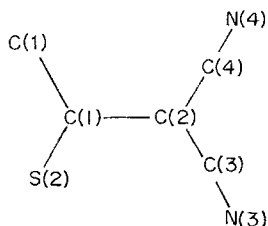**Table 2.** Geometrical features for covalent and ionic bonded i-mnt. Bond lengths are in Å, angles in °.

Compound	[Ni(i-mnt)$_2$]$^{2-}$ [8]		Na$_2$(i-mnt)·3H$_2$O[10]	K$_2$(i-mnt)·H$_2$O[9]
C(1)–S(1)	1.83(2)	1.87(2)	1.705(5)	1.713(3)
C(1)–S(2)	1.78(2)	1.78(2)	1.728(5)	1.713(3)
C(1)–C(2)	1.28(2)	1.28(2)	1.404(7)	1.405(7)
C(2)–C(3)	1.43(3)	1.43(3)	1.412(7)	1.420(4)
C(2)–C(4)	1.56(3)	1.51(3)	1.410(7)	1.420(4)
C(3)–N(3)	1.11(2)	1.09(2)	1.155(7)	1.143(4)
C(4)–N(4)	1.10(2)	1.13(2)	1.149(7)	1.143(4)
S(1)–C(1)–S(2)	104(1)	101.8(6)	122.8(3)	121.3(3)

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Kinetics of the thermal and photochemical decomposition of aquapentacyanoferrate(III) in aqueous solution[a]

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Summary

The kinetics of the thermal and photochemical decomposition of aquapentacyanoferrate(III) ion in aqueous solution in the presence of *o*-phenanthroline was studied spectrophotometrically. The first-order rate constant (k_θ) at 30° C [I = 1 M(NaCl)] for the thermal reaction is $(1.49 \pm 0.13) \times 10^{-6} \text{s}^{-1}$ with $\Delta H^{\neq} = (158 \pm 7) \text{kJ mol}^{-1}$ and $\Delta S^{\neq} = (42 \pm 4) \text{JK}^{-1} \text{mol}^{-1}$. The initial quantum yield for the photochemical reaction at pH = 7 is independent of the light intensity and is $(1.49 \pm 0.33) \times 10^{-2} \text{mol einstein}^{-1}$.

Introduction

The photolysis of aquapentacyanoferrate(III) ion in aqueous solution has been previously studied stoichiometrically, with reference to the photolysis of nitroprusside[1]. The photochemistry of nitroprusside has been studied repeatedly but, unfortunately, the results have led to divergent mechanistic conclusions, which include

almost all the types of photochemical reaction of coordination compounds[2–6]. It may be supposed that the variety of pathways proposed results from the experimental methods used in the earlier studies, which did not allow differentiation of primary from secondary products. Jarzynowski *et al.*[5] studied the reaction using flash photolysis and proposed the production of $[Fe(CN)_5H_2O]^{2-}$ in the primary process. The other reactions taking place in the overall photochemical reaction were not investigated. The present work reports a kinetic study of the thermal decomposition and the photochemical behaviour of aquapentacyanoferrate(III) in aqueous solution, aimed at clarifying the different steps occurring in the reactions following the primary act of the photochemical decomposition of nitroprusside. We found no report in the literature on the thermal and photochemical decompositions of pentacyanoferrate(III) complexes, $[Fe(CN)_5L]^{2-}$, so this is the first contribution on these subjects**.

Experimental

Absorbance measurements were performed with a Shimadzu UV-300 recording spectrophotometer with 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 of the irradiated solutions were analysed with the linear equations:

