pentaborane radical with hexafluoroacetone (eq 3 and 4). The absence of any 2-[$HO(C(CF_3)_2)_2O]B_5H_8$ may be a reflection of its low thermodynamic stability with respect to that of the apical isomer, and in fact, irreversible basal to apical isomerization for the pentaborane derivative 1-$(CF_3)_2PB_5H_8$ has previously been observed.[43] Alternatively, the absence of 2-substituted product may be due to decomposition resulting from oxygen bonding at the base. This latter explanation is consistent with the observation that 2-$CH_3OB_5H_8$ decomposes rapidly in the liquid phase.[22] In the reaction products of the 2,4-$C_2B_5H_7$/HFA cophotolysis, the strong preference for 5-position substitution is analogous to the known electrophilic methylation of 2,4-$C_2B_5H_7$ using Friedel–Crafts conditions.[19]

The reactions described above further exemplify the utility of photochemical techniques for the facile synthesis of novel polyhedral borane and carborane derivatives and suggest that the full potential of such photochemical approaches in this area has not been realized. Work is currently under way in this laboratory directed toward the development of other photochemical synthetic procedures for the production of new types of boron cluster compounds.

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Registry No. I, 91384-71-3; II, 91384-72-4; III, 91384-73-5; IV, 91384-74-6; V, 91384-75-7; $(CF_3)_2CO$, 684-16-2; B_5H_9, 19624-22-7; 2,4-$C_2B_5H_7$, 20693-69-0.

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Kinetics of the Stepwise Oxidation of Manganese(II) by Peroxodiphosphate (PDP) in Aqueous Perchloric Acid. Catalysis by Silver(I)

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The kinetics of the title reaction was investigated under isolated conditions ([Mn(II)] << [PDP]) at $I = 0.58$ M. The kinetics of the first stage of the reaction, during which Mn(II) is oxidized to Mn(IV) via a stable Mn(III) species, were monitored by following the increase in absorbance of Mn(IV) at 400 nm, where the other species in the reaction have negligible absorbance. The reaction exhibits an induction period followed by a binomial dependence of the type $a + b$[Mn(III)], a first-order dependence on [Ag(I)], and a complex dependence on [PDP]. It is also observed that further oxidation of Mn(IV) to Mn(VII) occurs only when the former is stoichiometrically formed from Mn(II). The plots of absorbance vs. time at 400 nm were found to pass through a steep maximum, after which the descending portions were linear. When [Mn(II)] was varied, with all other parameters kept constant, the maxima of the plots of absorbance vs. time obey Beer's law. The descending linear portions of these plots correspond to the oxidation of Mn(IV) to Mn(VII). An analysis of these plots suggests that this stage of the oxidation process exhibits a zero-order dependence on [Mn(IV)], first-order dependence on [Ag(I)], and a complex dependence on [PDP]. When the kinetic runs were monitored by following the increase in absorbance of Mn(VII) at 525 nm, the zero-order rate constants (k_0) were found to be identical with those evaluated from the slopes of the descending portions of the absorbance vs. time plots at 400 nm. The results for this stage of oxidation conform to the rate law $-d[Mn(IV)]/dt = d[Mn(VII)]/dt = k_0K_1K_2[PDP][Ag^+][H^+]/(1 + K_1[H^+] + K_1K_2[PDP][H^+])$, where K_1 and K_2 correspond to the equilibrium constants for the equilibria

$$H_2P_2O_8^{2-} + H^+ \overset{K_1}{\rightleftharpoons} H_3P_2O_8^- \qquad H_3P_2O_8^- + Ag^+ \overset{K_2}{\rightleftharpoons} \text{complex}$$

The k_0 values were found to be $(1.20 \pm 0.10) \times 10^{-4}$, $(1.85 \pm 0.10) \times 10^{-4}$, and $(2.33 \pm 0.14) \times 10^{-4}$ s^{-1} at 25, 30, and 35 °C, respectively.

