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Silent Discharge Reactions in Aqueous Solutions. IV. Systems of Ferrous-Cupric Ions and Ceric-Thallous Ions Acidified with 0.8 N Sulfuric Acid in Helium and Argon Atmospheres[*1]

Akira YOKOHATA and Satoru TSUDA

Department of Chemistry, Faculty of Engineering, Hiroshima University, Senda-machi, Hiroshima

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In this series of studies of silent discharge reactions, the G values of the hydrogen atom, the hydroxyl radical and hydrogen peroxide have successfully been determined in terms of the radiolysis of water by slow electrons: $G(\mathrm{H})=1.1$, $G(\mathrm{OH})=1.6$, and $G(\mathrm{H_2O_2})=1.0$ in helium, and $G(\mathrm{H})=0.6$, $G(\mathrm{OH})=0.7$ and $G(\mathrm{H_2O_2})=1.5$ in argon. Also, the absorbed dose has been estimated. In order to obtain further information regarding the nature of these radicals and the adequacy of these G values, the ferrous-cupric ions system and ceric-thallous ions system in atmospheres of helium and argon have now been investigated. The experimental results show that $G_{obs}(\mathrm{Fe^{3+}})$ in a ferrous-cupric ion system and $G_{obs}(\mathrm{Ce^{3+}})$ in a ceric-thallous ion system almost coincide with $G_{calc}(\mathrm{Fe^{3+}})$ $(=2G(\mathrm{H_2O_2})+G(\mathrm{OH})-G(\mathrm{H}))$ and $G_{calc}(\mathrm{Ce^{3+}})$ $(=2G(\mathrm{H_2O_2})+G(\mathrm{OH})+G(\mathrm{H}))$, as was to be expected from the previously determined G values. These findings suggest that the silent discharge reaction in these systems can be well interpreted in terms of the scavenging effect of cupric ions and thallous ions on the hydrogen atom and the hydroxyl radical, as in the case of radiation chemistry. Further, the present study has confirmed that the G values determined in the earlier experiment are reliable.

It has been reported[1] that, in helium or argon atmospheres, the chemical reactions in an aqueous solution of ferrous sulfate or ceric sulfate by silent discharge can be well interpreted by taking into consideration the actions on the solvent of slow electrons produced in the gaseous phase; that neither the effect of the metastable excited states of helium and argon nor that of luminescence can be important, and, further, that the silent discharge reaction apparently corresponds to the radiolysis caused by a particle with a high LET (linear energy transfer) value.

On the basis of the above reasoning, the following does rates, (E), and G values were successfully determined for the first time. In helium, $E=3.8\times10^6$R/hr, $G(\mathrm{H})=1.1$, $G(\mathrm{OH})=1.6$, and $G(\mathrm{H_2O_2})=1.0$; in argon, $E=7.2\times10^6$R/hr, $G(\mathrm{H})=0.6$, $G(\mathrm{OH})=0.7$, and $G(\mathrm{H_2O_2})=1.5$.

In order to obtain further information on the nature of these radicals and on the adequacy of these G values, the silent discharge reactions of the ferrous-cupric ion system and the ceric-thallous ion system were investigated.

According to radiation chemistry studies made on these systems,[2-9] $G(\mathrm{Fe^{3+}})$ can be finally given as in Eq. (1):

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

and $G(\mathrm{Ce^{3+}})$ as in Eq. (2):

$$G(\mathrm{Ce^{3+}}) = 2G(\mathrm{H_2O_2}) + G(\mathrm{OH}) + G(\mathrm{H}) \quad (2)$$

If our interpretation that the silent discharge reaction corresponds to radiolysis by slow electrons is appropriate, the $G_{obs}(\mathrm{Fe^{3+}})$ or $G_{obs}(\mathrm{Ce^{3+}})$ value obtained from the experiment should approximately coincide with the $G_{calc}(\mathrm{Fe^{3+}})$ or $G_{calc}(\mathrm{Ce^{3+}})$ estimated by applying $G(\mathrm{H_2O_2})$, $G(\mathrm{H})$, and $G(\mathrm{OH})$ to Eq. (1) or Eq. (2). This work, dealing with this problem, will present further evidence that the silent discharge reaction can, in large part, be adequately interpreted in terms of the radiolysis of water by slow electrons.

