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Silent Discharge Reactions in Aqueous Solutions. II. An Acidic Aqueous Solution of Ceric Sulfate in Atmospheres of Helium and Argon*

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In an atmosphere of helium or argon, the silent discharge reaction of an acidic aqueous solution of ceric sulfate has been investigated from the point of view of radiation chemistry. The results show the reduction of ceric ions to cerous ions. The situation is very similar to that in the case of radiation chemistry. From the known mechanism of the radiolysis of a ceric sulfate solution, the yield of "hydrogen atoms minus hydroxyl radicals" has been determined. Also, combining this yield with that of "hydrogen atoms plus hydroxyl radicals" previously obtained gave the respective yields of hydrogen atoms and hydroxyl radicals. Moreover, on the basis of the value of the dose rate previously determined, the G values of the hydrogen atom, the hydroxyl radical and the cerous ion were determined to be as follows: in helium: $G(H)=1.1$, $G(OH)=1.6$, $G(Ce^{3+})=1.6$; in argon: $G(H)=0.6$, $G(OH)=0.7$, $G(Ce^{3+})=2.9$. On the basis of these results, it may be concluded that the silent discharge reactions in an aqueous solution in inert gas can well be interpreted in terms of the radiolysis caused by the ionizing radiation of high LET.

In the previous report[1] it was pointed out, first, that in the atmospheres of helium and argon, the chemical reaction in an aqueous solution of ferrous sulfate by silent discharge may well be interpreted in terms of the actions of slow electrons generated in the gas phase on the solvent, and, then, that neither the effect of the metastable-excited states of helium and argon nor of the luminescence can be serious.

Using the methods described in that, the present work will deal with a silent discharge reaction, in the atmospheres of helium and argon, on an aqueous solution of ceric sulfate acidified with dilute sulfuric acid.

The reaction mechanism of this system has already been well established in the field of radiation chemistry,[2] in which ceric ions have been reduced to cerous ions.

The silent discharge also showed the reduction of ceric ions. As was established in the previous report, the net effect of slow electrons generated by the silent discharge may be considered to be similar to that of radiation chemistry introduced by alpha- or gamma-ray irradiation. Therefore, combining the yield of cerous ions with that of hydrogen peroxide should give the yield of "hydrogen atoms minus hydroxyl radicals" under given conditions. Accordingly, it may be expected that the yield of hydrogen atoms and hydroxyl radicals can be separately estimated by combining the yield of "hydrogen atoms plus hydroxyl radicals" (described in the previous report) with that of "hydrogen atoms minus hydroxyl radicals."

In this report, the G values of H, OH and Ce^{3+} in the silent discharge will be estimated. Also, it will be pointed out that, in atmospheres of helium and argon, the silent discharge reactions in the aqueous solutions can apparently be interpreted well in terms of the radiolysis caused by a particle of a high LET value.

Experimental

The discharge tube, the electric circuit, and the experimental conditions were the same as have previously been reported.

Merck guaranteed-reagent ceric sulfate was used without further purification. All the other materials were also of a reagent grade. The helium and argon (purity: >99.99%) were used without further treatment.

The ceric-ion concentration was measured directly by spectrophotometry, using the molar extinction coefficient of 5580 at 3200 Å (25°C).

Results

Figures 1a and 1b show the relationship between the amount of cerous ions formed and the duration time of the discharge in the cases of helium and argon respectively. The yield of cerous ions in a ceric sulfate solution acidified with 0.8 N sulfuric acid was independent of the concentration of ceric ions in the range from 1×10^{-3} M to 2×10^{-2} M. The effect of the solute concentration, however, was found at concentrations higher than 5×10^{-2} M (cf. Fig. 1b). The situation is very similar to the

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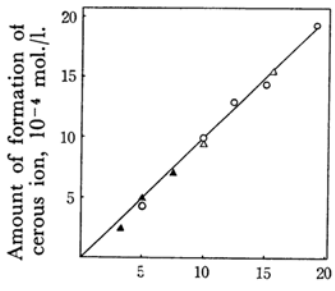
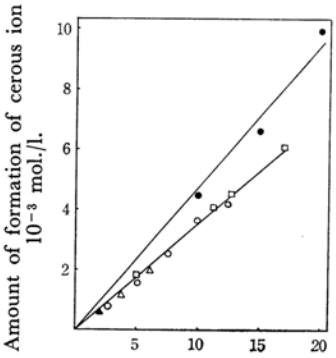
1) Part I of this series: A. Yokohata and S. Tsuda, This Bulletin, **39**, 46 (1966).