Of the oxidation states of manganese the +7, +4, +3, and +2 states are known to be stable in acid solution while +5 and +6 are known to be stable in alkaline medium. The kinetics of oxidation of Mn(II) to Mn(VII) by periodate and peroxodisulfate ions has been reported[1,2] without much information on the nature of the intermediate oxidation states of manganese. The peroxodisulfate ion is isoelectronic and isostructural with peroxodiphosphate ion (PDP), which in recent years has been reported to be an oxidizing agent for a variety of substrates. Creaser and Edwards have extensively reviewed the oxidation reactions of this ion and the nature of its species under different pH conditions.[3] Edwards et al. and Gupta et al.[4-9] were mainly responsible for the use of this salt in kinetic studies on the oxidation of inorganic substrates. While most of the peroxodisulfate oxidations were known to be catalyzed by Ag(I) ion, similar studies with PDP as oxidizing agent are comparatively scarce. Santappa et al.[10] have reported the use of Ag(I) ion as a catalyst in the oxidation of water by PDP. In this paper, we report the results of our kinetic study on the oxidation of Mn(II) by PDP catalyzed

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Table I. Stoichiometry for the Oxidation of Mn(II) to Mn(VII) by PDP[a]

starting materials			
$10^3 \times$ [Mn(II)], M	$10 \times$ [PDP], M	$10^3 \times$ $[PDP]_{consumed}$, M	$[PDP]_{consumed}/[Mn(II)]_{oxidized}$
2.0	5.630	4.9	2.45
2.0	3.378	4.9	2.45
3.0	5.630	7.4	2.47
3.0	3.378	7.4	2.47
4.0	3.378	9.9	2.48
4.0	2.252	9.9	2.48

[a] [Ag(I)] = 6.0×10^{-3} M; [H$^+$] = 0.08 M; $I = 0.58$ M; temp = 30 °C.

by Ag(I) ion in perchloric acid medium, undertaken to gain an insight into the nature of the intermediate oxidation states of manganese.

Materials

Tetrapotassium peroxodiphosphate ($K_4P_2O_8$) was a gift from FMC Corp. Potassium phosphate and KF present as impurities have no effect on the kinetics of the reaction, and hence the sample was used as such. Doubly distilled water was used for preparing all solutions, the second distillation being from permanganate. Aqueous solutions of PDP of desired strength were prepared and standardized iodometrically. The source of Mn(II) was a M & B (Analysed) sample of $MnSO_4 \cdot H_2O$. Aqueous solutions of this salt were prepared and standardized by the literature method.[12] Perchloric acid and sodium nitrate were of E. Merck GR grade and were used as such. A 0.06 M solution of BDH AnalaR silver nitrate was used as the catalyst. Manganese(IV) solution was prepared by the method of Sant et al.[13] by stirring, for about 9 h, a solution of potassium permanganate in 9 M H_2SO_4 and setting it aside overnight. It was standardized prior to use. Mn(III) in the presence of sodium pyrophosphate was prepared by the method of Walters et al.[14] All other chemicals were of analytical grade.

Kinetic Procedure and Rate Measurements

Mn(II), $HClO_4$, and other constituents in desired amounts were placed in an amber-colored reaction vessel and thermostated at 30 ± 0.1 °C unless otherwise mentioned. The reaction was initiated by adding the temperature-equilibrated PDP to the reaction mixture. The progress of the reaction was followed spectrophotometrically by measuring the change in absorbance of Mn(IV) at 400 nm and the increase in absorbance of Mn(VII) at 525 nm from time to time under isolated conditions. A Hilger UVISPEK spectrophotometer (H.700) with matched 2-cm glass cells, a thermostated cell compartment, and a VEB U10 circulation thermostat (±0.1 °C) were used for this purpose.

The optical densities (at 525 nm) of a series of solutions containing varying proportions of Mn(II), PDP, Ag(I), and H$^+$ were measured after 2–48 h and compared with those of accurately standardized solutions of potassium permanganate of identical concentration, under identical experimental conditions. In all these experiments [PDP] >> [Mn(II)]. Not only did the two absorbance values agree with each other but also the spectra of the two solutions recorded in the wavelength range 450–600 nm were found to overlap. This indicates that under these experimental conditions Mn(II) is quantitatively oxidized to Mn(VII) by PDP. In a preliminary investigation, the reaction in the absence of added Ag(I) salt has been found to be negligible within the time of a kinetic run involving the catalyzed reaction.

Stoichiometry

The number of moles of PDP required to completely oxidize Mn(II) to Mn(VII) was ascertained as follows.

