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Chemical Kinetics

KINETICS AND MECHANISM OF OXIDATION OF D-GLUCOSE BY HEXACYANOFERRATE(III) IN THE PRESENCE OF ETHYLENEDIAMINE

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For the first time, the kinetics of oxidation of D-Glucose by hexacyanoferrate-(III) in the presence of ethylenediamine has been studied. The reaction follows zero order kinetics with respect to [hexacyanoferrate (III)] and first order both with respect to [reducing sugar] and [hydroxide ion]. The effect of dielectric constant on the reaction rate has also been investigated. The reaction has been studied at four different temperatures and the data have been utilized for the evaluation of thermodynamic parameters. A general mechanism involving the formation of intermediate enediol anion has been proposed. It is found that the rate of enolization is the rate of oxidation. Formic acid and arabonic acid have been identified as the oxidation products.

Keywords: Kinetics & Mechanism; Oxidation; D-Glucose; Hexacyanoferrate-(III); Ethylenediamine; Reducing Sugar; Enolization; Formic & Arabonic Acids

INTRODUCTION

KINETIC studies of oxidation of reducing sugars by Cu(II) in the presence of complexing agents in alkaline medium were made by Singh *et al.* (1955). Their results were confirmed by Marshall and Waters (1960, 1961). Nath and Singh (1965) and Tiwari and Singh (1969) studied the oxidation kinetics of reducing sugars by hexacyanoferrate(III) in the presence of sodium hydroxide and ammonium hydroxide.

The essential kinetic features of the oxidation of D-Glucose by hexacyanoferrate-(III) in the presence of ethylenediamine has been studied for the first time. Our main aim was to find out whether the role of hexacyanoferrate(III) in the oxidation of D-Glucose is similar to the role of hexacyanoferrate(III) in the presence of sodium hydroxide and ammonium hydroxide. In this reaction, there is basic catalysis. In order to explain the role of ethylenediamine in this reaction the present study has been made.

EXPERIMENTAL

Potassium hexacyanoferrate(III), ceric sulphate, potassium chloride used were of A.R. (B.D.H.) grade samples. Ethylenediamine (Sisco chemicals) was used as such. The standard solution of D-glucose A.R (B.D.H.) was always prepared daily before commencement of work. The rate of the reaction was determined by

estimating the amount of ferrocyanide produced at different time intervals, against a standard solution of ceric sulphate using ferroin as redox indicator.

RESULTS AND DISCUSSION

In the oxidation of D-glucose by hexacyanoferrate(III) in the presence of ethylenediamine, the reaction has been studied with respect to hexacyanoferrate(III), keeping the concentration of other reactants constant. The ionic strength of the medium was maintained constant with the help of standard solution of potassium chloride.

A straight line is obtained by plotting remaining hexacyanoferrate(III) concentration against time (Fig. 1, curves A and B) indicating zero order kinetics with respect to [hexacyanoferrate (III)]. There is some deviation in the latter part of the kinetic run due to decrease in pH of the system caused by the gradual formation of acidic products. Table I shows the effect by variation of [hexacyanoferrate (III)] on the reaction rate. The K_s values obtained are practically constant confirming zero order dependence of the reaction rate on [hexacyanoferrate (III)].

