to any extent in acetonitrile. The possibility that this might be due to limited solubility is rejected since two resonance signals, assigned to PCl_4^+ and PCl_6^- ions, were observed in the ^{31}P nmr spectrum of phosphorus(V) chloride in acetonitrile under the same conditions.[1] The absence of a coordinated acetonitrile signal confirms our previous conclusion based upon infrared data[1] that acetonitrile is not entering into the first coordination sphere of the PCl_4^+ ion to alter its tetrahedral symmetry.

Although infrared spectral measurements[1,21] showed the presence of $SbCl_6^-$ ion in solutions of antimony(V) chloride in acetonitrile, no evidence could be found in the spectrum for tetrahedral $SbCl_4^+$ ion. The apparent solvation number of 0.82 indicates that two acetonitrile molecules are present in the first coordination sphere of the cation and supports the suggestion[1,21] that the cation is present as *trans*-$(CH_3CN)_2SbCl_4^+$. The possibility that $SbCl_5 \cdot CH_3CN$ is also present cannot be entirely excluded since it too has a solvation number of 1. However, in view of the high conductance of the solution[1] it cannot be present in any significant amounts. The slight reduction in the solvation number from the expected value of 1 indicates the presence of species of decreased solvation number such as Sb_2Cl_{10} or $(CH_3CN)Cl_4Sb^+,SbCl_6^-$.

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Catalysis of the Chlorine–Hydrogen Peroxide Reaction by the Manganese(III)–Manganese(II) Ion Pair

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The Mn(III)–Mn(II) ion pair catalyzes the Cl_2–H_2O_2 reaction by initiating a free-radical mechanism. In the saturation region ([Mn(II)] $\geq 0.01\ M$) the reaction is first order with respect to both Cl_2 and H_2O_2. A mechanism consistent with the data is

$$\mathrm{Mn(III)} + H_2O_2 \rightleftarrows MnO_2H^{2+} + H^+ \text{ (fast)}$$

$$MnO_2H^{2+} + Cl_2 \longrightarrow \mathrm{Mn(II)} + H^+ + Cl^- + O_2 + Cl\cdot$$

$$\mathrm{Mn(II)} + Cl\cdot \longrightarrow \mathrm{Mn(III)} + Cl^-$$

Introduction

The oxidation of hydrogen peroxide by chlorine in acid media

$$H_2O_2 + Cl_2 \longrightarrow 2H^+ + 2Cl^- + O_2$$

has been the subject of a number of investigations.[1–3] A mechanism for this reaction was suggested by Connick[3]

$$H_2O_2 + Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} HOOCl + H^+ + Cl^- \qquad (1)$$

$$HOOCl \xrightarrow{k_2} H^+ + Cl^- + O_2 \qquad (2)$$

This leads to the rate expression

$$-\frac{d[Cl_2]}{dt} = \frac{k_1k_2[H_2O_2][Cl_2]}{k_{-1}[H^+][Cl^-] + k_2} \qquad (I)$$

When the [HCl] is large and constant, this reduces to

$$-\frac{d[Cl_2]}{dt} = k_0[H_2O_2][Cl_2] \qquad (II)$$

where $k_0 = k_1k_2/k_{-1}[H^+][Cl^-]$ and is the pseudo-second-order rate constant.

The present study was undertaken to determine the catalytic effect of the Mn(III)–Mn(II) pair on the Cl_2–H_2O_2 reaction. This pair has previously been used to catalyze a number of other redox reactions[4,5] causing them to occur through a free-radical mechanism. Davies, Kirschenbaum, and Kusten[6] did a kinetic study of the reaction between Mn(III) and H_2O_2 in perchloric acid solutions and proposed the rate-determining steps

$$Mn^{3+} + H_2O_2 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} Mn^{2+} + H_2O_2^+ \qquad (3)$$

$$MnOH^{2+} + H_2O_2 \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} Mn^{2+} + HO_2 + H_2O \qquad (4)$$

where at 25.0° $k_3 = 7.3 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_4 = 3.2 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$. Other metal ions causing the rapid formation of the $HO_2\cdot$ free radical include Ce(IV)[7] and Co(III).[8]

As in these other studies the presence of the Mn(III)–Mn(II) pair causes the Cl_2–H_2O_2 reaction to proceed *via* a free-radical mechanism.

Experimental Section

Reagents.—Triply distilled water was used in the preparation of all solutions.

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[1] B. Makower and W. C. Bray, *J. Amer. Chem. Soc.*, **55**, 4765 (1933).

