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Silent Discharge Reactions in Aqueous Solutions. III. Acidic Aqueous Solutions of Ferrous Sulfate and Ceric Sulfate in a Hydrogen Atmosphere*

By Akira YOKOHATA and Satoru TSUDA

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

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A study has been made of silent discharge reactions in aqueous solutions of ferrous sulfate and ceric sulfate acidified with sulfuric acid in a hydrogen atmosphere. The present study has confirmed that silent discharge leads to the formation of hydrogen peroxide from water molecules in a dilute sulfuric acid solution, the oxidation of ferrous ions to ferric ions, and the reduction of ceric ions to cerous ions. The same reactions were previously studied in inert gases. A satisfactory interpretation can be made of their mechanisms by taking into consideration the action on the solvent of slow electrons produced in the gaseous phase. In a hydrogen atmosphere, the yields of the foregoing reactions were very small when compared with those in the case of inert gases; however, a good linear correlation was observed between the yield and the duration time of discharge. From these results it has been concluded that the yields can be well interpreted by taking into consideration the action of active species of hydrogen generated in the gaseous phase on the radicals formed from liquid water, besides the action of slow electrons; moreover, the action of active species on the solute cannot be serious. The absorbed dose in the solution was estimated to be approximately 1.9×10^7 r./hr. from the relation of the dissipated energy calculated electrically to the absorbed dose.

In previous reports(1) it has been pointed out that (1) in a helium or argon atmosphere the chemical reactions in an aqueous solution of ferrous sulfate or ceric sulfate by silient discharge can be well interpreted by taking into consideration the actions on the solvent of slow electrons produced in the gaseous phase, and that (2) neither the effect of the metastable excited state of helium and argon nor that of luminescence can be serious, while the silent discharge reaction apparently corresponds to the radiolysis caused by a particle of high LET (linear energy transfer).

The foregoing conclusions were drawn from a study of silent discharge in helium and argon atmospheres. However, in the case of gases other than inert gases, the reaction mechanisms may become complicated, for the effect of active species,(2-7) besides that of slow electrons, should also be taken into consideration.

In the current study, hydrogen gas was used as an atmosphere: the effect of active species of hydrogen generated in the gaseous phase was investigated, and the results were compared with those obtained with inert gases.

In acidic aqueous solutions, the experimental results showed the formation of hydrogen peroxide, the oxidation of ferrous ions to ferric ions, and the reduction of ceric ions to cerous ions. The reaction mechanisms were complicated by the formation of active species of hydrogen in the gaseous phase. However, the results could be well interpreted in terms of the radiolysis of an aqueous solution under the active species of hydrogen.

Experimental

The discharge tube and the electrical circuit were identical to those previously reported. All the experiments were performed at a constant solution volume of 10 ml. The surface of the solution vibrated gently during the discharge. This may be useful in renewing the surface of the solution. All the experiments were conducted at about 20°C after the oxygen dissolved in the solution had been completely removed by bubbling hydrogen gas into the solution. A constant discharge current of 1 mamp. was employed in most of the experiments, letting hydrogen gas flow at a velocity of about 120 ml./min. through the gas space of the discharge tube. The water used was purified by the multiple distillation procedure described by Johnson and Allen.(8) The Merck guaranteed reagents ferrous sulfate and ceric sulfate were used without further treatment. As pure hydrogen gas (99.95%) provided the same results

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

2) S. Miyamoto, *J. Chem. Soc. Japan (Nippon Kagaku Kaishi)*, **55**, 611 (1934).

3) T. Davis, S. Gordon and E. J. Hart, *J. Am. Chem. Soc.*, **80**, 4487 (1958).

4) G. Czapski and G. Stein, *J. Phys. Chem.*, **63**, 850 (1959).

5) M. Schiavello and G. G. Volpi, *J, Chem. Phys.*, **37**, 1510 (1962).

6) G. Czapski and G. Stein, *Israel J. Chem.*, **2**, 15 (1964).

7) H. A. Kazmi and L. D. J. Roy, *Can. J. Chem.*, **42**, 1145 (1964).

