Asian Journal of Chemistry Vol. 15, Nos. 3 & 4 (2003), 1724–1728

Kinetics and Mechanism of the Oxidation of Adonitol by Hexacyanoferrate(III) Ion in Aqueous Alkaline Medium

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The rate of oxidation of adonitol by hexacyanoferrate(III) ion in aqueous alkaline medium is directly proportional to the organic substrate and hydroxide ion concentration. The rate of hexacyanoferrate(III) ion is first order at considered concentrations. A probable mechanism has been suggested.

Key Words: Kinetics and mechanism, Adonitol, Hexacyanoferrate(III) Ion.

INTRODUCTION

The kinetics of oxidation of polyhydroxy alcohols have been less studied in alkaline medium. The data is available dealing with alkaline permanganate[1]. The kinetic data suggest that the oxidation involves the formation of a complex between the amount of substrate and $[Fe(CN)_6]^{2-}$. The complex gives the free radical and $[Fe(CN)_6]^{3-}$ ions.

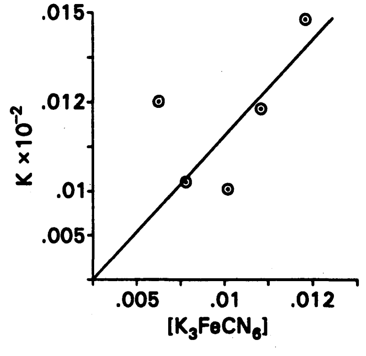
Oxidation kinetics of polyhydroxy alcohols has been studied by some workers[2–4].

RESULTS AND DISCUSSION

(a) Effect of variation of oxidant

At lower concentration of hexacyanoferrate(III) ion, the rate of reaction is found to be first order (Fig. 1). The concentration of hexacyanoferrate(III) varied for adonitol was 0.59×10^{-2} to 1.765×10^{-2} M.

The initial reaction rate values were calculated by plotting remainings of ferricyanide ion concentration against time.



Effect of variation of oxidant on rate of reaction
NaOH = 2.35×10^{-2} to 5.82×10^{-2} M.;
μ = 1 M at 30°C

Fig. 1

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TABLE-1
EFFECT OF VARIATION OF OXIDANT ON RATE OF REACTION
NaOH = 2.35×10^{-2} to 5.82 M $\times 10^{-2}$ (μ = 1 M at 30°C)

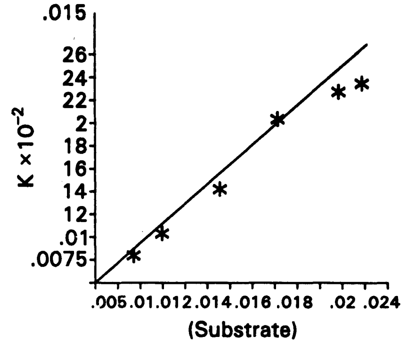
S.No.	$K_3[Fe(CN)_6]$	K $\times 10^{-2}$ (from graph)
1.	1.7646	1.260
2.	1.4700	1.134
3.	1.1760	1.100
4.	0.7350	1.090
5.	0.5900	1.005

(b) Effect of variation of susbstrate [Adonitol]

The substrate concentraion was varied from 2.35×10^{-2} M to 0.88×10^{-2} M. The rate of the reaction follows first-order kinetic, with respect to sodium hydroxide.

TABLE-2
EFFECT OF VARIATION OF ADONITOL ON RATE OF REACTION
NaOH = 2.35×10^{-2} to 5.82 M $\times 10^{-2}$
(μ = 1 M at 30°C)

S.No.	Adonitol $\times 10^{-2}$ M	K $\times 10^{-2}$ (from graph)
1.	0.88	0.860
2.	1.80	1.152
3.	1.47	1.450
4.	1.76	2.370
5.	2.05	2.370
6.	2.35	2.452

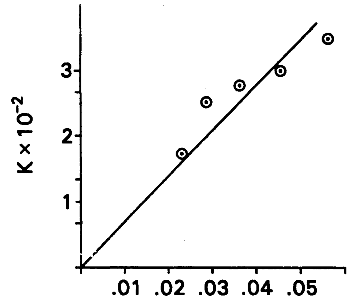


Effect of variation of adonitol on rate of reaction
NaOH = 2.35×10^{-2} to 5.82×10^{-2} M.;
μ = 1 M at 30°C

Fig. 2

(c) Effect of Variation of [NaOH] on the reaction rate

A graph between K_s values and [NaOH] gives a straight line passing through origin suggesting that order with respect to hydroxide ion is one. The concentration of NaOH is varied from 2.35×10^{-2} to 5.82×10^{-2} M.



