Kinetics & Mechanism of Cu(II)-catalysed Oxidation of Tartaric Acid by Alkaline Hexacyanoferrate(III)

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Cu(II) ion-catalysed oxidation of tartaric acid by hexacyanoferrate(III) has been investigated in alkaline medium. The reaction rate has first order dependence in the oxidant, tartaric acid, sodium hydroxide and the catalyst. A mechanism based on the formation of an intermediate Cu(II)-tartrate complex and its subsequent oxidation to Cu(III)-tartrate complex by hexacyanoferrate(III) has been suggested. The mechanism is substantiated by the results of a separate kinetic study of the oxidation of such intermediate complex which has been synthesized. Positive salt effect has been observed. Activation energy and entropy of activation have been evaluated as 6·15 kcal/mole and −53·6 e.u. respectively.

THE kinetics of oxidation of a number of organic and inorganic compounds by hexacyanoferrate(III) has been studied by a number of workers[1-4]. In many cases the uncatalysed reactions are slow and hence some suitable catalyst such as Os(VIII)[5-8] has been employed. Recently Wilson *et al.*[9-11] have investigated Cu(II)-catalysed oxidation of cystine and related thiols and hydroxylamine by hexacyanoferrate(III). The present paper deals with kinetics of oxidation of tartaric acid by hexacyanoferrate(III) in the presence of Cu(II) ion in alkaline medium.

Materials and Methods

The stock solution of potassium hexacyanoferrate(III) (AR, BDH) was prepared in doubly distilled water and standardized iodometrically[12]. All other chemicals used were of AR grade and their solutions were prepared in doubly distilled water. The solution of sodium hydroxide was always standardized before use. Aqueous solution of 1 : 1 Cu(II)-tartrate complex was prepared[13] by dissolving equimolar amounts of tartaric acid and copper sulphate in sodium hydroxide solution at $pH \approx 9$.

The kinetics of the reaction was followed by estimating the decrease in [hexacyanoferrate(III)] with time iodometrically. The method gave reproducible results. The results are interpreted in terms of initial rate of the reaction to avoid the interference due to reaction products. These rates were obtained from the slopes of hexacyanoferrate(III) reacted versus time plots for the first 10% of the reaction.

Results and Discussion

It was found that six moles of hexacyanoferrate(III) are consumed per mole of tartaric acid for its complete oxidation, which takes several days for completion to give formic acid, identified by chromotropic acid test[14] and CO_2.

The kinetics of the reaction was studied with equimolar [oxidant] and [substrate] $(0·01M)$ at [alkali]$= 0·4M$ and [catalyst]$= 2·5 \times 10^{-4}M$ at five different temperatures. It was observed that the disappearance of hexacyanoferrate(III) followed a second order path. The activation parameters calculated are: temperature coefficient $= 1·35$; energy of activation $= 6·15$ kcal/mole; frequency factor $= 5·56 \times 10^2$ sec^{-1}; and entropy of activation $= -53·6$ e.u.

The reaction rate has first order dependence on [hexacyanoferrate(III)] at lower concentration (up to $0·01M$) but deviates at higher concentrations. A plot of $1/[Fe(CN)_6^{3-}]$ vs $1/IR$ is linear, implying that the rate of reaction with respect to oxidant is governed by Eq. (1)

$$R = \frac{A C_{Fe[CN]_6^{3-}}}{1 + B C_{Fe[CN]_6^{3-}}} \qquad \ldots(1)$$

The constants A and B have been evaluated as $1·66 \times 10^{-2}$ and $16·6$ respectively from the slope and intercept of the linear plot. The reaction rate is first order with respect to tartaric acid up to $6·6 \times 10^{-3}M$ concentration beyond which it falls and has a first order dependence with respect to [alkali]. The reaction rate is directly proportional to [Cu(II)], indicating first order dependence in catalyst. Hexacyanoferrate(II) has a retarding effect on the reaction rate.

The reaction rate increases with an increase in the ionic strength of the reaction mixture by the addition of salts like potassium chloride and potassium sulphate (Table 1). Further, the absence of vinyl polymerization ruled out the possibility of a radical mechanism.

