba(OH)_2 \cdot 8H_2O$ (Fisher Scientific Co.) for neutralization. To prepare the ferrous perchlorate solution (*ca.* 0.05 M in 0.10 M $HClO_4$, subsequently used for analytical purposes), boiling, equivalent solutions of ferrous sulfate (dissolved $FeSO_4 \cdot 7H_2O$, Fisher Scientific Co.) and barium perchlorate were mixed, allowed to cool overnight, and filtered. Manganous perchlorate solution, obtained by mixing cold solutions of manganous sulfate (made from $MnSO_4 \cdot H_2O$, Fisher Scientific Co.) and excess barium perchlorate and filtering, gave the same results as were obtained with commercially prepared manganous perchlorate (G. Frederick Smith Chemical Co. $Mn(ClO_4)_2 \cdot 6H_2O$).[1] The concentration of Mn(II) was determined by the method of Mehlig.[17]

Manganese(III) solutions in $HClO_4$ were obtained by electrolytic oxidation of a large excess of manganese(II) at a platinum anode.[2] The solution was stirred using either a magnetic stirrer or a stream of purified nitrogen before and during electrolysis. In this way, Mn(III) solutions of concentrations up to *ca.* 10^{-3} M were conveniently prepared. The concentration of Mn(III) was determined as follows.[6] An aliquot of solution was added to an excess of Fe(II) at total perchloric acid concentration greater than 1 M. The resulting concentration of Fe(III) was determined spectrophotometrically at 260 mμ *vs.* an appropriate blank (extinction coefficient 2.88×10^3 M^{-1} cm^{-1};[18] relative error, $\leq \pm 1\%$). All aqueous solutions of uncomplexed Mn(III) are metastable. For this reason solutions were always freshly prepared immediately before use. No change in the optical density at 470 mμ or in the oxidizing titer of the stock solution took place in the time taken to carry out kinetic experiments. Tests for any contaminating chloride and sulfate in reagents were negative.

Hydrogen peroxide (Fisher, 30% w/v, unstablized) was diluted to *ca.* 5×10^{-2} M and analyzed immediately before use with standard 0.10 M Ce(IV) solution, using ferroin as indicator. No catalytic decomposition of H_2O_2 was observed on dilution of the stock solution in acidic Mn(II).[19] Solutions thus prepared were stable during the time taken for kinetic measurement. Dilute (*ca.* 5×10^{-3} M or less) solutions of hydrogen peroxide were determined by addition of an aliquot to an excess of iron(II). The iron(III) thus produced was determined as above, with a relative error in $[H_2O_2]_0$ measured in this way of $\pm 1\%$.[13a,18]

Stoichiometry.—The stoichiometry of the reaction was determined in acid perchlorate containing a high concentration of Mn(II) throughout. Under conditions where the excess of hydrogen peroxide was initially between two- and fivefold, the following procedure was employed. A sample from the hydrogen peroxide solution was taken before and after addition of a known amount of Mn(III), and the peroxide concentration was determined in each case as described above. When Mn(III) was in excess, determinations of [Mn(III)], as described, before and after addition of a known amount of hydrogen peroxide yielded the stoichiometry. Experiments in which Mn(III) and hydrogen

(7) C. F. Wells, *Nature*, **205**, 693 (1965). This value represents a revision of K_H given by G. Davies, Ph.D. Thesis, Birmingham, England, 1966. The standard deviation is ± 0.04 M at 25°.

(8) L. G. Sillén and A. E. Martell, Ed., "Stability Constants of Metal Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, p 210.

(9) H. Diebler and M. Eigen, Abstract, Proceedings of the 9th International Conference on Coordination Chemistry, St. Moritz, Switzerland, Sept 1966, p 360.

(10) W. C. Shumb, C. N. Satterfield, and R. L. Wentworth, "Hydrogen Peroxide," Reinhold Publishing Corp., New York, N. Y., 1955.

(11) G. Czapski, B. H. J. Bielski, and N. Sutin, *J. Phys. Chem.*, **67**, 201 (1963).

(12) J. H. Baxendale and C. F. Wells, *Trans. Faraday Soc.*, **53**, 800 (1957).

(13) (a) W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462 (1951); (b) *ibid.*, **47**, 591 (1951).

(14) E. Saito and B. H. J. Bielski, *J. Am. Chem. Soc.*, **83**, 4467 (1961); B. H. J. Bielski and E. Saito, *J. Phys. Chem.*, **66**, 2266 (1962).

(15) L. M. Dorfman and M. S. Matheson, *Progr. Reaction Kinetics*, **3**, 239 (1965).

(16) M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Ed., Pulse Radiolysis," Academic Press Inc., London, 1965.

(17) J. P. Mehlig, *Ind. Eng. Chem., Anal. Ed.*, **11**, 274 (1939); **13**, 819 (1941).

(18) R. Bastian, R. Weberling, and F. Palilla, *Anal. Chem.*, **28**, 459 (1956).

(19) D. B. Broughton and R. L. Wentworth, *J. Am. Chem. Soc.*, **69**, 741 (1947).

peroxide solutions were rapidly mixed under ordinary experimental conditions and over glass beads yielded the same stoichiometry, indicating the absence of surface catalysis.

When the peroxide was present in more than fivefold excess, the precision of this method decreased because of the relatively low concentration of Mn(III). That is, low initial [Mn(III)] produced insufficient reaction to allow the difference between the two peroxide determinations to exceed the experimental error in the determination itself. At these higher hydrogen peroxide concentrations a more precise procedure is to measure directly the oxygen produced upon reaction of a previously measured quantity of Mn(III).

The procedure adopted was to allow degassed solutions of manganese(III) and hydrogen peroxide to react in an evacuated vessel. The unreacted H_2O_2 was then decomposed by reaction with an excess of Fe(II), which quantitatively reduces hydrogen peroxide to water.[13a] The specially designed vessel used for this purpose is shown in Figure 1. After the reaction, the oxygen was pumped through a liquid nitrogen trap, into the calibrated volumes of a Toepler pump, where the pressure and volume of the gas were measured. The ambient temperature was also recorded at this time. The sample was then analyzed by gas chromatography. The relative error in the number of moles of oxygen thus determined is $\pm 3\%$.

