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# The Photochemistry of Aqueous Hexacyanoferrate(II) Solutions. II. Photo-oxidation Reaction at 2537Å

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The effects of 2537 Å radiation upon solutions of hexacyanoferrate(II) were investigated at 25°C, using specific scavengers for hydrated electrons ($N_2O$, $H_3O^+$, and $NO_3^-$) and for hydrogen atoms ($CH_3OH$ and $C_2H_5OH$). In the presence of $N_2O$ or $NO_3^-$, a photo-oxidation reaction giving hexacyanoferrate(III) was found to take place, the primary process being:

$$[Fe(CN)_6]^{4-} \xrightarrow{h\nu} [Fe(CN)_6]^{3-} + e^-_{aq}$$

The quantum yield of this photochemical process was determined to be 0.35 at 25°C. The $e^-_{aq}$ thus formed reacted with $N_2O$, $NO_3^-$, and $H_3O^+$, just like the hydrated electron produced in water irradiated with fast electrons or $\gamma$-rays.

The electronic spectrum of the hexacyanoferrate(II) ion[1] shows two kinds of absorption bands: the d-d and the charge transfer bands. In the preceding paper[2] we studied the aquation reaction of hexacyanoferrate(II) solutions irradiated at 3660 Å. Excitation by light at this wavelength corresponds to the d-d transitions. On the other hand, the irraditation of this complex with light in the charge-transfer band (*e. g.*, 2537 Å) results in an oxidation reaction giving hexacyanoferrate(III) and a hydrated electron. This was previously reported,[3] but no details of the experimental methods were given there; it is the purpose of this paper to present such details, together with the detailed results we have obtained. During this work chemical kinetic evidence for the formation of the hydrated electron in this system was obtained. Other similar studies have recently been published,[4,5] but those results do not quantitatively agree with those of this work, as will be seen later. Another aim of this work and of the preceding one was to get a correlation of the varying photochemical behavior of the transition metal complex with its different excited states.[6-8]

## Experimental

**Light Source and Actinometry.** The light source was a low-pressure mercury lamp operated at 530 V and 20 mA from a stabilized a. c. supply.

The reaction cell was immersed in a thermostated 0.1 M sodium chloride solution, which cut off all the light below 2000 Å. The only line absorbed appreciably by our solution ($10^{-3}$ M potassium hexacyanoferrate(II)) was the 2537 Å line.[9] The light output at 2537 Å was determined by a differential actinometric method using a ferric oxalate actinometer. In the first experiment, the actinometric solution in the reaction cell was irradiated directly. In the second experiment, a 1-cm-path-length filter (0.05 M benzene in an *n*-hexane solution), absorbing all the light below 2800 Å, was inserted between the reaction cell and the lamp. The chemical change upon illumination was determined in both cases by the spectrophotometric analysis of the ferrous ions produced.[10] From the difference between the two values, the absorbed light intensity at 2537 Å was determined to be $3.83 \times 10^{-6}$ einstein·$l^{-1}$ sec$^{-1}$, assuming a quantum yield of 1.2 for the actinometer.[11] The light intensity including the lines above 2800 Å was about 10% higher than this.

In all cases it could be assumed that the incident light in the reaction cell was completely absorbed by the hexacyanoferrate(II) ions. Absorption by any other solutes, such as nitrous oxide, nitrate ions, methanol and ethanol, was negligible at the concentration employed.

**Reaction Cell.** A spectrophotometer cell with a 1-cm optical path length was used as the reaction cell;

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

2) S. Ohno, This Bulletin, **40**, 1765 (1967).

3) S. Ohno and G. Tsuchihashi, paper presented at 14th Symposium of Coordination Chemistry, Fukuoka, November, 1964; S. Ohno and G. Tsuchihashi, This Bulletin, **38**, 1052 (1965).

4) M. Shirom and G. Stein, *Nature*, **204**, 778 (1964).

5) P. L. Airey and F. S. Dainton, *Proc. Roy. Soc. (London)*, **A291**, 340 (1966).

6) W. P. Griffith, *Quart. Rev.*, **16**, 188 (1962), p. 197.

7) A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958).

8) V. Balzani, V. Carassiti, L. Moggi and N. Sabbatini, *Inorg. Chem.*, **4**, 1247 (1965).