Since the final stage of oxidation, i.e. Mn(IV) → Mn(VII), has a zero-order dependence on Mn(II), the exact time required for complete oxidation of Mn(II) to Mn(VII) can be determined. A known amount of Mn(II) was then mixed with an excess of PDP under conditions identical with those employed in the kinetic runs referred to hereafter and allowed to react till the predetermined time. The reaction mixture was immediately quenched in an excess of standard iron(II) solution. The Mn(VII) formed and the remaining PDP present in the reaction mixture immediately oxidized Fe(II) to Fe(III). Excess Fe(II) was back-titrated with a standard solution of $K_2Cr_2O_7$ with barium diphenylaminesulfonate as indicator. From a knowledge of the concentration of Mn(VII) formed (deduced from a calibration curve), the amount of Fe(II) consumed by the excess PDP was calculated. From the initial concentration of PDP added and the amount that remained unconsumed, the amount of PDP required to completely oxidize the given amount of Mn(II) to Mn(VII) was then evaluated. The results are given in Table I. From the results in Table I, it is evident that 2 mol of Mn(II) must consume very nearly 5 mol of PDP for complete conversion to Mn(VII). As long as Mn(II) is present in the reaction mixture, no perceptive consumption of PDP by other reactions such as oxidation of water can be visualized. However, if the reaction mixtures were allowed to stand beyond the time required for complete formation of Mn(VII), PDP was found to react with water, causing appreciable errors in the amount of PDP consumed. Hence quenching is done immediately after the complete oxidation of Mn(II) to Mn(VII).

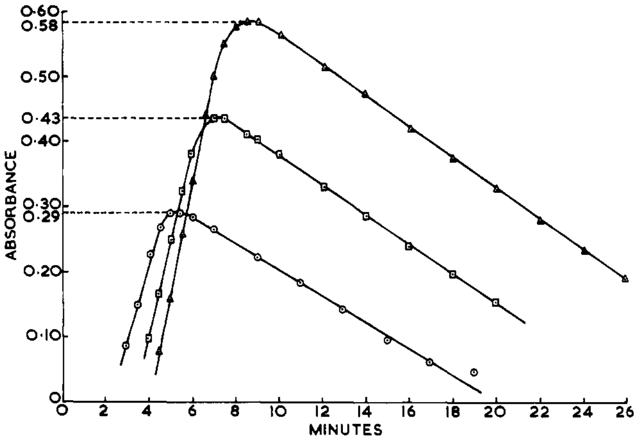

Figure 1. Plots of absorbance vs. time at 400 nm (2 cm path length cells) in the oxidation of Mn(II) with peroxodiphosphate ([PDP] = 1.0×10^{-2} M; [Ag(I)] = 3.0×10^{-3} M; [H$^+$] = 0.08 M; $I = 0.58$ M; temp = 30 °C). [Mn(II)]: (○) 2.2×10^{-4} M; (◊) 3.3×10^{-4} M; (△) 4.4×10^{-4} M.

Results and Discussion

The oxidation of Mn(II) to Mn(VII) by PDP is accompanied by an induction period during which a brownish yellow color develops, but no traces of Mn(VII) are formed. After the induction period, the pink color of the permanganate ion gradually appears. This induction period decreases with an increase in [PDP], [Ag(I)], and [H$^+$] but increases with an increase in [Mn(II)]. When [Mn(II)] was varied concentrations of the other species and the progress of the reaction followed at 400 nm (where Mn(VII) and the other species in the reaction mixture have negligible absorbance), the optical density gradually increased, reached a maximum, and then decreased linearly to a minimum as shown in Figure 1. It is evident from the figure that the absorption maxima for various [Mn(II)] obey Beer's law. It is well-known[15] that although at lower concentrations of the acid the hydrated manganese dioxide easily precipitates, the precipitation is delayed in the presence of phosphate ions, the clear brownish yellow solution obeying Beer's law. Further, no intermediate oxidation state of manganese has a brownish yellow color in the presence of the phosphate ion except Mn(IV). No significant change in optical absorption at 400 nm was noticed in our control experiments, in which Mn(IV) was added to

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an excess of PDP without any Ag(I) salt, while a gradual decrease was observed in the presence of Ag(I) salt, indicating Mn(IV) was not precipitated during the time in which it was further oxidized to Mn(VII). The absorbance values at 400 nm of solutions containing Mn(IV) and excess PDP without added Ag(I) were found to be identical with those obtained at the maximum of the absorbance vs. time plots of a kinetic run in which equivalent concentrations of Mn(II) were employed. This establishes that Mn(II) is quantitatively converted into Mn(IV) before it is further oxidized to Mn(VII).

