

MECHANISM OF OSMIUM TETROXIDE CATALYSED OXIDATION OF MALONATE ION BY HEXACYANOFERRATE (III) IN AQUEOUS ALKALINE MEDIUM

by M. P. SINGH, H. S. SINGH, B. SINGH, A. K. SINGH, and AMOD K. SINGH,
Department of Chemistry, University of Allahabad, Allahabad

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Kinetics of osmium tetroxide catalysed oxidation of malonate ion by hexacyanoferrate (III) ion has been studied in aqueous alkaline medium. The reaction order has been found to be independent of hexacyanoferrate (III) ion while the order with respect to both osmium tetroxide and hydroxyl ion comes out to be unity. The reaction kinetics follows first-order at low malonate ion and becomes zero at higher concentrations. The course of the reaction was considered to proceed through the formation of an activated malonate OsO_4 complex which decomposes giving reduced osmium (VI) followed by fast oxidation with hexacyanoferrate (III) ion. The energy of activation for the reduction process was calculated as 14.8 K. cal/mole.

INTRODUCTION

Reactions involving the catalytic oxidation of organic compounds are among the most interesting and useful chemical processes. Solymosi (1957) found qualitatively that the osmium (VIII) is an effective catalyst with alkaline ferricyanide. He studied a number of estimations but no kinetics was reported. Krishna and Singh (1966) attempted to investigate the mechanism of osmium tetroxide catalysed oxidation of methanol and ethanol with alkaline ferricyanide. Similarly the kinetics of oxidation of methylketones (cf. Singh, V. N. *et al.* 1969), mandelate ion, (Singh, N. P. *et al.* 1968), tartaric acid and malic acid (Singh, N. P. *et al.* 1970), lactate and glycolate (Lal *et al.* 1972), and aldehydes (Pandey *et al.* 1971) have been studied by alkaline ferricyanide using osmium tetroxide as catalyst. In the present study we are reporting a more definite information regarding the mechanism of osmium tetroxide catalysed oxidation of malonic acid with alkaline ferricyanide ion.

MATERIALS AND METHOD EMPLOYED

The sample of malonate was of L. R. B. D. H. grade. The sample (John Mathey & Co. Ltd) of OsO_4 was dissolved in the known strength of aqueous sodium hydroxide. Potassium ferricyanide, sodium hydroxide and potassium chloride were of G. R. (S. Merck) grade. The ionic strength of the medium was kept constant with standard solution of potassium chloride. The products were identified with the help of paper chromatography. The similar experimental procedure was employed as it is reported in previous papers (cf. Krishna & Singh 1966; Singh, V. N. *et al.* 1969; and Singh, N. P. *et al.* 1968, 1970).

RESULTS AND DISCUSSION

The osmium tetroxide catalysed oxidation of malonate ion in basic aqueous solution has been studied kinetically at constant ionic strength medium. Our results,

covering a much wider concentration, confirm that this reaction has a complicated feature. The kinetics of the reaction was followed by estimating the amount of ferrocyanide ion produced at different intervals of time with the help of a standard solution of ceric sulphate using ferro-ion as a redox indicator. The zero-order rate constant

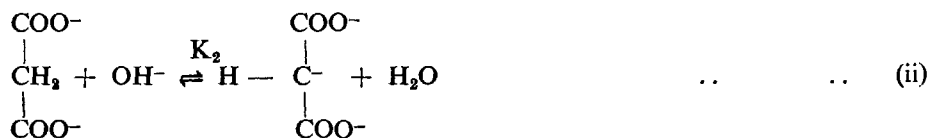
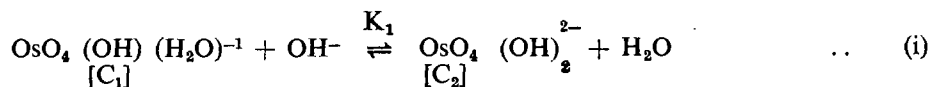
TABLE I
[Malonate] = 5.00×10^{-2} M
 $\mu = 2.50$ M

Temp 35°C

$[K_3Fe(CN)_6]$ $\times 10^3$ M	[NaOH] M	$[OsO_4] \times 10^5$ M	$(-dc/dt) \times 10^5$ mole lit ⁻¹ min ⁻¹	$-dc/dt/[OH^-]$ min ⁻¹
1.00	2.00	3.80	0.55	0.27
2.00	2.00	3.80	0.75	0.37
3.00	2.00	3.80	0.77	0.38
4.00	2.00	3.80	0.75	0.37
2.00	0.50	7.60	0.22	0.44
2.00	0.75	7.60	0.30	0.41
2.00	1.00	7.60	0.41	0.41
2.00	2.00	7.60	0.90	0.45