9) The longer wavelengths were poorly absorbed under the present experimental conditions. See the absorption spectrum of hexacyanoferrate(II) ion, *e. g.*, S. R. Cohen and R. A. Plane, *J. Phys. Chem.*, **61**, 1096 (1957).

10) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. 2, D. Van Nostrand Co., New York, N. Y. (1955), p. 316.

11) C. A. Parker, *Proc. Roy. Soc. (London)*, **A220**, 104 (1953).

this cell could be connected to a vacuum system through a valve. Another cell, *i. e.,* a quartz cylindrical cell 3-cm in diameter and holding about 50 m*l* of solution was employed for the gasometric analysis.

**Analysis.** The hexacyanoferrate(III) ion was identified by means of thin-layer chromatography.[12] It was further shown that $[Fe(CN)_6]^{3-}$ can be separated completely from $[Fe(CN)_5OH_2]^{3-}$, as well as from $[Fe(CN)_6]^{4-}$,[12] on a silica-gel layer (Silica-Rider of the Daiichi Pure Chemical Co., Ltd.), using an acetone-water-acetic acid (70 : 30 : 7) solution as the developing solvent. The concentration of the hexacyanoferrate(III) ion was determined by its absorption at 4200 Å ($\varepsilon=1030\pm40\ l\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$). The nitrite was determined spectrophotometrically after reaction with sulfanilic acid and $\alpha$-naphthylamine hydrochloride.[13] The acetaldehyde was determined as its 2, 4-dinitrophenylhydrazone.[14] The gaseous products, hydrogen and nitrogen, were analyzed by mass spectrometry after passing them through a trap cooled to −196°C.

**Procedure.** Deaerated solutions were prepared by bubbling argon through the solution for about 30 min, and by then outgassing it in a vacuum system for 30 sec every five minutes until the uncondensable gas pressure (at −196°C) above the solution was of the order of $10^{-4}$ mmHg. During the whole period the solution was vigorously shaken.

Nitrous oxide (Takachiho Chemical Industrial Co., Ltd.) was purified by freezing it several times in a liquid nitrogen trap and by then pumping the uncondensable gases out. Finally the trap was removed and the pressure was measured, after which the nitrous oxide was transferred into a reaction cell containing the degassed solution. Equilibration was carried out over a 1—2 hr period. The concentration of nitrous oxide in the solution was calculated from the data available on the dependence of the solubility (and of Henry's coefficient) for nitrous oxide in water on the temperature and the pressure.[15]

Photolyses were carried out at 25±0.2°C. At suitable intervals after the beginning of irradiation, the shutter separating the cell and the lamp was closed and the amount of the hexacyanoferrate(III) was determined. In the experiments using the cell for gasometric analysis, the solution was stirred by a magnetic stirrer during irradiation. After irradiation the stopcock was opened several times for about 30 sec, the water vapor was condensed in the trap (−196°C), and the gas was analyzed.

The other experimental techniques have been described in Part I.[2]

## Results

**Photochemistry in the Presence of Nitrous Oxide.** Deaerated neutral (pH ~6) solutions of $10^{-3}$ M potassium hexacyanoferrate(II) containing various amounts of dissolved nitrous oxide colored when irradiated at 2537 Å. The absorption spectrum of irradiated solutions, as well as the results of thin-layer chromatography, clearly indicated the formation of hexacyanoferrate(III) ions. Figure 1 presents the dependence of the yield of hexacyanoferrate(III) on the irradiation time at a constant light intensity ($3.83\times10^{-6}$ einstein$\cdot l^{-1}$sec$^{-1}$) and at 25°C. From the initial slopes of the curves, one can evaluate the initial quantum yields, which depend markedly on the nitrous oxide concentration. These results are represented in Fig. 2, curve 1. At high $N_2O$ concentrations ($>5\times10^{-3}$ M), a constant yield is obtained independent of the nitrous oxide concentration ($\gamma=0.71\pm0.02$).

