BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 46—52 (1966)

# Silent Discharge Reactions in Aqueous Solutions. I. An Acidic Aqueous Solution of Ferrous Sulfate in Atmospheres of Helium and Argon*

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(Received April 6, 1965)

In an atmosphere of helium or argon, the silent discharge reactions of aqueous solutions have been investigated from the point of view of radiation chemistry. A discharge tube with two coaxial glass tubes was used. In a dilute oxygen-free aqueous solution of sulfuric acid, hydrogen peroxide appeared as a result of discharge. Also, the oxidation of ferrous ions to ferric ions has been found. It has been confirmed, first, that neither the effect of metastable excited states of helium and argon nor that of luminescence is serious, and, second, that the reaction may well be interpreted by taking into consideration the actions of slow electrons generated in the gas phase on the liquid water. The yield of hydrogen atoms plus hydroxyl radicals has been estimated from the yields of hydrogen peroxide and ferric ions. The ratios of the yield of hydrogen peroxide to that of radicals show that the silent discharge reaction corresponds to the reaction by ionizing radiation of high LET, the value of which apparently equals 3eV./Å in helium and 8 eV./Å in argon. The $G(Fe^{3+})$

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* Presented in part at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

value and the absorbed dose ($E$) estimated were, respectively, as follows: In helium: $G(\mathrm{Fe}^{3+})=4.6$, $E=3.8\times10^6$ r./hr.; in argon: $G(\mathrm{Fe}^{3+})=4.3$, $E=7.2\times10^6$ r./hr.

In the field of silent discharge reaction, the work has hitherto been chiefly confined to studies of the gas phase; the study of the solutions is, however, currently receiving increasing attention.[1,2] The discharge reactions in the gas phase have been investigated exhaustively,[3-5] and their reaction mechanisms have been elucidated from the point of view of the reactivity of active species. In the studies of liquids,[6-8] the reaction mechanisms have also been interpreted as the reactions of active species generated in an atmosphere to solutes or solvents; the actions on them of low-energy electrons generated in an atmosphere have been neglected or forgotten.

As far as we have been able to determine, few studies of the silent discharge reactions in aqueous solutions from the point of view of radiation chemistry by the low-energy electron generated in an atmosphere have been made. Moreover, their importance has not adequately been explored.

We began our studies with the purpose of rectifying these omissions and so explored the mechanism of the silent discharge reactions, comparing this mechanism with the findings of radiation chemistry. The method we have developed also makes it possible to determine the apparent energy absorbed in a solution by silent discharge if adequate chemical systems are selected.

In the present work the oxidation of ferrous ion in the dilute sulfuric acid solution, well known as a chemical dosimeter, has been studied, using helium or argon as an atmosphere[9]; as has already been pointed out by Davis,[1] the contributions of their metastable-excited states to chemical reactions, to, for example, the oxidation of ferrous ion to ferric ion, seem to be very small.

According to our experimental results, hydrogen peroxide is formed in the dilute sulfuric acid solution; ferrous ion is oxidized to ferric ion, and the yield of ferric ions is always larger than that which would be expected from the oxidation by the hydrogen peroxide formed. Now, assuming that the net effect by the slow electrons is similar to that of the usual ionizing radiation,[10] the yield of hydrogen atoms plus hydroxyl radicals can be estimated from the yields of hydrogen peroxide and ferric ions according to the well-established reaction mechanism. Moreover, the ratio of the yield of hydrogen peroxide to that of radicals shows clearly that the silent discharge reaction[11] in the aqueous solutions corresponds to the reactions by ionizing radiations of high LET. Also, the apparent dose rate in each case of helium and argon under our experimental conditions was estimated by considering carefully our findings on the relations of LET and $G(\mathrm{Fe}^{3+})$.

## Experimental

**Apparatus.**—Most of the previous studies of the discharge reaction have been made by means of glow discharge. It is impossible, however, to study the aqueous solution by this method. In this work, a discharge tube of the ozonizer type (Fig. 1) was used; this makes the study of solutions possible. It is composed of two coaxial, hard-glass tubes; the part consisting of tin foil stuck on the 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). After the sample solution had been poured into the discharge tube, the discharge was made by applying a high tension between those two electrodes, letting helium or argon flow through the gas space of the discharge tube.

