Monatshefte für Chemie 110, 1455—1460 (1979) **Monatshefte für Chemie**

Mechanism of Hexacyanoferrate(III) Oxidation of 1-Propanol and 2-Propanol in Aqueous Alkaline Medium

H. S. Singh*, **V. P. Singh**, and **D. P. Pandey**[a]

Chemical Laboratories, University of Allahabad, Allahabad, India

[a] Department of Chemistry, Firoz Gandhi Post Graduate College, Raibarelli (U.P.), India

(Received 3 January 1978. Revised 14 August 1978. Accepted 14 September 1978)

Kinetic studies of the hexacyanoferrate(III) oxidation of 1-propanol and 2-propanol have been carried out in aqueous alkaline medium. The reaction velocity is of first order with respect to alcohols, alkali and hexacyanoferrate(III). The kinetic data suggest that the oxidation involves the formation of an anion of the substrate undergoes oxidation with hexacyanoferrate(III) via charge transfer process. The free radical thus produced is further oxidised to form the final products.

(Keywords: Kinetics; Mechanism; Oxidation of alcohols; Reduction)

Der Mechanismus der Hexacyanoferrat(III)-Oxidation von 1-Propanol und 2-Propanol in alkalischem, wäßrigen Milieu

Kinetische Studien ergaben für die Oxidation Abhängigkeiten erster Ordnung sowohl für die Alkohole, als auch für OH^- und Hexacyanoferrat(III). Die Daten legen nahe, daß das Substrat-Anion zunächst unter einfacher Ladungsübertragung oxidiert wird, wobei das gebildete freie Radikal weiterer Oxidation zu den endgültigen Reaktionsprodukten unterliegt.

Introduction

Earlier studies on alkaline hexacyanoferrate(III) oxidation of organic compounds showed that the anions derived from the organic substrates are frequently oxidized by hexacyanoferrate(III) via an electron transfer process[1]. Similarly *Singh* et al.[2,3] have suggested that the oxidation of aldehydes and ketones takes place via an electron transfer process; recently the kinetics of oxidation of a number of diols was examined[4] and the data led to assume that the oxidation proceeds

0026-9247/79/0110/1455/$ 01.20

via complex formation between the anions of the diols and hexacyanoferrate(III) ion. This duality of views regarding the mechanism of alkaline hexacyanoferrate(III) oxidation of organic compounds prompted to study the kinetics of oxidation of 1-propanol and 2-propanol; a probable reaction mechanism will be proposed explaining the kinetic data.

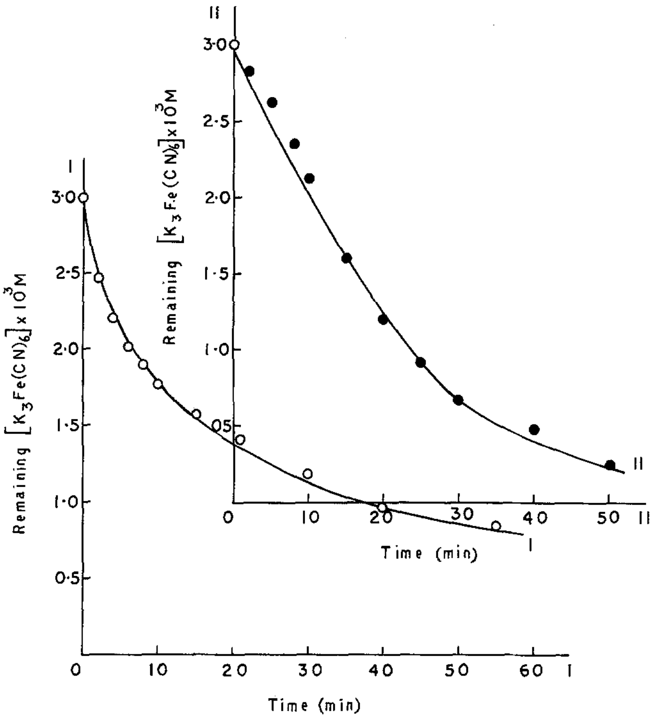

Fig. 1. I $[K_3Fe(CN)_6] = 3.00 \times 10^{-3}M$, [1-propanol] $= 2.5 \times 10^{-1}M$, $[NaOH] = 8.0 \times 10^{-1}M$, $\mu = 1.0M$, Temp. 35°. II $[K_3Fe(CN)_6] = 3.00 \times$ $\times 10^{-3}M$, [2-propanol] $= 1.2 \times 10^{-1}M$, $[NaOH] = 5.0 \times 10^{-1}M$, $\mu = 1.0M$, Temp. 30°

Results and Discussion

The oxidation of 1-propanol and 2-propanol by hexacyanoferrate(III) in aqueous alkaline medium was studied over a wide range of concentrations. The actual nature of the reaction is shown by the plots of unreacted hexacyanoferrate(III) concentration against time (Fig. 1), the slope giving the reaction rate $(-dc/dt)$. The rate of reaction is directly proportional to the concentration of hexacyanoferrate(III) (Fig. 2); the rate of reaction is also directly proportional to the concentration of hydroxide ion and the alcohols giving similar plots.