Effect of variation of [NaOH] on rate of reaction
NaOH = 2.35×10^{-2} to 5.82×10^{-2} M.;
μ = 1 M at 30°C

Fig. 3

TABLE-3
EFFECT OF VARIATION OF [NaOH] ON RATE OF REACTION
NaOH = 2.35×10^{-2} to 5.82×10^{-2} M ($\mu = 1$ M at 30°C)

S.No.	NaOH × 10^{-2} M	K × 10^{-2} (graphical)	K/NaOH
1.	2.35	1.84	0.7830
2.	2.90	2.86	0.9896
3.	3.52	2.94	0.8352
4.	4.05	3.17	0.7830
5.	5.80	3.84	0.6960

(d) Effect of variation of ionic strength on reaction rate

The ionic strength of the medium has been changed by using KCl at concentration of other reactants. The result indicates positive effect on ionic strength.

TABLE-4
EFFECT OF VARIATION OF IONIC STRENGTH
ON REACTION RATE
NaOH = 2.35×10^{-2} to 5.82 M × 10^{-2} ($\mu = 1$ M at 30°C)

S.No.	KCl × 10^{-2}	K × 10^{-2} M
1.	0.882	0.566
2.	1.764	6.200
3.	2.350	6.400

Mechanism

Taking the above observations in view at lower concentrations of reactants, the following rate expression may be suggested:

$$\frac{-d[\text{Fey}]}{dt} = [\text{Fe(CN)}_6]^{3-}[\text{OH}^-[\text{s}]] \qquad \text{(I)}$$

or

$$\text{Rate} = [\text{Fe(CN)}_6]^{3-}[\text{OH}]^1 \quad [\text{Adonitol}] \qquad (1)$$

where K is constant for adonitol. Literature reveals that the oxidation of organic substrate takes place both with $[Fe(CN)_6]^{3-}$ ion and $[Fe(CN)_6]^{2-}$ ion This is because when $[Fe(CN)_6]^{3-}$ ion is used as an oxidant in aqueous alkaline medium the following equilibrium exists:

$$3K^+ + [\text{Fe(CN)}_6]^{3-} \rightleftharpoons K_3[\text{Fe(CN)}_6]$$

It is also reported that the equilibrium[3] is also mainly towards right.

Thus, in order to explain the aforesaid results the reaction mechanism considering $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{2-}$ ion as oxidants is proposed in **Scheme-1**.

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

$$S + OH^- \underset{K^{-1}}{\overset{K_1}{\rightleftharpoons}} S^- + H_2O \tag{II}$$

$$S^- + [Fe(CN)_6]^{2-} \underset{Slow}{\overset{K_2}{\rightleftharpoons}} Complex\ (C_1) \tag{III}$$

$$S^- + [Fe(CN)_6]^{3-} \xrightarrow[Slow]{K_2} Complex\ (C_2) \tag{IV}$$

$$Complex\ (C_1) \xrightarrow[Fast]{K_4} S^\bullet + [Fe(CN)_6]^{3-} \tag{V}$$

$$Complex\ (C_2) \xrightarrow[Fast]{K_5} S^\bullet + [Fe(CN)_6]^{4-} \tag{VI}$$

$$S^\bullet + [Fe(CN)_6]^{2-} \xrightarrow{Fast} Product + [Fe(CN)_6]^{3-} \tag{VII}$$

$$S^\bullet + [Fe(CN)_6]^{3-} \xrightarrow{Fast} Product + [Fe(CN)_6]^{3-} \tag{VIII}$$

Scheme-1

The complexes formed in steps (III) and (IV) disproportionate at a faster rate as represented in steps (V) and (VI), but the oxidation rate would also depend on the concentration of the species of hexacyanoferrate(III) and (IV) and the rate of disappearance of hexacyanoferrate(III) ion concentration as

$$\frac{-d[Fey]}{dt} = K_2[s][KFe(CN)_6]^{2-} + K_3[s][KFe(CN)_6]^{3-} \tag{2}$$

In order to derive the final rate law equation it would be most appropriate to assume the total hexacyanoferrate(III) ion concentration as

$$[Fe(CN)_6^{3-}]_T = [Fe(CN)_6]^{3-} + [KFe(CN)_6]^{2-} \tag{3}$$

Thus considering the steady state condition and equation (3), the final rate law equation in terms of decreasing hexacyanoferrate(III) ion concentration would be given by equation (4).

$$\frac{-d[Fey]}{dt} = \frac{2K_1[s][OH][Fey]_T\{K_3 + K_2 + (KK^+)\}}{K_{-1}[1 + (KK^+)]] + [Fey]_T\{K_3 + K_2(KK^+)\}} \tag{4}$$

The derived rate law equation (4) is almost consistent with the observed kinetics, *i.e.*, it shows first order kinetics with respect to substrate and hydroxide ion concentration as well as the retarding trend with respect to hexacyanoferrate(III) ion concentration. The final oxidation product is the corresponding acid.

EXPERIMENTAL

The standard solution of hexacyanoferrate(III) ion was prepared fom AR (BDH) sample Adonitol used of AR (BDH). Stock solution of NaOH (AR, BDH) was prepared in double distilled water. The ionic strength of the medium was followed by estimating the amount of hexacyanoferrate(II) ion produced after a definite time interval with a solution of ceric(IV) sulphate using ferroin as a redox indicator, The products were identified by TLC.

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(*Received*: 17 February 2003; *Accepted*: 12 May 2003) AJC-3091