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Silent Discharge Reactions in Aqueous Solutions. VI. Aqueous Solution of Chloralhydrate in Atmospheres of Helium and Argon[*1]

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Although most of the reaction systems hitherto treated are limited to acidic solutions in the series of this present research, this work has been extended to neutral solutions. Silent discharge leads to production of hydrochloric acid from neutral aqueous chloralhydrate. A linear correlation was observed between yield of hydrochloric acid and electric discharge current. This finding has been successfully interpreted in terms of absorbed dose, the value of which can be estimated at a given electric discharge current. Yields of hydrochloric acid were not significantly affected by chloralhydrate concentration between 1×10^{-2} M and 1×10^{-3} M. The experiments of the radical scavenging effect of cupric ion and bromide ion showed that $K_{H+Cu^{2+}}/K_{H+CCl_3CH(OH)_2}\approx0.2$ and $K_{OH+Br^-}/K_{OH+CCl_3CH(OH)_2}\approx9$, and also that the following formula holds approximately irrespective of kind of gas used in low solute concentration and dose rate used in this work: values of hydrogen atom $G(\mathrm{HCl})\simeq3G(\mathrm{OH})+G(\mathrm{H})$. Moreover, these findings also suggested that the G values of and hydroxyl radical obtained in the acidic aqueous solution can be applied approximately to the neutral region. The relation of G(HCl) to solute concentration was qualitatively identical to gamma-ray irradiation, although they are different in detail because of the difference in value of LET and in the mechanism of radical formation.

In 1950 Andrews[1] reported that aqueous chloralhydrate was decomposed by X-rays to yield hydrochloric acid and other products. The acid yield was found to be linear with radiation dose and to increase by increasing the initial chloralhydrate concentration, but was reported to be independent of dose rate. With gamma-ray irradiation Freeman[2] observed essentially the same results as Andrews except that the acid yield was found to be dependent on (dose rate)$^{-1/2}$. Platford[3] used beta rays and compared the results with those from gamma-rays. Their results showed that no great difference existed between beta-ray radiolysis and gamma-ray radiolysis of aqueous chloralhydrate and that the decomposition reaction was proceeded by a chain mechanism. Kondo[4] suggested that hydroxyl radical may be important as chain initiators. The same free radical mechanism has been also suggested by McIntosh.[5]

In the present work, silent discharge reactions of neutral aqueous solution of chloralhydrate in the atmospheres of helium and argon were investigated, and compared with the results obtained by gamma rays irradiation.

Through the studies of acidic aqueous solutions[6] the authors reported that silent discharge reactions can be well interpreted in terms of the radiolysis caused by slow electrons generated in the atmosphere. If our interpretation is correct, decomposition of chloralhydrate should be naturally expected in neutral aqueous solution.

The results showed that chloralhydrate was decomposed by silent discharge to yield hydrochloric acid. It has been elucidated through experiments of radical scavengers that radicals produced from water by slow electrons play an important role in the formation of hydrochloric acid. In view of the G value of hydrochloric acid obtained by silent discharge reaction and of the effects of solute concentration and additives on that of hydrochloric acid, it has been also confirmed that the reaction mechanisms can be interpreted satisfactorily in terms of the radiolysis of water by slow electrons.

Experimental

The discharge tube and the electrical circuit used were identical with those previously reported. In this series a discharge tube of the ozonizer type was used.

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

[1] H. L. Andrews and P. A. Shore, *J. Chem. Phys.*, **18**, 1165 (1950).

[2] G. R. Freeman, A. B. Van Gleave and J. W. T. Spinks, *Can. J. Chem.*, **32**, 322 (1954).

[3] R. F. Platford and J. W. T. Spinks, *ibid.*, **37**, 1022 (1959).

[4] Y. Murata, I. Tachikawa and M. Kondo, *Dōitai to Hoshasen (Isotopes and Radiation)*, **2**, 200 (1959).