Mechanism — It is generally known that transitional metal ions with $3d^9$ structure are not easily oxidized by mild oxidants but complex formation with a suitable ligand provides favourable conditions for their oxidation to higher oxidation state. Hence, a mechanism involving the participation

TABLE 1 — EFFECT OF ADDED SALT ON THE
REACTION RATE

{$[Fe(CN)_6^{3-}]$ = [Tartaric acid] = $1 \times 10^{-2}M$,
[NaOH] = $4.0 \times 10^{-1}M$, $[CuSO_4]$ = $2.5 \times 10^{-4}M$, temp. 40°}

10[salts]M	Ionic strength M	10^4 IR M min^{-1}
nil	0·49	1·36
	KCl	
1·0	0·59	1·94
2·0	0·69	2·45
	K_2SO_4	
1·0	0·79	2·55
2·0	1·09	3·62

of coordination complex between Cu(II) and tartrate ion has been postulated as shown in Scheme 1.

The alkali dependence of the reaction rate suggests an attack of a OH$^-$ ion on tartrate ion resulting in the formation of a trivalent anion of tartaric acid (step-2). This step is essential prior to complex formation as has been reported in literature[15] that in tartrate-Cu(II) system one of the hydrogens of the alcoholic group is also replaced at high pH. This anion then forms a 1:1 coordination complex with Cu(II) ion by a reversible equilibria (step-3), which in turn is oxidized to a Cu(III)-tartrate com-

plex in the rate-controlling step-4. The positive salt effect and a negative value of entropy lends support to step-4 as rate determining one. The reversible nature of this step is supported by a pronounced negative effect of hexacyanoferrate(II) on the reaction rate. The Cu(III)-tartrate complex is then attacked by OH$^-$ to give Cu(I) and intermediate products (step-5). Cu(I) is then rapidly oxidized to Cu(II) by $Fe(CN)_6^{3-}$ ion (step-6). The intermediate products are oxidized in a fast step to final product formic acid by a series of reaction (step-7). The above mechanism is similar to that proposed by Wilson (loc. cit.) for the Cu(II)-catalysed oxidation of thiols by hexacyanoferrate (III). Recently the existance of Cu(III) ion in alkaline medium has been reported by Jaiswal and Yadav[16]. Such species has also been postulated in the Cu(II)-catalysed oxidation of tartaric acid by peroxidisulphate[17].

This mechanism finds further support from the results of a separate kinetic study of the oxidation of the synthesized Cu(II)-tartrate complex by alkaline hexacyanoferrate(III), which reveals that the rate of oxidation of this complex has a first order dependence on [complex], [oxidant] and [alkali]. This justifies the validity of steps (4) and (5) of the proposed mechanism.

Rate law — Applying steady state treatment to the various intermediates and necessary approximations for the initial stages of the reaction, the final rate term can be written in the form of Eq. (8)

$$\frac{-d}{dt} C_{Fe(CN)_6^{3-}} = \frac{K C_{T^2-} C_{Fe(CN)_6^{3-}} C_{Cu(II)} C_{OH^-}}{1 + K' C_{Fe(CN)_6^{2-}}} \quad \ldots(8)$$

where

$$K = \frac{2k_1 k_2 k_3}{k_{-1} k_{-2} C_{H_2O}} \text{ and } K' = \frac{k_3}{k_{-2}}$$

On reversing Eq. (8)

$$\frac{1}{\frac{-d}{dt} C_{Fe(CN)_6^{3-}}} = \frac{1}{K C_{T^2-} C_{Fe(CN)_6^{3-}} C_{Cu(II)} C_{OH^-}} + \frac{K'}{K C_{T^2-} C_{Cu(II)} C_{OH^-}} \quad \ldots(9)$$

Eq. (9) demands that a plot between $1/IR$ and $1/[Fe(CN)_6^{3-}]$ should be linear. This has actually been observed, thus justifying the validity of rate law Eq. (8). The values of the constants K and K' have been evaluated from the slope and intercept of linear plot which on substituting in Eq. (8) give the rate law (10)

$$\frac{-d}{dt} C_{Fe(CN)_6^{3-}} = \frac{16.66 \times 10^3 C_{Fe(CN)_6^{3-}} C_{T^2-} C_{OH^-} C_{Cu(II)}}{1 + 16.66 C_{Fe(CN)_6^{2-}}} \quad \ldots(10)$$