[2] B. Makower, *ibid.*, **56**, 1315 (1934).

[3] R. E. Connick, *ibid.*, **69**, 1509 (1947).

[4] H. Taube, *ibid.*, **69**, 1418 (1947).

[5] H. Taube, *ibid.*, **70**, 3928 (1948).

[6] G. Davies, L. J. Kirschenbaum, and K. Kusten, *Inorg. Chem.*, **7**, 146 (1968).

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

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

Hydrogen peroxide (Fisher, 30% Superoxol) was diluted to about 0.1 *M* and analyzed prior to use by iodometric titration using a starch indicator. Subsequent to reaction this solution was adjusted to the desired concentration and acidity (2 *M* HCl), and Mn(II) was added. No catalytic decomposition of the H_2O_2 by Mn(II) was detected.

Chlorine solutions were prepared either by the reaction of MnO_2 with 4 *M* HCl or by directly bubbling reagent grade Cl_2 (Matheson, Inc., $\geq 99.9\%$) into triply distilled water. No kinetic differences were observed using solutions prepared by either of the two methods. Chlorine solutions standardized by iodometric titration with a starch indicator were used in the preparation of a Beer's law curve at 328 nm. Due to the volatility of these solutions, concentrations were determined prior to each run using this curve.

The Mn(III) solutions were prepared by the method of Kalra and Gosh[9] through the quantitative reaction of reagent grade $MnSO_4$ and $KMnO_4$ in 4.67 *M* H_2SO_4

$$\mathrm{Mn(VII)} + 4\mathrm{Mn(II)} \longrightarrow 5\mathrm{Mn(III)}$$

A Beer's law curve was prepared from the above solutions at 275 nm and was used to determine the catalyst concentration prior to each run.

The manganous ion was prepared from Fisher reagent grade $MnSO_4 \cdot H_2O$ with no subsequent purification. The ionic strength was maintained by diluting all solutions in 2 *M* HCl. In those solutions where necessary, NaCl was used for the adjustment of ionic strength.

Kinetic Measurements.—Rates of reaction were followed by measuring the decrease in absorbance of Cl_2 at 328 nm using a Beckman DU monochromator with Aminco-Morrow stopped-flow apparatus[10] attached. The detector used was a 1P28 photomultiplier tube (PMT) powered by a Kepco Model ABC-500 dc power supply. The PMT output was fed into the Aminco high-performance kinetic photometer and then into a log adaptor attached to the Tektronix 3A8 operational amplifier. The logarithmic (absorbance) signal was then displayed using the Tektronix RM 564B storage oscilloscope. Figure 1 shows a typical oscilloscope trace of the reaction.

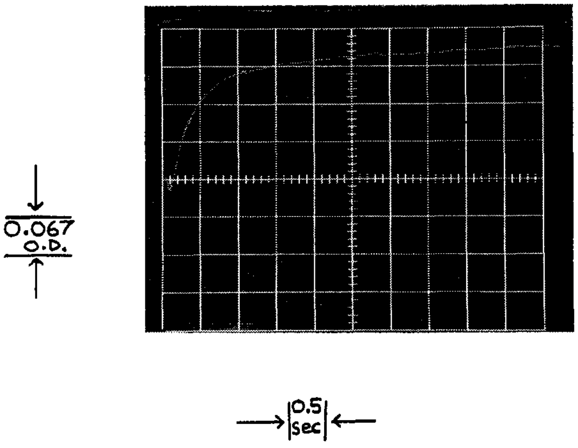

Figure 1.—Typical kinetic trace using stopped-flow apparatus.

Results and Discussion

Table I gives the conditions for all experiments and their observed rate constants, k_{obsd}. The pseudo-second-order rate constant k_0 (from eq II) for the uncatalyzed reaction in 2 *M* HCl increased linearly from 28 M^{-1} sec^{-1} in the absence of Mn(II) to 120 M^{-1} sec^{-1} when [Mn(II)] = 0.1 *M*. This behavior suggests the formation of $MnOOH^+$ which also reacts with the Cl_2 at a somewhat enhanced rate. In the presence of both Mn(II) and Mn(III) the reaction between H_2O_2 and Cl_2 proceeds at a greatly enhanced rate which, when $[\mathrm{Mn(II)}] \geq 0.01$ *M*, was not affected by changes in [Mn(II)]. Similar behavior by manganous ion has been observed in other chemical systems. Taube[4] has referred to this as the saturation region with respect to the manganous ion.