2) A. O. Allen, *Radiation Res.*, **1**, 85 (1954).



Duration time of discharge, min.

Fig. 1a



Duration time of discharge, min.

Fig. 1b

Fig. 1. Relationship between amount of formation of cerous ion and duration time of discharge.
a Helium b Argon
Initial concentrations of ceric ion
● 5×10^{-2} M, □ 2×10^{-2} M, ○ 5×10^{-3} M,
△ 3×10^{-3} M, ▲ 1×10^{-3} M

case in radiation chemistry. This point will be discussed later.

Discussion

Harlan and Hart,[3] using a concentrated solution, studied the upper limit of the usefulness of ceric dosimetry; they found that the relation between the change in the ceric-ion molarity and the dose absorbed was not linear. The initial slope corresponded to $G(Ce^{3+})=3.1$, and the final slope to $G=1.7$. Also, the effect of the solute concentration has been determined. For example, in the concentration range from 10^{-4} M to 10^{-3} M, $G(Ce^{3+})$ equals 2.50 and 2.9 at 0.1 M. In a 0.39 M ceric-sulfate solution, $G(Ce^{3+})$ increases to 3.1 because the $H+Ce^{4+}$ reaction now scavenges hydrogen atoms that normally combine to form hydrogen in dilute solutions,

3) J. T. Harlan and E. J. Hart, *Nucleonics*, **17** (No. 8), 102 (1959).

Taimuty et al.[4] irradiated the same system and obtained almost the same results. In the range from 1×10^{-3} M to 5×10^{-2} M, they got $G(Ce^{3+})=2.5$. Also, their results showed no dose-rate dependence; on the other hand a small effect of the temperature was found at temperatures higher than 27°C.

The present work will show that $Y(Ce^{3+})$ is independent of the ceric-ion concentration in the range from 1×10^{-3} M to 2×10^{-2} M within the range of experimental error, but that it is dependent on ceric ions in concentrations higher than 5×10^{-2} M. This point might well be interpreted by taking the $H+Ce^{4+}$ reaction into consideration in the same way as has been described by Harlan and Hart.

Now, in the same manner as was pointed out in the previous report, we may assume a radiolysis by the interaction of slow electrons with the water molecules.

Therefore, in the range of the linear correlation of each yield to the dose, the observed yield of cerous ion may be expressed by (1)[5,6]:

$$Y(Ce^{3+})=2Y(H_2O_2)+Y[(H)-(OH)] \qquad (1)$$

Table I shows $Y[(H)-(OH)]$ as estimated from (1) by combining the $Y(Ce^{3+})$ with the $Y(H_2O_2)$ previously obtained.[1] The cases of both helium and argon give a negative value: $Y(OH)>Y(H)$.

Hochanadel[7] has published the yields of the intermediate H, OH in the decomposition of a 0.4 M sulfuric acid solution as a function of the initial LET (linear energy transfer) value of the incident particle. In the LET range above 10 eV./Å, $G(OH)$ exceeds $G(H)$ and $G(H_2)$ exceeds $G(H_2O_2)$.

Table I. Yield of "hydrogen atom minus hydroxyl radical"

	$Y(H_2O_2)$ mol./l.	$Y(Ce^{3+})$ mol./l.	$Y[(H)-(OH)]$ mol./l.
He	6.5×10^{-4}	1.0×10^{-3}	-3×10^{-4}
Ar	1.8×10^{-3}	3.5×10^{-3}	-1×10^{-4}

Our results show that the silent discharge reactions apparently correspond to the reactions induced by particles with values of LET larger than about 10 (eV./Å). In the previous report we showed that the silent discharge reaction in helium

4) S. I. Taimuty, L. H. Towle and D. L. Peterson, ibid., **17** (No. 8), 103 (1959).