[5] R. G. McIntosh, R. L. Eager and J. W. T. Spinks, *Can. J. Chem.*, **42**, 2033 (1964); **43**, 3490 (1965).

[6] A. Yokohata and S. Tsuda, This Bulletin, **39**, 46, 53, 1636 (1966); **40**, 294 (1967).

After the dissolved oxygen in the solution was completely excluded by the method previously described, silent discharge was made in the state of gas flow. All experiments were made at a constant solution volume of 10 m*l* and at a constant discharge current of $I=1$ mA, unless otherwise stated.

In silent discharge in helium and argon, each apparent dose rate was 3.8×10^6 R/hr and 7.2×10^6 R/hr as previously determined.[6)]

Gamma-ray irradiations were carried out with cobalt-60 of 260 curie. The dose-rate (1.2×10^5/hr) was determined by a Fricke dosimeter, with $G(\mathrm{Fe}^{3+})=15.5$.

All reagents used were of the reagent grade. Helium (purity: >99.995) and argon (purity: >99.998) were used without further procedure. The water used was triply distilled.

Reactions were followed by titration of the acid produced on irradiation or silent discharge. The samples were titrated with 10^{-2} M sodium hydroxide solution from a microburette. Irradiated or discharged solutions were titrated to the same color as non-irradiated or non-discharged blank using bromophenol blue as an indicator. Sometimes chloride ions were determined by measuring the turbidity of silver chloride suspensions formed when a silver salt was added to an analyzed solution in 50% ethanol.[7)] It was confirmed that the discrepancy between acidimetry and turbidimetry was very small. All experiments were made at room temperature.

Results

Figure 1 shows the relation between the quantity of hydrochloric acid produced and dose under the gamma dose rate of 1.2×10^5 R/hr. As is well known, the dependency of solute concentration was observed.

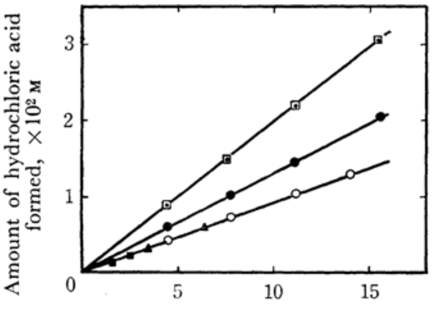

Fig. 1. Relationship between amount of hydrochloric acid formed and dose of gamma-rays.
Dose rate 1.2×10^5 R/hr
Initial concentration of chloralhydrate:

■ 1×10^{-3} M	▲ 5×10^{-3} M
○ 1×10^{-2} M	● 1×10^{-1} M
⊡ 1 M	

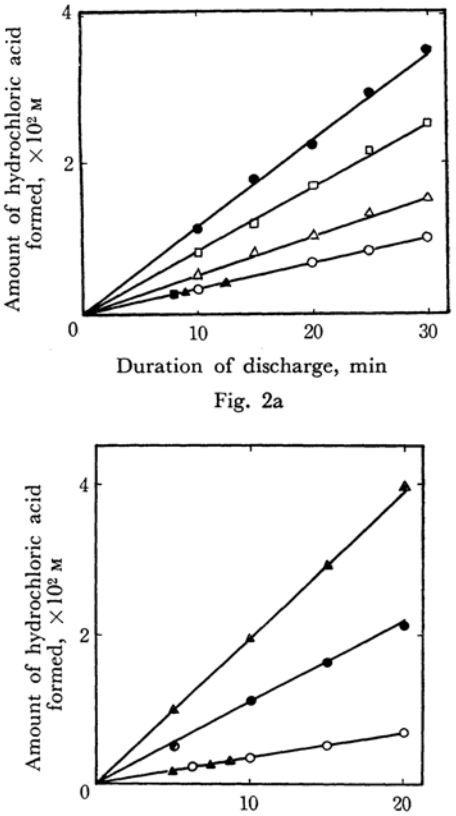

Fig. 2a

Fig. 2b

Fig. 2. Relationship between amount of hydrochloric acid formed and duration of discharge.
Initial concentration of chloralhydrate:

■ 1×10^{-3} M	▲ 5×10^{-3} M
○ 1×10^{-2} M	△ 2×10^{-2} M
□ 5×10^{-2} M	● 1×10^{-1} M
◬ 4×10^{-1} M	
a Case of helium	b Case of argon

Figures 2a and 2b show the relation between the quantity of hydrochloric acid produced and duration of discharge. In each case the results produced a good linear curve. In silent discharge, the effects of solute concentration were also seen.

Figure 3 summarizes the relation between the G value of hydrochloric acid and solute concentration. Since the apparent dose rates are already known in atmospheres of helium and argon, the G value of hydrochloric acid can be easily estimated. The choice of variables, $G(\mathrm{HCl})$ *vs.* log(concentration of chloralhydrate) was convenient in expanding the scale at low concentrations.

The results show that the situation of silent discharge reactions is identical to gamma irradiations. Figures 4a and 4b show the relation between the quantity of hydrochloric acid produced and electric discharge current, where the initial concentration of chloralhydrate is 5×10^{-3} M and duration

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

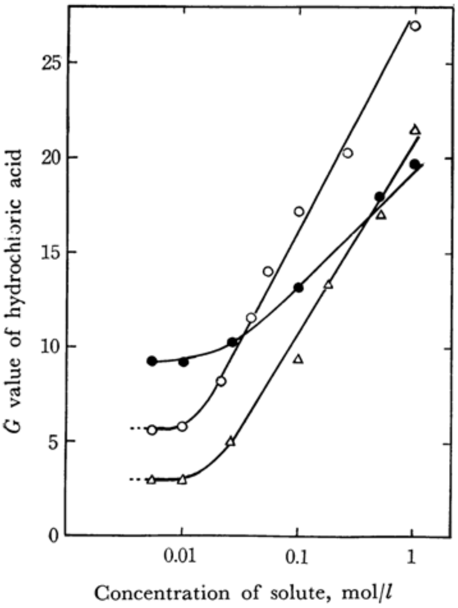

Fig. 3. The dependence of G(HCl) on the solute concentration.

● Gamma irradiation
○ Silent discharge in helium
△ Silent discharge in argon

of discharge is 10 min. In each case a linear correlation was found. Strictly speaking, however, the absorbed dose should be taken into consideration rather than the electric discharge current. This problem will be discussed later.

The Effect of Additive. To our knowledge, hardly any study has been made on the effects of additive in this system. In order to determine the behavior of radicals, potassium bromide and cupric sulfate were used as the scavenger of radicals. Bromide ion is effective for scavenging hydroxyl radical and cupric ion for reducing species. The effects of these additives are shown in Figs. 5 and 6.

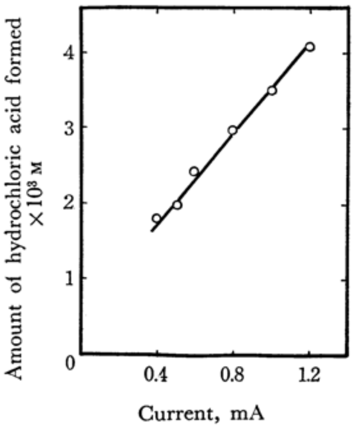

Fig. 4a

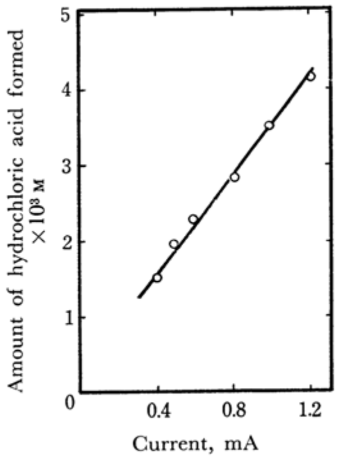

Fig. 4b

Fig. 4. Relationship between amount of hydrochloric acid formed and discharge current.
a Case of helium b Case of argon