When the kinetic runs were conducted with Mn(IV) as the substrate under conditions identical with those using Mn(II), no perceptible induction period was noticed. However, when Mn(II) is deliberately added to Mn(IV), not only is the induction period restored but it is found also to increase with increasing [Mn(II)]. These observations lead us to believe that the reactive intermediates from PDP or Ag(I) ion attack only the Mn(II) as long as it is present, but not the Mn(IV).

Oxidation of Mn(II) to Mn(IV). The progress of the reaction was followed by measuring the absorbance of the yellow-brown solution at 400 nm, where the other species present in the reaction mixture are transparent. This stage of the reaction is preceded by an induction period during which a transient pale violet color appears and gradually changes to a yellow-brown color. This is perhaps due to the formation and decay of Mn(III) stabilized by the diphosphate ions present in the solution. The observed induction period decreases with increasing [PDP], [Ag(I)], and [H$^+$] but increases with increase in [Mn(II)]. If A_∞ and A_t are the absorbances of the reaction mixture (at 400 nm) after the completion of the reaction and at time t, then $(A_\infty - A_t)$ is proportional to the concentration of the remaining substrate at time t. The $(A_\infty - A_t)$ values in different kinetic runs in which [Mn(II)] is varied are plotted vs. t, and tangents are drawn to the resultant curves at various specified values of $(A_\infty - A_t)$. The rates are then computed from the slopes of these tangents and are plotted against $(A_\infty - A_t)$. These yield a straight line with a positive intercept on the rate axis. This indicates that the oxidation of Mn(II) to Mn(IV) proceeds by both [Mn(II)]-dependent and -independent paths requiring a binomial dependence of the rate on [Mn(II)] in the rate expression, viz. $a + b$[Mn(II)], where a and b are constants. The rate was also found to increase with increasing [PDP], [Ag(I)], and [H$^+$]. When the kinetic runs were carried out by using 2.0 × 10^{-3} M Mn(II) instead of 3.0 × 10^{-4} M Mn(II), the pale violet intermediate observed during the induction period had an absorption maxima in the range 490–510 nm characteristic of Mn(III). To confirm that the species observed during the induction period is Mn(III), we have carried out further experiments keeping [Mn(II)] ≥ [PDP] in the presence of added phosphate and measuring the absorbance at 400 nm. No significant absorbance was noticed at this wavelength, suggesting that Mn(IV) is not formed under these conditions. From these observations, and also because of the stability of Mn(III) in the presence of diphosphate,[16] we believe that no Mn(IV) is formed until all the Mn(II) is converted to Mn(III) and the observed induction period is the time required for the formation of Mn(III). As a check, we have carried out kinetic runs using a previously prepared Mn(III)–pyrophosphate solution as the substrate instead of Mn(II), keeping all other species essentially the same. The reaction was found to exhibit the same kinetic pattern as that noticed after the induction period. The rates were found to agree in both cases. However, in kinetics runs using Mn(III)–pyrophosphate as the substrate, if Mn(II) is deliberately added, the induction period is restored. The extinction coefficient of Mn(IV) in the presence of added diphosphate at 400 nm was found to be 650 ± 7. This value was used to convert the absorbance of Mn(IV) solution into concentration.

Table II. Dependence of Rate on [Ag(I)] for the Oxidation of Mn(III) to Mn(IV)^a

10^3[Ag$^+$], M	10^7 × rate, M s^{-1} obsd^b	calcd^c	obsd^d
0.75	3.8	3.5	3.5
1.50	8.1	7.0	7.1
3.00	15.1	14.0	14.1
4.50	22.4	21.0	21.2
6.00	28.2	28.0	28.2

^{a} [Mn(III)] = 3.0 × 10^{-4} M; [PDP] = 2.0 × 10^{-2} M; [H$^+$] = 0.08 M; I = 0.58 M; temp = 30 °C. ^{b} Rate when Mn(II) is used. ^{c} The rates were calculated by using the equilibrium constants K_1 and K_2 obtained as mentioned (vide infra) in the oxidation of Mn(IV) to Mn(VII) and the slope and intercept values calculated from the plots of rate vs. [Mn(III)]. ^{d} Rate when Mn(III)-pyrophosphate is used.

