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The Photochemistry of Aqueous Hexacyanoferrate(II) Solutions. III. The Effect of Acetone on the Photo-oxidation Reaction at 2537 Å[1]

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The photochemistry of the hexacyanoferrate(II) ion was investigated at 2537 Å in the presence of acetone and of N_2O or NO_3^-. Acetone was found to act as a scavenger for the photochemically-produced electron, thus giving an acetone radical which can reduce the hexacyanoferrate(III) ion to the -(II) ion. The relative reaction rates of the electron, $k(e^-_{aq}+\text{acetone})/k(e^-_{aq}+N_2O)$ and $k(e^-_{aq}+\text{acetone})/k(e^-_{aq}+NO_3^-)$, were found to be 1.5 and 0.45 respectively. These rate ratios were found to vary with the ionic strength value in a way which indicates that e^-_{aq} has a unit negative charge and survives long enough for the establishment of its ionic atmosphere.

In a previous paper[2] it has been shown that, in the presence of an electron scavenger such as N_2O or NO_3^-, irradiation at 2537 Å causes a photo-oxidation reaction in aqueous hexacyanoferrate(II) solutions. Radiation chemical studies[3] indicate that acetone dissolved in aqueous solutions acts as an efficient scavenger for hydrated electrons. However, preliminary experiments have shown that the added acetone is not effective enough for a photo-oxidation to take place.

This paper aims to clarify the scavenging mechanism of acetone in competition with other electron scavengers (N_2O and NO_3^-) and to study possible subsequent reactions. This work also studies the effect of the changing ionic strength on the photochemistry of hexacyanoferrate(II) at 2537 Å in an attempt to get further insight into the nature of the reactive intermediate in this case.

Experimental

The experimental technique was similar to that previously described.[2] Acetone did not absorb the light at 2537 Å in any significant manner at the concentrations employed ($\varepsilon=10\ \text{mol}^{-1}\ l\ \text{cm}^{-1}$). Experiments were carried out at 25°C. The reaction vessel was a 1 cm-optical pass-length spectrophotometer cell.

Results

The $[Fe(CN)_6]^{4-}+N_2O+$Acetone) Systems. Experiments were carried out at 25°C with deaerated aqueous solutions of 10^{-3} M hexacyanoferrate(II) and varying concentrations of nitrous oxide and acetone. When the solution was irradiated at 2537 Å, hexacyanoferrate(III) ions were formed (Fig. 1). The yield *versus* time curves are linear when the concentration of added acetone is low. The quantum yield for the formation of $[Fe(CN)_6]^{3-}$ in the absence of acetone is 0.70±0.03. The curves depart from linearity when the concentration of acetone is high (curves 4 and 5 in Fig. 1), the rate of the formation of $[Fe(CN)_6]^{3-}$ falling off slightly after a short irradiation period and then reaching a constant value. Additional experiments were carried out in the presence of initially-added 5×10^{-5} M $[Fe(CN)_6]^{3-}$. A linear plot of the $[Fe(CN)_6]^{3-}$ yield *versus* the irradiation time was obtained in this system, indicating that the falling-off of the rate, seen in Fig. 1, may be accompanied

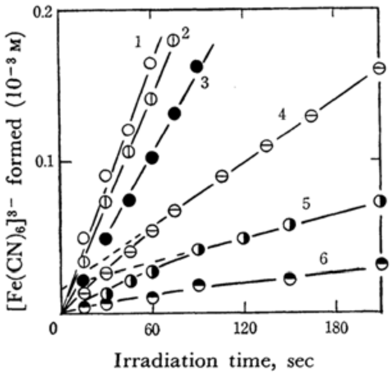

Fig. 1. The formation of $[Fe(CN)_6]^{3-}$ from solutions of 10^{-3} M $[Fe(CN)_6]^{4-}$ containing varying concentrations of N_2O and acetone.

	N_2O, M	Acetone, M
Curve 1:	1.87×10^{-2}	0
2:	2.46×10^{-2}	2.0×10^{-3}
3:	5.6×10^{-3}	2.0×10^{-3}
4:	7.06×10^{-3}	10^{-2}
5:	1.47×10^{-3}	10^{-2}
6:	0	10^{-2}

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[1] Partly presented at the 9th International Conference on Photochemistry, Tokyo, August, 1965.