$$A_\lambda = \Sigma \varepsilon_{i,\lambda} c_1 \tag{1}$$

200 W and 500 W Osram HBO high-pressure mercury lamps and a conventional optical train with quartz lenses were used to illuminate the reaction cell with a parallel light beam placed in the Shimadzu Model B cross-illumination attachment, modified to fit the optical train used. Combined Jena coloured-glass filters (UG2 + WG1) were employed to isolate the 365 nm mercury line. One-centimetre optical-path-length square quartz cells polished on all four sides were used for irradiations. The intensity of the light beam was measured using ferrioxalate actinometry[8,9]. The quantum yield for ferrous ion production in the photolysis of ferrioxalate solution was taken as 1.21 ± 0.06 mol einstein^{-1} at 365 nm[8]. Measurements were performed only after stabilization of the lamp emission, which took about 1 h. Values obtained for the intensity of the light impinging on the cell were $(1.59 \pm 0.09) \times 10^{-7}$ and $(6.37 \pm 0.08) \times 10^{-7}$ einstein min^{-1} for the 200 and 500 W lamps, respectively. We used an empirical value for the molar absorptivity of 550 M^{-1} cm^{-1} at 365 nm for the aquapentacyanoferrate(III) ion. The reported value[10] at 395 nm is 743 M^{-1} cm^{-1}.

A Sargent-Welch pH meter model LSX with a miniature Sargent-Welch combined glass electrode, which was calibrated against commercial standard buffers, was used for pH measurements.

Free cyanide ion concentration was measured with an Orion cyanide ion-selective electrode in solutions ob-

tained by displacing HCN from the photolyzed solutions at pH = 4 (AcOH-NaOAc buffer) with N_2, and bubbling the gas mixture into aqueous 0.1 N NaOH. Measurements were not directly done in the photolyzed solutions because the complexes present in the mixture interfered.

All chemicals used were reagent grade. Aqueous solutions of $[Fe(CN)_5H_2O]^{2-}$ were freshly prepared by literature procedures[10] and further diluted to *ca.* $3–5 \times 10^{-4}$ M. Enough NaCl was added to give a total ionic strength of 1.0 M.

Kinetic studies were carried out at pH values in the range 4–7 to avoid the formation of $[Fe(CN)_5OH]^{3-}$ in the solution (pK of $[Fe(CN)_5H_2O]^{2-} = 8.3$[10]) Rate constants are averages of three determinations.

Separation of the components of the reaction medium were performed by gel filtration with a Sephadex G-25 column prepared in the usual way[11]. $[Fe(CN)_2(o\text{-}phen)_2]$ (o-phen = o-phenanthroline) was isolated by extracting with $CHCl_3$. $[Fe(o\text{-}phen)_3]^{2+}$ was precipitated as the perchlorate by adding $NaClO_4$ to the reaction mixture. Characterization of the isolated complexes was performed by vibrational and electronic spectroscopies.

Results and discussion

In aqueous solutions, either buffered (pH = 4–7) or unbuffered, aquapentacyanoferrate(III) suffers a slow thermal aquation reaction whose rate is increased by irradiation and which returns to the original value when the irradiation is interrupted.
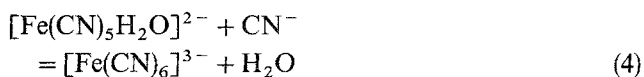
The thermal and photochemical reactions obey the following stoichiometry[1].

$$6[Fe(CN)_5H_2O]^{2-}$$
$$= 5[Fe(CN)_6]^{3-} + [Fe(H_2O)_6]^{3+} \tag{2}$$
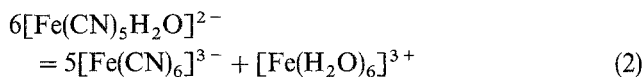
$[Fe(H_2O)_6]^{3+}$ hydrolyzes giving $[Fe(H_2O)_5OH]^{2+}$ and even $[Fe(H_2O)_4(OH)_2]^+$ at neutral pH because of its high acidity[12]. It seems probable that $[Fe(CN)_5H_2O]^{2-}$ first undergoes aquation to diaquotetracyanoferrate(III) according to Equation 3.

$$[Fe(CN)_5H_2O]^{2-} + H_2O$$
$$= [Fe(CN)_4(H_2O)_2]^- + CN^- \tag{3}$$
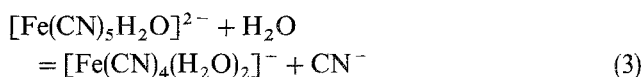
$[Fe(CN)_6]^{3-}$ ions may be formed as result of the following reaction (4).