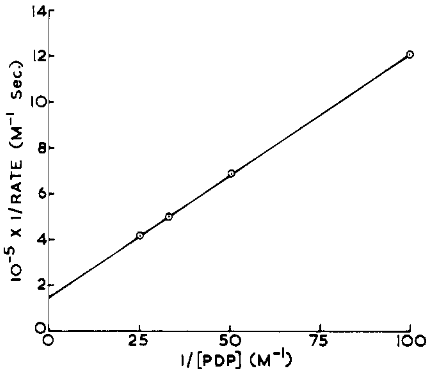

Figure 2. Dependence of rate on [PDP] with Mn(II) as substrate in the oxidation of Mn(II) with peroxodiphosphate ([Mn(II)] = 3.0 × 10^{-4} M; [Ag(I)] = 3.0 × 10^{-3} M; [H$^+$] = 0.08 M; I = 0.58 M).

Dependence on [Mn(III)]. When the concentration of Mn(II) or Mn(III)–pyrophosphate was varied from 1.0 × 10^{-4} to 8.0 × 10^{-4} M, with all other parameters kept constant, the rates were found to increase with increasing [substrate]. Further, a plot of rate vs. [Mn(III)] is a straight line with a positive intercept on the rate axis, indicating a binomial dependence of rate on [Mn(III)]. The slope and intercept values when Mn(II) ([PDP] = 2.0 × 10^{-2} M; [Ag(I)] = 3.0 × 10^{-3} M; [H$^+$] = 0.08 M; I = 0.58 M) is used are (1.69 ± 0.06) × 10^{-3} s^{-1} and (8.97 ± 0.18) × 10^{-7} M s^{-1}, respectively. The corresponding values when Mn(III)–pyrophosphate ([PDP] = 1.0 × 10^{-2} M; [Ag(I)] = 3.0 × 10^{-3} M; [H$^+$] = 0.08 M; I = 0.58 M) is used are (6.88 ± 0.12) × 10^{-4} s^{-1} and (4.45 ± 0.07) × 10^{-7} M s^{-1}, respectively.

Dependence on [Ag(I)]. With [Ag(I)] varying from 7.5 × 10^{-4} to 6.0 × 10^{-3} M at fixed concentrations of the other species, the plots of rate vs. [Ag(I)] were found to be linear, passing through the origin. This indicates that the reaction exhibits a first-order dependence on [Ag(I)] and proceeds entirely through a catalyzed path. The results are given in Table II.

Dependence on [PDP]. In kinetic runs in which [PDP] was varied in the range 0.5 × 10^{-2} to 6.0 × 10^{-2} M, with all other parameters kept constant, the plots of rate vs. [PDP] were found to be curved, tending toward a limiting value. However, when 1/(rate) was plotted against 1/[PDP], the plots were linear with a definite positive intercept on the 1/(rate) axis (Figures 2 and 3). This suggests that PDP in one of its forms is involved in complexation with one of the species in the reaction mixture.

Dependence on [H$^+$]. When the [H$^+$] was varied from 0.03 to 0.26 M at constant I = 0.58 M and at fixed concentrations

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[16] Berka, A.; Vulterin, J.; Zyka, J. *Int. Ser. Monogr. Anal. Chem.* **1965**, *22*, 10.

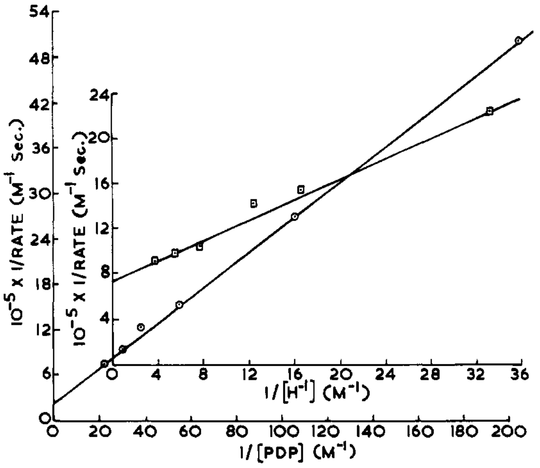

Figure 3. Dependence of rate on [PDP] (○) and on [H^+] (□) with Mn(III)–pyrophosphate as substrate in the oxidation of Mn(III)–pyrophosphate with peroxodiphosphate ([Mn(III)–pyrophosphate] = 3.0×10^{-4} M; [Ag(I)] = 1.5×10^{-3} M; $I = 0.58$ M): (○) [H^+] = 0.08 M; (□) [PDP] = 2.0×10^{-2} M.

