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Kinetics and Mechanism of Oxidation of Ethylglycol by Alkaline Hexacyanoferrate(III) Ions

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Kinetics of oxidation of ethylglycol by hexacyanoferrate(III) ions in aqueous alkaline medium has been reported. The reaction is first order with respect to hydroxide ion and substrate. The reaction also shows nearly first order kinetics at lower concentrations of hexacyanoferrate(III) ions which tends towards zero order at its higher concentrations. The course of reaction has been considered to proceed through the formation of activated complex between $KFe(CN)_6^{2-}$ and substrate anion which decomposes into product and $KFe(CN)_6^{3-}$.

INTRODUCTION

The kinetics of hexacyanoferrate(III) ion [Fey] oxidation of organic compounds has received much attention[1–3]. A large amount of data had been reported for the oxidation of diols[4, 5]. For collecting further information concerning the oxidation kinetics of diols in aqueous alkaline medium, we have studied the kinetics of oxidation of ethylglycol by Fey.

EXPERIMENTAL

An aqueous solution of ethylglycol of AR (BDH) grade was always prepared afresh. The samples of NaOH and Fey were of AR (BDH) grade. The ionic strength of the system was kept constant by using KCl of E. Merck grade.

The kinetic experiments were carried out by mixing the required quantity of glycol solution, maintained at a constant temperature into a mixed aqueous solution of NaOH and $K_3Fe(CN)_6$ kept in reaction flask at the same temperature.

The progress of the reaction was followed by estimating the amount of hexacyanoferrate(II) ions produced after definite interval of time with standard solution of ceric(IV) sulphate[6] using ferroin as indicator. Ethylglycollic acid was identified as the main reaction product on the basis of reference TLC employing a mixture of butanol, formic acid and water (12 : 2 : 15) as eluent.

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RESULT AND DISCUSSION

The results (Table-1) show nearly first order kinetics at lower concentrations of Fey tending towards zero order at its higher concentrations.

The values of rate have been calculated from the initial slope of the curve obtained on plotting the remaining (Fey) against time in order to avoid the possible error involved due to intervention of the products. It has been observed that the order of reaction is unity with respect to hydroxide ion and ethylglycol concentration even up to tenfold variation (Tables-2 and 3).

TABLE-1

[Ethylglycol] = 5·00 × 10^{-2} M; [OH^-] = 3·0 × 10^{-1} M; Temp = 25 ± 0.1°C

[Fey] × 10^3 M	2·0	3·0	4·0	5·0	6·0	8·0	9·0	10·0
Rate × 10^7 (mole L^{-1} min^{-1})	3·20	4·76	5·78	6·46	7·82	9·18	9·86	10·56

TABLE-2

[Ethylglycol] = 3·00 × 10^{-2} M; [Fey] = 3·00 × 10^{-3} M; μ = 1·0 M; Temp = 25 ± 0.1°C

[OH^-] × 10^1 M	0·25	0·50	1·00	2·00	3·00	5·00	7·00
Rate × 10^7 (mole L^{-1} min^{-1})	1·20	1·84	3·92	6·16	8·80	15·20	22·40

TABLE-3

[Fey] = 3·00 × 10^{-3} M; [OH^-] = 5·0 × 10^{-1} M; μ = 1·0 M; Temp = 25 ± 0·1°C

[Ethylglycol] × 10^3 M	0·50	1·00	2·00	4·00	5·00	6·00	8·00	9·00
Rate × 10^7 mole L^{-1} min^{-1}	1·43	1·56	2·20	9·24	11·00	14·70	19·80	22·00

A plot of log (rate) vs. $\sqrt{\mu}$ has been found to be a straight line with positive slope (Table-4) suggesting thereby the involvement of two similarly charged reacting species in the reaction. A plot of $rate^{-1}$ *vs.*· $[Fey]^{-1}$ has been found to be a straight line.

TABLE-4

[Fey] = 3·00 × 10^{-3} M; [Ethylglycol] = 3·00 × 10^{-2} M; [OH^-] = 3·0 × 10^{-1} M;
Temp. = 25 ± 0·1°C

μ/M	0·318	0·50	0·75	1·00	1·50	1·75
Rate × 10^7 (mole L^{-1} min^{-1})	3·20	3·42	3·84	4·16	4·76	5·10

