

KINETICS AND MECHANISM OF THE OXIDATION OF 1,3-PROPANEDIOL BY ACID PERMANGANATE IN THE PRESENCE OF FLUORIDE IONS

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INTRODUCTION

Oxidation of pinacol by Mn(III)-pyrophosphate has been reported by Drummond and Waters [1], who concluded that this diol reversibly displaces a chelated pyrophosphate group attached to Mn(III), followed by a reaction involving C-C bond rupture. Oxidation of acyclic glycols by acid permanganate in the presence of pyrophosphate are reported by Nath and others [2, 3]. Nath and others also studied the oxidation of 1,3-diols by acid permanganate in the presence of pyrophosphate [4], in which they proposed both Mn(III) and Mn(IV) as the oxidizing species. However, of the two, Mn(IV) has been shown to be the more powerful oxidizing species. The reaction involves a cyclic intermediate complex with Mn(III) or Mn(IV), followed by a C-C bond rupture. During the oxidation of benzyl alcohol, Nath and Banerji [5] noted the effect of fluoride ions in controlling the rate of permanganate oxidations. It was therefore thought worthwhile to study the oxidation of 1,3-propanediol by acid permanganate in the presence of fluoride ions to get a clear picture of the reacting species of the permanganate in these oxidations.

EXPERIMENTAL

1,3-Propanediol (BDH) was used after distillation under reduced pressure. Perchloric acid (70%, BDH) was used as a source of hydrogen ions. Sodium perchlorate (BDH) was used to maintain the constant ionic strength. All other chemicals used were chemically pure.

Kinetic Measurement

All reactions were carried out at $30 \pm 0.2^\circ\text{C}$ unless stated otherwise. The reactions were followed by quenching the aliquots (usually 5 ml), withdrawn at known intervals of time, in excess KI and titrating the liberated iodine against sodium thiosulphate. The concentration of 1,3-propanediol was always kept much greater (≥ 10 times) than that of the permanganate in all experiments.

Product Analysis

For product analysis, reaction mixtures containing excess of diol and other requisite reagents were left

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overnight to ensure complete reduction of permanganate. Characterization by different spot tests [6] shows that this diol gives formaldehyde and acetaldehyde as the reaction products under the kinetic conditions that apply. These products were further confirmed by GLC.

RESULTS

Oxidation of 1,3-propanediol by acid permanganate is usually very fast. To make the rate measurable, sufficient excess of fluoride was used. It is obvious from Table 1(a) that sodium fluoride reduces the rate until its concentration reaches $20 \times 10^{-2}\text{M}$, beyond which its further addition has no effect on the rate. Therefore, a fluoride concentration of $20 \times 10^{-2}\text{M}$ was used in all experiments.

In the presence of excess [Diol] and $[\text{H}^+]$, the disappearance of permanganate follows a first order rate law for the first 40–50% of the reaction, beyond which it becomes faster. The first order rate constant does not vary appreciably with different initial permanganate concentrations. The reaction, therefore, is of first order in permanganate (see Table 1(b)).

Table 1. Variation of Rate of Oxidation of 1,3-Propanediol with Various Parameters

[NaF] (M)	[KMnO ₄] (10 ⁴ M)	[Diol] (10 ² M)	[H ⁺] (M)	$k_1 \times 10^4$ (sec ⁻¹)
(a) Variation of [NaF]				
0.10	10	1.0	1.0	6.91
0.15	10	1.0	1.0	5.75
0.20	10	1.0	1.0	5.56
0.25	10	1.0	1.0	5.56
(b) Variation of [KMnO ₄]				
0.20	5	2.0	1.0	10.7
0.20	10	2.0	1.0	11.1
0.20	20	2.0	1.0	10.8
0.20	30	2.0	1.0	11.1
(c) Variation of [Diol]				
0.20	10	0.5	1.0	2.88
0.20	10	1.0	1.0	5.40
0.20	10	2.0	1.0	11.5
0.20	10	3.0	1.0	17.3
0.20	10	4.0	1.0	22.6
(d) Variation of [H ⁺]				
0.20	10	2.0	0.25	2.68
0.20	10	2.0	0.50	5.37
0.20	10	2.0	1.00	11.1
0.20	10	2.0	1.50	17.3

The rate varies linearly with the concentration of 1,3-propanediol (see Table 1(c)). $k_1/[\text{Diol}]$ works out to be constant within the kinetically permissible limits. Hence, the order with respect to the diol is also one.

Table 1(d) reflects that at constant ionic strength ($\mu=1.7\text{M}$), the rate varies linearly with the concentration of H^+ . As $k_1/[\text{H}^+]$ is constant, the order with respect to $[\text{H}^+]$ is again one.

The Mn(II) concentration was varied from $4 \times 10^{-4}\text{M}$ to $20 \times 10^{-4}\text{M}$. Table 2 records the results of the effect on the rate due to the addition of Mn(II). It is seen that the rate does not vary with the addition of Mn(II).

Table 2. Effect of Adding Mn(II) on Rate of Oxidation of 1,3-Propanediol

Mn ²⁺ $\times 10^{-4}(\text{M})$ $k_1 \times 10^4(\text{sec}^{-1})$	4.0 10.4	8.0 10.4	12.0 10.7	16.0 10.6	20.0 10.7
Note. [Diol] = $2 \times 10^{-2}\text{M}$; [NaF] = 0.2M ; $[\text{H}^+] = 1\text{M}$; [KMnO ₄] = $10 \times 10^{-4}\text{M}$.					