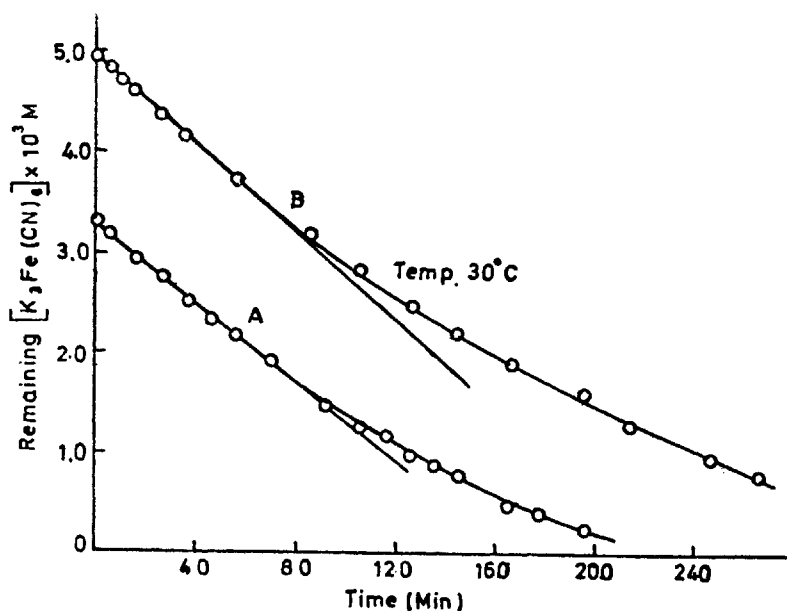


FIG. 1—Plot of remaining [Hexacyanoferrate(III)] against time.

- (A) $[K_3Fe(CN)_6] = 3.33 \times 10^{-3} M$; $[Glucose] = 10.00 \times 10^{-3} M$;
 $[ethylenediamine] = 2.00 \times 10^{-2} M$; $\mu = 0.20 M$.
- (B) $[K_3Fe(CN)_6] = 5.00 \times 10^{-3} M$; $[Glucose] = 10.00 \times 10^{-3} M$;
 $[ethylenediamine] = 2.00 \times 10^{-2} M$; $\mu = 0.20 M$.

Table II shows the effect of variation of [D-glucose] on the reaction rate. A perusal of this table shows that the reaction rate does not increase in the same

TABLE I

Effect of varying [hexacyanoferrate(III)] on the reaction rate at 30 °C
 [D-Glucose] = 10.0×10^{-2} M; [ethylenediamine] = 2.0×10^{-2} M; $\mu = 0.20$ M.

$[K_3Fe(CN)_6] \times 10^3$ M	$K_s \times 10^5$ mole lit ⁻¹ min ⁻¹
1.00	2.15
1.25	2.25
2.00	2.20
2.50	2.20
3.33	2.26
4.00	2.26
5.00	2.20
10.00	2.20

TABLE II

Effect of varying [D-glucose] on the reaction rate at 30 °C
 (A) $[K_3Fe(CN)_6] = 2.5 \times 10^{-3}$ M; [ethylenediamine] = 2.0×10^{-2} M; $\mu = 0.20$ M.

[Glucose] $\times 10^2$ M	pH	$[OH^-]$ $\times 10^4$ M	Observed $K_s \times 10^5$ mole lit ⁻¹ min ⁻¹	Actual K'_s $\times 10^5$ mole lit ⁻¹ min ⁻¹	Actual $K'_s \times 10^5$ [Glucose] min ⁻¹
0.50	10.75	8.318	0.27	0.27	0.54
0.75	10.75	8.318	0.44	0.44	0.58
1.00	10.73	7.943	0.57	0.59	0.59
1.25	10.73	7.943	0.70	0.73	0.58
2.50	10.71	7.586	1.25	1.38	0.55
5.00	10.67	6.918	2.00	2.70	0.54
7.50	10.63	6.310	3.00	3.95	0.53
10.00	10.62	6.166	4.00	5.40	0.54

(B) $[K_3Fe(CN)_6] = 2.5 \times 10^{-3}$ M; [ethylenediamine] = 2.0×10^{-2} M; $\mu = 0.20$ M.

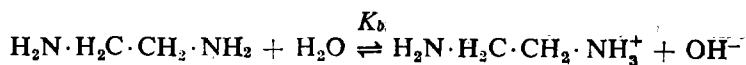
[Glucose] $\times 10^2$ M	pH	$[OH^-]$ $\times 10^4$ M	Observed $K_s \times 10^5$ mole lit ⁻¹ min ⁻¹	Actual $K'_s \times 10^5$ mole lit ⁻¹ min ⁻¹	Actual $K'_s \times 10^5$ [Glucose] min ⁻¹
1.0	10.55	5.248	0.30	0.30	0.30
1.5	10.55	5.248	0.47	0.47	0.31
2.0	10.55	5.248	6.58	0.58	0.29
4.0	10.49	4.571	0.83	1.10	0.27
8.0	10.43	3.981	1.60	2.11	0.26
10.0	10.43	3.981	2.64	2.82	0.28
20.0	10.31	3.020	2.75	4.87	0.24
25.0	10.26	2.691	3.33	6.49	0.26
50.0	10.07	1.738	4.80	14.49	0.28

