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The Photochemistry of Aqueous Hexacyanoferrate(II) Solutions. I. Photo-aquation Reaction at 3660 Å[1]

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The photochemistry of hexacyanoferrate(II) ions in aqueous solutions was studied at 3660 Å in the presence and in the absence of nitrous oxide as an electron scavenger. Only a photo-aquation reaction yielding aquopentacyanoferrate(II) and cyanide ions was observed to occur as the primary process. The formation of aquopentacyanoferrate(II) ions, determined spectrophotometrically after a reaction with sodium azide, was studied as a function of the irradiation time over a wide pH range (0.5 to 13). In neutral or alkaline solutions the amount of aquopentacyanoferrate(II) ions measured was small, because of an efficient thermal back reaction. The initial quantum yield depended on the pH; for example, the yield 0.52 at pH 0.65 and 0.89 at pH 4.0 for 0.01 M solutions at 25°C. The yield decreased with an increase in the hexacyanoferrate(II) concentration.

The photochemistry of hexacyanoferrate(II) ions in aqueous solutions has been the subject of many works.[2-11] Baudisch[2] reported the production of aquopentacyanoferrate(II) and cyanide ions:

$$[Fe(CN)_6]^{4-} + H_2O \rightarrow [Fe(CN)_5OH_2]^{3-} + CN^- \qquad (1)$$

The pH of the solution increases on exposure to light as a result of the hydrolysis of the cyanide ions produced. The reaction was followed either by measurements of the variations in pH[3-5] or

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[1] The preliminary report: S. Ohno and G. Tsuchihashi, paper presented at 14th Symposium of Coordination Chemistry, Fukuoda, November, 1964; S. Ohno and G. Tsuchihashi, This Bulletin, **38**, 1052 (1965).

[2] O. Baudisch, *Ber.*, **62**, 2706 (1929).

[3] S. Asperger, *Trans. Faraday Soc.*, **48**, 617 (1952).

[4] A. G. MacDiarmid and N. F. Hall, *J. Am. Chem. Soc.*, **75**, 5204 (1953).

[5] V. Carassiti and V. Balzani, *Ann. Chim. (Rome)*, **50**, 782 (1960).

[6] V. Balzani, V. Carassiti and R. Sotoloos, *ibid.*, **54**, 103 (1964).

[7] G. Emschwiller and J. Legros, *Compt. Rend.*, **239**, 1491 (1954).

[8] S. Asperger, I. Murati and O. Cupahin, *J. Chem. Soc.*, **1953**, 1041.

[9] G. Emschwiller and J. Legros, *Compt. Rend.*, **261**, 1537 (1965).

[10] S. Asperger, I. Murati and D. Pavlovic, *J. Chem. Soc.*, **1960**, 730.

[11] R. P. Mitra, D. V. S. Jain, A. K. Bannerjee and K. V. Raghavachari, *Nature*, **200**, 163 (1963).

by colorimetric determinations of the aquopentacyanoferrate(II) using nitrosobenzene.[7,8] The quantum yields of the photo-dissociation reaction (1) at 3660 Å were reported to be 0.44 for a 0.5 M solution of hexacyanoferrate(II) at pH 9.9[7] and 0.1 in a neutral unbuffered solution.[5] A more detailed study of the quantum yield and of its dependence on the pH and on the solute concentration seemed necessary.

The oxidation reaction in the photochemistry of hexacyanoferrate(II) ions had not been studied until recently.[*1] Mitra *et al.*[11] have now, however, reported the formation of Prussian blue (ferri-ferrocyanide) under acidic conditions (pH $\sim$1.5). Matheson *et al.*[12] observed, in the flash photolysis of an aqueous hexacyanoferrate(II) solution, a transient absorption due to the formation of hydrated electrons, and a permanent absorption which coincided with that of the hexacyanoferrate(III) ion. These authors used unfiltered light, however.

On the other hand, progress has been made in assigning the electronic spectrum of the hexacyanoferrate(II) ion,[13,14] and it is now possible to study the relationship between the wavelength of the exciting radiation and the nature of the consequent chemical reaction of the hexacyanoferrate(II).

We have, therefore, studied the photo-induced reactions of hexacyanoferrate(II) at various pH values, in the presence or in the absence of specific scavengers for hydrated electrons, employing two light sources of different wavelengths, in an attempt to develop a more precise understanding of the photochemistry of this complex. The results using light at 3660 Å will be described in this paper.

