BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1779—1783 (1967)

The Photochemistry of Aqueous Hexacyanoferrate(II) Solutions. IV. A Study of the Mechanism of the Photoelectron Detachment[1]

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(Received December 22, 1966)

The effects of environmental changes, such as temperature changes, the addition of salts, and the use of D_2O as a solvent, upon the absorption spectrum of the hexacyanoferrate(II) ion, as well as upon the photochemical yield of hydrated electrons, have been investigated. The results observed have then been tentatively interpreted in terms of a proposed mechanism: (1) the absorption of light quanta results in an "internal" metal-(d)→CN-(π^*) excited state; (2) the rate of the detachment of an electron from this excited state to the solvent is dependent on the size of the cavity occupied by the complex ion surrounded by the hydration layers of the water, and (3) environmental changes affect the size of the cavity, thus influencing the magnitude of the quantum yields of e^-_{ap}.

Recent photochemical studies have shown that some anions in aqueous solutions can produce hydrated electrons upon absorbing light in the ultraviolet region; these anions include halide,[2-4] hydroxide,[4,5] thiosulfate,[6] sulfate,[5] thiocyanate,[4]

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[1] Presented at the Symposium of Photochemistry, Osaka, October, 1966; Part III of this series, This Bulletin, **40**, 1776 (1967).

[2] J. Jortner, M. Ottolenghi and G. Stein, *J. Phys. Chem.*, **66**, 2037 (1962).

[3] J. Jortner, M. Ottolenghi and G. Stein, *ibid.*, **68**, 247 (1964).

[4] M. S. Matheson, W. A. Mulac and J. Rabani, *ibid.*, **67**, 2613 (1963).

[5] J. Barrett, M. F. Fox and A. L. Mansell, *ibid.*, **69**, 2996 (1965).

[6] R. Sperling and A. Treinin, *ibid.*, **68**, 897 (1964).

phenolate,7) hexacyanoferrate(II),4,8,9) and hexacyanocobaltate(III)10) ions. However, other anions, *e. g.*, azide,11) hexabromoplatinate(IV),12) manganate10) and hexacyanoferrate(III)10) ions, have been shown not to produce a hydrated electron.

The spectra of halide13−16) and thiosulfate6) ions have been investigated, and the initial act designated as a charge-transfer-to-solvent (CTTS) mechanism. The excited electron at a CTTS state is bound in the coulombic field of the oriented solvent medium. This state may dissociate, leading to the production of hydrated electrons.2) However, an electron detachment to the solvent may alsor result from the thermal ionization of an intramolecular excited state, as in the case of the phenolate ion.7)

The purpose of this paper is to clarify the mechanism by which the hydrated electron is formed from the irradiated hexacyanoferrate(II) ion, with special attention paid to the identification of the type of the primary act of light absorption—whether it is an "intramolecular" or an "intermolecular-(CTTS)" transition. Therefore, environmental effects such as temperature changes, the addition of inert salts, and a change in the solvent for D_2O, upon the spectrum of the hexacyanoferrate(II) ion, as well as upon the photochemical yields, were studied.

Experimental

Spectra were measured with a Shimadzu QR-50 spectrophotometer using a 1-cm quartz cell in a thermostatted holder. In every measurement, a reference solution was used which differed from the sample only by containing no potassium hexacyanoferrate(II) (sample: 2×10^{-5} M).

Deuterium oxide (99.7%, Showa Denko Co., Ltd.) was purified by treating it with ^{60}Co-γ irradiation, followed by ordinary distillation. The other materials used were of the purest grade available.

The molar extinction coefficient of hexacyanoferrate-(III) in D_2O was determined to be 1040 ± 40 mol^{-1}·*l* cm^{-1}, which may be compared with the value of 1030 ± 40 in H_2O, at 4200 Å. All the other experimental methods were described in Part II.

Results

Environmental Effects on the Spectrum of the Hexacyanoferrate(II) Ion. The irradiation of an aqueous hexacyanoferrate(II) solution with a light at 2537 Å corresponds to the strong absorption band whose maximum is situated at about 2180 Å (*cf.* Part II). In order to establish whether or not a charge-transfer-to-solvent transition is involved in this absorption, the effect of some environmental changes on the absorption maximum was investigated. The results are presented in Table 1. The effect of adding salts on the spectrum is also shown in Fig. 1. The marked blue shift of $h\nu_{max}$ characteristic of a CTTS band17) is not observed in any of the cases examined.

