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Reactivity of Glycolaldehyde towards Hexacyanoferrate(III) in Alkaline Medium and Mechanism of the Reaction

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The oxidative behaviour of glycolaldehyde towards hexacyanoferrate(III) in alkaline medium has been investigated. The reaction obeys the following rate expression:

$$-\frac{d[\mathrm{Fe(CN)}_6^{3-}]}{dt} = k_3[\mathrm{Fe(CN)}_6^{3-}][\text{glycolaldehyde}][\mathrm{OH}^-]$$

where $k_3 = 100.0 \pm 2$ mol^{-2} dm^6 s^{-1} at 298 K. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are 51 ± 4 kJ mol^{-1} and -35 ± 13 JK^{-1} mol^{-1} respectively. The reactions appear to proceed through the intermediate formation of alkoxide ion to glyoxal.

INTRODUCTION

Glycolaldehyde (hydroxy acetaldehyde) has been shown to exist in equilibrium with its enediol form.[1] The enediol is quantitatively oxidised to glyoxal by an excess methylene blue both in acid and alkaline medium. There is no literature data involving the oxidation of glycolaldehyde by metal ion oxidants in alkaline medium. Hexacyanoferrate(III) acts as a good oxidant both in alkaline[2, 3] and acid[4, 5] medium. However, the mechanism of the oxidation of glycolaldehyde by hexacyanoferrate(III) in alkaline medium is yet to be understood. The present report deals with the reactivity behaviour of glycolaldehyde towards hexacyanoferrate(III) in alkaline medium.

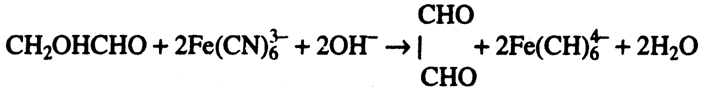
EXPERIMENTAL

Reagents: Potassium hexacyanoferrate(III) (S. Merck, India) was purified by recrystallization, first from hot water and then by precipitation with methanol from aqueous solution at 25°C. The fine orange crystals were dried over silica gel and stored in the dark to avoid possible decomposition to aquopentacyanoferrate(III) ions.[6] Its actual strength was determined by usual titration procedure. To a known quantity of hexacyanoferrate(III) solution an excess of potassium iodide followed by zinc sulphate were added and the liberated iodine was titrated against standard thiosulphate using starch as indicator. Glycolaldehyde (Fluka, A.G.) [Found: $C_4H_8O_4$, m. wt. = 120.1, mixture of stereoisomer, $H_2O < 1\%$, m.p. 85°C] was used. Glycolaldehyde was estimated as follows.[7] To a known quantity of the glycolaldehyde solution was added an excess of sodium hydrogen sulphite (containing 5% ethanol) followed by a known excess of iodine solution. The excess of iodine was back titrated against standard thiosulphate using starch as an indicator. Methanol was of E. Merck grade and distilled before use. All the solutions were prepared in doubly distilled water.

Instruments: Absorbances were measured on a Systronics (India) UV-Visible Spectrophotometer. IR spectra were recorded on KBr discs using a Shimadzu IR-200 Spectrophotometer. Cyclic voltammograms were recorded by Bio-Analytical System (BAS) CV-27 instrument in a dry argon atmosphere using a three electrode configuration. A planar working electrode and a saturated calomel electrode (SCE) were used as the reference. The melting point determinations were carried out on a Callen-Kamp melting point apparatus.

Kinetic measurement: The rate of disappearance of hexacyanoferrate(III) was followed spectrophotometrically at λ_{max} of 420 nm[8] ($\varepsilon = 1060 \pm 10$ mol^{-1} dm^3 cm^{-1}) under pseudo-first-order conditions. The spectrophotometer has its cell compartment kept at constant temperature by circulating water from a thermostat. The reactants previously equilibrated to bath temperature were mixed and the mixture was then transferred to the cell of path length 1 cm. Hexacyanoferrate(II) is nearly transparent at this wavelength. In each run, 10–15 experimental readings were taken and straight lines were obtained when values of log A (A = absorbance) were plotted against time. The pseudo-first-order rate constants were reproducible to within ± 3% in each reaction.