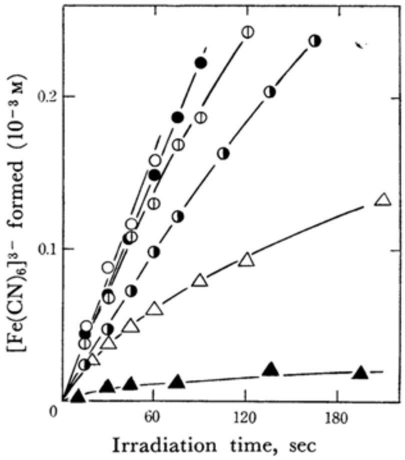

Fig. 1. Dependence of the yield of $[Fe(CN)_6]^{3-}$ on irradiation time at various $[N_2O]$.
Concentration of $N_2O$, ○: $1.87\times10^{-3}$ M
●: $5.2\times10^{-4}$ M ⦶: $2.6\times10^{-4}$ M
◑: $1.6\times10^{-4}$ M △: $8\times10^{-5}$ M
▲: none

Additional experiments were also carried out with $10^{-2}$ M solutions (20 m*l*) of potassium hexacyanoferrate(II) containing $1.6\times10^{-2}$ M $N_2O$. The gas evolved on irradiation for 20 min was found to be pure nitrogen. About 90% of the hexacyanoferrate(II) initially present was shown, by means of potentiometric titration with 0.01 N $Ce^{4+}$ solutions, to have been oxidized.

**Photochemistry in the Presence of Potassium Nitrate.** Evacuated solutions of $10^{-3}$ M potassium hexacyanoferrate(II) in the presence of nitrate ions were irradiated at 2537 Å and 25°C. Hexacyanoferrate(III) and nitrite ions were formed, the yields of the latter being approximately half those of the former (Fig. 3). Figure 2, curve 2, represents the dependence of the initial yield of hexacyanoferrate(III) on the nitrate ion concentration. The yield increases with an increase in the nitrate concentration until it reaches the same limiting value ($\gamma_{\mathrm{lim}}=0.71\pm0.02$) as when nitrous oxide is the scavenger.

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[12] Y. Tsunoda, T. Takeuchi and Y. Yoshino, *Sci. Papers Coll. Gen. Educ., Univ. Tokyo,* **14**, 55 (1964).
[13] Reference 10, p. 802.
[14] G. R. A. Johnson and G. Scholes, *Analyst,* **79**, 217 (1954).
[15] A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. 1, D. Van Nostrand Co., New York (1953), p. 1135.

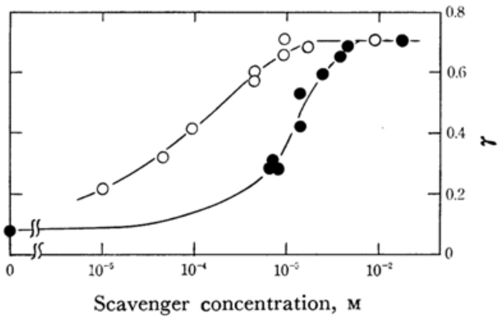

Fig. 2. Dependence of $\gamma$ on the scavenger concentration.
Curve 1 (●): $N_2O$ Curve 2 (○): $NO_3^-$

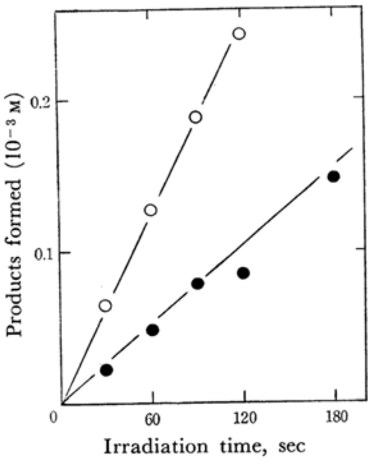

Fig. 3. Formation of $[Fe(CN)_6]^{3-}$ (○) and $NO_2^-$ (●) from $10^{-3}$ M $[Fe(CN)_6]^{4-}+10^{-3}$ M $NO_3^-$ solutions irradiated at 2537Å.

