

# Solvated Electron Formed in Water by the Silent Electric Discharge in Argon Atmosphere

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Based on radiation chemistry of water a study on the chemical changes resulting from the silent electric discharge of aqueous solution under argon atmosphere was made for the purpose of elucidating the nature of the reducing species formed. In the neutral aqueous  $\text{ClCH}_2\text{COOH}$  system the effects of such additives as  $\text{CH}_3\text{OH}$  and  $\text{NO}_3^-$  on the yield of  $\text{Cl}^-$  and in the system containing  $\text{NO}_3^-$  the yield of  $\text{NO}_2^-$  were investigated. Moreover, in the alkaline aqueous  $\text{K}_3\text{Fe}(\text{CN})_6$  system emphasis was placed on the yield of aquocomplex. In view of the non-dependence of the yield of  $\text{Cl}^-$  on the concentration of additive  $\text{NO}_3^-$  and of the low yields of  $\text{NO}_2^-$  and  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  produced, it was concluded that in the silent electric discharge the yield of solvated electrons which react with solutes in the bulk of water is very small ( $G \leq 0.06$ ). Reasons for the low yield of solvated electrons are briefly described.

The chemical effects of silent electric discharge and those of high energy radiations have been demonstrated to be identical in many respects.<sup>1-4</sup> Silent electric discharge may be considered to be a peculiar particle-accelerator of low energy having the following characteristics.

(1) The electrons at one atmospheric pressure have an energy distribution from just above zero to a value slightly higher than the ionization potential of the gas in which the discharge occurs.<sup>5,6</sup>

(2) Relatively low voltages (10—15 kV) result in the high currents ( $\sim 1$  mA). From the point of view of total power, the dose rate can be expected to be considerably high.

Consistent with theoretical considerations, our recent studies<sup>4</sup> have proved that most of the reactions of aqueous solutions induced by the silent electric discharge in the inert gas atmospheres 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, reducing radical or hydroxyl radical.

The apparent dose rate under our experimental conditions was  $7.2 \times 10^6$  R/hr as reported previously<sup>4</sup>) and each primary  $G$  value of radicals was estimated as follows:

$$^sG(\text{Red}) = 0.6, \quad ^sG(\text{OH}) = 0.7 \quad (1)^{*1}$$

They were almost independent of pH within the experimental error. The content of  $^sG(\text{Red})=0.6$ , however, is yet unknown. The present investigation was undertaken to estimate the yield of solvated electrons. Neutral aqueous monochloroacetic acid and alkaline aqueous potassium ferricyanide solutions were both selected as the reaction systems suitable for this purpose.

## Experimental

The discharge tube and the electrical circuit used were identical with those previously described.<sup>4</sup>) A discharge tube of the ozonizer type (Fig. 1) was composed of two coaxial hard-glass tubes; the tin foil wrapped

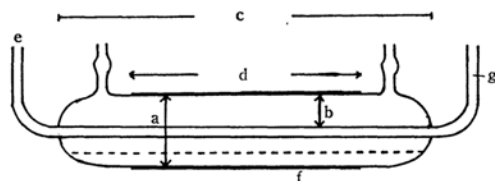


Fig. 1. Schematic diagram of discharge tube.

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

1) M. Freund and G. Földiák, *Erdöl und Kohle*, **10**, 758 (1957).

2) H. J. Pasman, J. C. Vlugter and C. J. Breukink, *Brennstoff-chemie*, **46**, 271 (1965).

3) Z. Paál and G. Földiák, "Radiation Chem. Proceedings of the 1962 Tihany Symposium," Akademiai Kiado, Budapest (1964), p. 445.

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

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

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

\*1 The symbol  $^sG$  means the effective  $G$  value in the silent electric discharge.  $^sG(\text{Red})$  means the  $^sG$  value of total reducing species.

around the outer was used as one electrode (f) and dilute sulfuric acid in the inner tube (g) as the other electrode (the high-tension side). After pouring the sample solution into the discharge tube, discharge was made by applying high tension to these two electrodes with argon flowing through the gas space of the discharge tube at a velocity of about 120 ml/min.

All experiments were made at a constant solution volume of 10 ml, at room temperature after removing the dissolved oxygen from the solution by bubbling argon gas into the solution, and at a constant discharge current of  $I=1$  mA.

