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Silent Discharge Reactions in Aqueous Solutions. VIII. Effects of Discharge Gap Distance and Discharge Current on the Yield of Decomposition Products Formed from Water in Argon Atmosphere

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In order to elucidate the effects of discharge gap distance and discharge current on $^{s}GH_2O_2$, ^{s}GOH and ^{s}GH, the study of this series was further made by using a new discharge apparatus. Both of acidic aqueous solutions of ferrous sulfate and ferrous sulfate-cupric sulfate have been selected as the reaction systems suitable for this purpose. Experiments were made in the range from 3 mm to 9 mm of discharge gap distance and from 0.2 mA to 0.5 mA of discharge current. Each ^{s}G value of H_2O_2, OH and H varied with gap distance (5→9 mm) and current (0.2 →0.5 mA) as follows; in the former, 1.0→1.2, 1.8→0.9 and 1.1→0.9: in the latter, 1.4→1.2, 0.6→ 0.9, 0.8→0.9. Based on the value of $Y(H_2O_2)/Y(H+OH)$, it was concluded that (1) the silent discharge reactions under a longer gap distance correspond to the radiolysis having a value of higher LET, that (2) although those under a lower current do also to a higher one, the effect of discharge current on the value of apparent LET is relatively small.

In the previous reports,[1] the authors have elucidated that in the silent discharge reactions of the aqueous solutions under the atmosphere of inert gas, the actions of the slow electrons generated in the gas phase to water molecules play a main

1) A. Yokohata and S. Tsuda, This Bulletin, **39**, 46, 53, 1636 (1966); **40**, 294, 1339, 2502, 2507 (1967).

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 intermediates like hydrogen atoms or hydroxyl radicals through the interaction of slow electrons with water molecules, in which the molecular products; hydrogen and hydrogen peroxide can also be obtained.

Each apparent G value (denoted by ^{s}G) determined through the series of this study was as follows:

In argon; $^{s}G(H)=0.6$, $^{s}G(OH)=0.7$ and $^{s}G(H_2O_2)=1.5$

Of course, these values are meaningful only in the discharge tube used by us and not so universal as in the radiation chemistry. They appear to vary with the shape of discharge tube, the discharge gap distance and the discharge current, because the numbers and the mode of the streamers produced by discharge depend on them.

In order to get more informations on these points, a new discharge apparatus to make possible the variation of discharge gap distance was devised. The effect of electric discharge current has been also checked.

It is of interest and important to clear up these problems in the field of silent discharge. The aqueous solutions of ferrous ions and ferrous-cupric ions acidified with 0.4 N sulfuric acid were selected as the reaction systems suitable for this purpose.

Experimental

Apparatus. Figure 1 shows an experimental apparatus. It is composed of a discharge vessel having an electrode (A) of glass disk on which a tin foil (a) is wrapped and a gas washing bottle (B). A glass disk connected with glass holder (b) by adhesive is movable up and down through the wax-sealed part (c), which makes the variation of discharge gap distance possible. This disk was used as one electrode of the high tension side, and the tin foil part wrapped on the outer side (d) of vessel as another electrode (earth side).

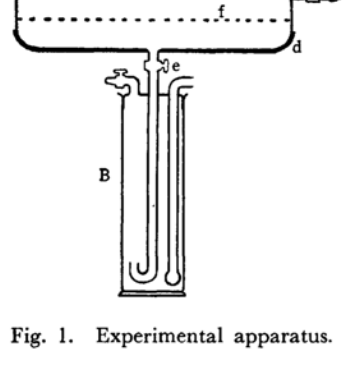

Fig. 1. Experimental apparatus.

After the sample solution deaerated previously by argon had been introduced into the vessel through the stopcock (e) of gas-washing bottle, the discharge was made by applying a high tension among those two electrodes, flowing argon gas through the vessel.

The discharge gap distance between the glass disk and the water surface was measured by the scale previously marked on the glass holder, while the level of the solution in the vessel was always kept constant (f).

The value of applied voltage was always calibrated by a static voltmeter. The electric discharge current was measured by the electric circuit shown in Fig. 2.

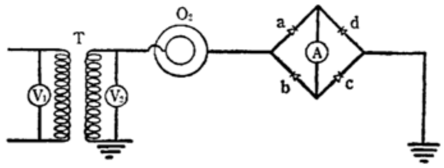

Fig. 2. Electric circuit.

