Stock solutions of hydrazinium ion were prepared by adding hydrazine hydrate to a boiled[26] solution of aqueous perchloric acid at equimolar concentration, effectively yielding $N_2H_5^+ClO_4^-$. The solution was standardized with potassium iodate.[27]

Other materials were reagent grade chemicals, or were prepared as described earlier.[28] For reactions in deuterated solvent, D_2O was used in the preparations described above, such that the reaction solutions contained a mole fraction of D $\geqslant 0.95$.

Methods. The kinetic data were obtained spectrophotometrically, by continuously monitoring the UV absorbance in a cell of 5-cm optical path with a Varian Cary Model 219 spectrophotometer with a thermostated cell holder. Data were mostly obtained at 290 nm, although some data were collected at 245 nm, with identical results. A Perkin-Elmer diode-array spectrophotometer was also used in some experiments.

The experiments were conducted anaerobically with $[N_2H_5^+]$ and $[H^+]$ in great excess over $[CrO_2^{2+}]$. Reactions conducted with oxygen present gave absorbance-time traces that did not reach a stable end point reading or fit first-order kinetics; such experiments are not considered further here. The data we report followed pseudo-first-order kinetics and were evaluated by the standard methods. In experiments where $HCrO_4^-$ was not present, however, the reactions also did not follow pseudo-first-order kinetics; the rate constant for the initial stage was obtained by a biphasic kinetic analysis.

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Registry No. $N_2H_5^+$, 18500-32-8; CrO_2^{2+}, 34021-34-6; $\cdot N_2H_4^+$, 20771-51-1; D_2, 7782-39-0.

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Reaction between Permanganate Ion and Hydrogen Peroxide: Kinetics and Mechanism of the Initial Phase of the Reaction[1]

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The reaction between permanganate ion and hydrogen peroxide, studied by stopped-flow experiments, occurs in three stages: a fast initial phase, an induction period, and an autocatalytic step. The reaction is autocatalytic because manganous ion, a product of the reaction, catalyzes the reaction by combining with permanganate ion to form a complex whose breakdown products react faster with peroxide than does the complex. Retardation of the first phase to give the induction period is also due to manganous ion, which preferentially binds to permanganate, forming a relatively nonreactive intermediate, thus shutting down the first phase. At 25.0 ± 0.5 °C and ionic strength 1.0 M ($NaClO_4$), the spectrophotometrically determined stoichiometry of the fast initial phase reaction is $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$. The rate law for the initial phase is $-{}^1/_2 d[MnO_4^-]/dt = (k_3 + k'[H^+])[MnO_4^-][H_2O_2]$ where k' is a composite rate constant that includes the protonation equilibrium constant of MnO_4^-, $k' = (3.1 \pm 0.5) \times 10^2$ M^{-2} s^{-1}, and $k_3 = 23.2 \pm 3.0$ M^{-1} s^{-1}. This reaction is explained by nucleophilic attack of H_2O_2 on manganese(VII) in an inner-sphere mechanism.

Introduction

Permanganate ion has several advantages as an analytical reagent.[3] Above all, it is a strong, vividly colored oxidant, serving as its own indicator. However, these advantages are only realized with rapidly reacting reductants, a requirement frequently fulfilled by adding manganous ion at the start of a titration. This expedient makes permanganate ion reactions generally useful, despite their often balky, irreproducible kinetics.[4]

For example, in closed (batch) reactions, under conditions of nearly equivalent permanganate ion and substrate concentrations or of excess substrate concentration, permanganate ion reactions exhibit complex dynamical behavior. With hydrogen peroxide as substrate, individual phases of the reaction show substrate inhibition and autocatalysis, while the initial rate exhibits maxima and minima in its dependence on substrate and product concentrations.[5,6] Similar behavior has been observed in the permanganate oxidation of the more slowly reacting oxalic acid.[7,8] In an open (flow) reactor, acidified permanganate ion-hydrogen peroxide exhibits bistability,[9] as does permanganate ion-oxalic acid.[10]

The Mn(II)/Mn(III) couple has been successfully introduced into oscillating reaction systems where a high oxidation potential is required, e.g., as a replacement for Ce(III)/Ce(IV).[11] However, its participation in oscillatory processes should be more widespread, owing to the several and relatively stable oxidation states between permanganate (+7) and manganous (+2) ions. Reactions of manganese with dioxygen species, especially, should be attractive candidates for the design of new chemical oscillators, if more were known about their kinetics.