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

as purified hydrogen gas, it was used without further purification in later experiments. The concentrations of sulfuric acid, ferrous sulfate and ceric sulfate solutions varied from 1.5 to 0.1 N, from 1×10^{-2} to 1×10^{-3} M and from 2×10^{-3} to 5×10^{-4} M respectively.

Results

In the gaseous phases, hardly any ozone or hydrogen peroxide was formed. Moreover, hardly any hydrogen sulfide was formed from the dilute aqueous solution of sulfuric acid.

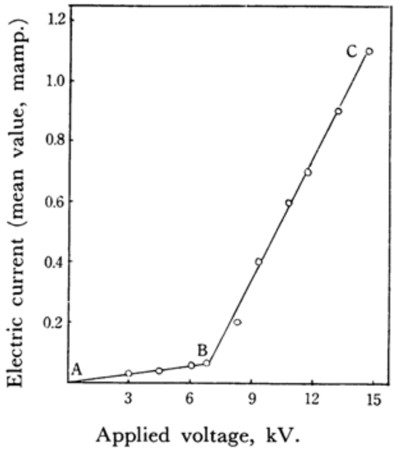

Fig. 1. Relation between applied voltage and electric current.

Figure 1 shows the relationship between the applied voltage and the electric current as measured by the method described in the previous report, where B is the firing voltage.

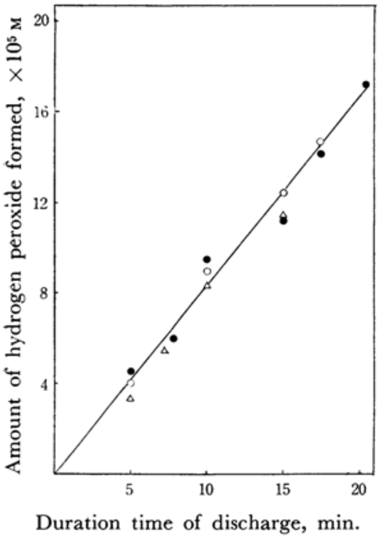

Fig. 2. Relationship between amount of hydrogen peroxide formed and duration time of discharge.
● 1.5 N H_2SO_4 ○ 0.8 N H_2SO_4
△ 0.1 N H_2SO_4

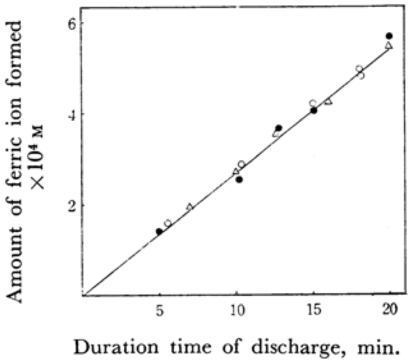

Fig. 3. Relationship between amount of ferric ion formed and duration time of discharge.
Initial concentration of ferric ion;
○ 1×10^{-3} M △ 5×10^{-3} M ● 1×10^{-2} M
H_2SO_4: 0.8 N

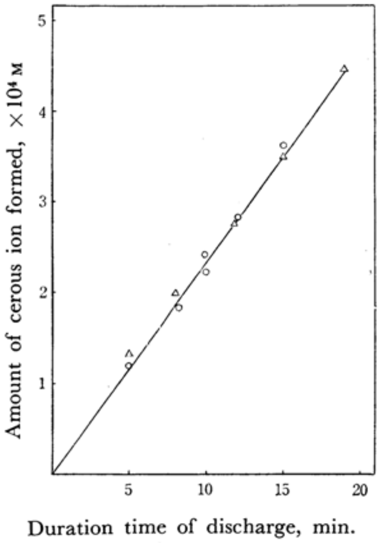

Fig. 4. Relationship between amount of cerous ion formed and duration time of discharge.
Initial concentration of ceric ion;
○ 5×10^{-4} M △ 2×10^{-3} M
0.8 N H_2SO_4

In a dilute aqueous solution of sulfuric acid, hydrogen peroxide appeared following the discharge. Also, in acidic solutions of ferrous sulfate and ceric sulfate, the oxidation of ferrous ions to ferric ions and the reduction of ceric ions to cerous ions were noted respectively. Figures 2, 3 and 4 show, respectively, the relationship between the amounts of hydrogen peroxide, ferric ion and cerous ion formed and the duration of the discharge. The results produced a good linear curve.