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

All experiments were made at room temperature, and at the constant solution volume of 100 m*l*. Flow velocity of argon 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 of reagent grade. Argon (purity$\gtrsim$99.998%) was used without further procedure.

Analysis. Ferric ion was determined from its optical density using a spectrophotometer at 304 mμ where $\varepsilon=2160\ M^{-1}cm^{-1}$. Hydrogen peroxide was determined by the Ghormley method.[2]

Results

Figure 3 shows the relation between the applied voltage and electric current under each discharge gap distance of 5, 7 and 9 mm. As previously described, the discharge tube may be considered to be a sort of condenser having the capacitance C,[3] which consists of two parts, C_{die} and C_a; the former depends on the thickness and surface area of the glass disk and of the part covered by tin foil on the vessel, and the latter, on the gap distance among the glass disk and the water surface.

In Fig. 3, B, B′, and B′′ show respectively the firing voltage (V_1) for gap distance of 5, 7 and 9 mm. The AB, AB′ and AB′′ parts before discharge are

2) A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, *J. Phys. Chem.*, **56**, 575 (1952).
3) T. Biyodo, *J. Japan Chem. (Kagaku-no-Ryoiki)*, **3**, 172 (1950).

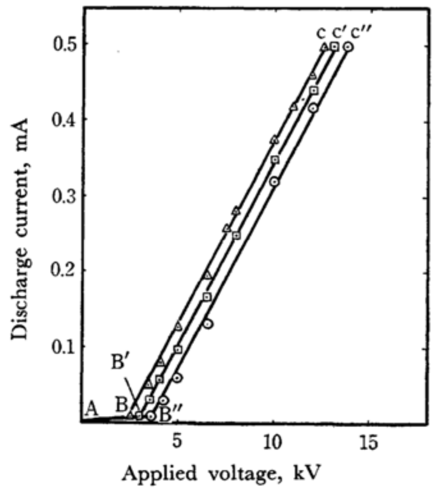

Fig. 3. Relation between applied voltage and discharge current.
Discharge gap distance: ⊙ 9 mm, ⊡ 7 mm, ⚠ 5 mm

expressed by the formula $I=\omega CV$. For BC, B′C′ and B″C″ during discharge, $I=\omega CV_1+\omega C_{die}(V-V_1)$: $\omega=2\pi f$; V_1: firing voltage; V: applied voltage; f: frequency.

Table 1 summarizes the values of C, C_{die} and C_a against each discharge gap distance. These values are the ones needed for when calculating the energy dissipated by the silent discharge, as discussed later.

TABLE 1. RELATION BETWEEN DISCHARGE GAP DISTANCE AND CAPACITANCE

Gap distance mm	C, pF	C_{die}, pF	C_a, pF
5	6.3_7	131	6.7_0
7	5.3_1	131	5.5_8
9	4.4_2	131	4.5_7

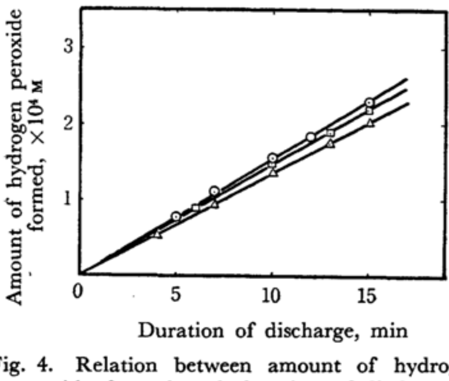

Fig. 4. Relation between amount of hydrogen peroxide formed and duration of discharge in 0.4 N sulfuric acid solution.
Discharge current: 0.5 mA
Discharge gap distance: ⊙ 9 mm, ⊡ 7 mm, ⚠ 5 mm

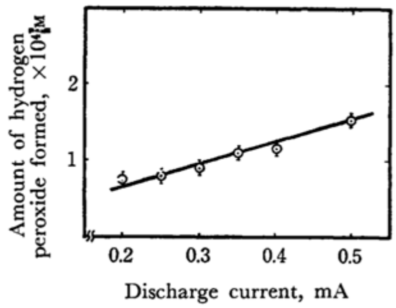

Fig. 5. Relation between amount of hydrogen peroxide formed and discharge current in 0.4 N sulfuric acid solution.
Discharge gap distance: 9 mm
Duration of discharge: 10 min