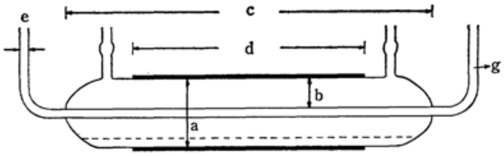

Fig. 1. Schematic diagram of discharge tube.

| | | | |
|---|---|---|---|
| a | 26 mm. | e | 10 mm.$\phi$ |
| b | 8 mm. | | |
| c | 300 mm. | --- | surface of solution |
| d | 230 mm. | — | tin foil |

All experiments were made at a constant volume of the solution, 10 ml. The surface of the solution was vibrated gently by the discharge. This may be useful for the renewal of the surface of the solution.

All experiments were made after the dissolved oxygen in the solution had been completely removed by bubbling helium or argon gas into the solution. Sometimes samples were degassed by four successive cycles of freezing, evacuation, and melting on a vacuum line.

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[1] T. W. Davis, S. Gordon and E. J. Hart, *J. Am. Chem. Soc.*, **80**, 4487 (1958).

[2] G. Gzapski and G. Stein, *Nature*, **182**, 598 (1958); *J. Phys. Chem.*, **63**, 850 (1959); *Israel J. Chem.*, **2**, 15 (1964).

[3] M. Suzuki, *Proc. Japan Acad.*, **26**, 20 (1950).

[4] K. Sugino, E. Inoue, T. Wakabayashi and T. Matsuda, *J. Elect. Chem. Japan*, **25**, 70 (1957).

[5] G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley & Sons, London (1939).

[6] T. Okamoto and H. Kobayashi, *J. Soc. Org. Synth. Chem. Japan*, **7**, 10 (1949).

[7] Y. Isomura, *J. Elect. Chem. Japan*, **17**, 9 (1949).

[8] M. Gotoda, *Railway Technical Research Report* (*Tetsudo Gizitsu Kenkyu Hōkoku*), No. 226, June (1961).

[9] Even though the effects of such ions as $\mathrm{Ar}^+$ and $\mathrm{He}^+$ have been considered, the effect would probably be very small since their mobility is quite low compared with that of electrons.

[10] It is generally accepted that the chemical change produced by a high-energy radiation, such as those of beta-, alpha- and gamma-rays, can be explained as the reaction by secondary electrons with a mean energy of about 100 eV.

[11] Since the electron energy is very small, most of the energy might be dissipated by one event. Accordingly, the term "LET", as herein used, may not be adequate, the electron generated by silent discharge being very slow.

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

Sometimes, a quartz discharge tube of the same size was used to test the effect of the light arising from the discharge. In this case. the test was made after the sample had been poured into the inner tube, g in Fig. 1. If the effect were predominant, some contributions would be expected; however, this was not the case.

Another discharge tube (Fig. 2) was also used. This is a vertical one. Samples were tested in the position of A. This experiment makes it possible to estimate the contributions of active species with a long life, such as $He^{m*}$ and $Ar^{m*}$, and also those of the oxidizing products, such as the trace of ozone formed in the gas phase.

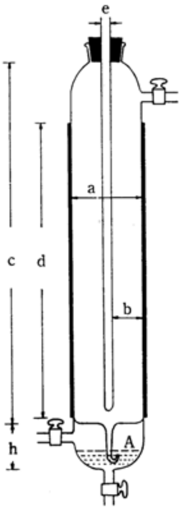

Fig. 2. Schematic diagram of discharge tube.

| | | | |
|---|---|---|---|
| a | 26 mm. | d | 230 mm. |
| b | 8 mm. | e | 10 mm.$\phi$ |
| c | 300 mm. | h | 40 mm. |

**Electric Circuit.**—An electric circuit (Fig. 3) was used for measuring the discharge current running through the discharge tube. In general the wave form shown in Fig. 4 is found, where V and I are the voltage and the current respectively. The phase difference was about 80 degrees.

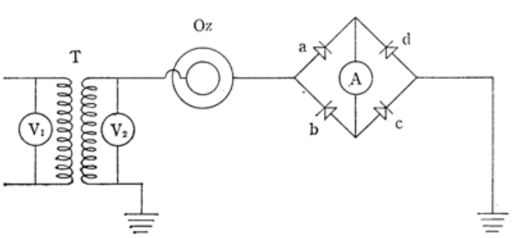

Fig. 3. Electric circuit.

