Inorganica Chimica Acta, *131* (1987) 113–117

Kinetics of the Thermal Decomposition of $[Fe(CN)_5H_2O]^{3-}$ in Aqueous Solutions Containing *o*-Phenanthroline with Reference to the Photolysis of $[Fe(CN)_5H_2O]^{2-}$

S. E. RONCO* and P. J. AYMONINO**

Química Inorgánica, Programa QUINOR, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 y 115, (1900) La Plata, Argentina

(Received August 4, 1986; revised January 22, 1987)

Abstract

Kinetics of the thermal decomposition of aquopentacyanoferrate(II) in aqueous solutions in the presence of *o*-phenanthroline were studied spectrophotometrically. The value found for the first order thermal rate constant (k_θ) at 30 °C, I = M (NaCl), was $(2.12 \pm 0.09) \times 10^{-4}$ s^{-1}. $\Delta H^{\neq} = (102 \pm 2)$ kJ mol^{-1} and $\Delta S^{\neq} = (23 \pm 14)$ J K^{-1} mol^{-1}. *o*-Phenanthroline gave place to important quantities of $[Fe(CN)_4(o\text{-phen})]^{2-}$ and $[Fe(o\text{-phen})_3]^{2+}$ and to smaller amounts of $[Fe(CN)_2(o\text{-phen})_2]$. The photochemical behavior of $[Fe(CN)_5H_2O]^{3-}$ was also investigated but it was found that UV light (365 nm wavelength) has no neat influence on it.

Introduction

The thermal and photochemical reactions of $[Fe(CN)_5H_2O]^{3-}$ were investigated in connection with the photolysis of $[Fe(CN)_5H_2O]^{2-}$ in aqueous solutions at slightly acid pH [1, 2]. Aquopentacyanoferrate(III) undergoes successive hydrolytic steps giving finally $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{3-}$ [1–3]. This latter ion is produced by the rapid attack of cyanide ions on aquopentacyanoferrate(III) [2]. Hexacyanoferrate(III) photolyzes producing $[Fe(CN)_5H_2O]^{3-}$ as one of the reaction products [4, 5]. The thermal decomposition of aquopentacyanoferrate(II) has been studied by several authors [6–8] who proposed the following stoichiometry for the reaction

$$6[Fe(CN)_5H_2O]^{3-} = 5[Fe(CN)_6]^{4-} + [Fe(H_2O)_6]^{2+} \qquad (1)$$

Intermediates could not be trapped on adding *o*-phenanthroline to the reacting medium and $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ were the only products reported for the reaction [8].

This work reports a kinetic study of the thermal decomposition of aquopentacyanoferrate(II) in aqueous solution at neutral pH. Intermediates trapped with *o*-phenanthroline initially added to the reaction mixture were $[Fe(CN)_4(o\text{-phen})]^{2-}$, $[Fe(o\text{-phen})_3]^{2+}$ and in a minor proportion, $[Fe(CN)_2(o\text{-phen})_2]$. The photochemical behaviour of $[Fe(CN)_5H_2O]^{3-}$ was also investigated, and it was found that UV light has no influence on the thermal reaction as expected from the photochemical behaviour of substituted pentacyanoferrate(II) complexes, $[Fe(CN)_5L]^{3-}$, which lose ligand L in the first stage [9–11].

Experimental

Absorbance measurements were performed with a Shimadzu UV-300 spectrophotometer with a temperature control. Spectra were resolved with a SAPCOM-1A data processor, and an Apple II Europlus computer was used to obtain the concentration of the components in the reaction medium. The electronic spectra were analyzed with the linear equations

$$A_{\lambda_i} = \Sigma \epsilon_{j,\lambda_i} c_j \qquad (2)$$

where A_{λ_i} is the absorbance at λ_i, ϵ_{j,λ_i}, the molar absorptivity of species j at λ_i, and c_j, its molar concentration. As a check for the procedure, synthetic mixtures of reactant and reaction products were analysed and results agreed within 96% with the expected values (see Fig. 2 below).

