

## Kinetics & Mechanism of Oxidation of Propane-1,2-diol & Butane-2,3-diol by Hexacyanoferrate(III) in Aqueous Alkaline Medium

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The oxidation of propane-1,2-diol and butane-2,3-diol by hexacyanoferrate(III) in aqueous alkaline medium has been found to be first order with respect to both hydroxide ion and the organic substrate in the lower concentration region, but tends to zero order at higher concentrations. However, under both the conditions the reaction is found to be first order with respect to [hexacyanoferrate(III)]. The kinetic data suggest that the oxidation involves formation of anions of the substrates which undergo oxidation with hexacyanoferrate (III) via the formation of complexes between the anion and hexacyanoferrate(III). The complex disproportionates into the free radical and  $KFe(CN)_6^-$  ion. The free radical produced is further oxidized to final oxidation products.

POTASSIUM permanganate and hexacyanoferrate(III) are the most common oxidants used in alkaline medium for the oxidation of organic compounds. Hexacyanoferrate(III) has been mainly employed in the systems which are obviously favourable for the extraction of a single electron from an electron-rich site in a molecule<sup>1</sup>. Although the kinetics and mechanism of hexacyanoferrate(III) oxidation of organic compounds have received much attention<sup>2</sup>, similar studies on diols are lacking. We present in this paper the results of investigation on the kinetics of oxidation of propane-1,2- and butane-2,3-diols by aq. alkaline hexacyanoferrate(III).

### Materials and Methods

All the reagents used were of AR grade and the solutions of potassium hexacyanoferrate(III), propane-1,2-diol and butane-2,3-diol were prepared in distilled water. The ionic strength of the medium was kept constant by adding aq. solution of KCl.

The reaction was followed by mixing the required quantity of diol solution with the solutions of  $K_3[Fe(CN)_6]$  at the desired temperature maintained with an accuracy of  $\pm 0.1^\circ$ . The amount of hexacyanoferrate(II) produced at different intervals of time was estimated titrimetrically<sup>2c</sup> against a standard solution of ceric(IV) sulphate using ferroin as indicator.

Ceric(IV) sulphate being an oxidizing agent could also oxidize diols, but it was observed that the estimation of hexacyanoferrate(II) by ceric(IV) sulphate in 4-5N  $H_2SO_4$  was not affected in the presence of diols. Several experiments were performed and always reproducible results were obtained, justifying the use of Ce(IV) sulphate for the estimation of hexacyanoferrate(II)

### Results and Discussion

The kinetics were studied over a wide range of concentrations. The actual nature of reaction can be shown by the plots of unreacted [hexacyanoferrate(III)] against time (Fig. 1), where the slope

( $-dc/dt$ ) values give the reaction rates. The pseudo first order reaction is quite obvious from the data in Table 1, where  $k_1$  values remain fairly constant. The complex feature of the reaction was obtained with the variation of  $[OH^-]$  and [diol]. The reaction rate which followed nearly first order kinetics with respect to low  $[OH^-]$ , tended to zero order at higher concentrations (Fig. 2). Similarly, the oxidation rate was directly proportional to [diol] in lower concentration region, but an appreciable retardation in the rate was observed at higher concentrations of the diols (Fig. 3).

Thus taking the above results into account, a general rate expression (1) might be written