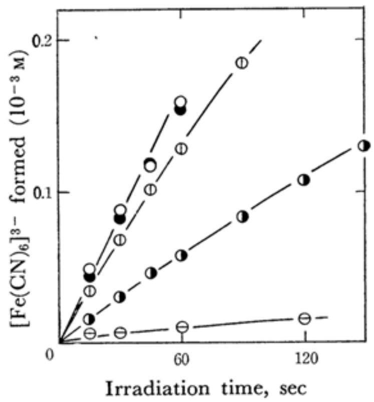

Fig. 4. Effect of added ethanol in the ($10^{-3}$ M $[Fe(CN)_6]^{4-}+1.6\times10^{-2}$ M $N_2O$) system.
The concentration of ethanol,
○: none ●: $10^{-4}$ M ⦶: $1.1\times10^{-3}$ M
◑: $10^{-2}$ M ⊖: 1 M

**The ($[Fe(CN)_6]^{4-}+N_2O+C_2H_5OH$) Systems.** Neutral solutions of $10^{-3}$ M potassium hexacyanoferrate(II) containing varying amounts of ethanol were irradiated in the presence of $1.6\times10^{-2}$ M $N_2O$. The results are shown in Fig. 4. The simultaneous formation of acetaldehyde was verified using 2, 4-dinitrophenylhydrazine.

**The ($[Fe(CN)_6]^{4-}+N_2O+HClO_4+CH_3OH$) Systems.** Solutions of $10^{-3}$ M $K_4[Fe(CN)_6]$ containing 1 M methanol were irradiated in the presence of varying amounts of $N_2O$ and $HClO_4$. The gases evolved, $N_2$ and $H_2$, were analyzed on a mass spectrogram. Table 1 shows some of these results.

TABLE 1. RATIO OF THE YIELDS, $\gamma(N_2)/\gamma(H_2)$, FROM THE PHOTOLYSIS OF AQUEOUS $[Fe(CN)_6]^{4-}$ SOLUTION ($10^{-3}$ M) CONTAINING 1 M $CH_3OH$ AND VARYING CONCENTRATIONS OF $N_2O$ AND $HClO_4$

| $[N_2O]$, M | $[HClO_4]$, M | $\gamma(N_2)/\gamma(H_2)$ |
|---|---|---|
| $2.2\times10^{-2}$ | 0 (pH=6) | >1000 |
| 0 | 0.1 | <0.02 |
| $1.96\times10^{-2}$ | $10^{-2}$ | 0.923 |
| $1.87\times10^{-2}$ | $2\times10^{-3}$ | 4.29 |
| 0 | 0 (pH=6) | no gas evolved |

**The ($[Fe(CN)_6]^{4-}+NO_3^-+CH_3OH$ or $C_2H_5OH$) Systems.** The effect of adding ethanol or methanol on the yield of hexacyanoferrate(III) in the presence of nitrate ions as the electron scavenger was studied in view of the marked effect of ethanol when nitrous oxide is the electron scavenger (Fig. 4). When evacuated solutions of $10^{-3}$ M $K_4[Fe(CN)_6]$ containing $10^{-3}$ M $KNO_3$

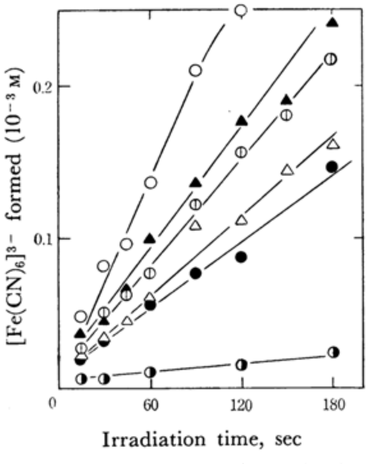

Fig. 5. The formation of $[Fe(CN)_6]^{3-}$ from solutions of ($10^{-3}$ M $[Fe(CN)_6]^{4-}+1$ M $C_2H_5OH$) containing varying amount of $N_2O$ and $NO_3^-$.

| | $N_2O$, M | $NO_3^-$, M |
|---|---|---|
| ○ : | 0 | $9.6\times10^{-4}$ |
| ▲ : | $1.05\times10^{-3}$ | $2.0\times10^{-3}$ |
| ⦶ : | $1.02\times10^{-3}$ | $9.6\times10^{-4}$ |
| △ : | $9.0\times10^{-4}$ | $6.0\times10^{-4}$ |
| ● : | $2.37\times10^{-3}$ | $9.6\times10^{-4}$ |
| ◑ : | $1.6\times10^{-2}$ | 0 |

were irradiated in the presence of 1 M $C_2H_5OH$ or 1 M $CH_3OH$, the quantum yield for the hexacyanoferrate(III) formation remained constant at 0.71±0.02.