of other species, plots of rate vs. [H^+] were found to be curved, leveling off after a certain [H^+]. In these plots allowance was made for the [H^+] removed through the reaction

$$P_2O_8^{4-} + 2H^+ \rightarrow H_2P_2O_8^{2-}$$

However, plots of 1/(rate) vs. 1/[H^+] were found to be linear with a definite positive intercept on the 1/(rate) axis (Figure 3). This suggests that H^+ is involved in the protonation equilibrium[6]

$$H_2P_2O_8^{2-} + H^+ \rightleftharpoons H_3P_2O_8^-$$

In view of these observations, a mechanism that explains the binomial dependence of the rate on [Mn(III)], first-order dependence on [Ag(I)], and complex dependence on [PDP] and [H^+] may be proposed as in Scheme I. We cannot follow the progress of the reaction Mn(II) → Mn(III) and establish its kinetic pattern, because of the low absorbance of Mn(III) species.

Scheme I

$$H_2P_2O_8^{2-} + H^+ \overset{K_1}{\rightleftharpoons} H_3P_2O_8^-$$

$$H_3P_2O_8^- + Ag^+ \overset{K_2}{\rightleftharpoons} \text{complex}$$

$$\text{complex} \xrightarrow[\text{slow}]{k_1} Ag^{2+} + HPO_4^{-\cdot} + H_2PO_4^-$$

$$\text{complex} + \text{Mn(III)} \xrightarrow[\text{slow}]{k_2} \text{Mn(IV)} + HPO_4^{-\cdot} + Ag^+ + H_2PO_4^-$$

$$HPO_4^{-\cdot} + Ag^+ \xrightarrow[\text{fast}]{} Ag^{2+} + HPO_4^{2-}$$

$$\text{Mn(III)} + Ag^{2+} \xrightarrow[\text{fast}]{} \text{Mn(IV)} + Ag^+$$

$$\text{rate} = \frac{K_1K_2[Ag^+][H_2P_2O_8^{2-}][H^+]}{1 + K_1[H^+] + K_1K_2[H_2P_2O_8^{2-}][H^+]}[k_1 + k_2[\text{Mn(III)}]]$$

Oxidation of Mn(IV) to Mn(VII). The oxidation of Mn(IV) to Mn(VII) is followed, after all Mn(II) is converted to Mn(IV), by measuring the increase in absorbance of Mn(VII) at 525 nm or the decrease in absorbance of Mn(IV) with time at 400 nm. Plots of [Mn(IV)] vs. time were found to be linear up to at least 90% completion of the reaction at moderate and higher concentrations of PDP and Ag(I). Our control experiments indicate that the hydrolysis of PDP to peroxomonophosphoric acid under the acidities employed here is negligible during the reaction at moderate or high concentrations of the catalyst. At lower concentrations of the catalyst and oxidant, the linearity of the plots is limited to 60–70% completion of the reaction. The rate constants are reproducible within ±5%. The zero-order rate constants (k_0') were calculated from the plots of [Mn(IV)] or [Mn(VII)] vs. time. The k_0' values calculated by following Mn(VII) at 525 nm agree within 3% with the k_0' values computed by following the decrease in absorbance at 400 nm under the same experimental conditions. We have also carried out kinetic runs using previously prepared Mn(IV) instead of Mn(II) as the substrate. The k_0' values from these experiments are found to be in good agreement with those obtained by using Mn(II) as the substrate.

Table III. Dependence of the Zero-Order Rate Constant on [Ag(I)] for the Oxidation of Mn(IV) to Mn(VII)[a]

$10^3 \times$ [Ag(I)], M	$10^7k_0'$, M s^{-1}					
	25 °C	30 °C			35 °C	
	obsd	obsd	calcd	obsd[b]	obsd	calcd
1.50		1.1	1.0	1.0	1.6	1.6
3.00	1.1	2.0	1.9	1.8	3.0	3.2
6.00	2.2	4.1	3.8	3.9	5.9	6.4
9.00	3.4	6.3	5.7	6.0	9.3	9.6
12.00	4.6	8.3	7.6	7.8	11.9	12.8

[a] [Mn(II)] = 2.0×10^{-4} M; [PDP] = 2.0×10^{-2} M; [H^+] = 0.08 M; $I = 0.58$ M. [b] Mn(IV) used instead of Mn(II).