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

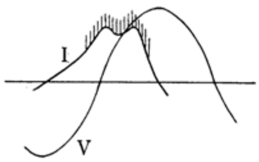

Fig. 4. General waveform of discharge current.
I Discharge current
V Voltage

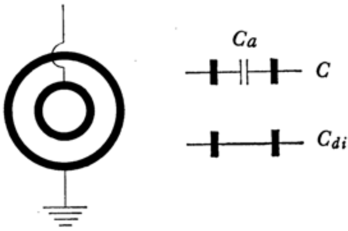

Fig. 5. Cut-away diagram of discharge tube.

The discharge tube is a sort of condenser, the capacitance of which is shown by $C$ and which consists of two parts $C_{die}$ and $C_a$; the former depends on the thickness of the outer and inner glass tubes, and the latter, on the gap distance of the discharge tube (Fig. 5). The capacitance during discharge may be approximately shown by $C_{die}$, because it has a short circuit because of the discharge.[12)]

**Materials.**—The water used was purified by the multiple distillation described by Johnson and Allen.[13)] Reagent-grade sulfuric acid and ferrous ammonium sulfate were used without further purification. Helium and argon (purity: >99.99%) were also used without further treatment.

**Analysis.**—The amount of hydrogen peroxide produced in the dilute sulfuric acid solution was determined by the method of Ghormley.[14)] The ferric ions in ferrous sulfate solutions were determined by light absorption at 3040 Å.

## Results

Figure 6 shows the relation between the applied voltage and the electric current when 10 ml. of solution is contained in the discharge tube, where B or B′ shows the firing voltage ($V_1$) for helium and argon respectively. The AB or AB′ part before discharge is expressed by the formula[10)] $I=\omega CV$. For BC or 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. Most of the experiments were made at a constant discharge current, $I=1$ mamp. The electric current as measured by the method shown in Fig. 2 shows the low frequency component principally, not the high frequency component. For the latter another method, such as

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[12)] T. Biyodo, *J. Japan Chem.* (*Kagaku-no-Ryoiki*), **3**, 172 (1950).

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

[14)] A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, *J. Phys. Chem.*, **56**, 575 (1952).

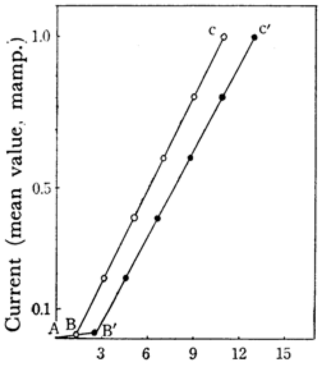

Fig. 6. Relation between applied voltage and electric current.
○ case of helium
● case of argon

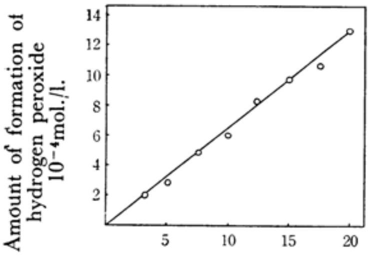

Fig. 7a.

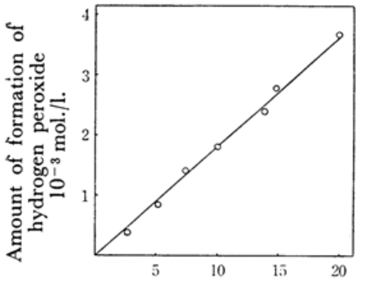

Fig. 7b.

Fig. 7. Relationship between amount of formation of hydrogen peroxide and duration time of discharge in $0.8\,\text{N}$ sulfuric acid.
a case of helium b case of argon

one using a thermoammeter, seems to be needed. Recently we have made extensive studies of this point,[15] but we will not discuss them here.

**The Formation of Hydrogen Peroxide from a Dilute Aqueous Solution of Sulfuric Acid.**—In the oxygen-free aqueous solution of sulfuric acid, hydrogen peroxide appeared as a result of discharge in argon or helium. The concentration of sulfuric acid in the range from $2\times10^{-2}\,\text{N}$ to $1.5\,\text{N}$ had no effect on the yield of hydrogen peroxide within the range of experimental error (Figs. 7a and 7b). The yield of hydrogen peroxide also showed a good linear correlation with the duration of discharge. A larger amount of hydrogen peroxide was found in argon than in helium. Although the formation of hydrogen peroxide from the water vapor in the gas phase may be expected, it was negligibly small under our experimental conditions, in which the gas passed at a velocity of about 120 ml./min. and the duration time of the discharge (20 min.) was very short.