The discharge tube was washed with a mixture of methylalcohol and a saturated aqueous solution of sodium hydroxide besides the usual cleaning solution, and dried by evacuation.

Gamma-ray irradiations were carried out using a 260 curie  $^{60}\text{Co}$  source. The dose rate ( $1.57 \times 10^5 \text{R/hr}$ ) was determined by the Fricke dosimeter, taking  $G(\text{Fe}^{3+}) = 15.5$ .

**Materials.** Reagents used were of the reagent grade. Argon gas (pyrity: 99.998%) was used without further procedure. Triply-distilled water was used in all the runs.

**Analysis.** Microquantities of chloride were determined by the turbidimetric method.<sup>7)</sup> The turbidity was measured at 350 m $\mu$  with a spectrophotometer. Nitrite ions were determined colorimetrically at 540 m $\mu$ .<sup>8)</sup>

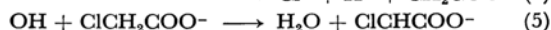
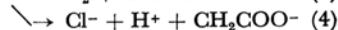
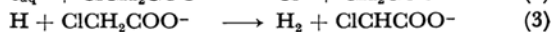
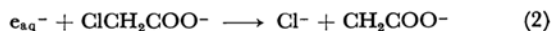
The aquopentacyanide ion,  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ , was determined spectrophotometrically by the method using  $\text{NaN}_3$ .<sup>9,10)</sup> A calibration curve was obtained by the following procedure:  $\text{Na}_3\text{Fe}(\text{CN})_5\text{OH}_2$  was prepared according to the method of Hofmann<sup>11)</sup> and was purified by passing through an alumina chromatographic column and eluting with water. Its content in the eluted solution was determined by the ceric titration. An aliquot (2 ml) of the solution containing the various amounts of  $\text{Na}_3\text{Fe}(\text{CN})_5\text{OH}_2$  was pipetted in a 10 ml-volumetric flask to which 0.3 M  $\text{CH}_3\text{COOH}$ -0.3 M  $\text{NaN}_3$  was added, and after 15–20 min the optical density at 560 m $\mu$  was measured. The molecular extinction coefficient thus obtained was  $1.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at pH 4–6. The presence of  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{CN})_6^{3-}$  did not interfere with this measurement.

## Results and Discussion

### Neutral Monochloroacetic Acid Solution.

It is well known<sup>12)</sup> that in the field of  $\gamma$ -radiolysis the formation of inorganic chloride on irradiation of deaerated solution of  $\text{ClCH}_2\text{COOH}$  is a result of reaction of the reducing species (mainly  $e_{aq}^-$ )

with the solute. The reaction of OH radicals has been believed to result in dehydrogenation rather than dechlorination. The H-radicals among the reducing species induce principally the hydrogen abstraction reaction with a small possibility of dechlorination.<sup>13)</sup> The reaction mechanism is shown as follows.



The silent electric discharge also leads to the formation of inorganic chloride. Figure 2 shows the relationship between the yield and the duration of discharge, in which a good linear correlation can be seen. The yield of  $\text{Cl}^-$  was independent of the solute concentration in the range from  $1 \times 10^{-3}$  to  $1 \times 10^{-2} \text{ M}$  (pH=6.5).

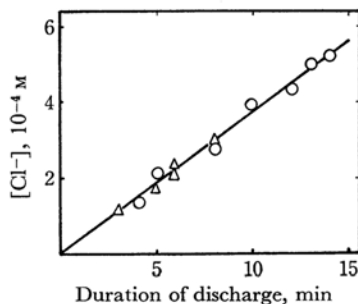


Fig. 2. Silent electric discharge of neutral aqueous solution of  $\text{ClCH}_2\text{COOH}$ .

○, 0.01 M  $\text{ClCH}_2\text{COOH}$

△, 0.001 M  $\text{ClCH}_2\text{COOH}$

If the above-mentioned mechanism can be accepted and reaction (4) can be ignored because  $k_4=0.09$   $k_3$ ,<sup>13)</sup> the yield of  $e_{aq}^-$  should equal the yield of  $\text{Cl}^-$ . Our recent work, however, showed the formation of inorganic chloride in a considerable amount even under the experimental conditions in which reaction (2) could not be expected to

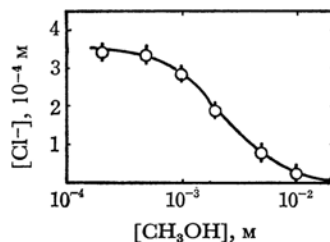


Fig. 3. Effect of  $\text{CH}_3\text{OH}$  on  $\text{Cl}^-$  yield in the silent electric discharge of neutral aqueous solution of  $\text{ClCH}_2\text{COOH}$  ( $1 \times 10^{-2} \text{ M}$ ).