**The ($[Fe(CN)_6]^{4-} + NO_3^- + N_2O + C_2H_5OH$) Systems.** Solutions of $10^{-3}$ M $K_4[Fe(CN)_6]$ containing varying amounts of $NO_3^-$ and $N_2O$ were irradiated in the presence of 1 M $C_2H_5OH$. Figure 5 presents the dependence of the yield of hexacyanoferrate(III) on the irradiation time in these systems. The hexacyanoferrate(III) plots have positive intercepts.

**Photochemistry in the Absence of an Electron Scavenger.** The irradiation at 2537 Å of a deaerated solution of $10^{-3}$ M potassium hexacyanoferrate(II) in the neutral pH region caused no significant change in the optical density at 4200 Å. In acidic solutions, however, such an irradiation caused an aquation reaction. The quantum yield of the initial formation of aquopentacyanoferrate(II), as measured using sodium azide,[2] was of the order of 0.7[16] for an 0.1 N $HClO_4$ solution containing $10^{-3}$ M potassium hexacyanoferrate(II).

## Discussion

**Photochemistry in the Presence of Electron Scavengers.** Nitrous oxide is known to react rapidly with hydrated electrons produced in aqueous systems by ionizing radiations leading to the formation of nitrogen.[17,18] The hydrogen ion is also an electron scavenger,[19] converting it into an H atom which will, in turn, be scavenged by methanol to yield molecular hydrogen.[18,20] The results presented in Table 1 can be interpreted on the basis of the following reaction scheme, involving a photochemical process which leads to the production of hydrated electrons:

$$[Fe(CN)_6]^{4-} \xrightarrow{h\nu} [Fe(CN)_6]^{3-} + e^-_{aq} \tag{1}$$

$$e^-_{aq} + N_2O \rightarrow N_2 + O^-_{aq}\ (\rightarrow OH + OH^-) \tag{2}$$

$$e^-_{aq} + H_3O^+ \rightarrow H + H_2O \tag{3}$$

$$H + CH_3OH \rightarrow H_2 + CH_2OH \tag{4}$$

$$OH + CH_3OH \rightarrow H_2O + CH_2OH \tag*{(5)$^{19b)}$}$$

$$CH_2OH + [Fe(CN)_6]^{3-} \rightarrow H^+ + HCHO + [Fe(CN)_6]^{4-} \tag*{(6)$^{20)}$}$$

and it is known that $k_2=8.7\times 10^{9}$,[21] $k_3=2.3\times 10^{10}$,[21] and $k_4=2\times 10^6\ M^{-1}sec^{-1}$.[22] It should be noted that we can exclude one possible photochemical process:[23]

$$[Fe(CN)_6]^{4-},\ H_2O \xrightarrow{h\nu} [Fe(CN)_6)]^{3-} + H + OH^- \tag{7}$$

in which an H atom is formed directly by the electron capture of one of the water molecules in the hydration shell, as in the case of ferrous ions,[24] since there is no $H_2$ evolution from an 1 M $CH_3OH$-containing solution in the absence of $H_3O^+$ (Table 1). Methanol would act as an efficient scavenger for H atoms, if present, leading to the evolution of $H_2$. Other possible reactions of the H atom formed by Reaction (3), such as:

$$H + N_2O \rightarrow N_2 + OH \tag{8}$$

$$H + H_3O^+ \rightarrow H_2^+ + H_2O \tag{9}$$

$$H + [Fe(CN)_6]^{3-} \rightarrow H^+ + [Fe(CN)_6]^{4-} \tag*{(10)$^{25)}$}$$

may also be excluded, as Reactions (8) and (9) are slow ($k_8=1.25\times 10^4$ and $k_9=2.6\times 10^3\ M^{-1}\cdot sec^{-1}$)[26] compared with Reaction (4) and as the $[Fe(CN)_6]^{3-}$ concentration may not be sufficient to permit Reaction (10) to compete significantly with Reaction (4).