Table IV. Dependence of the Zero-Order Rate Constant on [PDP][a]

$10^2 \times$ [PDP], M	$10^7k_0'$, M s^{-1}					
	25 °C	30 °C			35 °C[c]	
	obsd	obsd	calcd	obsd[b]	obsd	calcd
0.5	0.7	1.4	1.3	1.4		
1.0	1.3	2.2	2.3	2.3	1.9	2.1
2.0	2.2	4.1	3.8	3.5	3.0	3.2
3.0	3.0	5.4	4.9	4.7	3.7	3.9
4.0	3.4	6.1	5.7	5.6	4.2	4.4
5.0	3.8	6.6	6.3	6.1		
6.0					4.9	4.8

[a] [Mn(II)] = 2.0×10^{-4} M; [Ag(I)] = 6.0×10^{-3} M; [H^+] = 0.08 M; $I = 0.58$ M. [b] Mn(IV) used instead of Mn(II). [c] 3.0×10^{-3} M Ag(I) used.

Table V. Dependence of the Zero-Order Rate Constant on [H^+][a]

10[H^+], M	$10^7k_0'$, M s^{-1}			
	30 °C[b]		35 °C	
	obsd	calcd	obsd	calcd
0.30	2.0	2.1	1.9	2.0
0.55			2.6	2.7
0.80	3.0	3.8	3.0	3.2
1.30	4.7	4.8	3.4	3.8
1.80	5.0	5.3		

[a] [Mn(II)] = 2.0×10^{-4} M; [PDP] = 2.0×10^{-2} M; [Ag(I)] = 3.0×10^{-3} M; $I = 0.58$ M. [b] 6.0×10^{-3} M Ag(I) used.

The salient features of the oxidation of Mn(IV) to Mn(VII) are as follows: (1) In the concentration range of Mn(II) from 1.0×10^{-4} to 4.0×10^{-4} M the reaction is zero order in Mn(IV) when [Mn(II)] << [PDP]. The k_0' values are independent of initial [Mn(II)]. (2) The reaction is first order in Ag(I) (Table III). (3) The plots of $1/k_0'$ vs. 1/[PDP] are linear with a positive intercept on the $1/k_0'$ axis suggesting the formation of a complex between Ag(I) and PDP (Table IV). (4) The reaction is acid catalyzed. The plot of $1/k_0'$ vs. 1/[H^+] at constant $I = 0.58$ M is linear with a positive intercept on the $1/k_0'$ axis (Table v). (5) Increasing the ionic strength of the medium with sodium nitrate decreases the rate. (6) The reaction is markedly inhibited by allyl acetate. The reaction induces polymerization of acrylonitrile. This indicates the formation of radical intermediates during the reaction. (7) The presence of HSO_4^- changes the kinetic pattern of the oxidation of Mn(IV) to Mn(VII).

The foregoing kinetic results suggest that under the experimental conditions $H_3P_2O_8^-$ forms a 1:1 complex with Ag^+ ion which then decomposes in a rate-determining step to give reactive intermediates. These reactive intermediates then attack Mn(IV) to give Mn(VII) in a series of fast steps:

$$H_2P_2O_8^{2-} + H^+ \overset{K_1}{\rightleftharpoons} H_3P_2O_8^-$$

$$H_3P_2O_8^- + Ag^+ \overset{K_2}{\rightleftharpoons} \text{complex}$$

$$\text{complex} \xrightarrow[k_0]{\text{slow}} \text{intermediates}$$

$$\text{Mn(IV)} + \text{intermediates} \xrightarrow{\text{fast}} \text{products}$$

On the basis of this mechanism the rate law can be derived as

$$k_0' = \frac{k_0'K_1K_2[Ag^+][H_2P_2O_8^{2-}][H^+]}{1 + K_1[H^+] + K_1K_2[H_2P_2O_8^{2-}][H^+]}$$

From the slopes and intercepts of the plots between $1/k_0'$ vs. 1/[PDP] and $1/k_0'$ vs. $1/[H^+]$, the values of K_1, K_2, and k_0 can be calculated. The values of K_1 and K_2 are found to be K_1 = 4.0 (30 °C) and 4.8 (35 °C) L mol^{-1} and K_2 = 109 (30 °C) and 155 (35 °C) L mol^{-1}.