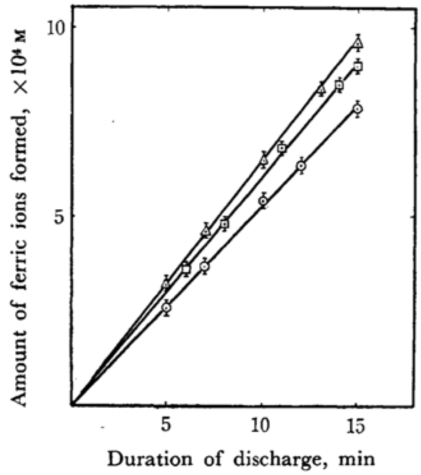

Fig. 6a

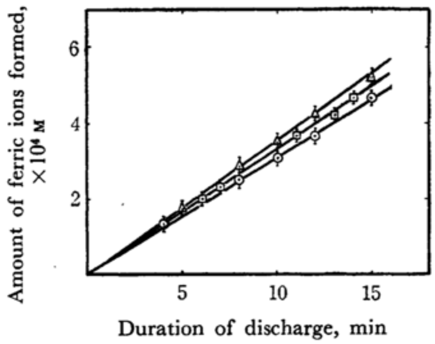

Fig. 6b

Fig. 6. Relation between amount of ferric ions formed and duration of discharge.
Discharge current: 0.5 mA
Dischrge gap distance:
⊙ 9 mm, ⊡ 7 mm, ⚠ 5 mm
a Ferrous ion system: 2×10^{-3} M $FeSO_4$, 0.4 N H_2SO_4
b Ferrous-cupric ion system: 2×10^{-3} M $FeSO_4-2\times10^{-2}$ M $CuSO_4$, 0.4 N H_2SO_4

In the aqueous solution of 0.4 N sulfuric acid deaerated by argon, silent discharge leads to the formation of hydrogen peroxide.

Figure 4 shows the relation between the amount of hydrogen peroxide formed and the duration of discharge under the constant electric discharge current, 0.5 mA, where the discharge gap distance was changed in the range from 5 mm to 9 mm. In every case a good linearity has been found.

Figure 5 shows the relation between the amount of hydrogen peroxide formed and discharge current under a condition of discharge gap distance = 9 mm and duration of discharge = 10 min. In the experimental condition from 0.2 mA to 0.5 mA a good linearity was also found respectively.

As shown in the previous reports,[1] the silent discharge leads to the oxidation of ferrous ions to ferric ions. Then, the yield of ferric ions was independent of the concentration of ferrous ions in the range from 2×10^{-3} M to 4×10^{-1} M, and of the concentration of sulfuric acid in the range from 2×10^{-2} N to 1.5 N.

On the other hand, the addition of cupric ions reduces the yield of ferric ions because of the competition reaction of cupric ions and ferrous ions for the hydrogen atom. Then, it is also known that the existence of cupric ions of about 10 times as much as the ferrous ions is sufficient to scavenge the hydrogen atoms through the competition with ferrous ions.[1] In the ferrous ion system 2×10^{-3} M ferrous sulfate, and in the ferrous-cupric ion system 2×10^{-3} M ferrous sulfate and 2×10^{-2} M cupric sulfate were used respectively.

Figure 6 shows the relation between the amount of ferric ions formed and the duration of discharge (Fig. 6a for ferrous ion system and Fig. 6b for ferrous-cupric ion system), where the discharge current was 0.5 mA and the discharge gap distance was changed in the range from 5 mm to 9 mm. In all cases a good linearity has been found.

Figure 7 shows the relation between the amount of ferric ions formed and electric discharge current (Fig. 7a for ferrous ion system and Fig. 7b for ferrous-cupric ion system), where the discharge gap distance was 9 mm and the discharge current was changed in the range from 0.2 mA to 0.5 mA. In both cases a good linearity has been also found.