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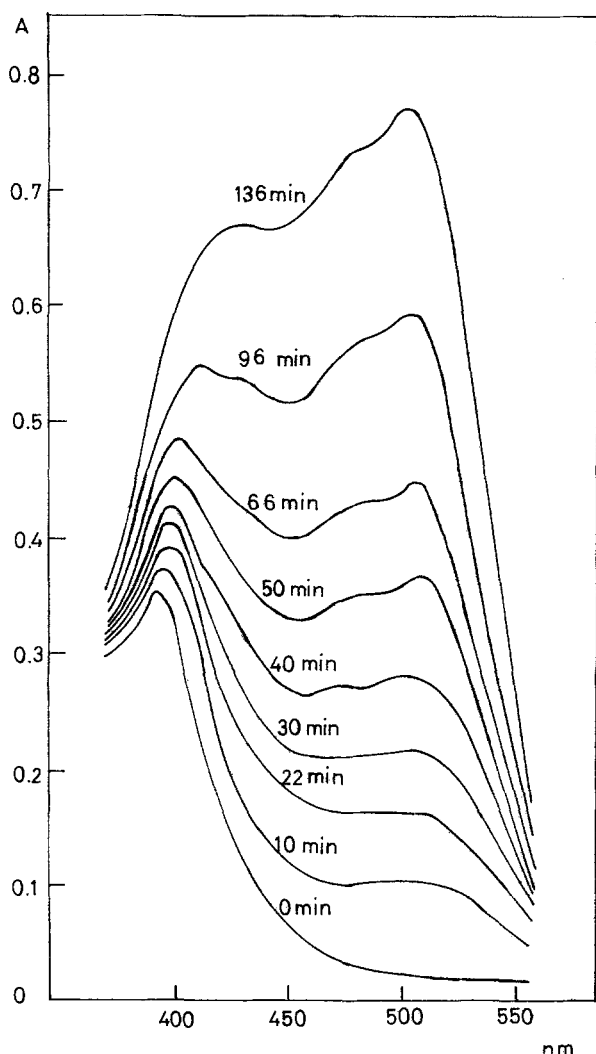$$= [Fe(CN)_6]^{3-} + H_2O \tag{4}$$

Some of the intermediates of the thermal and photochemical reactions were trapped with o-phenanthroline. Since the cyanide ion reduces the iron(III) cyano(o-phenanthroline) complexes[13] in the reaction mixture, $[Fe(CN)_4(o\text{-}phen)]^{2-}$ and, in a small amount, $[Fe(CN)_2(o\text{-}phen)_2]$ are formed. Interestingly, Schilt[14] proposed a rapid and complete disproportionation of the neutral complex in water, giving $[Fe(o\text{-}phen)_3]^{2+}$ and $[Fe(CN)_4(o\text{-}phen)]^{2-}$ a proposal which was later refuted by Margerum and Morgenthaler[15] who showed that $[Fe(CN)_2(o\text{-}phen)_2]$ is stable in water. $[Fe(o\text{-}phen)_3]^{3+}$ is stable only in solutions of high acidity. In neutral solutions, $[Fe(o\text{-}phen)_3]^{3+}$ undergoes fairly rapid spontaneous reduction to $[Fe(o\text{-}phen)_3]^{2+}$ with a rate constant which increased with pH. In aqueous basic solutions the reduction rate constant value is (210 ± 1) M^{-1} s^{-1} (25° C)[16]. As u.v. light accelerates this reaction, in the

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** **Note added in proof.** After submitting the paper for publication, we became acquainted with a publication by M. W. Fuller, K.-M. F. Le Brocq, E. Leslie and I. R. Wilson, *Aust. J. Chem.*, **39**, 1411 (1986), were the formation of $[Fe(CN)_5H_2O]^{2-}$ is confirmed as the first chemical step in the photolysis of $[Fe(CN)_6]^{3-}$ in acidic solutions (in the absence of a sequestering agent) followed by condensation to $[Fe_2(CN)_{10}]^{4-}$ and further reduction to $[Fe(CN)_{10}]^{5-}$.