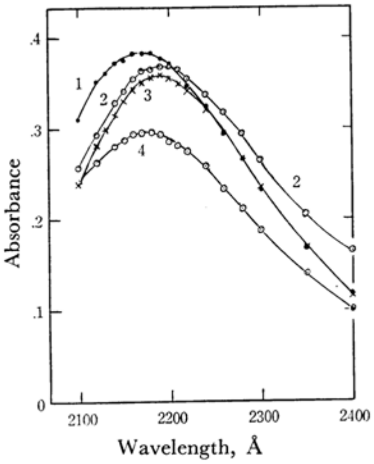

Fig. 1. Absorption band of $K_4[Fe(CN)_6]$ (2×10^{-5} M) alone (1) and in the presence of 1 M Na_2SO_4 (2), 1 M sucrose (3) and 2 M $NaClO_4$ (4).

Environmental Effects on the Quantum Yield, Γ. The results presented in Part II of this series showed that the presence of 1.6×10^{-2} M

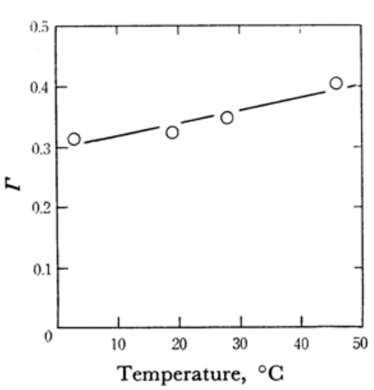

Fig. 2. Temperature effect on Γ.
$[K_4[Fe(CN)_6]]=10^{-3}$ M, and $[N_2O]=2\times10^{-2}$ M

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7) J. Jortner, M. Ottolenghi and G. Stein, *J. Am. Chem. Soc.*, **85**, 2712 (1963).

8) S. Ohno and G. Tsuchihashi, This Bulletin, **38**, 1052 (1965).

9) P. L. Airey and F. S. Dainton, *Proc. Roy. Soc.*, **A 291**, 340, 478 (1966).

10) S. Ohno, To be published.

11) I. Burak and A. Treinin, *J. Am. Chem. Soc.*, **87**, 4031 (1965).

12) S. A. Penkett and A. W. Adamson, *ibid.*, **87**, 2514 (1965).

13) M. Smith and M. C. R. Symons, *Trans. Faraday Soc.*, **54**, 338, 346 (1958).

14) T. R. Griffiths and M. C. R. Symons, *ibid.*, **56**, 1125 (1960).

15) G. Stein and A. Treinin, *ibid.*, **55**, 1086, 1091 (1959).

16) G. Stein and A. Treinin, *ibid.*, **56**, 1393 (1960).

17) It should be noted that the changes in $h\nu_{max}$, not in ε_{max}, are to be considered as a diagnostic test for a CTTS band. See Refs. 13—16.

TABLE 1. $h\nu_{max}$ (Å) AND ε_{max} FOR $K_4[Fe(CN)_6]$ IN VARIOUS ENVIRONMENTS

Run	Solvent	Added salt (M)	Temp(°C)	$h\nu_{max}$(Å)	$\triangle h\nu_{max}$ (to Run 2)	ε_{max}
1	H_2O	—	14	2175±5	−5	20000
2	H_2O	—	27	2180±5	—	19200
3	H_2O	—	35	2170±5	−10	18900
4	H_2O	Na_2SO_4 (1)	27	2190±5	+10	18500
5	H_2O	sucrose (1)	27	2190±5	+10	18000
6	H_2O	$NaClO_4$ (2)	27	2175±5	−5	14900
7	D_2O	—	27	2175±5	−5	—

N_2O is sufficient to scavenge all the hydrated electron produced photochemically in an aqueous hexacyanoferrate(II) solution. Under these conditions, the observed quantum yield of hexacyanoferrate(III), γ, corresponds to the value of $2\times\Gamma$, Γ being the quantum yield for the primary formation of hydrated electrons. The dependence of Γ upon changes in the temperature, the addition of inert electrolytes, such as Na_2SO_4 and $NaClO_4$, and a change in the solvent from H_2O to D_2O was also investigated. The results are shown in Figs. 2—4.