To provide a better understanding of the kinetics of analytical procedures utilizing permanganate ion and to determine the origins of complex dynamical behavior in the permanganate-hydrogen peroxide reaction, we are investigating the different phases of this system. We report here a study of the kinetics of the initial phase of the permanganate ion-hydrogen peroxide reaction by stopped-flow spectrophotometry.

Experimental Section

Materials. The following reagents were used without further purification: manganous perchlorate (G. Frederick Smith Chemical Co.), hydrogen peroxide (30%), potassium permanganate, perchloric acid (70-72%), and sodium perchlorate (Fisher Scientific Co.). Stock solutions of sodium perchlorate (4.0 M) were first filtered before being used as the inert electrolyte to maintain ionic strength at unity.

Potassium permanganate solutions were prepared and standardized against sodium oxalate.[12] The procedure was performed only once to

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obtain an absorptivity coefficient for permanganate at 525 nm of 2340 M^{-1} cm^{-1}. Approximately 5×10^{-3}, M stock solutions were prepared fresh each day and standardized spectrophotometrically on a Beckman Model 25 spectrophotometer.

Hydrogen peroxide solutions were standardized by using either standard 0.1 N cerium sulfate solution (Fisher Scientific Co.)[13] or potassium permanganate,[14] which had been standardized by the method mentioned above. Tris(1,10-phenanthroline)iron(II) sulfate was used as indicator in the cerium sulfate titrations. Hydrogen peroxide solutions were prepared fresh before each set of experiments.

Manganous perchlorate solutions were used for a week before fresh solutions were prepared. Stock perchloric acid solutions (6.0 M) were prepared and standardized by titrating against standard 0.1 N sodium hydroxide (Fisher Scientific Co.) with methyl orange as the indicator.

Methods. Stoichiometric determinations were carried out spectrophotometrically by monitoring absorbances of the reaction solutions at 525 and 420 nm. However, in acid solutions, permanganate ions can react with product manganous ions to give Mn(III) ions, which absorb maximally at 420 nm.[15] Thus, when one starts with excess permanganate, the exact stoichiometric equivalents are achieved when the absorbance at 525 nm reaches its lowest value without appreciable absorbance at 420 nm.

Kinetic measurements were made with a Gibson-type stopped-flow spectrophotometer with stainless-steel drive syringe barrels.[16] The reaction was followed by monitoring the absorbance of permanganate at 525 nm. Hydrogen peroxide was mixed with sodium perchlorate in one of the solution reservoirs, and potassium permanganate, perchloric acid, and sodium perchlorate were mixed in the other. In the case of experiments performed with Mn^{2+} ions initially added, manganous perchlorate was added to the hydrogen peroxide reservoir.

The trace from the stopped-flow apparatus was captured on a Biomation 610B transient recorder and digitalized. The digitalized trace was then fed into a PDP-11/23 minicomputer where it was analyzed by the initial rate method.

Results

Permanganate ion reacts with hydrogen peroxide in acidic medium to give oxygen, manganous ions, and water according to reaction I.[17] Our spectrophotometric studies confirmed this stoichiometry.

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2 \quad \text{(I)}$$

Stopped-flow experiments show that the reaction has, depending upon initial acid, peroxide, and manganous ion concentrations, one, two, or I.[17] These phases are a fast initial process, an induction period, and an autocatalytic process. The last two phases have been routinely observed in previous studies of this reaction, but not the first phase. Our study concerns the first phase, which, in the absence of initially added manganous ions, comprises 6–20% of the reaction.

Parts a (short time span) and b (long time span) of Figure 1 show all three phases. In all cases, the reaction starts fast, slows down during the induction period, and then picks up speed again. The autocatalytic phase, however, does not attain the rate of the initial phase. No pseudo-first-order kinetics were observed even though peroxide and acid were in excess, except for the initial phase when both acid and peroxide concentrations were very high. In these conditions, one could easily separate the initial step from the third step because the induction period became much longer.

A series of experiments were carried out to determine the acid, hydrogen peroxide, permanganate, and manganous ion dependences of the initial rate of the first phase.

