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# Silent Discharge Reactions in Aqueous Solutions. VII. Alkaline Aqueous Solution of Potassium Ferricyanide in Atmospheres of Helium and Argon[*1]

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The silent discharge reactions of aqueous solution have been extended to an alkaline region. Potassium ferricyanide was selected as reaction system. The results show the reduction of ferricyanide ions. The situation is very similar to that in the case of radiation chemistry. The $G$ value of the disappearance of ferricyanide ions was almost the same as that of cerous ions formed from the acidified ceric solution by silent discharge reaction under the same experimental condition. Moreover, the yield of hydrogen peroxide produced in the alkaline solution was almost the same as those of acidic and neutral solutions. Those findings suggest that the radical yields will be also almost equal, irrespective of pH in the range studied. This work gives a further evidence that most of silent discharge reactions of the aqueous solutions in inert gases can be well interpreted in terms of the radiolysis by slow electrons generated in the gas phase.

One of the problems of the radiation chemistry of aqueous solutions much discussed recently is that of the yields of the various primary intermediates in the higher pH range where reported primary yields are not in agreement.[1]

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[*1] Presented in part at the 8th Conference of the Radiation Chemistry (Japan), Tokyo, November, 1965.

[1] A. O. Allen, *Radiation Res.*, suppl., **4**, 54 (1964).

In the previous reports,²⁾ the authors have elucidated that in the silent discharge reactions of the acidic or neutral aqueous solutions under the atmospheres of helium and argon, the actions of the slow electrons generated in the gas phase to water molecules play a main role. In other words, the silent discharge reactions can be well interpreted in terms of an indirect effect; the primary one being the radiolysis of the water to give the intermediate like hydrogen atoms or hydroxyl radicals through the interaction of slow electrons with water molecules.

Each $G$ value determined through the series of this study was as follows in the acidic region:

In argon;

$$G(\mathrm{H})=0.6,\ G(\mathrm{OH})=0.7 \text{ and } G(\mathrm{H_2O_2})=1.5$$

In helium;

$$G(\mathrm{H})=1.1,\ G(\mathrm{OH})=1.6 \text{ and } G(\mathrm{H_2O_2})=1.0$$

In the present work, the study of the aqueous solution has been extended to the higher pH range. Dainton *et al.*³⁾⁴⁾ and Hughes *et al.*⁵⁾ have reported the radiolysis of the alkaline potassium ferricyanide system by gamma rays. According to their results, the disappearance of ferricyanide ions is proportional to dose and independent of ferricyanide concentration and of dissolved oxygen. Also, the decrement of ferricyanide ions is reported to be expressed by Eq. (1)

$$G(-\mathrm{Fe(CN)_6}^{3-}) = 2G\mathrm{H_2O_2} + G\mathrm{Red} - G\mathrm{OH} \quad (1)$$

On the other hand, in the ceric sulfate solution acidified with 0.8 N sulfuric acid, the $G$ value of cerous ions formed by the silent discharge reaction was previously reported by us to be expressed in the same equation as Eq. (1).²⁾ Therefore, if it is assumed that the effect of pH is very small on the yields of the primary products of the radiolysis by slow electrons, a quantity of decrement of ferricyanide ions should be consistent with those of ceric ions at least in order of magnitude.

It is of interest and significant to clear up this problem in the field of silent discharge. The present work deals with this problem.

## Experimental

**Apparatus.** The discharge tube, the electric circuit, and the experimental conditions employed were identical with those previously reported. In this series a discharge tube of the ozonizer type (Fig. 1) was used. It is composed of two coaxial, hard-glass tubes; the part consisting of tin foil stuck on outer tube was used for one electrode, and the part containing the dilute sulfuric acid in the inner tube (g) was used for the other electrode (high-tension side).

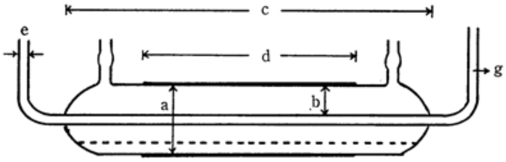

Fig. 1. Schematic diagram of discharge tube.
a 26 mm ---- surface of solution
b 8 mm —— tin foil
c 300 mm
d 230 mm
e 10 mm

After the sample solution had been poured into the discharge tube the discharge was made by applying a high tension among those two electrodes, flowing helium or argon through the gas space of discharge tube.