$(-dc/dt)$ given in Table I are the average values obtained from the slope of the remaining ferricyanide against time plot. Fig. 1 shows a typical zero-order plot and clearly confirms that the reaction rate follows zero-order kinetics with respect to ferricyanide ion. The effect of variation of hydroxyl ion also indicates the first order kinetics (Table I). The results presented in Fig. 2 substantiates that the reaction follows first order kinetics at lower malonate ion concentrations and tend towards zero order kinetics at its higher concentrations. The osmium tetroxide concentration was varied and the results are shown in the Fig. 3. A straight line with a positive intercept at y -axis shows the first order kinetics with respect to osmium tetroxide. The intercept at y -axis also indicates that the oxidation of malonate ion is taking place even without osmium tetroxide. Indeed the uncatalysed part is so small that the actual catalysed route will not be effected.

Taking into account these results, a probable scheme for the oxidation of malonate ion might be considered as follows :



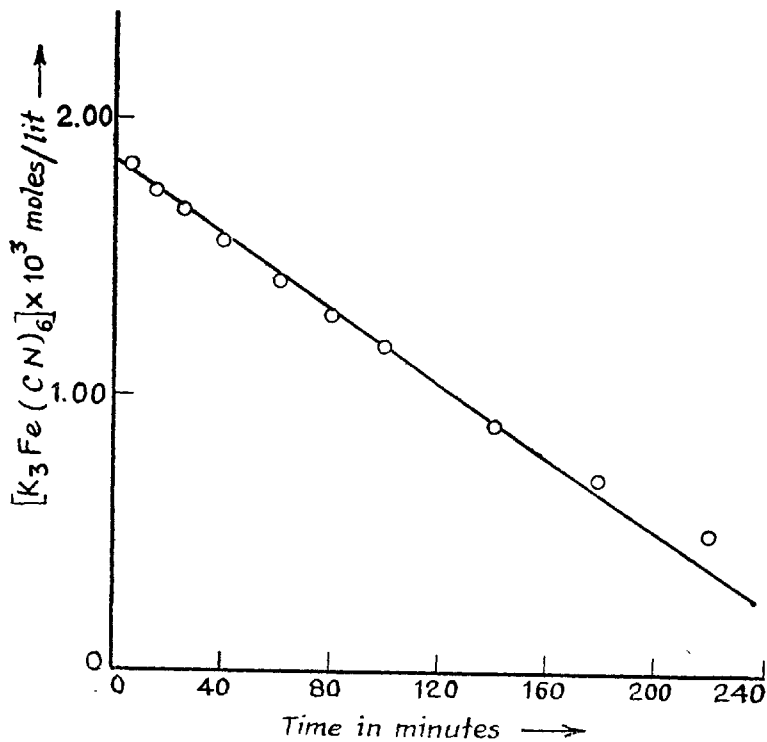
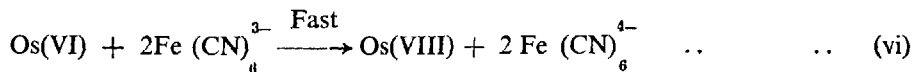
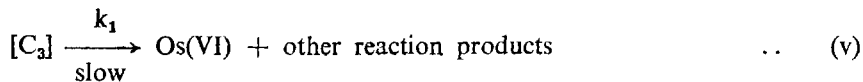
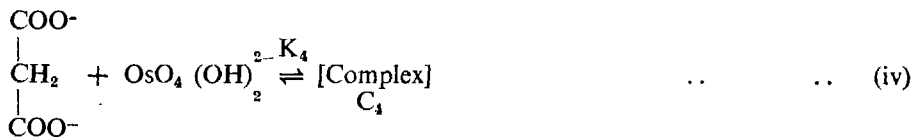
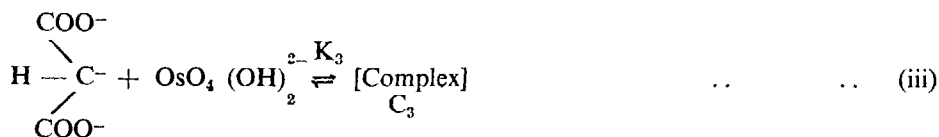


FIG. 1. Temp 35°C [Malonate] = 5.00×10^{-2} M [OsO₄] = 3.80×10^{-5} M
[NaOH] = 2.00 M $\mu = 2.50$ M



