

Kinetics of Oxidation of Hypophosphorous & Phosphorous Acids by Mn(III) Sulphate

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The kinetics of oxidation of hypophosphorous and phosphorous acids by Mn(III) sulphate in sulphuric acid have been studied spectrophotometrically. The oxidation shows first order dependence in [substrate] and [Mn³⁺] and an inverse first order dependence in [H⁺]. The energy and entropy of activation have been calculated to be 14.9 ± 1.2 (kcal mole⁻¹) and -11.4 ± 4.0 (e.u.), respectively for hypophosphorous acid, and 23.8 ± 1.5 (kcal mole⁻¹) and +1.1 ± 4.5 (e.u.), respectively for phosphorous acid.

KINETICS of the oxidation of some organic compounds by Mn(III) are reported in the literature¹. The oxidation of phosphites by different oxidizing agents such as halogens and the halates has been the subject of a number of detailed kinetic studies². The main reaction in these studies was the conversion of hypophosphite to phosphite. The subsequent reaction whereby phosphite is oxidized to phosphate was considerably slower^{3,8}. However, the oxidation of hypophosphorous and phosphorous acids by Mn(III) has not received attention. The present paper describes the kinetics of oxidation of both hypophosphorous and phosphorous acids by Mn(III).

Materials and Methods

All the chemicals used were of analar BDH or equivalent grades. Mn(III) sulphate was prepared by the oxidation of Mn(II) sulphate with potassium permanganate⁹. Its solution was stored in blue bottles and placed in a refrigerator when not in use. The solution was standardized occasionally before use by titrating it against standard ferrous ammonium sulphate. All solutions were prepared in doubly distilled water.

Kinetic measurements — The kinetics of reactions were followed spectrophotometrically on a Beckman DU model spectrophotometer using a cell of 1 cm path-length at 500 nm ($\epsilon_{\text{max}} = 107 \pm 3.0 \text{ M}^{-1} \text{ cm}^{-1}$) where Mn(III) shows maximum absorbance. The details have been described earlier^{10,11}. The experiments were carried out in large excess of [Mn(II)] so as to minimize the disproportionation of Mn(III).

Rate law — Equation (1) was used to evaluate the second order rate constant (k_2) for the oxidation of hypophosphorous acid by Mn(III).

$$\frac{1}{b-x} = \frac{k_2}{2}t + \frac{1}{b} \quad \dots(1)$$

which on differentiation gives Eq. (2).

$$\frac{dx}{dt} = k_2 \left(a - \frac{x}{2} \right) (b-x) \quad \dots(2)$$

When $b = 2a$, Eq. (2) becomes

$$\frac{dx}{dt} = \frac{k_2}{2}(b-x)^2 \quad \dots(3)$$

where a and b are the initial molar concentrations of hypophosphorous acid and Mn(III), respectively, and x = amount of Mn(III) which has disappeared at time t in minutes. The values of k_2 were calculated from the slope values of $1/(b-x)$ versus time plots (Fig. 1).

The pseudo first order rate constant (k_1) for the oxidation of phosphorous acid was calculated from the slope of $\log [\text{Mn(III)}]$ versus time plot. The error in the analysis of rate constants was within ± 5%. In most of the experiments, satisfactory results were obtained which were reproducible to ± 3%. It was observed that decomposition of Mn(III) was not more than 5% per hour even at higher temperatures, and blank experiments were

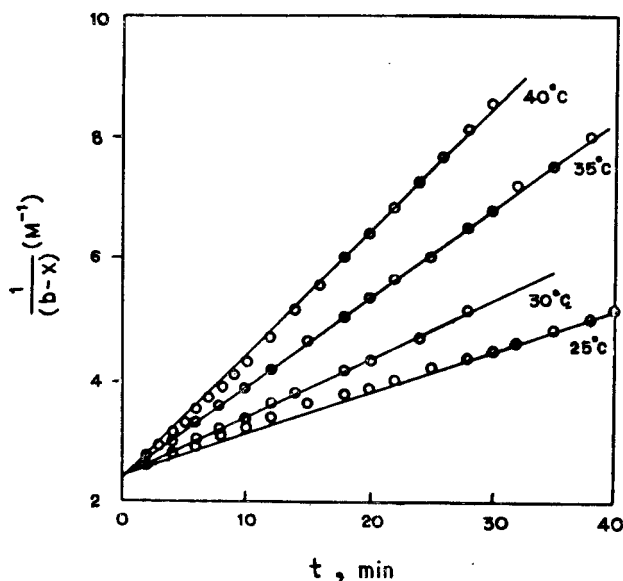


Fig. 1 — Typical second order plots of oxidation of hypophosphorous acid by Mn(III) sulphate in sulphuric acid at different temperatures

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performed where decomposition was appreciable. The rate of decrease in [Mn(III)] was followed up to at least 80% reaction.