Hydrogen Peroxide Dependence. Figure 1 shows the effect of hydrogen peroxide on all the phases. Higher hydrogen peroxide concentrations increase the rate of the initial phase. In low H_2O_2 concentrations there is a smooth transition from the initial phase to the autocatalytic phase, and the induction period is barely noticeable. Increasing $[H_2O_2]$ lengthens the induction period, and the absorbance at the end of the first phase increases, indicating formation of a new species that absorbs substantially at 525 nm. High $[H_2O_2]$ retards autocatalysis; at high enough $[H_2O_2]$, the autocatalysis finally disappears altogether, with the rate of the third phase substantially reduced, and the system is dominated by the initial phase. A plot of initial rate vs. $[H_2O_2]$ in low-[acid] environments gives a linear plot that passes through the origin (Figure 2a).

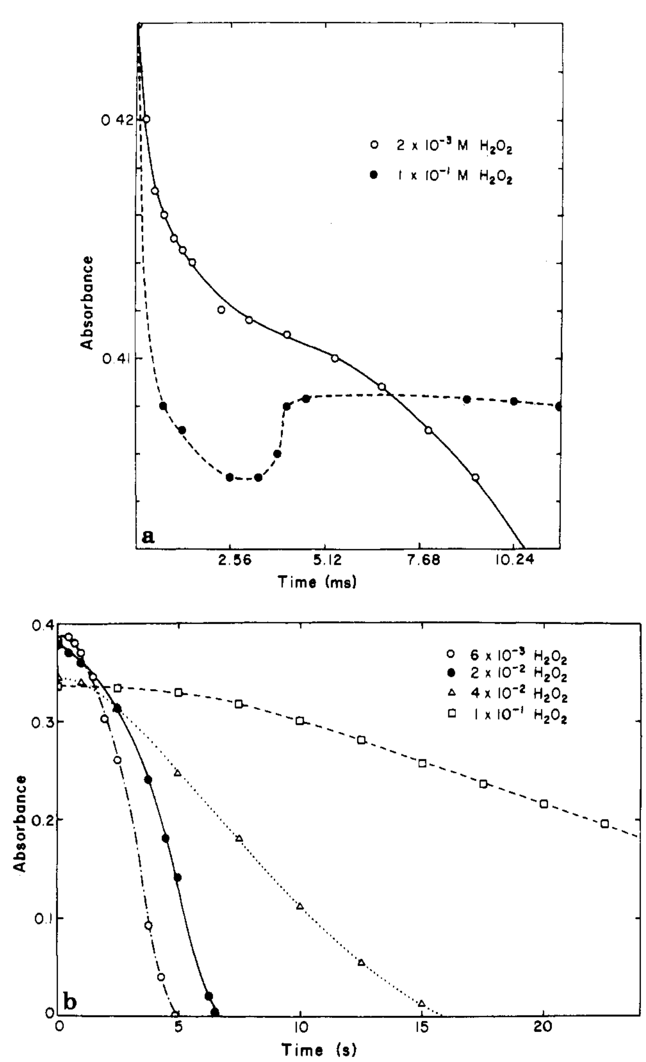

Figure 1. (a) Optical density trace at 525 nm showing the effect of hydrogen peroxide on the initial phase of the reaction: $[H^+]_0 = 0.01$ M; $[MnO_4^-]_0 = 2 \times 10^{-4}$ M. (b) Effect of increasing initial hydrogen peroxide on the autocatalytic phase of the reaction: $[H^+]_0 = 0.01$ M; $[MnO_4^-]_0 = 2 \times 10^{-4}$ M.

Acid Dependence. Acid has a positive effect on the rates of both the initial phase and the autocatalytic phase (Figure 3). As in the case of the H_2O_2 dependence, at high acid concentrations, more of the reaction proceeds via the initial phase before the induction period begins. Not only does acid help shorten the induction period, it also enhances the autocatalysis and generally makes the overall reaction faster. The effect of acid is, however, greatly reduced in high $[H_2O_2]$. While high $[H_2O_2]$ can eliminate the autocatalysis, high acid concentrations do not cause such an effect within the hydrogen peroxide and hydrogen ion concentrations of this study. Figure 2b shows the dependence of the initial rate on the acid concentration.