In the range from 0.1 N to 1.5 N of sulfuric acid, the yield of hydrogen peroxide was independent of the concentration of sulfuric acid. An independence of the solute concentration with relation to the yield was also found when the ferrous ion concentration ranged from 1×10^{-2} M to 1×10^{-3} M, and when that of ceric ions ranged from 2×10^{-3} M to 5×10^{-4} M.

The yield of each product was obtained as follows:

$$Y(H_2O_2) = 8.3\times10^{-5}\text{ M},\ Y(Fe^{3+}) = 2.7\times10^{-4}\text{ M},$$
$$Y(Ce^{3+}) = 2.3\times10^{-4}\text{ M}$$

where Y shows the yield with the discharge current at 1 mamp. and with the duration of discharge at 10 min. These yields were very small when compared with those in helium and argon.

These points will be discussed in detail later.

Discussion

The Estimation of the Absorbed Dose in the Aqueous Solution.—It is very important to determine the absorbed dose in silent discharge chemistry. However, the estimation of the absorbed dose has been little studied. In our previous reports, we pointed out that, in an inert gas atmosphere, it is possible to estimate the absorbed dose in silent discharge by chemical dosimetry. Furthermore, it was shown that Eq. 1 holds good:

$$A(\text{He})/A(\text{Ar}) = E(\text{He})/E(\text{Ar}) \tag{1}$$

where A is the value calculated by Eq. 3 from the standpoint of electrical engineering and gives the total energy dissipated per second by silent discharge. E gives the absorbed dose in the solution per second. Equation 1 shows that E is proportional to A and that the proportional constant is independent of the kind of gas, at least in the cases of helium and argon.

At the present stage, no adequate method is available to check experimentally whether Eq. 1 applies to other gases or not. However, in view of the fact that Eq. 1 holds good in helium and argon, despite the difference in such properties as the ionization potential, the mean free path, the firing voltage, and the absolute value of A, it may be said that Eq. 1 applies to other gases. If so, Eq. 2 can be obtained:

$$A(H_2)/A(X) \simeq E(H_2)/E(X) \tag{2}$$

where X is helium or argon. Since $A(H_2)$ and $A(X)$ can be calculated by Eq. 3 and since $E(X)$ is known, $E(H_2)$ can be determined from 2. In Eq. 3,[9] C_{die} and C_a depend on the shape of the discharge tube, while V_i and V_d depend on the kind of gas used under given experimental conditions.

$$A=\frac{f(C_{die}+C_a)(V_i+V_d)\{2E_m-(V_i+V_d)(1+C_a/C_{die})\}}{1+C_a/C_{die}} \tag{3}$$

where

f : the frequency of the electric source used
C_{die} : the total capacitance of the insulator
C_a : the capacitance due to the gap space in the 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

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.[10]

Under our experimental conditions, C_{die}= 180pF, C_a=36pF, V_i=1.3 kV. and E_m=15.4 kV. in helium, while V_i=6.9 kV. and E_m=19 kV. in hydrogen. By applying these values to Eq. 3, the ratio of the dissipated energy in helium and hydrogen may be estimated. Table I shows the calculated results when V_d/V_i=0.2 and 0.4. In this study the mean value for $A(H_2)/A(\text{He})$ was assumed to be 5. As E(He) is equal to 3.8×10^6 r./hr., $E(H_2)$ is estimated to be about 1.9×10^7 r./hr. This value, of course, varies with the value of the electric discharge current. Shown here are the values in the case of 1 mamp. This also gives the average integral dose absorbed by the aqueous solution in the apparatus used by the authors, where the volume of the solution is 10 ml.

TABLE I. CALCULATED RATIO OF $A(H_2)$ TO A(He)

V_d/V_i	$A(H_2)/A(\text{He})$
0.2	5.2
0.4	4.9

An Estimation of the Apparent LET.—In order to estimate theoretically the radical or molecular yield from the absorbed dose, it is necessary to ascertain the LET values of electrons produced in a hydrogen atmosphere by silent discharge.[11]

Generally speaking, in silent discharge at one atmospheric pressure, electrons have an energy distribution from just above zero to somewhat above the ionization potential of the gas in which the discharge occurs.[12]

In view of the fact[13] that the ionization potential of the hydrogen molecule is equal to 15.4 eV., that of argon, to 15.7 eV., and that of helium, to 24.5 eV., the LET values of electrons in a hydrogen atmosphere may closely resemble that in argon. Therefore, a value of about 8(eV./Å) was

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

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

[11] The G value depends on the LET value.