Experimental

The discharge tube and the electrical circuit used in the current experiment were identical with those previously described. In this series a discharge tube of the ozonizer type (Fig. 1) was used. It has two coaxial hard-glass tubes; the tin foil wrapped around the outer

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[*1] Presented in part at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

1) Parts I and II of this series: A. Yokohata and S. Tsuda, This Bulletin, **39**, 46, 53 (1966).

2) E. J. Hart, *Radiation Res.*, **2**, 33 (1955).

3) A. Danno, H. Hotta, A. Terakawa, K. Shimada and S. Ōno, *Dōitai to Hoshasen (Isotopes and Radiation)*, **3**, 488 (1959).

4) S. Tsuda, *Memoirs of the Faculty of Engineering of Hiroshima University*, **2** (No. 3), 191 (1960).

5) T. J. Sworski, *Radiation Res.*, **4**, 483 (1956).

6) D. M. Donaldson and N. Miller, *Trans. Faraday Soc.*, **52**, 652 (1956).

7) N. F. Barr and R. H. Schuler, *J. Phys. Chem.*, **63**, 808 (1959).

8) M. Lefort and X. Tarrago, *ibid.*, **63**, 833 (1959).

9) J. Weiss and N. Miller, *ibid.*, **63**, 888 (1959).

tube was used as one electrode, while the dilute sulfuric acid in the inner tube (g) was used as the other electrode (the high-tension side). After the sample solution had been poured into the discharge tube, the discharge was made by applying high tension to these two electrodes, thus permitting helium or argon to flow through the gas space of the discharge tube.

All experiments were made at a constant solution volume of 10 m*l*. The surface of the solution was vibrated gently by the discharge. This was useful in renewing the surface of the solution. Experiments were made after completely removing the dissolved oxygen from the solution by bubbling helium or argon gas into the solution.

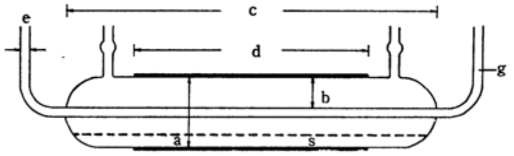

Fig. 1. Schematic diagram of discharge tube.

a 26 mm
b 8 mm
c 300 mm
d 230 mm
e 10 mmϕ
--- surface of solution
—— tin foil

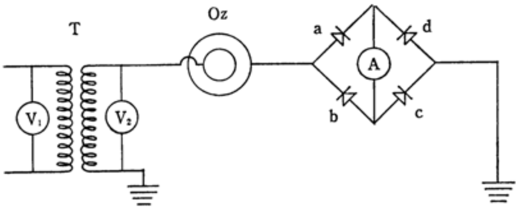

Fig. 2. Electric circuit.

V_1 Voltmeter
V_2 Static electric voltmeter
a, b, c, d Cu_2O rectifier
A Direct ammeter
Oz Discharge tube
T Transformer

The electrical circuit shown in Fig. 2 was used in measuring the discharge current running through the discharge tube. The experiments were made at a constant discharge current of $I = 1$ mA.

Materials. The water was purified by the multiple distillation procedure described by Johnson and Allen.[10] Guaranteed reagent ferrous ammonium sulfate, ceric sulfate, cupric sulfate (Merck), and c. p. thallous sulfate were used without further purification. Helium and argon (purity: >99.99%) were also used without further treatment.

Analysis. The ferric ion and ceric ion concentrations were measured directly by spectrophotometry.

Results

Ferrous-Cupric Ion System. The aqueous solution with a ferrous sulfate concentration of 5×10^{-3} M, acidified with 0.8 N sulfuric acid, was used. The concentration of additive cupric ions was changed from 10^{-5} M to 10^{-1} M.