irradiated solutions [Fe(*o*-phen)$_3$]$^{2+}$ appears rather than [Fe(*o*-phen)$_3$]$^{3+(1)}$. Under u.v.-irradiation [Fe(CN)$_4$(*o*-phen)]$^{2-}$ turns slowly into [Fe(CN)$_2$(*o*-phen)$_2$], the quantum yield being low (0.38 × 10^{-3} mol einstein^{-1})[17]. The thermal decomposition of [Fe(CN)$_2$(*o*-phen)]$^{2-}$ is also very slow[17]. [Fe(CN)$_2$(*o*-phen)$_2$] itself is very inert, both thermally and photochemically[18]. It seems therefore reasonable to suppose that the formation of [Fe(*o*-phen)$_3$]$^{2+}$, even after short irradiation times[1,19], is due to the reaction of *o*-phenanthroline with aquahydroxocomplexes of iron(III), which parallels the formation of [Fe(CN)$_4$(*o*-phen)]$^{2-}$ and [Fe(CN)$_2$(*o*-phen)$_2$] from the respective aquacyanocomplexes.

Figure 1 shows successive spectral changes observed in

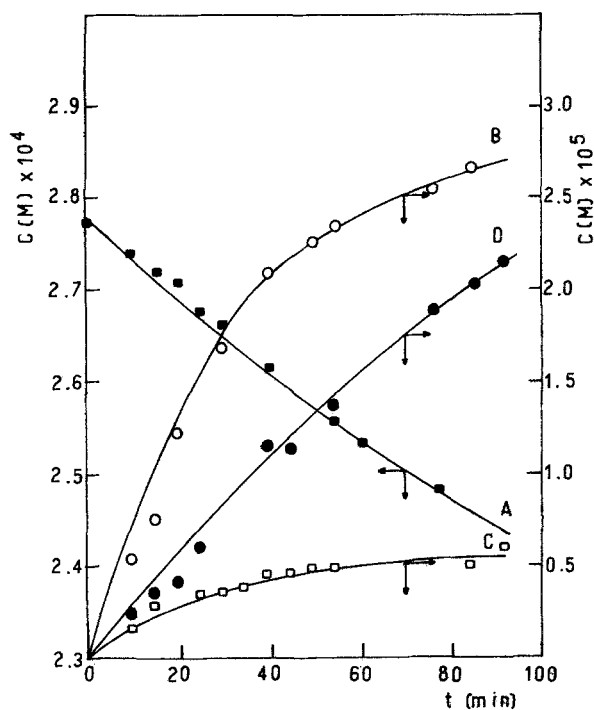an irradiated solution of [Fe(CN)$_5$H$_2$O]$^{2-}$. Spectra were analysed assuming that only [Fe(CN)$_5$H$_2$O]$^{2-}$, [Fe(CN)$_6$]$^{3-}$, [Fe(CN)$_4$(*o*-phen)]$^{2-}$ and [Fe(*o*-phen)$_3$]$^{2+}$ were present in the mixture in significant amounts. [Fe(CN)$_2$(*o*-phen)$_2$], [Fe(CN)$_5$H$_2$O]$^{3-}$, and [Fe(CN)$_6$]$^{4-}$ were proved to be present in very small quantities and the presence of other components (intermediate aquacomplexes) were considered negligible when the progress of the reaction was less than 10%. It is to be noted that [Fe(CN)$_5$H$_2$O]$^{3-}$ and [Fe(CN)$_6$]$^{4-}$ are products of the photoreduction of [Fe(CN)$_6$]$^{3-(20,21)}$.

Absorbances at four wavelengths were required therefore for the quantitative analysis of the mixtures. Values of molar absorptivities and wavelengths used are given in Table 1. Figure 2 shows the concentrations of the four ions at different reaction times. Plots of ln[Fe(CN)$_5$H$_2$O^{2-}] versus time were found to be linear, in agreement with first-order kinetics. Thus, the following rate equation was deduced for the primary process.

$$-\frac{d[Fe(CN)_5H_2O^{2-}]}{dt} = k_t[Fe(CN)_5H_2O^{2-}]$$

$$= (k_\theta + k_\phi)[Fe(CN)_5H_2O^{2-}] \qquad (5)$$

Figure 1. Spectral changes observed in a 4.5 × 10^{-4} M solution of [Fe(CN)$_5$H$_2$O]$^{2-}$ and 2 × 10^{-2} M in *o*-phenanthroline when irradiated.

