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The Reactions of the OH Radical Arising from Nitrous Oxide in an Aqueous Hexacyanoferrate(II) Solution Illuminated at 2537Å[1]

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A method for the determination of the relative rate constants for reactions of the OH radical is described. The OH radical is generated from the reaction between N_2O and the photochemically-produced electron in a solution of 10^{-3} M hexacyanoferrate(II) irradiated at 2537 Å. The method has been applied to the determination of the rate constants for the reactions of OH with methanol, ethanol, 2-propanol, formate, bromide, glycine, and boric acid relative to that with $[Fe(CN)_6]^{4-}$. The values found are compared with those obtained by other methods, and their significance is discussed.

The reaction of the OH radical in aqueous solutions has been studied by several methods: (1) the employment of the Fenton reagent ($Fe^{2+}+H_2O_2$), (2) the photolysis of H_2O_2-containing solutions, and (3) the radiolysis of aqueous solutions. Methods based on the pulse radiolysis technique for the determination of rate constants for OH radical reactions are now being developed by several authors.[2-4]

We have already reported, in an abbreviated form, a new method based on the photolysis of ($[Fe(CN)_6]^{4-}+N_2O$) solutions.[5] Let us here briefly describe that method. The OH radical generated from N_2O on reaction with the photochemically-produced electron may react competitively with $[Fe(CN_6)]^{4-}$ and an added solute, if it reacts at all (Reactions (3) and (4)):

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

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

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

$$OH + \text{solute} \rightarrow \text{products} \quad (4)$$

The formation of OH, or at least an entity which resembles OH in its nature, by way of Reaction (2) is now widely accepted.[6] Provided that the solute added does not significantly react with e^-_{aq} in comparison with Reaction (2) (these conditions are easily achieved by employing high concentrations of N_2O, $k(e^-_{aq}+N_2O)$ being 0.87×10^{10} $M^{-1}\,sec^{-1}$ [7]), the relative rate constants (k_4/k_3) may be obtained by measuring the amounts of each product formed by Reactions (3) and (4).

This paper aims to obtain the relative rate constants of OH-radical reactions by measuring spectrophotometrically the $[Fe(CN)_6]^{3-}$ produced in the cases of methanol, ethanol, 2-propanol, formate, bromide, *etc.* and to compare them with other published values.

Experimental

The experimental methods have been described previously.[8] The methanol, ethanol, 2-propanol, sodium formate, potassium bromide, glycine, and boric acid were all of the purest grade available and were used without further purifications.

Results

Figure 1 represents the yields of hexacyanoferrate(III) against the irradiation time from solutions of 10^{-3} M $[Fe(CN)_6]^{4-}$ containing 1.6×10^{-2} M N_2O in the presence of various concentrations of 2-propanol. The 2-propanol may react with OH radicals produced by Reaction (2):[9]

$$OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2COH \quad (5)$$

followed by:

$$(CH_3)_2COH + [Fe(CN)_6]^{3-} \rightarrow (CH_3)_2CO + H^+ + [Fe(CN)_6]^{4-} \quad (6)$$

Some support for Reaction (6) comes from the

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

[3] J. K. Thomas, *ibid.*, **61**, 702 (1965).

[4] E. Heckel, A. Henglein and G. Beck, *Chem. Ber.*, **70**, 149 (1966).

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[9] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, **1963**, 3119; R. Livingston and H. Zeldes, *J. Chem. Phys.*, **44**, 1245 (1966).

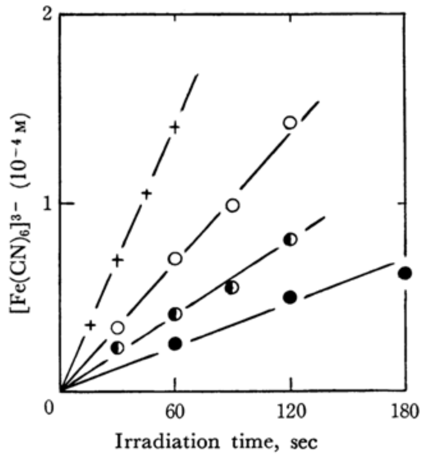

Fig. 1. The formation of $[Fe(CN)_6]^{3-}$ from (10^{-3} M $[Fe(CN)_6]^{4-}+1.6\times10^{-2}$ M N_2O) solutions containing 2-propanol.
[2-propanol]: (+) 0; (○) 5.0×10^{-3}; (◐) 1.07×10^{-2}; (●) 2.15×10^{-2} M