Stoichiometry and product analysis—The reaction mixture in excess glycolaldehyde was allowed to stand for several hours and the unreacted substrate was then estimated.[7] The reaction takes place as shown below:



$$CH_2OHCHO + 2Fe(CN)_6^{3-} + 2OH^- \rightarrow \begin{array}{c} CHO \\ | \\ CHO \end{array} + 2Fe(CH)_6^{4-} + 2H_2O$$

In another experiment, the reaction mixture containing an excess of glycolaldehyde over the oxidant was allowed to stand for several hours. After the reaction was complete the mixture was extracted thrice with diethyl ether. After removal of the ether a little freshly sublimed *o*-aminophenol and ignited calcium oxide were added which gave an intense red colour[9] indicating the presence of glyoxal. Another portion of the reaction mixture was heated on a water-bath and the fraction distilling at 50–60°C was collected. Addition of 2,4-dinitrophenyl hydrazine solution of the distillate gave an orange precipitate which was washed, recrystallized from ethanol and analyzed [Found: C = 40.40, H = 2.60, N = 26.60%, calculated for $C_{14}H_8N_8O_8$, C = 40.19, H = 2.39, N = 26.79%, m.p. 320–322°C, lit.[10] m.p. 318°C].

A broad band at 3500–3300 cm^{-1} due to O—H stretching was observed in the IR spectrum of pure glycolaldehyde but was absent in the IR spectrum of the 2,4-DNP derivatives of the oxidation product. Moreover, the IR spectra of the 2,4-DNP derivatives obtained from the oxidation product and that from authentic glyoxal were identical.

RESULTS AND DISCUSSION

The pseudo-first-order rate constants (k_{obs}) studied with varying concentrations of hexacyanoferrate(III) ions were independent of the oxidant concentration. The values of k_{obs} at 303 K are found to be $(2.62 \pm 0.02) \times 10^{-3}$ s^{-1} at $[Fe(CN)_6^{3-}]$, [glycolaldehyde] and $[OH^-]$ of $(1-10) \times 10^{-4}$, 10×10^{-3} and 2.0×10^{-3} mol dm^{-3} respectively. The effect of varying glycolaldehyde concentration on the rate of the reaction was studied at different glycolaldehyde concentrations but at constant concentrations of other reactants. The values of k_{obs} when plotted against [glycolaldehyde] gave straight line passing through the origin.

The reaction was also studied at different hydroxyl ion concentrations, varied by the addition of potassium hydroxide. The ionic strength of each run was adjusted constant to $\mu = 0.1$ mol dm^{-3} by the addition of potassium chloride. The rate increases with the increase in [OH$^-$]. The values of k_{obs} along with k_3 ($k_3 = k_{obs}$/[glycolaldehyde][OH$^-$]) are recorded in Table 1.

TABLE-1

MEASURED RATE CONSTANTS IN THE OXIDATION OF GLYCOLALDEHYDE BY HEXACYANOFERRATE(III) AT [Fe(CN)$_6^{3-}$] = 1.0 × 10^3 mol dm^{-3}

