Interaction of potassium hexacyanoferrate (II) with histidine

Ramesh Bembi and Wahid U. Malik*

Department of Chemistry, University of Roorkee, Roorkee 247667

MS received 7 April 1975; in final form 11 October 1976

Abstract

L-histidine substitutes cyano groups of $K_4Fe(CN)_6$ at pH 7·0 on irradiation with ultraviolet light. The reaction follows first order kinetics with reference to $K_4Fe(CN)_6$ and zero order with reference to histidine. The kinetic data shows the primary process to be aquation of $Fe(CN)_6^{4-}$ while the final product is formed through a rapid dark reaction of histidine with $Fe(CN)_4(H_2O)_2^{2-}$ to give the product $K_2Fe(CN)_2(histidine)_2$. The final product has been subjected to chemical and infrared spectral analysis.

1. Introduction

Malik and Aslam[1,2] showed on the basis of spectrophotometric and polarographic studies that amino acids substitute cyano groups of $K_4Fe(CN)_6$ in neutial or alkaline solutions on irradiation with ultraviolet light. Their studies revealed that L histidine at pH 7·0 on interaction with $K_4Fe(CN)_6$ gives a light green solution. Therefore, spectrophotometric kinetic studies were carried out with L-histidine to elucidate the mechanism of the reaction.

2. Experimental

Solutions of potassium hexacyanoferrate (II) (AnalaR grade, BDH) were prepared in double distilled water and its strength determined by titrating potentiometrically against $KMnO_4$. Solutions of L-histidine were prepared in double distilled water by dissolving known amounts. L-histidine (AR; BDH) was checked for its purity by thin layer chromatography and was found to give a single spot.

A pH of 7·0 was maintained by using KOH-Boric acid buffer.[3]

The progress of the reaction was followed on a Unicam SP 500 spectrophotometer at 425 nm using 10 mm silica cells. Solutions placed in a thermo-

---

* Present address: Bundelkhand University, Jhansi (UP).

A 4–April 77

static water bath maintained at 25 $\pm$ 0·1° C were exposed to ultraviolet light with an ultraviolet lamp (Wotan Ultravitalux, Gur 53 $\sim$, 220–230 V, 300 mnX, made in Germany) which gave ultraviolet light of wavelength around 350 nm. The lamp was placed at a distance of 3 ft from the reaction vessel. An ionic strength of 1·0 was maintained by adding the requisite amount of KCl. The absorbance of the solutions was measured at intervals of 5 min for 90 to 100 min. The rate of the reaction was calculated by Guggenheim's method[4] for first order reactions. The first order plots between log $[O.D._{T+t} -O.D._T]$ versus $T + t$ were linear to about 60% completion of the reaction.

[Fe (CN)$_4$ (1, 10 phenanthroline)]$^{2-}$ was prepared from K$_4$Fe (CN)$_6$ by the method of Schilt.[5] K$_3$Fe (CN)$_5$ H$_2$O was prepared from sodium nitroprusside by treatment with hydroxylamine hydrochloride.[6]

Iron was estimated after decomposing the complex by prolonged boiling with HCl in presence of a pinch of sodium bisulphite. The resulting solution was treated with hydroxylamine hydrochloride in presence of H$_2$SO$_4$ to reduce Fe (III) to Fe (II). Iron was then estimated spectrophotometrically using 1, 10 phenanthroline and adjusting the pH to 4·5 with dilute NH$_4$OH.

Carbon and nitrogen were estimated at the microanalytical laboratory Chemistry Department, Panjab University, Chandigarh.

Infrared spectra were recorded on Beckmann IR 20 infrared spectrophotometer in KBr discs.

ISOLATION OF THE COMPLEX

10 ml of 0·1 M L-histidine was mixed with 5 ml of 0·1 M K$_4$Fe (CN)$_6$ and the volume made up to 150 ml with buffer of pH 7·0. The solution was exposed to ultraviolet light (wavelength around 350 nm) for 3 hr. The clear green solution was concentrated at room temperature under vacuum until it became turbid, after which three times its volume of absolute alcohol was added. The solution was then shook vigorously, allowed to stand for four hours and centrifuged. The residue was washed several times with alcohol, then ether and dried under vacuum.

PREPARATION OF K$_2$Fe (CN)$_4$ (H$_2$O)$_2$

To 100 ml of a 0·01 M solution of K$_2$Fe (CN)$_4$ (1, 10 phenanthroline), about 1·5 gm of KOH was added and the solution shaken vigorously. After 5 min the precipitated 1, 10 phenanthroline was centrifuged out and discarded. The supernatant liquid was acidified with dilute HNO$_3$ and treated with about 50 ml of 0·05 M AgNO$_3$, which resulted in the precipitation of

the silver salt, $Ag_2Fe(CN)_4(H_2O)_2$. The precipitate was filtered off, washed with alcohol, then ether and dried in vacuum. The silver salt was subjected to chemical analysis and infrared spectral analysis.