To identify the reaction products, the components of the reacted media were separated by gel filtration with a Sephadex G-25 column prepared in the usual way [12]. $[Fe(CN)_2(o\text{-phen})_2]$ was previously extracted with $CHCl_3$. Characterization

---

*Doctoral Fellow of CONICET, Argentina.

**Author to whom correspondence should be addressed, Member of the Carrera del Investigador Científico, CONICET, Argentina.

0020-1693/87/$3.50

of the isolated complexes were performed using vibrational and electronic spectroscopies [13].

All chemicals used were reagent grade. Aqueous solutions of $[Fe(CN)_5H_2O]^{3-}$ were freshly prepared by aquation of $[Fe(CN)_5NH_3]^{3-}$ [14] which was introduced as $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$. This salt was synthetized by a literature procedure [15]. The solutions were diluted to *ca.* $0.5–5 \times 10^{-4}$ M. Deoxygenated water was used and a slight amount of ascorbic acid was added to help to prevent the oxidation of $[Fe(CN)_5H_2O]^{3-}$. Enough NaCl was added to have 1.0 M total ionic strength.

Kinetic studies were done in the thermostated 1 cm path length optical cell of the spectrophotometer with solutions initially neutral and in the temperature range 20–45 °C (±0.1 °C). Results reported are averages of not less than three determinations.

To perform the photochemical experiments, a 200 W Osram HBO high-pressure mercury lamp and a conventional optical train with quartz lenses were used to illuminate with a parallel light beam the reaction cell placed in the Shimadzu cross-illumination attachment Model B, modified to fit the optical train used. Combined Jena glass-colored filters (UG2 + WG3) were employed to isolate the 366 nm mercury line. One centimeter optical path length square cells polished at the four sides were used for irradiations and simultaneous obtainment of the absorption spectra. The intensity of the light beam was measured using ferrioxalate actinometry [16, 17].

Results and Discussion

$[Fe(CN)_5H_2O]^{3-}$ Formation in the Thermal and Photochemical Decompositions of $[Fe(CN)_5H_2O]^{2-}$

It seems probable that the ferricyanide ion produced in those reactions performed in aqueous neutral or slightly acid solutions [1, 3]] undergoes further photochemical reduction and aquation forming $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5H_2O]^{2-}$ [4, 5]. By further reactions, both products could give place to $[Fe(CN)_5H_2O]^{3-}$ [4, 18]. As a test, we irradiated solutions of $[Fe(CN)_6]^{3-}$ initially neutral, and in the spectra obtained at short irradiation periods only ferricyanide and ferrocyanide ions were found. We proved also the simultaneous formation of $OH^{\bullet}$ radicals (which could be due to the oxidation of OH^- by $[Fe(CN)_6]^{3-}$ (*cf.* [4]) by the bleaching of the yellow colour of *p*-nitrosodimethylaniline (RNO) (a test which is specific for these radicals [19, 20]). Figure 1 shows successive absorption spectra of a 5.0×10^{-4} M solution of ferricyanide and 1.8×10^{-5} M in RNO under irradiation. The reduction of absorbance at 440 nm (the wavelength of the absorption maximum of RNO ($\epsilon_{440} = 34200$ M^{-1} cm^{-1})) is clearly seen. The green complex $[Fe(CN)_5RNO]^{3-}$ [19] was not detected proving the absence of $[Fe(CN)_5H_2O]^{3-}$ at short irradiation times. Moreover, when the reaction was performed in the presence of nitrosobenzene (ϕNO) instead of RNO, no absorption in the 530 nm region (λ_{max} of $[Fe(CN)_5\phi NO]^{3-}$ [4]) was observed but it appeared however at longer irradiation times, as shown by the successive spectra reproduced in Fig. 2. Thus, it seems probable that $[Fe(CN)_6]^{3-}$ is photoreduced to $[Fe(CN)_6]^{4-}$, which further aquates to $[Fe(CN)_5H_2O]^{3-}$.