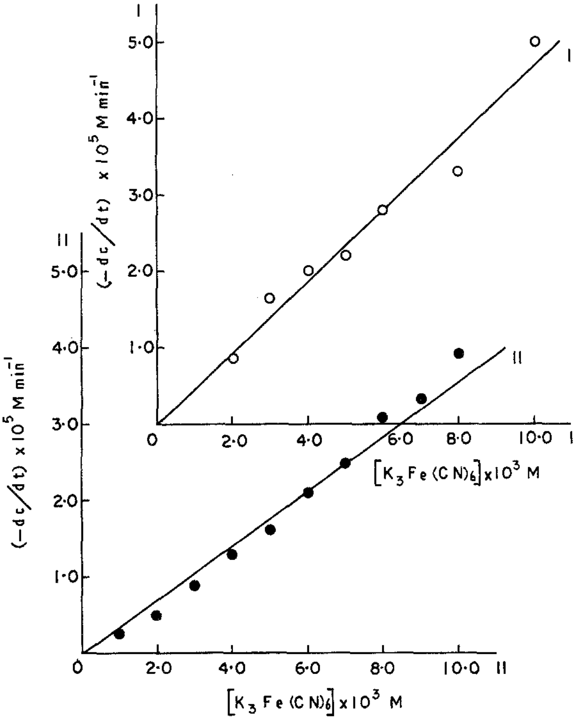

Fig. 2. I [1-propanol] = 2.50 × $10^{-1}M$, [NaOH] = 8.00 × $10^{-1}M$, $\mu = 1.00M$, Temp. 35°. II [2-propanol] = 1.20 × $10^{-1}M$, [NaOH] = 5.00 × $10^{-1}M$, $\mu = 1.00M$, Temp. 30°

Thus, taking the above results into consideration the following rate expression might be written for the oxidation of primary and secondary alcohols.

$$\frac{-\mathrm{d}\,[Fey]}{\mathrm{d}t} = \mathrm{k}\ [S]\ [\mathrm{OH}^-]\ [\mathrm{Fe(CN)_6}]^{3-} \qquad (1)$$

Where k is specific rate constant, $[Fey]$ and $[S]$ represents the hexacyanoferrate(III) and alcohol concentration respectively. The observed third order rate constant was found to be 4.0 × $10^{-1}\,M^{-2}\,\mathrm{min}^{-1}$ for 1-propanol and 6.2 × $10^{-2}\,M^{-2}\,\mathrm{min}^{-1}$ for 2-propanol at the temperature 35° and 30° respectively.

In view of the above experimental results a probable scheme of oxidation for both types (primary and secondary) of alcohols by alkaline hexacyanoferrate(III) ion via the formation of anion (S^-) as an intermediate might be considered as follows:

$$S + \mathrm{OH}^- \underset{K_{-1}}{\overset{k_1}{\rightleftharpoons}} S^- + \mathrm{H_2O} \tag{I}$$

$$S^- + \mathrm{Fe(CN)_6}^{3-} \underset{\text{slow}}{\overset{k_2}{\rightarrow}} S^{\cdot} + \mathrm{Fe(CN)_6}^{4-} \tag{II}$$

$$S^{\cdot} + \mathrm{Fe(CN)_6}^{3-} \underset{\text{fast}}{\overset{k_3}{\rightarrow}} \text{Intermediate product} + \mathrm{Fe(CN)_6}^{4-} \tag{III}$$

Now assuming steady state condition for the concentration of S^-, the rate law might be derived as follows:

$$\frac{-\mathrm{d}[S^-]}{\mathrm{d}t} = k_1[S]\,[\mathrm{OH}^-] - k_{-1}[S^-]\,[\mathrm{H_2O}] - k_2[S^-]\,[\mathrm{Fe(CN)_6}^{3-}] \tag{2}$$

Now keeping the experimental conditions in mind and solving equ. (2) the final rate equation will be:

$$\frac{-\mathrm{d}[Fey]}{\mathrm{d}t} = \frac{2\,k_1k_2[S]\,[\mathrm{OH}^-]\,[\mathrm{Fe(CN)_6}]^{3-}}{k_{-1}[\mathrm{H_2O}] + k_2[\mathrm{Fe(CN)_6}]^{3-}} \tag{3}$$

To the first approximation, if we assume that k_{-1} $[\mathrm{H_2O}] \gg k_2[\mathrm{Fe(CN)_6}]^{3-}$, the rate law (3) reduces to (4):

$$\frac{-\mathrm{d}[Fey]}{\mathrm{d}t} = \frac{2\,k_1k_2[S]\,[\mathrm{OH}^-]\,[\mathrm{Fe(CN)_6}]^{3-}}{k_{-1}[\mathrm{H_2O}]} \tag{4}$$

The rate law (4) clearly explains the experimental results i.e., first order kinetics with respect to hexacyanoferrate(III), alcohols, and hydroxide ion concentration.