The validity of the rate law is further demonstrated by calculating the rate of reaction from Eq. (10) at different concentrations of the reactants and comparing these values with those observed experimentally. Table 2 incorporates the observed and calculated values of initial rates under identical conditions at 40° which shows a considerable degree of agreement between the two values justifying the validity of rate law and hence the mechanism.
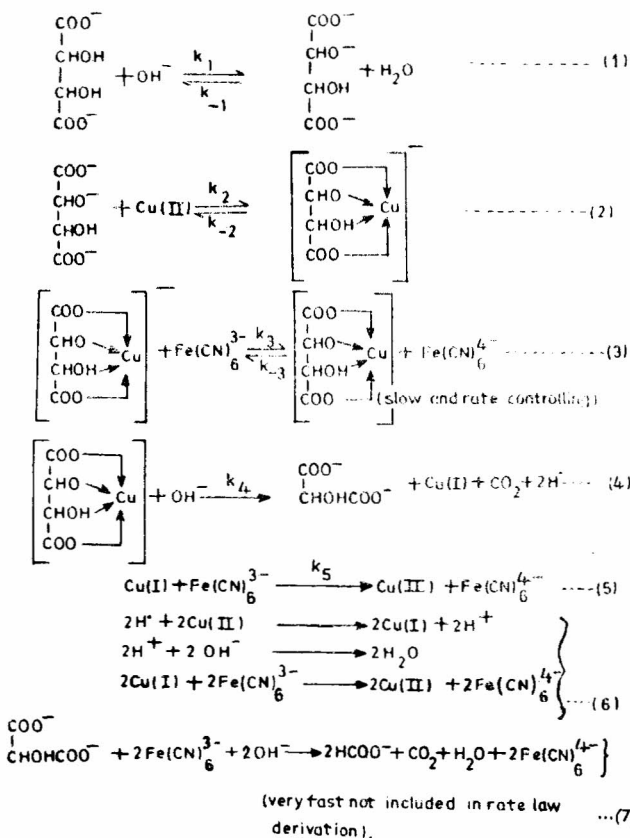
Scheme 1

TABLE 2 — OBSERVED AND CALCULATED REACTION RATES

{[Tartaric acid] $= 1.0 \times 10^{-2}M$; [NaOH] $= 4.0 \times 10^{-1}M$; temp. 40°}

$10^3[Fe(CN)_6^{3-}]$ M	$10^4[CuSO_4]$ M	IR mole litre^{-1} min^{-1} $\times 10^4$	
		Obs.	Calc.
20·0	2·5	2·50	2·50
10·0	2·5	1·45	1·43
5·0	2·5	0·66	0·77
4·0	2·5	0·60	0·62
2·5	2·5	0·36	0·39
2·0	2·5	0·31	0·32
10·0	10·0	5·00	5·71
10·0	5·0	2·50	2·85
10·0	1·66	1·11	0·95
10·0	1·25	0·67	0·71

Acknowledgement

References

1. THYAGARAJAN, B. S., *Chem. Rev.*, **58** (1958), 439.
2. SANT, B. R. & SANT, B. S., *Talanta*, **3** (1960), 261.
3. SOLYMOSI, F., *Talanta*, **4** (1960), 211.
4. WILSON, I. R., *Rev. pure appl. Chem. Austr.*, **16** (1966), 103.
5. MEHROTRA, U. S. & MUSHRAN, S. P., *J. Indian chem. Soc.*, **45** (1968), 526.
6. SINGH, V. N., SINGH, H. S. & SAXENA, B. B. L., *J. Am. chem. Soc.*, **91** (1969), 2643.
7. MUSHRAN, S. P., JINDAL, V. K. & AGARWAL, M. C., *J. chem. Soc.*, A (1971), 622.
8. MATHUR, P. C. & SRIVASTAVA, S. S., *J. Indian chem. Soc.*, **53** (1976), 576.
9. BRIDGART, G. J., FULTER, M. W. & WILSON, I. R., *J. chem. Soc., Dalton Trans.*, (1973), 1274.
10. BRIDGART, G. J. & WILSON, I. R., *J. chem. Soc., Dalton Trans.*, (1973), 1281.
11. BRIDGART, G. J., WATER, W. A. & WILSON, I. R., *J. chem. Soc., Dalton Trans.*, (1973), 1582.
12. VOGEL, A. I., *A text book of quantitative inorganic analysis* (John Wiley, New York), 1951, 356.
13. TIKHONOV, A. S. & BEL'SKAYA, V. P., *Shorvik Stateipo Obschei Khim Akad Nauk USSR*, **2** (1953), 1211.
14. FEIGL, F, *Spot test in organic analysis* (Elsevier, New York), 1960, 368.
15. BOBTELSKY, M. & JORDON, J., *J. Am chem. Soc.*, **67** (1945), 1824.
16. JAISWAL, P. K. & YADAV, K. L., *Indian J. Chem.*, (1973), 837.
17. AGARWAL, S. C. & SAXENA, L. K., *Agra Univ. Jour. (Science)*, **23** (1974), 53.