Stoichiometry—The reducing substrates when mixed with a large excess of Mn(III) acidified with sulphuric acid and kept for 24 hr, consumed about two equivalents of oxidants per mole of the substrate. Phosphorous acid $\sim(10^{-3}M)$ which is the product of oxidation of hypophosphorous acid was not further oxidized under the conditions used for the oxidation of hypophosphorous acid, since the addition of ammonium molybdate to the reaction mixture failed to give any precipitate of ammonium phosphomolybdate. Phosphorous acid was oxidized only when its concentration was $10^{-1}M$ or more.

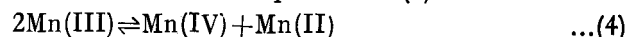
Results and Discussion

Effects of varying reactants—The oxidation of hypophosphorous acid by Mn(III) was studied at different initial $[H_3PO_2]$. The values of $k_1/[H_3PO_2]$ are given in Table 1. The order in each reactant was found to be one since the total order is two. The oxidation of phosphorous acid was carried out under the condition $[H_3PO_3] \gg [\text{oxidant}]$. To determine order with respect to Mn(III), the reactions were carried out at different concentrations of the oxidant. The order with respect to Mn(III) is one since first order rate constant was found to be independent of the initial [Mn(III)]. Experiments performed with varying $[H_3PO_3]$ gave the values of $k_1/[H_3PO_3]$ to be constant (Table 1) indicating that the order with respect to $[H_3PO_3]$ is unity.

Effect of varying $[H^+]$ —The acidity of reaction mixture was varied by the addition of H_2SO_4 . Each reaction was carried out at constant [Mn(III)]

and [substrate] but ionic strength could not be maintained constant. The products $k_2[H_2SO_4]$ are recorded in Table 2 which indicate that the rates are directly proportional to $[H^+]$.

Effects of added salts—Addition of sodium sulphate increased the reaction rate (k_2) whereas addition of Mn(II) did not show any effect on k_2 in the concentration range $(0.25-2.0) \times 10^{-2}M$. This is in agreement with the observation made earlier¹² in the oxidation of cyclohexanone by Mn(III) sulphate. The absence of any effect of the added Mn(II) on the rate of oxidation indicates the non-involvement of equilibrium (4).



Effect of varying temperature on the second order rate constants—The values of k_2 were found to be 2.26×10^{-4} , 3.69×10^{-4} , 4.86×10^{-4} and 7.0×10^{-4} litre mole⁻¹ sec⁻¹ at 25°, 30°, 35° and 40°, respectively for the oxidation of hypophosphorous acid whereas k_2 values for the other reaction were 1.66×10^{-4} , 2.82×10^{-4} , 4.72×10^{-4} and 8.88×10^{-4} litre mole⁻¹ sec⁻¹ at 35°, 40°, 45° and 50°, respectively. It is to be mentioned that the value 3.69×10^{-4} litre mole⁻¹ sec⁻¹ of k_2 at 30° for the oxidation of hypophosphite ion is the average value of five determinations recorded in Table 1. The reactions were studied at $[Mn(III)] = 4.0 \times 10^{-3}M$ and $[H_2SO_4] = 6.0M$. The concentrations of hypophosphorous and phosphorous acids were $2.0 \times 10^{-3}M$ and $2.07 \times 10^{-1}M$, respectively. The energies of activation were calculated¹¹ from the slope of the conventional plot of $\log k_2$ versus $1/T$. The values of k_2 and activation parameters for the oxidations of hypophosphorous, phosphorous and phenylphosphorous¹⁴ acids at $[H_2SO_4] = 6.0M$ are summarized in Table 3. The rate constants follow

TABLE 1 — EFFECT OF VARYING [SUBSTRATES] ON THE PSEUDO FIRST ORDER RATE CONSTANTS

{For hypophosphorous acid oxidation: $[Mn(III)] = 4.0 \times 10^{-3}M$; $[H_2SO_4] = 6.0M$, temperature, 30°; for phosphorous acid oxidation: $[Mn(III)] = 4.0 \times 10^{-3}M$; $[H_2SO_4] = 2.4M$, temperature, 35°}

Oxidation of H_3PO_2			Oxidation of H_3PO_3		
$[H_3PO_2] \times 10^3$ <i>M</i>	$k_1 \times 10^4$ sec ⁻¹	$k_1/[H_3PO_2] \times 10$ litre mole ⁻¹ sec ⁻¹	$[H_3PO_3] \times 10$ <i>M</i>	$k_1 \times 10^4$ sec ⁻¹	$k_1/[H_3PO_3] \times 10^4$ litre mole ⁻¹ sec ⁻¹
2.0	7.83	3.9	2.07	0.775	3.74
3.0	11.10	3.7	2.48	0.967	3.9
4.0	14.78	3.7	2.90	1.03	3.55
8.0	28.8	3.6	3.31	1.20	3.62
10.0	35.5	3.55	3.73	1.38	3.7

TABLE 2 — VARIATION OF SECOND ORDER RATE CONSTANT WITH THE CHANGE IN ACIDITY

{For hypophosphorous acid oxidation: $[H_3PO_2] = 5.0 \times 10^{-3}M$; $[Mn(III)] = 10 \times 10^{-3}M$; temperature, 20°; for phosphorous acid oxidation: $[H_3PO_3] = 2.07 \times 10^{-1}M$; $[Mn(III)] = 4.0 \times 10^{-3}M$ }

