BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2035—2038 (1967)

The Reactions of the Photochemically Produced Electron in Aqueous Hexacyanoferrate(II) Solutions[1]

Shin-ichi OHNO

Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki

(Received February 24, 1967)

The reactions of the photochemically-produced electron, e^-_{aq}, in an aqueous solution of hexacyanoferrate(II) were studied when $H_2PO_4^-$, NO_3^-, H_2O_2, CO_2, $[Fe(CN)_6]^{3-}$ and H_3BO_3 were used as the solute. The relative reaction rates, obtained by competition kinetics, are compared with those calculated using the published data on the absolute rate constants. The agreements are satisfactory in some cases, but not in other cases (*e. g.*, $H_2PO_4^-$, H_2O_2 and CO_2), for which a possible explanation is given. This explanation includes the postulation of an electron-transfer reaction between the solutes employed; it is shown that information on the efficiency of this electron-transfer reaction may be obtained by using the relative rates obtained both from competition kinetics and from pulse radiolysis.

The absolute rate constants for reactions of hydrated electrons, e^-_{aq}, have now been measured by using the pulse radiolysis technique.[2,3] This method, following the decay of the spectrum of e^-_{aq}, provides the rate of the disappearance of the e^-_{aq} reacting with solutes.

This paper aims to determine, from competition studies, the relative rates of the reactions of several solutes with e^-_{aq} produced in aqueous hexacyanoferrate(II) solutions illuminated with light at 2537 Å, and to compare them with those calculated using the data of pulse radiolysis.

The advantages of the present system for studying the reaction of e^-_{aq} are: 1) e^-_{aq} is the only reactive species produced photochemically, while in the radiolysis study several other reactive species, such as H, OH, H_2O_2, and H_2O^*, must also be considered.

2) Among the several ions which are known to generate e^-_{aq} by ultraviolet light, the $[Fe(CN)_6]^{4-}$ provides one of the simplest systems, since the $[Fe(CN)_6]^{4-}$ ion itself does not react with e^-_{aq}, and since the species remaining after photoelectron detachment ($[Fe(CN)_6]^{3-}$) is a chemically stable entity and has a negative charge, putting the detached e^-_{aq} in the negative Coulomb field.

3) Since the $[Fe(CN)_6]^{4-}$ ion has a sufficient absorption coefficient at 2537 Å, light absorption is complete even at a low concentration, where any possible interference induced by $[Fe(CN)_6]^{4-}$ is negligible.

4) The system can be used over the whole pH range, and the amount of the $[Fe(CN)_6]^{3-}$ produced can be readily followed spectrophotometrically.

This article is a full presentation of the details of the results which were briefly reported previously in this Bulletin.[4]

Experimental

The experimental technique was the same as that described previously.[5] Commercially-available carbon dioxide was purified by a method similar to that used in the case of nitrous oxide.[5] Its concentration was estimated from the equilibrium pressure over the solution (pH ~6). The other chemicals used (KNO_3, KH_2PO_4 and H_3BO_3) were of the purest grade available.

Results and Discussion

The (N_2O–$H_2PO_4^-$) System. When deaerated solutions of 10^{-3} M hexacyanoferrate(II) containing N_2O and $H_2PO_4^-$ are illuminated with light with a wavelength at 2537 Å, the following reactions can occur:[5]

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

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

$$e^-_{aq} + H_2PO_4^- \rightarrow H + HPO_4^{2-} \quad (3)^{6)}$$

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

$$H + [Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{4-} + H^+ \quad (5)$$

---

[1] The Photochemistry of Aqueous Hexacyanoferrate(II) Solutions. V. For Part IV, S. Ohno, This Bulletin, **40**, 1779 (1967).

[2] S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani and J. K. Thomas, *Discussions Faraday Soc.*, **36**, 193 (1963).

[3] J. H. Baxendale, E. M. Fielden, C. Capellos, J. M. Franius, J. V. Davies, M. Ebert, C. W. Gilbert, J. P. Keene, E. J. Land, A. J. Swallow and J. M. Nosworthy, *Nature*, **201**, 468 (1964).

[4] S. Ohno, This Bulletin, **38**, 2018 (1965).

[5] S. Ohno, *ibid.*, **40**, 1770 (1967).

[6] J. Jortner, M. Ottolenghi, J. Rabani and G. Stein, *J. Chem. Phys.*, **37**, 2488 (1962).

