JOURNAL OF CATALYSIS 49, 135–140 (1977)

Kinetics and Mechanism of the Osmium Tetroxide-Catalyzed Oxidation of 2-Methylpentane-2,4-diol and Butane-1,4-diol with Hexacyanoferrate (III) Ion in Aqueous Alkaline Medium

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Received February 2, 1976; revised April 5, 1977

Kinetic data for the rate of the osmium tetroxide-catalyzed oxidation of butane-1,4-diol and 2-methylpentane-2,4-diol with hexacyanoferrate (III) are reported. The results thus obtained suggest that the oxidation proceeds via formation of an activated complex between the diol anion and osmium tetroxide, which slowly disproportionates to an intermediate product and the osmium (VI) species. The osmium (VI) species thus produced is oxidized rapidly to osmium (VIII) species with hexacyanoferrate (III) ion. The oxidation products are confirmed, and a possible reaction path for their formation is proposed.

INTRODUCTION

Oxidation reactions incorporating certain selective catalysts are of considerable academic and technological importance. However, in contrast to the many oxidation reactions using heterogeneous catalysts which have received continuous attention for several years, it is only relatively recently that the oxidation of organic substrates involving homogeneous catalysts has been subjected to mechanistic studies. Very recently, osmium (VIII) catalyst has been reported in the ferricyanide oxidation of olefins (*1*), α-hydroxy acids (*2*), aldehydes (*3*), ketones (*4*), alcohols (*5*) and digols (*6*) in aqueous alkaline media. However, the mechanism of oxidation of diols has not yet been studied, and, in the present study, we have carried out the oxidation of butane-1,4-diol and 2-methylpentane-2,4-diol with aqueous hexacyanoferrate (III) in an alkaline medium using osmium tetroxide as a homogeneous catalyst. The details of the results are presented, and, accordingly, a reaction mechanism is proposed.

RESULTS AND DISCUSSION

The kinetic data for the osmium tetroxide-catalyzed oxidation of 2-methylpentane-2,4-diol and butane-1,4-diol with aqueous hexacyanoferrate (III) in an alkaline medium at constant ionic strength, obtained over a wide range of concentrations is given in Table 1 and Figs. 1–3.

Figure 1 shows a zero-order plot for the rate of oxidation of 2-methylpentane-2,4,-diol and butane-1,4-diol. It is obvious from these plots that the zero-order velocity constants begin to increase after a certain stage of the reaction. From these data we may conclude that this increase in the zero-order rate constant values is due to further oxidation of the intermediate product. In order to avoid possible intervention by the products, the initial

ISSN 0021-9517

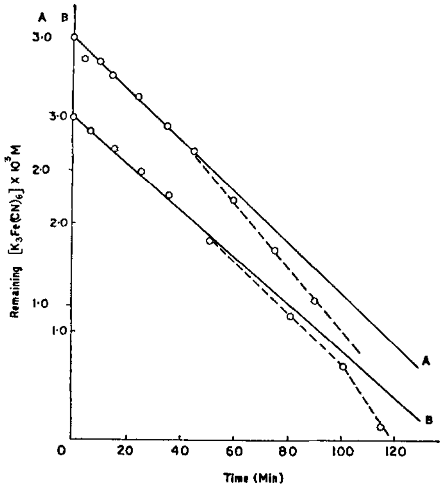

FIG. 1. Reaction features with respect to ferricyanide: A. $[K_3Fe(CN)_6] = 3.00 \times 10^{-3}$ *M*; [NaOH] $= 9.00 \times 10^{-3}$ *M*; [2-methyl-2,4-pentane diol] $= 1.00 \times 10^{-2}$ *M*; $[OsO_4] = 10.50 \times 10^{-5}$ *M*; $\mu = 1.00$ *M*; temp.: 30°C. B. $[K_3Fe(CN)_6] = 3.00 \times 10^{-3}$ *M*; [NaOH] $= 2.00 \times 10^{-2}$ *M*; [butane-1,4-diol] $= 2.00 \times 10^{-2}$ *M*; $[OsO_4] = 3.90 \times 10^{-5}$ *M*; $\mu = 0.50$ *M*; temp.: 30°C.

reaction velocity $(-dc/dt)$ was calculated by plotting the remaining hexacyanoferrate (III) versus time. The initial $(-dc/dt)$ values at different initial hexacyanoferrate (III) ion concentrations are listed in Table 1 and show the reaction rate to be independent of hexacyanoferrate (III) ion concentration.