For preparing solutions of $K_2Fe(CN)_4(H_2O)_2$, the requisite amount of the silver salt was treated with a 0·1 M KOH solution and the silver hydroxide precipitate filtered out. The pH of the filtrate was then adjusted with dilute HCl and the volume made up to known amounts with water.
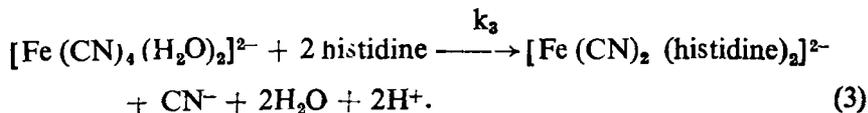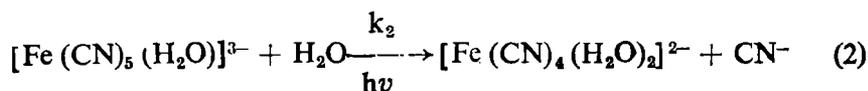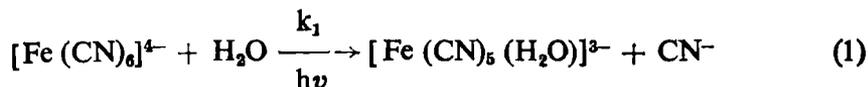
3. RESULTS AND DISCUSSION

The reaction shows first order dependence on $[Fe(CN)_6]^{4-}$ and is independent of histidine concentration (Table 1). Since $K_4Fe(CN)_6$ undergoes aquation[7,8] on irradiation with ultraviolet light, photochemical aquation of $K_4Fe(CN)_6$ is the primary step and the final product should be obtained through a rapid dark reaction of histidine with the aquation product. Separate experiments, however, reveal that the first aquation product, $[Fe(CN)_5(H_2O)]^{3-}$, does not react in dark with histidine. On the other hand, the reaction between $K_3Fe(CN)_5(H_2O)$ and histidine proceeds on irradiation with ultraviolet light, the product obtained thereby being the same as that obtained from $K_4Fe(CN)_6$. This reaction again shows first order dependence on $[Fe(CN)_5(H_2O)]^{3-}$ and is independent of histidine concentration (Table 1). It may, therefore, be concluded that $[Fe(CN)_5(H_2O)]^{3-}$ undergoes further aquation before reacting with histidine. Balzani et al.[9-11] while studying the photochemical reaction between $K_4Fe(CN)_6$

Table 1. Rates of the reaction at different concentrations of the reactants.

pH = 7·0			$\mu = 1\cdot0$	Temp. = 25°C
	Histidine — 0·5 × 10⁻³ M		k min⁻¹ (× 10³) for reaction of histidine with	
Conc. H 10⁻³ M	k min⁻¹ (X 10³) for reaction with		$K_4Fe(CN)_6$ (0·5 × 10⁻³ M)	$K_3Fe(CN)_5 H_2O$ (0·5 × 10⁻³ M)
	$K_4Fe(CN)_4$	$K_3Fe(CN)_5 H_2O$		
0·2	1·02	1·15	2·40	2·41
0·4	2·00	2·06	2·45	2·53
0·5	2·51	2·43	2·50	2·43
0·6	3·12	3·52	2·51	2·47
0·8	4·01	4·43	2·47	2·61
1·0	5·00	5·67	2·70	2·38

and 1, 10 phenanthroline have also proposed slow stepwise photoaquation of $K_4Fe(CN)_6$.

To verify the above, $[Fe(CN)_4(H_2O)_2]^{2-}$ was prepared by the hydrolysis of $[Fe(CN)_4 (1, 10 phenanthroline)]^{2-}$ with $KOH \cdot [Fe(CN)_4(H_2O)_2]^{2-}$ thus obtained was found to react with histidine rapidly in the dark and the resulting product was identical with the one obtained from $K_4Fe(CN)_6$. The following mechanism may thus be assigned to the reaction:

$$[Fe(CN)_6]^{4-} + H_2O \xrightarrow[hv]{k_1} [Fe(CN)_5(H_2O)]^{3-} + CN^- \qquad (1)$$

$$[Fe(CN)_5(H_2O)]^{3-} + H_2O \xrightarrow[hv]{k_2} [Fe(CN)_4(H_2O)_2]^{2-} + CN^- \qquad (2)$$

$$[Fe(CN)_4(H_2O)_2]^{2-} + 2\,histidine \xrightarrow{k_3} [Fe(CN)_2(histidine)_2]^{2-}$$
$$+ CN^- + 2H_2O + 2H^+. \qquad (3)$$