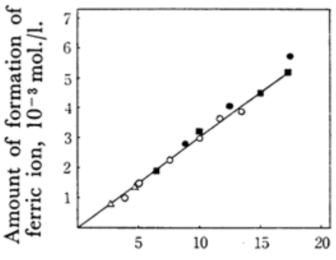

Fig. 8a.

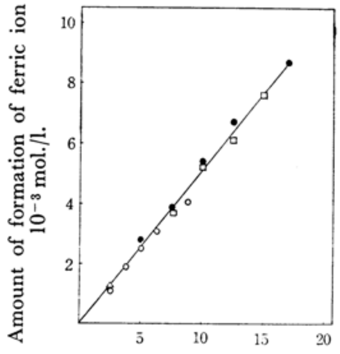

Fig. 8b.

Fig. 8. Relationship between amount of formation of ferric ion and duration time of discharge.

| a case of helium | b case of argon |
|---|---|
| ● $4\times10^{-1}$ mol./l. | □ $4\times10^{-2}$ mol./l. |
| ■ $1\times10^{-2}$ mol./l. | ○ $5\times10^{-3}$ mol./l. |
| △ $2\times10^{-3}$ mol./l. | |

The formation of hydrogen peroxide, therefore, may be considered to be caused by the actions of low energy electrons generated by discharge on water molecules, just as in radiation chemistry.

**The Formation of Ferric Ions.**—Ferric ions were found to be formed in an aqueous ferrous sulfate solution acidified with sulfuric acid. Figures 8a and 8b show the relationship between the amount of ferric ions formed and the duration of the discharge in a helium or an argon atmosphere respectively. The yield of ferric ions was independent of the concentration of ferrous ions in the

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[15] A. Yokohata and S. Tsuda, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **86**, 682, 686, 689 (1965).

range from $2\times10^{-3}$ M to $4\times10^{-1}$ M, and of the concentration of sulfuric acid in the range from $2\times10^{-2}$ N to 1.5 N; it also showed a good linear correlation with the duration of discharge. These results suggest that the mechanism of the silent discharge reaction may be interpreted as that of radiolysis by slow electrons.

## Discussion

The silent discharge on aqueous solutions in an atmosphere of helium or argon will give many numbers of electrons; excited molecules such as $He^{m*}$ and $Ar^{m*}$, and atoms or radicals like the H-atom and the OH-radical due to the interaction of the water molecule with an electron or an excited molecule such as $He^{m*}$; it is also accompanied by a weak luminescence. Accordingly, the effect of the silent discharge may naturally be considered to be the superposed effect caused by those electrons, active species, and luminescence.

It is, however, very important to clarify which of them plays the main role. This is our purpose in the present study.

**The Effect of Active Species.**—First, let us consider the effect of the excited molecule alone. It is very difficult to clear up this effect quantitatively, but it is possible to do so qualitatively. For this purpose, the discharge tube shown in Fig. 2 was used. 10 ml. samples were tested in the position of A. After the oxygen dissolved in a sample in the A section had been completely excluded by bubbling argon or helium in, a discharge was made. In order to pass the discharged gas rapidly into the sample solution, the gas was sent forth through the capillary tube. The experimental results showed only a very small amount of ferric ions under such these conditions: duration time of discharge =30 min.; flow velocity of gas =120 ml./min., and electric current=1 mamp. If the effect of the excited molecules is predominant, larger amounts of ferric ion may be expected.

Our results are consistent with the work by Davis et al.,1) in which the oxidation of ferrous ions was checked by introducing argon treated by glow discharge into an aqueous solution. They found only a very slow oxidation. Therefore, the effect of the excited molecule itself may be concluded to be very small. However, when water vapor is present, the situation may be different.

In the study of the total ionization in gases by single alpha-particles, Jesse16) showed that the number of ion pairs in pure helium or neon is greatly increased by the addition of a small amout of almost any impurity; he then suggested that the additional ionization arose from reactions of the following type:

$$He^* + X \rightarrow He + X^+ + e^- \qquad (1)$$

The metastable-excited states of helium have a sufficiently long life to encounter an impure atom or molecule and ionize it in a collision of the second kind (the Penning effect). With helium, most of the contaminants show this effect. As expected, other ionizing radiations (beta-rays, gamma-rays) show exactly the same effect.