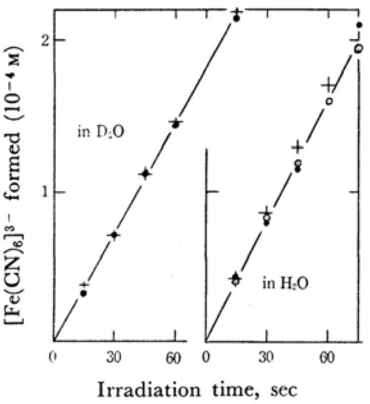

Fig. 3. Comparison of the $[Fe(CN)_6]^{3-}$ yields in H_2O and in D_2O at 25°C and $[N_2O]=1.6-2.0\times10^{-2}$ M.

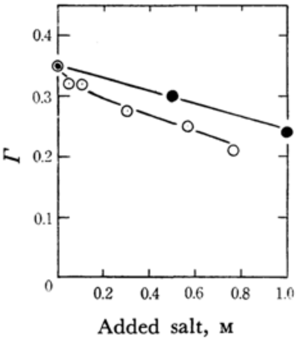

Fig. 4. Dependence of Γ on added salts at 25°C and $[N_2O]=1.6\times10^{-2}$ M, (●): $NaClO_4$, (○): Na_2SO_4 (data from Part II).

Discussion

The results of previous papers are: (1) Nitrous oxide, nitrate ions, acetone, and hydrogen ions can be reduced in aqueous solutions of hexacyanoferrate(II) illuminated with a light at 2537 Å, (2) The reactive species participating in these systems has a charge of −1 according to the Brönsted-Bjerrum theory of ionic reactions; thus, it can be identified as the hydrated electron, e^-_{aq}, and (3) The limiting quantum yield of e^-_{aq}, Γ, obtained at high concentrations of the electron scavenger is less than unity, namely, 0.35.

While these results show that the solutes do not interact directly with the spectroscopic excited state of the hexacyanoferrate(II) ion, but react with the e^-_{aq} produced by a secondary process, the exact nature of the excited state responsible for the electron release remains unclear. Two possibilities may be considered: (a) The charge-transfer-to-solvent (CTTS) state which results from an intermolecular excitation involving an electron transfer from the ion to the solvent, and (b) An intramolecular excitation state, $^1T_{1u}$, indentified by Gray[18] on the basis of a derived molecular orbital energy scheme.

Discrimination between the Two Possibilities of the Excited State. In a CTTS mechanism, an excited electron is bound in the electric field of the solvent molecules oriented to the ion just before the light absorption. The production of the hydrated electron from this state has previously been discussed in the case of the halide ions.[2,3]

It is well known that the CTTS bands of the halide ions in solution are sensitive to environmental changes and exhibit typical shifts of the absorption maximum upon changes in the temperature[13-15] and upon the addition of solutes.[13,16] Similar environmental changes are expected for polyvalent anions.[19] These spectroscopic studies claim that the environmental changes influence the effective ionic radius, r_0, *i. e.*, the size of the cavity

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[18] H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).

[19] A. Treinin, *J. Phys. Chem.*, **68**, 893 (1964).

[20] M. Halmann and I. Platzner, *Proc. Chem. Soc.*, 261 (1964).

occupied by the ion in its solvation sphere. A decrease in temperature or an increase in pressure results in the contraction of the cavity. Added solutes, influencing the structure of the solvent water, indirectly modify the solvation environment of the ion and thus the r_0. For example, solutes decreasing the concentrations of free water molecules available for the formation of the cavity would diminish the r_0.[16] The decrease in r_0 results in a shift to shorter wavelengths for all negative ions absorbing by means of a CTTS mechanism.

The results presented in Fig. 1 and in Table 1 clearly indicate the absence of blue shifts characteristic of a CTTS band. It should be mentioned that the band of the iodide ion is shifted by 18—19 Å in the presence of 2 M $NaClO_4$ or 1 M Na_2SO_4, and by 28 Å in the presence of 1M sucrose,[16] while the increase in the temperature (11—41°C) causes a shift of 20 Å to a shorter wavelength.[15]

Moreover, Halmann and Platzner[20] have proposed a large blue shift (400—800 cm^{-1}) in the absorption of anions when water as a solvent is replaced by D_2O as being diagnostic for a CTTS mechanism. Ions which show either a small blue shift or a red shift upon this change of solvent are regarded as undergoing internal excitation in the initial act of absorption. From the results shown in Table 1, by Run 7, the absorption of light by $[Fe(CN)_6]^{4-}$ may not be classified as a CTTS mechanism.