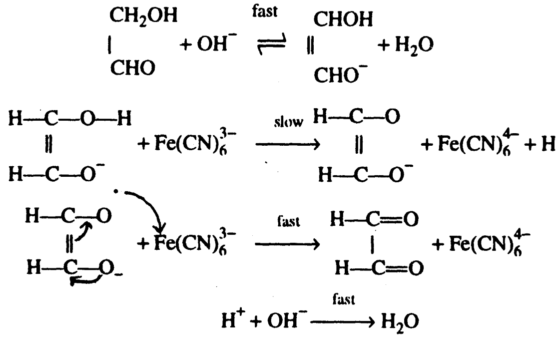
[sub] × 10^{-3} mol dm^{-3}	[OH$^-$] × 10^{-3} mol dm^{-3}	[Methanol] (v/v) %	Temp. K	$k_{obs} \times 10^3$ s^{-1}	$k_3 \times 10^{-2}$ mol^{-2} dm^6 s^{-1}
2.5	2.0		298	0.51	1.02
5.0	2.0		298	1.03	1.03
8.0	2.0		298	1.63	1.02
10.0	2.0		298	2.01	1.00
15.0	2.0		298	3.05	1.01
17.0	2.0		298	3.45	1.01
20.0	2.0		298	4.09	1.02
10.0	2.0		303	2.62	1.31
10.0	2.0		308	3.84	1.92
10.0	2.0		313	5.70	2.85
10.0	0.8		303	1.04	1.30
10.0	1.6		303	2.07	1.29
10.0	2.0		303	2.62	1.31
10.0	2.2		303	2.86	1.30
10.0	2.4		303	3.15	1.31
10.0	3.0		303	3.90	1.30
10.0	3.5		303	4.57	1.31
10.0	4.0		303	5.23	1.31
10.0	2.0	0	298	2.01	
10.0	2.0	10	298	1.61	
10.0	2.0	20	298	1.45	
10.0	2.0	30	298	1.32	
10.0	2.0	40	298	1.15	
10.0	2.0	50	298	1.00	

The values of k_3 were computed at different temperatures which are (100 ± 2), (130 ± 2.5), (192 ± 3) and (285 ± 4) $mol^{-2}\ dm^6\ s^{-1}$ at 298, 303, 308 and 313 K respectively. Activation enthalpy ($\Delta H^{\neq}$) was then calculated from least square plot of log (k_3/T) against 1/T followed by an estimation of $\Delta S^{\neq}$. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are 51 ± 4 kJ mol^{-1} and −35 ± 13 $JK^{-1}\ mol^{-1}$ respectively.

Solvent effect was studied by varying the dielectric constants of the medium by the addition of methanol (v/v). Methanol was unreactive towards reaction with hexacyanoferrate(III) under comparable condition of experiments. The rate decreases as dielectric constant falls. The dielectric constants of the mixtures were calculated from the work of Akerlof.[11] The plot of log k_{obs} against $1/\varepsilon$ (ε = dielectric constant) yields a straight line with a negative slope. The results indicate that the reaction occurs between two similarly charged ions.[12]

The reaction is first order with respect to [glycolaldehyde], $[Fe(CN)_6^{3-}]$ and $[OH^-]$. The results from cyclic voltammetric experiment indicate that glycolaldehyde undergoes oxidation initially to glyoxal at −0.80 V at 298 K and subsequently glyoxal to glyoxalic acid at + 0.44 V at the same temperature where both steps are irreversible. The reduction potential of $Fe(CN)_6^{-3} + e \rightleftharpoons Fe(CN)_6^{4-}$ couple has been reported[13] to be 0.36 V. However, the potential is a function of potassium ion concentration and using equal concentration of two negative ions, the observed potential has been shown to be around 0.48 V. We have measured cyclic voltametrically the potential of the same couple at [KOH] = 2.0×10^{-3} mol dm^{-3} which is 0.3125 V at 298 K. The reaction may be explained by either of the Schemes 1 or 2. The enolization of glycolaldehyde followed by the electron transfer from enolate to hexacyanoferrate(III) can be explained as mentioned below (Scheme 1).