Figure 2 shows the exact dependence of the reaction rate on hydroxyl ion and diol concentration. It is obvious that, at low concentrations of OH^- and diol, the reaction velocity follows first-order dependence (solid lines in Fig. 2) but tends toward zero-order dependence at higher concentrations (dotted lines in Fig. 2).

The order with respect to osmium tetroxide is unity in both diols. Thus, at very low concentrations of hydroxyl ion and diol, these results give rise to rate law (1).

$$-\frac{d}{dt}[\text{Fey}] = k[\text{S}][\text{OH}^-][\text{OsO}_4] \qquad (1)$$

where

$$[\text{Fey}] = [\text{Fe(CN)}_6]^{3-} \text{ and } [\text{S}] = [\text{diol}]$$

The values of *k* are calculated to be 1.4×10^4 and 2.40×10^4 M^{-2} min^{-1} for butane-1,4-diol and 2-methylpentane-2,4-diol, respectively.

Before attempting to propose the oxidation mechanism of these diols, it is noteworthy at this stage to discuss the species of Os (VIII) existing in alkaline medium. Osmium tetroxide in alkaline medium has been reported to exist as octahedral complexes of the form (*7*) *trans*-$OsO_4(OH)(H_2O)^-$ and $OsO_4(OH)_2{}^{2-}$. These species might be considered via equilibrium step (II) of the proposed scheme for the reaction. It is also observed that the $OsO_4(OH)_2{}^{2-}$ is the only reacting species of osmium tetroxide, (*2*) and the equilibrium will usually be shifted to the right (*8*).

In the light of these observations, the following probable oxidation mechanism for these diols is proposed:

$$\text{S} + \text{OH}^- \overset{K}{\rightleftharpoons} \text{S}^- + \text{H}_2\text{O} \qquad \text{(I)}$$

$$\underset{\text{(C)}}{\text{OsO}_4(\text{OH})(\text{H}_2\text{O})^-} + \text{OH}^- \overset{K_1}{\rightleftharpoons} \underset{(\text{C}_1)}{\text{OsO}_4(\text{OH})^{2-}_2} + \text{H}_2\text{O} \qquad \text{(II)}$$

$$\text{S}^- + \text{OsO}_4(\text{OH})^{2-}_2 \overset{K_2}{\rightleftharpoons} \text{Complex } (\text{C}_2) \qquad \text{(III)}$$

$$\text{C}_2 \xrightarrow[\text{(slow)}]{k_1} \text{Os(VI)} + \text{intermediate products}, \qquad \text{(IV)}$$

where C, C_1, and C_2 represent $OsO_4(OH)H_2O^-$, $OsO_4(OH)^{2-}_2$ and complex, respectively.

Now, from this proposed mechanism the total Os (VIII) may be obtained from Eq. (2):

$$[\text{Os(VIII)}]_{\text{total}} = \text{C} + \text{C}_1 + \text{C}_2. \qquad (2)$$

TABLE 1

Effect of Variation of Hexacyanoferrate(III) Concentration on the Reaction Rate[a]

A. $[K_3Fe(CN)_6] \times 10^4\ M$	5.00	10.00	15.00	20.00	25.00	30.00	35.00	45.00	50.00
$-dc/dt \times 10^5$ (mol·liter^{-1}·min^{-1})	1.53	1.65	1.50	1.50	1.50	1.50	1.60	1.57	1.60
B. $[K_3Fe(CN)_6] \times 10^4\ M$	5.00	10.00	30.00	40.00	50.00	60.00			
$-dc/dt \times 10^5$ (mol·liter^{-1}·min^{-1})	2.00	2.10	2.00	2.09	2.00	2.04			

[a] A: [NaOH] = $9.00 \times 10^{-3}\ M$; [2-methylpentane-2,4-diol] = $1.00 \times 10^{-2}\ M$; $[OsO_4] = 10.50 \times 10^{-5}\ M$; $\mu = 1.00\ M$; temperature: 30°C. B: [NaOH] = $2.00 \times 10^{-2}\ M$; [butane-1,4-diol] = $2.00 \times 10^{-3}\ M$; $[OsO_4] = 3.80 \times 10^{-5}\ M$; $\mu = 0.50\ M$; temperature: 30°C.