According to Reaction Schemes (1), (2), (3) and (4), the ratio of the yields, $\gamma(H_2)/\gamma(N_2)$, should be represented by:

$$\gamma(H_2)/\gamma(N_2) = k_3[H_3O^+]/k_2[N_2O] \tag{11}$$

Using the data of Table 1, the rate constant ratio, $k_3/k_2=2.2$, was calculated to be in fair agreement with the value ($k_3/k_2=2.7$) obtained by radiation chemical studies.[21,27]

In neutral solutions of $[Fe(CN)_6]^{4-}$ containing only $N_2O$ as the scavenger, Reactions (1) and (2) would take place, followed by:

$$OH + [Fe(CN)_6]^{4-} \rightarrow OH^- + [Fe(CN)_6]^{3-} \tag{12}$$

The dependence of the yields of $[Fe(CN)_6]^{3-}$ on the $N_2O$ concentration (Fig. 2, curve 1) indicates that Reaction (2) competes with a back reaction, presumably:

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[16] Emschwiller and Legros reported $\gamma=0.1$—0.2 for 0.01—0.5 M solution of $K_4[Fe(CN)_6]$ at pH 10 (G. Emschwiller and J. Legros, *Compt. Rend.*, **261**, 1537 (1965)), their solution not being stirred during irradiation; see G. Emschwiller, *Ric. Sci., Suppl.*, **27**, 1 (1957).

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

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

[19] a) J. Jortner, M. Ottolenghi and G. Stein, *ibid.*, **66**, 2029 (1962); b) J. H. Baxendale and G. Hughes, *Z. Physik. Chem.*, **14**, 306 (1958).

[20] G. Hughes and C. Willis, *Discussions Faraday Soc.*, **36**, 223 (1963).

[21] S. Gordon, E. J. Hart, M. S. Matheson and J. Rabani, *ibid.*, **36**, 193 (1963).

[22] J. P. Sweet and T. K. Thomas, *J. Phys. Chem.*, **68**, 1363 (1964).

[23] Airey and Dainton[5] reached the same conclusion using 2-propanol as the H atom scavenger.

[24] J. Jortner and G. Stein, *J. Phys. Chem.*, **66**, 1258, 1264 (1962).

[25] $k_{10}=10^7\ M^{-1}\ sec^{-1}$, G. Czapski and G. Stein, *J. Phys. Chem.*, **64**, 219 (1960); $k_{10}=2\times 10^8\ M^{-1}\ sec^{-1}$, J. Rabani and G. Stein, *J. Chem. Phys.*, **37**, 1865 (1962).

[26] F. S. Dainton and S. A. Sills, *Proc. Chem. Soc.*, **1962**, 223.

[27] G. V. Buxton and F. S. Dainton, *Proc. Roy. Soc. (London)*, **A287**, 427 (1965).

$$[Fe(CN)_6]^{3-} + e^-_{aq} \rightarrow [Fe(CN)_6]^{4-} \quad (13)$$

The limiting constant quantum yield of $[Fe(CN)_6]^{3-}$, $\gamma_{lim}=0.71\pm0.02$, obtained at a high $[N_2O]$ value, would correspond to the total scavenging of the hydrated electrons produced by Process (1).

In the case of nitrate ions used as the scavenger, the reaction sequence may be represented by photoreaction (1), together with Reaction (13) and the processes:

$$e^-_{aq} + NO_3^- \rightarrow NO_2 + 2OH^- \quad (14)^{28)}$$

$$2NO_2 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+ \quad (15)^{28)}$$

$$NO_2 + [Fe(CN)_6]^{4-} \rightarrow NO_2^- + [Fe(CN)_6]^{3-} \quad (16)$$

though Reaction (14) can possibly be replaced by Reactions (17) and (18):29)

$$e^-_{aq} + NO_3^- \rightarrow NO_3{}^{2-}{}_{aq} \quad (17)$$

$$NO_3{}^{2-}{}_{aq} \rightarrow NO_2 + 2OH^- \quad (18)$$

Another reaction sequence, which would involve Reaction (19), as suggested from the results of a study of the $\gamma$-radiolysis of deaerated aqueous 2-propanol-nitrate solutions:30)

$$e^-_{aq} + NO_3^- \rightarrow NO_2^- + OH + OH^- \quad (19)$$

followed by Reaction (12), may be excluded for reasons to be discussed later. In this system, too, the same constant quatum yield corresponding to the total electron scavenging was obtained at high nitrate ion concentrations (Fig. 2, curve 2). To explain the yields of hexacyanoferrate(III) and nitrite ions (Fig. 3), it is postulated that the $NO_2$ formed by Reaction (14) (or by Reactions (17) and (18)) does not disproportionate *via* Reaction (15), as is usually supposed,29,31) but reacts instead with the hexacyanoferrate(II) present to give nitrite ions (Reaction (16)).