Permanganate Ion Dependence. Permanganate ion concentrations were varied from 5×10^{-5} to 5×10^{-4} M in different combinations of acid and peroxide concentrations. In all cases, the initial rate increased linearly with $[MnO_4^-]$. Plots of initial

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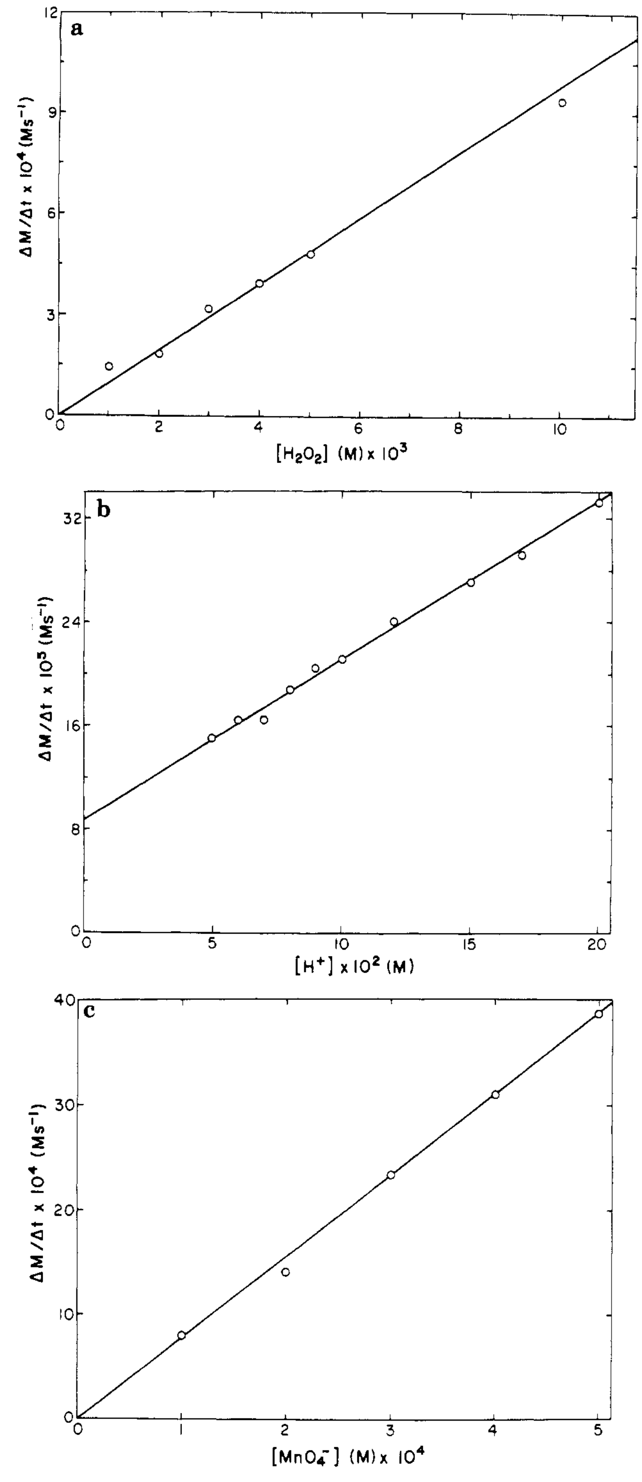

Figure 2. (a) Plot of initial rate, $\Delta[MnO_4^-]/\Delta t$, vs. $[H_2O_2]$: $[HClO_4]_0 = 1 \times 10^{-2}$ M; $[MnO_4]_0 = 2 \times 10^{-4}$ M. (b) Hydrogen ion dependence of the initial rate. Slope gives $k'$and intercept gives k_3; $[H_2O_2]_0 = 2 \times 10^{-3}$ M, and $[MnO_4]_0 = 2 \times 10^{-4}$ M. (c) Permanganate dependence of the initial rate: $[HClO_4] = 5 \times 10^{-2}$ M; $[H_2O_2]_0 = 2.03 \times 10^{-2}$ M.