Experimental

Light Source. The light source was a high-pressure mercury lamp (Toshiba H-400 P) operated at 130 V a. c. and 3.3 A with voltage stabilization. A combination of two glass filters (Toshiba UV-35 and -D1A) with a narrow band-pass centered at 3660 Å was used to isolate this wavelength. The absence of appreciable transmission for the other photoactive wavelengths emitted by the lamp was checked by measuring the absorption spectrum of the filters with a Shimadzu QR-50 spectrophotometer.

Reaction Cell. A 2×5×10 cm quartz cell with a 2-cm optical pass length was used as the reaction cell. The homogeneity of the solutions was maintained during irradiation by bubbling in purified nitrogen. The cell was kept in a thermostat equipped with an optically-flat quartz window on the side through which the radiation came to the cell.

Materials. All the chemicals used were of a reagent grade. Potassium hexacyanoferrate(II) was recrystallized from a hot aqueous solution and air dried. The other chemicals were used without additional purification. Solutions were prepared with triply-distilled water (ordinary distillation followed by distillations from acidic permanganate and dilute alkaline permanganate solutions. pH of the water: 6.0±0.2).

Analysis. The amount of aquopentacyanoferrate(II) ions produced by the photolysis was determined spectrophotometrically after a reaction with sodium azide.[2] A calibration curve was obtained as follows: sodium aquopentacyanoferrate(II) was prepared according to the method of Hofmann[15] and purified by passing it through an alumina chromatographic column and eluting it with water.[16,17] Its content in the eluted solution was determined by ceric titration.[18] An aliquot (2 m*l*) of a solution containing various amounts of sodium aquopentacyanoferrate(II) was pipetted in a 10-m*l* volumetric flask, a solution of 0.3 M CH_3COOH - 0.3 M NaN_3 was added, and then, after 15—20 min, the optical density at 5600 Å was measured. Acetic acid was employed to adjust the pH of the solution, since the absorption at 5600 Å was found to be pH-dependent (Fig. 1). The molar extinction coefficient thus obtained was 1430±50 at pH 4—6; it was not interfered with by the presence of hexacyanoferrate(II) and -(III) under the conditions employed. Aquopentacyanoferrate(III) could be easily identified by its

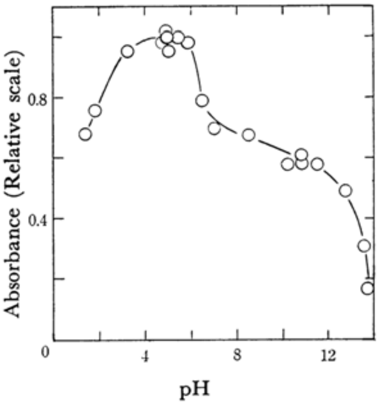

Fig. 1. Effect of pH on the absorbance at 5600 Å in the reaction mixture ($[Fe(CN)_5OH_2]^{3-}+NaN_3$).

[*1] After this work had been nearly finished, the photo-oxidation of $[Fe(CN)_6]^{4-}$ by light at 2537 Å in the presence of N_2O was reported; see Part II of this series.

12) M. S. Matheson, W. A. Mulac and J. Rabani *J. Phys. Chem.*, **67**, 2613 (1963).

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

14) M. B. Robin, *Inorg. Chem.*, **1**, 337 (1962).

15) "Handbuch der Präparativen Anorganischen Chemie," ed. by G. Brauer, Ferdinand enke Verlag, Stuttgart (1954), p. 1363.

16) A. G. MacDiarmid and N. F. Hall, *J. Am. Chem. Soc.*, **76**, 4222 (1954).

17) After this work had been practically finished, the paper of Legros became available in which she took advantage of a stoichiometric reaction between $HgCl_2$ and the hexacyanoferrate(II). Thus she obtained a calibration curve of the $[Fe(CN)_5C_6H_5NO]^{3-}$ without preparing the aquopentacyanoferrate(II) followed by a rather difficult purification process. See J. Legros, *J. Chim. Phys.*, **61**, 909 (1964).