Figure 3 shows the relationship between the amount of ferric ions formed and the duration of the discharge (Fig. 3a for helium and Fig. 3b for argon). The concentration of the additive cupric ions used was 0.1 M. In each case the relation of the ferric-ion yield to the duration of discharge was linear.

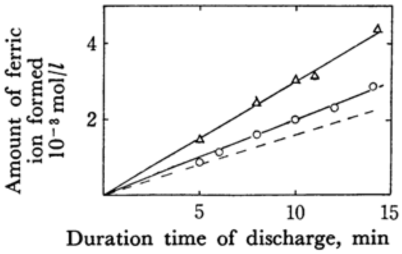

Fig. 3a.

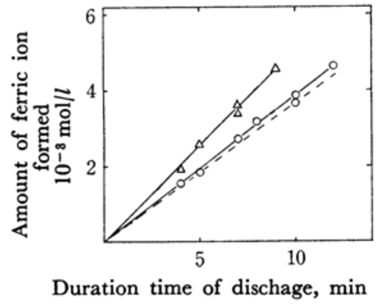

Fig. 3b.

Fig. 3. Relationship between amount of ferric ion formed and duration time of discharge.

a case of helium b case of argon
○ Cu^{2+}: 1×10^{-1} M Fe^{2+}: 5×10^{-3} M
△ no Cu^{2+} added
--- expected line

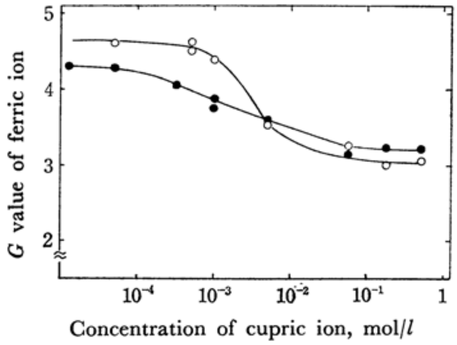

Fig. 4. Effect of cupric ion concentration on $G(Fe^{3+})$ in ferrous-cupric ions system; initial concentration of Fe^{3+}: 5×10^{-3} M
○ case of helium ● case of argon

Figure 4 shows the effect of the cupric ion concentration on the $G(Fe^{3+})$ value as estimated from the amount of ferric ions formed and the previously-determined dose. With an increase in the cupric

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[10] E. R. Johnson and A. O. Allen, *J. Am. Chem. Soc.*, **74**, 4147 (1952).

ion concentration, $G(Fe^{3+})$ gradually decreased until it reached a constant value of 3.0 in helium and 3.2 in argon.

Ceric-Thallous Ion System. In helium, an aqueous solution with a ceric sulfate concentration of 5×10^{-3} M, acidified with 0.8 N sulfuric acid, was used, while in argon a solution with a 1×10^{-2} M concentration, acidified with 0.8 N sulfuric acid, was used. The concentration of additive thallous ions was changed from 10^{-5} M to 10^{-2} M.

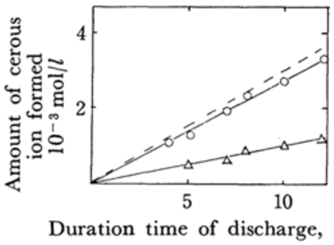

Fig. 5a

○ Tl^+: 5×10^{-3} M Ce^{4+}: 5×10^{-3} M
△ no Tl^+ added
--- expected curve

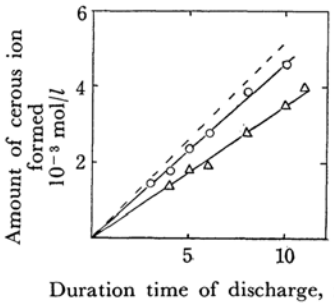

Fig. 5b

○ Tl^+: 1×10^{-2} M Ce^{4+}: 1×10^{-2} M
△ no Tl^+ added
--- expected curve

Fig. 5. Relationship between amount of cerous ion formed and duration time of discharge.

