

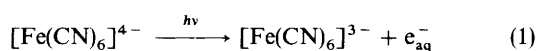
# Effects of Temperature on the Photo-oxidation Quantum Yield of Aqueous Hexacyanoferrate(II) Anion

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The photo-oxidation quantum yield of aqueous hexacyanoferrate(II) anion in the presence of N<sub>2</sub>O is found to be moderately dependent on temperature at 253.7 nm, but at 228.8 nm only very slightly dependent, and with a substantially lower quantum yield. In considering models of the photoionization process, it is deduced that, at least at the lower wavelength of irradiation, the charge-transfer metal-to-ligand state produced by light absorption does not quantitatively populate the CTTS state believed to be the intermediate in solvated electron production. At 253.7 nm, where the slope of the plot of  $\ln(\phi_e^{-1} - 1)$  against  $T^{-1}$  is somewhat less than for iodide ion, the involvement of some other fate for the CTML state (but to a much lesser extent than at the higher quantum energy) is a clear possibility.

Previous studies<sup>1-7</sup> of the photo-oxidation of aqueous hexacyanoferrate(II) ion:



have investigated the identity of the reducing species formed in the primary process,<sup>1,2</sup> the dependence of the quantum yield on excitation wavelength,<sup>3</sup> the occurrence of photo-aquation reactions<sup>4-7</sup> and unusual kinetic salt effects exhibited<sup>2</sup> by the hydrated electron produced in step (1).

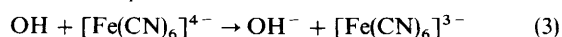
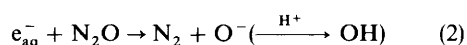
While some experiments over a range of temperatures were reported by Ohno,<sup>4</sup> it was considered desirable to carry out a more extensive study of the effect of temperature on the quantum yield of step (1).

In many cases where the solvated electron can be generated photochemically<sup>8</sup> from a reducing anion, the excitation process involved is classed as belonging to the 'charge-transfer-to-solvent' (CTTS) type, denoting an absorption process not present in the ionic lattice and occurring because the electron can be promoted to a spherically symmetrical orbital in the potential well formed by the oriented solvent molecules of the polar solvent. While halide ions, apart from fluoride, clearly exhibit CTTS spectra, characterised by perceptible shifts in the absorption edge due to changes in solvent polarity, temperature or applied pressure,<sup>9</sup> the situation in regard to hexacyanoferrate(II) anion is less clear cut. While the intense band at 218 nm has the characteristics of a metal-to-ligand charge transfer absorption and has been so assigned,<sup>10,11</sup> pressure effects on its long-wavelength edge are consistent<sup>12</sup> with CTTS behaviour. However, this peak exhibits no blue shift with temperature,<sup>7</sup> as is generally found with halide ions and regarded as a CTTS characteristic.

Since the effect of temperature on the quantum yield of the hydrated electron from singly charged anions involving CTTS states has been well documented earlier,<sup>13-15</sup> the temperature dependence established in this present study may be expected to have clear implications regarding the electronic states involved in the photoionization of hexacyanoferrate(II) anion.

## Experimental

It was decided to use N<sub>2</sub>O to scavenge the hydrated electron produced in the primary process and thus prevent the recombination of the products of step (1).



Also, the visible absorption band of the product ion was employed to monitor the extent of the photoreaction.

AnalaR (BDH) potassium hexacyanoferrate(II) was used, along with doubly distilled water. To minimise thermal oxidation of the solutions by dissolved oxygen, the doubly distilled water was deoxygenated by boiling while bubbling argon through it, before the weighed salt was added to it. Anaesthetic-grade N<sub>2</sub>O was further purified by fractional distillation and by pumping at 77 K to remove non-condensable gases. All glassware and the photolysis vessels were carefully cleaned with permanganic acid followed by a nitric acid-hydrogen peroxide mixture and then numerous rinsings.