TABLE I[a]

Expt no.	$10^3[Cl_2]_0$, *M*	$10^3[H_2O_2]_0$, *M*	10^6[Mn(III)], *M*	[Mn(II)], *M*	k_{obsd}, M^{-1} sec^{-1}
1	2.0	2.0	0.00	0.00	28
2	2.0	2.0	0.00	0.010	35
3	2.0	2.0	0.00	0.050	70
4	2.0	2.0	0.00	0.10	120
5	2.0	2.0	2.5	0.10	2.0×10^2
6	2.0	2.0	5.0	0.10	2.6×10^2
7	2.0	2.0	10.0	0.10	3.8×10^2
	2.0	2.0	28.0	0.10	8.0×10^2
9	2.0	2.0	55.0	0.10	1.4×10^3
10	2.0	2.0	83.0	0.10	1.9×10^3
11	2.0	2.0	110	0.10	2.1×10^3
12	2.0	2.0	55.0	0.050	1.4×10^3
13	2.0	2.0	55.0	0.010	1.4×10^3
14	3.0	0.50	55.0	0.10	3.30[b]
15	2.0	2.0	28.0	0.10	16.9×10^2[c]

[a] The temperature in all runs was 30.0 ± 0.1°. [b] In experiment 14 only, k_{obsd} is a first-order rate constant. [c] In experiments 1–14, [HCl] = 2 *M*. In experiment 15, [HCl] = 1 *M*.

The total rate of loss of Cl_2 is the sum of the uncatalyzed and catalyzed reactions where the uncatalyzed reaction contains Mn(II) at the same concentration as does the catalyzed reaction. In the saturation region the observed rate law in 2 *M* HCl was found to be

$$-\frac{d[Cl_2]}{dt} = k_{\mathrm{obsd}}[H_2O_2][Cl_2] \qquad \text{(III)}$$

When the manganous ion concentration was reduced to 0.005 *M* and smaller, a dependency upon the manganous ion concentration was observed indicating a change in the rate expression. In addition, a change in the overall order of the reaction was observed. At lower manganous ion concentrations ($<10^{-4}$ *M*) the reaction was found to be between first and second order rather than strictly second order overall.

A free-radical mechanism consistent with our results for the catalyzed reaction in the saturation region is

$$\mathrm{Mn(III)} + H_2O_2 \overset{K_5}{\rightleftharpoons} MnO_2H^{2+} + H^+ \quad \text{(fast)} \qquad (5)$$

$$MnO_2H^{2+} + Cl_2 \xrightarrow{k_6} \mathrm{Mn(II)} + H^+ + Cl^- + O_2 + Cl\cdot \qquad (6)$$

$$\mathrm{Mn(II)} + Cl\cdot \xrightarrow{k_7} \mathrm{Mn(III)} + Cl^- \qquad (7)$$

Step 7 accounts for the regeneration of Mn(III).

It is assumed in step 5 that the complexation of Mn(III) by H_2O_2 is only partial; otherwise saturation in rate as H_2O_2 is increased would be observed. This was not noted. Therefore the [Mn(III)] in the rate law that follows is the same as the stoichiometric [Mn(III)]. The resulting rate expression is

$$-\frac{d[Cl_2]}{dt} = K_5k_6\frac{[\mathrm{Mn(III)}][H_2O_2][Cl_2]}{[H^+]} = k_c[\mathrm{Mn(III)}][H_2O_2][Cl_2] \qquad \text{(IV)}$$

where $k_c = K_5k_6/[H^+]$. The total rate of loss of Cl_2 for both the catalyzed and uncatalyzed reactions in the saturation region is

$$-\frac{d[Cl_2]}{dt} = \{k_0 + k_c[\mathrm{Mn(III)}]\}[H_2O_2][Cl_2] = k_{\mathrm{obsd}}[H_2O_2][Cl_2] \qquad \text{(V)}$$

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(9) H. L. Kalra and S. Gosh, *Z. Phys. Chem.*, **21**, 228 (1965).

(10) J. I. Morrow, *Chem. Instrum.*, **2**, 375 (1970).

where

$$k_{obsd} = k_0 + k_c[\text{Mn(III)}] \qquad \text{(VI)}$$

When the [Mn(II)] is lowered sufficiently, the chain-ending step involving the recombination of atomic chlorine would compete with reaction 7

$$\text{Cl}\cdot + \text{Cl}\cdot \longrightarrow \text{Cl}_2 \qquad (8)$$

This necessitates deviations from integral orders at lower manganous ion concentrations as was observed.