[2] Part II of this series, This Bulletin, **40**, 1770 (1967).

[3] a) J. Rabani and G. Stein, *J. Chem. Phys.*, **37**, 1865 (1962). b) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani and J. K. Thomas, *Discussions Faraday Soc.*, **36**, 193 (1963).

by an accumulation of the hexacyanoferrate(III) produced.

The ($[Fe(CN)_6]^{4-}+NO_3^-+$Acetone) Systems. Evacuated solutions containing 10^{-3} M $[Fe(CN)_6]^{4-}$, 10^{-3} M NO_3^-, and varying concentration of acetone were irradiated at 2537 Å and 25°C. When there was no acetone, the hexacyanoferrate(III) was formed in a quantum yield of 0.7. Additions of acetone lowered the yield (*cf.* Fig. 2). A good linear relationship between the yields and the irradiation time was not obtained in this system.

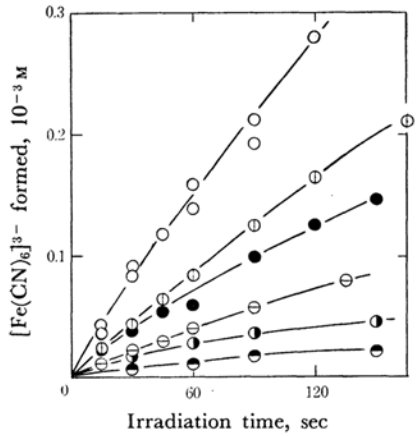

Fig. 2. The effect of added acetone in the (10^{-3} M $[Fe(CN)_6]^{4-}+10^{-3}$ M NO_3^-) systems. The concentration of acetone, ○: 0, ⦶: 0.00137 M, ●: 0.00274 M, ⊖: 0.00548 M, ◑: 0.01 M, ◒: 0.01 M in the absence of NO_3^-

The Effect of a Changing Ionic Strength. The effect of an added inert salt, Na_2SO_4, on the photochemical yield was studied in order to get an insight into the nature of the reactive species. Such a study had previously been used to discriminate between two forms of reducing species in the radiation chemistry of aqueous systems.[4,5]

Solutions of 10^{-3} M $K_4[Fe(CN)_6]$ containing varying amounts of added sodium sulfate were irradiated at 2537 Å and 25°C in the presence of the electron scavengers (N_2O, NO_3^- and acetone), and the yields of $[Fe(CN)_6]^{3-}$, γ, were measured. The results are included in Tables 1 and 2, which demonstrate that the added Na_2SO_4 affects the yields in the presence of acetone. Figure 3 presents the yields of $[Fe(CN)_6]^{3-}$, γ_0, in acetone-free solutions containing amounts of N_2O large enough to scavenge all the electrons produced.[2)]

Table 1. The effect of added Na_2SO_4 on γ for solutions of 10^{-3} M $[Fe(CN)_6]^{4-}$ containing N_2O and acetone (Concentration in M)

Na_2SO_4	N_2O	Acetone	γ
0	9.6×10^{-3}	2.74×10^{-3}	0.435
0.1	9.89×10^{-3}	2.74×10^{-3}	0.408
0.1	9.89×10^{-3}	2.74×10^{-3}	0.390

Table 2. The effect of added Na_2SO_4 on γ for solutions of 10^{-3} M $[Fe(CN)_6]^{4-}$ containing KNO_3 (10^{-3} M) and acetone (2.74×10^{-3} M)

Na_2SO_4, M	γ
0	0.271
0.022	0.315
0.045	0.311
0.070	0.311
0.209	0.324

Discussion

Acetone as an Electron Scavenger. The preceding paper[2)] has shown that the presence of 1.6×10^{-2} M N_2O or of 10^{-3} M NO_3^- is sufficient to scavenge all the electrons produced photochemically in a 10^{-3} M $K_4[Fe(CN)_6]$ solution. The following reactions were suggested in the case of N_2O as the scavenger:

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

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

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

The effect of added acetone represented in Fig. 1 may be interpreted in terms of a competition between the acetone (Reaction (4), followed by (5)):

$$(CH_3)_2CO + e^-_{aq} \rightarrow (CH_3)_2COH + OH^- \qquad (4)$$

$$[Fe(CN)_6]^{3-} + (CH_3)_2COH \rightarrow [Fe(CN)_6]^{4-} + (CH_3)_2CO + H^+ \qquad (5)$$

and N_2O (Reaction (2), followed by (3)) for the photochemically-produced electron.