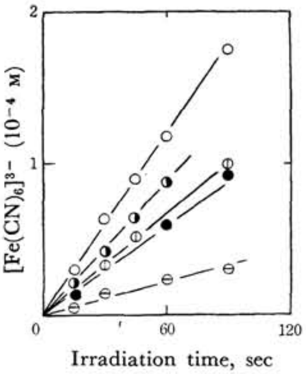

Fig. 1. The production of $[Fe(CN)_6]^{3-}$ as a function of irradiation time from solutions of 10^{-3} M $[Fe(CN)_6]^{4-}$ containing N_2O and $H_2PO_4^-$.

	N_2O, M	$H_2PO_4^-$, M
○	1.5×10^{-2}	0
◑	8.5×10^{-3}	0.2
⦶	3.8×10^{-3}	0.2
●	2.9×10^{-3}	0.2
⊖	0	0.2

The competition between Reactions (2) and (3) leads to the expression:

$$\frac{\gamma_0}{\gamma} = 1 + \frac{k_3[H_2PO_4^-]}{k_2[N_2O]} \qquad (6)$$

where γ denotes the yield of the hexacyanoferrate(III) and where γ_0 refers to the value in the absence of $H_2PO_4^-$. Figure 1 shows the yields of $[Fe(CN)_6]^{3-}$ as a function of the irradiation time in the presence of varying concentrations of $H_2PO_4^-$ and N_2O. The analysis of these results according to Eq. (6) gave the k_3/k_2 ratio of 0.016±0.001, which is too low a value compared with the 0.17⁷⁾ obtained from the data of the pulse radiolysis. However, this discrepancy can be resolved if an intermediate in Reaction (3) is assumed, as Thomas did,⁸⁾ and, further, an electron transfer from this intermediate to N_2O (Reaction (7)):

$$e^-_{aq} + H_2PO_4^- \rightarrow H_2PO_4{}^{2-}{}_{aq} \qquad (3a)$$

$$H_2PO_4{}^{2-}{}_{aq} \rightarrow H + HPO_4^{2-} \qquad (3b)$$

$$H_2PO_4{}^{2-}{}_{aq} + N_2O \rightarrow H_2PO_4^- + N_2 + OH + OH^- \qquad (7)$$

The rate constant provided by the pulse radiolysis refers to Reaction (3a). From the (1), (2), (3a), (3b), (4), (5), and (7) reaction sequence, the yield of $[Fe(CN)_6]^{3-}$, γ, should be represented by:

$$\gamma = \Gamma + \Gamma\frac{k_2[N_2O]}{k_2[N_2O]+k_{3a}[H_2PO_4^-]} + \Gamma\frac{k_{3a}[H_2PO_4^-]}{k_2[N_2O]+k_{3a}[H_2PO_4^-]} \times \frac{k_7[N_2O]-k_{3b}}{k_7[N_2O]+k_{3b}}$$

where Γ denotes the quantum yield of Reaction (1). This can be rearranged to the form;

$$\frac{\gamma_0}{\gamma_0-\gamma} = \left[1 + \frac{k_2[N_2O]}{k_{3a}[H_2PO_4^-]}\right]\left[1 + \frac{k_7[N_2O]}{k_{3b}}\right] \qquad (8)$$

k_2 and k_{3a} being 8.7×10^9 and 1.5×10^9 M⁻¹ sec⁻¹ respectively.⁷⁾ Figure 2 presents the plot of $[\gamma_0/(\gamma_0-\gamma)]/[1+k_2[N_2O]/k_{3a}[H_2PO_4^-]]$ against $[N_2O]$, where $k_7/k_{3b}=250\pm50$ M⁻¹ may be obtained.

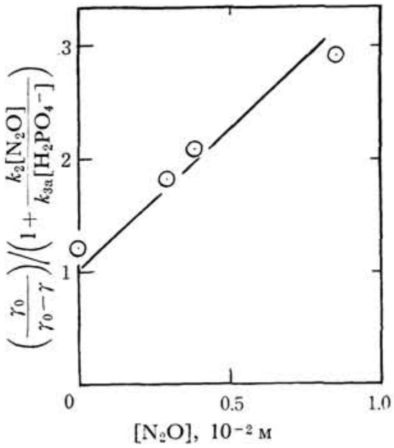

Fig. 2. Calculation of k_7/k_{3b} (Test of Eq. (8)).