a case of helium b case of argon

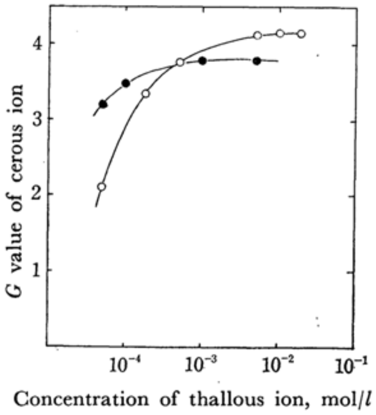

Fig. 6. Effect of thallous ion concentration on $G(Ce^{3+})$ in ceric-thallous ions system.
○ case of helium Ce^{4+}: 5×10^{-3} M
● case of argon Ce^{4+}: 1×10^{-2} M

Figure 5 shows the relationship between the amount of cerous ions formed and the duration of the discharge (Fig. 5a for helium and Fig. 5b for argon). The concentrations of the additive thallous ions were 5×10^{-3} M for helium and 1×10^{-2} M for argon. In both cases, there was a good linearity between the cerous-ion yield and the duration of the discharge.

Figure 6 shows the effect of the thallous ion concentration on the $G(Ge^{3+})$ value as estimated from the amount of cerous ions formed and the dose previously determined. With an increase in the thallous ion concentration, $G(Ce^{3+})$ gradually increased, reaching a constant value of 4.2 in helium and 3.8 in argon.

Discussion

Ferrous-Cupric Ion System. In the absence of cupric ions, a good linear correlation of the ferric-ion yield to the duration of the discharge had been reported. It had also been shown that these results could be interpreted well in terms of radiolysis caused by particles with a high LET value. One hydrogen atom and one hydroxyl radical oxidize one ferrous ion, while one hydrogen peroxide oxidizes two ferrous ions.

If our interpretation is correct, the experimental results obtained from the mixed system of ferrous and cupric ions should also be interpreted on basis of the known radiolysis of the ferrous-cupric ion system.

The reaction mechanism proposed for gamma-rays is as follows:

$$H_2O \rightsquigarrow H,\ OH,\ H_2O_2,\ H_2 \qquad (3)$$

$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^- \qquad (4)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH \qquad (5)$$

$$Fe^{2+} + H + H^+ \rightarrow Fe^{3+} + H_2 \qquad (6)$$

$$Cu^{2+} + H \rightarrow Cu^+ + H^+ \qquad (7)$$

$$Fe^{3+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+} \qquad (8)$$

The addition of cupric ions reduces the yield of ferric ions because of the occurrence of reaction (7), removing hydrogen atoms, followed by the reduction of ferric ions via reaction (8). In this case, in view of the competition between reactions (6) and (7), $G(Fe^{3+})$ depends on the cupric ion concentration. Reaction (7) proceeds much more rapidly than reaction (6) because the ratio of the rate constant of reaction (7) to that of (6), k_7/k_6, has been known to be in the order of 10^2.[11] Therefore, $G(Fe^{3+})$ decreases with an increasing concentration of cupric ions until finally it should be given as:

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[11] M. Burton, J. S. Kirby-Smith and J. L. Magee, "Comparative Effects of Radiation," John Wiley & Sons, New York (1960), p. 216; A. O. Allen and W. G. Rothschild, *Radiation Res.*, **7**, 591 (1957).

$$G(Fe^{3+}) = 2G(H_2O_2) + G(OH) - G(H) \quad (9)$$

By applying the previously-determined values of $G(H_2O_2)$, $G(OH)$, and $G(H)$ in 9, the following $G(Fe^{3+})$ values should be expected: in helium, $G_{calc}(Fe^{3+})=2.5$; in argon, $G_{calc}(Fe^{3+})=3.1$. By using these $G_{calc}(Fe^{3+})$ values and the dose value previously determined, we can derive theoretically the relation of the yield of ferric ions to the duration of the discharge. In Figs. 3a and 3b, these relations are shown with broken lines.