For each experimental study the final oxidation products have been extracted and identified chromatographically. Propionic acid is the final oxidation product of 1-propanol, acetic acid and oxalic acid are the final oxidation products from 2-propanol (acetone is formed as an intermediate product and this in turn is further oxidized to the final oxidation products via pyruvic aldehyde; the oxidation path of acetones is described in[3,4]).

These results clearly substantiate that the reaction proceeds via a charge transfer process as it has already been observed in the course of the oxidation of acetone, ethylmethylketone and formaldehyde by aqueous alkaline hexacyanoferrate(III)[2,3]. During the course of the oxidation of 1,2-propanediol, 2,3-butanediol[4a], 2-methyl-2,4-pentanediol and 1,5-pentanediol[4b], pinacol[4c], and glycerol[4d] by alkaline hexacyanoferrate(III) in aqueous alkaline medium, it has been observed that the reaction rate follows first order kinetics with respect to hexacyanoferrate(III) in each substrate. The effect of variation of the diols (triols) and hydroxide ion concentration shows first order kinetics with respect to these reactants at lower concentration, whereas at higher concentration the reaction velocity tends towards zero-order kinetics. These observations clearly indicate that there might be complex formation between the organic substrate anion and hexacyanoferrate(III) ion. In the present studies the charge transfer process is completely ruled out. *Michaelis* and *Menten*[5] have also observed similar results during enzyme catalyzed reaction and they have also proposed a complex formation reaction mechanism. It is quite obvious that the diols have greater tendency of complex formation as compared to simple alcohols. During the course of oxidation of alcohols by alkaline permanganate, *Stewart*[6] has also observed a hydride ion transfer process. Thus on the basis of these previous results, it is quite justified to assume the charge transfer process during the course of oxidation of 1-propanol and 2-propanol by alkaline hexacyanoferrate(III).

Materials and Methods

All the reagent used were of AR (B. D. H.) grade except sodium hydroxide which is of G. R. (S. Merck). All the solutions were prepared in distilled water. The ionic strength of the medium was kept constant by adding aqueous solution of KCl.

The reaction was followed by mixing the required quantity of alcohol solution with the solutions of $K_3Fe(CN)_6$, NaOH and KCl at the desired temperature maintained with an accuracy of $\pm 0.1°$. The amount of hexacyanoferrate(II) produced at different intervals of time was estimated titrimetrically[3] against standard solution of ceric(IV) sulphate using ferroin as redox indicator.

Ceric(IV) sulphate as oxidizing agent could also oxidize alcohols, but it was observed that the estimation of hexacyanoferrate(II) by ceric(IV) sulphate in $4—5N\text{-}H_2SO_4$ was not affected in the presence of alcohols. Several experiments were performed; reproducible results were obtained in all cases, justifying the use of Ce(IV) sulphate for the estimation of hexacyanoferrate(II).

Acknowledgement

The authors are indebted to Dr. *M. P. Singh* and to the U.G.C., Government of India, for financial assistance.

References

[1] *I. R. Wilson*, Rev. Pure appl. Chem. **16**, 103 (1966).

[2] *V. N. Singh*, *M. C. Gangwar*, *B. B. L. Saxena*, and *M. P. Singh*, Canad. J. Chem. **47**, 105 (1969).

[3] *V. N. Singh*, *M. P. Singh*, and *B. B. L. Saxena*, Indian J. Chem. **8**, 529 (1970).

[4] a. *H. S. Singh*, *V. P. Singh*, and *P. N. Srivastava*, Indian J. Chem. **15 A**, 111 (1977). b. *H. S. Singh*, *V. P. Singh*, *J. M. Singh*, and *P. N. Srivastava*, Indian J. Chem., in press. c. *H. S. Singh*, *V. P. Singh*, *J. M. Singh*, and *P. N. Srivastava*, Indian National Science Academy **43**, 24 (1977). d. *H. S. Singh*, *V. P. Singh*, *J. M. Singh*, and *P. N. Srivastava*, J. Indian Chem. Soc., in press.

[5] *L. Michaelis* and *M. L. Menten*, Biochem. Z. **49**, 333 (1913).

[6] *R. Stewart*, J. Amer. Chem. Soc. **79**, 3057 (1957).