The Photochemistry of Hexacyanoferrate(II) Ions in Aqueous Solutions

By Shin-ichi OHNO and Gen-ichi TSUCHIHASHI*

(Received April 15, 1965)

Aqueous hexacyanoferrate(II) solutions decompose in ultraviolet light to give the aquopentacyanoferrate(II) ion.(1) Recently, Matheson et al.(2) observed a transient absorption due to the hydrated electron, e^-_{aq}, in the flash photolysis of aqueous hexacyanoferrate(II) solutions. We have studied the photo-induced reaction of aqueous hexacyanoferrate(II) solutions at various pH values, employing two light sources of different wavelengths. We have observed that illumination with a 3660 Å light causes only a ligand substitution reaction:

$$[Fe(CN)_6]^{4-} \xrightarrow[H_2O]{3660\,\text{Å}} [Fe(CN)_5OH_2]^{3-} + CN^- \qquad (1)$$

---

* Present Adress: Sagami Chemical Research Center, Onuma, Sagamihara-shi, Kanagawa.

1) S. Ašperger, *Trans. Faraday Soc.*, **48**, 617 (1952).

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

As a result of activation with a 2537 Å light, on the other hand, a photo-oxidation reaction was found to take place, giving hexacyanoferrate(III) and "reducing species (r. s.)":

$$[\mathrm{Fe(CN)_6}]^{4-} \xrightarrow[\mathrm{H_2O}]{2537\,\text{Å}} [\mathrm{Fe(CN)_6}]^{3-} + \text{“r.s.”}(\mathrm{e^-}_{\mathrm{aq}}) \qquad (2)$$

The reducing species thus formed displayed a reactivity similar to that of the hydrated electron produced in water irradiated by fast electrons or γ-rays.[3]

The pH-buffered solutions of 10^{-2} M potassium hexacyanoferrate(II) were irradiated with a 3660 Å light from a high pressure mercury lamp, the solution being stirred by bubbling nitrogen gas. The quantum yield of the initial formation of aquopentacyanoferrate(II) was 0.89 at pH 4.0, the maximum value obtained, and 0.52 at pH 0.65.

Photo-oxidation reaction 2 was studied by using a 2537 Å light from a low pressure mercury lamp. The irradiation of the deaerated solution of 10^{-3} M potassium hexacyanoferrate(II) alone caused no significant change in the optical density at 420 mμ. The same solution, however, became colored when irradiated in the presence of nitrous oxide or nitrate ions.[5] The absorption spectra of the solution, as well as the results of thin-layer chromatography, clearly indicate the formation of hexacyanoferrate(III) ions, which may be attributed to reaction 2, followed by:

$$\mathrm{e^-}_{\mathrm{aq}} + \mathrm{N_2O} \longrightarrow \mathrm{N_2} + \mathrm{OH} + \mathrm{OH^-} \qquad (3)$$

$$\mathrm{OH} + [\mathrm{Fe(CN)_6}]^{4-} \longrightarrow [\mathrm{Fe(CN)_6}]^{3-} + \mathrm{OH^-} \qquad (4)$$

or

$$\mathrm{e^-}_{\mathrm{aq}} + \mathrm{NO_3^-} \longrightarrow \mathrm{NO_2} + 2\mathrm{OH^-} \qquad (5)$$

$$\mathrm{NO_2} + [\mathrm{Fe(CN)_6}]^{4-} \longrightarrow [\mathrm{Fe(CN)_6}]^{3-} + \mathrm{NO_2^-} \qquad (6)$$

The yield of hexacyanoferrate(III) ions increased with the increase in the concentration of nitrous oxide or nitrate ions to reach a limiting value. The quantum yield of the formation of $\mathrm{e^-}_{\mathrm{aq}}$ was determined to be 0.35. We also noted that no noticeable amount of hexacyanoferrate(III) was produced with a 3660 Å light, regardless of whether an electron scavenger, such as $\mathrm{N_2O}$ or $\mathrm{NO_3^-}$, was present or not.

Further, acetone appeared to compete with reaction 3 or 5 for $\mathrm{e^-}_{\mathrm{aq}}$, and ethanol, with reaction 4 for OH. From kinetic data, the rate constant ratios were calculated te be $k(\mathrm{e^-}_{\mathrm{ap}}+\text{acetone})/k_3=1.5$, $k(\mathrm{e^-}_{\mathrm{ap}}+\text{acetone})/k_5=0.45$ and $k(\mathrm{OH}+\text{ethanol})/k_4=0.16$. Agreements with the reported values are satisfactory.[3]

We may, therefore, conclude that the irradiation of hexacyanoferrate(II) ions with a 2537 Å light (the charge-transfer-to-solvent type of excitation[4]) brings about an electron release to the solvent, while activation by a 3660 Å light (the ligand-field transition type) causes only a ligand substitution reaction. The present photochemical study offers a new method of investigating, in a direct manner, the reactions of hydrated electrons with a variety of inorganic and organic substances: several such studies are now in progress.

Japan Atomic Energy Research Institute
Tokai-mura, Ibaraki

---

[3] "Radiation Research Supplement" Vol 4, Academic Press, New York and London (1964).

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