7) E. N. Luce, E. C. Denice and F. E. Akerlund, *Ind. Eng. Chem.*, **15**, 365 (1943).

8) T. Rigg, G. Scholes and J. Weiss, *J. Chem. Soc.*, **1952**, 3034.

9) O. Baudisch, *Ber.*, **62**, 2706 (1929).

10) S. Ohno, *This Bulletin*, **40**, 1765 (1967).

11) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie" Ferdinand Enke Verlag, Stuttgart (1954), 1363.

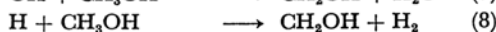
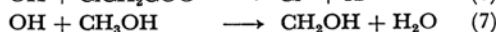
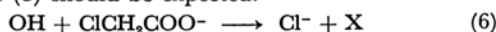
12) E. Hayon and A. O. Allen, *J. Phys. Chem.*, **65**, 2181 (1961).

13) J. Jortner and J. Rabani, *J. Am. Chem. Soc.*, **83**, 4868 (1961); *J. Phys. Chem.*, **66**, 2078, 2081 (1962).

occur.\*<sup>2</sup> This finding is noteworthy in that the possibility of dechlorination reaction due to OH is suggested. Thus, a more detailed experiment was undertaken.

Figure 3 shows the effect of additive CH<sub>3</sub>OH on the yield of Cl<sup>-</sup> obtained by the silent electric discharge with discharge current at 1 mA and duration at 10 min. It is of great interest that there was a strong suppressive effect of CH<sub>3</sub>OH.

When [CH<sub>3</sub>OH]/[ClCH<sub>2</sub>COOH] < 2, CH<sub>3</sub>OH cannot compete with the ClCH<sub>2</sub>COO<sup>-</sup> for e<sub>aq</sub><sup>-</sup>, because the rate constant of reaction of e<sub>aq</sub><sup>-</sup> with ClCH<sub>2</sub>COO<sup>-</sup>,  $k_2 = 3.8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ ,<sup>14</sup> is much larger than that with CH<sub>3</sub>OH,  $k_{e_{aq}^- + \text{CH}_3\text{OH}} < 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ .<sup>15</sup> These findings lead to the possibility that in the case of silent electric discharge the radicals (*i. e.* OH, H) to be scavenged by CH<sub>3</sub>OH play an important role in the formation of Cl<sup>-</sup>. Thus, the competition of (6) with (7) and of (4) with (8) should be expected.



where X means the reaction product. However, since the yield of Cl<sup>-</sup> observed ( $^*G(\text{Cl}^-) = 0.3$ ) is much larger than the yield expected ( $^*G(\text{Cl}^-) = 0.06$ ) to be produced *via* reaction (4) on the basis of  $^*G(\text{Red}) = 0.6$  and  $k_4 = 0.09 k_3$  the contribution of hydrogen atom may not be considered to be significant. Thus, the possibility of (6) is strongly suggested.

If the occurrence of reaction (6) is possible, the considerable yield of Cl<sup>-</sup> should be expected even by the addition of electron scavengers such as NO<sub>3</sub><sup>-</sup>. Indeed, as shown later, experiments of  $\gamma$ -ray irradiation came up to our expectation. This residual amount is too much to be expected from H atoms and can be suppressed almost completely by the addition of 0.1M CH<sub>3</sub>OH. These findings tend to confirm the possibility of the occurrence of reaction (6).

Our study provides further evidence that Cl<sup>-</sup> can be formed by the reaction of the Fenton reagent with ClCH<sub>2</sub>COOH but also be suppressed by the addition of CH<sub>3</sub>OH.