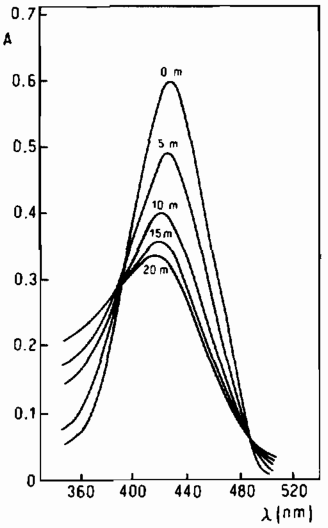

Fig. 1. Consecutive spectral changes observed in a 5×10^{-4} M solution of $[Fe(CN)_6]^{3-}$ and 1.8×10^{-5} M in *p*-nitrosodimethylaniline (RNO) when irradiated with 366 nm wavelength light.

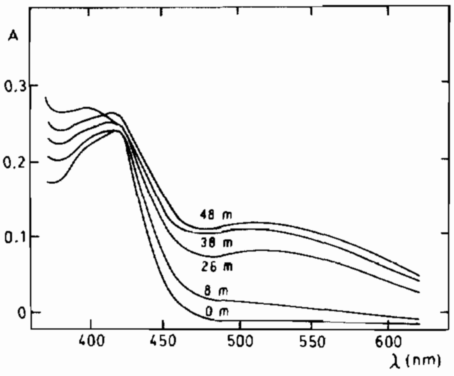

Fig. 2. Successive spectral changes observed in a 3×10^{-4} M solution of $[Fe(CN)_6]^{3-}$ and 10^{-2} M in ϕNO on irradiation.

Thermal Decomposition of $[Fe(CN)_5H_2O]^{3-}$

This reaction obeys the stoichiometry of eqn. (1) [6–8] which is analogous to the stoichiometry of the thermal and photochemical decomposition reactions of $[Fe(CN)_5H_2O]^{2-}$ in aqueous solutions [1–3]. Probably, $[Fe(CN)_5H_2O]^{3-}$ produces first diaquotetracyanoferrate(II) according to the equation

$$[Fe(CN)_5H_2O]^{3-} + H_2O = [Fe(CN)_4(H_2O)_2]^{2-} + CN^- \qquad (3)$$

The intermediate aquates further in successive steps giving $[Fe(H_2O)_6]^{2+}$ as the final product. $[Fe(CN)_6]^{4-}$ ions may be formed as result of the following reaction