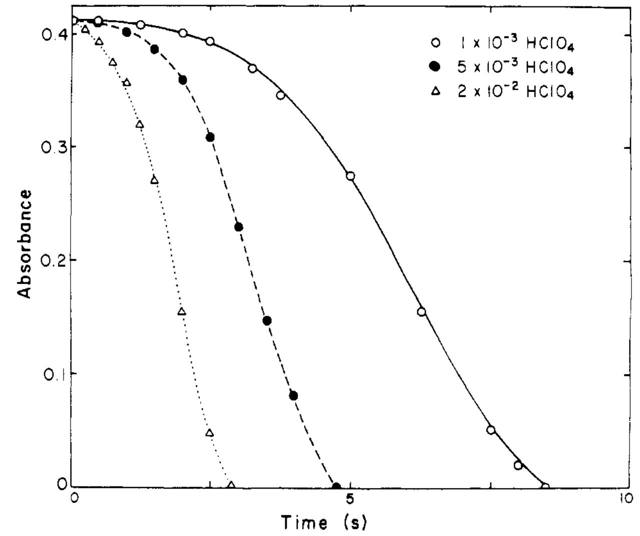

Figure 3. Effect of increasing initial acid concentration. The effect is opposite to that observed with hydrogen peroxide (Figure 1b): $[H_2O_2]_0 = 0.01$ M, $[MnO_4^-]_0 = 1.85 \times 10^{-4}$ M.

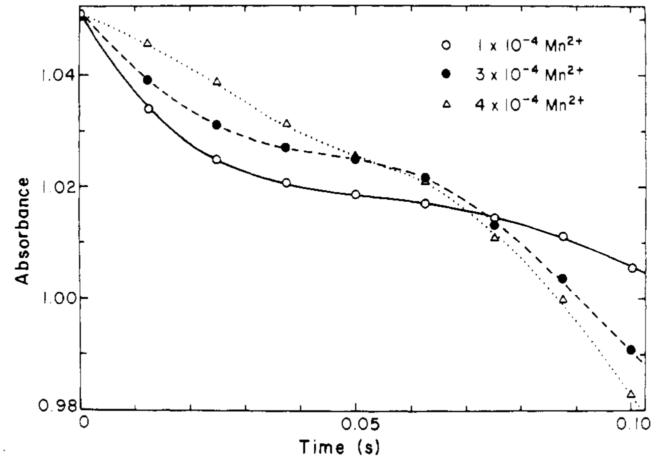

Figure 4. Higher initial manganous ion concentrations (i) eliminating the initial phase, (ii) reducing the duration of induction period, and (iii) increasing the rate of the autocatalytic step: $[HClO_4]_0 = 0.05$ M; $[H_2O_2]_0 = 0.1$ M; $[MnO_4^-]_0 = 4.83 \times 10^{-4}$ M.

rate vs. $[MnO_4^-]$ all pass through the origin (Figure 2c). In low $[MnO_4^-]$ ($<3 \times 10^{-4}$ M), the overall rate of reaction (all three phases) increased with increasing $[MnO_4^-]$ until a saturation value was reached.

Manganous Ion Dependence. The effect of manganous ion on the rate of the initial phase was difficult to obtain because, as can be seen from Figure 4, increasing $[Mn^{2+}]$ progressively eliminated the initial phase and the induction period. By adjusting the range of data points used for the calculation of the initial rate based upon the duration of the first phase, we obtained a plausible $[Mn^{2+}]$ dependence. In high $[Mn^{2+}]$ ($[Mn^{2+}] > [MnO_4^-]$), there was initially a rapid increase in rate with $[Mn^{2+}]$ quickly followed by saturation. However, at micromolar $[Mn^{2+}]$ (5–50 μM), a plot of initial rate vs. $[Mn^{2+}]$ was linear with a positive intercept. Linearity was rapidly lost as $[Mn^{2+}]$ started to exceed substantially $[MnO_4^-]$. In high $[Mn^{2+}]$ (10^{-3} M with $[MnO_4^-] = 2 \times 10^{-4}$ M), the reaction became insensitive to changes in acid and peroxide concentrations. In these conditions, too, the initial phase and the induction period totally disappear, leaving only the third phase. The sigmoidal progress curve, which denotes autocatalysis, also disappears, and instead a straight-line absorbance decay is observed. The decay becomes exponential as $[Mn^{2+}]$ is increased further.

