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# Some Remarks on the Reactions of Ferricyanide Ions with Hydrogen Atoms in Alkaline Aqueous Solutions

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In the radiolysis of the deaerated alkaline aqueous solutions of potassium ferricyanide, there seems to be no doubt[1-4] that aquocomplex ($Fe(CN)_5H_2O^{3-}$) is formed *via* the reactions of ferricyanide ions with the reducing species (mainly $e_{aq}^-$). However, the role of hydrogen atoms in the formation of aquocomplex is not well known.[5] In order to make it clear, a technique introducing hydrogen atoms generated in a microwave discharge into the alkaline aqueous solution of potassium ferricyanide was used, and the mechanism of formation of aquocomplex was successfully investigated, in relation to the concentration of hydroxyl ions.

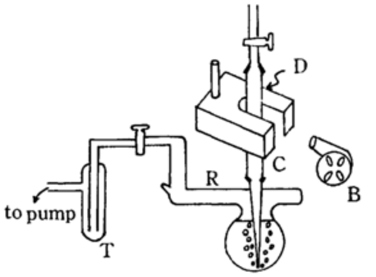

Fig. 1. Schematic diagram of apparatus.
B: blower C: cavity D: discharge tube
R: reaction vessel T: trap

## Experimental

The apparatus consists of a conventional discharge flow system. Hydrogen atoms were produced at a moderately high pressure (13—14 mmHg[*1]) by 2450 Mc/sec microwave generator feeding a resonant cavity. Hydrogen (purity: $>99.95\%$) was used without further purification. Gas flow was controlled by a needle valve to maintain their velocity at $5\times10^{-5}$ M/min through the reaction section. The reaction section consists of the discharge tube of quartz and the reaction vessel of hard glass (Fig. 1). The gas stream was finally removed from the line with a vacuum pump.

The experimental procedure was as follows. After the system was evacuated to $<10^{-3}$ mmHg, a stream of hydrogen was passed through the system. The electrical circuit to the discharge tube was then closed. A few minutes was required for sweeping out the residual air in the system with the hydrogen stream. As soon as the red hydrogen arc appeared in the tube, the current was shut off; then 10 m*l* of the pre-deaerated sample solution was introduced into the reaction vessel by a syringe through the rubber stopper. Electric power was usually adjusted to 100 W and the reaction vessel was maintained at about 3°C by means of an ice bath.

Reproducible results were obtained only when the equipment was throughly cleaned before each run.

All reagents used were of research grade. Concentration of aquocomplex ($Fe(CN)_5H_2O^{3-}$) was determined spectrophotometrically by the method using $NaN_3$.[2,4]

## Results and Discussion

A preliminary experiment of the effect of initial concentration of ferricyanide ions on the reduction yield of ferricyanide ions showed no effect in the range from $5\times10^{-3}$M to $5\times10^{-2}$M. This indicates that in this concentration range all hydrogen atoms reaching the solution are utilized to reduce ferricyanide ions. Thus, in this work the solution of $5\times10^{-3}$M or $1\times10^{-2}$M of ferricyanide ions was used.

Figure 2 shows the relation between the amount of aquocomplex formed and the duration of dis-

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1) E. Masri and M. Haïssinsky, *J. Chim. Phys.*, **60**, 397 (1960).

2) S. Ohno and G. Tsuchihashi, *Radioisotopes*, **16**, 434 (1967).

3) C. E. Burchill, F. S. Dainton and D. Smithies, *Trans. Faraday Soc.*, **63**, 932 (1967).

4) A. Yokohata, This Bulletin, **42**, 658 (1969).

5) G. Navon and G. Stein, *J. Phys. Chem.*, **70**, 3630 (1966).

[*1] Contains water vapor. Although the formation of OH radicals through the dissociation of water vapor can be expected, they will react with the large excess of molecular hydrogen. ($OH+H_2\rightarrow H+H_2O$): T. W. Davis, S. Gordon and E. J. Hart, *J. Am. Chem. Soc.*, **80**, 4487 (1958).