Kinetics.—Since the reaction between Mn(III) and hydrogen peroxide is rapid in perchlorate media, the reaction was studied with a rapid-mixing, stopped-flow apparatus[20] (constructed of quartz and glass). Mixing is complete within the time required for the solution to flow from the mixing jets to the observation chamber (*ca.* 5 msec).[20] The temperature of the solutions in the pushing syringes was maintained at 25 $\pm 1°$. These syringes are enclosed in an aluminum block through which water is circulated from a thermostat. A sufficient volume of solution is forced through the apparatus each time to ensure proper flushing of the observation chamber.

A freshly prepared stock solution of Mn(III) was mixed with a series of solutions of hydrogen peroxide containing identical concentrations of Mn(II) and $HClO_4$, respectively. The disappearance of manganese(III) was followed spectrophotometrically at 470 mμ. The range over which the initial [Mn(III)] can be varied is limited by three factors.

(i) The concentration of Mn(III) which is stable in perchlorate media is restricted by the disproportionation reaction.

(ii) In consequence of (i), the optical densities being measured were small, even at 470 mμ, where the extinction coefficient is a maximum in the visible region.[1,2,6]

(iii) The advantage of working at shorter wavelengths, where the absorption band has a greater extinction coefficient than that at 470 mμ, was offset by a decrease in total signal due to inherent limitations in instrumentation.

The reaction trace was recorded on a storage oscilloscope and afterward photographed. Each run was repeated at least twice and the results were averaged, the reproducibility being generally better than $\pm 5\%$. An example of a kinetic run is shown in Figure 2.

Experiments with the largest possible $[H_2O_2]_0$ compatible with the resolution time of the apparatus gave linear first-order plots for [Mn(III)] disappearance. At lower concentrations of peroxide, reaction I should give a linear plot of log $[(2b - x)/(a - x)]$ *vs.* time,[21] where a and b are the initial concentrations of manganese(III) and hydrogen peroxide, respectively, and x is the [Mn(III)] which has been consumed at time t. An example of such a plot, shown in Figure 3, is linear, within experimental error, indicating that the over-all order of the reaction is two, and the order with respect to each component is unity. The apparent second-order rate constant, k_{app}, was calculated in each case from the equation $k_{app} = 2.303(\text{slope})/(2b - a)$ and was in good agreement with that calculated from the linear first-order plot when $[H_2O_2]_0$ was in sufficient excess.

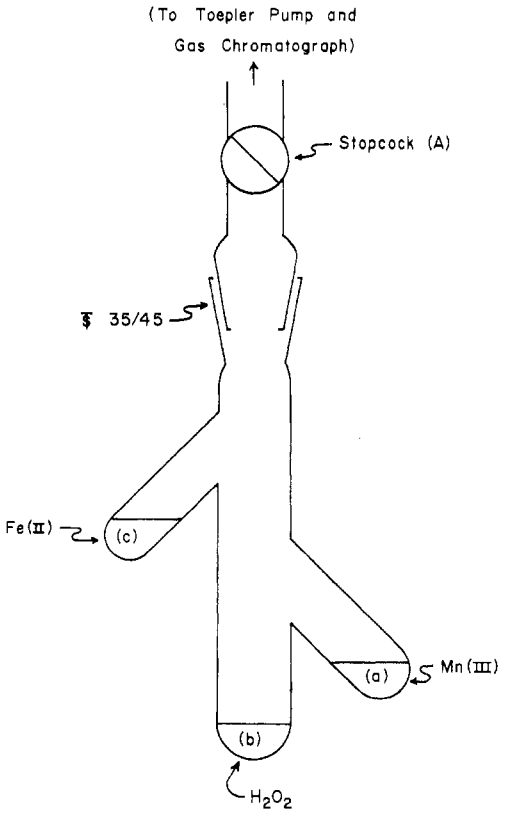


Figure 1.—Stoichiometry in the presence of excess H_2O_2. In this experiment the order of addition of reagents is significant. After degassing, valve A is closed, leaving an evacuated vessel with three frozen solutions. With (c) frozen, (a) is added to (b). The Mn(III) is quantitatively consumed, producing O_2, and leaving unreacted H_2O_2. The Fe(II) solution is then thawed, and (b) is added to (c). Thus, the unreacted H_2O_2 is exposed to an excess of Fe(II) and is quantitatively reduced to H_2O, evolving no further oxygen.

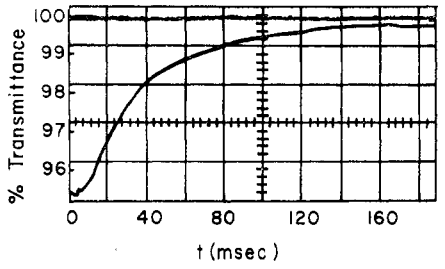


Figure 2.—Oscillograph of a stopped-flow experiment. The ordinate has been calibrated in percentage of light transmitted, the abscissa is time in milliseconds. For this trace the experimental conditions are: $a = [Mn(III)]_0 = 6.30 \times 10^{-4}$ M, $b = [H_2O_2]_0 = 1.69 \times 10^{-3}$ M, $[Mn(II)] = 9.0 \times 10^{-1}$ M, $[HClO_4] = 2.00$ M, total ionic strength = 4.70 M, temperature = 25°, and path length = 6.9 mm. Data points from this and all other traces were taken after the first 10 msec had elapsed.

Results

Stoichiometry. (A) Spectrophotometric Analysis.—The results of several determinations of the stoichiometry by spectrometric analysis in solution are shown in Table II. It is evident that, for changes in concentration of the reactants, $\Delta[Mn(III)]/\Delta[H_2O_2] = 2$, over

(20) P. Hurwitz and K. Kustin, *Trans. Faraday Soc.*, **62**, 427 (1966).

(21) S. W. Benson, "The Fundamentals of Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1960, Chapter II.