Data Treatment

The acid dependence results suggest two routes, one affected by acid and another that is not. The following simplified scheme fits the data:

$$MnO_4^- + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HMnO_4 \quad \text{rapid equilibrium} \tag{II}$$

$$HMnO_4 + H_2O_2 \xrightarrow{k_2} HX \quad \text{rate limiting} \tag{IIIA}$$

$$MnO_4^- + H_2O_2 \xrightarrow{k_3} X^- \quad \text{rate limiting} \tag{IIIB}$$

The rate of reaction thus becomes

$$-\tfrac{1}{2}d[MnO_4^-]/dt = [MnO_4^-][H_2O_2](k_3 + k'[H^+]) \quad (1)$$

where $k' = k_1k_2/k_{-1}$.

The intercept of the acid dependence plots gives $k_3 = 21.4 \pm 3.5$ M^{-1} s^{-1} and the slope gives $k' = (3.04 \pm 0.6) \times 10^2$ M^{-2} s^{-1}. Permanganate and hydrogen peroxide dependence plots cannot give individual values for k_3 and k', but from the two slopes one can obtain expressions for k_3 and k'. From a solution of the two simultaneous equations generated, the following values were obtained: $k_3 = 23.2 \pm 3.0$ M^{-1} s^{-1}; and $k' = (3.1 \pm 0.5) \times 10^2$ M^{-2} s^{-1}.

Low $[Mn^{2+}]$ dependence experiments gave an expression for k_3 and k' that differed by about 5% from the expressions that gave the above values.

If reaction II is reversible and competitive with (IIIA) and (IIIB), the steady-state assumption may be applied to $[HMnO_4]$ to give the rate law

$$-\tfrac{1}{2}d[MnO_4^-]/dt = [MnO_4^-][H_2O_2]\left(k_3 + \frac{k_1k_2[H^+]}{k_{-1} + k_2[H_2O_2]}\right) \quad (2)$$

However, since saturation with respect to $[H_2O_2]$ in the first phase is not observed, and since pK_a for (II) is about −2.25,[18] we assume reaction II is always in equilibrium. Equation 1 represents the simplified scheme.

After formation of HX and X^-, subsequent reactions leading to formation of Mn^{2+} and oxygen are more rapid. The initial phase should be able to proceed up to the formation of manganous ion before the induction period begins. For stoichiometric purposes, let X^- be a manganese(VII), H_2O_2-containing complex that rapidly produces dioxygen, and a reduced manganese species. Addition of reactions IV–VII gives the desired stoichiometry. This particular route has been chosen so that the oxygen–oxygen bond of the peroxide molecule is not cleaved, since all the molecular oxygen liberated in the reaction should come from the peroxide oxygen atoms.[19]

$$MnO_4^- + H_2O_2 + 2H^+ = MnO_2^+ + O_2 + 2H_2O \quad (IV)$$

$$MnO_2^+ + H_2O_2 = MnO_2^- + O_2 + 2H^+ \quad (V)$$

$$MnO_2^- + H_2O_2 + 3H^+ = Mn^{2+} + HO_2 + 2H_2O \quad (VI)$$

$$HO_2 = {}^1\!/_2H_2O_2 + {}^1\!/_2O_2 \quad (VII)$$

Discussion

This study is concerned with two separate problems: (1) explaining the observation of three phases in the inital permanganate ion–hydrogen peroxide reaction; (2) accounting for the experimentally determined single-step rate law, eq 2, in terms of a molecular mechanism. For the observed kinetics, we present an overall reaction sequence in a section on dynamics. In a second section on mechanism, we discuss a molecular mechanism in light of recent studies on the kinetics and mechanisms of permanganate ion and hydrogen peroxide reactions.

Reaction Dynamics. In addition to explaining the presence of three phases, we wish to account for the behavior of each phase as concentrations and acidity are changed. The following sequence of reactions (Figure 5) accomplishes these goals, explaining the dynamical behavior of the permanganate ion–hydrogen peroxide reaction in a stopped-flow spectrophotometer.

