Oxidation of Bivalent Manganese by Peroxomonophosphoric Acid Catalysed by Cobalt(II) – A Kinetic Study

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Abstract

The kinetics of oxidation of bivalent manganese to the heptavalent state by peroxomonophosphoric acid was investigated spectrophotometrically in a perchloric acid medium. The reaction was found to be negligible in absence of a suitable catalyst. In the presence of traces of Co(II), the reaction is found to proceed with a measurable speed following first order kinetics and binomial dependence on [Mn(II)], first order in [Co(II)] and fractional order dependence on [PMPA] and $[H^+]$. The reaction was found to be autocatalytic, the Mn(IV) formed as a transient reactive species catalysing its further oxidation to Mn(VII). A mechanism consistent with the observed kinetics is proposed and the rate law derived.

Introduction

Of the known oxidation states of manganese, the +7, +4, +3 and +2 are known to be the only species stable in acid solution, while the +6 and +5 states are reported to be stable in alkaline solution. Perhaps next to iron, cobalt and zinc, it is the only transition metal ion that is of significant importance in the metabolism of plants and animals. It has an important role in photosynthesis as a promoter of oxidative phosphorylation. It is well known that manganese deficiency causes significant reduction in life expectancy and causes 'aprysolene disease'. In view of its importance in various fields of human activity, a study of the mechanism of oxidation of manganese will be of paramount importance. A quantitative method for the determination of manganese comprises of its oxidation to stable manganese(VII) species using a variety of oxidising agents like peroxodisulphate [1], periodate [2], peroxodiphosphate [3] etc. Although Creaser and Edwards [4] categorically reported that manganese(II) is oxidised to manganese(VII) by peroxomonophosphoric acid, the details of the quantitative study are not available. In an earlier communication from our laboratory, the kinetics of the stepwise oxidation of manganese(II) to manganese(VII) by peroxodiphosphate catalysed by Ag^+ was reported [5]. In continuation of our studies, we have investigated the mechanism of oxidation of manganese(II) to manganese(VII) by peroxomonophosphoric acid catalysed by Co(II). We report in this communication the results of our study. On a perusal of the literature of the oxidation reactions of peroxomonophosphoric acid, we have noticed that there are no reports on the use of catalysts in its oxidation reactions.

Experimental

Reagents

Tetrapotassium peroxodiphosphate (PDP) was a gift from FMC Corporation. The sample was used as such. Peroxomonophosphoric acid (PMPA) was prepared by acid hydrolysis of PDP following the procedure of Gupta *et al.* [6]. All the solutions were prepared with doubly distilled deionized water.

The Mn(II) sample was a BDH AnalaR $MnSO_4 \cdot H_2O$. Solutions of desired strength were prepared and standardised against standard EDTA [7]. The source of Co(II) was a BDH AnalaR $Co(NO_3)_2 \cdot 6H_2O$. The $HClO_4$ solution was prepared from E. Merck's 70% perchloric acid by appropriate dilution. All the solutions were standardised by literature methods. Ionic strength was maintained by $LiClO_4$, which is prepared by carefully neutralising Li_2CO_3 with $HClO_4$.

Apparatus

The kinetics of the reaction were monitored spectrophotometrically by measuring the increase in absorbance of Mn(VII) at 525 nm using a Carl-Zeiss spekol spectrocolorimeter in conjunction with an EK5 attachment and a CENCO circulation-cum immersion thermostat.

Kinetic Procedure

Mn(II), Co(II), $HClO_4$, $LiClO_4$ in desired amounts were taken in a 25 ml volumetric flask and thermo-

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stated at 30 ± 0.1 °C. The reaction was initiated by adding the temperature equilibrated PMPA to the reaction mixture. The reaction mixture was immediately transferred to the optical cell of the spectrocolorimeter and the increase in the optical density (D_t) of the reaction mixture at 525 nm against a reagent blank, was noted from time to time.

Stoichiometry

The optical densities (at 525 nm) of a series of solutions containing varying proportions of Mn(II), PMPA, Co(II) and H^+ were measured after completion of the reaction (as indicated by a constancy in the reading of the instrument) and compared with those of accurately standardised solutions of potassium permanganate of identical concentration, under identical experimental conditions. In all these experiments $[Mn(II)] \ll [PMPA]$. The spectra of the two solutions recorded in the wavelength range 400–600 nm were found to overlap. This indicates that under the experimental conditions Mn(II) is quantitatively oxidised to Mn(VII) by PMPA.