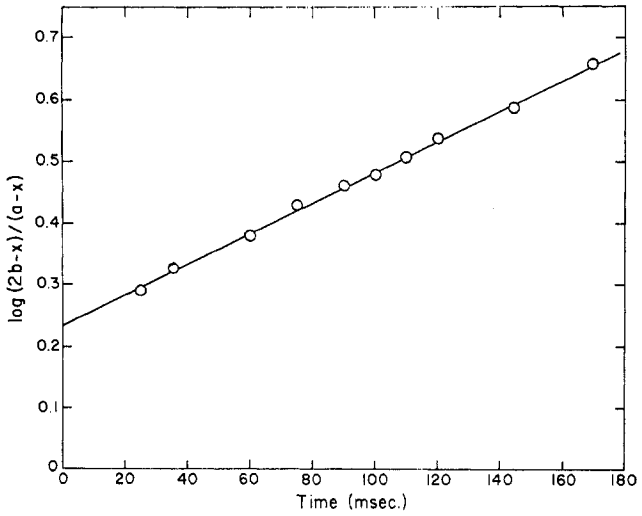


Figure 3.—Typical second-order plot. Per cent transmission was converted to optical density, so that the parameter x could be calculated. For this run the experimental conditions were as follows: $a = [Mn(III)]_0 = 6.10 \times 10^{-4}$ M, $b = [H_2O_2]_0 = 4.82 \times 10^{-4}$ M, $[Mn(II)] = 9.0 \times 10^{-1}$ M, $[HClO_4] = 2.00$ M, and total ionic strength = 4.70 M.

TABLE II

STOICHIOMETRY BY SPECTROPHOTOMETRIC ANALYSIS AT VARIOUS ACIDITIES[a] AND AT 25°

$[HClO_4]$	$10^4[Mn(III)]_0$	$10^4[Mn(III)]_\infty$	$10^4 \cdot [H_2O_2]_0$	$10^4 \cdot [H_2O_2]_\infty$	$\Delta[Mn(III)]/\Delta[H_2O_2]$
3.70[b]	4.02	2.80	0.61	0	2.00
	4.05	2.21	0.92	0	2.00
	4.15	1.08	1.53	0	2.00
1.00[c]	6.37	3.33	1.58	0	1.92
	6.34	3.94	1.26	0	1.90
	6.35	4.54	0.95	0	1.91
	6.30	5.06	0.63	0	1.97
3.70[b]	4.54	0	9.33	7.12	2.06
	4.56	0	10.02	7.68	1.95
	4.51	0	10.03	7.72	1.95
2.50[d]	5.04	0	22.3	19.5	1.80
	5.04	0	22.3	20.0	2.19
	5.04	0	22.3	19.8	2.02
				Av	1.97 ± 0.09

[a] All concentrations, M. [b] $[Mn(II)] = 0.10$ M. [c] $[Mn(II)] = 1.00$ M. [d] $[Mn(II)] = 0.50$ M.

the acidity range 1.00–3.70 M $HClO_4$, up to a fivefold excess of hydrogen peroxide. However, as mentioned previously (Experimental Section; *cf.*, also, Table II, results for $[H_2O_2]_0 = 2.23 \times 10^{-3}$ M), the uncertainty in the final stoichiometric ratio is higher at the higher $[H_2O_2]_0$.

(B) Oxygen Analysis.—Oxygen produced by a reaction in the vessel shown in Figure 1 will be contaminated with air due to incomplete degassing and residual air in the line. The amount of air thus carried along is relatively small, but, in any event, does not invalidate the results, since it can be accounted for. That is, by using the chromatographic column to separate, detect, and measure oxygen and nitrogen, the total volume of gas collected, V, could be corrected for this air as follows. Samples of air were passed through the column and the chromatographic ratio $N_2/O_2' = y$ was determined, where N_2 and O_2' represent the integrated areas for residual nitrogen and oxygen, respectively. Let V_{O_2} represent the volume of oxygen due to (I). Then, if the corresponding ratio for the sample is $N_2/(O_2 + O_2') = 1/z$, we have $V_{O_2} = V(yz - 1)/y(z + 1)$, with $V = V_{O_2} + V_{air}$.

The use of this technique with respect to results in 2.50 M $HClO_4$, with $[Mn(II)] = 0.50$ M, is illustrated in Table III. Blank experiments with no Mn(III) present show that (1) no oxygen is produced when hydrogen peroxide reacts with an *excess* of Fe(II) and (2) the decomposition of H_2O_2 by solid MnO_2 proceeds quantitatively, leading to the conclusion that oxygen can be determined to an accuracy of ±3% in this apparatus. An experiment in which 6.05×10^{-6} mole of Mn(III) was allowed to react with an approximately fivefold excess of H_2O_2 showed that the stoichiometry of reaction I is two (*i.e.*, $\Delta[Mn(III)]/\Delta[H_2O_2] = 2$), confirming the spectrophotometric results. However, similar experiments (of which one is shown in Table III), in which the excess of H_2O_2 was increased to *ca.* 50-fold, produced a larger quantity of oxygen than would be predicted from the above ratio. We conclude that some catalytic decomposition of H_2O_2 is being induced as a result of reaction with Mn(III) at these higher peroxide concentrations.

Kinetics.—Kinetic results obtained from experiments within an acidity range of 1.00–3.70 M $HClO_4$ at 25° are shown in Table IV. In each run the initial concentrations are such that no Mn(III) remains at the end of a reaction. The following trends are evident throughout these results. At fixed values of $[HClO_4]$, $[Mn(II)]$, and $[Mn(III)]_0$, the apparent bimolecular rate constant, k_{app}, decreases as $[H_2O_2]_0$ increases. Since $[Mn(III)]_0$ shows little variation, it is also evident that k_{app} increases as $[Mn(II)]$ decreases when $[H_2O_2]_0$ is constant. These relationships may be verified by examining Figures 4 and 5.