Initially, no Mn^{2+} is present; phase 1 of the reaction follows pathways A and F. Almost as soon as Mn^{2+} is formed, it competes with H_2O_2 for MnO_4^-, via route B. Since this process is faster than path A, the MnO_4^- is depleted, forming a complex that reacts slowly with H_2O_2 (path C). When Mn^{2+} is initially present, competition between paths A and B starts immediately; path B prevails, and the complex forms. The result is phase 2, an induction period. As the complex slowly reacts with H_2O_2 to give Mn^{2+}, the Mn^{2+} attacks the complex (path D) to give a reactive intermediate, most likely Mn(III), which reacts rapidly with H_2O_2 (path E). More Mn^{2+} is produced, consuming complex and H_2O_2 via paths D and E in an autocatalytic buildup, which is phase 3 of the reaction.

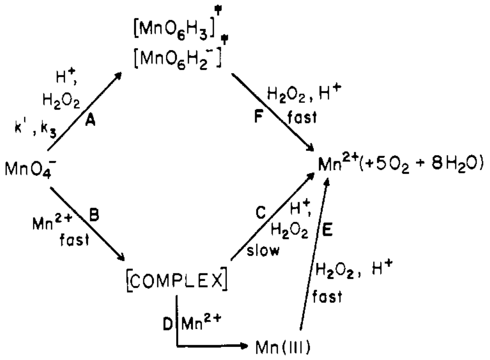

Figure 5. Schematic diagram explaining the first three phases in the reaction between permanganate ion and hydrogen peroxide.

Reaction Mechanism. The transfer of reducing agent from hydrogen peroxide to the manganese center in permanganate can take place through an outer-sphere flow of electrons or through an inner-sphere flow of either electrons or atoms. One technique used to decide between inner- and outer-sphere mechanisms is application of the Marcus cross-reaction test to measured rate constants (k_2 or k_3).[20] However, since the self-exchange rate constant for the hydrogen peroxide/superoxide couple in the highly acidic media used in this study is not known and the self-exchange rate constant between $HMnO_4$ and $HMnO_4^-$ may be very different from the self-exchange rate constant between MnO_4^- and MnO_4^{2-} determined in alkaline media, application of the cross-reaction test to the permanganate ion–hydrogen peroxide reaction is not reliable at this time. Therefore, we examine rate and mechanistic information from relevant systems to make a mechanistic assignment in the system under study.

Consider first evidence for inner-sphere permanganate ion reactions. With U(IV),[21] $PtCl_4^{2-}$,[22] Ti(III),[23] and V(IV),[24] permanganate reacts rapidly, serving as a nucleophile for these strong electrophilic reagents. (The much slower chromium(III) reaction involves neither Mn(VII) nor Cr(III) in the rate-determining step.[25]) The most significant feature of these studies occurs with uranium(IV) and platinum(II), where the use of tracers shows that all oxygen in the products U(VI) and Pt(IV) comes from permanganate, which establishes the existence of bridged activated complexes. However, hydrogen peroxide is nucleophilic, not electrophilic, so we next consider the evidence for permanganate serving as an electrophile for nucleophilic substrates.

The kinetics of permanganate oxidations of several simple inorganic substrates, Br^-,[26] I^-,[27] CN^-,[28] and $HClO_2$,[29] have been assigned to the inner-sphere mechanism. In the halide and cyanide reactions, H^+ attacks the activated complex; indeed, the cyanide study has a two-term rate law, one term showing an inverse $[OH^-]$ dependence, arising from removal of H^+ from the activated complex due to reaction with OH^-. In the reaction with chlorine(III), $[H^+]$ dependence was ascribed to the different reactivities of $HClO_2$ and ClO_2^-, the undissociated acid reacting faster.

Studies of permanganate oxidations of organic substrates are even more numerous, since the availability of a parent compound

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and its derivatives allows investigators to observe reactions of many related substrates. Classes of compounds include aldehydes,[30] phenols,[31] and uracils[32] studied by stopped-flow and diols[33] studied by conventional spectrophotometry. (The very rapid initial reaction with oxalate produces Mn(III) within the resolution time of the stopped-flow apparatus,[34] and no conclusion could be drawn with respect to the Mn(VII)–oxalate interaction.) Except for the diol reaction,[33] interpreted as $HMnO_4$ more reactive than MnO_4^-, the [H^+] dependence has been assigned to protonation of substrate, with protonated species more reactive, except for phenolate more reactive than phenol.

