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Formation of the Intermediate Complex in the Oxidation of Thiourea by Hexacyanoferrate(III) in Acidic Media

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A spectrophotometric study of the redox reaction of hexacyanoferrate(III) and thiourea under acidic conditions reveals the existence of an intermediate complex resulting from the outer-sphere complex formation between the oxidant and the substrate. The visible absorption spectrum of the complex has a maximum at 560 nm, the absorption coefficient and the equilibrium constant values being 38.25 L mol^{-1} cm^{-1} and 16.5 respectively. The thione-thiol equilibrium of thiourea as well as the unprotonated form of hexacyanoferrate(III) ion play significant role in the formation of the intermediate complex. Variation of hydrogen ion concentration has enabled the derivation of the rate constant values at 30°C and I = 1.0 M to vary between 4.254 to 12.562×10^{-4} sec^{-1}.

Key Words: Formation, Intermediate complex, Oxidation, Thiourea, Hexacyanoferrate(III).

INTRODUCTION

Oxidation of organic substrates by metal ions often involves metal-substrate complex formation as intermediates[1]. Although most of these intermediates are short lived, some have existence long enough to be probed kinetically[2]. In this respect the oxidation of sulphur containing ligands by iron(III) ion needs special mention in view of the importance of iron-sulphur complexes in redox catalysis in living systems[3]. The present paper deals with the kinetic and mechanistic study of the formation of the blue-purple intermediate complex prior to the overall redox process of thiourea oxidation by hexacyanoferrate(III). Although the redox process has been investigated, little is known[4] about the intermediate metal-substrate complex whose stability is condition specific.

EXPERIMENTAL

All reagents used were of AR grade. Deionised water was used to prepare the solution. To remove traces of Cu^{2+} present, all solutions were passed through a cation exchange resin[5]. The iron content in the stock solution of hexacyanoferrate(III) as well as in the experimental solutions at different intervals of time was determined by literature method[6]. Stock solutions of perchloric acid were standardised against disodium tetraborate. Sodium perchlorate solution was used to maintain the ionic strength at 1.0 M. The kinetic runs were carried out under pseudo-first order conditions and at constant temperature (30 ± 0.05°C) by following the complex formation at 560 nm using Shimadzu –160 A UV-visible spectrophotometer.

RESULTS AND DISCUSSION

The stoichiometry of the complex is determined as 1 : 1 by Job's Continuous Variation method. The complex formation equilibrium can be represented by

$$[Fe(CN)_6]^{3-} + TUH^+ = [Fe(CN)_6 - TU]^{3-} + H^+ \qquad (1)$$

where TUH^+ is the protonated form of thiourea. Preliminary investigations revealed that under conditions of high H^+ concentration and excess hexacyanoferrate(III), the rate of complex formation greatly exceeded that of the redox step[7]. Hence these conditions were maintained throughout the study. Under such conditions, although the shape of the spectrum remained unaltered for fairly good length of time, the Fe(III) ion concentration recorded a tendency to decrease approximately after ten minutes from the start of reaction. Moreover, under these conditions, the subsequent complex redox process resulted in the precipitation of products which hindered spectral measurements. Hence the maximum absorbance values under different reaction conditions were restricted to measurement at the tenth minute from the beginning.

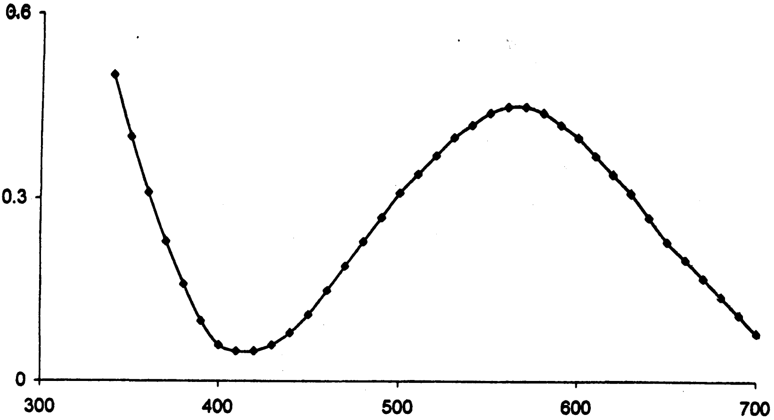

Fig. 1. Spectrum of the intermediate: $Fe(CN)_6]^{3-}$ = 0.05 mol dm^{-3}; [TU] = 0.005 mol dm^{-3}; $[H^+]$ = 0.4 mol dm^{-3}; I = 1.0 mol dm^{-3}; 30°C.