Taking the above observation in view, the general rate exypression might be suggested for the oxidation at lower concentration of ethylglycol as:

$$-\frac{d[Fey]}{dt} = f[S][OH][Fe(CN)_6^{3-}] \qquad (1)$$

The dependence of reaction rate on $[OH^-]$ indicates that OH^- is involved actively in the reaction. As reported earlier in the oxidation of alcohols[7, 8] by potassium permanganate in alkaline medium the alkoxide ion is formed in the following way:

$$R\text{—}CH_2OH + OH^- \rightarrow RCH_2O^- + H_2O$$

In view of the above experimental results the probable mechanism for the oxidation of ethylglycol by alkaline [Fey] might be formulated as follows:

$$K^+ + [Fe(CN)_6^{3-}] \overset{K}{\rightleftharpoons} [KFe(CN)_6^{2-}] \tag{I}$$

$$S^+[OH^-] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S^- + H_2O \tag{II}$$

$$S^- + [KFe(CN)_6^{2-}] \xrightarrow[\text{(slow)}]{k_2} \text{Complex (C)} \tag{III}$$

$$\text{Complex (C)} \xrightarrow[\text{(fast)}]{k_3} S^\circ + [KFe(CN)_6^{3-}] \tag{IV}$$

$$S^\circ + [KFe(CN)_6^{2-}] \xrightarrow[\text{(fast)}]{k_4} \text{Product} + [KFe(CN)_6^{3-}] \tag{V}$$

where 'S' represents the substrate and 'C' is a labile complex between substrate anion and $[KFe(CN)_6^{2-}]$. In step (III) the complex formed will disproportionate at a faster rate as represented in step (IV) and so the reversibility of step (III) will not arise. The formation of complex of organic substrate and $[KFe(CN)_6^{2-}]$ is evident from the retarding trend of rate with an increase in [Fey]. The positive salt effect supports the view that the reaction is occuring between alkoxide ion and $[KFe(CN)_6^{2-}]$.

Now considering steady state condition and the total [Fey] concentration being represented by $[Fey]_T$ whereas $[Fey]_T = [Fe(CN)_6^{3-}] + [KFe(CN)_6^{2-}]$, the rate law can be given as follows:

$$-\frac{d[Fey]}{dt} = \frac{2Kk_1k_2[S][OH^-][Fey]_T[K^+]}{k_{-1}[H_2O]\{1 + K[K^+]\} + k_2K[K^+][Fey]_T} \tag{2}$$

This equation clearly explains the first order kinetics with respect to [ethylglycol] and $[OH^-]$. It also explains first order kinetics with respect to [Fey] tending towards zero order at its higher concentration:

The previous workers[9, 10] have reported that step (I) is mainly towards right. Thus $K[K^+] \gg 1$ and equation (1) reduces to

$$-\frac{d[Fey]}{dt} = \frac{2k_1k_2[S][OH^-][Fey]_T}{k_{-1}[H_2O] + k_2[Fey]_T}$$

At low [Fey], $k_2[Fey]_T$ will be quite small as compared to unity and the inequality $k_{-1}[H_2O] \gg K_2[Fey]_T$ will hold good. Thus equation reduces to:

$$-\frac{d[Fey]}{dt} = \frac{2k_1k_2[OH^-][Fey]_T[S]}{k_{-1}[H_2O]} \tag{3}$$

The above equation explains first order kinetics with respect to substrate, hydroxide ion and [Fey] at low concentrations. At high [Fey], inequality $k_{-1}[H_2O] \ggg k_2[Fey]_T$ would not be applicable because the value of $k_2[Fey]_T$ would increase with increase in [Fey]. Thus the rate of reaction would not be directly poportional to [Fey].

Further the validity of rate law can be tested by rewriting the equation (2).

$$\frac{1}{d[Fey]/dt} = \frac{k_{-1}[H_2O]}{2k_1k_2[S][OH^-][Fey]_T} + \frac{1}{2k_1[S][OH^-]} \tag{3}$$

The plots of rate^{-1} *vs.* reciprocal of $[Fey]_T^{-1}$ gives a straight line with a positive intercept at rate-axis, indicating the validity of rate equation. The values of k_1k_2/k_{-1} and k_1 as calculated from the slope and intercept of this plot, have been evaluated under two different condition (Table-5, 6)

TABLE-5

[Ethylglycol] = 5·00 × 10^{-2} M; [OH^-] = 3·0 × 10^{-1} M; μ = 1·0 M; Temp = 25 ± 0·1°C

$[Fey]^{-1} \times 10^{-3}$	0·50	0·33	0·25	0·20	0·17	0·125	0·11	0·10
$Rate^{-1} \times 10^{-7}$	0·31	0·21	0·17	0·15	0·13	0·11	0·10	0·09
k_1k_2/k_{-1}	4·90 × 10^{-3}							
k_1	4·76 × 10^{-5}							

TABLE-6

[Ethylglycol] = 7·5 × 10^{-2}M; [OH^-] = 4 × 10^{-1}M; μ = 1·0M; Temp. = 25 ± 0·1°C

$[Fey]^{-1} \times 10^{-3}$	0·50	0·33	0·25	0·20	0·14	0·125	0·10
$Rate^{-1} \times 10^{-7}$	0·25	0·16	0·125	0·13	0·11	0·10	0·09
k_1k_2/k_{-1}	6·67 × 10^{-3}						
.k_1	5·56 × 10^{-3}						

The results show a good agreement betweem the two values of constants, supporting thereby the rate law and mechanism proposed by us.

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