In the absence of electron scavenger, however, there was hardly any effect of additive CH<sub>3</sub>OH on the  $\gamma$ -radiolysis. This suggests that reaction (6) is important only in little or no presence of e<sub>aq</sub><sup>-</sup>. In the present stage, the reaction scheme must await further study.\*<sup>3</sup> In any event, the main

point here is that most of Cl<sup>-</sup> produced by the silent electric discharge is due to the reaction of the active species (mainly OH) other than e<sub>aq</sub><sup>-</sup> with ClCH<sub>2</sub>COO<sup>-</sup>.

**Effect of Nitrate Ions Added in the ClCH<sub>2</sub>-COOH System.** Figure 4 shows the effect of NO<sub>3</sub><sup>-</sup> on the yield of Cl<sup>-</sup> and NO<sub>2</sub><sup>-</sup> in the  $\gamma$ -irradiated solution of 0.01M ClCH<sub>2</sub>COOH (deaerated, pH 6.5). The increment in NO<sub>2</sub><sup>-</sup> yield and the decrement in Cl<sup>-</sup> yield with an increasing NO<sub>3</sub><sup>-</sup> concentration suggest the competition of (2) with (9), followed by (10) and (11).<sup>16</sup>

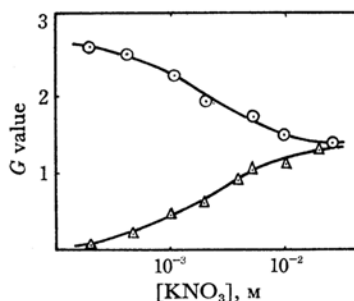
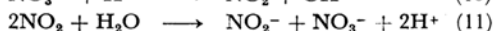
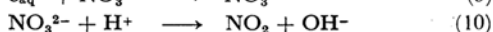


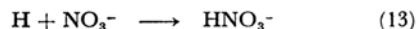
Fig. 4. Effect of KNO<sub>3</sub> on  $G(\text{Cl}^-)$  and  $G(\text{NO}_2^-)$  in  $\gamma$ -radiolysis of neutral aqueous solution of ClCH<sub>2</sub>COOH ( $1 \times 10^{-2} \text{ M}$ ).

○,  $G(\text{Cl}^-)$     △,  $G(\text{NO}_2^-)$

If above mechanism is accepted, Eq. (12) can be derived in the presence of sufficient amount of NO<sub>3</sub><sup>-</sup> to scavenge all of e<sub>aq</sub><sup>-</sup>.

$$G(\text{NO}_2^-) = 0.5 G(e_{aq}^-) \quad (12)$$

Reaction (13) might be also expected, since  $k_{\text{H} + \text{NO}_3^-} \approx 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ <sup>17</sup> and  $k_{\text{H} + \text{ClCH}_2\text{COO}^-} = 1.9 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ <sup>18</sup>.



However, as the yield of NO<sub>2</sub><sup>-</sup> below pH 3 where a considerable amount of H could be expected by the reaction of e<sub>aq</sub><sup>-</sup> with H<sup>+</sup> was negligibly small, HNO<sub>3</sub><sup>-</sup> disappears probably through the reactions with solute or intermediates to yield products other than NO<sub>2</sub><sup>-</sup>.

If, as discussed above, NO<sub>2</sub><sup>-</sup> is produced *via* reactions (9)–(11), a simple competition of (2) with (9) leads to Eq. (14).

$$\frac{1}{G(\text{NO}_2^-)} = \frac{2}{G(e_{aq}^-)} + \frac{2}{G(e_{aq}^-)} \frac{k_2[\text{ClCH}_2\text{COO}^-]}{k_9[\text{NO}_3^-]} \quad (14)$$

16) J. T. Allan, *J. Phys. Chem.*, **68**, 2697 (1964).

17) T. J. Sworski, "Proceedings of the Fifth Informal Conference on the Radiation Chemistry of Water," Univ. of Notre Dame, Indiana (1966), p. 28.

18) M. G. Scholes and M. Simic, *J. Phys. Chem.*, **68**, 1738 (1964).

\*<sup>2</sup> Presented at the 21th Annual Meeting of the Chemical Society of Japan, Osaka, March, 1968.

14) D. M. Brown, F. S. Dainton, J. P. Keene and D. C. Walker, *Proc. Chem. Soc.*, **1964**, 266.

15) E. J. Hart, J. K. Thomas and S. Gordon, *Radiation Res. Suppl.*, **4**, 74 (1964).

\*<sup>3</sup> The rate constant of (6) and additional details will be considered in a publication of the radiolysis of the system containing CH<sub>3</sub>OH and N<sub>2</sub>O.