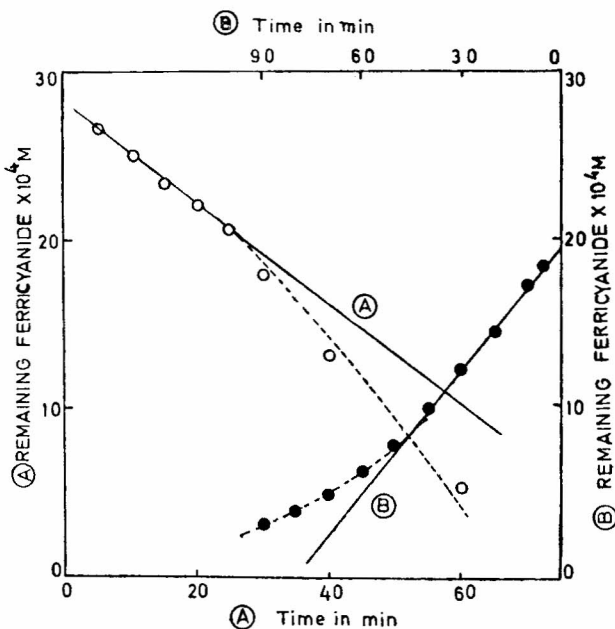


Fig. 1 — Plots of unreacted [hexacyanoferrate(III)] against time {For curve A:  $[K_3Fe(CN)_6] = 3.0 \times 10^{-3}M$ ; [propane-1,2-diol] =  $1.0M$ ;  $[NaOH] = 1.0M$ ; for curve B:  $[K_3Fe(CN)_6] = 2.0 \times 10^{-3}M$ ; [butane-2,3-diol] =  $0.4M$ ;  $[NaOH] = 0.4M$ }

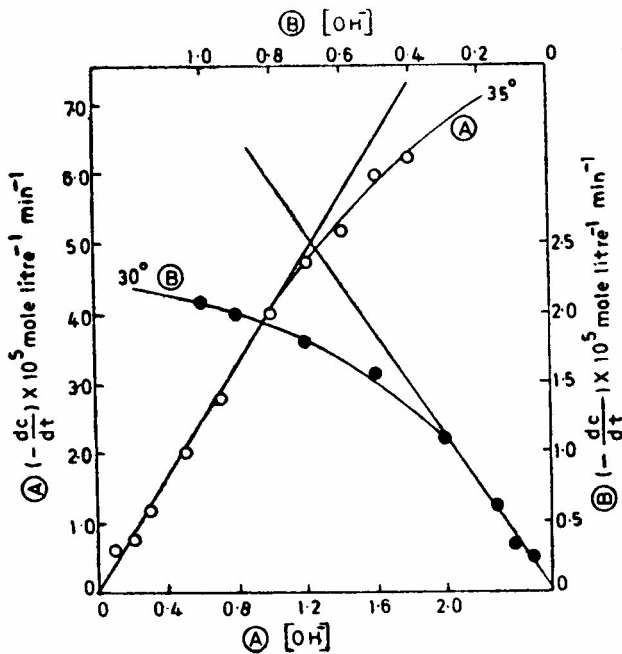


Fig. 2 — Plots of reaction rate  $(-dc/dt)$  against  $[\text{OH}^-]$  {For curve A:  $[\text{K}_3\text{Fe}(\text{CN})_6] = 3.0 \times 10^{-3} \text{ M}$ ;  $[\text{propane-1,2-diol}] = 1.0 \text{ M}$ ;  $\mu = 2.0 \text{ M}$ ; for curve B:  $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.0 \times 10^{-3} \text{ M}$ ;  $[\text{butane-2,3-diol}] = 0.4 \text{ M}$ ;  $\mu = 2.0 \text{ M}$ }

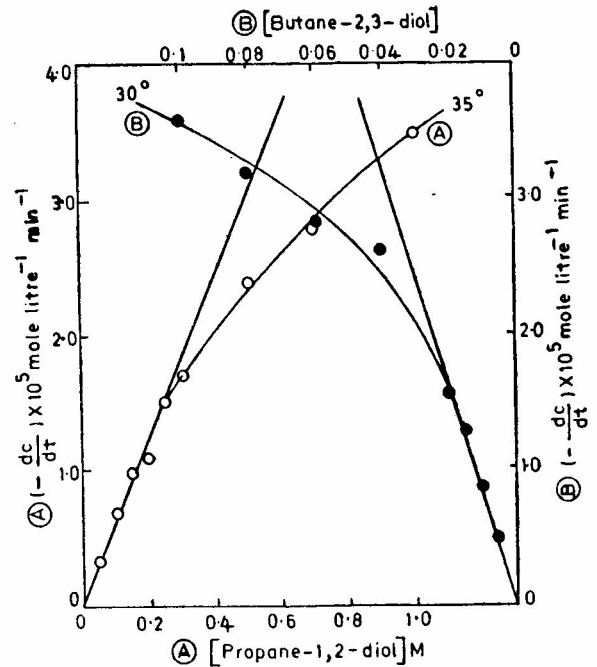


Fig. 3 — Plots of reaction rate  $(-dc/dt)$  against  $[\text{diol}]$  {For curve A:  $[\text{K}_3\text{Fe}(\text{CN})_6] = 3.0 \times 10^{-3} \text{ M}$ ;  $[\text{NaOH}] = 0.8 \text{ M}$ ;  $\mu = 2.0 \text{ M}$ ; for curve B:  $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.0 \times 10^{-3} \text{ M}$ ;  $[\text{NaOH}] = 1.0 \text{ M}$ ;  $\mu = 2.0 \text{ M}$ }