Figure 2. Concentration changes of the component ions of a 2.8 × 10^{-4} M solution of [Fe(CN)$_5$H$_2$O]$^{2-}$ and 2 × 10^{-2} M in *o*-phenanthroline upon irradiation. (A) [Fe(CN)$_5$H$_2$O]$^{2-}$, (B) [Fe(CN)$_6$]$^{3-}$, (C) [Fe(CN)$_4$(*o*-phen)]$^{2-}$, (D) [Fe(*o*-phen)$_3$]$^{2+}$.

Table 1. Molar absorptivities at selected wavelengths for the main species involved in the thermal and photochemical reactions[a].

Species	ε_{365}	ε_{395}	ε_{420}	ε_{470}	ε_{510}
[Fe(CN)$_5$H$_2$O]$^{2-}$	550	743[b]	328	0	0
[Fe(CN)$_6$]$^{3-}$	655	628	1100[c]	0	0
[Fe(CN)$_4$(*o*-phen)]$^{2-}$	1030	1710	3025	4750[d]	3226
[Fe(*o*-phen)$_3$]$^{2+}$	700	3245	6170	8950	11100[d]

[a]Data in M^{-1}cm^{-1}; [b]Reference 10; [c]Reference 22; [d]Reference 7.

where $k_t = (1.73 \pm 0.01) \times 10^{-5} \mathrm{s}^{-1}$ [30° C, $I = 1$ M (NaCl), $I_0 = 1.59 \pm 0.09) \times 10^{-7}$ einstein min^{-1}] is the total rate constant for the photochemical and thermal reactions, k_θ is the rate constant of the thermal reaction and k_ϕ, of the photochemical reaction.
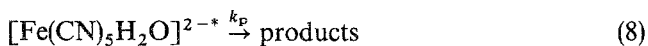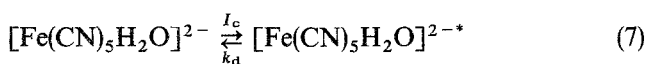
For the thermal reaction, the measured value of the rate constant, k_θ, is $(1.49 \pm 0.13) \times 10^{-6} \mathrm{s}^{-1}$ [30° C, $I = 1$ M (NaCl)]. The k_θ values at different temperatures are given in Table 2. The Eyring plot provides the following activation parameters: $\Delta^{\neq} = (158 \pm 7) \mathrm{kJ\,mol}^{-1}$ and $\Delta S^{\neq} = (42 \pm 4) \mathrm{J\,K}^{-1}\mathrm{mol}^{-1}$. Therefore, reaction 3 seems to be the rate-limiting step. It should be of D or, more likely, I_d type[23]. Interestingly, no report could be found in the literature on the kinetics of reaction 4. The high affinity of cyanide ions for $[\mathrm{Fe(CN)_5H_2O}]^{2-}$ $(K_{[\mathrm{Fe(CN)_6}]^{3-}} = 5 \times 10^{8}$[24]) is to be noted in this connection.

Table 3 shows the direct relationship between rate constant and light intensity. The following equation is obeyed[9].

$$n = \log(k_\phi/k^i_\phi)/\log(I_0/I^i_0) \tag{6}$$

where n is the order of the light intensity, k^i_ϕ is the rate constant for an intensity I^i_0 of the incident beam (full light intensity I_0 reduced to I^i_0 with wire gratings). Table 3 gives $n = 1.01 \pm 0.06$.

The photochemical behaviour of the system can be described by the following equations.

$$[\mathrm{Fe(CN)_5H_2O}]^{2-} \underset{k_d}{\overset{I_c}{\rightleftarrows}} [\mathrm{Fe(CN)_5H_2O}]^{2-*} \tag{7}$$

$$[\mathrm{Fe(CN)_5H_2O}]^{2-*} \overset{k_p}{\rightarrow} \text{products} \tag{8}$$

where I_c is the average number of moles of photons absorbed by the reactant per unit volume and unit time, $[\mathrm{Fe(CN)_5H_2O}]^{2-*}$ represents the excited species, k_d is the rate constant of the deactivation reactions and k_p is the rate constant of the product-forming reaction. Introducing the quantum yield $\Phi = k_p/k_p + k_d$, and applying the steady-state approximation for the concentration of the

Table 2. Rate constants for the thermal process.