18) F. Burriel-Marti, F. Lucena-Conde and S. Bolle, *Anal. Chim. Acta*, **7**, 302 (1952).

violet color; it showed a maximum at 5650 Å ($\varepsilon=500$ mol^{-1} l cm^{-1}).[19]

The formation of free cyanide ions was verified and measured by the method using sodium picrate[20] after precipitating and removing all the existing cyanide-complexes as their cadmium salts.[16,21] A part of the hydrogen cyanide produced was carried off from the solution by a stream of bubbling nitrogen. This was trapped in an 0.5 M sodium carbonate solution[20] and then analyzed.

Ferrous ions were measured by means of the 2, 2′-dipyridyl method[22] using an acetate buffer.

Procedure. The solution was made free from oxygen prior to irradiation by bubbling in nitrogen for about 30 min. The lamp was lit preliminarily for 15 min, and then a mechanical shutter separating the cell and the lamp was opened and the solution was irradiated. The rates of the photochemical reactions were determined by removing aliquots (mostly 2 ml) from the reaction cell at various intervals. The products were analyzed immediately.

The pH-buffered solutions were made using perchloric acid, sodium oxide, potassium biphthalate, and potassium monohydrogen phosphate, and were adjusted by means of adding sodium perchlorate so that all had the same ionic strength value.

The method of preparing the nitrous oxide-containing solution will be described in Part II of this series.

Actinometry. Actinometry was carried out in a reaction cell using a 0.01 M ferric oxalate actinometer solution. The quantum yield for the formation of ferrous ions was taken to be 1.0 at 3660 Å.[23] The light intensity thus obtained in a typical experiment was 2.3×10^{-6} einstein l^{-1} sec^{-1}. In those cases where the hexacyanoferrate(II) concentration was low ($<10^{-2}$ M) and the conditions of total absorption could not be attained, the required correction for the light quanta absorbed was made in calculating the quantum yields. The molar extinction coefficient of hexacyanoferrate(II) at 3660 Å is about 77,[3,24] the path of the solution being 2 cm in the present case. The acid or buffer used did not absorb this wavelength.

Results and Discussion

Reaction Products. Oxygen-free solutions of 10^{-2} M potassium hexacyanoferrate(II) at various pH values were irradiated at 3660 Å and 25°C. The results are presented in Table 1.

On irradiation the acidic solution gave first a yellow and then a brown color; these colors may be ascribed to the formation of aquopentacyanoferrate(II) ions (Reaction (1): The absorption maximum of aquopentacyanoferrate(II) is at 3900—4000 Å[25]). When the solution was removed from the light and was left in contact with air, it developed a blue color and finally produced a blue precipitate, whose color, however, disappeared when an alkali was added, giving a precipitate of Fe(III) hydroxide. Thus it seems probable that the formation of Fe(III) results from the decomposition of aquopentacyanoferrate(II) under the influence of oxygen, and that the formation of Prussian blue reported by Mitra *et al.*[11] can be attributed to the presence of air in their solution.

The formation of ferrous ions is probably due to the photo-induced decomposition of the aquopentacyanoferrate(II) ion:

$$[Fe(CN)_5OH_2]^{3-} \rightarrow Fe^{2+} + 5\,CN^- \qquad (2)$$

since after a sufficient period of irradiation the absorption of light by the aquopentacyanoferrate(II) produced becomes significant (ε at 3660 Å is 170 mol^{-1} l cm^{-1} [10,25]) and since the occurrence of Reaction (2) has already been checked at pH 6.[10]

As compared with the acid solution, the neutral and alkaline solutions were rather insensivtive to light (*Cf*. Table 1). Irradiation did not produce any significant change in the absorption spectrum. It must be noted, however, that the pH of a neutral, unbuffered solution of 10^{-2} M potassium hexacyanoferrate(II) increased from the original 6.0 and became constant at 8.8 after about 2 min of irradiation. This increase in pH has already been ascribed to Reaction (1), followed by:[3-5]

$$CN^- + H_2O \rightarrow HCN + OH^- \qquad (3)$$

In the irradiated solutions examined, no absorption was observed at 5650 Å (a characteristic band

TABLE 1. AMOUNTS OF THE PRODUCTS (IN 10^{-3} M) IN THE IRRADIATED SOLUTION OF 10^{-2} M $K_4[Fe(CN)_6]$ AT DIFFERENT CONDITIONS

Medium	Irradiation time, min	$[Fe(CN)_5OH_2]^{3-}$	$[Fe(CN)_5OH_2]^{2-}$	Fe^{2+}	CN^-
0.1 N $HClO_4$	60	1.6	<0.01	0.11	~1.3
Neutral	120	0.06	<0.01	<0.01	~0.1
0.1 N NaOH	100	<0.01	<0.01	<0.01	<0.01

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[19] M. Haissinsky and R. Julien, *J. Chim. Phys.*, **57**, 666 (1960).