Using the limiting value for the formation of hexacyanoferrate(III), $\gamma_{lim}=0.71$, obtained in two scavenger systems, for which the schemes are represented by Reactions (1), (2), and (12), and by Reactions (1), (14) and (16), respectively, one can get $\Gamma=0.35$ at 25°C for the quantum yield of the production of hydrated electrons in the photochemistry of aqueous hexacyanoferrate(II) solutions at 2537 Å.32)

**Effect of Added Alcohols in the Presence of $N_2O$ or $NO_3^-$.** Ethanol reacts rapidly with an OH radical:

$$C_2H_5OH + OH \rightarrow CH_3CHOH + H_2O \quad (20)$$

the $k_{20}$ being $10^9\ \mathrm{M}^{-1}\ \mathrm{sec}^{-1}$.33) The resulting organic free radical may be expected, by analogy with Reaction (6), to reduce hexacyanoferrate(III):

$$CH_3CHOH + [Fe(CN)_6]^{3-} \rightarrow CH_3CHO + H^+ + [Fe(CN)_6]^{4-} \quad (21)$$

The results of Fig. 4 can well be interpreted on the basis of Reactions (1), (2), (12), (20) and (21), the formation of acetaldehyde having been verified. Under these conditions, the yield of $[Fe(CN)_6]^{3-}$, $\gamma$, is represented by:

$$\gamma = \Gamma + \Gamma\frac{k_{12}[Fe(CN)_6{}^{4-}] - k_{20}[C_2H_5OH]}{k_{12}[Fe(CN)_6{}^{4-}] + k_{20}[C_2H_5OH]} \quad (22)$$

where $\Gamma=0.35$ at 25°C and $[Fe(CN)_6{}^{4-}]=10^{-3}\ \mathrm{M}$. Equation (22) may thus be rearranged to give:

$$\frac{1}{\gamma} = \frac{1}{0.7} + \frac{1}{0.7}\frac{k_{20}}{10^{-3}k_{12}}[C_2H_5OH] \quad (23)$$

A plot of $1/\gamma$ against $[C_2H_5OH]$ is shown in Fig. 6, from which it may be deduced that $k_{20}/k_{12}=0.16$. Other values obtained using the radiation chemical data are 0.11$^{34)}$ and 0.21.35) The agreement is satisfactory, confirming the reaction mechanism described above.

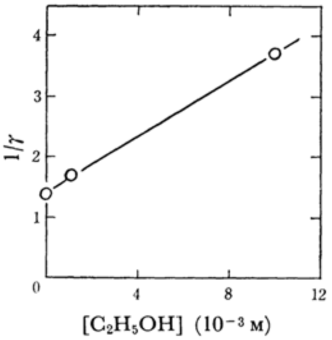

Fig. 6. The plot of $1/\gamma$ against $[C_2H_5OH]$ (Test of Eq. (23)). Conditions as in Fig. 4.

If Reaction (19) occurred, the subsequent reactions would be the same as in the case of Reaction (2); a marked decrease in the hexacyanoferrate(III) yield upon the addition of ethanol (or methanol) would likewise be predicted. Experimental results have shown that such is not the case, thus excluding any reaction mechanism involving Reaction (19).

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28) M. L. Hyder, *J. Phys. Chem.*, **69**, 1858 (1965).

29) J. T. Allan, *ibid.*, **68**, 2697 (1964); T. Sawai, This Bulletin, **39**, 955 (1966).

30) A. Appleby, G. Scholes and M. Simic, *J. Am. Chem. Soc.*, **85**, 3891 (1963).

31) M. Haissinsky, *J. Chim. Phys.*, **10**, 1141 (1965).

