

Kinetics & Mechanism of Alkaline Ferricyanide Oxidation of 2-Methylpentane-2,4-diol & Pentane-1,5-diol

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Oxidation of 2-methylpentane-2,4-diol and pentane-1,5-diol by hexacyanoferrate(III) in aqueous alkaline medium has been studied. The reaction is first order with respect to hexacyanoferrate(III). The first order kinetics has been observed with respect to both OH⁻ and diol at low concentrations; the first order tends towards zero-order at higher concentrations. A probable reaction mechanism has been proposed.

THE earlier studies on alkaline hexacyanoferrate(III) oxidation of organic compounds showed that the anion derived from the organic substrates are frequently oxidized by hexacyanoferrate(III) via an electron transfer process¹. Recently, Singh and coworkers^{2,3} suggested that the oxidation of aldehydes and ketones also takes place via an electron transfer process. Whereas in one of the studies in which the oxidation of iodide ion was carried out with hexacyanoferrate(III), formation of an intermediate complex was assumed⁴. Similarly another type of bridging was found in the reaction of Co(II) ethylenediamine tetraacetate with hexacyanoferrate(III)⁵, in the first reversible equilibrium. The complex was then assumed to disproportionate slowly to products in the subsequent step. This duality of views regarding the mechanism of alkaline hexacyanoferrate(III) oxidation of organic compounds led us to study the kinetics of oxidation and 2-methyl-2,4-pentane- and pentane-1,5-diols. A probable reaction mechanism has been proposed to explain the experimental results.

Materials and Methods

The solutions of 2-methylpentane-2,4-diol and pentane-1,5-diol (Fluka), potassium hexacyanoferrate(III), potassium chloride and sodium hydroxide (AR, BDH grade) were prepared in doubly distilled water.

After equilibrating the solutions of the reactants [hexacyanoferrate(III), NaOH and diols] at the desired temperature, these were mixed and the amount of hexacyanoferrate(II) produced at different time intervals was estimated by titrating against a standard solution of ceric(IV) sulphate using ferroin as an indicator.

Ceric(IV) sulphate being an oxidizing agent could also oxidize diols but it was observed that the estimation of hexacyanoferrate(II) ion by ceric(IV) sulphate was not affected in the presence of diols.

Product analysis — 2-Methyl-lactic acid, acetic acid and oxalic acid have been identified as the oxidation products of 2-methyl-pentane-2,4-diol and

glutaric acid as the final oxidation product in the case of pentane-1,5-diol.

Results and Discussion

Pseudo-first order rate constants (k_1) have been obtained from the relation (1) and the values are given in Table 1. These values are fairly constant for the oxidation of 2-methylpentane-2,4-diol but decrease on increasing the [hexacyanoferrate(III)] in the case of pentane-1,5-diol. Such an anomalous behaviour in the case of pentane-1,5-diol might

$$k_1 = - \left(\frac{dc}{dt} \right) / [\text{hexacyanoferrate(III)}] \quad \dots (1)$$