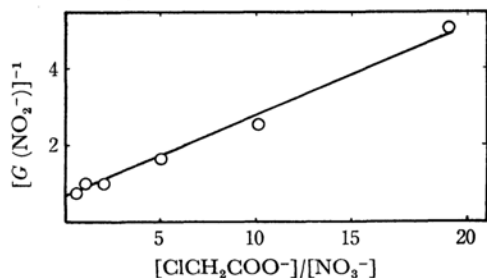


Fig. 5. A plot of  $1/G(\text{NO}_2^-)$  against  $[\text{ClCH}_2\text{COO}^-]/[\text{NO}_3^-]$  (Eq. (14)).

In Fig. 5  $1/G(\text{NO}_2^-)$  is plotted against  $[\text{ClCH}_2\text{COO}^-]/[\text{NO}_3^-]$ . A straight line in Fig. 5 supports the validity of the simple competition mentioned above. Thus,  $k_2/k_9=0.15$  can be estimated by using a value of  $G(e_{aq}^-)=2.8$ .  $K_9=1.1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ <sup>19</sup> gives  $k_2=1.7 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ , which is almost consistent with other workers (3.8 or  $1.2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ ).<sup>14,20</sup>

On the other hand, nitrite ion was also formed in the silent electric discharge. Figure 6 shows the relationship between the yield of  $\text{NO}_2^-$  and duration of discharge for aqueous solution of  $0.01 \text{ M ClCH}_2\text{COO}^- + 0.1 \text{ M NO}_3^-$  (pH=6.5). Figure 7 shows the dependence of the yield of  $\text{Cl}^-$  and  $\text{NO}_2^-$  on

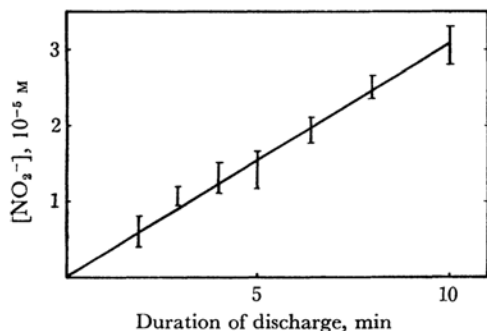


Fig. 6. Silent electric discharge of neutral aqueous solution of  $0.01 \text{ M ClCH}_2\text{COOH} + 0.1 \text{ M KNO}_3$ .

the  $\text{NO}_3^-$  concentration. A linear curve in Fig. 6 gives  $^*G(\text{NO}_2^-) \approx 0.03$ , which is very small when compared with  $^*G(\text{Red})=0.6$ . Because  $k_2/k_9=0.15$ , most of the  $e_{aq}^-$  should react with  $\text{NO}_3^-$  to yield  $\text{NO}_2^-$  in the experimental conditions where  $[\text{ClCH}_2\text{COO}^-]/[\text{NO}_3^-] < 0.1$ . Of course, H atoms may make a small contribution to this yield. Thus  $^*G(e_{aq}^-)$  estimated by Eq. (12) gives the maximum value.

$$^*G(e_{aq}^-) \leq 0.06 \quad (15)$$

Non-dependence of the yield of  $\text{Cl}^-$  on the additive  $\text{NO}_3^-$  known as a strong electron scavenger (Fig. 7) is of interest. It is one of other evidences

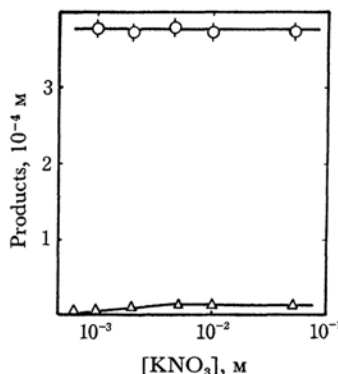


Fig. 7. Dependency of yields of  $\text{Cl}^-$  and  $\text{NO}_2^-$  on  $[\text{NO}_3^-]$  in the silent electric discharge. Initial concentration of  $\text{ClCH}_2\text{COOH}$ ,  $1 \times 10^{-2} \text{ M}$  (pH=6.5)

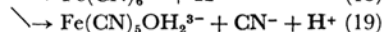
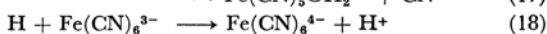
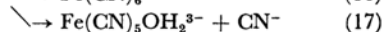
○,  $\text{Cl}^-$     △,  $\text{NO}_2^-$

that in the silent electric discharge the yield of the solvated electrons can be concluded to be very small.