Oxygen dissolved in the sample solution was completely excluded by bubbling helium or argon gas into solution. Sometimes samples were degassed by four successive cycles of freezing, evacuation, and melting on a vacuum line.

For the washing of the discharge tube, a mixed solution of alcohol and saturated aqueous solution of sodium hydroxide was used, besides the usual cleaning solution. The discharge tube was dried by evacuation.

All experiments were made at room temperature and at constant volume of the solution, 10 m*l*. Flow velocity of gas was about 120 m*l*/min.

**Materials.** For the reliable performance, triple distilled water was always used throughout the work. All other materials were also of reagent grade. Helium and Argon (purity;>99.998%) were used without further procedure.

**Procedure.** Ferricyanide ion was determined from its optical density using a spectrophotometer at 420 m$\mu$ where $\varepsilon=1030$. Hydrogen peroxide was determined by the Ghormley method.⁶⁾ To verify the accuracy of the method with solutions of pH 12, hydrogen peroxide solution of known concentration were brought to the desired pH and analyzed. No effect due to high pH could be detected with hydrogen peroxide solutions which had been neutralized with potassium acid phthalate immediately before analysis.

In this work, the production of cyanide ion was checked. It was determined by the colorimetric method using the picric acid.⁷⁾

## Results

The silent discharge leads to the reduction of ferricyanide ions to ferrocyanide ions in 0.01—0.1 N sodium hydroxide solutions. Figures 2a and 2b show the relationship between the disappearance of ferricyanide ions and duration of discharge under 1 mA of electric discharge current; Fig. 2a

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2) A. Yokohata and S. Tsuda, This Bulletin, **39**, 46, 53, 1636 (1966); **40**, 294, 1339 (1967).

3) F. S. Dainton and W. S. Watt, *Nature,* **195**, 1294 (1962).

4) F. S. Dainton and W. S. Watt, *Proc. Roy. Soc.,* **A 275**, 447 (1963).

5) G. Hughes and C. Willis, *Discussions Faraday Soc.,* **36**, 223 (1963).

6) C. J. Hochanadel, *J. Phys. Chem.,* **56**, 587 (1952).

7) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. 2, D. Van Nostrand Co., Inc., New York (1949), p. 864.

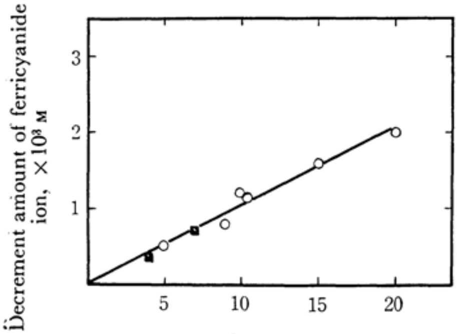

Fig. 2a

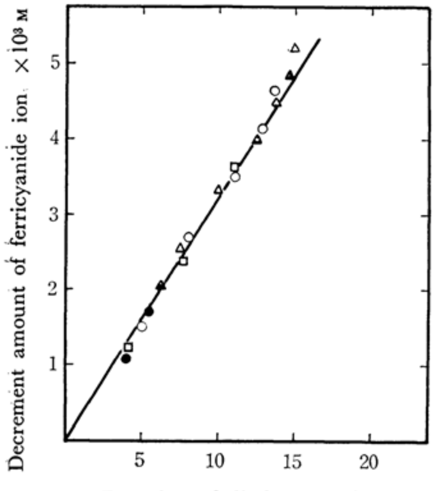

Fig. 2b

Fig. 2. Relationship between decrement amount of ferricyanide ion and duration of discharge.
■ $1\times10^{-3}$ M $Fe(CN)_6^{3-}$ 0.1 N NaOH
● $2\times10^{-3}$ M $Fe(CN)_6^{3-}$ 0.1 N NaOH
○ $5\times10^{-3}$ M $Fe(CN)_6^{3-}$ 0.1 N NaOH
□ $5\times10^{-3}$ M $Fe(CN)_6^{3-}$ 0.01 N NaOH
△ $1\times10^{-2}$ M $Fe(CN)_6^{3-}$ 0.1 N NaOH
▲ $1\times10^{-2}$ M $Fe(CN)_6^{3-}$ 0.01 N NaOH
a Case of helium b Case of argon

for helium; Fig. 2b for argon. In each case a good linearity has been found. The effects of initial concentrations of potassium ferricyanide ($1\times10^{-3}$—$1\times10^{-2}$ M) and of sodium hydroxide (0.01—0.1 N) have not been found within the range of experimental error. Most of the experiments were made at $5\times10^{-3}$ M of the solute concentration.