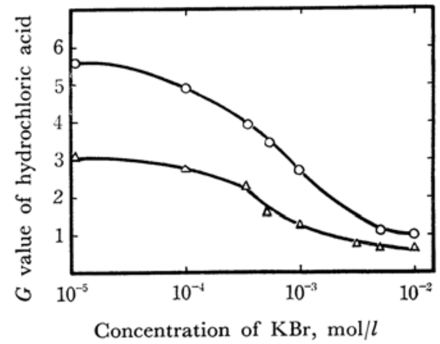

Fig. 5. Scavenging effect of potassium bromide. Initial concentration of chloralhydrate: 5×10^{-3} M
○ Helium △ Argon

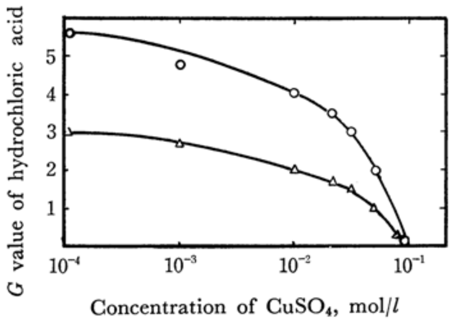

Fig. 6. Scavenging effect of cupric sulfate. Initial concentration of chloralhydrate: 5×10^{-3} M
○ Helium △ Argon

Discussion

The Effect of Electric Discharge Current. As described previously,⁶⁾ energy A dissipated per second by silent discharge is given by the following formula.8)

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

where the values of C_{die}, *etc.* have been known in our experimental condition. By applying the maximum voltage (E_m) for each electric current to Eq. (1), it can be estimated. Table 1 shows the relation between the maximum value of applied voltage and electric discharge current.

TABLE 1. RELATION BETWEEN ELECTRIC DISCHARGE CURRENT AND THE MAXIMUM VALUE OF APPLIED VOLTAGE

I mA	E_m, kV	
	Helium	Argon
0.4	7.3	9.1
0.6	9.8	12.3
0.8	12.6	15.1
1.0	15.4	17.2

Based on the findings that the ratio of dissipated energy A to absorbed dose E is constant and the apparent dose rate under 1 mA of electric discharge current is 3.8×10^6 R/hr in helium and 7.2×10^6 R/hr in argon,6) the absorbed doses at a given electric discharge current can be calculated using Eq. (1). Thus, it has become possible to arrange the effect of electric discharge current in terms of absorbed dose. Table 2 shows the relation between electric discharge current and absorbed dose. The relatively good proportional correlation can be found.

TABLE 2. RELATION BETWEEN ELECTRIC DISCHARGE CURRENT AND ABSORBED DOSE

I mA	Absorbed dose, 10^5R	
	Helium	Argon
0.4	2.7	5.6
0.6	3.8	8.1
0.8	5.1	10
1.0	6.3	12

The Effects of Solute Concentration. As shown in Figs. 2a and 2b, the dependency of G value of hydrochloric acid on solute concentration was observed also in this work, while it is independent in the range less than 0.01 M. The trend of the curve is similar to that obtained with gamma-ray irradiation. The absolute G values, however, are different from each other; for gamma-ray irradiations (1.2×10^5 R/hr) $G=9.0$; for silent discharge in helium (3.8×10^6 R/hr) $G=5.6$ and in argon (7.2×10^6 R/hr) $G=3.0$. These relatively small values suggest that in low concentrations chain reactions cannot be expected, or even when expected the chain is very short.

In the present stage when it is very difficult to set up a reaction scheme, because of lack of knowledge on reaction products, it is not feasible to discuss in detail the underlying reasons for the difference in each G value. However, it is qualitatively possible to interpret them by the behavior of the radicals.