#### Alkaline Aqueous Solution of Potassium Ferricyanide.

In order to secure a further evidence on the yield of solvated electrons, a study was extended to another system,  $\text{K}_3\text{Fe}(\text{CN})_6$ - $0.1 \text{ N NaOH}$  solution. In this system the attention was directed toward the reaction of  $e_{aq}^-$  to  $\text{Fe}(\text{CN})_6^{3-}$ .

It has been recently reported by Haïssinsky *et al.*<sup>21</sup> that aquopentacyanide is formed *via* following competitive reaction.



More recently, Burchill *et al.*<sup>22</sup> reported that the product which gives a colored complex with nitroso-benzene ( $\text{Fe}(\text{CN})_5\text{PhNO}^{3-}$ ) is diminished by the presence of oxygen or  $\text{N}_2\text{O}$ , and therefore the product may be formed by Eq. (17). On the other hand, the formation of aquopentacyanide was also confirmed<sup>23</sup> by using  $\text{NaN}_3$  instead of nitroso-benzene.

In the present work, the  $\text{NaN}_3$  method was applied for the determination of the solvated electrons formed by the silent electric discharge.

In the silent electric discharge,<sup>24</sup> the product which gives a colored complex with  $\text{NaN}_3$  was also found. Figure 8 shows that the relation of the yield of product to the duration of discharge is linear

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

22) C. E. Burchill, F. S. Dainton and D. Smithies, *Trans. Faraday Soc.*, **63**, 932 (1967).

23) S. Ohno and G. Tsuchihashi, *Radioisotopes (Japan)*, **16**, 434 (1967).

24) The disappearance of ferricyanide ions has been reported<sup>4)</sup> to be  $^*G(-\text{Fe}(\text{CN})_6^{3-})=2.8$ .

19) J. K. Thomas, S. Gordon and E. J. Hart, *ibid.*, **68**, 1524 (1964).

20) M. Anbar and E. J. Hart, *ibid.*, **69**, 271 (1965).

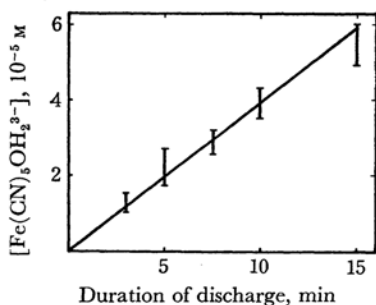


Fig. 8. Silent electric discharge of alkaline aqueous solution of  $5 \times 10^{-3} \text{ M Fe(CN)}_6^{3-}$  (0.1N NaOH).

and that the yield is independent of the concentration in the range from  $5 \times 10^{-3} \text{ M}$  to  $1 \times 10^{-2} \text{ M Fe(CN)}_6^{3-}$  within the experimental error. Then the  $^sG$  value of the product can be estimated to be about 0.03.

In clarifying the relation between  $G(e_{aq}^-)$  and the  $G$  value of the product, the  $\gamma$ -ray experiment of the deaerated system was done in the same concentration range. The yield of the product ( $G(\text{Fe(CN)}_5\text{OH}_2^{3-}) = 1.4$ ) was almost independent of the concentration in the range from  $5 \times 10^{-3} \text{ M}$  to  $1 \times 10^{-2} \text{ M Fe(CN)}_6^{3-}$  and larger than the yield in lower concentration.\*<sup>5</sup>

On the other hand, the strong suppressive effect of  $\text{N}_2\text{O}$  on the yield of the product was also confirmed in this experiment (Fig. 9). Thus, there seems to be no doubt that the product originates mostly from the reaction of  $e_{aq}^-$  with  $\text{Fe(CN)}_6^{3-}$ .