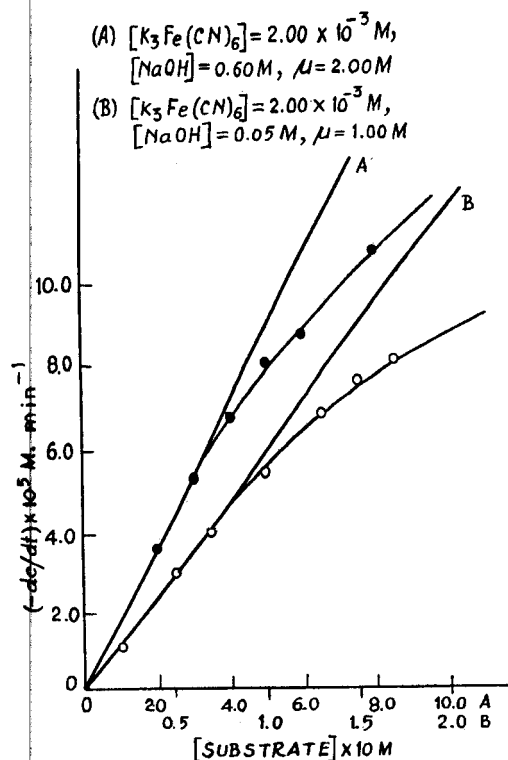
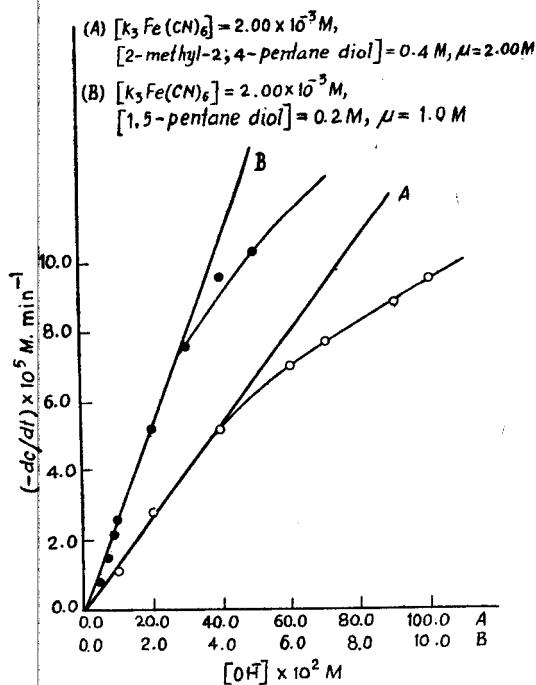
be due to the glutaric acid formed during the course of reaction. The complicated feature of the reaction was observed with varying [OH⁻] and

TABLE 1 — RATE CONSTANTS AT VARYING CONCENTRATIONS OF HEXACYANOFERRATE(III)

{(1) [NaOH] = 15 × 10⁻³M; [2-methyl-pentane-2,4-diol] = 0.1M; temp. = 35°}

{(2) [NaOH] = 4 × 10⁻²M; [pentane-1,5-diol] = 0.1M}

[K ₃ Fe(CN) ₆] × 10 ³ M		$-\frac{dc}{dt} \times 10^5$	$k_1 \times 10^3$
Initial	Consumed	moles litre ⁻¹ min ⁻¹	(min ⁻¹)
OXIDATION OF 2-METHYLPENTANE-2,4-DIOL			
0.50	0.43	0.80	1.93
1.00	0.91	1.60	1.36
1.50	1.37	1.50	1.06
2.00	1.82	2.10	1.10
3.00	2.89	3.20	1.09
4.00	3.86	4.20	1.01
OXIDATION OF PENTANE-1,5-DIOL			
0.50	0.39	2.00	7.82
0.80	0.65	4.00	6.45
1.00	0.85	4.50	5.34
3.00	2.80	6.60	2.37
5.00	4.80	8.20	1.66
7.00	6.80	2.10	1.36


 Fig. 1 — Plot of $(-dc/dt)$ versus [substrate] at 35°

 Fig. 2 — Plot of $(-dc/dt)$ versus $[OH^-]$ at 35°

[diols]. The reaction rate is directly proportional to the $[OH^-]$ and [diols] at lower concentrations but tends towards zero-order at higher concentrations (Figs. 1 and 2).

Thus, considering the above facts the general rate (2) may be suggested for the oxidation of these diols at lower concentrations of alkali and diols

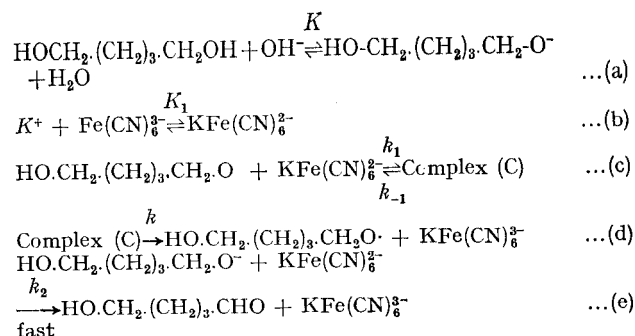
$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = k_r [S][OH^-][Fe(CN)_6^{3-}] \quad \dots(2)$$

where S represents the [diols] and k_r is the specific rate constant. The values of third order rate constant (k_r) have been calculated by dividing