On the other hand, some authors[9,21] have thought that the intense band of $[Fe(CN)_6]^{4-}$ below 3000 Å was due to a CTTS mechanism. This idea is based on the pressure effect on the spectrum observed by Fyfe.[22] He found that the absorption edge at 2800 Å was shifted to shorter wavelengths by a pressure change of 2000 atm in the case of $[Fe(CN)_6]^{4-}$. However, in our opinion, the shift observed gives no information regarding the pressure sensitivity of the band maximum, since it could well have been caused by a broadening or a sharpening of the spectrum.[14] Thus the results of Fyfe can not be used for the purpose of identifying a CTTS transition in the present case.

Therefore, the excited state which is responsible for an electron detachment in the case of hexacyanoferrate(II) ions may be classified as an "internal" state ($^1T_{1u}$) arising from a metal-(d) to CN(π-antibonding) excitation.

Proposed Mechanism of the Photoelectron Detachment. We will now propose the following mechanism, where { } represents the non-equilibrium state resulting from the electron transfer according to the Franck-Condon principle:

$$[Fe(CN)_6]^{4-}(aq) \xrightarrow{h\nu} {}^1T_{1u}(aq) \tag{1}$$

$$^1T_{1u}(aq) \xrightarrow{E_x} \{[Fe(CN)_6]^{3-}(aq)\} + e \tag{2}$$

$$^1T_{1u}(aq) \longrightarrow [Fe(CN)_6]^{4-}(aq) \tag{3}$$

The $^1T_{1u}(aq)$ state may either eject an electron to the solvent (Eq. (2)) or decay back to the ground state (Eq. (3)). The two processes compete with each other and determine the quantum yield, Γ, for the formation of the hydrated electron. E_x is the energy required for the electron detachment from the $^1T_{1u}(aq)$ state without changing the positions of all the nuclei. It may be assumed that the magnitude of E_x is a factor governing the rate of electron detachment. It would be of interest to see how the size of the cavity occupied by the excited ion, $^1T_{1u}$, affects the value of E_x, thus influencing the value of Γ, though the primary act of light absorption ("internal" excitation) is not affected by the cavity radius.

Consider the following cycle, which resembles that discussed by Stein and Treinin in their treatment of the CTTS excitation of the ion:[15]

$$\begin{tikzcd}
{}^1T_{1u}(aq) \arrow[r, "E_x"] \arrow[d, "E_1"] & \{[Fe(CN)_6]^{3-}(aq)\} + e \arrow[d, "E_3"] \\
{}^1T_{1u} + \{aq\} \arrow[r, "E_2"] & \{[Fe(CN)_6]^{3-}\} + \{aq\} + e
\end{tikzcd}$$

E_2 is the vertical ionization potential of the ion ($^1T_{1u}$) in the gas phase. E_1 and E_3 are calculated assuming that the ($^1T_{1u}$) ion occupies a cavity with a radius of r_x in a continuous medium with a static dielectric constant, D_s, and an "optical" dielectric constant, D_{op}. E_1 is the sum of the interaction energy of a charge, $Z\boldsymbol{e}$, with the persistent polarization of the organized medium and of the electronic polarization caused by this charge:

$$E_1 = \frac{Z^2\boldsymbol{e}^2}{r_x}(1/D_{op} - 1/D_s) + \frac{Z^2\boldsymbol{e}^2}{2r_x}(1 - 1/D_{op}) \tag{4}$$

E_3 can be represented similarly by taking into account the interactions for a $(Z-1)$ charge in the same medium as in the case of a Z charge:

$$E_3 = \frac{(Z-1)Z\boldsymbol{e}^2}{r_x}(1/D_{op} - 1/D_s) + \frac{(Z-1)^2\boldsymbol{e}^2}{2r_x}(1 - 1/D_{op}) \tag{5}$$

Thus, the following expression is derived from the cycle:

$$E_x = E_1 + E_2 - E_3 = E_2 + \boldsymbol{e}^2\left(\frac{Z}{r_x}\right)\left(1 - \frac{1}{2Z} + \frac{1}{2ZD_{op}} - \frac{1}{D_s}\right) \tag{6}$$

Hence, for the present system ($Z=4$, $D_{op}=1.77$, $D_s=80$);

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[21] M. Shirom and G. Stein, *Nature*, **204**, 778 (1964).