Therefore, in the range from  $5 \times 10^{-3} \text{ M}$  to  $1 \times 10^{-2} \text{ M Fe(CN)}_6^{3-}$ , Eq. (20) can be obtained by using a value of  $G(e_{aq}^-) = 2.8$ .

$$G(e_{aq}^-) \approx 2G(\text{Fe(CN)}_5\text{OH}_2^{3-}) \quad (20)$$

By applying the yield of the product obtained in the silent electric discharge ( $^sG(\text{Fe(CN)}_5\text{OH}_2^{3-}) = 0.03$ ) to Eq. (20),  $^sG(e_{aq}^-)$  can be estimated to be about 0.06. A part of the yield, however, might be due to the H atom. Thus, this gives a maximum value.

$$^sG(e_{aq}^-) \lesssim 0.06 \quad (21)$$

**General Discussion.** In the case of the silent electric discharge clusters of intermediates will be formed densely on the surface of water by the impact of low energy particles (mainly  $e^-$ ). In the clusters, the primary main product will be an excited water molecule since the energy of the electron is most probably less than the ionization

\*<sup>5</sup> We confirmed that at a relatively low concentration of  $\text{Fe(CN)}_6^{3-}$  (e.g.  $5 \times 10^{-4} \text{ M}$ ), the yield of the product which gives a coloured complex with  $\text{NaN}_3$  ( $G(\text{Fe(CN)}_5\text{OH}_2^{3-}) = 0.5$ ) is approximately consistent with that<sup>22)</sup> of nitrosobenzene method, and that the product has a dependency on the concentration of  $\text{Fe(CN)}_6^{3-}$  as pointed out by Haissinsky.

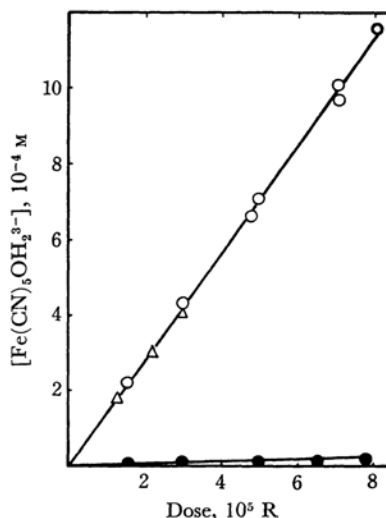


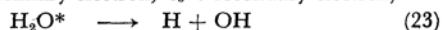
Fig. 9.  $\gamma$ -Ray radiolysis of alkaline aqueous solution of  $\text{K}_3\text{Fe(CN)}_6$  (0.1N NaOH).

○,  $5 \times 10^{-3} \text{ M Fe(CN)}_6^{3-}$   
 △,  $1 \times 10^{-2} \text{ M Fe(CN)}_6^{3-}$   
 ●,  $5 \times 10^{-3} \text{ M Fe(CN)}_6^{3-} + 2 \times 10^{-2} \text{ M N}_2\text{O}$

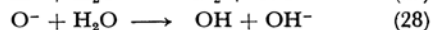
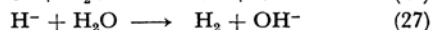
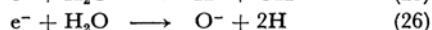
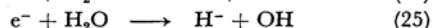
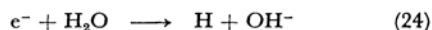
potential of water molecule. Thus the main reducing species produced from radiolysis by the silent electric discharge can be considered to be hydrogen atom formed mainly through the excitation of water molecule:



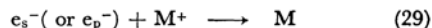
( $e_p^-$ : primary electron,  $e_s^-$ : secondary electron)



In addition, the formation of negative ions would be also naturally expected<sup>24)</sup> although they ( $\text{H}^-$  and  $\text{O}^-$ ) would disappear *via* reactions (27) and (28).



A part of the primary or secondary electrons might also probably disappear *via* neutralization reaction with the positive ions  $\text{M}^+$  ( $\text{Ar}^+$ , etc.) on the surface of water:



Of course, a part of them might be also solvated to give  $e_{aq}^-$ , but most of the solvated electrons produced are expected to combine *via* reaction (30) before they escape from the clusters of intermediates to react with the solute in the bulk.



The foregoing, although speculative, may provide an adequate explanation for the small yield of

24) M. Burton, "Comparative Effect of Radiation," John Wiley & Sons, New York (1960), p. 152.

the solvated electron in the bulk of water.

In the present stage, however, it is very difficult to discuss quantitatively the fate of slow electrons.

It is our conclusion that in the silent electric discharge the yield of solvated electrons which react with solutes in bulk of water is very small ( $G \leq 0.06$ ).

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