It was previously showed6) that in silent discharge of acidic aqueous solution in the atmospheres of helium and argon the following G values can be estimated. In helium, $G(H_2O_2)=1.0$; $G(H)=1.1$ and $G(OH)=1.6$ while in argon, $G(H_2O_2)=1.5$, $G(H)=0.6$ and $G(OH)=0.7$. The total yield of radicals is larger in helium than argon.9) If radicals produced from water molecules play an important role in the formation of hydrochloric acid,5) the former will lead to a larger G value of hydrochloric acid. This also will be discussed later in the relation to the effect of additives.

In the range of solute concentration larger than 0.01 M, the G value of hydrochloric acid appears to increase with increment in solute concentration. The tendency is very similar in gamma irradiation and silent discharges, although the degree of increment is slightly different.

In gamma irradiations, the following formula had been proposed under 1 M of solute concentration in de-aerated solution.

$$G(\mathrm{HCl}) = 75/\sqrt{I} + A \tag{2}$$

where I is the dose rate (kR/hr). A has a value of about 11.10) $C_{obs}(\mathrm{HCl})\approx19$ obtained under the dose rate of 1×10^5 R/hr is almost identical with $G_{calc}(\mathrm{HCl})\approx18$ calculated from Eq. (2). Thus, G values of 12.2 and 11.9 can be respectively estimated under the dose rates of 3.8×10^6 R/hr and 7.2×10^6 R/hr. On the other hand, in silent discharge reactions in atmospheres of helium and

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8) f: the frequency of 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

9) As shown in Part I of this series, in an atmosphere of helium, the chemical effect of the silent discharge apparently corresponds to that of the ionizing radiation with a LET of about 3 eV/Å, while in argon it corresponds to a radiation with a LET of about 8 eV/Å. The difference between helium and argon is thought mainly 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.

10) Value obtained experimentally by Kondo *et al.*4) They reported that this is probably caused by direct effects.

argon, *G* values of 27 and 22 have been obtained, respectively. The lack of agreement between the experimental and the calculated values may be qualitatively explained as differences in LET value or in the mechanism of radical formation. Since the electron energy produced in silent discharge is very low, the excited state of water may play a more important role than the ionized state. In the present stage, however, the detailed mechanisms are not well known and are yet to be resolved.

The Effect of Additives. As shown in Figs. 5 and 6, the effects of potassium bromide and cupric sulfate on the yield of hydrochloric acid are remarkable. In this work the effects in solute concentration of 5×10^{-3} M are discussed, because the direct effect cannot be expected in such a low concentration.

It is tentatively assumed on the basis of radiolysis that decomposition of aqueous chloralhydrate proceeds through the following mechanism:

$$\mathrm{H_2O} \xrightarrow{\text{slow electron}} \mathrm{H}^{11)},\ \mathrm{OH} \tag{3}$$

$$\mathrm{CCl_3CH(OH)_2} + \mathrm{OH} \rightarrow \mathrm{HCl} + \mathrm{A} \tag{4a}$$

$$\mathrm{CCl_3CH(OH)_2} + \mathrm{H} \rightarrow \mathrm{HCl} + \mathrm{A'} \tag{4b}$$

A or A′ may react successively with chloralhydrate to yield hydrochloric acid. Thus the yield of hydrochloric acid may be expressed by Eq. (5):

$$G(\mathrm{HCl}) = aG(\mathrm{OH}) + bG(\mathrm{H}) \tag{5}$$

In the presence of radical scavengers such as bromide ion or cupric ion, reactions (6) or (7) will compete with (4).

$$\mathrm{Br^-} + \mathrm{OH} \rightarrow \mathrm{Br} + \mathrm{OH^-} \tag{6}$$

$$\mathrm{Cu^{2+}} + \mathrm{H} \rightarrow \mathrm{Cu^+} + \mathrm{H^+} \tag{7}$$

The presence of non-scavengible parts in the additive of bromide ions will lead to Eq. (8) through the simple competitive kinetics between (4a) and (6):

$$\frac{1}{G(\mathrm{HCl}) - G_0(\mathrm{HCl})} = \frac{1}{aG(\mathrm{OH})} + \frac{1}{aG(\mathrm{OH})}\,\frac{\mathrm{K_6[Br^-]}}{\mathrm{K_4[R]}} \tag{8}$$

where G_0(HCl) is the *G* value of the part not scavenged by additive of bromide ion.