With organic substrates bearing carbon–carbon double bonds, inner-sphere mechanisms appear to be the rule,[35] and considerable effort has been put into the detection of reduced organomanganese intermediates.[32] For organic substrates, the activated complex structure may either be cyclic, with substrate bonding to two oxo ligands,[32] or direct-bonded, with a nucleophilic site becoming attached directly to the manganese center.[36] Both possibilities for activated complex structure have arisen in connection with the above mentioned inorganic substrates, i.e., cycloaddition for uranium(IV) and platinum(II) and direct Mn–nucleophile bonding for Br^-, I^-, and CN^-.

Outer-sphere permanganate oxidations with large substitution-inert anions such as $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $Mo(CN)_8^{4-}$ are most likely accomplished by direct electron transfer. Although $HMnO_4$ is more reactive than MnO_4^- in these systems, electron rather than hydride transfer appears to be operative; protonation seems to lower the free energy barrier to activated complex formation. Organic free radicals ($RCH_2\cdot$) generated pulse radiolytically react very rapidly with MnO_4^-, all at very nearly the same rate.[38] The positively charged molybdenum(V) dimer, $Mo_2O_4^{2+}$, provides an example of an outer-sphere mechanism with an electrophile, in which $HMnO_4$ is more reactive than MnO_4^-.[39] Two sulfur-containing anions, SO_3^{2-}[40] and $S_2O_3^{2-}$,[41] react rapidly with permanganate ion in alkaline media, where short-lived intermediates of Mn(VI) and Mn(V) have been detected in the reaction with SO_3^{2-}.

In addition to the previously mentioned rapid oxalate oxidation, for which no mechanistic conclusions could be drawn, conventional studies of H_3PO_3[42] and $HN(CH_3)_2$[43] show complex rate laws, from which no inner- vs. outer-sphere mechanistic conclusions were drawn.

For permanganate as oxidant, a clear distinction between inner- and outer-sphere substrates does not appear to exist. Electrophiles such as VO^{2+} and $Mo_2O_4^{2+}$ can be found in both categories. Thiosulfate and sulfite, nucleophiles thought of as being poor ($S_2O_3^{2-}$) and good (SO_3^{2-}),[44] both undergo outer-sphere reactions. In this connection, hydrogen peroxide is considered to be a good nucleophile—HO_2^- might even be classified as a "super" nucleophile.[44] In summation, for permanganate, outer-sphere reduction mechanisms appear to be in the minority. We now consider mechanisms where hydrogen peroxide acts as reductant.

Metal–hydrogen peroxide complexes have been well established in the oxidation of hydrogen peroxide; most of these mechanisms appear to be inner-sphere.[45] A possible exception is d^4 manganese(III).[46] Oxidation of HO_2^- by silver(III), present as $Ag(OH)_4^-$, involves a silver(III)–HO_2^- complex, and is most likely inner-sphere.[45] A nonmetallic species that is capable of oxidizing hydrogen peroxide to dioxygen is chlorine. The most recent conclusion about the complex kinetics behavior exhibited by the Cl(0)/Cl(I)–H_2O_2 reaction is "that reaction takes place by nucleophilic attack by peroxide upon the chlorine atom," forming an inner-sphere complex.[47]

It therefore seems most likely that the initial phase of the manganese(VIII)–H_2O_2 reaction in acid follows an inner-sphere mechanism. Increased rate of reaction with increasing [H^+] can be assigned to greater reactivity of $HMnO_4$ compared with MnO_4^-, since H_2O_2 is so weakly acidic. Attack on permanganate by H_2O_2 to form a cyclo intermediate would require H bonding, since the O–O bond distance in H_2O_2 is much smaller than an O–O edge distance in tetrahedral permanganate.[48] It is also difficult to see how electron transfer could be accomplished through H bonds, and hydride transfer, though not to be excluded, does not seem to be likely. Direct linkage to one of the manganese–oxide resonance forms, such as $^+Mn{-}O^-$,[36] which might be enhanced by H bonding prior to such an attachment, seems to be the preferred mode of attack.

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Registry No. MnO_4^-, 14333-13-2; H_2O_2, 7722-84-1; Mn^{2+}, 16397-91-4.

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