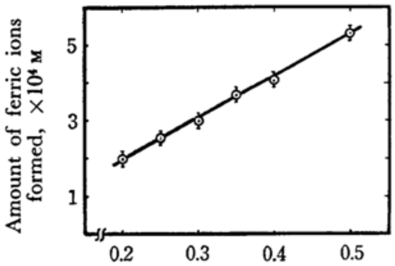

Fig. 7a

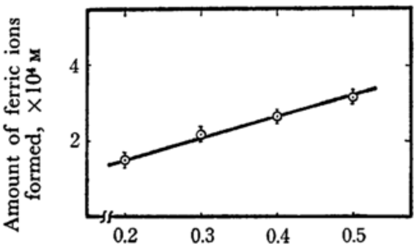

Fig. 7b

Fig. 7. Relation between amount of ferric ions formed and discharge current.
Discharge gap distance: 9 mm
Duration of discharge: 10 min
a Ferrous ion system: 2×10^{-3} M $FeSO_4$, 0.4 N H_2SO_4
b Ferrous-cupric ion system: 2×10^{-3} M $FeSO_4-2\times10^{-2}$ M $CuSO_4$, 0.4 N H_2SO_4

Discussion

On the basis of the well-known reaction mechanisms of the radiolysis of these systems, Eqs. (1) and (2) can be obtained. For the ferrous ion system,

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

For the ferrous-cupric ions system,

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

Since the silent discharge reactions correspond to ones induced by ionizing radiations of high LET (linear energy transfer), Eqs. (3) and (4) should be obtained respectively.[1]

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

$$Y(Fe^{3+}) = 2Y(H_2O_2) + Y(OH) - Y(H) \quad (4)$$

where, Y shows respectively the yield of each product under a given discharge conditions. Thus, Y(OH) and Y(H) can be separately estimated from $Y(Fe^{3+})$ in the ferrous ion system, $Y(Fe^{3+})$ in the ferrous-cupric ion system, and $Y(H_2O_2)$ in the aqueous 0.4 N sulfuric acid.

TABLE 2. RELATION BETWEEN DISCHARGE GAP DISTANCE AND Y VALUE

Gap distance mm	$Y(H_2O_2)$ $\times10^4$ M	Y(H+OH) $\times10^4$ M	Y(OH−H) $\times10^4$ M	$Y(H_2O_2)/Y$(H+OH)
5	1.3_6	3.7_8	0.8_1	0.36
7	1.4_7	3.1_1	0.4_0	0.47
9	1.5_5	2.2_4	0.0_6	0.69

By the same treatment as described in the previous report,[1] we can estimate $G(Fe^{3+})$ value from the value of apparent LET estimated on the basis of the relation between $G(H_2O_2)/G(H+OH)$ and LET. By combining $G(Fe^{3+})$ value estimated in this way with $Y(Fe^{3+})$, the absorbed dose can be determined. Of course, this means the dose determined by a chemical dosimeter; in other word, ones normalized to the scale of radiation chemistry. Let us call it "the apparent dose." The significance and the usefullness of this dose have been discussed in detail through the series of this study.

Effect of Discharge Gap Distance. Table 2 shows the respective value of $Y(H_2O_2)$, $Y(H+OH)$, $Y(OH-H)$ and $Y(H_2O_2)/Y(H+OH)$ under each discharge gap distance of 5, 7 and 9 mm, where discharge current=0.5 mA and duration of discharge=10 min. Thus, it can be understood that the silent discharge reactions of the aqueous solutions in argon atmosphere under each discharge gap distance of 5 mm, 7 mm and 9 mm correspond to the ones induced by the ionizing radiations having the value of LET of about 2, 4 and 6 (eV/Å).

By the use of each $G(Fe^{3+})$ value estimated from the value of LET,[4] the apparent dose rate can be respectively estimated to be 7.9×10^5 R/hr in 5 mm, 8.0×10^5 R/hr in 7 mm and 7.5×10^5 R/hr in 9 mm.

In general, the energy dissipated per second by the silent discharge is known to be expressed as follows:[5]

$$A = \frac{\left[\begin{array}{l} f(C_{die}+C_a)(V_i+V_d)\{2E_m- \\ (V_i+V_d)(1+C_a/C_{die})\} \end{array}\right]}{1+C_a/C_{die}} \qquad (5)$$

where V_i is correlated by the $V_i=V_1(C_{die}/(C_a+C_{die}))$ formula to the firing voltage, V_1. Table 3 shows the results of the calculation of A for each case of $V_d/V_i=0.2$ and 0.4.[1]

Since it is very difficult to determine exactly a value of firing voltage, the values calculated from Eq. (5) should be considered to be approximate ones.