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

[13] K. Watanabe, T. Nakayama and J. Mottl, *J. Quant. Spectry. Radiation Transfer*, **2**, 369 (1962).

assumed for the LET value of electrons in hydrogen.[14]

The Formation of Hydrogen Peroxide.—The silent discharge reaction in a hydrogen atmosphere showed the formation of hydrogen peroxide from dilute aqueous solutions of sulfuric acid. As precursor of hydrogen peroxide, the hydroxyl radical has heretofore been proposed, but recent studies have also suggested contribution of the excited state of water.[15] Inasmuch as details of this new mechanism are yet to be elucidated, this remains a problem for future study. In this study an attempt will be made to explain the mechanism involved from the previously-proposed theory of the recombination reaction of hydroxyl radicals.

Two processes can be considered for the formation of hydroxyl radical, that is, the interaction of (a) water vapor and (b) liquid water, with slow electrons. As has been pointed out by Hart et al.,[3] however, the process a cannot be great in the presence of a large excess of molecular hydrogen. Therefore, the process b should be considered:

$$\text{lig.H}_2\text{O} \underset{\text{slow electron}}{\rightsquigarrow} \text{OH, H} \qquad (4)$$

$$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \qquad (5)$$

The estimated yield of hydrogen peroxide calculated on the basis of the absorbed dose and the $G\,(\text{H}_2\text{O}_2)$ value, $Y_{cal}(\text{H}_2\text{O}_2)$, should be about 4.4×10^{-3} M. In the experiment, however, the value of $Y\,(\text{H}_2\text{O}_2)$ was only 8.3×10^{-5} M. This discrepancy might be ascribed to the radiolysis of an aqueous solution under the active species of hydrogen. In silent discharge, the radicals from liquid water are formed mainly just below the surface, because the energy of the electrons is very small. Therefore, a scavenging action of active species of hydrogen on these radicals may be expected:

$$\text{H}_{\text{at}} + \text{OH} \rightarrow \text{R} \qquad (6)$$

$$\text{H}_{\text{at}} + \text{H} \rightarrow \text{S} \qquad (7)$$

where H_{at} is the active species of hydrogen (H, H^+, etc.) generated in the atmosphere. R and S are the reaction products (H_2O or H_2 is mainly expected respectively). Therefore, this scavenging reaction 6 should lead to a decreased yield of hydrogen peroxide. In fact, as will be shown later, the estimated yield of hydroxyl radicals and hydrogen atoms were both very small. This is suggestive evidence that reactions 6 and 7 should be considered.

Other cases can also be mentioned. First, the action of the hydroxyl radical on hydrogen molecules dissolved in the solution-reaction 8; second, the action of hydrogen atoms on hydrogen peroxide in the solution-reaction 9, and third, the action of active species of hydrogen in the gaseous phase on hydrogen peroxide-reaction 10.[16]

$$\text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O} \qquad (8)$$

$$\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH} \qquad (9)$$

$$\text{H}_{\text{at}} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH} \qquad (10)$$

These reactions lead to the formation of another radical, in company with the disappearance of one radical. As will be shown later, however, the $Y\,(\text{H})$ and $Y(\text{OH})$ estimated from the experiments on ferrous sulfate and ceric sulfate being very small, reactions 8, 9 and 10 may not be serious.

The Formation of Ferric Ions.—The estimated yield of ferric ions, calculated on the basis of the absorbed dose and the $G(\text{Fe}^{3+})$ value, $Y_{cal}(\text{Fe}^{3+})$ should be about 1.3×10^{-2} M. However, the experiment gave the value of $Y(\text{Fe}^{3+})$ to be only 2.7×10^{-4} M, with the solute concentration ranging from 1×10^{-2} M to 1×10^{-3} M.