In the series at $[HClO_4] = 2.00$ M, with $[Mn(III)]_0 = a = 4.17 \times 10^{-4}$ M and $[Mn(II)] = 0.075$ M, Figure 4 shows that a linear relationship exists between $1/k_{app}$ and $[H_2O_2]_0/[Mn(III)]_0$ (*i.e.*, b/a). Values of $1/k_{app}$ at fixed values of b/a were obtained nomographically from plots similar to Figure 4 for each series in which a and $[Mn(II)]$ are constant. Values of b/a equal to 0.0, 1.0, 2.0, 3.0, and 4.0 were chosen for this purpose. The values of $1/k_{app}$ for different b/a were plotted against the corresponding values of $[Mn(II)]/a$; Figure 5 demonstrates that a linear relationship exists between these parameters at each value of b/a. The lines drawn through each of these sets of data have essentially the same slope. Corresponding relationships were obtained at other acidities.

These relationships can be expressed in the form of the empirical equation

$$\frac{1}{k_{app}} = A + B\frac{[Mn(II)]}{a} + C\frac{b}{a} \qquad \text{(i)}$$

Values of A, B, and C at different acidities are collected in Table V, and their relation to the mechanism will be discussed in the next section.

TABLE III

STOICHIOMETRY BY OXYGEN ANALYSIS AT 25°, $[HClO_4] = 2.50\ M$, $[Mn(II)] = 0.50\ M$

Mn(III) consumed, mole	H_2O_2, initial, mole	Vol collected, ml	Pressure, mm	y	z	O_2 produced, mole
0	2.5×10^{-5} [a]	0.467	7.16	2.23	0.45	0
0	2.285×10^{-5} [b]	1.075	26.42	2.25	6.20	1.22×10^{-5}
6.05×10^{-6}	3×10^{-5}	0.467	19.65	2.40	2.80	3.09×10^{-6}
7.05×10^{-6}	35×10^{-5}	5.847	5.10	2.30	3.90	11.33×10^{-6}

[a] H_2O_2 decomposed with excess Fe(II). [b] H_2O_2 decomposed with *ca.* 1 g of freshly prepared MnO_2.

TABLE IV

KINETIC DATA AT 25°[a]

[Mn(II)]	μ	10^4[Mn(III)]$_0$	$10^4[H_2O_2]_0$	$10^{-3}k_{app}$, M^{-1} sec^{-1}
	(a) $[HClO_4] = 3.70\ M$			
0.40	4.90	3.84	5.2	14.7
			10.4	13.9
			13.0	12.3
			18.2	10.1
0.25	4.45	3.71	6.2	23.1
			10.2	13.3
			14.4	12.2
			20.5	9.1
0.10	4.00	4.00	5.4	22.2
			13.5	13.4
			18.8	12.3
0.04	3.82	3.62	5.4	36.5
			10.8	20.4
			13.5	16.4
			18.9	10.0
	(b) $[HClO_4] = 2.96\ M$			
0.60	4.76	3.91	7.3	9.8
			9.7	8.5
			12.2	7.5
0.30	3.86	4.08	4.7	16.2
			7.0	12.5
			9.3	11.7
0.15	3.41	5.43	5.1	22.9
			7.6	18.5
			10.2	18.5
			12.7	15.5
0.09	3.23	5.14	4.3	26.3
			6.5	24.2
			8.6	24.4
			10.8	18.6
	(c) $[HClO_4] = 2.00\ M$			
0.90	4.70	6.30	12.1	10.9
			16.9	9.7
			24.1	8.5
0.67	4.00	4.34	5.4	13.1
			13.6	12.0
			19.0	10.4
0.30	2.90	4.02	4.9	16.7
			12.2	12.7
			17.1	10.2
0.15[b]	4.05	4.72	5.8	24.3
			14.6	17.2
			29.2	9.3
0.15	2.45	7.00	5.0	33.7
			12.5	23.7
			25.0	13.3
0.075	2.23	4.17	5.4	24.5
			13.6	20.4
			19.0	13.3
			27.2	11.4
	(d) $[HClO_4] = 1.00\ M$			
1.20	4.60	3.92	5.1	16.6
			10.1	11.3
			12.7	12.6
			17.8	10.3
0.60	2.80	4.99	5.3	21.9
			10.6	17.2
			13.3	15.4
			18.6	12.3
0.90[c]	3.70	4.24	7.2	13.0
			10.9	11.3
			14.5	9.7
			18.1	9.9
0.60[c]	2.80	2.78	5.2	15.2
			7.7	12.7
			10.3	14.2
			12.9	13.3

[a] All concentrations, M. [b] In this experiment $[NaClO_4] = 1.60\ M$. [c] Since $[Mn(II)]/a = 214 \pm 2$ in these cases, the results were combined in a least-squares calculation.

TABLE V

VALUES OF THE KINETIC PARAMETERS A, B, AND C AT DIFFERENT ACIDITIES AT 25°

$[HClO_4]$[a]	10^5A[b]	10^8B[b]	10^5C[b]
3.70	1.6	2.70	1.39
2.96	1.7	4.66	1.86
2.00	1.4	4.14	1.32
1.00	2.1	1.12	1.16

[a] M. [b] M sec.

Finally, we note from Table IV that the ionic strength varies throughout, without any apparent effect on the kinetics of (I). Indeed, no effect on the rate could be observed when sodium perchlorate was added to the solution to control the ionic strength (see Table IV, Figure 5, and ref 11).

Treatment of Data

The preceding observations can be explained, and rate equations identical with the empirical rate law can be derived, with the postulation of a radical mechanism; in particular, with $H_2O_2^+$ as an intermediate. An additional hypothesis is that the protolytic reactions are rapid with respect to all other reactions, so that the quotients