The photolysis cells were of the same design<sup>16</sup> as used previously. Alternative methods of sample preparation were used, with no difference detected in the subsequent behaviour of the samples. By one method, the solution was degassed by four cycles of freeze-pump-thaw and then equilibrated with N<sub>2</sub>O at ca. 600 Torr.† By the other method the solution was degassed and saturated with N<sub>2</sub>O by bubbling this gas through it for 15 min, using a rubber seal and two syringe needles.

In each case, the build-up of the concentration of hexacyanoferrate(III) anion was monitored at 420 nm in the photolysis cell using a Perkin-Elmer Lambda-5 spectrophotometer with a custom-designed box around the cell assembly to exclude light. These measurements were all made with the samples at 293 K, regardless of the temperature of irradiation.

Since this product ion absorbs intensely at the wavelengths of irradiation, a correction is necessary in respect of the incident light absorbed by it and thus unavailable to cause photo-oxidation of the substrate. It was assumed that during photolysis the magnetic follower sufficed to keep the solution homogeneous: to this end, very high concentrations of substrate in which nearly all of the incoming light would be absorbed in much less than 1 mm were avoided because then fully efficient stirring might have been rendered almost impossible.

Denoting by  $C_2$  and  $\epsilon_2$  the concentration of hexacyanoferrate(II) ion and its absorption coefficient and using  $C_3$  and  $\epsilon_3$  for the corresponding parameters of hexacyanoferrate(III) ion, the fraction of the incident light absorbed by the substrate ion is given by  $C_2\epsilon_2/(C_2\epsilon_2 + C_3\epsilon_3)$ . If the volume of the sample is  $V$  and  $I$  represents the flux of light, in einstein s<sup>-1</sup>, entering the cell and being totally absorbed within it, then the rate of increase of

† 1 Torr = 101 325/760 Pa.

hexacyanoferrate(III) ion concentration is

$$\frac{dC_3}{dt} = \frac{\varepsilon_2 C_2}{\varepsilon_2 C_2 + \varepsilon_3 C_3} \times \frac{\phi(\text{ferri})I}{V} \quad (4)$$

where  $\phi(\text{ferri})$  represents the number of product ions formed per quantum absorbed by the substrate ion.

Since in this system the ratio of the absorption coefficient of the product ion at 420 nm to  $\varepsilon_2$  is unfavourably low, it is not practicable to restrict photolysis to depletion of substrate concentration by only a small fraction. Thus in making a correction for the light absorbed by the product ion, it is not sensible to make the approximation<sup>16</sup> that  $C_2$  is constant. However, one may assume that  $(C_2 + C_3)$  remains constant at  $C$ , the initial concentration of the substrate. Thus eqn. (4) becomes

$$\left(1 + \frac{\varepsilon_3 C_3}{\varepsilon_2 (C - C_3)}\right) dC_3 = \frac{\phi(\text{ferri})I}{V} dt \quad (5)$$

Integrating and putting  $C_3 = 0$  when  $t = 0$ , one obtains

$$\phi(\text{ferri}) = \frac{V}{It} \left[ C_3 \left(1 - \frac{\varepsilon_3}{\varepsilon_2}\right) + \frac{C\varepsilon_3}{\varepsilon_2} \ln\left(\frac{C}{C - C_3}\right) \right] \quad (6)$$

which incorporates a more substantial correction than was employed previously<sup>16</sup> on the iron(II)/iron(III) system. Moreover, this correction takes no account of the photoaquation of hexacyanoferrate(III) anion at 254 nm, but it has been found<sup>17</sup> that the quantum yield of this process is quite low.

Actinometry was performed using the ferrioxalate system,<sup>18</sup> with corrections as previously described<sup>16</sup> for the actinic effect of the longer-wavelength lines. In the case of the low-pressure mercury lamp this is a small correction, but with the cadmium lamp it represents *ca.* 67% of the total actinic effect and is the origin of the much greater uncertainty in the quantum yields obtained at this lower wavelength.