Thus, considering the equilibrium conditions for steps (I), (II), and (III) and solving in terms of total osmium (VIII) concentration, the final rate law is derived in Eq. (3):

$$-\frac{d[\mathrm{Fey}]}{dt} = \frac{2k_1KK_1K_2[\mathrm{S}][\mathrm{Os(VIII)}]_t[\mathrm{OH}]^{2-}}{1+K_1[\mathrm{OH}^-]\{1+KK_2[\mathrm{S}][\mathrm{OH}^-]\}}. \qquad (3)$$

Since K_1 is the equilibrium constant for step (II), in which the equilibrium is more inclined toward the right, due to greater formation of $OsO_4\ (OH)^{2-}{}_2$, hence, the inequality $K_1[OH^-] \gg 1$ will evidently exist, and the rate equation, Eq. (3), is reduced to Eq. (4):

$$-\frac{d[\mathrm{Fey}]}{dt} = \frac{2k_1KK_2[\mathrm{S}][\mathrm{Os(VIII)}]_t[\mathrm{OH}^-]}{1+KK_2[\mathrm{S}][\mathrm{OH}^-]}. \qquad (4)$$

The rate law, Eq. (4), apparently accounts for the observed kinetics. At very low concentrations of hydroxide ion and diols the inequality $1 \gg KK_2[S][OH^-]$ is evident, and the rate law, Eq. (4), is reduced to

$$-\frac{d[\mathrm{Fey}]}{dt} = 2k_1KK_2[\mathrm{S}][\mathrm{Os(VIII)}]_t[\mathrm{OH}^-] \qquad (5)$$

which explains well the experimental results obtained at these low concentrations (Fig. 2). The values of k_1KK_2 calculated from the slopes of the straight lines are 1.07×10^3 and 1.14×10^3 in the case of 2-methylpentane-2, 4-diol and 7.40×10^2 and 7.30×10^2 in the case of butane-2,4-diol from hydroxyl ion and subtrate variation, respectively.

At sufficiently higher concentrations of hydroxyl ion and diols the above inequality will be valid in the reverse direction, i.e., $KK_2\ [S][OH^-] \gg 1$, and Eq. (4) is reduced to Eq. (6):

$$-\frac{d[\mathrm{Fey}]}{dt} = 2k_1[\mathrm{Os(VIII)}]_t. \qquad (6)$$

Equation (6) clearly explains the zero-order kinetics with respect to hydroxyl ion and diols at their higher concentrations. The values of k_1 were not calculated due to the absence of perfect zero-order kinetics at higher concentrations.

Further verification of the rate law, Eq. (4), can again be obtained according to:

$$\frac{1}{v_i} = \frac{1}{2k_1KK_2[\mathrm{S}][\mathrm{Os(VIII)}]_t[\mathrm{OH}^-]} + \frac{1}{2k_1[\mathrm{Os(VIII)}]_t}, \qquad (7)$$

where $1/v_i = 1/-d[\mathrm{Fey}]/dt$.

A plot of the reciprocal of the reaction velocity against the reciprocal of the hydroxyl ion or diol concentration should give a straight line with a positive intercept