The $(NO_3^- - H_2O_2)$ System. When the nitrate ion is used as the electron scavenger, the transient formation of $NO_3{}^{2-}{}_{aq}$ and NO_2 have recently been suggested.⁹⁻¹¹⁾ In solutions (pH 6) of 10^{-3} M $K_4[Fe(CN)_6]$ in the presence of KNO_3 and H_2O_2,¹²⁾ the photochemical reaction (1) may be followed by:

$$e^-_{aq} + H_2O_2 \rightarrow OH + OH^- \qquad (9)$$

$$e^-_{aq} + NO_3^- \rightarrow NO_3{}^{2-}{}_{aq} \qquad (10)$$

$$NO_3{}^{2-}{}_{aq} \rightarrow NO_2 + 2OH^- \qquad (11)$$

$$NO_2 + [Fe(CN)_6]^{4-} \rightarrow NO_2^- + [Fe(CN)_6]^{3-} \qquad (12)$$

$$NO_3{}^{2-}{}_{aq} + H_2O_2 \rightarrow NO_3^- + OH + OH^- \qquad (13)$$

as well as by Reaction (4). The occurrence of Reaction (13) may be supported by the fact that H_2O_2 can easily decompose to give OH and OH^-

---

7) k_2 is 8.7×10^9 M⁻¹ sec⁻¹ from Ref. 2. Two values have been reported for k_{3a} by Thomas *et al.*, namely, 6×10^9 in Ref. 8 and 1.5×10^9 M⁻¹ sec⁻¹ in J. K. Thomas, S. Gordon and E. J. Hart, *J. Phys. Chem.*, **68**, 1524 (1964). The latter value is taken here.

8) J. K. Thomas, *Discussions Faraday Soc.*, **36**, 68 (1963).

9) J. T. Allan, *J. Phys. Chem.*, **68**, 2697 (1964); T. Sawai, This Bulletin, **39**, 955 (1966).

10) M. Haissinsky, *J. Chim. Phys.*, **62**, 1141 (1965); E. Hayon, *Trans. Faraday Soc.*, **61**, 734 (1965).

11) L. Kevan, *J. Phys. Chem.*, **70**, 2529 (1966).

12) Suchsy stems with $[H_2O_2]$ values of up to ~10^{-3} M are stable for at least an hour in the absence of ultraviolet light.

on reaction with some reducing agents, Fe^{2+}, Ti^{3+}, e^-_{aq}, *etc.* The stationary-state treatment for the intermediates, e^-_{aq}, OH, $NO_3{}^{2-}{}_{aq}$, and NO_2, gives the following relation:

$$\frac{\gamma_0(NO_2{}^-)}{\gamma(NO_2{}^-)} = \left[1+\frac{k_9[H_2O_2]}{k_{10}[NO_3{}^-]}\right]\left[1+\frac{k_{13}}{k_{11}}[H_2O_2]\right] \quad (14)$$

where $\gamma(NO_2{}^-)$ and $\gamma_0(NO_2{}^-)$ are the yields for $NO_2{}^-$ in the presence and in the absence of H_2O_2 respectively. k_9 and k_{10} are taken to be 1.2×10^{10} and 1.1×10^{10} $M^{-1}\,sec^{-1}$ respectively, according to Gordon *et al.*2) Figure 3 represents the plot of the experimental results according to Eq. (14), demonstrating their consistency with the mechanism presented above. From these results, $k_{13}/k_{11}=430\pm100$ M^{-1} may be obtained at pH 6.

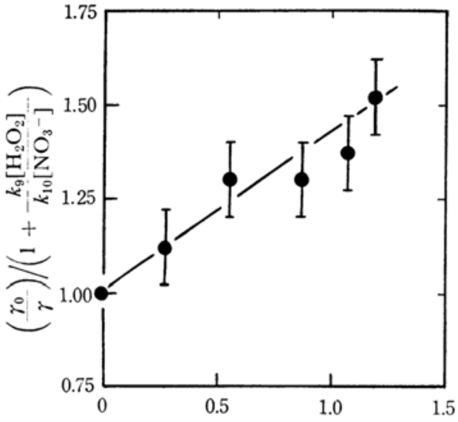

Fig. 3. Calculation of k_{13}/k_{11} (Test of Eq. (14)).