$$[Fe(CN)_5H_2O]^{3-} + CN^- = [Fe(CN)_6]^{4-} + H_2O \qquad (4)$$

with a rate constant value of (1.5 ± 0.2) M^{-1} s^{-1} [18]. We were able to trap with *o*-phenanthroline (*cf.* [8]) some of the intermediate complexes as well as Fe^{2+} formed in the thermal reaction. So, in the reaction media $[Fe(CN)_4(o\text{-phen})]^{2-}$ appeared and, in minor proportions, $[Fe(CN)_2(o\text{-phen})_2]$, together with $[Fe(o\text{-phen})_3]^{2+}$. As $[Fe(CN)_4(o\text{-phen})]^{2-}$ and $[Fe(CN)_2(o\text{-phen})_2]$ are thermally very inert [21, 22], it seems reasonable to suppose that the production of $[Fe(o\text{-phen})_3]^{2+}$ was mainly due to the reaction between $[Fe(H_2O)_6]^{2+}$ and *o*-phenanthroline and not to further reactions of $[Fe(CN)_4(o\text{-phen})]^{2-}$ and $[Fe(CN)_2(o\text{-phen})_2]$ [3, 21]. Figure 3 shows successive spectra obtained with a solution of $[Fe(CN)_5H_2O]^{3-}$ in the presence of *o*-phenanthroline, at 26 °C. The slight absorbance decrease noted at the first stage of the reaction did not appear at temperatures above 32 °C. Spectra were analyzed considering that only $[Fe(CN)_5H_2O]^{3-}$, $[Fe(CN)_4(o\text{-phen})]^{2-}$ and $[Fe(o\text{-phen})_3]^{2+}$ were present in the reaction mixture in significant amounts. For the calculations, ferrocyanide was discarded due to its low absorbance in the visible region [23], introducing practically no error in the analysis of the spectra. Absorbances at three wavelengths were required therefore for the quantitative analysis of the mixtures. Values of molar absorptivities and wavelengths used are given in Table I. Figure 4, curve a, shows the spectrum of a solution 6.0×10^{-4} M in $[Fe(CN)_5H_2O]^{3-}$ and 2×10^{-2} M in *o*-phenanthroline irradiated for 157 min. Curve b reproduces a spectrum synthetized with the data processor using the concentrations of the component ions which result from the spectral analysis of Fig. 3(a). The difference noted between these spectra is due to the absorbance of the ligand *o*-phenanthroline which was not taken into account in the calculated spectrum. Figure 5 illustrates how concentrations of reactant and products changed with time. Data were taken from Fig. 3.

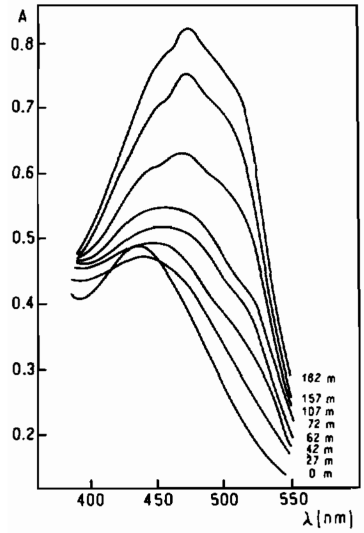

Fig. 3. Successive spectral changes observed in a solution 6.1×10^{-4} M in $[Fe(CN)_5H_2O]^{3-}$ and 2×10^{-2} M in *o*-phenanthroline.

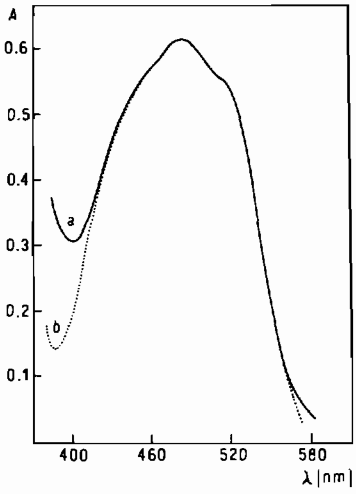

Fig. 4. (a) Measured spectrum of a 6.0×10^{-4} M and 2×10^{-2} M solution of $[Fe(CN)_5H_2O]^{3-}$ and *o*-phenanthroline, respectively, irradiated during 157 minutes; (b) calculated spectrum.

TABLE I. Molar Absorptivities at Selected Wavelengths for the Main Species Involved in the Thermal Reaction (M^{-1} cm^{-1})

Species	ϵ_{440}	ϵ_{470}	ϵ_{510}
$[Fe(CN)_5H_2O]^{3-}$	640[a]	425	100
$[Fe(CN)_4(o\text{-phen})]^{2-}$	4333	4750[b]	3226
$[Fe(o\text{-phen})_3]^{2+}$	7666	8950	11100[b]

[a] Ref. 19. [b] Ref. 2.