## Results and Discussion

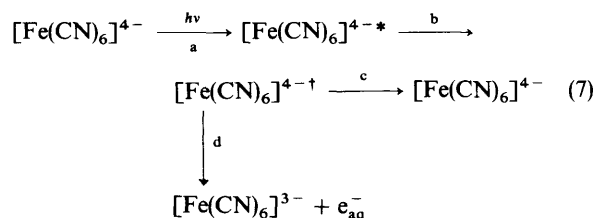
Experiments with  $8 \times 10^{-4}$  mol dm<sup>-3</sup> solutions of potassium hexacyanoferrate(II) using 253.7 nm light showed an appreciable increase in  $\phi(\text{ferri})$  with increasing temperature as shown in Table 1, where each value is the mean of at least five individual measurements.

In another series of experiments using solutions of concentration  $2 \times 10^{-4}$  mol dm<sup>-3</sup> with 228.8 nm light, lower values of  $\phi(\text{ferri})$  were found, showing less variation with temperature. At this wavelength the results shown in Table 1 are the mean of six experiments.

Eqns. (1)–(3) above imply that  $\phi(\text{ferri})$  should be precisely twice  $\phi_{e^-}$ , the quantum yield of step (1). Some previous studies of this system using a low-pressure mercury lamp have found<sup>7,19</sup> that, based on the increase in absorbance at 420 nm, the yield of hexacyanoferrate(III) ion is less than twice

the yield of gaseous N<sub>2</sub>. The discrepancy is attributed to the concurrence with step (1) of photoaquation reactions, but clearly the yield of N<sub>2</sub> is the more indicative of the photoionization process. Thus, based on these earlier studies, we take  $\phi_{e^-}$  as  $0.59\phi(\text{ferri})$ , treating this factor as being independent of temperature, as it appeared to be.<sup>19</sup>

The spectroscopic evidence suggests the following sequence in the photoionization process:



where \* denotes the charge-transfer metal-to-ligand (CTML) state populated initially and † the CTTS state to which it relaxes and which may either undergo a radiationless transition to the ground state or dissociate to yield the hydrated electron and the oxidised ion. On this basis the quantum yield is given by

$$\phi_{e^-} = \frac{k_d}{k_c + k_d} \quad (8)$$

Writing each rate constant in terms of its Arrhenius parameters, this leads to

$$\ln\left(\frac{1}{\phi_{e^-}} - 1\right) = \ln \frac{A_c}{A_d} + \frac{(E_d - E_c)}{RT} \quad (9)$$

In Fig. 1 the appropriate function of the quantum yield is plotted against  $T^{-1}$ , from which, for 253.7 nm light,  $(E_d - E_c)$  is evaluated as  $13.2 \pm 2$  kJ mol<sup>-1</sup>.

Since step (c) is regarded as independent of temperature whereas step (d) occurs because of the rotational motion of solvent molecules around the CTTS state facilitating electron escape,<sup>14</sup> this parameter is expected to be close to the activation energy<sup>20</sup> for the self-diffusion of water (19.6 kJ mol<sup>-1</sup>). While the agreement with this value is not good, the present value compares well with some found earlier for substituted phenolates,<sup>15</sup> although it is less than was obtained for aqueous iodide ion.<sup>13,14</sup> The difference in behaviour could be