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} \text{ with hexacyanoferrate(III), } OH^- \text{ and}$$

diol concentrations and these values were found to be $1.66 \times 10^{-3} \text{ mole}^{-2} \text{ litre}^2 \text{ sec}^{-1}$ for 2-methylpentane-2,4-diol and $7.83 \times 10^{-2} \text{ mole}^{-2} \text{ litre}^2 \text{ sec}^{-1}$ for pentane-1,5-diol at 30° .

Mechanism — Keeping these experimental facts in view a probable reaction mechanism is shown in Scheme 1.



Scheme 1

where C represents a complex between diol anion and $KFe(CN)_6^{2-}$. Similar steps might be proposed for 2-methylpentane-2,4-diol.

The formation of the alkoxide ion of the diol (step a) is supported by the observations of Stewart and coworkers⁶ who have studied the kinetics of permanganate oxidation of alcohols in alkaline medium and suggested that the alkoxide ion formed by the ionization of alcohols is one of the reacting species. It has already been reported by several workers^{7,8} that the step (b) of the proposed reaction scheme will be mainly towards right.

Now considering the steady state condition and the total hexacyanoferrate(III) as $[Fe(CN)_6^{3-}]_T = [Fe(CN)_6^{3-}] + [KFe(CN)_6^{2-}] + \text{Complex}$ the rate law in terms of decreasing [hexacyanoferrate(III) ion] would be

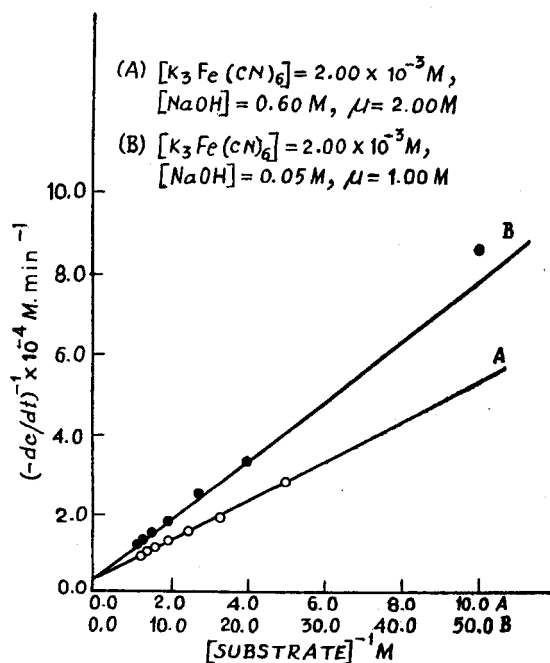
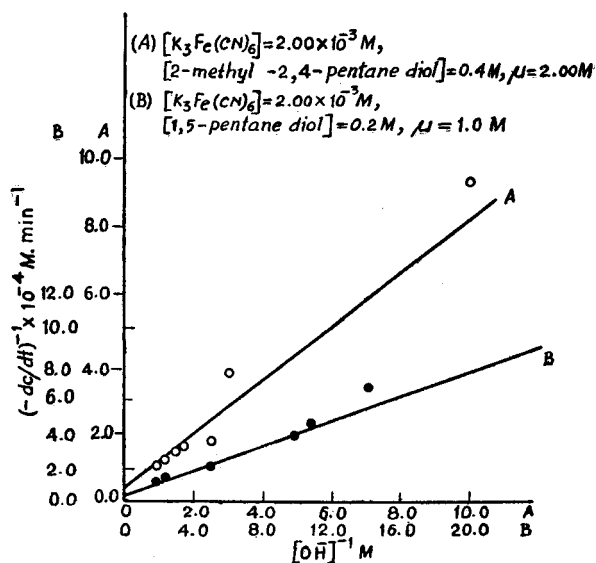
$$\begin{aligned} v_i &= \frac{-d[Fe(CN)_6^{3-}]}{dt} \\ &= \frac{2kk_1KK_1[K^+][S][OH^-][Fe(CN)_6^{3-}]_T}{(k+k_{-1})\{1+K_1[K^+]+k_1KK_1[K^+][S][OH^-]\}} \quad \dots(3) \end{aligned}$$

Eq. (3) is apparently consistent with the observed kinetics. It shows the first-order kinetics with respect to hexacyanoferrate(III) ion and also explains the observed complex kinetic feature of the reaction rate with respect to [diol] and $[OH^-]$.