The stoichiometry of the reaction was established by following the method reported by us in our earlier communication [5] and was found to be 5 moles of PMPA for every 2 moles of Mn(II) oxidised.

Results

Our control experiments have shown that the oxidation of Mn(II) to Mn(VII) by PMPA in the absence of a Co(II) catalyst is negligible; no perceptible increase in absorbance of the reaction mixture was noticed even after 12 h of standing. However, in the presence of Co(II), the pink colour of permanganic acid in the reaction mixture gradually intensifies and attains maximum optical density within 50 to 60 min under the given experimental conditions depending upon the initial concentration of Mn(II) in the reaction mixture. Since the reaction was carried out under isolation conditions, *i.e.* $[Mn(II)] \ll [PMPA]$, the maximum optical density of the reaction mixture in each case under the specified experimental conditions is found to be proportional to [Mn(II)], as confirmed by the system adhering to Beer's law. Unlike in the oxidation with PDP, no intermediate brown colour of the Mn(IV) species was noticed in this case. At the end of each kinetic run, the optical density of the reaction mixture, which attains a constant value, remains fairly stable for over one hour, thereafter it gradually decreases. This is perhaps due to the secondary reaction between permanganic acid and hydrogen peroxide formed by the slow hydrolysis of the excess oxidant in the reaction mixture. When the optical densities were plotted against time, a sigmoid curve (Fig. 1) characteristic of an autocatalytic reaction was obtained.

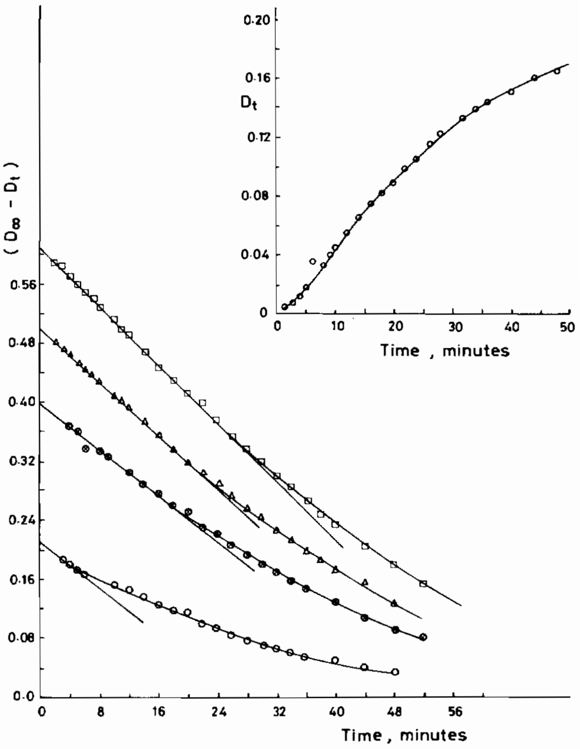

Fig. 1. Effect of varying [Mn(II)] on the rate of oxidation of Mn(II) by PMPA. A plot of $(D_\alpha - D_t)$ *vs.* time. Inset: autocatalysis curve. ○, $[Mn(II)] = 8 \times 10^{-5}$ M; ⊕, $[Mn(II)] = 16 \times 10^{-5}$ M; △, $[Mn(II)] = 20 \times 10^{-5}$ M; □, $[Mn(II)] = 24 \times 10^{-5}$ M.

Dependence on [Mn(II)]

When kinetic runs were carried out by varying the concentration of Mn(II) in the limits 8×10^{-5} to 24×10^{-5} M keeping all other parameters constant and maintaining isolation conditions, *i.e.* $[Mn(II)] \ll [PMPA]$, the plots of optical density of Mn(VII) *versus* time (Fig. 1) were found to be linear upto a certain stage of the reaction and thereafter show significant deviations from linearity. With increasing [Mn(II)], the linear portion increases suggesting a zero order dependence on [Mn(II)]. When the log (optical density) *versus* time plots were drawn, the plots consist of two intersecting straight lines. The straight lines corresponding to the later stage of the reaction are parallel to each other indicating that this stage of the reaction conforms to the first order dependence on [Mn(II)] and the overall reaction bears a binomial dependence of the type a + b [Mn(II)]. The order of magnitude of the zero order rate constants is the same as that deduced from the initial linear portions of the $(D_\infty - D_t)$ *versus* time plots. When Mn(III) pyrophosphate or manganese(VII) was added deliberately to the reaction mixture,

TABLE I. Dependence of the First Order Rate Constants on the Concentrations of Reactants for the Oxidation of Mn(II) by PMPA: $I = 0.2$ M, $T = 30 \pm 0.1$ °C.