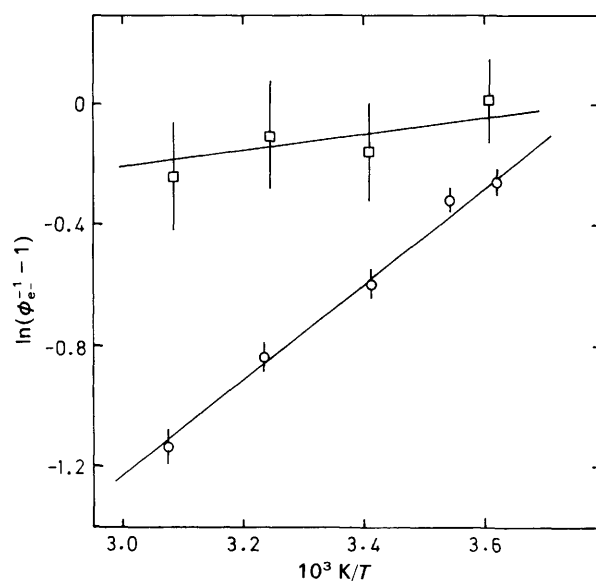


Fig. 1 Plot of  $\ln(\phi_{e^-}^{-1} - 1)$  against  $T^{-1}$  for the data at irradiation wavelengths 253.7 (○) and 228.8 nm (□)

Table 1 Variation of the quantum yield of ferricyanide ion,  $\phi(\text{ferri})$ , with temperature and wavelength

T/K	$\phi(\text{ferri})$	
	253.7 nm	228.8 nm
276	0.96 ± 0.04	
277		0.84 ± 0.06
282	0.99 ± 0.03	
293	1.09 ± 0.04	0.91 ± 0.07
308		0.89 ± 0.08
309	1.19 ± 0.03	
324		0.95 ± 0.08
325	1.29 ± 0.04	

partly attributable to the differing charges on the ion, leading to different extents to which the behaviour of neighbouring solvent molecules is influenced by the proximity of the anion.

When the data obtained with 228.8 nm light are treated in the same way there is obtained the much less steep line shown in Fig. 1, from which  $(E_d - E_c)$  is found to be  $2.4 \pm 4$  kJ mol<sup>-1</sup>. In this case, agreement with the activation energy for the self-diffusion of water is so poor that one must question the applicability of the model.

While there is no clear precedent for using the relation,  $\phi_{e-} = 0.59\phi(\text{ferri})$  at 228.8 nm in the way that there is at 253.7 nm, it should be pointed out (i) that this factor has only a minor effect on the gradient of the plot of  $\ln(\phi_{e-}^{-1} - 1)$  against  $T^{-1}$ , and (ii) that the UV spectra of solutions irradiated at 228.8 nm closely resembled those of solutions illuminated at 253.7 nm, which argues against any appreciable difference in the relative roles of photoionization and photo-aquation at the two wavelengths.

However, at the shorter wavelength the quantum yields are much lower, just as was reported initially<sup>3</sup> by Shirom and Stein. It does seem likely that at 228.8 nm, where the quantum is 0.5 eV greater, the model proposed above is not fully correct, in that it should not imply that all CTML states lead to the CTTS state. If they were to, it is difficult to see why the electron quantum yield should be lower than at 253.7 nm since, with at least the same if not greater excitation energy in the CTTS state, the ratio  $k_d/(k_c + k_d)$  can hardly be less. So one must conclude that, at least when it is populated by absorption of 228.8 nm light, the CTML state has an alternative fate that cannot lead to photoionization. This is probably internal conversion to the lowest excited singlet state. Let us call this step (e). We now have, for the hydrated electron quantum yield,

$$\phi_{e-} = \left( \frac{k_b}{k_b + k_e} \right) \left( \frac{k_d}{k_d + k_c} \right) \quad (10)$$

in place of eqn. (8).

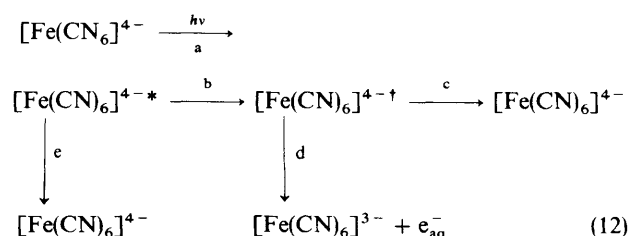
Using the expansion of each rate constant in terms of its Arrhenius parameters, it can be shown that, on the basis of eqn. (10), the gradient predicted in Fig. 1 is given by

$$R \frac{d \ln(\phi_{e-}^{-1} - 1)}{d(1/T)} = \frac{\frac{k_e}{k_b}(E_b - E_e) + \frac{k_c}{k_d}(E_d - E_c) + \frac{k_e k_c}{k_b k_d}(E_b - E_e + E_d - E_c)}{\frac{k_e}{k_b} + \frac{k_c}{k_d} + \frac{k_e k_c}{k_b k_d}} \quad (11)$$