In silent discharge, the mechanism of oxidizing ferrous ions to ferric ions in an acidic solution might be shown as follows:

$$\text{OH} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- \qquad (11)$$

$$\text{H} + \text{H}^+ + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{H}_2 \qquad (12)$$

$$\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH} + \text{OH}^- \qquad (13)$$

The yield of ferric ions, $Y(\text{Fe}^{3+})$, should, then, be expressed by Eq. 14:

$$Y(\text{Fe}^{3+}) = 2Y(\text{H}_2\text{O}_2) + Y(\text{H}) + Y(\text{OH}) \qquad (14)$$

Even if reaction 8 is caused by dissolved hydrogen molecules, the yield of ferric ions would be independent of 8, because one hydrogen atom and one hydroxyl radical oxidize one ferrous ion, and also one hydrogen atom obtained via 8 oxidizes one ferrous ion via 12. Therefore, with regard to the discrepancy between the observed yield and the calculated ferric ion yield, we must assign the reactions to reasons other than 8. Also, the value of $Y(\text{H}+\text{OH})$ estimated by 14, about 1×10^{-4} M, was very small when compared with the calculated value of about 4.4×10^{-3} M. This suggests that only a small part of the yield of hydrogen atoms and hydroxyl radicals expected theoretically from the radiolysis of water by slow electrons contributes to the oxidation of ferrous ions to ferric ions. The above facts are suggestive evidence which support reactions 6 and 7.

In addition, ferric ions produced via reactions 11—13 may be reduced by the active species generated in the gaseous phase:

$$\text{H}_{\text{at}} + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{H}^+ \qquad (15)$$

This reaction, however, may be not important in

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[14] Accordingly, the G value can be assigned as follows:
$G(\text{H})=0.7$, $G(\text{OH})=0.7$, $G(\text{H}_2\text{O}_2)=1.4$, $G(\text{Fe}^{3+})=4.2$, $G(\text{Ce}^{3+})=2.8$.

[15] M. Anbar, S. Guttmann and G. Stein, *J. Chem. Phys.*, **34**, 703 (1961).

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

the range of a good linear correlation between the yield and the duration of discharge.

The Formation of Cerous Ions.—The estimated yield of cerous ions, calculated on the basis of the absorbed dose and the $G(\mathrm{Ce}^{3+})$ value, should be about 8.9×10^{-3} M. However, the experiment gave a yield of only 2.3×10^{-4} M within the range from 2×10^{-3} M to 5×10^{-4} M in a solute concentration in a 0.8 N sulfuric acid solution. With regard to the discrepancy between the observed and calculated values, the following reasons might be mentioned.

In the case of gamma-ray irradiation and also silent discharge in an inert gas atmosphere, $Y(\mathrm{Ce}^{3+})$ can be expressed by Eq. 16.[1]

$$Y(\mathrm{Ce}^{3+}) = 2Y(\mathrm{H_2O_2}) + Y(\mathrm{H}) - Y(\mathrm{OH}) \qquad (16)$$

In a hydrogen atmosphere, if the active species of hydrogen act directly on the solute, a comparatively large increment in $Y(\mathrm{Ce}^{3+})$ may be expected when compared with the case of inert gas. The experimental value of $Y(\mathrm{Ce}^{3+})$, however, was very small, contrary to expectation. This suggests that the action of active species on the solute cannot be serious. Also, for the same reason, it might be said that the reaction of the hydrogen molecule on the hydroxyl radical (8) cannot be serious. Next, by combining Eq. 16 with 14, the values of $Y(\mathrm{H})$ and $Y(\mathrm{OH})$ can be separately estimated; that is, $Y(\mathrm{H})=8\times10^{-5}$ M and $Y(\mathrm{OH})=2\times10^{-5}$ M. Both values are very small when compared with the calculated values, $Y_{cal}(\mathrm{H})=2.2\times10^{-3}$ M and $Y_{cal}(\mathrm{OH})=2.2\times10^{-3}$ M. The above is also suggestive evidence for the adequacy of reactions 6 and 7.

It is our conclusion that the scavenging action of the active species of hydrogen on the hydroxyl radical and the hydrogen atom formed from liquid water by slow electrons plays an important role.