Bromide ion is known to scavenge the reducing species in addition to hydroxyl radical.

$$\mathrm{H} + \mathrm{Br} \rightarrow \mathrm{H^+} + \mathrm{Br^-} \tag{9}$$

In this reaction system, however, reaction (9) may not occur, because of a large value of $K_{\mathrm{H+CCl_3CH(OH)_2}}$ as shown in later. The presence of a part not scavenged by even the additive of bromide ions may be well interpreted by this concept.

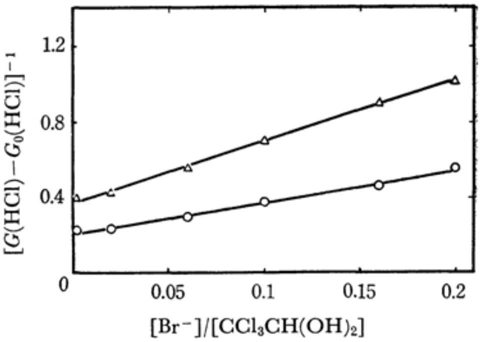

Fig. 7. Competition plot for the hydrochloric acid yield in the chloralhydrate-bromide ion system.
Chloralhydrate concentration: 5×10^{-3} M
○ Helium △ Argon

On the other hand, as shown in Fig. 6, the formation of hydrochloric acid was strongly suppressed by the additive cupric ions. This result suggests that hydroxyl radical in addition to hydrogen atom can be also scavenged. In the experiments with pulsed electron beam, Baxendale12) suggests that, in the absence of an efficient hydroxyl radical scavenger, the possible reaction could also be:

$$\mathrm{Cu^{2+}} + \mathrm{OH} = \mathrm{Cu^{3+}} + \mathrm{OH^-} \tag{10}$$

Moreover, the following reaction may be considered.13)

$$\mathrm{Cu^+} + \mathrm{OH} = \mathrm{Cu^{2+}} + \mathrm{OH^-} \tag{11}$$

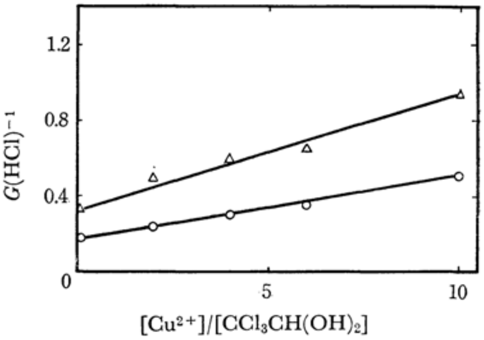

Fig. 8. Competition plot for the hydrochloric acid yield in the chloralhydrate-cupric ion system.
Chloralhydrate concentration: 5×10^{-3} M
○ Helium △ Argon

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11) Although in this series we have generally assumed that the reducing species formed in liquid water by silent discharge is hydrogen atom, the existence of solvated electron may be also expected in neutral solutions. A recent work, however, has shown that in silent discharge the major reducing species is hydrogen atoms (to be published). For the sake of simplicity, we have continued, therefore, to treat the reducing species as hydrogen atom under all conditions of pH.

12) J. H. Baxendale, E. M. Fielden and J. P. Keene, *Proc. Roy. Soc. (London)*, **A286**, 320 (1965).

13) O. Micic and I. Draganic, *J. Phys. Chem.*, **70**, 2212 (1966).