$$K_H = \frac{[MnOH^{2+}][H^+]}{[Mn^{3+}]}$$

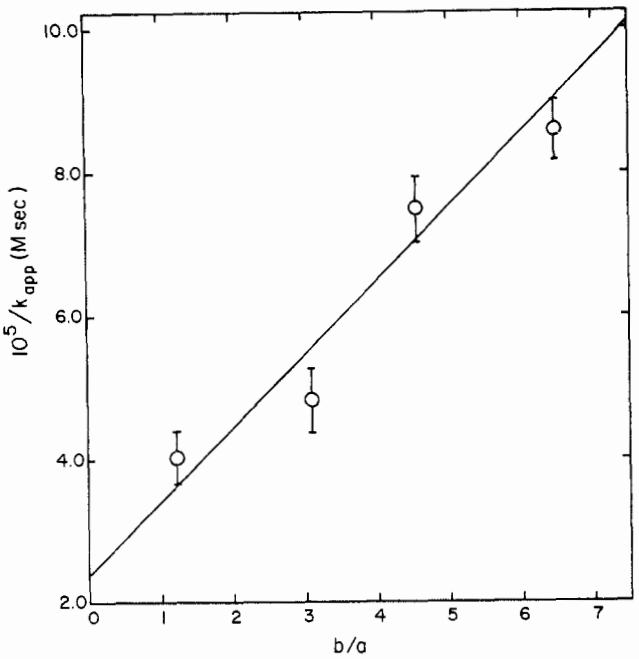


Figure 4.—Plot of $1/k_{app}$ *vs.* b/a for [Mn(II)] = 0.075 M and $[Mn(III)]_0 = 4.17 \times 10^{-4}$ M at $[HClO_4]$ = 2.00 M and μ = 2.23 M.

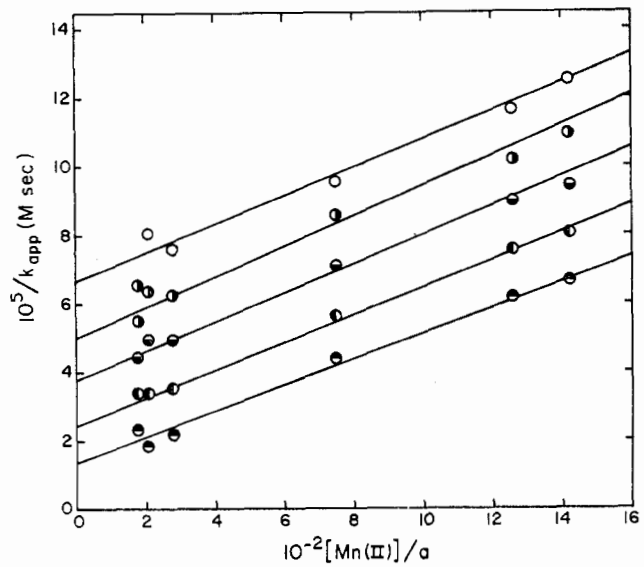


Figure 5.—Plot of $1/k_{app}$ *vs.* [Mn(II)]/a for different b/a at $[HClO_4]$ = 2.00 M. Ionic strength varies between 2.23 and 4.70 M. The value of b/a in each plot is as follows: ○, 4.0; ◑, 3.0; ◒, 2.0; ◐, 1.0; ◓, 0.0.

and

$$K_a = \frac{[HO_2][H^+]}{[H_2O_2^+]}$$

are assumed to be constant throughout the entire course of the reaction.

If the concentration of complexed Mn(III) species is inappreciable, a mechanism which gives a dependence of k_{app} on $[H_2O_2]_0$ is

$$Mn^{3+} + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mn^{2+} + H_2O_2^+ \qquad (1)$$

$$MnOH^{2+} + H_2O_2 \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} Mn^{2+} + HO_2 + H_2O \qquad (1')$$

$$Mn^{3+} + H_2O_2^+ \xrightarrow{k_2} Mn^{2+} + 2H^+ + O_2 \qquad (2)$$

$$MnOH^{2+} + H_2O_2^+ \xrightarrow{k_2'} Mn^{2+} + H_3O^+ + O_2 \qquad (2')$$

$$H_2O_2 + H_2O_2^+ \xrightarrow{k_3} OH + H_3O^+ + O_2 \qquad (3)$$

$$Mn^{2+} + OH \xrightarrow{k_4} Mn(III) + OH^- \qquad (4)$$

Letting [Mn(III)] represent total oxidized manganese and defining the rate according to

$$\text{rate} = \frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[Mn(III)]}{dt} = \ldots \qquad (II)$$

we may apply the steady-state assumption to $[H_2O_2^+]$ and [OH] to obtain

$$-\frac{1}{2}\frac{d[Mn(III)]}{dt} = k_{app}[Mn(III)][H_2O_2] \qquad (III)$$

where, at constant acidity, with $[Mn(III)]_0 \equiv a$ and initial hydrogen peroxide concentration, $[H_2O_2]_0 \equiv b$, it can be shown that

$$\frac{1}{k_{app}} = \frac{1}{k^h_1}\left[1 + \frac{k^h_{-1}}{k^h_2}\frac{[Mn^{2+}]}{a} + \frac{k_3}{k^h_2}\left(\frac{b}{a}\right)\right] \qquad (IV)$$

which is identical with the empirical rate law (i) with $A \equiv 1/k^h_1$, $B \equiv k^h_{-1}/k^h_1k^h_2$, and $C \equiv k_3/k^h_1k^h_2$.

Complexation has been implicated in the rates of redox reactions involving metal ions. It has been known for some time that hydrogen peroxide readily forms complexes with cations.[22] In the case of manganese(III), temperature-jump studies of complex formation with various ligands have established the relative rapidity of this type of reaction, with Mn^{3+} reacting more rapidly than $MnOH^{2+}$.[9] Partial resolution into single-step rate constants is possible by examining the behavior of the system under conditions of varying acidity. The rate constant for the most rapid step in the mechanism, k_4, cannot be determined in this fashion.

We may begin this analysis by assuming the existence of complexed manganese(III) species. In the simplest case this process could be represented by the reaction

$$Mn(III) + H_2O_2 \underset{}{\overset{K^h_c}{\rightleftharpoons}} Mn^{III}\cdot H_2O_2 \qquad (5)$$

with the acid-dependent stability constant

$$K^h_c = \frac{[Mn^{III}\cdot H_2O_2]}{[Mn(III)][H_2O_2]} \qquad (V)$$

No direct experimental evidence could be obtained for the existence of such species since the extinction coefficient at time t = 0 does not vary appreciably with $[H_2O_2]_0$. Nevertheless, this observation does not *a priori* rule out the presence of complexed species. In fact, the conclusions to be drawn are as follows: (a) K^h_c is small enough to make the contribution of the complex to the initial optical density too small to detect; (b) K^h_c is not small, but the extinction coefficient of the complex is similar to that of uncomplexed manganese(III). It can easily be shown that if complexes need be considered in the mechanism and that, if reaction 5 is very rapid, then the right-hand side of eq IV

(22) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1946, p 368.

has to be multiplied by $(1 + K^{h}_{c}[H_2O_2])$, where $[H_2O_2]$ is the concentration of *uncomplexed* hydrogen peroxide. The modified form of eq IV can only be evaluated under certain conditions, namely, (i) if K^{h}_{c} is small, in which case $[H_2O_2] \equiv b$ and eq IV is essentially unchanged, or (ii) if $b >> a$, whence $[H_2O_2] \equiv b$. This case cannot be experimentally realized because of the rapidity of the reaction at the relatively high values of $[Mn(III)]_0$ which are used.