According to this scheme, the quantum yield of $[Fe(CN)_6]^{3-}$, γ, should be represented by:

$$\gamma = \Gamma + \Gamma\frac{k_2[N_2O] - k_4[(CH_3)_2CO]}{k_2[N_2O] + k_4[(CH_3)_2CO]} \qquad (6)$$

where Γ (=0.35) is the quantum yield of the process 1. The value of γ can be obtained from the slope of the linear part of the curve in Fig. 1. It should be mentioned that the initial slope of the curve should not be taken, because initially, when there are practically no $[Fe(CN)_6]^{3-}$ ions present, Reaction (5) can not easily occur; therefore, the organic radical, $(CH_3)_2COH$, may disappear by another possible process:

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4) E. Collinson, F. S. Dainton, D. R. Smith and S. Tazuke, *Proc. Chem. Soc.*, 140 (1962).

5) G. Czapski and H. A. Schwarz, *J. Phys. Chem.*, **66**, 471 (1962).

$$2\ (CH_3)_2COH \rightarrow \text{products} \tag{7}$$

or:

$$(CH_3)_2COH + N_2O \rightarrow (CH_3)_2CO + N_2 + OH \tag{8}$$

followed by Reaction (3), thus leading to an increase in the yield of $[Fe(CN_6)]^{3-}$. The occurrence of Reaction (8) in alkaline solutions has previously been suggested.6)

Equation (6) can be rearranged to the form:

$$\frac{1}{\gamma} = \frac{1}{\gamma_0} + \frac{1}{\gamma_0}\frac{k_4}{k_2}\frac{[(CH_3)_2CO]}{[N_2O]} \tag{9}$$

where $\gamma_0(=2\Gamma)$ is the value of γ at [acetone]=0. The plot of $1/\gamma$ *vs.* [acetone]/$[N_2O]$ is presented in Fig. 4, where:

$$\frac{k_4}{k_2} = \frac{\text{(slope)}}{\text{(intercept)}} = 1.5$$

This value is a little higher than the values, $k(e^-{}_{aq}+\text{acetone})/k(e^-{}_{aq}+N_2O)=0.68$,3b) and 0.987), obtained from other radiation chemical studies.

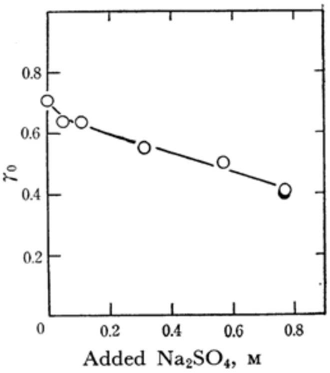

Fig. 3. The effect of added Na_2SO_4 on γ_0 in the photolysis of 10^{-3} M $[Fe(CN)_6]^{4-}$ at 25°C.
○: $[N_2O]=1.6\times10^{-2}$ M
●: $[N_2O]=2.5\times10^{-2}$ M

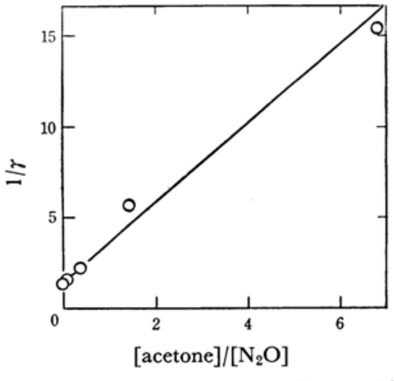

Fig. 4. The plot of $1/\gamma$ against [acetone]/$[N_2O]$; test of Eq. (9).

In the presence of NO_3^- as the electron scavenger, a competition between NO_3^- and acetone for the electron may be represented by;

$$e^-{}_{aq} + NO_3^- \rightarrow NO_2 + 2OH^- \tag{10}$$

$$NO_2 + [Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + NO_2^- \tag{11}$$

together with Reactions (4) and (5). The competition kinetics may be represented by the relationship:

$$\frac{1}{\gamma} = \frac{1}{\gamma_0} + \frac{1}{\gamma_0}\frac{k_4}{k_{10}[NO_3^-]}[(CH_3)_2CO] \tag{12}$$

where γ_0 is the yield of $[Fe(CN)_6]^{3-}$ in the absence of acetone. The experimental results of Fig. 2 satisfy the relationship of Eq. (12) (*cf.* Fig. 5) and lead to a value:

$$\frac{k_4}{k_{10}} = \frac{\text{(slope)}}{\text{(intercept)}}[NO_3^-] = 0.45$$

The value calculated using the data of pulse radiolysis3b) is $k_4/k_{10}=0.54$.