[20] F. B. Fischer and J. S. Brown, *Anal. Chem.*, **24**, 1440 (1952).

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[23] C. A. Parker, *Proc. Roy. Soc. (London)*, **A220**, 104 (1953).

[24] S. R. Cohen and R. A. Plane, *J. Phys. Chem.*, **61**, 1096 (1957).

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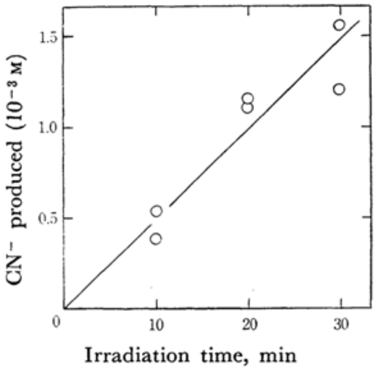

Fig. 2. The formation of CN^- ions in the 0.1 N $HClO_4$ solution of 10^{-2} M $K_4[Fe(CN)_6]$; light intensity = 1.24×10^{-4} einstein l^{-1} min^{-1}.

of aquopentacyanoferrate(III)).

Figure 2 represents the plot of the concentration of free cyanide ions produced *vs.* the irradiation time for a solution of 10^{-2} M potassium hexacyanoferrate(II) in 0.1 N perchloric acid at a constant light intensity.

In view of the results of the flash photolysis,[12] deaerated solutions of 10^{-2} M potassium hexacyanoferrate(II) were irradiated at 3660 Å in the presence of nitrous oxide. The nitrous oxide was used as an electron scavenger,[26,27] converting the hydrated electron, if present, into an OH radical which would oxidize hexacyanoferrate(II) and so yield hexacyanoferrate(III).[25,28] The formation of hexacyanoferrate(III) was searched for by measuring its absorption at 4200 Å. The results are presented in Fig. 3, where the results using a light of 2537 Å[29] are also shown for the sake of comparison. Hexacyanoferrate(III) was not formed in significant amounts in the case of 3660 Å, whether nitrous oxide was present or not.

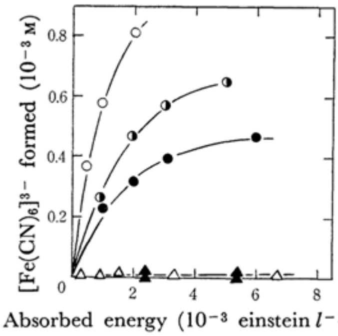

Fig. 3. Effect of N_2O in the photochemistry of $[Fe(CN)_6]^{4-}$ solution;

	Wavelength, Å	N_2O, M
○ :	2537	6.5×10^{-3}
◑ :	2537	2.0×10^{-3}
● :	2537	1.1×10^{-3}
△ :	3660	8.1×10^{-3}
▲ :	3660	0

The Effect of pH on the Quantum Yields of Photo-aquation Reaction. Figure 4 presents the dependence of the yield of aquopentacyanoferrate(II) on the irradiation time for a 10^{-2} M potassium hexacyanoferrate(II) solution at various pH values. The initial quantum yields were calculated from the initial slopes of the curves; these are plotted in Fig. 5. The value, especially at a high pH region, is not accurate, as the curves depart from linearity, indicating an efficient back reaction:

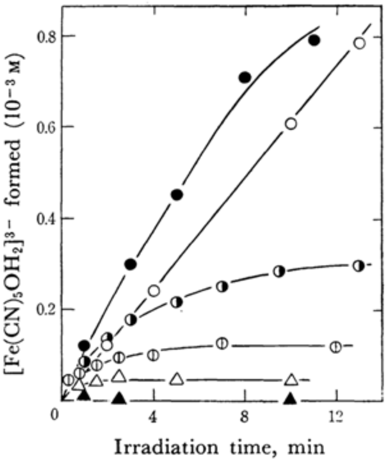

Fig. 4. Yield of $[Fe(CN)_5OH_2]^{3-}$ *vs.* irradiation time at various pH values for 10^{-2} M $K_4[Fe(CN)_6]$ solution. pH=0.95 (○); 2.84 (●); 5.13 (◑); 6.0 (⦶); 7.1 (△); 13.0 (▲)