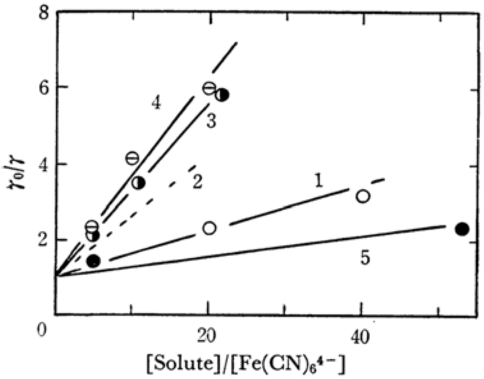

Fig. 2. Evaluation of the relative rate constants.
(1) methanol; (2) ethanol;⁷⁾ (3) 2-propanol; (4) formate; (5) glycine

analogous reactions of CH_2OH and CH_3CHOH with $[Fe(CN)_6]^{3-}$.⁸⁾ On the basis of the reaction mechanism represented by Reactions (1), (2), (3), (5) and (6), the following relation is obtained:

$$\frac{\gamma_0}{\gamma} = 1 + \frac{k_5[\text{2-propanol}]}{k_3[\text{Fe(CN)}_6{}^{4-}]} \qquad (7)$$

where γ_0 and γ are the yields of $[Fe(CN)_6]^{3-}$ in the absence and in the presence of 2-propanol respectively. The experimental results of Fig. 1 satisfy the conditions of Eq. (7), as is evident from the straight line in Fig. 2 (curve 3). The slope of this curve gives $k_5/k_3=0.23$.

When other OH-scavengers are employed, the following reactions are assumed on analogy with Reactions (5) and (6):

$$\left\{\begin{array}{ll} \text{OH} + \text{CH}_3\text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH} & (8) \\ \text{CH}_2\text{OH} + \text{ferri} \rightarrow \text{HCHO} + \text{H}^+ + \text{ferro} & (9) \end{array}\right.$$

$$\left\{\begin{array}{ll} \text{OH} + \text{HCOO}^- \rightarrow \text{H}_2\text{O} + \text{COO}^- & (10) \\ \text{COO}^- + \text{ferri} \rightarrow \text{CO}_2 + \text{ferro} & (11) \end{array}\right.$$

$$\left\{\begin{array}{ll} \text{OH}+\text{NH}_2\text{CH}_2\text{COOH} \rightarrow & \\ \qquad \text{H}_2\text{O} + \text{NH}_2\text{CHCOOH} & (12)^{10)} \\ \text{NH}_2\text{CHCOOH} + \text{ferri} \rightarrow & \\ \qquad \text{NHCHCOOH} + \text{H}^+ + \text{ferro} & (13) \end{array}\right.$$

where ferro and ferri denote the hexacyanoferrate-(II) and -(III) respectively. The experimental results for these scavengers are included in Fig. 2. The slopes of the lines give the following values: $k_8/k_3=0.061$, $k_{10}/k_3=0.26$ and $k_{12}/k_3=0.028$.

The relative rates of the reactions of OH with Br^- and H_3BO_3 were found to be as follows. When KBr was added to the (10^{-3} M $[Fe(CN)_6]^{4-}+1.6\times10^{-2}$ M $N_2O+4\times10^{-2}$ M CH_3OH) system, the yield of $[Fe(CN)_6]^{3-}$ increased. This is likely to be due to Reactions (14) and (15) replacing Reactions (8) and (9) respectively:

$$\text{OH} + \text{Br}^- \rightarrow \text{OH}^- + \text{Br} \qquad (14)$$

$$\text{Br} + \text{ferro} \rightarrow \text{Br}^- + \text{ferri} \qquad (15)$$

The competition among Reactions (3), (8), and (14) for OH leads to the expression:

$$\gamma = \Gamma + \Gamma\frac{k_3[\text{ferro}]+k_{14}[\text{Br}^-]-k_8[\text{CH}_3\text{OH}]}{k_3[\text{ferro}]+k_{14}[\text{Br}^-]+k_8[\text{CH}_3\text{OH}]}$$

$$\frac{\gamma}{\gamma_0-\gamma} = \frac{k_3[\text{ferro}]}{k_8[\text{CH}_3\text{OH}]} + \frac{1}{[\text{CH}_3\text{OH}]}\frac{k_{14}}{k_8}[\text{Br}^-] \qquad (16)$$

where Γ is the quantum yield of Reaction (1), γ_0 is the yield of $[Fe(CN)_6]^{3-}$ in the absence of CH_3OH, $[\text{ferro}]=10^{-3}$, $[CH_3OH]=4\times10^{-2}$ M, and $k_3/k_8=1/0.061$, as above. The experimental data plotted according to Eq. (16) are shown in Fig. 3, where $k_{14}/k_8=0.88$ may be calculated.