Plots of $\ln[Fe(CN)_5H_2O^{3-}]$ *versus* time were found to be linear, in agreement with first order kinetics. Thus, the following rate equation was deduced for the primary process of the thermal reaction

$$-\frac{d[Fe(CN)_5H_2O^{3-}]}{dt} = k_\theta[Fe(CN)_5H_2O^{3-}] \qquad (5)$$

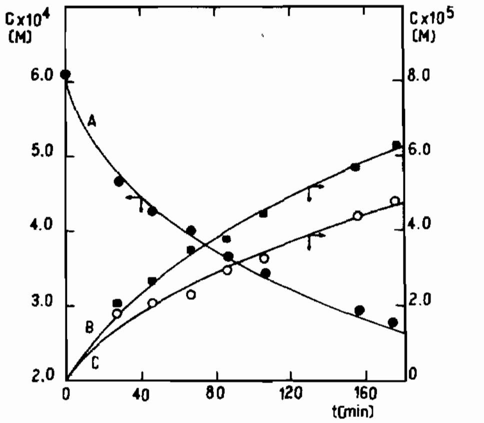

Fig. 5. Concentration changes of reactant and products in reaction of Fig. 3. A, $[Fe(CN)_5H_2O]^{3-}$; B, $[Fe(CN)_4(o\text{-phen})]^{2-}$; C, $[Fe(o\text{-phen})_3]^{2+}$.

where $k_\theta = (2.12 \pm 0.09) \times 10^{-4}$ s^{-1} [30 °C, $I = 1$ M (NaCl)] is the thermal reaction rate constant. Changes in the initial concentrations of $[Fe(CN)_5H_2O]^{3-}$ and *o*-phenanthroline, between 0.5×10^{-4} M and 6×10^{-4} M, and 10^{-3} and 10^{-1} M, respectively, did not affect the kinetic behaviour. It is to be noted that the formation of $[Fe(o\text{-phen})_3]^{2+}$ prevents the catalytic action of Fe^{2+} on the air oxidation of $[Fe(CN)_5H_2O]^{3-}$, which in the presence of free Fe^{2+} proceeds even in the dark [24] and could therefore interfere with the kinetic measuremens.

k_θ values at different temperatures are given in Table II. The Eyring plot, which gave a straight line, provided the following activation parameter values: $\Delta H^{\neq} = (102 \pm 2)$ kJ mol^{-1} and $\Delta S^{\neq} = (23 \pm 14)$ J K^{-1} mol^{-1}.

From the analysis of the spectra we found that about 0.27 mol of $[Fe(o\text{-phen})_3]^{2+}$ and 0.18 mol of $[Fe(CN)_4(o\text{-phen})]^{2-}$ were formed per mole of $[Fe(CN)_5H_2O]^{3-}$. Interestingly, the ratio between $[Fe(o\text{-phen})_3]^{2+}$ and $[Fe(CN)_4(o\text{-phen})]^{2-}$ concentrations remained constant during the reaction (see Fig. 5). It should be noted that the formation of $[Fe(CN)_4(o\text{-phen})]^{2-}$ was not reported previously [8].

TABLE II. Reaction Rate Constants for the Thermal Process

T (°C)	k_θ $\times 10^4$ (s^{-1})
16.5	0.30
20.5	0.49
26.5	1.23
32.2	2.32
39.0	7.43
42.9	11.34

TABLE III. Comparison Between Reaction Rate Constants

T (°C)	I_0 $\times 10^7$ (einstein min^{-1})^a	k_θ $\times 10^4$ (s^{-1})^b	k_i $\times 10^4$ (s^{-1})^c
25.0	0.89	1.00	0.99
34.4	2.71	3.64	3.27
39.5	2.72	7.10	7.12

$^a\lambda_i = 366$ nm. ^{b}Thermal rate constant. ^{c}Rate constant under irradiation.