proportion in which the [sugar] is raised. It is also seen that with the change in [D-glucose], there is a slight change in the pH of the system (Column 2, Table II). The actual order of the reaction with respect to [D-glucose] will be therefore obtained by varying the [sugar] at constant pH or constant $[\text{OH}^-]$. Hence K'_s values have been calculated by taking into consideration the K_s value in each run and the K_s value equivalent to decrease in pH in the following manner:

$$\text{Actual } K'_s \text{ value} = \text{observed } K_s \text{ value} + K_s \text{ value equivalent to decrease in pH.}$$

By the decrease in pH, equivalent K_s value has been calculated in each run as there is direct proportionality with respect to $[\text{OH}^-]$. The values of $K'_s/[\text{D-glucose}]$ are fairly constant indicating first order dependence of the reaction rate on [D-glucose].

The pH value for different [ethylenediamine] were measured and corresponding $[\text{OH}^-]$ was calculated. The values of $K_s/[\text{OH}^-]$ are fairly constant (Column 6, Table III) showing first order kinetics with respect to $[\text{OH}^-]$. The plot of K_s vs. [ethylenediamine]^{1/2} is linear passing through the origin (Fig. 2). This shows that the dissociation of ethylenediamine is given by,



Hence,

$$[\text{OH}^-] = \sqrt{K_b[\text{ethylenediamine}]}$$

TABLE III

Effect of varying [ethylenediamine] on the reaction rate at 30 °C

$K_3\text{Fe}(\text{CN})_6 = 2.5 \times 10^{-3}\text{M}$; $[\text{Glucose}] = 10.0 \times 10^{-3}\text{M}$; $\mu = 0.20\text{M}$.

[ethylenediamine] $\times 10^2\text{M}$	[ethylenediamine] ^{1/2} $\times 10\text{M}$	pH	$[\text{OH}^-]$ $\times 10^4\text{M}$	$K_s \times 10^5$ mole lit ⁻¹ min ⁻¹	$\frac{K_s \times 10^5}{[\text{OH}^-]}$ min ⁻¹
1.0	1.00	10.13	1.99	1.25	0.62
2.0	1.41	10.39	3.63	2.20	0.61
4.0	2.00	10.57	5.49	2.93	0.54
5.0	2.23	10.64	6.46	3.55	0.55
10.0	3.16	10.73	7.94	4.44	0.56
12.5	3.54	10.77	8.71	5.00	0.57

Table IV shows the effect of variation of the dielectric constant on the rate of the reaction. It has been observed that the rate constant decreases slightly with the decrease in dielectric constant of the medium. Further a plot of $\log_{10} K_s$ vs. $1/D$

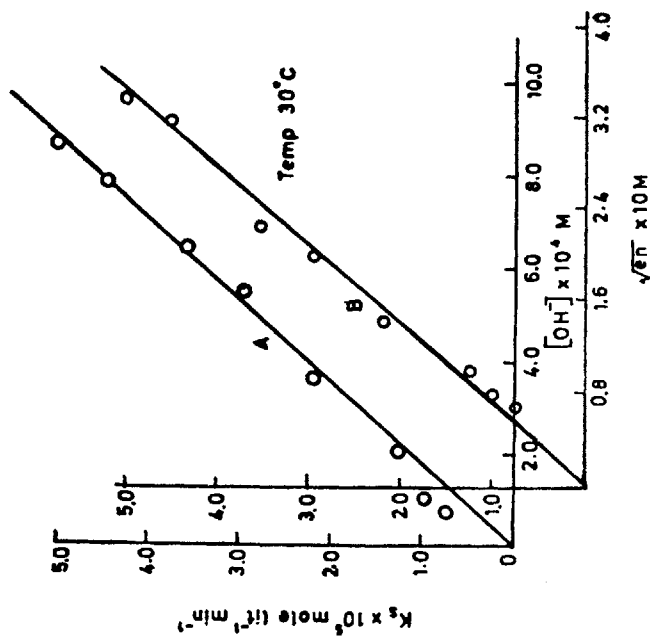


FIG. 2 (A).—Plot of reaction rate (K_p) against hydroxide ion concentration $[K_2Fe(CN)_6] = 2.5 \times 10^{-3} \text{ M}$; $[Glucose] = 10.00 \times 10^{-3} \text{ M}$; $\mu = 0.20 \text{ M}$.