$[Mn^{2+}] \times 10^5$ M	[PMPA] $\times 10^3$ M	$[H^+] \times 10^2$ M	$[Co^{2+}] \times 10^4$ *M*	$k_1 \times 10^3$ min^{-1}	$k_2 \times 10^3$ min^{-1}
8.0	8.0	2.0	4.0	23.03	41.45
16.0	8.0	2.0	4.0	23.03	46.06
20.0	8.0	2.0	4.0	24.41	46.06
24.0	8.0	2.0	4.0	24.64	46.06
16.0	4.0	2.0	4.0	50.66	110.5
16.0	5.33	2.0	4.0	52.97	101.3
16.0	8.0	2.0	4.0	64.48	110.54
16.0	10.66	2.0	4.0	78.30	125.74
16.0	8.0	1.0	4.0	43.98	59.88
16.0	8.0	1.5	4.0	30.63	45.13
16.0	8.0	2.0	4.0	25.33	41.45
16.0	8.0	4.0	4.0	15.33	21.48
16.0	8.0	2.0	2.0	11.83	17.08
16.0	8.0	2.0	4.0	23.03	33.62
16.0	8.0	2.0	8.0	50.66	78.30
16.0	8.0	2.0	12.0	78.99	110.54

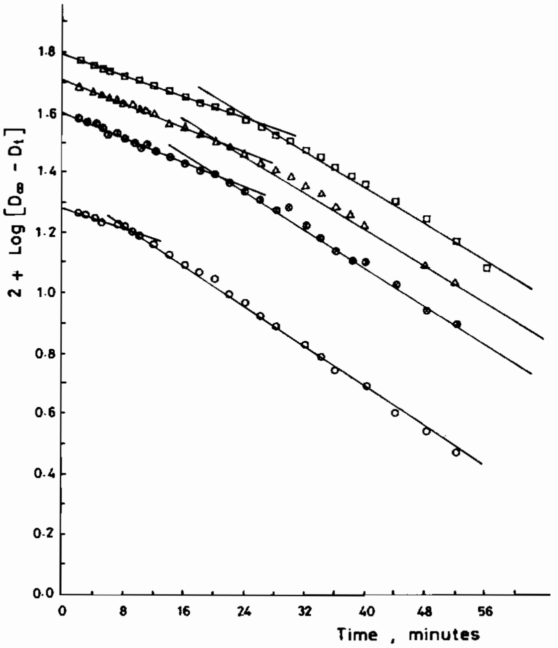

Fig. 2. Effect of varying [Mn(II)] on the rate of oxidation of Mn(II) by PMPA. A plot of $2 + \log(D_\alpha - D_t)$ *vs.* time. ○, [Mn(II)] = 8×10^{-5} M; ⊕, [Mn(II)] = 16×10^{-5} M; △, [Mn(II)] = 20×10^{-5} M; □, [Mn(II)] = 24×10^{-5} M.

the plots of log $(D_\infty - D_t)$ *versus* time were still the same, suggesting that they have no specific influence on the course of the reaction.

Dependence on [PMPA]

With increasing [PMPA] (from 4×10^{-3} to 10.6×10^{-3} M), other parameters being kept constant, the pseudo first order rate constants were found to increase (Table I) suggesting a pre-equilibrium step preceding the rate determining step. The plots of 1/rate *versus* 1/(PMPA) were found to be linear with a finite intercept on the 1/rate axis and a positive slope suggesting that PMPA is involved in complexation in one of the pre-equilibria.

Dependence on [Co(II)]

The effect of varying [Co(II)] (from 2×10^{-4} to 12×10^{-4} M) on the rate, at a fixed concentration of the other reactants and a fixed temperature 30 ± 0.1 °C, was investigated. It was found that the rate increases with increasing [Co(II)] (Table I) and the plots of the pseudo first order rate constants (k') *versus* [Co(II)] were found to be linear passing through the origin suggesting the first order dependence of the rate on [Co(II)].

Dependence on [H⁺]

When the kinetic runs were conducted with varying $[H^+]$ and the other parameters remained constant, the rate was found to decrease with increasing $[H^+]$ (Table I). A plot of 1/rate *versus* $[H^+]$ was found to be linear with a finite intercept on the 1/rate axis suggesting a fractional order dependence of the rate on $[H^+]$.