It is assumed for instance that the complex C_4 is stable as regards the decomposition, and so the rate of the reaction would be

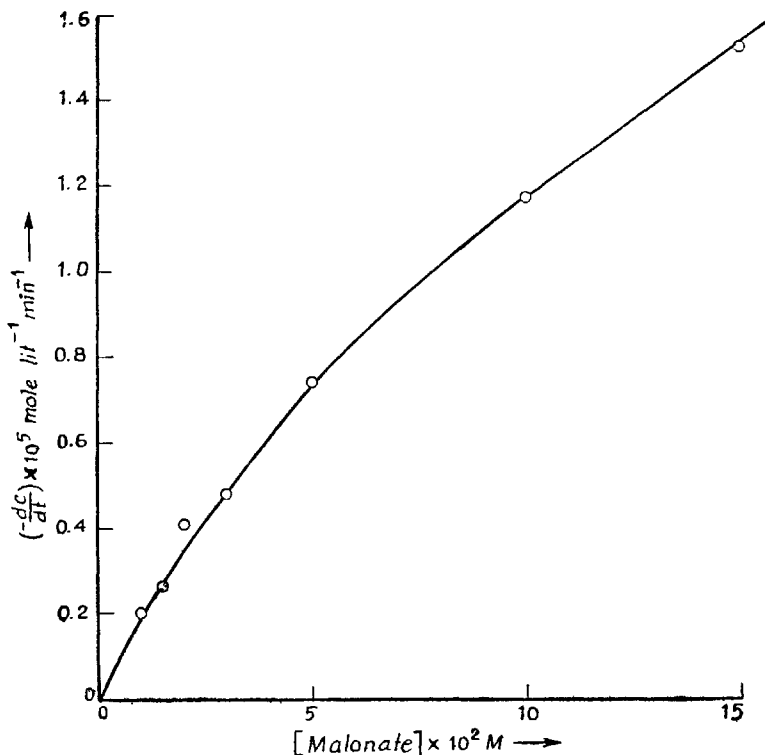


FIG. 2. Temp. 35°C $[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M$ $[OsO_4] = 3.80 \times 10^{-5} M$
 $[NaOH] = 2.00 M$ $\mu = 2.5 M$

$$-\frac{d[Fe_y]}{dt} = 2 k_1 [C_3] \quad \dots \quad (1)$$

where $Fe_y = [Fe(CN)_6]^{3-}$.

It is worth mentioning at this stage that osmium tetroxide (Griffith 1965) exists in the form of the equilibrium in alkaline medium. It is also reported that the species $OsO_4(OH)_2^{2-}$ acts as a catalyst (Cotton & Wilkinson 1966)

Now the total concentration of the Os(VIII) might be written as,

$$[Os(VIII)]_T = C_1 + C_2 + C_3 + C_4 \quad \dots \quad (2)$$

Solving equation in terms of the concentration of the C_2 , it becomes as equation (3)

$$[Os(VIII)]_T = \frac{C_2}{K_1 [OH^-]} + C_2 + K_3 [L^-] C_2 + K_4 [L] C_2 \quad \dots \quad (3)$$

Here L and L⁻ are the malonate and malonate anion as shown in step (ii).

From equation (3), the value of C_2 comes out to be

$$[C_2] = \frac{K_1 [OH^-] [Os(VIII)]_T}{1 + K_1 [OH^-] [1 + K_4 [L] + K_2 K_3 [L] (OH^-)]} \quad \dots \quad (4)$$

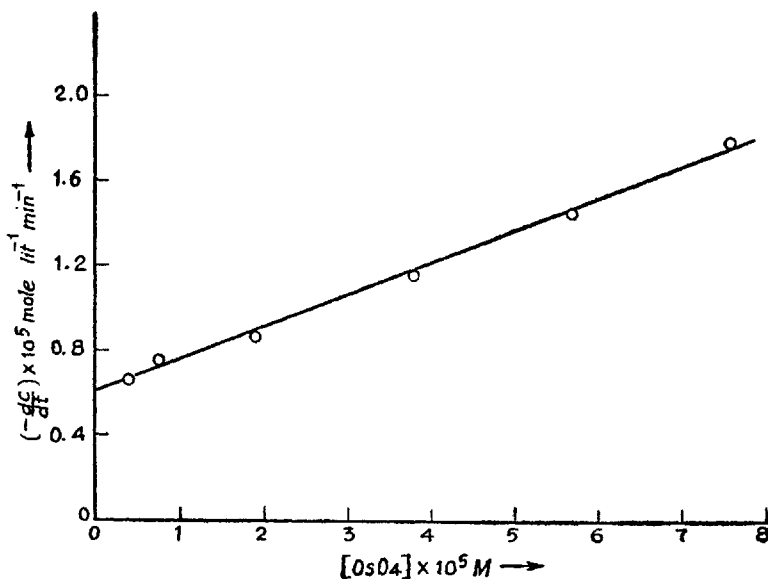


FIG. 3. Temp. 35°C $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ M $[Malonate] = 1.00 \times 10^{-3}$ M
 $[NaOH] = 2.00$ M $\mu = 2.5$ M