If K^{h}_{c} is appreciable, then $[H_2O_2] \not\equiv b$, and b cannot be evaluated. Thus no extensive quantitative account of complexation can be undertaken. This consideration does not prevent a complete analysis of the coefficients A and B, however, since all experimental plots can be extrapolated to $[H_2O_2] = b = 0$. If K^{h}_{c} is finite, then neglect of the factor $(1 + K^{h}_{c}[H_2O_2])$ in eq IV will result in too high an estimate for the ratio k_3/k^{h}_{2}.

According to the present mechanism (eq 1–4)

$$A = \frac{1}{k^{h}_{1}} = \frac{[H^+] + K_H}{k_1[H^+] + k_{1'}K_H} \qquad \text{(VI)}$$

and a plot of $([H^+] + K_H)/A$ *vs.* $[H^+]$ should be linear. Figure 6 shows the experimental relationship, from which k_1 and $k_{1'}$ may be determined (Table VI). The variation of the ratio B/A with acidity can be used to calculate further relationships, as follows. Let

$$D = B[H^+]/A([H^+] + K_H) = \alpha\left[\frac{\beta[H^+] + K_a}{\gamma[H^+] + K_H}\right] \qquad \text{(VII)}$$

where $\alpha = k_{-1'}/k_{2'}$, $\beta = k_{-1}/k_{-1'}$, and $\gamma = k_2/k_{2'}$. The function D increases with decreasing $[H^+]$ as shown in Figure 7, indicating that $\beta[H^+]$ is always less than K_a (*i.e.*, that $\beta << 1$). From the slope and intercept of the plot in Figure 7 the values $\alpha \cong 0.05$ and $\gamma \cong 0.7$ may be obtained. Hence $k_{-1} < k_{-1'} < k_{2'}$ and $k_{2'} \cong k_2$. Finally, we note from Table V that the coefficient C is apparently insensitive to changes in acidity. Table VI summarizes the kinetic findings.

TABLE VI
SUMMARY OF RATE CONSTANTS AND RATE CONSTANT RATIOS AT 25°

$k_1 = 7.3 \times 10^4\ M^{-1}\ \text{sec}^{-1}$
$k_{1'} = 3.2 \times 10^4\ M^{-1}\ \text{sec}^{-1}$
$k_{-1}/k_{-1'} \ll 1$
$k_2/k_{2'} \simeq 0.7$

Discussion

The results of the present study may be compared with those of the oxidation of hydrogen peroxide in other systems.

For two other metal ions, Ce(IV) and Co(III), the kinetics of oxidation of hydrogen peroxide bear certain similarities to this work. In each case, a step like (1) or (1′) is involved. For ceric ion,[11] however, the observed rate constant is higher ($10^6\ F^{-1}\ \text{sec}^{-1}$ in 0.80 M H_2SO_4), while for cobaltic ion[12] it is considerably lower ($1.5 \times 10^3\ F^{-1}\ \text{sec}^{-1}$ in 1.02 M $HClO_4$). Since the oxidizing power ascends in the order Ce(IV) < Mn(III) < Co(III) in these different media, a linear free-energy relationship such as that described by the Marcus theory[23] for electron-transfer reactions is precluded. Indeed, exchange rates for the Ce(IV)–Ce(III), Mn(III)–Mn(II), and Co(III)–Co(II) couples follow the order Mn < Ce < Co.[2,24] Thus, cobalt(III), with the highest redox potential and most rapid exchange rate, reacts most slowly of the three metals with hydrogen peroxide. In the cobalt(III) study cited,[12] the data indicated complex formation. A similar interpretation was made for the iron(III) reaction at very high concentrations of H_2O_2.[25]

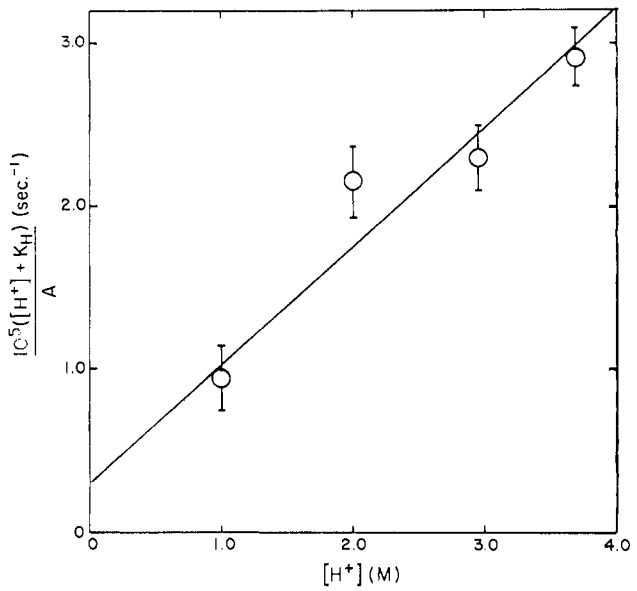


Figure 6.—Plot of $10^5([H^+] + K_H)/A$ *vs.* $[H^+]$ at 25°, using the value $K_H = 0.93\ M$.