Effect of Temperature

The kinetic runs were conducted at varying temperatures in the range 28.5 to 39.2 °C, keeping all other parameters constant. The pseudo first order rate constants (k') were found to adhere to the Arrhenius law. The energy and entropy of activation were found to be 119.55 kJ mol^{-1} and −217.5 J K^{-1} mol^{-1} at $T = 30.0 \pm 0.1$ °C respectively.

Discussion

The salient features of the kinetic study are:

(1) the rate of the reaction has binominal dependence of the type a + b[Mn(II)] on [Mn(II)],

(2) fractional order dependence on [PMPA] and $[H^+]$ and

(3) first order dependence on [Co(II)].

Recently the kinetics of oxidation of Mn(II) with peroxomonosulphuric acid was reported by Lawrence and Ward [8]. They reported that the product is colloidal MnO_2 and the reaction is autocatalytic, and no traces of MnO_4^- are formed. But in our studies, we have not observed any brown colour due to Mn(IV); even if Mn(IV) is formed as a transient species it is further rapidly oxidised to Mn(VII) by the reactive intermediate, namely molecular oxygen formed in the rate determining step. In view of these observations, we propose the following tentative mechanism, which explains all the observed results.

$$H_3PO_5 \overset{K_1}{\rightleftharpoons} H_2PO_5^- + H^+$$

$$Co^{2+} + H_2PO_5^- \overset{K_2}{\rightleftharpoons} [CoH_2PO_5^-]^+$$

$$[CoH_2PO_5^-]^+ \xrightarrow[\text{slow}]{k_1} Co^{2+} + H_2PO_4^- + \tfrac{1}{2}O_2$$

$$[CoH_2PO_5^-]^+ + Mn^{2+} \xrightarrow[\text{slow}]{k_2} MnO^{++} + Co^{2+} + H_2PO_4^-$$

$$MnO^{++} + Mn^{2+} \overset{\text{rapid}}{\rightleftharpoons} MnO^+ + Mn^{3+}$$

$$MnO^{++} + \tfrac{1}{2}O_2 \xrightarrow[\text{fast}]{} \text{Products}$$

The above mechanism leads to the rate law

$$\text{rate} = \frac{K_1K_2[Co^{2+}]_t[H_3PO_5]_t}{K_1 + [H^+] + K_1K_2[H_3PO_5]_t}\{k_1 + k_2[Mn(II)]_t\}$$

k_2 being the effective rate constant which is used for calculations.

From the rate law it follows that plots of 1/rate *versus* 1/[PMPA], 1/rate *versus* $[H^+]$ should be linear with a finite positive intercept on the 1/rate axis which was actually found to be the case. Further, a plot of rate *versus* [Mn(II)] should also be linear with a finite positive intercept corresponding to the [Mn(II)]-independent path. This was also found to be true. The intercept corresponding to this zero order rate constant was of the same order of magnitude as that computed from the plots $(D_\infty - D_t)$ *versus* time plots. From the slope intercept values of the 1/rate *versus* 1/[PMPA] and 1/rate *versus* $[H^+]$, the first protonation constant of PMPA was calculated to be 12.18×10^{-3} at 30 ± 0.1 °C which compares well with the reported value of 8×10^{-2} at 25 ± 0.1 °C by Battagalia and Edwards [9]. This agreement lends further support to our above proposed mechanism.

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Appendix 1

Mechanism and Derivation of Rate Law

$$H_3PO_5 \overset{K_1}{\rightleftharpoons} H^+ + H_2PO_5^-$$

$$Co^{2+} + H_2PO_5^- \overset{K_2}{\rightleftharpoons} CoH_2PO_5^+$$

$$CoH_2PO_5^+ \xrightarrow[\text{slow}]{k_1} Co^{2+} + H_2PO_4^- + \tfrac{1}{2}O_2$$

$$CoH_2PO_5^+ + Mn^{2+} \xrightarrow[\text{slow}]{k_2} MnO^{++} + Co^{2+} + H_2PO_4^-$$

$$MnO^{++} + Mn^{2+} \overset{\text{fast}}{\rightleftharpoons} MnO^+ + Mn^{3+}$$

$$MnO^{++} + \tfrac{1}{2}O_2 \xrightarrow[\text{rapid}]{} \text{products}$$

$$MnO^+ + \tfrac{1}{2}O_2 \xrightarrow[\text{rapid}]{} \text{products}$$