TABLE 3. CALCULATED RESULTS OF DISSIPATED ENERGY UNDER EACH DISCHARGE GAP DISTANCE OF 5, 7 AND 9 mm (NORMALIZED TO THE CASE OF 5 mm)

Discharge gap distance mm	V_d/V_i	Dissipated energy
5		1
7	0.2	1.2
9		1.4
5		1
7	0.4	1.2
9		1.4

In spite of the fact that the dissipated energy increases with increasing discharge gap distance, the absorbed dose determined was almost the same. This finding suggests that the chemical utilization efficiency is rather better in a short discharge gap distance.

Table 4 shows each ${}^sG$ value of hydrogen peroxide, hydroxyl radical and hydrogen atom in relation to discharge gap distance. The increments of ${}^sG(H_2O_2)$ and the decrement of ${}^sG(OH)$ or ${}^sG(H)$ with the increasing discharge gap distance tend to confirm that the silent discharge reactions under a longer gap distance correspond to them induced by the ionizing radiations having a higher LET.

TABLE 4. RELATION BETWEEN DISCHARGE GAP DISTANCE AND ${}^sG$ VALUE; DISCHARGE CURRENT=0.5 mA

Gap distance mm	${}^sG(H_2O_2)$	${}^sG(OH)$	${}^sG(H)$
5	1.0	1.8	1.1
7	1.1	1.3	1.0
9	1.2	0.9	0.9

In general, a higher applied voltage is needed for with an increasing discharge gap distance under

TABLE 5. RELATIONS OF THE VALUES OF Y AND APPARENT LET TO EACH DISCHARGE CURRENT; DISCHARGE GAP DISTANCE=9 mm

Discharge current, mA	$Y(H_2O_2)$ $\times10^4$ M	$Y(H+OH)$ $\times10^4$ M	$Y(OH-H)$ $\times10^4$ M	$\frac{Y(H_2O_2)}{Y(H+OH)}$	LET eV/Å
0.2	0.6_7	0.6_7	0.1_6	1.0	8
0.3	0.9_7	1.2	0.1_1	0.8	7
0.4	1.2_5	1.7	0.1_0	0.7	6
0.5	1.5_5	2.2	0.0_2	0.7	6

4) A. O. Allen, "Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Company, New York (1961), p. 54.

5) S. Fuji and N. Takimura, *Bulletin of the Electrotechnical Laboratory (Denki Shikensho Hokoku)*, **16**, 837 (1952).

A: the energy dissipated per second by the silent discharge

f: the frequency of the electric source used

C_{die}: the total capacitance of the insulator

C_a: the capacitance due to the gap distance in the discharge tube

V_i: the voltage across the gap space at the firing voltage

V_d: the stopping voltage

E_m: the maximum value of the applied voltage a constant discharge current. A higher applied voltage would result in a localty of discharge which will induce the chemical reactions corresponding to them by a more densely ionizing radiations. The findings obtained support this interpretation.

Effect of Discharge Current. By the same procedure as above mentioned, the effect of discharge current was checked. Table 5 shows the respective value of $Y(H_2O_2)$, $Y(H+OH)$, $Y(OH-H)$, $Y(H_2O_2)/Y(H+OH)$ and apparent LET under each discharge current of 0.2, 0.3, 0.4 and 0.5 mA, where discharge gap distance= 9 mm and duration of discharge=10 min. From the value of apparent LET, the apparent dose rates under each discharge current of 0.2, 0.3, 0.4 and 0.5 mA were respectively estimated to be 2.9×10^5 R/hr, 4.4×10^5 R/hr, 6.0×10^5 R/hr and 7.5×10^5 R/hr. Table 6 shows the relation between each ${}^sG$ value of products and discharge current.

TABLE 6. RELATION BETWEEN DISCHARGE CURRENT AND ${}^sG$ VALUE; DISCHARGE GAP DISTANCE=9 mm

Discharge current mA	${}^sG(H_2O_2)$	${}^sG(OH)$	${}^sG(H)$
0.2	1.4	0.6	0.8
0.3	1.3	0.8	0.9
0.4	1.3	0.8	0.8
0.5	1.2	0.9	0.9

These findings show that the silent discharge reactions under a lower current tend to correspond to the radiolysis having a value of higher LET. However, it can be concluded that the effect of discharge current on the value of apparent LET is relatively small.