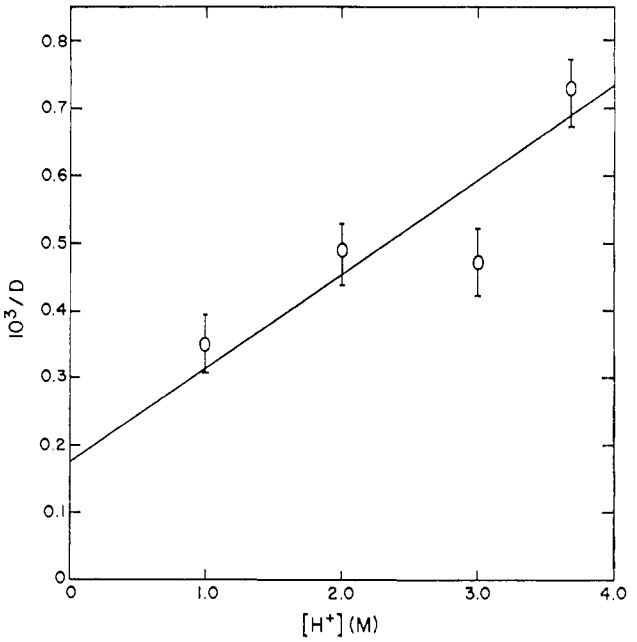


Figure 7.—Plot of $1/D$ *vs.* $[H^-]$ at 25°, using the value $K_H = 0.93\ M$.

(23) R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1965), and earlier papers in this series.
(24) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).
(25) M. L. Haggett, P. Jones, and W. F. K. Wynne-Jones, *Discussions Faraday Soc.*, **29**, 153 (1960); P. Jones, R. Kitching, M. L. Tobe, and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **55**, 79 (1959).

If we write steps 1 and 1′ as

$$\mathrm{Mn(III) + H_2O_2} \overset{K^h_c}{\rightleftharpoons} \mathrm{H_2O_2 \cdot Mn^{III}}$$

$$\mathrm{H_2O_2 \cdot Mn^{III}} \overset{k^h_s}{\longrightarrow} \mathrm{Mn(II) + H_2O_2^+} \qquad \mathrm{H_2O_2 \cdot Mn^{III}} \overset{k^h_{-s}*}{\longrightarrow} \mathrm{Mn(II) + H_2O_2^+}$$

$$\mathrm{Mn(II) + H_2O_2^+} \overset{k^h_{-s}}{\longrightarrow} \mathrm{H_2O_2 \cdot Mn^{III}} \qquad \mathrm{Mn(II) + H_2O_2^+} \overset{k^h_s*}{\longrightarrow} \mathrm{H_2O_2 \cdot Mn^{III}}$$

the apparent rate constant for the cyclic mechanism is

$$k^h_I = k^h_s + k^h_s{}^* K^h_c$$

$$k^h_{-I} = k^h_{-s} + k^h_{-s}{}^*$$

The over-all cyclic step thus described is a composite of two separate cycles involving the molecular species Mn^{3+} and $MnOH^{2+}$. Then

$$k_1 = k_s + k_s{}^* K_c; \; k_{-1} = k_{-s} + k_{-s}{}^*$$

and

$$k_{1'} = k_{s'} + k_{s'}{}^* K_{c'}; \; k_{-1'} = k_{-s'} + k_{-s'}{}^*$$

where the unprimed and primed terms refer to reactions of Mn^{3+} and $MnOH^{2+}$, respectively.

The initial step in the reaction appears to be an electron transfer to manganese(III), producing the $H_2O_2^+$ free radical. Mass spectrometric studies of the formation of $H_2O_2^+$ indicate that a nonbonding electron is removed, the ion thus being relatively stable in the gas phase.[26] In the first step, the nonhydroxylated Mn(III) species react more rapidly than $MnOH^{2+}$ species, as the acidity dependence has shown. In this regard, reaction of manganese(III) with the $H_2O_2^+$ radical is similar to that with the parent hydrogen peroxide. In neither step, however, is the difference between the rate constants of the two metal ion species large, and it may only reflect the reduction in available sites on the metal ion due to blocking by the hydroxide ligand.

The second step of the reaction may involve H atom transfer. The presence of the hydroxide ligand in the inner coordination sphere would aid reaction, since it could function as a stable site on the metal ion for attachment of the transferred H atom. Abstraction of an electron from the positively charged $H_2O_2^+$ would be inhibited, a problem circumvented by atom transfer. The ratios in Table VI indicate that $k_{-1'} > k_{-1}$.

Negatively charged and strongly complexing ligands catalyze the rates of exchange reactions.[27] An explanation, in part, for this observation is that complexation labilizes the water molecules still bound to the central metal ion, thus lowering the Franck–Condon barrier (if present) to completed electron transfer.[23] That this effect does not seem to be operating for step 1′ as opposed to step 1 may indicate that some other factor may be playing a role here.

The electronic structure of manganese(III) is that of a d^4 system. Such species, even in a field of six identical ligands, would be expected to show a Jahn–Teller distortion.[28] The ground-state configuration for paramagnetic $Mn(H_2O)_6^{3+}$ is ${}^5E_g(t_{2g}{}^3e_g)$ (in O_h).[28c] The ground states for the diamagnetic complexes $Co(H_2O)_6^{3+}$ and $Ce(H_2O)_x^{4+}$ are ${}^1A_{1g}(t_{2g}{}^6)$ and ${}^1S_0(5d^0)$, respectively.[28b] The rate of reaction seems to increase with the number of additional electrons that can be accommodated in the metal d orbitals, which is a maximum for cerium(IV) and a minimum for cobalt(III).

We will now consider the dependence of k_{app} on $1/[H_2O_2]_0$. The observation of a catalyzed reaction at high $[H_2O_2]_0$ indicates that Mn(III) and H_2O_2 compete for the radical $H_2O_2^+$. If hydroxyl radicals are produced in step 3 they would be rapidly scavenged by Mn(II) which is present at high concentration, since reactions analogous to (4) are known to have rate constants which are close to the diffusion-controlled limit.[15,16] Reaction between hydroxyl radical and perchlorate is known to be very slow.[29] Reactions such as

$$\mathrm{OH + H_2O_2 \longrightarrow H_2O + HO_2}$$

and

$$\mathrm{OH + Mn(III) \longrightarrow OH^- + Mn(IV)}$$

are thus probably not important under the present conditions.