Manganic Ion Dependency and Attrition.—Figure 2 shows k_{obsd} plotted against the Mn(III) concentration. As predicted from eq VI the plot is linear (to $[\text{Mn(III)}] \approx 7 \times 10^{-5}$ M) with a slope of 2.6×10^7 M^{-2} sec^{-1} ($=k_c$) and an intercept of 1.3×10^2 M^{-1} sec^{-1} ($=k_0$). This value of k_0 obtained by extrapolation is in good agreement with that obtained when the reaction was run without Mn(III) present. Above a manganic ion concentration of $\sim 7 \times 10^{-5}$ M, attrition of the catalyst occurs and hence the rate constant k_{obsd} no longer increases linearly with increasing [Mn(III)]. The most likely attrition reaction is

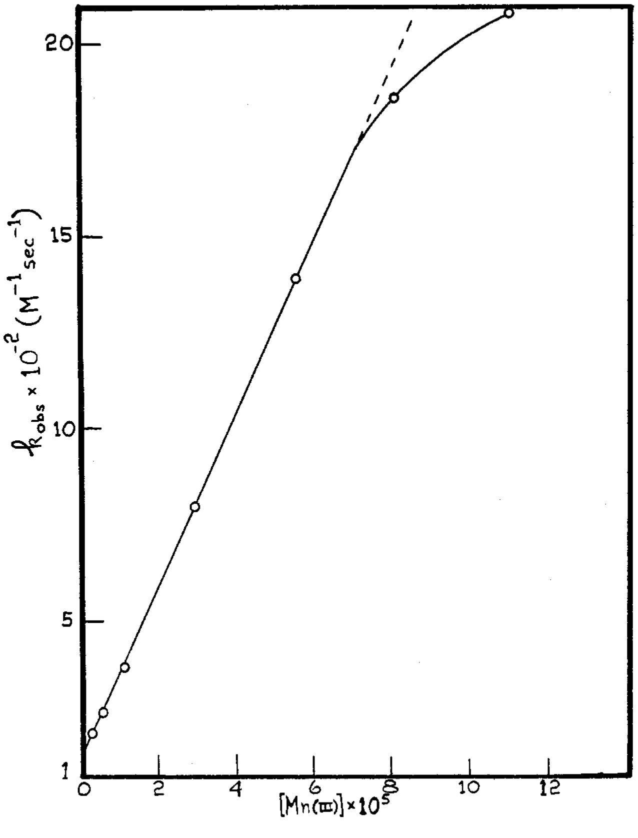

Figure 2.—Plot of k_{obsd} vs. [Mn(III)]; [Mn(II)] = 0.10 M; [HCl] = 2 M.

$$\text{MnO}_2\text{H}^{2+} + \text{Mn(III)} \longrightarrow 2\text{Mn(II)} + \text{O}_2 + \text{H}^+ \qquad (9)$$

Hydrogen Ion Dependency.—The mechanism predicts that k_c $(=K_5k_6/[\text{H}^+])$ should be inversely proportional to the [H$^+$]. That this is so is shown by the results of experiments 8 and 15 (Table I).

It is interesting to note that reaction 5 may be viewed as the sum of two other rapid reactions

$$\text{Mn(II)} + \text{H}_2\text{O}_2 \overset{K_{10}}{\rightleftarrows} \text{MnOOH}^+ + \text{H}^+ \qquad (10)$$

$$\text{MnOOH}^+ + \text{Mn(III)} \overset{K_{11}}{\rightleftarrows} \text{MnOOH}^{2+} + \text{Mn(II)} \qquad (11)$$

These suggest that the overall reaction may also be initiated by complexation of Mn(II) rather than Mn(III) by H_2O_2. This would be consistent with the observed effect of Mn(II) alone on the Cl_2–H_2O_2 reaction, thereby implying the formation of an MnOOH$^+$ species. Inclusion of reactions 10 and 11 in place of reaction 5 in the suggested mechanism results only in replacing K_5 wherever it appears with the product $K_{10} \cdot K_{11}$.

Summary

Addition of the Mn(III)–Mn(II) ion pair to Cl_2–H_2O_2 solutions greatly enhances the rate of reaction between Cl_2 and H_2O_2 by initiating a free-radical mechanism. In the saturation region, the reaction is first order with respect to both Cl_2 and H_2O_2 and inversely proportional to [H$^+$]. A mechanism was proposed that suggests the presence of MnOOH^{2+} and possibly MnOOH$^+$ as intermediates.