If the rapid reaction of cupric ions or cuprous ions with hydroxyl radicals can be assumed, this complete suppression can be well accounted for. Of course this assumption is tentative. There may exist another possibility. As is evident from Fig. 8, plotting of $1/G(\mathrm{HCl})$ against $[\mathrm{Cu}^{2+}]/[\mathrm{R}]$ gives a good linear curve. This finding will lead to (12).

$$\frac{1}{G(\mathrm{HCl})}=\frac{1}{bG(\mathrm{H})+aG(\mathrm{OH})}+\frac{1}{bG(\mathrm{H})+aG(\mathrm{OH})}\times\frac{\mathrm{K}_7[\mathrm{Cu}^{2+}]}{\mathrm{K}_4[\mathrm{R}]} \quad (12)$$

Thus, from Figs. 7 and 8, $K_{\mathrm{OH+Br}^-}/K_{\mathrm{OH+CCl_3CH(OH)_2}}\approx 9$ and $K_{\mathrm{Cu^{2+}+H}}/K_{\mathrm{CCl_3CH(OH)_2+H}}\approx 0.2$ can be obtained.14) Each value was almost the same irrespective of the kind of gas used. $G_0(\mathrm{HCl})=1$ in helium and $G_0(\mathrm{HCl})=0.6$ in argon lead to $b=1$. Accordingly, $a=3$ can be obtained irrespective of the kind of gas used;

$$G(\mathrm{HCl})\simeq 3G(\mathrm{OH})+G(\mathrm{H}) \quad (13)$$

These findings also suggest that the same reaction mechanism governs every case in atmospheres of helium and argon.

It is also interesting to note that in gamma-ray irradiation, G values ($G(\mathrm{HCl})_{calc}=9.6$) estimated by applying the yield of reducing species and hydroxyl radicals15) known in the neutral solution to Eq. (13) is almost consistent with those obtained from the experiment ($G(\mathrm{HCl})_{obs}=9.2$).

In the field of radiation chemistry, it is now known that the yields of the radicals produced in the low pH range differ from those in neutral solution. The situation may be the same in the radiolysis by slow electrons. In this work, we have continued to discuss on the basis of the G values of hydrogen atom and hydroxyl radical estimated in the acidic solution. However, in view of the findings that Eq. (13) holds well in the gamma-ray irradiation, it would be reasonable that in the silent discharge each G value obtained in acidic aqueous solution can be applied approximately to the neutral region.

It is our conclusion that silent discharge reactions of aqueous solutions in atmospheres of helium and argon can be well interpreted in terms of the radiolysis by slow electrons generated in the gas phase and that the scavenging effects of additive ions can be also explained in the same manner as radiation chemistry.

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14) Then, the following rate constants can be estimated: $K_{\mathrm{OH+CCl_3CH(OH_2)}}\approx 5\times10^7\ \mathrm{M^{-1}\,sec^{-1}}$; The value was calculated using $K_{\mathrm{OH+Br^-}}/K_{\mathrm{OH+C_2H_5OH}}=0.6$ and $K_{\mathrm{OH+C_2H_5OH}}=7.2\times10^8\ \mathrm{M^{-1}\,sec^{-1}}$: A. Hummel and A. O. Allen, *Radiation Res.*, **17**, 302 (1962). J. K. Thomas, *Trans. Faraday Soc.*, **61**, 702 (1965). $K_{\mathrm{H+CCl_3CH(OH)_2}}\gtrsim 6\times10^8$; The value was also estimated using $K_{\mathrm{H+Cu^{2+}}}=1.3\times10^8\ \mathrm{M^{-1}\,sec^{-1}}$ or $6\times10^8\ \mathrm{M^{-1}\,sec^{-1}}$: E. Hayon, *J. Chim. Phys.*, **62**, 391 (1965). A. Appleby, *J. Am. Chem. Soc.*, **67**, 1610 (1963).

15) E. Hayon, *Trans. Faraday Soc.*, **60**, 723 (1964).