TABLE 1 — PSEUDO FIRST ORDER RATE CONSTANTS IN PROPANE-1,2-DIOL AND BUTAN-2,3-DIOL

$[\text{K}_3\text{Fe}(\text{CN})_6]_0 \times 10^3 \text{ M}$	$[\text{K}_3\text{Fe}(\text{CN})_6]_0 \times 10^3 \text{ M}$	$\frac{dc}{dt} \times 10^5$ moles litre <sup>-1</sup> min <sup>-1</sup>	$k_1 = \frac{-dc/dt}{[\text{K}_3\text{Fe}(\text{CN})_6]_0 (-dc/dt)}$ (min <sup>-1</sup> )
PROPANE-1,2-DIOL, TEMP. = 35°			
1.00	0.94	1.00	1.06
2.00	1.90	2.00	1.05
3.00	2.82	3.00	1.06
4.00	3.76	4.00	1.06
6.00	5.70	6.00	1.05
8.00	7.50	8.00	1.06
10.00	9.50	10.02	1.05
BUTANE-2,3-DIOL, TEMP. = 30°			
1.00	0.80	0.70	0.88
2.00	1.61	1.30	0.80
4.00	3.20	2.60	0.88
6.00	4.80	3.70	0.77
8.00	6.64	5.20	0.78
10.00	8.30	6.50	0.78

for the alkaline hexacyanoferrate(III) oxidation of diols.

The complex (C) is formed between the diol anion and  $\text{KFe}(\text{CN})_6^{3-}$  ion.

In the mechanistic study of alcohol-permanganate reaction<sup>3</sup> in alkaline medium, it was reported that alkoxide ion formed as a result of ionization of the alcohol was one of the reacting species (step-i). Several workers<sup>4,5</sup> have also reported that  $\text{KFe}(\text{CN})_6^{3-}$  ion formed in the equilibrium step-(ii) lies well towards right.

Now considering the steady state condition and the total [hexacyanoferrate(III)] as:

$$[\text{Fe}(\text{CN})_6^{3-}]_{\text{Total}} = [\text{Fe}(\text{CN})_6^{3-}] + [\text{KFe}(\text{CN})_6^{3-}] + [\text{complex}] \quad \dots(2)$$

the rate law in terms of decreasing concentration of hexacyanoferrate(III) ion would be:

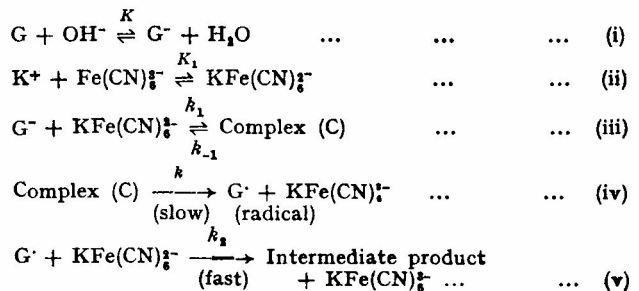
$$v_i = \frac{-[d\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{2kh_2KK_1[\text{K}^+][\text{G}][\text{OH}^-][\text{Fe}(\text{CN})_6^{3-}]_{\text{Total}}}{(k+k_1)\{1+K_1[\text{K}^+]+k_1KK_1[\text{K}^+][\text{G}][\text{OH}^-]\}} \quad \dots(3)$$

for the reaction at low concentrations of diols and hydroxide ion.

$$\frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = k[\text{G}][\text{OH}^-][\text{Fe}(\text{CN})_6^{3-}] \quad \dots(1)$$

where  $k$  is the specific rate constant and G represents diols. The observed third order rate constant was found to be  $0.63 \times 10^{-3}$  and  $13.87 \times 10^{-3}$  litre moles<sup>-2</sup> sec<sup>-1</sup> for propane-1,2-diol and butane-2,3-diol respectively at 30°.