The reaction of the *unprotonated* hydroperoxy radical

$$\mathrm{HO_2 + H_2O_2} \overset{k_{3'}}{\longrightarrow} \mathrm{OH + H_2O + O_2} \qquad (3')$$

has been studied previously. The main evidence for its existence comes from investigations of the photochemical[30] and Co^{60} γ-ray[31–33] decomposition of H_2O_2 solutions. Analyses of radiolytic data have produced values for the rate constant[33] which are at variance with the directly determined value. The determination carried out by Hart and Matheson[33] is a direct examination of (3′) by a fast-reaction technique. Averaging their values with that of the photochemical study[30] yields $k_{3'} = (6.5 \pm 1.2) \times 10^2\ M^{-1}\ \mathrm{sec}^{-1}$.

Another source of information on the rate of the reaction between hydroperoxy radical and hydrogen peroxide is the oxidation of H_2O_2 by $S_2O_8^{2-}$.[34] In this case, it was found that the reaction between hydroperoxy free radical and hydrogen peroxide had a rate constant approximately 1.5×10^{-3} times as large as the corresponding constant for the reaction between peroxydisulfate and the radical. It was also found that this ratio depended upon ionic strength. Moreover, Edwards[35] has pointed out that the reactions

(26) A. J. B. Robertson, *Trans. Faraday Soc.*, **48**, 228 (1952).

(27) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press Co., New York, N. Y., 1966, Chapter 3, especially Table 3-1; J. Halpern and L. E. Orgel, *Discussions Faraday Soc.*, **29**, 16 (1960).

(28) (a) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (b) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N.Y., 1966; (c) J. P. Fackler, Jr., and I. D. Chawla, *Inorg. Chem.*, **3**, 1130 (1964).

(29) D. Katakis and A. O. Allen, *J. Phys. Chem.*, **68**, 3107 (1964).

(30) D. E. Lea, *Trans. Faraday Soc.*, **45**, 81 (1949).

(31) H. Fricke, *J. Chem. Phys.*, **3**, 364 (1935); *Cold Spring Harbor Symp. Quant. Biol.*, **3**, 55 (1935); E. R. Johnson, *J. Chem. Phys.*, **19**, 1204 (1951).

(32) B. V. Ershler, M. A. Nezhevenko, and G. G. Myasishcheva, *Dokl. Akad. Nauk SSSR*, **126**, 126 (1959).

(33) E. J. Hart and M. S. Matheson, *Discussions Faraday Soc.*, **12**, 169 (1952); *cf.* discussion sections in this volume.

(34) M. S. Tsao and W. K. Wilmarth, "Free Radicals in Inorganic Chemistry," R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1962, p 43.

(35) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, p 172.

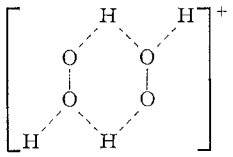
$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$

and

$$OH + OH \longrightarrow H_2O_2$$

which have high rate constants ($5.4 \times 10^6\ M^{-1}\ sec^{-1}$ [36] and $1.2 \times 10^{10}\ M^{-1}\ sec^{-1}$,[37] respectively), are not required to interpret the kinetics of the $S_2O_8^{2-}$–H_2O_2 reaction.[34] These considerations indicate: (1) the presence of the HO_2–H_2O_2 reaction is also detectable in another system with competing radical reactions and (2) the reaction environment is important in determining which radical processes predominate in a given system[35,38] and may significantly affect the magnitude of the third step in the present scheme.

Hydrogen peroxide interacts very strongly with water, as certain parameters such as the excess entropy of mixing and others indicate.[39,40] Association of H_2O_2 molecules with H_2O_2 by hydrogen bonding is inferred from Raman studies of liquid and solid phases.[41] Moreover, in both the Hart and Matheson study and in a study of proton exchange in aqueous hydrogen peroxide near neutrality by nmr,[42] cyclic complexes have been postulated as intermediates. The observation of catalysis with $[Mn(III)]_0 \simeq 5 \times 10^{-4}\ M$ and $[H_2O_2]_0$ as low as $2.5 \times 10^{-2}\ M$ indicates that $k_3 > k_{3'}$. This increase in rate constant can be related to the increased symmetry of the cyclic intermediate



and the increased rate of decomposition of the intermediate due to stronger interaction with the solvent.

As pointed out previously, the accurate determination of stoichiometry within the kinetic concentration range shows that $k_3 < k_2 \gtrsim k_{2'}$. The dependence of k_{app} on $1/[H_2O_2]_0$ can also be used to indicate the presence of complexed Mn(III) species as follows. If complexed Mn(III) species are present, then it can be shown that

$$Cb/a = K^h_c[H_2O_2][A + (B[Mn^{2+}]/a) + (Ak_3b/k^h_2a)] + (Ak_3b/k^h_2a) \quad \text{(VIII)}$$

At the highest peroxide concentration we may make the approximation $b = [H_2O_2]$. Now, from the observed stoichiometry $k_3 < k^h_2$ and it is evident from the values of the coefficients in Table V that

$$C \simeq AK^h_c a \quad \text{(IX)}$$

Substitution of values of A and C from Table V into eq IX, with $a = 5 \times 10^{-4}\ M$, yields an average value of K^h_c of *ca.* $1.7 \times 10^3\ M^{-1}$ over the experimental acidity range. Under the above conditions, with this value of K^h_c and with $b = 3 \times 10^{-3}\ M$, the percentages of $[Mn(III)]_0$ and $[H_2O_2]_0$ in the form of complexed species would be 82 and 14, respectively. The value of K^h_c so obtained is higher than the value of *ca.* $3 \times 10^2\ M^{-1}$ calculated from a study of the oxidation of hydrogen peroxide by Co(III).[12] However, experimental restrictions in the present study prevent a more quantitative treatment of the data at the present time.

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(37) J. Rabani and M. S. Matheson, *J. Am. Chem. Soc.*, **86**, 3175 (1964).
(38) J. O. Edwards in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 67.
(39) G. Scatchard, G. M. Kavanagh, and L. B. Ticknor, *J. Am. Chem. Soc.*, **74**, 3715 (1952).
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