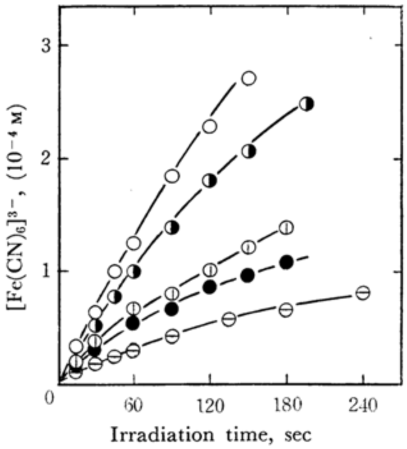

Fig. 4. The formation of $[Fe(CN)_6]^{3-}$ from 10^{-3} M $[Fe(CN)_6]^{4-}$ solutions containing 10^{-3} M $NO_3{}^-$ and CO_2. $[CO_2]$: (○) 0; (◑) 2.68×10^{-3}; (⦶) 6.65×10^{-3}; (●) 9.14×10^{-3}; (⊖) 2.80×10^{-2} M

If Reaction (13) is not assumed to occur, then $k_9/k_{10}=2.1$4) is calculated; this is not in good agreement with the value of 1.1 obtained from the pulse radiolysis study.

The ($NO_3{}^-$–CO_2) System. Figure 4 represents the dependence of the yield of $[Fe(CN)_6]^{3-}$ on the irradiation time. The yield-irradiation time curves are not linear, as may be seen. From the reaction mechanism presented by Reactions (10), (11), and (12), and by Reactions (15) and (16);13)

$$e^-_{aq} + CO_2 \rightarrow CO_2{}^- \quad (15)$$

$$CO_2{}^- + [Fe(CN)_6]^{3-} \rightarrow CO_2 + [Fe(CN)_6]^{4-} \quad (16)$$

the relation expressed by Eq. (17) is obtained:

$$\frac{\gamma_0}{\gamma} = 1+\frac{k_{15}[CO_2]}{k_{10}[NO_3{}^-]} \quad (17)$$

The plot of γ_0/γ *vs.* $[CO_2]/[NO_3{}^-]$, γ being calculated using the initial slope of the curves in Fig. 4, is presented in Fig. 5, curve 1. This would give $k_{15}/k_{10}=0.09$, which is too low a value compared with that of pulse radiolysis ($k_{15}/k_{10}=0.70$).2)

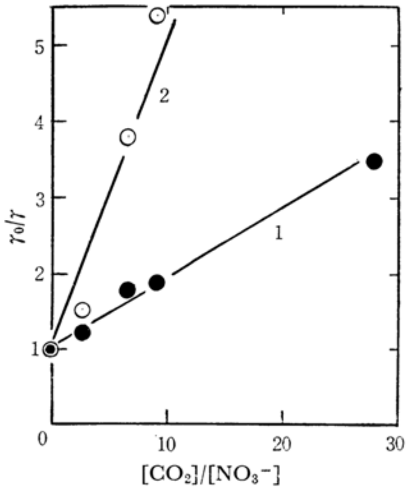

Fig. 5. The plots according to Eq. (17).

However, if one estimates the value of γ using the slope of the curves at the point where $[Fe(CN)_6{}^{3-}]=0.1\times10^{-3}$ M, then one gets $k_{15}/k_{10}=0.38$ (curve 2 of Fig. 4), which is closer to the value of the pulse radiolysis. Thus, one may conclude that, at the initial stage of reaction, where the concentration of $[Fe(CN)_6]^{3-}$ is low, Reaction (16) is in competition with Reaction (18):

$$CO_2{}^- + NO_3{}^- \rightarrow CO_2 + NO_3{}^{2-}{}_{aq} \quad (18)$$

followed by Reactions (11) and (12).

---

13) The pH of the solution containing CO_2 in the present system was found to be 5.75. Thus, the reaction between e^-_{aq} and H_3O^+ may be neglected.