In view of the above experimental facts, a probable mechanism shown in Scheme 1 is suggested



Scheme 1

The rate law (3) predicts the observed retardation at higher concentrations of hydroxide ion and the diols. Under these conditions as found by previous workers<sup>5,6</sup>, the inequality  $K_1[K^+] \gg 1$  would hold good and the rate law (3) reduces to Eq. (4).

$$v_i = \frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{2kk_1K[\text{G}][\text{OH}^-][\text{Fe}(\text{CN})_6^{3-}]_{\text{Total}}}{(k+k_1)+k_1K[\text{G}][\text{OH}^-]} \quad \dots(4)$$

However, sufficiently low concentrations of hydroxide ion and the diols, the inequality  $k+k_1 \gg k_1K[\text{G}][\text{OH}^-]$  will be quite valid and the rate law (4) reduces to Eq. (5)

$$v_i = \frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{2kk_1K}{k+k_1} [\text{G}][\text{OH}^-][\text{Fe}(\text{CN})_6^{3-}]_{\text{Total}} \quad \dots(5)$$

The rate law (5) clearly accounts for the first order kinetics with respect to hexacyanoferrate(III), hydroxide ion and the diols at very low concentrations of hydroxide ion and the substrates. The values of  $kk_1K/(k+k_1)$  calculated from the linear curves in Figs. 2 and 3 (i.e. at very low concentrations of hydroxide ion and diols) are quite close to each other (Table 2). This agreement in the values of  $kk_1K/(k+k_1)$  obtained from two different methods (by varying hydroxide ion and diol concentration) clearly substantiates the validity of the rate law (5).

At higher concentrations of hydroxide ion and the diols, the values of  $k_1K[\text{G}][\text{OH}^-]$  will be quite large and thus the retarding trend due to the hydroxide ion and diols, and the inequality  $(k+k_1) \gg k_1K[\text{G}][\text{OH}^-]$  will not be valid. Thus, at higher  $[\text{OH}^-]$  and [diols], further verification of the rate expression

(4) might be made by writing it as:

$$\frac{1}{v_i} = \frac{k+k_1}{2kk_1K[\text{G}][\text{OH}^-][\text{Fe}(\text{CN})_6^{3-}]_{\text{Total}}} + \frac{1}{2k[\text{Fe}(\text{CN})_6^{3-}]_{\text{Total}}} \quad \dots(6)$$

According to Eq. (6), the plot of  $1/v_i$  against  $1/[\text{OH}^-]$  or  $1/[\text{G}]$  should be linear with a positive intercept at  $y$ -axis. The linear curves (Figs. 4 and 5) with a positive intercept at  $y$ -axis obtained

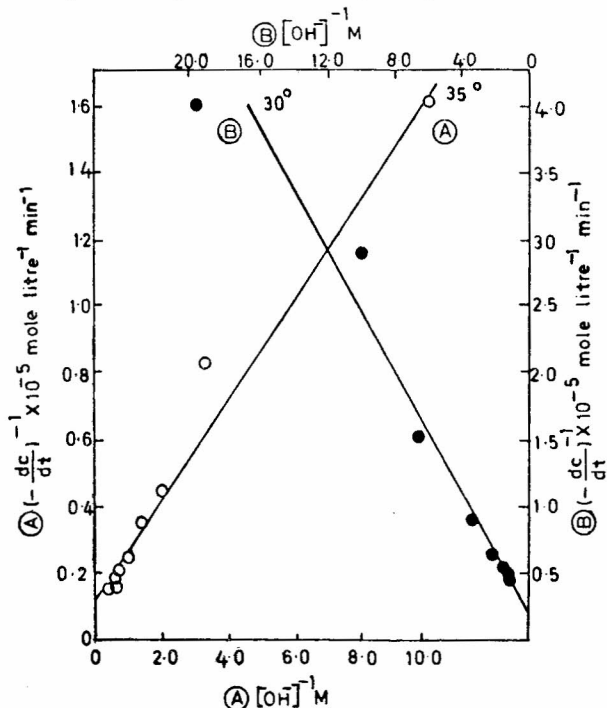


Fig. 4 — Plots of reaction rate  $(-dc/dt)$  against  $1/[\text{OH}^-]$  {For curve A:  $[\text{K}_3\text{Fe}(\text{CN})_6] = 3.0 \times 10^{-3}M$ ; [propane-1,2-diol] =  $1.0M$ ;  $\mu = 2.0M$ ; for curve B:  $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.0 \times 10^{-3}M$ ; [butane-2,3-diol] =  $4.0 \times 10^{-3}M$ ;  $\mu = 2.0M$ }