If a, b, c represent the initial concentration of hexacyanoferrate(III), thiourea and hydrogen ion respectively, then using equation (1), the absorption coefficient and the equilibrium constant values can be obtained from the linear relation

$$\frac{ab}{cA_{max}} = \frac{1}{\varepsilon l k} + \frac{1}{\varepsilon l}\frac{a+b}{c} \qquad (2)$$

where A_{max} is the absorbance at the tenth minute at 560 nm under a particular set of conditions for complex formation. Thus using different concentrations of hydrogen ion and hexacyanoferrate(III) at constant initial concentration of thiourea as well as ionic strength, all the data according to eqn. (2) are found to be incorporated in a single line (Fig. 2). This justifies the complex formation according to eqn. (1) and the release of one proton on complexation. From the slope and intercept of this line, the ε and K values are determined as 38.25 L $mol^{-1}cm^{-1}$ and 16.5 respectively.

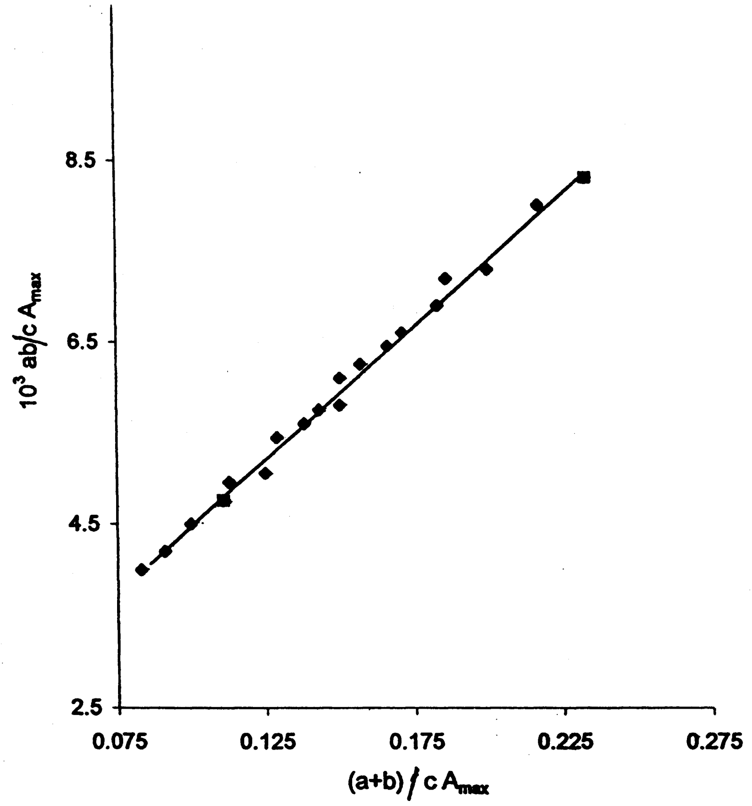

Fig. 2 Determination of ε and K at 30°C; $[Fe(CN)_6]^{3-}$ = 0.04 – 0.065 mol dm^{-3}; $[H^+]$ = 0.3 – 0.55 mol dm^{-3}; [TU] = 0.005 mol dm^{-3}.

The rate of complex formation is consistent with the rate law

$$\frac{d[Fe(CN)_6 - TU]^{3-}}{dt} = k_{obs}[TU]_T \qquad (3)$$

where $[TU]_T$ is the total thiourea concentration. Table-1 lists the k_{obs} values at different initial concentrations of reactants. The data in Table-1 indicate that the rate of complex formation is dependent on both the thiourea and hexacyanofer-

TABLE-1
EXPERIMENTAL AND CALCULATED RATE CONSTANT VALUES FOR THE INTERMEDIATE COMPLEX FORMATION REACTION BETWEEN HEXACYANOFERRATE(III) AND THIOUREA