In the case of H_3BO_3, the reactions corresponding to Reactions (14) and (15) are:

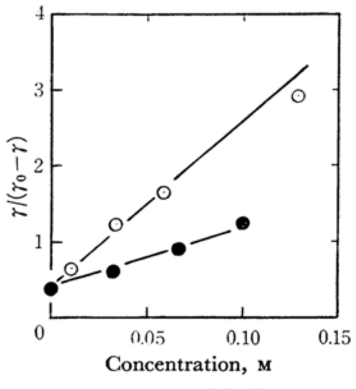

Fig. 3. Evaluation of k_{14}/k_8 and k_{17}/k_8.
(○) Br^-; (●) H_3BO_3

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10) R. L. S. Willix and W. M. Garrison, *J. Phys. Chem.*, **69**, 1579 (1965).

$$OH + H_3BO_3 \rightarrow H_2O + H_2BO_3 \qquad (17)$$

$$H_2BO_3 + \text{ferro} \rightarrow H_2BO_3^- + \text{ferri} \qquad (18)$$

The occurrence of Reaction (17) has already been considered by Haissinsky *et al.* (1952).[11] Support for Reaction (18) comes from the fact that the addition of 0.1 M H_3BO_3 to the ($[Fe(CN)_6]^{4-}$ + N_2O) solution containing no CH_3OH causes no change in the yield of $[Fe(CN)_6]^{3-}$, demonstrating that, if Reaction (17) occurs at all, its product, H_2BO_3, would oxidize $[Fe(CN)_6]^{4-}$ stoichiometrically equally to what the OH radical does. The reaction scheme represented by Reactions (1), (2), (3), (8), (9), (17), and (18) leads to an expression similar to Eq. (16). From the experimental plots shown in Fig. 3, k_{17}/k_8 may be calculated to be 0.3.

Discussion

The reaction rate constants of the OH radical obtained in this work and by other methods are summarized in Table 1. Relative values are normalized to $k(OH+[Fe(CN)_6]^{4-})=100$ by setting one of the relative rate constants of other authors as equal to one of the values in the first column in the table. The second column includes those presented by Allen,[12] and the third, those obtained by Kraljić and Trumbore[13] utilizing the radiolysis of *p*-nitrosodimethylaniline. The fourth column refers to the pulse radiolysis data obtained by Thomas using the iodide solution as a reference system,[3] and the last column refers to those of Fenton's reagent.[14] The data of the photolysis of an H_2O_2-containing solution are limited and not available for the present comparison.

As can be easily seen, the values obtained by the present method are in fair agreement with those of radiation chemistry. This gives strong support, from the kinetical point of view, for the assumption that N_2O reacts with e^-_{aq} to produce the same intermediate as the OH radical which appears in the radiolysis of water.

Allen quoted two values, differing by a factor of ten, for the reactivity of Br^-. The higher value was obtained from competition between H_2O_2 and Br^- towards OH, while the lower one obtained by comparing the reactivity of Br^- with that of ethanol, which was obtained through comparison with formate ions. The present results, as well as those of Kraljić and Trumbore, support Allen's lower value. One may further obtain $k(OH+Br^-)=5\times10^8\ M^{-1}\ sec^{-1}$ from the present results, since $k(OH+[Fe(CN)_6]^{4-})=10^{10}\ M^{-1}\ sec^{-1}$ has been reported in the pulse radiolysis study.[15] However, Ferradini and Koulkès-Pujo[16] reported a rather high value ($3.6\times10^{10}\ M^{-1}\ sec^{-1}$) for the rate constant of the Br^-+OH reaction; thus, the question is still open.

The reactivity of alcohols towards OH shown in Table 1 is in the following order:

methanol < ethanol < 2-propanol

except for the data on Fenton's reagent. It is possible that some of the rates measured using Fenton's reagent refer to the HSO_4 radical rather than to the OH radical,[4,17] since the measurements were carried out in a sulfuric acid medium. Further, a recent ESR study claims that the existence of the OH radical as an active intermediate of Fenton's reagent is very doubtful.[18]

The present method has several advantages for studying the OH radical reaction over the methods using Fenton's reagent or over the photolysis of peroxide solutions. There is no need to consider the possible reaction of other oxidizing species

TABLE 1. RELATIVE REACTION RATES OF OH RADICAL

	This work	Allen[12]	Kraljić and Trumbore[13]	Thomas[3]	Merz and Waters[14]
$[Fe(CN)_6]^{4-}$	100	=100	=100	220	—
Methanol	6.1	—	8.6	=6.1	=6.1
Ethanol	16[7]	11	14.6	9.3	10
2-Propanol	23	—	17.0	23	7.9
Formate ion	26	25	32	32	—
Bromide ion	5.4	65 6.5	8.9	—	—
Glycine	2.8	—	—	—	—
Boric acid	1.9	—	—	—	—

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11) J. Pucheault, M. Lefort and M. Haissinsky, *J. Chim. Phys.*, **49**, 286, 294 (1952).
12) A. O. Allen, *Radiation Res. Suppl.*, **4**, 54 (1964).
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18) T. Shiga, *J. Phys. Chem.*, **69**, 3805 (1965).

such as HO_2, which arises from the reaction:

$$OH + H_2O_2 \rightarrow H_2O + HO_2$$

Since the reaction of $[Fe(CN)_6]^{4-}$ with OH is fast, possible interference due to more complex kinetics is greatly reduced because of the low $[Fe(CN)_6]^{4-}$ concentrations employed. The system is simple and suitable as a reference system for competition reactions, and can be used for neutral and alkaline solutions. Its main disadvantage is that it can not be applied to a system containing a solute which absorbs light strongly in the same region as does $[Fe(CN)_6]^{4-}$.

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