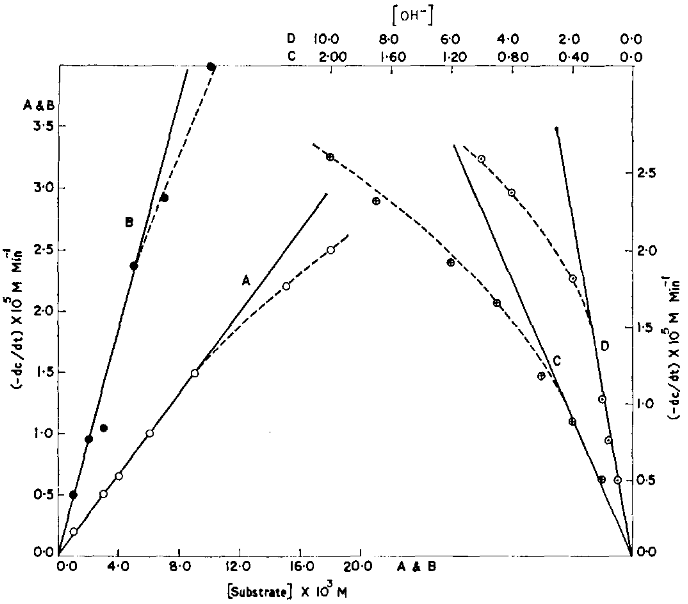

FIG. 2. Effect of variation in concentrations of substrate and hydroxide ion on the reaction rate. A. $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ *M*; $[NaOH] = 7.00 \times 10^{-3}$ *M*; $[OsO_4] = 10.50 \times 10^{-5}$ *M*; $\mu = 1.00$ *M*; temp.: 30°C. B. $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ *M*, $[NaOH] = 8.00 \times 10^{-3}$ *M*; $[OsO_4] = 3.60 \times 10^{-5}$ *M*; $\mu = 0.50$ *M*; temp.: 30°C. C. $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ *M*; [2-methylpentane-2,4-diol] $= 1.00 \times 10^{-2}$ *M*; $[OsO_4] = 10.50 \times 10^{-5}$ *M*; $\mu = 1.00$ *M*, temp.: 30°C. D. $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ *M*; [butane-1,4-diol] $= 2.00 \times 10^{-2}$ *M*; $[OsO_4] = 3.60 \times 10^{-5}$ *M*; $\mu = 0.50$ *M*; temp.: 30°C.

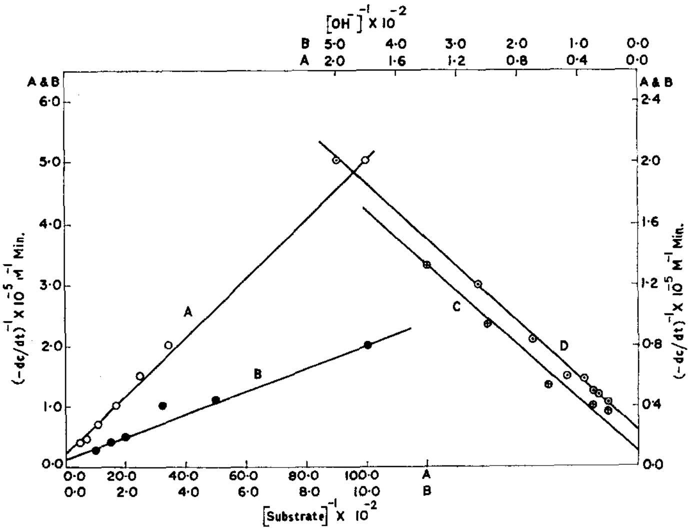

FIG. 3. Plot of $(-dc/dt)^{-1}$ vs $[\text{substrate}]^{-1}$ and $(-dc/dt)^{-1}$ vs $[OH^-]^{-1}$ for: A. $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ *M*; $[NaOH] = 7.00 \times 10^{-3}$ *M*; $[OsO_4] = 10.50 \times 10^{-5}$ *M*; $\mu = 1.00$ *M*; temp.: 30°C. B. $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ *M*; $[NaOH] = 8.00 \times 10^{-3}$ *M*; $[OsO_4] = 3.90 \times 10^{-5}$ *M*; $\mu = 0.50$ *M*; temp.: 30°C. C. $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ *M*; [2-methylpentane 2,4-diol] $= 1.00 \times 10^{-2}$ *M*; $[OsO_4] = 10.50 \times 10^{-5}$ *M*; $\mu = 1.00$ *M*; temp.: 30°C. D. $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ *M*; [butane-1,4-diol] $= 2.00 \times 10^{-2}$ *M*; $[OsO_4] = 3.60 \times 10^{-5}$ *M*; $\mu = 0.50$ *M*; temp.: 30°C.

on the y axis. Such plots are given in Fig. 3. The values of k_1KK_2 have been calculated from the slope of the straight line and are 8.33×10^2 and 8.60×10^2 for butane-1,4-diol and 1.39×10^3 and 1.36×10^3 for 2-methylpentane-2,4-diol from the hydroxide ion and substrate variation, respectively. Similarly, from the intercept the values of k_1 have been calculated as 1.60 and 1.30 for butane-1,4-diol and 0.20 and 0.21 for 2-methylpentane-2,4-diol from the hydroxide ion and the substrate variation, respectively.

The close similarity in k_1KK_2 values obtained from two different methods [from Eqs. (5) and (7)] clearly indicates the validity of the rate law, Eq. (4), and, hence, the corresponding reaction mechanism. Similarly, the values of k_1 obtained from different variations (from hydroxide ion and diol variation) are quite close to each other. This degree of agreement again shows the validity of the rate law, Eq. (4), and, hence, confirms the proposed reaction mechanism.