$10^5 kg(\mathrm{s}^{-1})$	$t(° C)$
0.285	32.6
0.309	33.8
1.17	39.9
3.11	44.5

Table 3. Relationship between light intensity and rate constant of the photochemical reaction.

$I^i_0 \times 10^7$ (einstein min^{-1})	$k^i_\phi \times 10^5$ (s^{-1})
3.22	6.16
0.95	1.79
0.73	1.32
0.40	0.51
0.35	0.58
0.34	0.46
0.28	0.46
0.25	0.33

excited complex, the following rate equation is obtained.

$$-\mathrm{d}[\mathrm{Fe(CN)_5(H_2O)^{2-}}]/\mathrm{d}t$$
$$= I_c\Phi + k_\theta[\mathrm{Fe(CN)_5(H_2O)^{2-}}] \tag{9}$$

where

$$I_c = I_0(1 - 10^{-\Sigma\varepsilon_i c_i l})\varepsilon_1 c_1/\Sigma\varepsilon_i c_i \tag{10}$$

The factor $I_0(1 - 10^{-\Sigma\varepsilon_i c_i l})$ measures the light intensity absorbed by $[\mathrm{Fe(CN)_5H_2O}]^{2-}$ and the products, and the ratio $\varepsilon_1 c_1/\Sigma\varepsilon_i c_i$ gives the fraction of light absorbed by the reactant (the summation $\Sigma\varepsilon_i c_i$ is extended over all substances absorbing the exciting light to take into account the inner filter action). Molar absorptivities at the irradiation wavelength (365 nm) used in calculations are given in Table 1. Quantum yields were obtained with Equation 9. Values for reaction time were plotted against percentage of reaction and the initial value of Φ was obtained by extrapolation to 0% reaction, giving $(1.49 \pm 0.33) \times 10^{-2}$ mol einstein^{-1}.

As the initial quantum yield is independent of the light intensity, as shown by Table 4, a single photon process should be operating.

In unbuffered solutions, both thermal and photochemical reactions cause a pH increase, as illustrated by Figure 3, due to the liberation of cyanide ions in the hydrolytic steps of the aquocyanocomplexes. Assuming that the protonation of CN$^-$ ions (pK of HCN $= 9.36$[25])

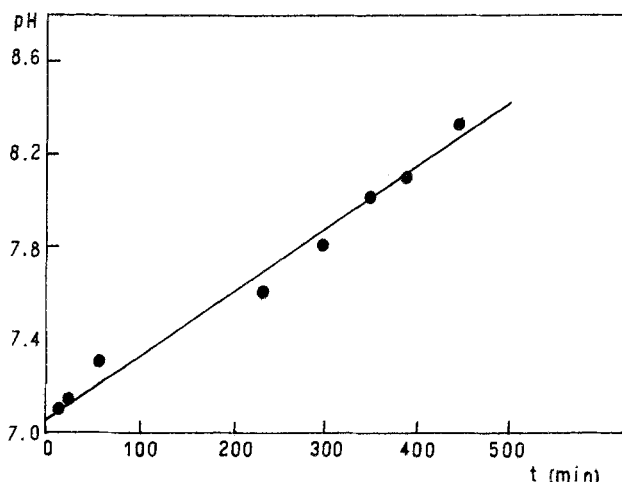**Table 4.** Initial quantum yields at different intensities of absorbed light.

$I_c \times 10^8$ (einstein min^{-1})	$\Phi_0 \times 10^2$ (mol einstein^{-1})
1.51	1.36
2.49	1.74
2.62	1.47
3.12	1.46
3.36	1.42
3.56	1.81
3.92	1.42
5.38	1.68
6.47	1.56
7.29	1.62
8.64	1.84

Figure 3. pH changes during photolysis of a solution 6.5×10^{-4} M in $[\mathrm{Fe(CN)_5H_2O}]^{2-}$ and 2×10^{-2} M in *o*-phenanthroline.

is responsible for the pH changes, the concentrations of free cyanide ions were calculated. The low values obtained (maximum $ca. 10^{-8}$ M) confirmed that the cyanide ions were rapidly consumed in the formation of $[Fe(CN)_6]^{3-}$ (4).