$$[Fe(CN)_5OH_2]^{3-} + CN^- \rightarrow [Fe(CN)_6]^{4-} \qquad (4)$$

This was confirmed by the observation that the

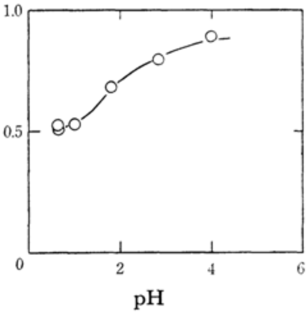

Fig. 5. Initial quantum yield for the aquation reaction as a function of pH.

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26) F. S. Dainton and D. B. Peterson, *Proc. Roy. Soc. (London)*, **A267**, 443 (1962).

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

28) E. Masri and M. Haissinsky, *J. Chim. Phys.*, **60**, 397 (1963).

29) Part II of this series.

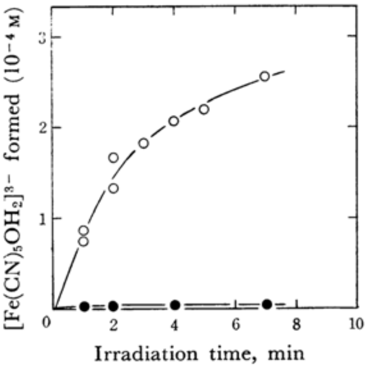

Fig. 6. Effect of added KCN on the formation of $[Fe(CN)_5OH_2]^{3-}$ from 10^{-2} M $K_4[Fe(CN)_6]$ solutions at pH 5.2.

○ : No added KCN
● : $+5.7\times10^{-4}$ M KCN

addition of potassium cyanide, favoring Reaction (4), effectively suppressed the yield (Fig. 6).

Hexacyanoferrate(II) exists in protonated forms (mono- and di-) in an acid solution.[30] Even with this knowledge, however, it is still not possible to understand the dependence of the initial yield on the pH shown in Fig. 5, for we still lack data for the pH region above 4.

Dependence of the Yield on the Concentration. Figure 7 shows the dependence of the yield of aquopentacyanoferrate(II) at equal light quanta absorbed on the solute concentration in 0.1 N perchloric acid solutions. The yield decreases with an increase in the concentration.

The Nautre of the Absorption Act and the Primary Process. The absorption of light at 3660 Å in the present system is in the region of the weak ligand field band.[13] This is the transition between the orbitals which are mainly localized on the central metal, namely, $t_{2g}\rightarrow e_g$. This excitation might cause a repulsion between the ligand and the metal ion, as has been suggested by Adams *et al.*;[31] hence, a ligand dissociation reaction, (1), would take place. However, the dependence of the yield on the concentration (Fig. 7) suggests that Reaction (1) represents an overall reaction of a more complicated process. The process may involve an initial photo-act, as is expressed by:

$$[Fe(CN)_6]^{4-}\ t_{2g} \xrightarrow{h\nu} [Fe(CN)_6]^{4-}\ e_g \qquad (5)$$

followed by the deactivation of the e_g-state through some possible processes, one of them probably being a collision with another hexacyanoferrate(II) ion.

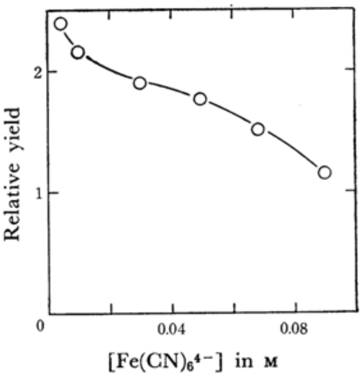

Fig. 7. Dependence of the yield of $[Fe(CN)_5OH_2]^{3-}$ on hexacyanoferrate(II) concentration in 0.1 N $HClO_4$.

Conclusions

We can conclude that the irradiation of hexacyanoferrate(II) ions with a light of 3660 Å (the ligand-field transition type of excitation) causes only a ligand substitution reaction, leading to the formation of aquopentacyanoferrate(II). This reaction is less important on the basic side than on the acid side, as the result of an efficient thermal back reaction. An oxidation reaction in the case of $[Fe(CN)_6]^{4-}$ ions irradiated at 3660 Å seems not to take place as the primary photochemical process, but it may occur as a secondary process in the presence of air.

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