Now considering the views of previous workers^{7,8} the inequality $K_1[K^+] \gg 1$ would manifest and the rate law (3) reduces to Eq. (4).

$$v_i = \frac{-d[Fe(CN)_6^{3-}]}{dt} = \frac{2kk_1K[S][OH^-][Fe]_T}{(k+k_{-1})+kK[S][OH^-]} \quad \dots(4)$$

At very low $[OH^-]$ and [diol] the inequality $(k+k_{-1}) \gg k_1K[S][OH^-]$ will hold good and under this condition the rate law (4) reduces to Eq. (5).


 Fig. 3 — Plot of $(-dc/dt)^{-1}$ versus $[substrate]^{-1}$

 Fig. 4 — Plot of $(-dc/dt)^{-1}$ versus $[OH^-]^{-1}$

$$v_i = \frac{-d[Fe(CN)_6^{3-}]}{dt} = \frac{2kk_1K[S][OH^-][Fey]_r}{k+k_{-1}} \quad \dots(5)$$

The rate law (5) clearly accounts for the first-order kinetics with respect to hexacyanoferrate(III), hydroxyl ion and diols at very low concentrations of hydroxyl ion and diols. Thus, the rate law (5) obtained at low concentration clearly supports the reaction mechanism. The values of $k+k_{-1}/kk_1K$ were calculated from the linear plots in Figs. 1 and 2 (i.e. at very low concentration of diol and hydroxyl ion) and the values are given in Table 2. A perusal of Table 2 indicates that the values obtained from

TABLE 2 — RATE CONSTANTS AT VERY LOW CONCENTRATIONS OF HYDROXYL ION AND DIOLS

$\frac{k+k_{-1}}{kk_1K}$ (from Figs. 1 and 2)	$\frac{k+k_{-1}}{kk_1K}$ (from Figs. 3 and 4)	$k_1 \times 10^3$	Variation
2-METHYLPENTANE-2,4-DIOL			
11.90	16.00	6.25	$[OH^-]$
13.70	13.20	8.33	(Diol)
PENTANE-1,5-DIOL			
0.31	0.28	9.26	$[OH^-]$
0.33	0.30	8.33	(Diol)

two different sets of conditions, viz. varying $[diol]$ and $[OH^-]$ are quite close to each other, thereby substantiating the validity of rate law (5).

At higher $[OH^-]$ and $[diol]$ the values of $k_1K[S][OH^-]$ will be quite large and, thus, the retarding trend due to the OH^- and diols would be obtained and the previous inequality will not be valid and, therefore, at higher $[OH^-]$ and $[diol]$ the rate expression (4) can be rewritten as

$$\frac{1}{v_i} = \frac{k+k_{-1}}{2kk_1K[S][OH^-][Fe(CN)_6^{3-}]} + \frac{1}{2k[Fe(CN)_6^{3-}]} \quad \dots(6)$$

This Eq. (6) predicts that a plot of $1/\text{rate}$ against $1/[S]$ or $1/[OH^-]$ should be linear with a positive intercept at y-axis. Such a trend is shown in Figs. 3 and 4. From the intercept and slope, the values of k and $k+k_{-1}/kk_1K$ have been calculated respectively and the values are given in Table 2.

Here again the values of $k+k_{-1}/kk_1K$, obtained under two sets of conditions, viz. varying $[diol]$ and $[OH^-]$ are in good agreement. This also confirms the validity of rate law (4). Hence a proposed reaction scheme appears to be quite probable.

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