I = 1.0 mol dm^{-3}, Temp. = 30°C

[TU] × 10^3 (mol dm^{-3})	[H^+] (mol dm^{-3})	[$Fe(CN)_6^{3-}$] × 10^2 (mol dm^{-3})	(k_{obs} × 10^4 sec^{-1})	(k_{cal} × 10^4 sec^{-1})
3.0	0.40	4.0	8.275	
3.5			8.090	
4.0			8.299	
4.5			8.712	
5.0			8.315	
4.0	0.20	4.0	4.254	4.266
	0.25		5.255	5.296
	0.30		6.302	6.305
	0.35		7.293	7.310
	0.40		8.299	8.312
	0.45		9.285	9.293
	0.50		10.256	10.253
4.0	0.30	4.0	6.402	
		4.5	7.852	
		5.0	8.000	
		5.5	8.921	
		6.0	9.966	
	0.35	4.0	7.293	
		4.5	8.511	
		5.0	9.356	
		5.5	9.935	
		6.0	10.610	
	0.40	4.0	8.299	
		4.5	10.009	
		5.0	10.800	
		5.5	11.321	
		6.0	12.562	

rate(III) concentrations to the first power only $k_{obs} = k[Fe(CN)_6^{3-}]$). However, the dependence on the hydrogen ion concentration is found to be complex in nature. Addition of cyanide ion did not appreciably affect the rate constant values thus excluding the possibility of decomposition or hydrolysis of hexacyanoferrate(III) under the condition of study. Based on the above observations the following mechanism is suggested for the complexation reaction.

$$TU + H^+ \overset{K_1}{\rightleftarrows} TUH^+ \qquad (4)$$

$$Fe(CN)_6^{3-} + TUH^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [Fe(CN)_6 - TU]^{3-} + H^+ \tag{5}$$

$$Fe(CN)_6^{3-} + TU^+ \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} [Fe(CN)_6 - TU]^{3-} \tag{6}$$

The equations (7) and (8) represent the expected kinetic behaviour[8] for the forward reaction which results in the formation of the intermediate complex. Considering the stability constant value for the intermediate complex (16.5), the reverse reactions are omitted in the derivation.

$$k = \frac{k_{obs}}{[Fe(CN)_6^{3-}]} = \frac{k_2K_1[H^+] + k_3}{1 + K_1[H^+]} \tag{7}$$

$$\frac{1}{k} = \frac{1}{k_2K_1[H^+]} + \frac{1}{k_2} \tag{8}$$

(when $k_3 << k_2K_1[H^+]$)

From the plot of 1/k *vs.* 1/[H$^+$], the values of k_2 and K_1 are obtained as 4.15×10^{-1} and 0.13 respectively. The latter value agrees well with the literature value[9] of 1.1×10^{-1} for the protonation constant of thiourea. Analysis of the data[10] in Table-1 yields the values of k_2, k_3 and K_1 as 4.23×10^{-1}, 2.66×10^{-5} and 1.29×10^{-1} respectively. The very low value of k_3 suggests that the protonated form of thiourea is the predominant reacting species in complex formation. This gains further support from the observation shown in Fig. 2. Using the values of k_2, k_3 and K_1, the rate constant values at different hydrogen ion concentrations have been calculated (kcal) and shown in Table-1. The agreement between the experimental and calculated rate constant values further supports the reaction mechanism.

REFERENCES

1. H. Sigel and R.B. Martin, *Chem. Rev.*, **82**, 385 (1982).
2. K.J. Ellis and A. McAuley, *J. Chem. Soc. Dalton Trans.*, 1533 (1973).
3. D. Banerjea, Coordination Chemistry, Tata McGraw-Hill, New Delhi, pp. 358, 367 (1993).
4. M.D. Lilani, G.K. Sharma and R. Shanker, *Indian J. Chem.*, **25A**, 370 (1986).
5. G.J. Bridgart, W.A. Waters and I.R. Wilson, *J. Chem. Soc. Dalton Trans.*, 1582 (1973).
6. A.I. Vogel, Quantitative Inorganic Analysis, Longmans Green, London, pp. 371–372 (1961).
7. J.C. Bailar, H.J. Emeleus, R. Nyholm and A.F. Trotman-Dickenson, Comprehensive Inorganic Chemistry, Pergamon Press, New York, p. 1047 (1973).
8. R.G. Wilkins, The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes, Allyn and Bacon, Boston, p. 45 (1974).
9. N.A. Lange, Handbook of Chemistry, McGraw-Hill, New York, p. 1215 (1967).
10. S.D. Bhattamisra and S. Tripathy, *J. Chem. Soc. Dalton Trans.*, 1907 (1993).

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