Now the rate could be written as

$$\frac{-d[Fe]}{dt} = 2k_1 [C_3] = 2k_1 K_2 K_3 [L] [OH^-] [C_2] \quad \dots \quad (5)$$

From equations (4) and (5)

$$\frac{-d[Fe]}{dt} = \frac{2k_1 K_1 K_2 K_3 [L] [Os(VIII)]_T [OH^-]^2}{1 + K_1 [OH^-] [1 + K_4 [L] + K_2 K_3 [L] [OH^-]}. \quad \dots \quad (6)$$

Under the conditions $K_1 [OH^-] \gg 1$, equation (6) reduces to eq. (7)

$$\frac{-d[Fe]}{dt} = \frac{2k_1 K_2 K_3 [L] [Os(VIII)]_T [OH^-]}{1 + K_4 [L] + K_2 K_3 [L] [OH^-]} \quad \dots \quad (7)$$

Since it was assumed that the complex formed in step (iv) is resistant to decomposition, C_4 might be assumed to be more stable. Also if K_2 is of very low magnitude, K_3 and K_4 are nearly of the same order, the validity of the inequality $K_4 [L] \gg K_2 K_3 [L] [OH^-]$ might be assumed. This equation (7) reduces to eq. (8).

$$v = \frac{-d[Fe]}{dt} = \frac{2k_1 K_2 K_3 [L] [Os(VIII)]_T [OH^-]}{1 + K_4 [L]} \quad \dots \quad (8)$$

At very low concentration of the organic substrate, we can assume that $K_4 [L]$ so eq. (8) reduces to eq. (9)

$$v = \frac{-d[Fe]}{dt} = 2k_1 K_2 K_3 [L] [Os(VIII)]_T [OH^-] \quad \dots \quad (9)$$

Equation (9) clearly explains the first order kinetics with respect to malonate, catalyst and hydroxyl ion. This is in good agreement with the experimental results.

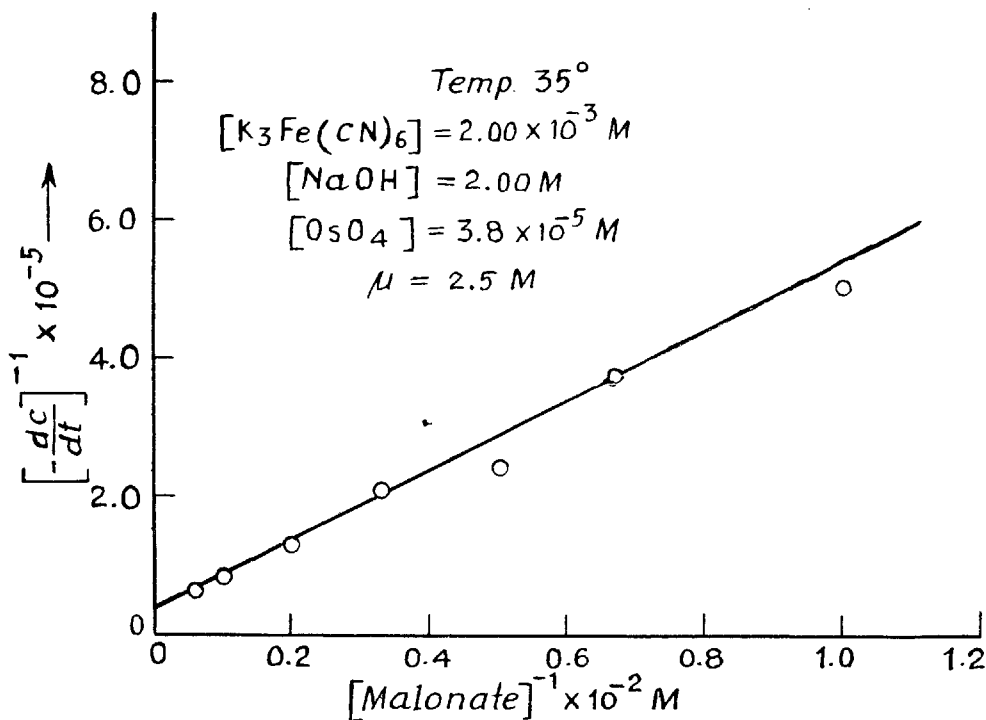


FIG. 4

The validity of the equation (8), however, might be verified by rewriting it as eq. (10)

$$\frac{1}{v} = \frac{1}{2k_1K_2K_3[L][Os(VIII)]_T[OH^-]} + \frac{K_4}{2k_1K_2K_3[Os(VIII)]_T[OH^-]} \quad (10)$$