5) The following reaction scheme may be expected:

$$H_2O \rightsquigarrow H, OH, H_2O_2, H_2$$
$$H + Ce^{4+} \rightarrow Ce^{3+} + H^+$$
$$H_2O_2 + 2Ce^{4+} \rightarrow 2Ce^{3+} + 2H^+ + O_2$$
$$OH + Ce^{3+} \rightarrow Ce^{4+} + OH^-$$

Accordingly, $G(Ce^{3+}) = 2G(H_2O_2) + G(H) - G(OH)$

6) Y shows the yield of products under these given conditions: discharge current: 1 mamp., and duration time of discharge: 10 min.

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

and in argon under given conditions apparently corresponded to that by particles with the LET values of 3 and 8 (eV./Å) respectively. A small discrepancy can be seen in helium. In estimating the value of LET, however, it seems to be more reasonable to take into consideration the ratio of $Y(H_2O_2)$ to $Y[(H)+(OH)]$ than the ratio of $Y(OH)$ to $Y(H)$. Accordingly, the values of 3 (eV./Å) in helium and 8(eV./Å) in argon were used in this work.

Of couse, the yield of hydrogen atoms and hydroxyl radicals from the water vapor may also be present in the case of a silent discharge on an aqueous solution. Our interest, however, was in the net yield of H and OH.

We previously reported the yield of the "hydrogen atom plus the hydroxyl radical":

$$\left.\begin{array}{ll}\text{In helium:} & Y[(H)+(OH)]=1.7\times10^{-3}\ \text{M}\\ \text{In argon:} & Y[(H)+(OH)]=1.5\times10^{-3}\ \text{M}\end{array}\right\} \quad (2)$$

Combining (2) with the results shown in Table I gives these yields of H and OH:

$$\left.\begin{array}{ll}\text{In helum:} & Y(H)=0.7\times10^{-3}\ \text{M}\\ & Y(OH)=1.0\times10^{-3}\ \text{M}\\ \text{In argon:} & Y(H)=0.7\times10^{-3}\ \text{M}\\ & Y(OH)=0.8\times10^{-3}\ \text{M}\end{array}\right\} \quad (3)$$

These values will hereafter be checked further by means of studies of other chemical systems.

Table II shows the relation between G_{obs} and G_{est}. Each G_{obs} indicates a G value obtained by combining $Y(H)$, $Y(OH)$ and $Y(H_2O_2)$ with the dose previously determined. Each G_{est} means a G value estimated from the figure[7] showing the relations of $G(H)$, $G(OH)$ and $G(H_2O_2)$ to LET, using 3 (eV./Å) in helium and 8 (eV./Å) in argon as the LET values. The correspondence of G_{obs} to G_{est} is relatively good, except for $G(OH)$ in helium.

Table II. Relation between G_{est} and G_{obs}

	He		Ar	
	G_{est}	G_{obs}	G_{est}	G_{obs}
H	1.2	1.1	0.7	0.6
OH	1.0	1.6	0.7	0.7
H_2O_2	1.2	1.0	1.4	1.5

Also, the values of $G(Ce^{3+})=1.6$ in helium and $G(Ce^{3+})=2.9$ in argon were obtained. The differences in $G(Ce^{3+})$ in helium and in argon, and also between $G_{obs}(OH)$ and $G_{est}(OH)$ in helium, may be due to the different discharge characters, the locality of the discharge being higher in argon than in helium. Besides, the difference in the formation mode of the hydrogen atom and of the hydroxyl radical from the water vapor may be a reason (cf. part I). These points will be left as a future problem.

It is our conclusion that silent discharge reactions in an aqueous solution in atmospheres of helium and argon may apparently be well interpreted in terms of radiolysis caused by a particle with a high LET value.