Scheme-1



$$\begin{matrix}CH_2OH\\ |\\ CHO\end{matrix} + OH^- \overset{fast}{\rightleftharpoons} \begin{matrix}CHOH\\ \|\\ CHO^-\end{matrix} + H_2O \qquad (1)$$

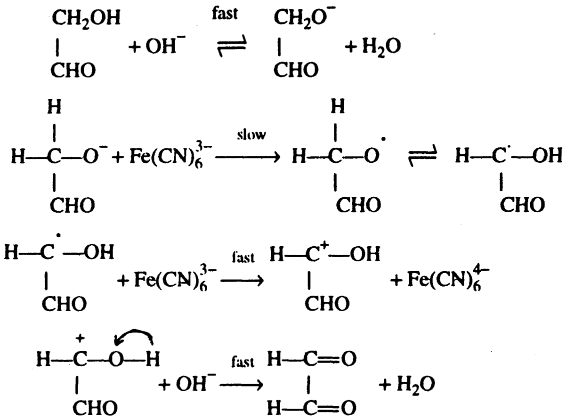
$$\begin{matrix}H—C—O—H\\ \|\\ H—C—O^-\end{matrix} + Fe(CN)_6^{3-} \xrightarrow{slow} \begin{matrix}H—C—O\\ \|\\ H—C—O^-\end{matrix} + Fe(CN)_6^{4-} + H^+ \qquad (2)$$

$$\begin{matrix}H—C—\dot{O}\\ \|\\ H—C—O^-\end{matrix} + Fe(CN)_6^{3-} \xrightarrow{fast} \begin{matrix}H—C=O\\ |\\ H—C=O\end{matrix} + Fe(CN)_6^{4-} \qquad (3)$$

$$H^+ + OH^- \xrightarrow{fast} H_2O \qquad (4)$$

The radical ions of the types as mentioned above are involved in the oxidations of ascorbic acid and of reducing sugars.[14] However, the enolization reaction of glycolaldehyde is associated with very high enthalpy of activation of 82.9 kJ mol^{-1}. The enthalpy of activation calculated in this reaction is much lower than this value. Consequently initial formation of radical ion (step 2) followed by its reaction with hexacyanoferrate(III) (step 3) to give glyoxal may be discounted. On the other hand, first order dependence on substrate and hydroxyl ion can be explained by the fact that OH^- reacts with glycolaldehyde to give an alkoxide ion (step 5) followed by its reaction with hexacyanoferrate(III) to give free radical as shown in step 6 of Scheme 2. The free radical reacts with hexacyanoferrate(III) to give carbonium ion (step 7). The latter subsequently by reacting with OH^- gives the product (step 8).

Scheme-2



$$\begin{array}{c}CH_2OH\\|\\CHO\end{array} + OH^- \overset{\text{fast}}{\rightleftharpoons} \begin{array}{c}CH_2O^-\\|\\CHO\end{array} + H_2O \qquad (5)$$

$$H-\begin{array}{c}H\\|\\C\\|\\CHO\end{array}-O^- + Fe(CN)_6^{3-} \xrightarrow{\text{slow}} H-\begin{array}{c}H\\|\\C\\|\\CHO\end{array}-\dot{O} \rightleftharpoons H-\begin{array}{c}\dot{C}\\|\\CHO\end{array}-OH \qquad (6)$$

$$H-\begin{array}{c}\dot{C}\\|\\CHO\end{array}-OH + Fe(CN)_6^{3-} \xrightarrow{\text{fast}} H-\begin{array}{c}C^+\\|\\CHO\end{array}-OH + Fe(CN)_6^{4-} \qquad (7)$$

$$H-\begin{array}{c}\overset{+}{C}\\|\\CHO\end{array}-O-H + OH^- \xrightarrow{\text{fast}} \begin{array}{c}H-C=O\\|\\H-C=O\end{array} + H_2O \qquad (8)$$

Thus the oxidation of glycolaldehyde takes place to give glyoxal and further oxidation of glyoxal to glyoxalic acid does not occur under the condition at which experiments were carried out. The experimentally obtained redox potentials of glyoxal → glyoxalic acid and also $Fe(CN)_6^{3-} \rightarrow Fe(CN)_6^{4-}$ couple corroborate the above contention.

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