In argon, the coincidence of the theoretical curve with the observed curve is very good. In helium, however, a small discrepancy has been found.

The Ceric-Thallous Ion System. Sworski⁵⁾ studied the radiolysis of the ceric-thallous ion system by gamma-rays and found an increment in the initial G value of the cerous ion from 2.30 to 7.92 upon the addition of thallous ions in a 0.8 N sulfuric acid solution. The reaction mechanisms are shown as follows:

$$Tl^{+} + OH \rightarrow Tl^{2+} + OH^{-} \quad (10)$$

$$Tl^{2+} + Ce^{4+} \rightarrow Tl^{3+} + Ce^{3+} \quad (11)$$

$$Ce^{4+} + H \rightarrow Ce^{3+} + H^{+} \quad (12)$$

$$2Ce^{4+} + H_2O_2 \rightarrow 2Ce^{3+} + 2H^{+} + O_2 \quad (13)$$

Therefore, $G(Ce^{3+})$ should be finally given as:

$$G(Ce^{3+}) = 2G(H_2O_2) + G(H) + G(OH) \quad (14)$$

By the same treatment as was used for the ferrous-cupric ion system, the theoretical curve showing the relation of the cerous ion yield to the duration of the discharge can be derived. In Figs. 5a and 5b, this relation is shown with a broken line. The coincidence of the theoretical curve with the observed curve is comparatively good.

On the basis of these findings, we can conclude that hydrogen atoms and hydroxyl radicals are mainly produced through the interaction of water molecules with slow electrons, and that their behavior with the radical scavenger can apparently be well interpreted with reference to radiolysis.

It should be emphasized that these findings provide further evidence for the adequacy of our interpretation.

Strictly speaking, however, a small discrepancy between the theoretical curve and the observed curve can be seen. The theoretical value of the ferric-ion yield is slightly smaller than the observed value, while the situation is reversed in the case of cerium.

In estimating the theoretical values, we always use the constant G value for hydrogen peroxide. As is well known, however, the initial G value of hydrogen peroxide falls off with some exponent of the concentration of the additive with a scavenging effect on the hydroxyl radical. According to Burton and Kurien,¹²⁾ for gamma-rays the exponent is one third, while for 3.4 MeV alpha-rays it is 0.15. Accordingly, the addition of thallous ions should result in a decrease in the amount of hydrogen peroxide. Therefore, in estimating the theoretical values a slightly smaller value of $G(H_2O_2)$ should be used. It then becomes possible to interpret the discrepancy without difficulty. However, since the exponent becomes smaller as the LET increases, the decrease in $G(H_2O_2)$ is expected to be very small in our case.

Even though the above interpretation is accepted, no effect of the addition of thallous ions on the hydroxyl radical yield should be expected. In their study of the radiolysis of potassium ferricyanide in an alkaline aqueous solution, Hughes and Willis¹³⁾ investigated the effect of potassium ferrocyanide; they showed that potassium ferrocyanide scavenges only the precursor of hydrogen peroxide and has no effect on the yield of hydroxyl radicals. However, this has not yet been completely established, and also it is not clear whether thallous ions behave the same behavior as potassium ferrocyanide or not. Moreover, this interpretation can not be applied to the case of the ferrous-cupric ions system. In the present stage of cold plasma chemistry, when there are many problems left to be resolved, as was pointed out in the first report, it seems to be very difficult to proceed to more detailed discussions. We should like here to point out, however, that the discrepancy is rather small in order.

It is our conclusion that most of the silent discharge reactions in an aqueous solution in atmospheres of helium and argon can apparently be well interpreted in terms of radiolysis.

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12) M. Burton and K. C. Kurien, *J. Phys. Chem.*, **63**, 899 (1959).

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