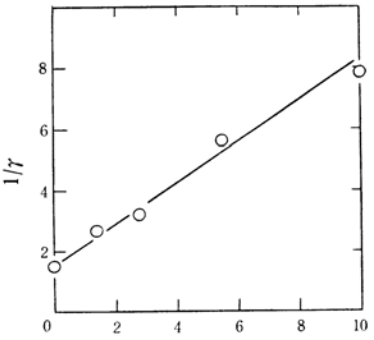

Fig. 5. Test of Eq. (12). Conditions as in Fig. 2.

It will now be of interest to compare the present results with those obtained in Part II.2) From the values of $k_4/k_{10}=0.45$ and $k_4/k_2=1.5$, one gets $k_2/k_{10}=0.30$, which is in fair agreement with the value (0.33) obtained from an independent study reported in Part II. Such a double check yields stronger support for the reaction mechanisms suggested in the present work.

Ionic-strength Effect on k_4/k_2 and k_4/k_{10}. Radiation chemists have made use of the Brönsted-Bjerrum theory of ionic reactions8) to provide proof that the reducing species ($e^-{}_{aq}$) in irradiated aqueous systems has a unit negative charge. This theory states that the rate constant, k, at an ionic strength, μ, will vary with the ionic strength of the solution according to the equation:

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6) G. Scholes, M. Simic and J. J. Weiss, *Discussions Faraday Soc.*, **36**, 214 (1963).

7) J. T. Allan and C. M. Beck, *J. Am. Chem. Soc.*, **86**, 1483 (1964).

8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York (1962), p. 150.

$$\log_{10}\frac{k}{k_0} = 1.02(Z_{e^-{}_{aq}})(Z_s)\ \frac{\mu^{1/2}}{1+\alpha\mu^{1/2}} \qquad (13)$$

where k_0 is the rate constant at zero ionic strength, α is a parameter close to unity, and $Z_{e^-{}_{aq}}$ and Z_s are the charges on $e^-{}_{aq}$ and the solute respectively. In the present systems, the expected value for $Z_{e^-{}_{aq}}$ being -1, k_{10} will increase ($Z_s=-1$), and k_4 and k_2 will be unchanged ($Z_s=0$) with an increase in the ionic strength. Hence, the k_4/k_2 ratio would be unaffected by the ionic strength, while k_4/k_{10} would decrease with the ionic strength. The ratios of the rate constants, k_4/k_2 and k_4/k_{10}, at various ionic strengths may be calculated using the data of Fig. 3 and Tables 1 and 2. The results, shown in Fig. 6, indicate that a behavior consistent with $Z_{e^-{}_{aq}}=-1$ is obtained and that the electron produced photochemically in the present system has time to form an ionic atmosphere before it is scavenged by the solute. If it reacts with the solute before the establishment of its ionic atmosphere, then any ionic-strength effects should be largely absent.[9] Thus, further evidence has been obtained for the production of the hydrated electron as the reactive intermediate in our photochemical system.

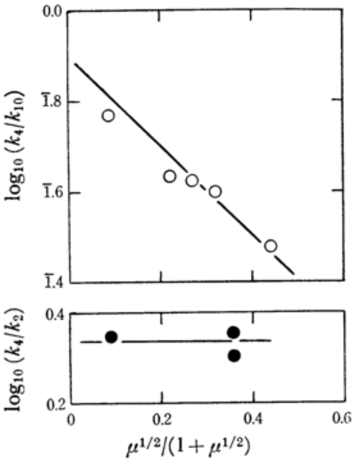

Fig. 6. The dependence of k_4/k_2 (●) and k_4/k_{10} (○) on ionic strength μ at 25°C. Conditions as in Tables 1 and 2.

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[9] F. S. Dainton, *Discussions Faraday Soc.*, **36**, 300 (1963).