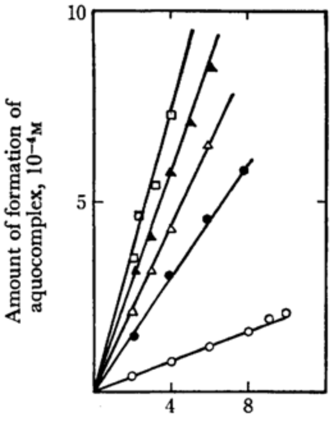

Fig. 2. Relation between the amount of formation of aquocomplex and duration of discharge.
Initial concentration: $5\times10^{-3}$M $Fe(CN)_6^{3-}$
○ 0.1M NaOH ● 0.5M NaOH
△ 1.0M NaOH ▲ 2.0M NaOH
□ 3.0M NaOH

charge in the concentration range of hydroxyl ions from 0.1M to 3M. The increment of aquocomplex yield with increasing concentration of hydroxyl ions has been found.

The following reaction scheme can be expected in this system.*[2]

$$H + Fe(CN)_6^{3-} \rightarrow Fe(CN)_6^{4-} + H^+ \quad (1)$$
$$\searrow Fe(CN)_5H_2O^{3-} + CN^- + H^+ \quad (2)$$
$$H + OH^- \rightarrow e^-_{aq} \quad (3)$$
$$e^-_{aq} + Fe(CN)_6^{3-} \rightarrow Fe(CN)_6^{4-} \quad (4)$$
$$\searrow Fe(CN)_5H_2O^{3-} + CN^- \quad (5)$$

If reaction (2) is ignored,[4] Eqs. (6) and (7) result in.*[3]

$$Y(-Fe(CN)_6^{3-}) = Y(H) \quad (6)$$

$$Y(Fe(CN)_5H_2O^{3-}) = Y(H)\frac{1}{1+k_1/k_3\cdot[Fe(CN)_6^{3-}]/[OH^-]}\cdot\frac{1}{1+k_4/k_5} \quad (7)$$

Equation (7) can be reformed to Eq. (8)

$$\frac{1}{Y(Fe(CN)_5H_2O^{3-})} = \frac{1+k_4/k_5}{Y(H)}\left(1+\frac{k_1[Fe(CN)_6^{3-}]}{k_3[OH^-]}\right) \quad (8)$$

A good linearity of a plot of $1/Y(Fe(CN)_5H_2O^{3-})$ against $[Fe(CN)_6^{3-}]/[OH^-]$ (Fig. 3) gives a value of 230*[4] for $k_1/k_3$ where $k_4/k_5 \approx 1$[4] and $Y(H) = 2.0\times10^{-3}$M determined in this experiment are used. If we take $k_1 = 4\times10^9$M$^{-1}$ sec$^{-1}$,[6] $k_3$ is estimated to be $\sim1.7\times10^7$M$^{-1}$ sec$^{-1}$ which is almost consistent in order of magnitude with $2.3\times10^7$M$^{-1}$ sec$^{-1}$ [7] obtained from the radiolytic experiment. In other words, these findings show that the assumption of exclusion of reaction (2) is allowable, at least in alkaline region.

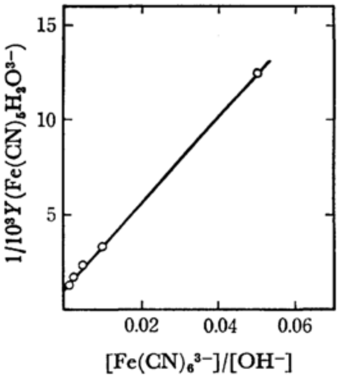

Fig. 3. A plot of $1/Fe(CN)_5H_2O^{3-}$ against $[Fe(CN)_6^{3-}]/[OH^-]$

It is our conclusion that (1) the increment of yield of aquocomplex with an increasing concentration of hydroxyl ions can be well interpreted in terms of the solvated electron formed *via* the reaction of hydrogen atoms with hydroxyl ions, and that (2) the contribution of hydrogen atoms themselves to the formation of aquocomplex can be ignored in alkaline region.

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*[2] Molecular hydrogen does not reduce ferricyanide.

*[3] $Y$(X) means the yield of product X formed during 4 min of the duration of discharge.

*[4] This value can be expected to be independent of temperature, if the same activation energy (∼5 kcal) for the reactions (1) and (3) is assumed, as seen in Navon's report: G. Navon and G. Stein, *J. Phys. Chem.*, **69**, 1384 (1965).

6) J. Rabani, *ibid.*, **66**, 361 (1962).

7) J. Rabani, in "Solvated Electron," R. F. Gould, Ed., Am. Chem. Soc., Washington., D. C. (1965), p. 242.