TABLE 2 — VALUES OF  $kk_1K/(k+k_1)$  OBTAINED FROM THE LINEAR CURVES OF  $(-dc/dt)$  VERSUS  $1/[\text{OH}^-]$  OR  $1/[\text{DIOL}]$  FOR PROPANE-1,2-DIOL AND BUTANE-2,3-DIOL

$kk_1K/(k+k_1)$	Variation
PROPANE-1,2-DIOL	
$1.30 \times 10^{-2}$	[Diol]
$1.00 \times 10^{-2}$	$[\text{OH}^-]$
BUTANE-2,3-DIOL	
$2.08 \times 10^{-1}$	[Diol]
$2.25 \times 10^{-1}$	$[\text{OH}^-]$

TABLE 3 — VALUES OF  $kk_1K/(k+k_1)$  AND  $k$  OBTAINED FROM THE INTERCEPT AND SLOPE VALUES RESPECTIVELY OF THE PLOTS OF  $1/v_i$  VERSUS  $1/[\text{OH}^-]$  OR  $1/[\text{DIOL}]$

$kk_1K/(k+k_1)$	$k \times 10^{-2}$ min <sup>-1</sup>	Variation
PROPANE-1,2-DIOL		
$1.48 \times 10^{-2}$	1.11	[Diol]
$1.20 \times 10^{-2}$	1.20	$[\text{OH}^-]$
BUTANE-2,3-DIOL		
$2.50 \times 10^{-1}$	1.25	[Diol]
$2.50 \times 10^{-1}$	1.25	$[\text{OH}^-]$

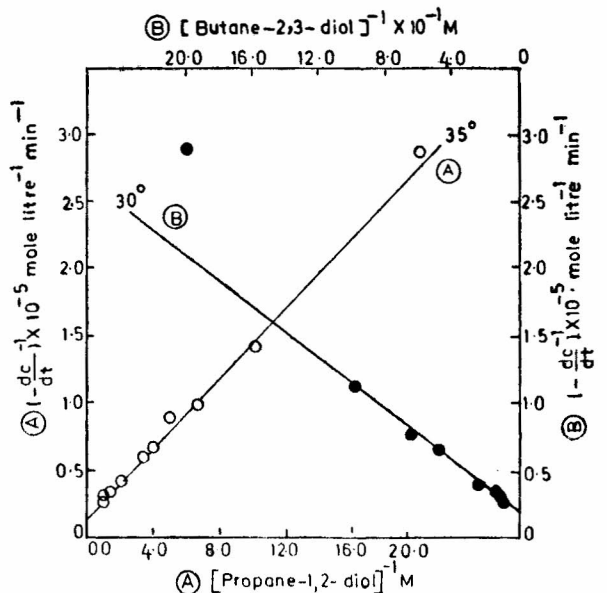
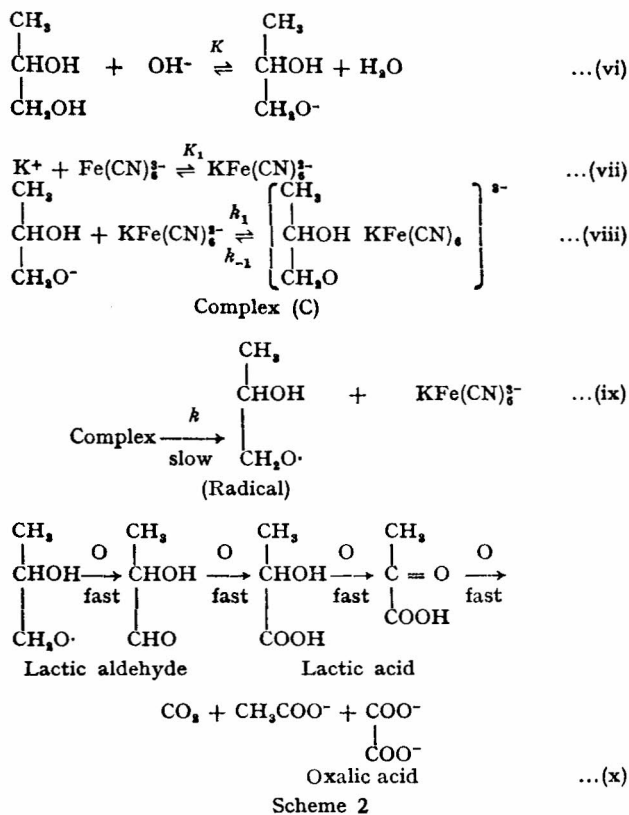