A typical example of the dependence of disappearance of ferricyanide ions against the electric discharge current is shown in Fig. 3: for argon. A linear correlation has been also obtained.

Moreover, it had been confirmed that, as shown in Fig. 4, the quantity of hydrogen peroxide formed in 0.01 N sodium hydroxide by the silent discharge was almost consistent with that formed in 0.8 N sulfuric acid or pure water.

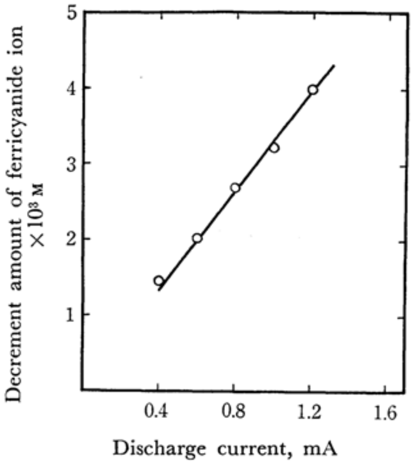

Fig. 3. Relationship between decrement amount of ferricyanide ion and electric discharge current.

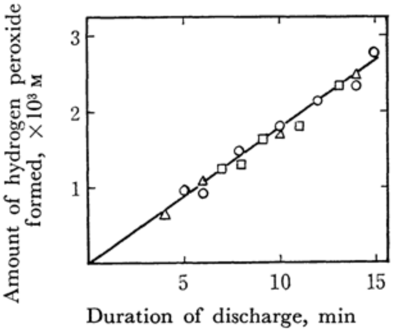

Fig. 4. Relationship between amount of hydrogen peroxide formed and duration of discharge. Discharge current=1 mA
○ In 0.01 N sodium hydroxide
△ In pure water
□ In 0.8 N sulfuric acid

Although the formation of cyanide ion has been found, the yield was negligibly small in comparison with the disappearance of ferricyanide ions,[8]—$2(\pm1)\times10^{-5}$ M for helium and $4(\pm1)\times10^{-5}$ M for argon under the condition of 10 min of discharge duration and 1 mA of electric discharge current.

## Discussion

In the silent discharge under one atmosphere, the electrons generated in the gas phase have an energy distribution from just above zero to somewhat above the ionization potential of the gas in which discharge occurs.[9] The most probable energy appears to be less than 10 eV.

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[8] The results for gamma irradiation will be published later, and they will show an relatively large amount of cyanide ions has been found.

[9] N. R. Dibelius, J. C. Fraser, M. Kawahata and C. D. Doyle, *Chem. Eng. Progress,* **60**, 41 (1964).

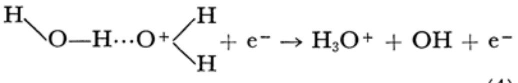
In the gamma-irradiations, Hochanadel[10] pointed out the possibilities of various elementary reactions expected from the irradiated water. Of the many possible ones, only a few are considered to be important. These are as follows.

Primary process

$$H_2O^* \ (\sim 7.4\ \text{eV}) \rightarrow OH + H + \sim 2\ \text{eV} \qquad (2)$$

$$H_2O^+ + e^- \ (\sim 12.56\ \text{eV}) \qquad (3)$$

or



$$H_2O{-}H\cdots O^+H_2 + e^- \rightarrow H_3O^+ + OH + e^- \qquad (4)$$

Secondary process

$$H_2O^+ + e^- \rightarrow H_2O^* \rightarrow OH + H \qquad (5)$$

$$H_3O^+ + e^- \rightarrow H_3O \rightarrow H_2O + H \qquad (6)$$

$$H_2O + e^-_{aq} \rightarrow H + OH^-_{aq} \qquad (7)$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \qquad (8)$$

Hayon and Weiss[11] found that two different kind of reducing radicals are necessary to explain some observations on the radiolysis of chloroacetic acid solution. Independently, Hart and Boag[12] found that the water irradiated at a very high intensity showed a transient coloration, the absorption spectrum being very similar to that of the well-known solvated electron in liquid ammonia. Today no one doubts that the major primary reducing radical formed in water radiolysis is a solvated electron ($e^-_{aq}$).