Since the rate is found to be independent of CN^- concentration, the reverse dark reaction in steps 1 and 2 is very slow as compared to the photochemical aquation, hence steps 1 and 2 may be considered as unidirectional while the solution is being exposed to ultraviolet light. The rate of the reaction will be the rate of formation of $[Fe(CN)_4(H_2O)_2]^{2-}$ giving rise to the following rate equation:

$$\frac{d}{dt}[Fe(CN)_4(H_2O)_2]^{2-} = K'[Fe(CN)_6]^{4-}.$$

Chemical analysis of the reaction product conformed to $K_2Fe(CN)_2$ (hist.)$_2$. As in other cyano complexes,[12–14] the infrared spectra shows the typical $C \equiv N$ stretching band at $2000\ cm^{-1}$. The absence of a band around $1720\ cm^{-1}$ and appearance of a strong absorption band at $1620\ cm^{-1}$ due to asymmetric stretching[15] of the COO^- group shows coordination of the metal to histidine through the oxygen of the carboxylic group. The symmetric stretching of the carboxylic group (coordinated) appears at $1390\ cm^{-1}$. Histidine does not show any absorption in the normal N–H stretching region[15] (3500–3300 cm^{-1}) but shows a band at $3120\ cm^{-1}$ due to NH_3 stretching. The appearance of this band at $3420\ cm^{-1}$ in the spectra of the complex indicates coordination of the amino acid to the metal through the nitrogen of the amino group. This is further supported by the shift in the C–N frequency of the $C-NH_2$ group of histidine from $1150\ cm^{-1}$ to $1130\ cm^{-1}$. Histidine is only bidentate in this complex because the imidazole ring nitrogen is not involved in coordination since the bands due to C–N and $C = N$ groups

of the imidazole residue of histidine (in the 1600–1300 cm^{-1} region) do not show any shifts in the spectra of the complex. The Fe–C stretching band[16] appears at 580 cm^{-1} and the Fe–N stretching band at 410 cm^{-1}. Thus histidine is bound to iron through the nitrogen of the amino group and oxygen of the carboxylic group. The complex may thus be assigned the following type of structure:
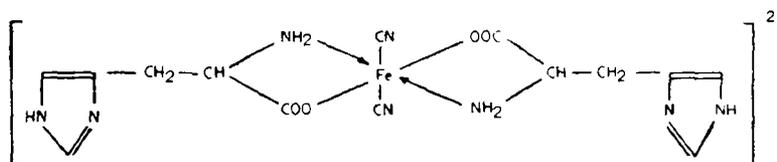
ACKNOWLEDGEMENT

REFERENCES

1. Malik, W. U. and Aslam, M., *Indian J. Chem.* **8** 736 (1970).

2. Malik, W. U. and Aslam, M., *J. Electroanal. Chem.* **25** 147 (1970).

3. Britton, H. T. S., *Hydrogen Ion*, Chapman and Hall, Essex, Vol. I (1956).

4. Guggenheim, E. A., *Phil. Mag.* **1** 538 (1926).

5. Schilt, A. A., *J. Am. Chem. Soc.* **79** 6421 (1957); **82** 3000 (1960).

6. Brauer, G., *Handbook of Preparative Inorganic Chemistry*, Academic Press. New York, (1965).

7. Asperger, S., *Trans. Faraday Soc.* **48** 617 (1952).

8. Asperger, S., Murati, I. and Cupahin, O., *J. Chem. Soc.* p. 1041 (1953).

9. Balzani, V., Carrassitti, V. and Sotoloos, R., *Ann. Chim.* (Rome), **54** 103 (1964).

10. Balzani, V., Carrassitti, V. and Moggi, L., *Ann. Chim.* (Rome), **54** 251 (1964).

11. Balzani, V. and Carrassitti, V., *Photochemistry of coordination compounds*, Academic Press London (1970).

12. Bonino, G. B. and Febri, G., *Alti. Accd. Zazl. Lincei, Rend. Classes, Sci. fig. mat. e, nat* **19** 386 (1959); **20** 414 (1956).

13. Miller, F. A. and Wilkens, G., *Anal. Chem.* **26** 3627 (1956).

14. Herrirgton, E. F. G. and Kynaston, W., *J. Chem. Soc.* p. 3555 (1955).

15. Rao, C. N. R., *Chemical Applications of Infrared Spectroscopy*, Academic Press, London (1963).

16. Nakamoto, K., *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley, New York (1962).