The (NO_3^-–O_2) System. The addition of O_2-($[O_2]=1.2\times10^{-3}$ M) to the (10^{-3} M $[Fe(CN)_6]^{4-}$ + 10^{-3} M NO_3^-) system suppressed the yield of $[Fe(CN)_6]^{3-}$ from 0.63 to 0.21±0.02. This is attributable to the reactions:

$$e^-_{aq} + O_2 \rightarrow O_2^- \tag{19}$$

$$O_2^- + [Fe(CN)_6]^{3-} \rightarrow O_2 + [Fe(CN)_6]^{4-} \tag{20}$$

With the help of Eq. (21);

$$\frac{\gamma_0}{\gamma} = 1 + \frac{k_{19}[O_2]}{k_{10}[NO_3^-]} \tag{21}$$

$k_{19}/k_{10}=1.7\pm0.3$ may then be calculated; this is in good agreement with the value obtained by the pulse radiolysis study.[2]

The (N_2O–$[Fe(CN)_6]^{3-}$) System. In a solution of (10^{-3} M $[Fe(CN)_6]^{4-}+10^{-3}$ M $[Fe(CN)_6]^{3-}$ $+3.2\times10^{-3}$ M N_2O) irradiated at 2537 Å, the rate of the production of measured $[Fe(CN)_6]^{3-}$ was $\gamma=0.38$. The ratio of the light quanta absorbed by $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ may be expressed by $\varphi=\varepsilon_{II}[Fe(CN)_6{}^{4-}]/\varepsilon_{III}[Fe(CN)_6{}^{3-}]$, where ε_{II} and ε_{III} are the absorption coefficients at 2537 Å and are 3000 and 1000 $M^{-1}\,cm^{-1}$ respectively. It may be further assumed that the absorption of light by $[Fe(CN)_6]^{3-}$ does not affect the observed yield of the $[Fe(CN)_6]^{3-}$ formed photochemically, as the irradiation at 2537 Å of a solution containing only 10^{-3} M $[Fe(CN)_6]^{3-}$ has been shown to cause only a negligibly small change in the optical density at 4200 Å by which the concentration of $[Fe(CN)_6]^{3-}$ is determined. Thus, the relative rates of Reactions (2) and (22):

$$e^-_{aq} + [Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{4-} \tag{22}$$

can be obtained using the following equation:

$$\frac{\gamma_0}{\gamma} = \left(1+\frac{1}{\varphi}\right)\left(1+\frac{k_{22}[Fe(CN)_6{}^{3-}]}{k_2[N_2O]}\right) \tag{23}$$

The introduction of the appropriate numerical values into Eq. (23) gives $k_{22}/k_2=1.2$.

The (N_2O–H_3BO_3) System. A solution of 10^{-3} M $K_4[Fe(CN)_6]$ containing H_3BO_3 in the presence of 1 M CH_3OH was found to produce H_2 gas on illumination, while the system containing only 1 M CH_3OH but no H_3BO_3 liberated no H_2 gas. In these experiments the pH of the solution was kept at pH 7.2 to 7.5 by adding sodium tetraborate to prevent the reaction of H_3O^+ with e^-_{aq}. The reactions after the photochemical production of e^-_{aq} are likely to be:[14]

$$e^-_{aq} + H_3BO_3 \rightarrow H + H_2BO_3^- \tag{24}$$

$$H + CH_3OH \rightarrow H_2 + CH_2OH \tag{25}$$

From the solutions containing (1.2×10^{-3} M N_2O- + 0.5 M H_3BO_3 + 1 M CH_3OH), the ratio of the yields of the gases evolved was found to be $\gamma(N_2)/\gamma(H_2)=7.6$. Thus, k_2/k_{24} can be calculated to be 3×10^3, and hence $k_{24}=3\times10^6\ M^{-1}\,sec^{-1}$, taking $k_2=8.7\times10^9\ M^{-1}\,sec^{-1}$.[2]

The Non-reactive Solutes. The addition of some other solutes, such as 0.1 M KCl, 1 M CH_3OH,[5] 0.1 M K_2HPO_4 and 0.1 M $NaClO_4$, to either the ($[Fe(CN)_6]^{4-}+N_2O$) or the ($[Fe(CN)_6]^{4-}+NO_3^-$) system gave no evidence for the reaction of e^-_{aq} towards these solutes.

The author wishes to thank Professor Shizuo Fujiwara of the University of Tokyo and Dr. Akibumi Danno for their guidance and advice in performing this work; Drs. Gen-ichi Tsuchihashi and Akira Sugimori for their helpful discussions, and Drs. Kenji Motojima and Mitsuru Koike for their advice in preparing the manuscript.

---

[14] On the basis of the experimental results given in S. Ohno, This Bulletin, **39**, 2560 (1966), similar arguments may be applied in obtaining the evidence of the reaction: $e^-_{aq} + HCN \rightarrow H + CN^-$.