In these experiments the concentration of hexacyanoferrate (III) was kept in large excess as compared to diols. After completion of the reaction, the products were identified using paper chromatograpy. In the case of butane-1,4-diol, the oxidation product is succinic acid. Similarly, methyl lactic acid, oxalic acid, and acetic acid have been confirmed as the final oxidation products of 2-methylpentane-2,4-diol. Thus, on the basis of the above final oxidation products, the following probable steps are proposed.

Oxidation of butane-1,4-diol

$$\mathrm{HOCH_2{-}CH_2{-}CH_2{-}CH_2O^- + OsO_4(OH)^{2-}{}_2} \overset{K_2}{\rightleftharpoons}$$

$$\mathrm{HOCH_2{-}CH_2{-}CH_2{-}CH_2{-}O{-}OsO_4(OH)^{3-}{}_2} \qquad \text{(III)}$$

complex (C_2)

$$\text{Complex } (\mathrm{C_2}) \xrightarrow[\text{Slow}]{k_1} \mathrm{HOCH_2{-}CH_2{-}CH_2CHO + OsO_3(OH)^{3-}{}_3} \qquad \text{(IV)}$$

$$\mathrm{OsO_3(OH)^{3-}{}_3 + OH^- + 2Fe(CN)^{3-}{}_6 \longrightarrow OsO_4(OH)^{2-}{}_2 + 2Fe(CN)^{4-}{}_6 + H_2O}$$

$$\mathrm{OHC{-}CH_2{-}CH_2{-}CHO} \xrightarrow[\text{fast}]{0} \mathrm{{-}OOC{-}CH_2{-}CH_2{-}CHO} \xrightarrow[\text{fast}]{0} \mathrm{)\bar{O}OC{-}CH_2{-}CH_2{-}CO\bar{O}}$$

succinic acid

The second alcoholic group of the diol will again follow the similar path, and, ultimately, succinic aldehyde will be formed.

In the same way, a similar oxidation path might be proposed for the oxidation of 2-methylpentane-2,4-diol with alkaline hexacyanoferrate (III) using osmium tetroxide as a homogeneous catalyst.

On comparing the values of k_1KK_2 and k_1 obtained in the case of two diols, it is quite clear that the rate of complex formation is in the following order, i.e., 2-methylpentane-2,4-diol > butane-1,4-diol, whereas the rate of disproportionation is faster in butane-1,4-diol as compared to 2 methylpentane-2,4-diol.

It is well known that osmium exist in eight coordination number, but, in the proposed reaction mechanism, the water molecule is not included in order to keep the structure of the molecule simple.

The results presented in Fig. 1 clearly indicate that, as soon succinic aldehyde is formed, its oxidation occurs very rapidly, and, because of this, an abnormal increase in reaction velocity is obtained. Similarly, in the oxidation of 2-methylpentane-2,4-diol, the oxidation product, methyl lactic acid and acetaldehyde, is obtained as the intermediate product. The oxidation of this intermediate product is again more rapid than that of 2-methylpentane-2,4-diol. Thus, the experimental results have been explained on the basis of the observed initial reaction velocities.

EXPERIMENTAL

2-Methylpentane-2,4-diol and butane-1,4-diol were purchased from Fluka. Potassium hexacyanoferrate (III), potassium chloride, and sodium hydroxide were all of A.R.B.D.H. grade. The sample of osmium tetroxide was from Johnson Matthey & Co., Ltd. The solution of potassium hexacyanoferrate (III) and the diols were prepared by dissolving an exact weighed quantity of sample in distilled water, and, also, a weighed quantity of osmium tetroxide was dissolved in NaOH solution of known strength (8.92×10^{-2} N). The initiation of reaction was followed by mixing the required quantity of diol solution maintained at a constant temperature into the mixed solutions of ferricyanide, osmium tetroxide, KCl, and sodium hydroxide maintained at the same temperature. The kinetics of the reduction of hexacyanoferrate (III) was followed by estimating the amount of hexacyanoferrate (II) produced at different intervals of time with the help of a standard solution of ceric (IV) sulfate using ferroin as a redox indicator.

Since ceric (IV) sulfate is an oxidizing agent, it can also oxidize diols, but it was observed that the estimation of hexacyanoferrate (II) ion by ceric (IV) sulfate is not affected in the presence of diols.

After complete reduction of the hexacyanoferrat (III) ion, the organic acid was separated by extracting into ether followed by aqueous ammonia. The ammoniacal solution was employed to detect the anion of the organic acid by means of paper chromatography.

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