32) Measuring the yield of nitrogen from $N_2O$-containing solutions, Airey and Dainton5) obtained $\Gamma=0.66$ for $K_4[Fe(CN)_6]$ and $\Gamma=0.48$ for lanthanum hexacyanoferrate(II) system. The results of Shirom and Stein,4) on the other hand, gave $\Gamma=1.0$ when $N_2O$ was used as the electron scavenger, but $\Gamma=0.33$ when phosphate ions were used as the electron scavenger and the amount of $H_2$ produced by the dehydrogenation of ethanol by the hydrogen atoms formed in the following way is measured:

$$e^-_{aq} + H_2PO_4^- \rightarrow H + HPO_4^{2-}$$

33) G. E. Adams, J. W. Boag and B. D. Michael, *Trans. Faraday Soc.*, **61**, 1417 (1965).

34) J. Rabani and G. Stein, *ibid.*, **58**, 2150 (1962).

**Evaluation of $k_2/k_{14}$.** In a photochemical system (pH=6) containing varying amounts of $N_2O$ and $NO_3^-$ in the presence of 1 M $C_2H_5OH$, the photochemically-produced electron would react according to either Reaction (2) followed by Reactions (20) and (21), or Reaction (14) followed by Reaction (16). Then it follows that:

$$\frac{1}{\gamma}=\frac{1}{0.7}\left(1+\frac{k_2[N_2O]}{k_{14}[NO_3^-]}\right) \qquad (24)$$

The hexacyanoferrate(III) plots of Fig. 5 have positive intercepts. At the beginning of the irradiation, the concentration of $[Fe(CN)_6]^{3-}$ is not yet sufficient to permit Reaction (21) to take place; therefore, the organic radical, $CH_3CHOH$, might disappear *via* another process, such as:

$$CH_3CHOH + NO_3^- \rightarrow HCHO + NO_2 + OH^- \qquad (25)$$

followed by Reaction (16). This would result in a high yield of hexacyanoferrate(III) and, hence, a positive intercept. The results of Fig. 5 (except those at the initial stages of irradiation) satisfy well the conditions of Eq. (24) (Fig. 7) and lead to a value of $k_2/k_{14}=0.33$. Direct measurements of $k_2/k_{14}$ by $\gamma$-radiolysis give 0.79,[21] 0.69,[36] and 0.37.[37]

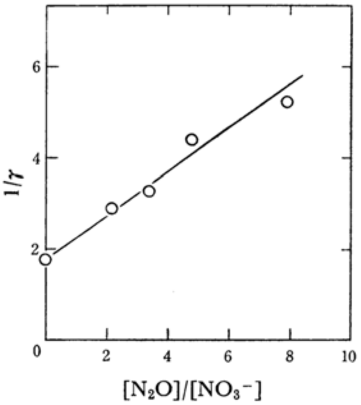

Fig. 7. Test of Eq. (24). Conditions as in Fig. 5.

**The Nature of the Absorption Act and the Primary Process.** The results presented in this work give chemical kinetic evidence for the formation of the hydrated electron in solution of hexacyanoferrate(II) irradiated at 2537 Å. The absorption of light at 2537 Å by the hexacyanoferrate(II) ion may be attributed to the charge-transfer band, which is identified as metal-$t_{2g}$→CN-$\pi$-antibonding-$t_{1u}$:[1]

$$[Fe(CN)_6]^{4-}\ t_{2g} \xrightarrow{h\nu} [Fe(CN)_6]^{4-}\ t_{1u} \qquad (26)$$

This excited state might be capable of an electron transfer to the adjacent solvent molecules, resulting in the formation of a hydrated electron. Alternatively, it may decay back to the ground state. The competition between these two processes determines the quantum yield, $\Gamma$. The fact that $\Gamma$ is smaller than unity (about one-third) suggests that the scavenging process does not involve any direct interaction of the scavenger with the spectroscopic excited state, but, rather, that the scavenger interacts with the species produced by the secondary process, most probably the hydrated electron.

## Conclusions

We have arrived at the conclusion that the absorption of light quanta in the region of the electron-transfer band of the hexacyanoferrate(II) ion leads to an oxidation reaction giving hexacyanoferrate(III) and the hydrated electron, while, as has been shown in the preceding paper, the absorption of light in the region of the ligand-field band leads only to a ligand dissociation reaction. The photochemically-produced electron in the present systems displays a reactivity towards some solutes ($N_2O$, $NO_3^-$ and $H_3O^+$) just like the hydrated electron observed in radiation chemistry. The present photochemical study thus offers a new method of investigating, in a direct manner, the nature of this electron and its reactions with a variety of inorganic and organic substances; some results of such studies will be published later.

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