FIG. 2 (B).—Plot of reaction rate (K_p) against

$\sqrt{\text{ethylenediamine concentration}}$. $[K_2Fe(CN)_6] = 2.50 \times 10^{-3} \text{ M}$; $[Glucose] = 10.00 \times 10^{-3} \text{ M}$; $\mu = 0.20 \text{ M}$.

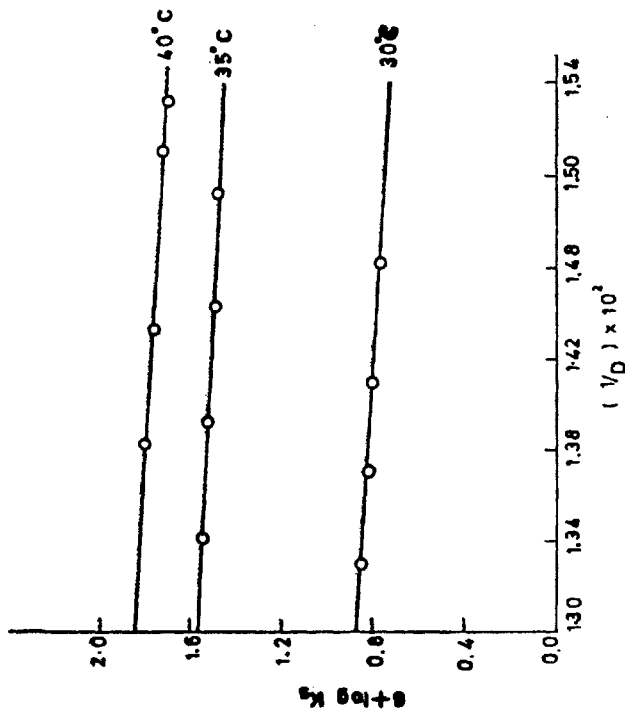


FIG. 3.—Plot of reaction rate (K_p) against $1/D$. $[K_2Fe(CN)_6] = 2.50 \times 10^{-3} \text{ M}$; $[Glucose] = 10.00 \times 10^{-3} \text{ M}$; $[ethylenediamine] = 2.00 \times 10^{-3} \text{ M}$; $\mu = 0.20 \text{ M}$.

TABLE IV

Effect of varying dielectric constant on the reaction rate

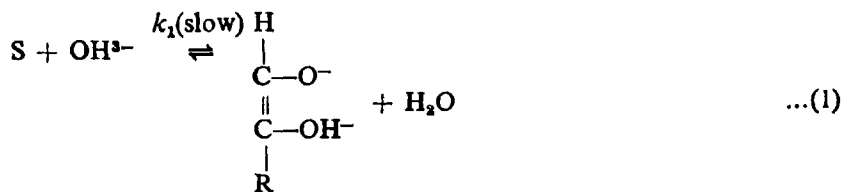
$[K_3Fe(CN)_6] = 2.5 \times 10^{-3}M$; (ethylenediamine) = $2.0 \times 10^{-2}M$; [Glucose] = $10.0 \times 10^{-2}M$; $\mu = 0.20 M$.