Oxidation of H_3PO_2			Oxidation of H_3PO_3		
$[H_2SO_4]$ <i>M</i>	$k_2 \times 10$ litre mole ⁻¹ sec ⁻¹	$k_2 \times [H_2SO_4] \times 10$	$[H_2SO_4]$ <i>M</i>	$k_2 \times 10^4$ litre mole ⁻¹ sec ⁻¹	$k_2[H_2SO_4] \times 10^4$
2.0	4.85	9.7	2.4	3.74	9.98
4.0	2.63	10.5	3.2	3.56	11.4
6.0	1.87	11.2	5.0	2.22	11.1
8.0	1.27	10.4	6.0	1.66	9.96

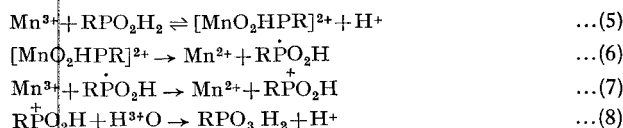
TABLE 3 — MEASURED SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS OF DIFFERENT REDOX REACTIONS

Substrate	k_2^* (litre mole ⁻¹ sec ⁻¹)	ΔE^\ddagger (kcal mole ⁻¹)	ΔS^\ddagger (e.u.)
H ₃ PO ₂	4.86×10^{-1}	14.9 ± 1.2	-11.4 ± 4.0
H ₃ PO ₃	1.66×10^{-4}	23.8 ± 1.5	1.1 ± 4.5
PhPO ₂ H ₂ (ref. 14)	6.5×10^{-3}	19.8 ± 1.0	-4.48 ± 2.0

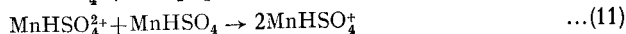
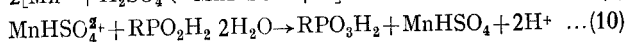
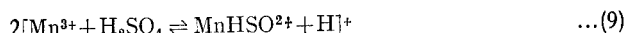
*Temperature, 35° and [H₂SO₄] = 6.0M.

the order H₃PO₂ > PhPO₂H₂ > H₃PO₃. The plot of ΔS^\ddagger versus ΔE^\ddagger was linear indicating that all the three reactions might be occurring by the same mechanism.

The second order rate constants for the oxidation of hypophosphorous and phosphorous acids were calculated to be 4.86×10^{-1} and 1.66×10^{-4} litre mole⁻¹ sec⁻¹ respectively at [H₂SO₄] = 6.0M and 35°. This shows that hypophosphorous acid is oxidized to phosphorous acid and further oxidation of phosphorous acid is too slow under the condition at which hypophosphorous acid is oxidized. The first dissociation constants¹³ for the respective acids are 8.0×10^{-2} and 5.1×10^{-2} and hence in the presence of sufficient mineral acid, they will remain undissociated (RPO₂H₂ form where R = H for hypophosphorous and R = OH for phosphorous acids). It is, therefore, suggested that the undissociated substrate molecule will react with Mn(III). The observed first order dependence in substrate and Mn(III) as well as the inverse dependence on [H⁺] can be explained according to the alternative Schemes 1 and 2. Cooper *et al.*¹⁶ have studied the reduction of V(V) by H₃PO₂, which also involves complex formation prior to the electron transfer process and the electron transfer was slow enough as compared to the present reaction to enable the determination of the stability constant for V(V)-H₃PO₂ complex. The stability constant for Mn(III)-RPO₂H₂ complex is very small since the kinetic evidence for intermediate compound formation is insignificant. The 1:1 complex which is formed by the reaction between Mn(III) and, RPO₂H₂ may decompose to give Mn(II) and a free radical according to step (6) in Scheme 1. The free radical further picks up another Mn(III) and the latter is subsequently reduced to Mn(II). The stable products are formed according to step (8) (Scheme 1). Alternatively, it may be proposed



Scheme 1



Scheme 2

that MnHSO₄²⁺ behaves as a two-equivalent oxidant and oxidizes the substrate according to step (10) (Scheme 2).

Addition of acrylamide to the reaction mixture failed to give any cloudy suspension in either reaction, indicating that free radicals are not involved in the reactions. The hydrogen atom in —OH groups are ionizable whereas P—H bonds formed in phosphorous acids are not ionizable and have reducing properties. NMR studies have also proved the existence of P—H bonds in phosphites.

Although it was pointed out earlier¹⁵ that R—P $\begin{matrix} \text{OH} \\ \diagdown \\ \text{OH} \end{matrix}$ is a better electron donor than its reorganized

structure R—P $\begin{matrix} \text{H} \\ \diagup \\ \text{O} \end{matrix}$ —OH(II), the oxidation of the com-

pound through P—H bond cleavage cannot be totally ruled out. Again, hypophosphorous acid has two hydrogen atoms attached to phosphorus atom. The replacement of one H of hypophosphorous acid by OH makes phosphorous acid more stable thereby requiring more energy to rupture P—H bond of phosphorous acid. The measured rate constants presented in Table 3 also support the above contention.

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