Thus, the products of the decomposition of liquid water by ionizing radiations are given by

$$H_2O \rightsquigarrow H_2,\ H_2O_2,\ H,\ e^-_{aq},\ OH,\ (H_3O^+) \qquad (9)$$

In the case of the slow electrons produced by the silent discharge the "clusters of intermediate" will be formed on the surface of water by electron impact. In the clusters resulting, the original main products will be the excited water molecules, $H_2O^*$, and not the ionized water molecules, $H_2O^+$, because the most probable energy of the electrons is less than the ionization potential of water molecules. Accordingly the possibility of the formation of the solvated electrons will also be very small. In fact, our recent work has shown that in the silent discharge the major reducing species is hydrogen atoms.[13] The present belief of the authors is that the hydrogen atoms and the hydroxyl radicals are produced by the reaction (2).[14]

Then, from the known chemistry of ferro-ferricyanide solution[3-5] and the products of water, the following reaction scheme can be naturally expected in the silent discharge.

$$H + Fe(CN)_6{}^{3-} \rightarrow H^+ + Fe(CN)_6{}^{4-} \qquad (10)$$

$$H_2O_2 + 2Fe(CN)_6{}^{3-} \rightarrow 2Fe(CN)_6{}^{4-} + 2H^+ + O_2 \qquad (11)$$

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

As the oxygen *via* (11) is produced in accordance with the progress of reaction, reactions (13), (14) and (15) may occur:

$$H + O_2 \rightarrow HO_2 \qquad (13)$$

$$HO_2 + Fe(CN)_6{}^{3-} \rightarrow H^+ + O_2 + Fe(CN)_6{}^{4-} \qquad (14)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (15)$$

According to the recent work[15] the p$K$ value for the dissociation of the hydroxyl radical is 11.8 and that of hydrogen peroxide is also the same.[16,17]

$$OH \rightleftarrows O^- + H^+ \qquad (16)$$

$$H_2O_2 \rightleftarrows HO_2{}^- + H^+ \qquad (17)$$

Therefore, at pH 13, reactions (11) and (12) should be replaced by (18) and (19).

$$HO_2{}^- + 2Fe(CN)_6{}^{3-} \rightarrow 2Fe(CN)_6{}^{4-} + O_2 + H^+ \qquad (18)$$

$$O^- + Fe(CN)_6{}^{4-} \xrightarrow{H_2O} 2OH^- + Fe(CN)_6{}^{3-} \qquad (19)$$

On the other hand, the conversion of a hydrogen atom to a solvated electron in an alkaline solution has been proposed by Baxendale and Hughes[18] as an equilibrium

$$H + OH^- \rightleftarrows e^-_{aq} \qquad (20)$$

In our experimental conditions, however, it may not be necessary to consider the competitive reaction of (20) and (10), because the rate constant of reaction (20)[19] ($K_{20}=1.5$—$2.3\times10^7\ \text{M}^{-1}\ \text{sec}^{-1}$) is much lower than of reaction 10[20] ($K_{10}=4\times10^9\ \text{M}^{-1}\ \text{sec}^{-1}$).

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[10] M. Burton, "Comparative Effects of Radiation," John Wiley & sons, Inc., New York (1960), p. 152.

[11] E. Hayon and J. Weiss, *Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva,* **29**, 80 (1959).

[12] E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.,* **84**, 4090 (1962).

[13] The details will be published later.

[14] In the radiation chemistry, Allan *et al.* and Hayon provided some evidences for hydrogen atoms being formed presumably from excited water molecules by the reaction (2) with the amount of hydrogen atoms as much as $G\simeq0.5$; J. T. Allan and G. Scholes, *Nature,* **187**, 218 (1960), E. Hayon, *Trans. Faraday Soc.,* **60**, 1059 (1964).

[15] J. L. Weeks and J. Rabani, *J. Phys. Chem.,* **70**, 2100 (1966).

[16] M. G. Evans and N. Uri, *Trans. Faraday Soc.,* **45**, 224 (1949).

[17] J. Jortner and G. Stein, *Bull. Res. Council Israel,* **A6**, 239 (1957).

[18] J. H. Baxendale and G. Hughes, *Z. Physik. Chem. (Frankfurt),* **14**, 306 (1958).

[19] S. Matheson, *Radiation Res, Suppl.,* **4**, 1 (1964).

[20] J. Rabani, *J. Phys. Chem.,* **66**, 361 (1962).