Edwards et al.[3] have reported the first, second, third, and fourth dissociation constants of $H_4P_2O_8$ to be $\simeq 2.0$, $\simeq 3 \times 10^{-1}$, $(6.6 \pm 0.3) \times 10^{-6}$, and $(2.1 \pm 0.1) \times 10^{-8}$ M, respectively. Because of the very low magnitude of the third and fourth dissociation constants, $P_2O_8^{4-}$ exists as $H_2P_2O_8^{2-}$ under the acid conditions employed in this investigation. The value of K_1 in the above mechanism corresponds to the inverse of the second dissociation constant reported by Edwards et al., and the agreement here is good. The values of k_0 at 25, 30, and 35 °C were found to be $(1.20 \pm 0.10) \times 10^{-4}$, $(1.85 \pm 0.10) \times 10^{-4}$, and $(2.33 \pm 0.14) \times 10^{-4}$ s^{-1}, respectively. From the estimated parameters k_0, K_1, and K_2 and the rate laws, the rates were calculated and compared with observed rates. These were shown in different tables.

Activation Parameters. The energy of activation and entropy of activation for the oxidation of Mn(IV) to Mn(VII) were computed from the rate constants (k_0) of the rate-determining step at three temperatures where the Arrhenius plot was linear. The energy of activation was found to be 47 ± 4 kJ mol^{-1}, and the entropy of activation was found to be −130 ± 10 J K^{-1} mol^{-1}.

On interesting observation is that under the same experimental conditions peroxodisulfate is not capable of oxidizing Mn(II) to Mn(VII) without precipitation of hydrated manganese dioxide due to its inability to stabilize Mn(III) and Mn(IV) formed as intermediates, whereas in the present investigation PDP itself is capable of stabilizing both Mn(III) and Mn(IV) for some time. If this is the case, in the presence of added phosphate, peroxodisulfate should oxidize Mn(II) to Mn(VII) with Mn(III) and Mn(IV) as the stable intermediates. The results of our preliminary investigation confirm this.

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Registry No. $P_2O_8^{4-}$, 15538-83-7; Mn, 7439-96-5; Ag, 7440-22-4.

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Mono- and Binuclear Iridium Carbonyl Hydrides Containing Bis(tertiary phosphine) Ligands

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New mono- and binuclear iridium(I) carbonyl halide complexes containing the bis(tertiary phosphine) ligands $Ph_2P(CH_2)_nPPh_2$ (n = 2, dppe; n = 3, dppp) have been prepared, and the formation of iridium(III) hydrides by H_2 oxidative addition has been studied. The binuclear complexes $[IrX(CO)(dppp)]_2$ (X = Br, I) possess trans phosphine donors, with the dppp ligands bridging the Ir(I) centers. Addition of H_2 yields the tetrahydride species $[IrH_2X(CO)(dppp)]_2$ in which the trans phosphine arrangement at each iridium is maintained. However, upon heating, cleavage of the dimers is noted, leading to the mononuclear species $IrH_2X(CO)(dppp)$. For X = I, mononuclear dppp complexes are also prepared starting with the reaction of $IrI_2(CO)_2^-$ + dppp under CO to yield $IrI(CO)_2(dppp)$. All of the dppe complexes are mononuclear, with dppe acting as a chelate. The necessarily cis disposition of phosphine donors in the mononuclear chelates is readily evidenced by ^1H NMR spectroscopy of the hydride complexes. Reversible addition of CO to IrX(CO)(dppe) (X = Br, I) is also observed.

Introduction

Metal hydrides play an important role in many metal-catalyzed reactions such as hydrogenation, hydroformylation, the water-gas shift reaction, and CO reduction chemistry.[1] For this reason, the preparation and reaction chemistry of transition-metal hydride complexes have been studied extensively. The oxidative addition of H_2 to a metal complex is one of the most important methods of hydride preparation, and one of the most relevant in the context of catalytic properties, since this reaction represents a principal mode for the activation of H_2. Since Vaska's initial report in 1962,[2] it has been known that d^8 iridium(I) phosphine complexes are particularly active with regard to H_2 oxidative addition.[1c] This reaction invariably proceeds with cis stereochemistry at the metal center and, in the case of *trans*-$IrCl(CO)(PPh_3)_2$ and its analogues,

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