Temp. °C	% of Ethanol by volume	D	$1/D \times 10^3$	$K_s \times 10^5$ mole lit ⁻¹ min ⁻¹	$6 + \log K_s$
40	5	72.08	1.38	6.15	1.79
	10	69.53	1.43	5.71	1.76
	15	66.16	1.51	5.33	1.73
	20	65.32	1.53	5.00	1.70
35	5	74.15	1.34	34.78	1.54
	10	71.67	1.39	33.33	1.52
	15	69.36	1.44	30.77	1.49
	20	67.32	1.49	29.66	1.47
30	5	75.15	1.33	7.27	0.86
	10	72.83	1.37	6.67	0.82
	15	70.95	1.41	6.16	0.79
	20	68.44	1.46	5.71	0.76

gives a straight line with a negative slope (Fig. 3). This shows the reaction is occurring between negative ion and dipole molecule in accordance with the equation of Amis and Jaffe for ion-dipolar reactions,

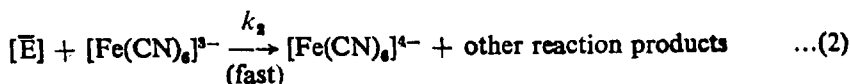
$$\ln k' = \ln k'_{\infty} + \frac{\epsilon z_B \cos \theta_0}{DkTr_0} \left(\mu_0^* - \frac{\mu^*(1 + x_{r_0})}{e} \right)$$

On the basis of aforesaid results, the probable mechanistic path for the oxidation of D-glucose by hexacyanoferrate(III) in the presence of ethylenediamine is proposed:



1, 2 enediol anion

(\bar{E})



Where S and \bar{E} represent the reducing sugar and enediol anion respectively. Considering steps (1) and (2)

$$-\frac{d[\text{Fe}(\text{CN})_6]^{3-}}{dt} = k_2[\bar{E}][\text{Fe}(\text{CN})_6]^{3-} \quad \dots(3)$$

Applying steady state condition for the enediol anion, the rate law in terms of decrease of $[\text{Fe}(\text{CN})_6]^{3-}$ might be derived as shown below:

$$-\frac{d[\text{Fe}(\text{CN})_6]^{3-}}{dt} = \frac{k_1[S][\text{OH}^-][\text{Fe}(\text{CN})_6]^{3-}}{k_1/k_2 + [\text{Fe}(\text{CN})_6]^{3-}} \quad \dots(4)$$

Since $k_2 > k_{-1}$, k_{-1}/k_2 may be neglected. The eqn. (3) reduces to

$$-\frac{d[\text{Fe}(\text{CN})_6]^{3-}}{dt} = k_1[S][\text{OH}^-] \quad \dots(5)$$

The rate law (5) clearly confirms first order kinetics with respect to both $[\text{OH}^-]$ and [reducing sugar] and zero order kinetics with respect to [hexacyanoferrate (III)] concentration. The formation of enediol anion as an intermediate in the inter conversion of reducing sugars was suggested by Anet (1964), Speck (1958) and Isbell *et al.* (1971). The rate law indicates that the rate of enolization is actually the rate of oxidation.

Positive salt effect has been observed. At low ionic strength, secondary salt effect is observed, while at higher ionic strength there is deviation due to primary salt effect being prominent.

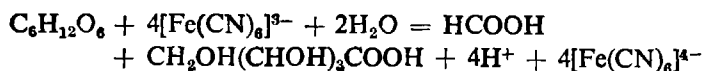
The thermodynamic parameters have been calculated at 35 °C and are given below:

Specific rate constant (K_r) $\times 10^3$ mole ⁻¹ lit sec ⁻¹	ΔE kcal/mole	ΔS e.u.	ΔF kcal/mole	A mole ⁻¹ lit sec ⁻¹
2.17	20.16	-1.28	21.00	9.16

In the present study of the oxidation of D-glucose by hexacyanoferrate(III) in the presence of ethylenediamine, there is decrease in entropy due to the solvation of the activated state rather than the reactants.

Stoichiometry

The total amount of ferricyanide ion consumed by one mole of reducing sugar was determined in the following manner: A number of sets were taken in which the concentration of ferricyanide was kept in excess of the concentration of reducing sugar. All the sets were kept for about a month and then the produced ferricyanide equivalent to the oxidized sugar was estimated as described previously. Ten to twelve determinations for stoichiometry showed that 4 moles of ferricyanide are consumed per mole of D-glucose.



Formic acid and arabonic acid have thus been confirmed as the oxidation products through equivalence and kinetic studies, as shown above and also by thin layer chromatography, using as solvent butanol saturated with ammonia on silica gel plate.

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