Progressive aquation of the aquacyanocomplexes was followed using the above procedure of displacing the CN^- ions as HCN from the reacting solution. Figure 4 shows the increase of free CN^- concentration produced during the photochemical reaction, which is consistent with the reaction described by equations 2, 3 and 4, as shown by the results of the appropriate calculations.

The production of $[Fe(o\text{-phen})_3]^{2+}$ is mainly due to a series of reactions involving the Fe^{III} aquahydroxocomplexes (see above). Contributions from the photochemical or thermal decomposition of $[Fe(CN)_4(o\text{-phen})]^{2-}$ should be considered of minor importance. Rate constants for the formation of $[Fe(CN)_4(o\text{-phen})]^{2-}$, k_1, and of $[Fe(o\text{-phen})_3]^{2+}$, k_2, were measured giving a mean k_2/k_1 ratio of 2.42 ± 0.18, which seems to be independent of light intensity and temperature, as shown in Table 5.

The ferricyanide ion formed in the reaction presumably undergoes photochemical and thermal reaction. It could produce, in the first step, either $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5H_2O]^{2-(20)}$ or only the latter[21].

Conclusions

The thermal and photochemical decomposition reactions of $[Fe(CN)_5H_2O]^{2-}$ are both first-order in the reactant concentration. The photochemical reaction implies a
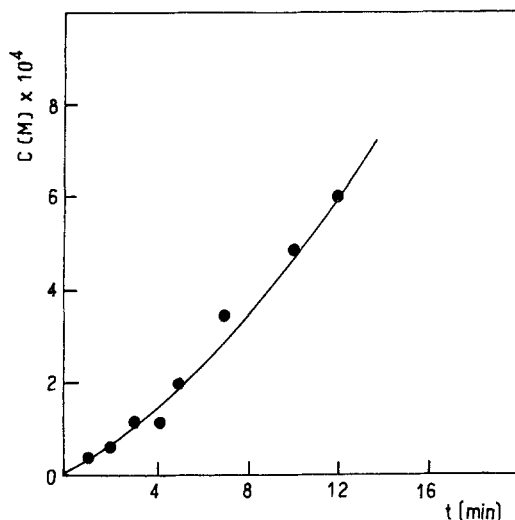
Figure 4. Experimental cumulative cyanide ion concentration in a 4.3×10^{-4} M solution of $[Fe(CN)_5H_2O]^{2-}$ and 2×10^{-2} M in o-phenanthroline during irradiation ($I_0 = 1.11 \times 10^{-5}$ einstein min^{-1}).

Table 5. Rate constants of production of $[Fe(CN)_4(o\text{-phen})]^{2-}$ (k_1) and $[Fe(o\text{-phen})_3]^{2+}$ (k_2).

I_0(einstein min^{-1}) $\times 10^{-7}$	t (°C)	k_1(s^{-1}) $\times 10^6$	k_2(s^{-1}) $\times 10^6$	k_2/k_1
0.424	33.7	0.74	1.89	2.57
0.499	35.5	1.99	5.24	2.62
0.586	36.8	2.86	6.49	2.26
1.964	36.2	7.16	16.10	2.25
3.082	32.6	7.81	17.70	2.26
2.097	43.8	9.47	24.34	2.57

single-photon process, as shown by the constancy of the initial quantum yield and by the first-order dependence of the reaction rate on light intensity. The common initial step of both reactions seems to be the replacement of one cyanide group by water, followed by further hydrolysis leading to iron(III) aquahydroxocomplexes. Cyanide ions produced in the hydrolytic steps react rapidly with undecomposed $[Fe(CN)_5H_2O]^{2-}$, yielding $[Fe(CN)_6]^{3-}$. In the presence of o-phenanthroline mixed Fe^{II} cyano(o-phenanthroline) and $[Fe(o\text{-phen})_3]^{2+}$ complexes are formed.

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