Since the presence of water vapor should be considered in our case, the following reaction may occur in the gas phase:

$$He^* + H_2O \rightarrow He + H_2O^+ + e^- \qquad (2)$$

However, it can, alternatively, result in the "dissociation" of the molecule.17)

$$He^* + H_2O \rightarrow He + H + OH \qquad (3)$$

One of the reaction products may be electronically excited. If the hydrogen exists in the excited state, reaction 4 may be expected:

$$H^* + H_2O \rightarrow H_2 + OH \qquad (4)$$

In argon also the circumstances are just the same, except that the excitation energy of the metastable state is smaller than that of helium. Since the excitation energy of argon is smaller than the ionization potential of the water vapor molecule, a reaction like 2 may not be expected.

As has already been pointed out,1) the effect of water vapor cannot be neglected. In the present stage, it is very difficult to estimate separately the effects of H-atoms and OH-radicals arising from the water vapor and those arising from the interaction of liquid water with the slow electrons generated in the gas phase. However, we have already obtained the experimental result that the yield of hydrogen peroxide formed in the gas phase is negligibly small under the experimental conditions. This seems to show that the contribution of the hydroxyl radical from the water vapor is not very great. Also, hydrogen atoms will not naturally make an important contribution.

**The Effect of Luminescence.**—The silent discharge gives a luminescence, although the intensity is weak. Therefore, photochemical reactions18) may be expected, although their contribution in this case is thought to be small.

In order to clear up this point, we made an experiment, where a quartz discharge tube was used; the aqueous ferrous sulfate solution to be tested was put in an inner tube (Fig. 1. g). Since quartz is transparent for light of wavelengths of $\lambda>2000$Å, it might be possible to learn the order of contributions due to photons of the wavelengths $\lambda>2000$Å by this experiment. Experimental results showed that this effect was negligibly small.

Evidence that the light below 2000Å is effective in the flash photolysis of aqueous ferrous sulfate

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16) W. P. Jesse and J. Sadauskis, *Phys. Rev.*, **88**, 417 (1952); **100**, 1755 (1955).

17) R. L. Platzman, *Vortex*, **23**, 372 (1962).

18) T. Rigg and J. Weiss, *J. Chem. Phys.*, **20**, 1194 (1952).

has recently been given by Baxendale and Mansell.[19] They concluded that the observed $Fe^{2+} \rightarrow Fe^{3+}$ oxidation was an indirect effect, the primary one being the photolysis of water to give products which oxidize $Fe^{2+}$. Although the contribution of ultraviolet rays ($<2000$Å) may exist in our case, we have not yet performed any experiment to test such effects because of the great difficulty. However, judging from the fact that the effect of luminescence was clearly negligibly small in the case of nitrogen molecule which has $\lambda \fallingdotseq$ 2000Å ($E=6.1$ eV.) as a resonance line,[20] the resonance lines of helium and argon are also too weak to make contributions.[21]

**The Effect of Electrons.**—As has been mentioned above, the effects of the metastable-excited state of helium and argon and of the luminescence cannot be serious.

However, the contributions of hydrogen atoms and hydroxyl radicals from the water vapor cannot be neglected, although they might also not be very large. The yield of hydrogen peroxide from the water vapor was very small. On the other hand, our present work shows that the yield of hydrogen peroxide formed in the aqueous solutions is fairly great (Table I). Also, the yield of ferric ions was always larger than that which could be expected from the oxidation by the hydrogen peroxide formed. These phenomena may be interpreted by taking into consideration the actions of the slow electrons generated in the gas phase on the solvent.

About the energy distribution of electrons produced by such silent discharge under an atmospheric pressure, we do not yet have any exact information. The electrons, however, may be considered to have an energy distribution from just above zero to somewhat above the ionization potential for the gas in which the discharge occurs.[22,23] On the other hand, to produce a hydrogen atom and a hydroxyl radical through the excited state of a water molecule, it is well known that the energy 7.4 eV. is necessary.[24] Accordingly, in the silent discharge also, the formation of a hydrogen atom and a hydroxyl radical can be expected. In other words, the effect of electrons may be interpreted in the same way as in radiation chemistry:

$$H_2O \rightsquigarrow H, OH, H_2, H_2O_2 \qquad (5)$$

Some part of the hydrogen atoms and the hydroxyl radicals may come from the water vapor. The overall reaction, however, proceeds irrespective of whether they are produced from the water vapor or the liquid water,

Therefore,[25] the following relation is obtained:

$$Y(Fe^{3+}) = 2Y(H_2O_2) + Y(OH) + Y(H) \qquad (6)$$

where $Y$ shows the yield of each product under given conditions.