Fig. 5 — Plots of reaction rate  $(-dc/dt)$  against  $1/[\text{diol}]$  {For curve A:  $[\text{K}_3\text{Fe}(\text{CN})_6] = 3.0 \times 10^{-3}M$ ;  $[\text{NaOH}] = 0.8M$ ;  $\mu = 2.0M$ ; for curve B:  $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.0 \times 10^{-3}M$ ;  $[\text{NaOH}] = 1.0M$ ;  $\mu = 2.0M$ }



in the present study support the validity of the rate law (4). From the intercept of such plots and slope, the values of  $k$  and  $kk_1K/(k+k_{-1})$  was calculated respectively, and are given in Table 3.

The values of  $kk_1K/(k+k_{-1})$  and  $k$  obtained from the two different methods, i.e. from variations in  $[\text{OH}^-]$  and  $[\text{diols}]$ , are quite close to each other. These results support the proposed mechanism (Scheme 1) for the oxidation of diols.

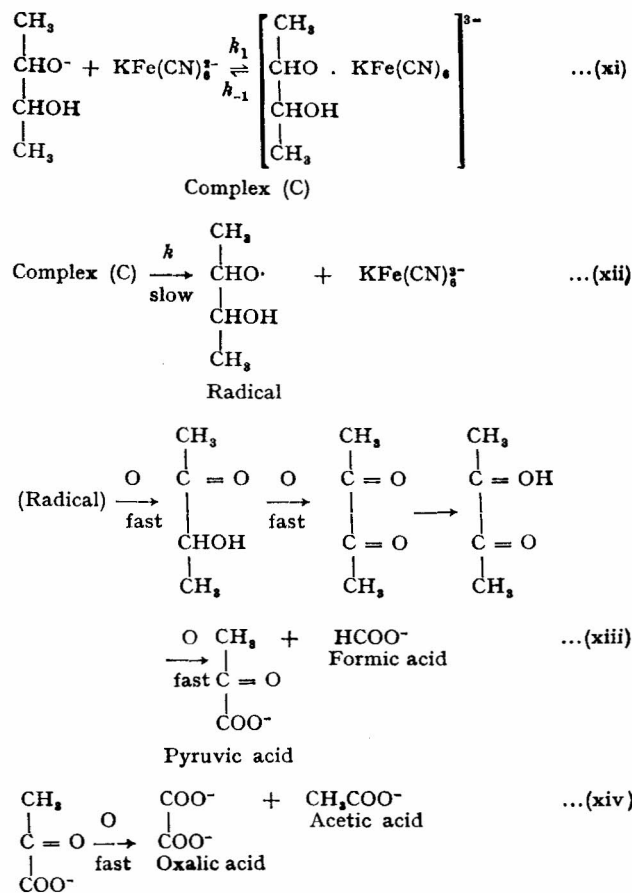
A close examination of the values of  $kk_1K/(k+k_{-1})$  and  $k$  shows that the values are greater for butane-2,3-diol as compared to those for propane-1,2-diol. This leads to the conclusion that the rate of complex formation and its disproportionation increases with the homologation of the diol.

The oxidation products of propane-1,2-diol were identified co-chromatographically as oxalic acid and acetic acid. On the basis of these results the oxidation of propane-1,2-diol probably takes place as shown in Scheme 2.

Similarly on the basis of the final oxidation products confirmed by co-chromatography in the oxidation of butane-2,3-diol, Scheme 3 may be proposed for the oxidation of butane-2,3-diol with hexacyanoferrate(III) in the presence of NaOH.

The formation of oxalic acid from pyruvaldehyde (Scheme 3) might be assumed on the basis of the contention of Litter<sup>6</sup> who pointed out that one of the common mode of oxidation of aldehydes and ketones involves oxidation at  $\alpha$ -position.

It is difficult to predict the actual structure of the complex, but on the basis of the experimental



results, the prediction of the complex between the diol anion and  $\text{KFe}(\text{CN})_6^{3-}$  ion is quite justified. A similar type of bridging has been reported in the reaction between  $\text{Co}(\text{II})$  ethylenediamine tetraacetate and hexacyanoferrate(III)<sup>7</sup>. The little information available on glycol-permanganate reaction also indicates a cyclic ester as an intermediate.

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