[22] W. S. Fyfe, *J. Chem. Phys.*, **37**, 1894 (1962).

$$E_x = E_2 + \frac{1240}{r_x} \text{ (in kcal mol}^{-1}\text{, Å)} \qquad (7)$$

Differentiation gives:

$$\mathrm{d}E_x/\mathrm{d}r_x = -1240/r_x^2 \qquad (8)$$

This means that any environmental effect which causes a contraction of the cavity occupied by the $^1T_{1u}$ state would result in a larger E_x value, and hence a decrease in the quantum yield of hydrated electrons, Γ. (a) A decrease in the temperature, (b) replacing H_2O as the solvent by D_2O, and (c) the addition of electrolytes—all these would lead to a decrease in r_x, as has been stated in the preceding section. The experimental results shown in Figs. 2—4 are in accord with this view, as will be seen below.

The Effect of Environmental Changes on Γ. The change in ionic radii with the temperature ($\mathrm{d}r_x/\mathrm{d}T$) has previously been discussed and estimated to be of the order of 10^{-3} Å deg^{-1} for the iodide ion.[16] This might predict a decrease by 2—3 kcal in E_x for the temperature change of 30 degrees, if $r_x = 4$ Å assumed.[23] This could explain the observed increase of Γ with an increase in the temperature, shown in Fig. 2.

D_2O has a slightly higher dipole moment ($\sim 1.5\%$)[24] and is generally supposed to hydrate the ion more strongly than H_2O does. A difference in the r_x values in H_2O and D_2O by 0.02—0.03 Å would account for the observed difference in Γ shown in Fig. 3, the magnitude of this difference corresponds to that which might be caused by a temperature change of 20—30 degrees.

Added salts have a marked effect on Γ (Fig. 4), which can be well understood in terms of the contraction of the cavity caused by the presence of electrolytes, as has been discussed above. It is of importance to mention that, in the case of the iodide ion where the primary act of light absorption brings about the binding of an electron by the solvent (a CTTS mechanism), no effect of added salts on Γ was observed.[3] In this case, the value of Γ is a result of the competition between the deactivation of the CTTS state and its dissociation into an iodine atom and a hydrated electron. The excited electron in the CTTS state is already trapped by the solvent out of the cavity and no more needs the energy, E_x, necessary to escape from the cavity. Therefore, the change in the cavity radius will not affect Γ in the case of a CTTS mechanism; instead, the factors influencing the movement of the fragments produced would affect Γ.

Conclusions

The present results are consistent with the view that the primary act of light absorption which is responsible for the formation of a hydrated electron in an aqueous hexacyanoferrate(II) solution is an "internal" excitation, metal-(d) to ligand- π-antibonding. This excited state can eject an electron to the solvent, leading to the formation of the hydrated electron. The efficiency of this process may be determined by the size of the cavity occupied by the ion from which the electron is transfered to the solvent.

A similar mechanism might be operative in the case of the $[Co(CN)_6]^{3-}$ ion, where light at 2537 Å was found to liberate H_2 in an acidified solution containing 1 M CH_3OH.[10] The results can be interpreted in terms of an internal excitation, metal-(d)→CN-(π^*),[18] leading to the formation of hydrated electrons. On the other hand, the illumination of $[MnO_4]^{2-}$, $[Fe(CN)_6]^{3-}$, and $[CrO_4]^{2-}$ in the wavelength region of the electron transfer band (from a ligand to a metal type) gave no evidence for the formation of a hydrated electron.[10] Further systematic study using the metal complex ions will provide a better, more detailed insight into the mechanism, especially the nature of the excited state responsible for the electron-detachment process.

The author is grateful to Professor Niro Matsuura of the University of Tokyo for his many helpful discussions.

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[23] The Fe–C and C–N bond lengths in $[Fe(CNCH_3)_6]Cl_2 \cdot 3H_2O$ are reported to be 1.85 and 1.18 Å respectively (H. M. Powell and G. W. R. Bartindale, *J. Chem. Soc.*, **1945**, 799). The radius of a cavity is likely to be a little larger than the crystallographic radius; see Ref. 15. Thus the value $r_x = 4$ Å will be taken here.

[24] E. Whalley, *Trans. Faraday Soc.*, **53**, 1578 (1957).