Table I shows each value of $Y(H_2O_2)$, $Y(Fe^{3+})$, $Y(H+OH)$ estimated by (6), and $Y(H_2O_2)/Y(H+OH)$ in the cases of helium and argon respectively.

TABLE I. ESTIMATION OF $Y(H_2O_2)/Y[(H)+(OH)]$

| | $Y(H_2O_2)$ mol./l. | $Y(Fe^{3+})$ mol./l. | $Y[(H)+(OH)]$ mol./l. | $Y(H_2O_2)/Y[(H)+(OH)]$ |
|---|---|---|---|---|
| He | $6.5\times10^{-4}$ | $3.0\times10^{-3}$ | $1.7\times10^{-3}$ | 0.38 |
| Ar | $1.8\times10^{-3}$ | $5.1\times10^{-3}$ | $1.5\times10^{-3}$ | 1.2 |

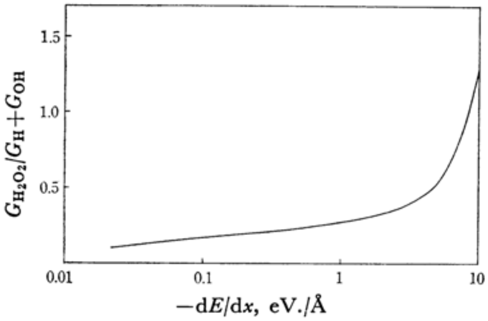

Fig. 9. Relation between $G_{H_2O_2}/G_H+G_{OH}$ and $-dE/dx$.

Figure 9 shows the relations between $G(H_2O_2)/G(H+OH)$ and LET, arranged using the data from Allen, Lefort and Barr.[26-28] The linear energy transfer (LET) in Fig. 9 is expressed by $-dE/dx$ (eV./Å), where $^{60}Co$ gamma rays: LET 0.02 eV./Å, 40 keV. electron: 0.08 eV./Å, 18 MeV. deuteron: 0.5 eV./Å and 5.5 MeV. alpha-rays: 9 eV./Å, as is already known,[29]

The radical yields decrease with an increase in the LET, and molecular yields increase until the radical yields approach zero at a sufficiently high LET.

By comparing the results in Table I with Fig. 9, the following interesting conclusions can be derived. In an atmosphere of helium, the chemical effect of the silent discharge apparently corresponds to that of the ionizing radiation with a LET of

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[19] J. H. Baxendale and A. L. Mansell, *Nature*, **190**, 622 (1961).

[20] G. Herzberg, "Molecular Spectra and Molecular Structure (I. Spectra of Diatomic Molecules)," D. Van Nostrand Company, New York (1963), p. 448.

[21] A long exposure time (for example, 1—4 hr.) was necessary to take spectrograms with a small "Riken" quartz spectrograph and with "Sakura S. G. 100" photographic plates.

[22] L. B. Loeb, "Basic Processes of Gaseous Electronics," Univ. of California Press, Berkeley (1955), p. 269.

[23] H. Kokado, Y. Mori and I. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **78**, 151 (1957).

[24] M. Burton, J. S. Kirby-Smith and J. L. Magee, "Comparative Effects of Radiation," John Wiley & Sons, New York (1960), p. 179.

[25] $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH$
$OH + Fe^{2+} \rightarrow Fe^{3+} + OH^-$
$H + H^+ + Fe^{2+} \rightarrow Fe^{3+} + H_2$

[26] A. O. Allen, *Radiation Res.*, **1**, 85 (1954).

[27] M. Lefort, *J. Chem. Phys.*, **54**, 782 (1957).

[28] N. F. Barr and R. H. Schuler, *Radiation Res.*, **7**, 302 (1957).

[29] A. O. Allen, "Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Company, New York (1961), p. 10.

about 3 eV./Å, while in argon it corresponds to a radiation with a LET of about 8 eV./Å. In argon it seems to be very close to the effect of alpha rays. This is consistent with Hochanadel's finding that, for very low-energy electrons, the radicals are formed in high concentrations along the track in the same way as for alpha particles and low-energy protons.[30]

The slight difference between helium and argon is thought to be due to their different discharge characters; in the former the discharge is very gentle and the high frequency part of the discharge current is very small, while in the latter the discharge is quite vigorous and the high frequency part is relatively large.[15] Also, from the relation between $-dE/dx$ and $G(\mathrm{Fe}^{3+})$[31] it becomes possible to estimate the apparent $G(\mathrm{Fe}^{3+})$ in helium and in argon. The former is $G(\mathrm{Fe}^{3+}) \doteqdot 4.6$, and the latter, $G(\mathrm{Fe}^{3+}) \doteqdot 4.3$.