A plot of $\frac{1}{v}$ against $\frac{1}{\text{malonate}}$ should be a straight line. Fig. 4 clearly demonstrates that the plot is a straight line. The intercept of the line gives the value of $K_4/K_1K_2K_3$ and the slope gives the value of $k_1K_2K_3$. Knowing the value of $k_1K_2K_3$ as 1.28, the value of K_4 was calculated as 7.83.

The validity of the rate law (8) might be demonstrated by substituting the value of $k_1K_2K_3$ and K_4 in it. The equation then becomes

$$\frac{-d[Fe]_y}{dt} = \frac{2 \times 1.28 \times [L][Os(VIII)][OH^-]}{1 + 7.83[L]} \quad \dots \quad (11)$$

From equation (11), the value of the rate was calculated for different sets of experiments. Thus the values obtained are summarized in the Table II. A perusal of this table clearly indicates that there is a considerable degree of agreement between the observed and the calculated values and hence confirms the proposed mechanism.

The oxidation products were identified as meso-oxalic acid and oxalic acid after the complete oxidation. Thus, the oxidation might be shown as follows:

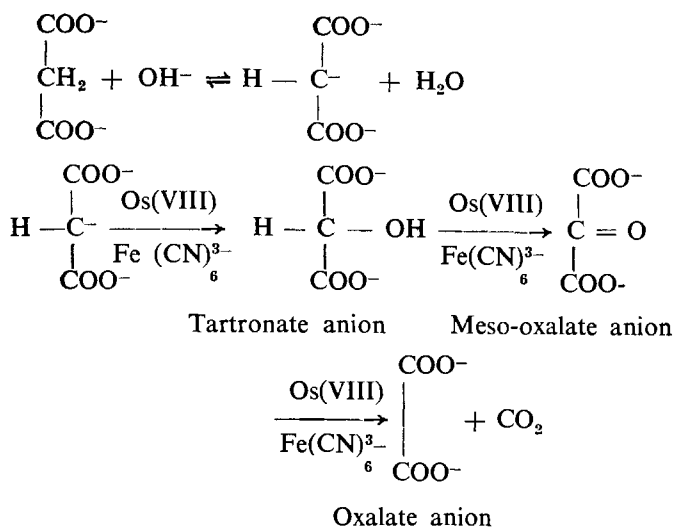


TABLE II

Observed and calculated data for the rate of oxidation of Malonate at 35°C

$$\begin{aligned}
 [\text{K}_3\text{Fe(CN)}_6] &= 2.00 \times 10^{-3}\text{M} \\
 \mu &= 2.50\text{M}
 \end{aligned}$$

[Malonate] $\times 10^2\text{M}$	[OsO ₄] $\times 10^5\text{M}$	[OH ⁻] M	$-dc/dt \times 10^5 \text{ mole lit}^{-1} \text{ min}^{-1}$	
			Observed	Calculated
1.00	3.80	2.00	0.20	0.18
1.50	3.80	2.00	0.26	0.26
2.00	3.80	2.00	0.41	0.34
3.00	3.80	2.00	0.48	0.48
5.00	3.80	2.00	0.74	0.70
10.00	3.80	2.00	0.74	0.70
15.00	3.80	2.00	1.52	1.34
5.00	7.60	0.50	0.22	0.37
5.00	7.60	0.75	0.30	0.52
5.00	7.60	1.00	0.41	0.69
5.00	7.60	2.00	0.90	1.30
10.00	1.90	2.00	0.86	0.54
10.00	3.80	2.00	1.17	1.09
10.00	7.60	2.00	1.80	2.18

The decomposition of the complexes C₃ and C₄ involves the internal oxidation switched in which two electrons are taken up by the Os(VIII) species. As the attack

takes place at the methylene carbon of the malonate, the greater electron density at this carbon atom would favour the decomposition assumed. As complex C_3 is rich in this respect, so its decomposition would be easier to that of the C_4 . Although the decomposition of C_4 cannot be denied, yet its rate appears to be negligible as compared to C_3 .

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