Table 3 shows the effect of change of temperature from 25 to 40°C ($\pm 0.2^\circ\text{C}$) on the rate of reaction.

The activation parameters were calculated by the procedure as enumerated by Frost and Pearson [7]. Thus, a plot of $\log k_1$ against $1/T$ gave a straight line, and from the slope the energy of activation, E_a , was evaluated.

$$E_a = -\text{slope} \times R.$$

From this, the enthalpy of activation was calculated using the relationship

$$\Delta H^\ddagger = E_a - RT,$$

which is applicable for the reactions in solutions. The

Table 3. Effect of Temperature on Reaction Rate

Temperature (K)	$k_1 \times 10^4$ (sec ⁻¹)	$K \times 10^{-2}$ (1 ² ·mol ⁻² ·sec ⁻¹)
298	3.45	3.45
303	5.37	5.37
308	8.44	8.44
313	12.66	12.66
ΔH^\ddagger (kJ·mol ⁻¹)	ΔS^\ddagger (J·mol ⁻¹ ·K ⁻¹)	ΔF^\ddagger (kJ·mol ⁻¹)
68.5	-42.2	81.5

Note. [Diol] = $1.0 \times 10^{-2}\text{M}$; $[\text{H}^+] = 1\text{M}$; [NaF] = 0.2M ; [KMnO₄] = $10 \times 10^{-4}\text{M}$.

entropy of activation was calculated by the following equation:

$$\frac{\Delta S^\ddagger}{19.14} = \log K - \log \frac{kT}{h} + \frac{\Delta H^\ddagger}{19.14T}$$

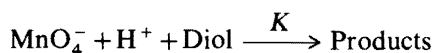
The calculated thermodynamic parameters are also recorded in Table 3. The error limits in the values of ΔH^\ddagger , ΔS^\ddagger , and ΔF^\ddagger are $\pm 4.0 \text{ kJ}\cdot\text{mol}^{-1}$, $\pm 8.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and $\pm 6 \text{ kJ}\cdot\text{mol}^{-1}$ respectively.

Derivation of Rate Law

The pseudo first order rate constant, k_1 , is given by the expression:

$$\frac{-d[\text{MnO}_4^-]}{dt} = k_1 [\text{MnO}_4^-] \quad (1)$$

The chemical equation expressing the oxidation of the diol may be given as follows:



where K is the specific rate constant, which is expressed as follows:

$$\frac{-d[\text{MnO}_4^-]}{dt} = K [\text{MnO}_4^-] [\text{H}^+] [\text{Diol}] \quad (2)$$

Since Equations (1) and (2) are equal,

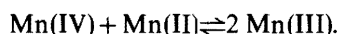
$$k_1 [\text{MnO}_4^-] = K [\text{MnO}_4^-] [\text{H}^+] [\text{Diol}]$$

or

$$K = \frac{k_1}{[\text{H}^+] [\text{Diol}]}$$

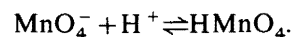
DISCUSSION

The phenomenon of autocatalysis is well-known in the oxidation reactions of acid permanganate [8]. Oxidation of 1,3-propanediol by acid permanganate also shows autocatalysis due to the involvement of Mn(III) and Mn(IV). To suppress the autocatalyst, a large excess of sodium fluoride was therefore used [9]. Mn(II) is known to effect the oxidation rates of several compounds [10, 11], where the oxidizing species are Mn(III) and/or Mn(IV), and this is due to the effect of Mn(II) on the equilibrium:



If the Mn(III) is involved in the oxidation, the rate should increase to a limiting value; and if Mn(IV) is

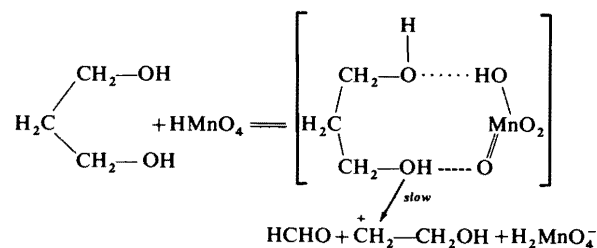
taking part in the reaction, the rate should have been retarded at high Mn(II) concentrations. However, the rate of oxidation of the diol by acid permanganate, in the presence of fluoride ions, is not altered by addition of Mn(II). This suggests that intermediate valency states of manganese, i.e., Mn(III) and/or Mn(IV), are not involved in the reaction. The linear dependence of rate on $[\text{H}^+]$ is due to the protonation of MnO_4^- to give more powerful oxidizing species, HMnO_4 [5]:



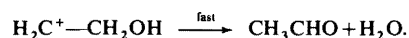
No effect on the rate due to the variation of ionic strength suggests a reaction between neutral molecules. Bakore and Narain [12] have reported that reactions involving a C-C bond rupture have small values of the entropy of activation. The observed entropy of activation of $-42.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is consistent with the idea of a C-C bond rupture in the oxidation of the diol by acid permanganate in the presence of fluoride ions.

The detection of formaldehyde and acetaldehyde as the reaction products [6] under the conditions of the kinetics experiments further confirms a C-C bond rupture in this reaction.

The following mechanism is proposed, consistent with the result of product analysis, thermodynamic parameters, and kinetic data:



and



A C-C bond rupture takes place in the rate determining step. The observed enthalpy of the reaction also suggests a C-C bond rupture via intermediate complex formation, as pointed out by Duke [13].

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