Most recently, Haissînsky *et al.*[21] reported a remarkable reaction scheme. The competitive reactions for the disappearance of ferricyanide ion by the gamma irradiations are as follows;

$$\mathrm{Fe(CN)_6^{3-}} + \mathrm{e^-_{aq}} - \left| \begin{array}{lr} \to \mathrm{Fe(CN)_6^{4-}} & (21) \\ \to \mathrm{Fe(CN)_5OH_2^{3-}} + \mathrm{CN^-} & (22) \end{array} \right.$$

$$\mathrm{Fe(CN)_6^{3-}} + \mathrm{H}$$

$$- \left| \begin{array}{lr} \longrightarrow \mathrm{Fe(CN_6)^{4-}} + \mathrm{H^+} & (10) \\ \xrightarrow{\mathrm{H_2O}} \mathrm{Fe(CN)_5OH_2^{3-}} + \mathrm{CN^-} + \mathrm{H^+} & (23) \end{array} \right.$$

They concluded that the rate constant of reaction (23) is $0.82 \times 10^9\,\mathrm{M^{-1}\,sec^{-1}}$, and in the alkaline region, the ratio of yields, $G(\mathrm{Fe(CN)_5OH_2^{3-}})/G(-\mathrm{Fe(CN)_6^{3-}})$, is 0.3/2.3. In the silent discharge also, the same reaction mechanisms can be expected from the formation of cyanide ions. That quantity, however, was negligibly small compared with disappearance of ferricyanide ion. Thus, this finding is qualitatively consistent[22] with Haissînsky's conclusion that the ratio of rate constant, $K_{23}/K_{10}$, is very small.

On the basis of the reactions above mentioned, the net yield would be expressed in Eq. (24);

$$G(-\mathrm{Fe(CN)_6^{3-}}) = 2G\mathrm{H_2O_2} + G\mathrm{H} - G\mathrm{OH} \quad (24)$$

where $H_2O_2$, H and OH are used only as formal representations of the species, independent of their precise nature.

By combining the dose rate of the silent discharge determined already with the yield of disappearance of ferricyanide ions shown in Figs. 2a and 2b, the $G$ value of disappearance of ferricyanide ions can be estimated. Table 1 shows the relation between $G(-\mathrm{Fe(CN)_6^{3-}})$ and $G\mathrm{Ce^{3+}}$ obtained previously.[2]

TABLE 1. RELATION BETWEEN $G(-\mathrm{Fe(CN)_6^{3-}})$ AND $G\mathrm{Ce^{3+}}$

| Atmosphere | $G(-\mathrm{Fe(CN)_6^{3-}})$ | $G\mathrm{Ce^{3+}}$ |
|---|---|---|
| Helium | 1.6 | 1.6 |
| Argon | 2.8 | 2.9 |

The consistency of both is good within the experimental error. This finding and the independency of the yield of hydrogen peroxide on pH lead to the same value of ($G$H$-G$OH) irrespective of pH in the range studied by us, under the respective atmosphere. In this work, each value of $G$H and $G$OH has not been determined separately. However, considering that in the silent discharge the radicals are mainly formed from the excited state of water molecules, each $G$ value of the radicals does not appear to be influenced by pH. On the basis of this view and the above experimental findings, it may be mentioned that the radical yields (H, OH) are approximately independent of pH under the experimental conditions. This is also consistent with the view of Hayon[23] and Hart[24] that the $G$ value of hydrogen atoms formed by the irradiation of ionizing radiation is independent of pH.

The linear correlation between the decrement amount of ferricyanide ions and the electric discharge current has been also found. This phenomena should be emphasized as one of the characteristics of the silent discharge reactions, which were discussed in details in the 6th report.

It is our conclusion that the silent discharge reactions can be well interpreted with an indirect effect of the slow electrons to water molecules, the primary one being the radiolysis of water to give the intermediates like hydrogen atom or hydroxyl radical, irrespective of pH.

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[21] M. Haissînsky, A. M. Koulkès and É. Masri, *J. Chim. Phys.*, **63**, 1129 (1966).

[22] It is difficult to discuss quantitatively, because cyanide ions are decomposed itself by the radiolysis; A. Yokohata and S. Tsuda, *Doitai to Hoshasen (Isotopes and Radiation)*, **4**, 393 (1961).

[23] E. Hayon, *J. Phys. Chem.*, **68**, 1242 (1964).

[24] E. J. Hart, "Proceeding of the Fifth Informal Conference on the Radiation Chemistry of Water," Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana (1966), p. 26.