**The Estimation of the Apparent Dose Absorbed.**[32]—It is very important to ascertain the absorbed energy or the dose in the silent-discharge chemistry. As a method of measuring the total dissipated energy, the electrical method using a synchroscope has been proposed.[33] In our experience, however, this method was very difficult because the high-frequency component of the electric current fluctuates very vigorously. An approach by theoretical calculations has also been made. The following formula has been proposed for the energy dissipated per second by the silent discharge[34]:

$$A=\frac{f(C_{die}+C_a)(V_i+V_d)\{2E_m-(V_i+V_d)(1+C_a/C_{die})\}}{1+C_a/C_{die}} \qquad (7)$$

$A$ : 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

Of couse, this formula is an approximate one, in which the contributions of the high-frequency parts are neglected. Also, $V_i$ means the voltage in the gas space and is correlated by the $V_i=V_1(C_{die}/(C_a+C_{die}))$ formula to the firing voltage, $V_1$. Now, let us suppose that discharge occurs when the voltage of the gap space attains $V_i$ and stops at $V_d$. The relation between $V_d$ and $V_i$ is not well known, but the value of $V_d/V_i$ is said to be approximately 0.4—0.2[35]

In our experimental conditions $C_{die}=180$ pF,[36] $C_a=36$ pF, $V_i=1.3$ kV. and $E_m=15.4$kV. in helium, and $V_i=2.4$kV. and $E_m=17.2$ kV. in argon. By putting these values into (7), the ratio of the energy dissipated by the silent discharge in helium and argon can be estimated.[37] Table II shows the results of the calculation for each case of $V_d/V_i=$ 0.2 and 0.4.

TABLE II. CALCULATION RESULTS OF DISSIPATED ENERGY IN HELIUM AND ARGON (NORMALIZED TO THE CASE OF HELIUM)

| Kind of atmosphere | $V_d/V_i$ | Dissipated energy |
|---|---|---|
| He | 0.2 | 1 |
| Ar |  | 2.0 |
| He | 0.4 | 1 |
| Ar |  | 2.0 |

Next, let us estimate approximately in roentgen units the dose absorbed in helium and in argon. By combining $G(\mathrm{Fe}^{3+})=4.6$ with $Y(\mathrm{Fe}^{3+})=3.0\times 10^{-3}$ M in helium and $G(\mathrm{Fe}^{3+})=4.3$ with $Y(\mathrm{Fe}^{3+})=5.1\times 10^{-3}$ M in argon, it becomes possible to estimate them. In helium, the apparent dose rate equals about $3.8\times 10^6$ r./hr. and in argon to $7.2\times 10^6$ r./hr. These values, of course, vary with the value of the electric discharge current. This is the case of 1 mamp. The values also indicate the average integral dose absorbed by the aqueous solution in the apparatus used by the authors, where a solution with a volume of 10 ml. is used. The dose rate in argon is larger than that in helium and its ratio is about 1.9, which is almost consistent with the calculated result.

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[30] C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).

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

[32] The absorbed dose cannot be measured directly by the instruments connected in the circuit, since a part of it has been changed to heat or light. The extent of the real chemical utilization can best be measured by chemical dosimetry.

[33] M. Suzuki, "Ozonizer Handbook," Koronasha, Tokyo (1960), p. 232.

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

[35] M. Suzuki, *J. Electrochem. Soc. Japan* (*Denki Kagaku*), **24**, 354 (1956).

[36] This value was estimated approximately from a curve showing the relation between the applied voltage and the discharge current.

[37] The value of $A$ means the total energy dissipated per second by the silent discharge. The energy absorbed in a solution occupies only a small amount ($x$%) of $A$. Since it is impossible to estimate the value of $x$, the absolute value of $A$ is not so important. The value of the $A_{\mathrm{Ar}}/A_{\mathrm{He}}$ ratio, however, would be useful for us as a means to check the value of the absorbed dose as measured by the chemical dosimeter.