If  $(E_b - E_e)$  were the same as  $(E_d - E_c)$  then eqn. (11) predicts the same gradient as from the earlier model. However, it is improbable that step (b) would be influenced by temperature to such an extent, if at all, and so, provided  $k_e$  is non-zero, a lesser gradient must be expected. However, if one accepts that  $(E_d - E_c)$  has the significance and size discussed above, to account for the negligible slope of the 228.8 nm line in Fig. 1 it would seem that  $(E_b - E_e)$  must be very small, or perhaps even negative.

The latter possibility would imply that step (e) is dependent on temperature to a greater extent than is step (b). These two steps are, of course, totally different in nature. The former is an internal transition of the transition-metal complex, whereas the latter involves the neighbouring molecules of solvent. With the greater mobility of these at a higher temperature creating more opportunities for the CTML  $\rightarrow$  CTTS transition to take place, it would be expected that step (e) could well be accelerated by temperature to a greater extent than step (b).

Thus it may be seen that a modified scheme is necessary at 228.8 nm and can account both for the diminution of the quantum yield and for its much lesser temperature dependence than at 253.7 nm. However, it may be that this revised scheme should also be invoked at 253.7 nm, although with a lower ratio of  $k_e/k_b$  than at 228.8 nm, since it could provide a more convincing explanation for the dependence of the electron quantum yield on temperature being less than expected.



## References

- 1 M. S. Matheson, W. Mulac and J. Rabani, *J. Phys. Chem.*, 1963, **67**, 2613.
- 2 P. L. Airey and F. S. Dainton, *Proc. R. Soc. London, Ser. A*, 1966, **291**, 340.
- 3 M. Shirom and G. Stein, *Nature (London)*, 1964, **204**, 778; *J. Chem. Phys.*, 1971, **55**, 3372.
- 4 S. Ohno, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 1765; 1779.
- 5 M. Shirom and G. Stein, *J. Chem. Phys.*, 1971, **55**, 3379.
- 6 V. Gaspar and M. Beck, *Magy. Kem. Foly.*, 1982, **88**, 433.
- 7 W. L. Waltz and A. W. Adamson, *J. Phys. Chem.*, 1969, **73**, 4250.
- 8 J. C. Mialocq, *J. Chim. Phys.*, 1988, **85**, 31.
- 9 M. J. Blandamer and M. F. Fox, *Chem. Rev.*, 1970, **70**, 59.
- 10 H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, 1963, **85**, 2922.
- 11 J. J. Alexander and H. B. Gray, *Coord. Chem. Rev.*, 1967, **2**, 29.
- 12 W. S. Fyfe, *J. Chem. Phys.*, 1962, **37**, 1894.
- 13 J. Jortner, M. Ottolenghi and G. Stein, *J. Phys. Chem.*, 1962, **66**, 2029.
- 14 F. S. Dainton and S. R. Logan, *Proc. R. Soc. London, Ser. A*, 1965, **287**, 281.
- 15 J. A. H. Cook and S. R. Logan, *J. Photochem.*, 1974, **3**, 89.
- 16 S. R. Logan, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 615.
- 17 M. W. Fuller, K. M. F. Le Brocq, E. Leslie and I. R. Wilson, *Aust. J. Chem.*, 1986, **39**, 1411.
- 18 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, 1956, **235**, 518.
- 19 J. A. H. Cook, D.Phil. Thesis, New University of Ulster, Coleraine, 1971.
- 20 J. H. Wang, *J. Am. Chem. Soc.*, 1951, **73**, 510.

Paper 0/05009A; Received 7th November, 1990