$[Fe(CN)_5H_2O]^{3-}$ *Behavior Under UV Light*

Irradiation practically did not change the rate of the thermal reaction as shown by Table III which presents values found for the reaction rate constants of the dark reaction and of the reaction performed under irradiation at different intensities of incident light. It has been suggested [9–11] that the initial reaction of the visible–near UV photochemical decomposition of substituted pentacyanoferrate(II) complexes, $[Fe(CN)_5L]^{3-}$, in aqueous solutions, is the replacement of L by water as represented by eqn. (6)

$$[Fe(CN)_5L]^{3-} + H_2O \xrightarrow{h\nu} [Fe(CN)_5H_2O]^{3-} + L \qquad (6)$$

The alternative photoreaction leading to the aquotetracyano-L-ferrate(II) species has been reported to be of minor importance or nonexistent when the wavelength of light is 366 nm [10, 11]. To put into evidence for aquopentacyanoferrate(II) such an initial photochemical act (loss of water), O^{18} enriched water should be used as solvent. Irradiation with 366 nm light should then merely induce water exchange between $[Fe(CN)_5H_2O]^{3-}$ and the solution while the thermal reaction leads to cyanide solvolysis.

Acknowledgements

To CONICET (Programa QUINOR), SUBCYT, and CICPBA, Argentina, for financial support.

References

1 S. E. Ronco and P. J. Aymonino, *Inorg. Chim. Acta, 77,* L31 (1983).
2 S. E. Ronco and P. J. Aymonino, *Transition Met. Chem.*, in press.
3 V. Balzani, V. Carassiti and R. Soto Loos, *Ann. Chim. Rome, 54,* 103 (1964).
4 J. Legros, *C.R., 265,* 225 (1967).
5 L. Moggi, F. Balleta, V. Balzani and F. Scandola, *J. Inorg. Nucl. Chem., 28,* 2589 (1966).
6 G. Emschwiller, *C.R., 270,* 1362 (1970).
7 G. Emschwiller, *C.R., 274,* 1500 (1972).

8 J. A. Olabe and H. O. Zerga, *Inorg. Chem.*, *22*, 4156 (1983).
9 G. L. Geoffrey and M. S. Wrighton, 'Organometallic Photochemistry', Academic Press, New York, 1970, p. 270.
10 J. E. Figard and J. D. Petersen, *Inorg. Chem.*, *17*, 1059 (1978).
11 H, E. Toma and N. Y. Murakami Iha, *Inorg. Chem.*, *21*, 3573 (1982).
12 'Sephadex, Gel Filtration in Theory and Practice', Pharmacia Fine Chemicals, 1975.
13 (a) A. A. Schilt, *J. Am. Chem. Soc.*, *82*, 3000 (1960); (b) A. J. McCaffery, S. F. Mason and B. J. Norman, *J. Chem. Soc. A*, 1428 (1969); (c) J. J. Alexander and H. B. Gray, *J. Am. Chem. Soc.*, *90*, 4260 (1968).
14 A. D. James, R. S. Murray and C. E. Higginson, *J. Chem. Soc., Dalton Trans.*, 1273 (1974).
15 J. D. Kenney, T. P. Flynn and J. B. Gallini, *J. Inorg. Nucl. Chem.*, *20*, 75 (1962).
16 (a) C. A. Parker, *Proc. R. Soc. London, Ser. A*, *220*, 104 (1953); (b) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, *225*, 518 (1956).
17 J. G. Calvert and J. N. Pitts, 'Photochemistry', Wiley, New York, 1966.
18 V. Gáspár and M. T. Beck, *Polyhedron*, *2*, 387 (1983).
19 J. Kraljić and C. N. Trumbore, *J. Am. Chem. Soc.*, *87*, 2548 (1965).
20 B. Sieklucka, A. Kanas and A. Samotus, *Transition Met. Chem.*, *7*, 131 (1982).
21 V. Balzani, V. Carassiti and L. Moggi, *Ann. Chim. Rome*, *54*, 251 (1964).
22 V. Balzani, V. Carassiti and L. Moggi, *Inorg. Chem.*, *3*, 1253 (1964).
23 J. Alexander and H. B. Gray, *J. Am. Chem. Soc.*, *90*, 4262 (1968).
24 H. E. Toma, *Inorg. Chim. Acta*, *15*, 205 (1975).