Chemical Behavior of Intermediates Produced in Sulfuric Acid Glass by Gamma Irradiation. II. Yield of Trapped Hydrogen Atoms in the System Containing Metallic Ions

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The yield of trapped hydrogen atoms, H_t, in gamma-irradiated sulfuric acid glass is remarkably increased by adding a small amount, 10^{-2} M, of metallic ions. The increase is followed with a slow decrease at the higher solute concentrations. The efficiency of the formation depends on the kind of cationic solute. The largest $G(H_t)$ is observed in a system containing Co^{2+} ions; it amounts to 8.7. These findings can be explained by a mechanism in which not only mobile electrons produced by the initial ionic processes, but also excited states of the matrix molecule, contribute to the H_t formation. The excitation energy is transferred from the matrix molecule to the solute, which consequently undergoes ionization; the resulting electron causes the H_t formation. This mechanism seems to be supported by the observation that the yield of H_t increases with a decrease in the charge-transfer energy of the solute in the rigid matrix.

The photochemical production of hydrogen atom in an aqueous acidic solution containing Fe^{2+} ions was first found by Weiss *et al.*[1] Afterwards, it was proposed that its primary process is the formation of an excited state of the Fe^{2+} ion, from which an electron is transferred to the water molecule of the surrounding hydration shell.[2,3] This explanation was also given for the photochemical reaction in other frozen solutions.[3,4]

On the other hand, it has been considered that H_t in the gamma-irradiated acidic frozen solution is produced only through ionic processes. In their spectrophotometric study of irradiated glasses containing transition metals, Brown and Dainton[5] have found that some kinds of solutes are reduced according to:

$$M^{n+} + e_m^- \longrightarrow M^{(n-1)+} \tag{1}$$

where $M^{n+}=Mn^{2+}$, Ni^{2+} *etc.* Since the mobile electron is considered to be a precursor of H_t in the acidic matrix, a decrease in the H_t yield can be anticipated for these systems containing cationic solutes.

In the present systematic study, however, a remarkable increase in the H_t yield was observed only upon the addition of a small amount of the transition-metal ion to the sulfuric acid glass. The yield curves always have maxima and their trends are analogous to those obtained photochemically by Moorthy and Weiss.[3] The largest G value amounts to 8.7, which is much larger than the value reported for H_t formation through ionic processes in the pure matrix: $G(H_t) \simeq 1.2$.[6] Although the primary processes are somewhat different from those in the photochemical production, excited states of the water molecule seem to play an important role in the formation. In the gamma irradiation, a secondary electron excites the matrix molecule during the slowing-down processes. Then an excitation energy seems to be transferred from the molecule to the solute, which consequently undergoes ionization.

Experimental

Sample Preparation. The water was redistilled. The sulfuric acid and all the chemicals from the Kanto Kagaku Co., Ltd. were of an analytical reagent grade. A small amount of cationic sulfate was added to an aqueous solution of 6 M sulfuric acid, after which the solution was cooled to 77 K.

The samples for ESR measurements were prepared as has previously been described.[7] On the other hand, the samples for gas-chromatographic analysis were degassed and then sealed in Pyrex cells with breakable seals. The sample volume was constantly 10 ml.

Irradiation and Measurement. The gamma irradiations were carried out by means of a 45 kCi ^{60}Co source at the dose rate of 6.4×10^{18} eV g^{-1} hr^{-1}. The dose absorbed was determined by Fricke dosimetry. The sample was usually exposed in the dark at 77 K for one hr.

The ESR spectra were obtained with an X-band Hitachi 771-type spectrometer equipped with 100 kHz modulator and were scanned without power saturation. The absolute H_t yields were determined by comparison with the signal intensity of a calibrated amount of the DPPH radical in a tetrahyrdofuran solution frozen at 77 K. The relative H_t yields were obtained from the signal intensity of the higher field. The SO_4^- yield was relatively determined from the signal height in the central part of the spectrum where its anisotropic singlet appeared. For the measurements of the H_2 yield, the irradiated sample was melted and the H_2 gas was recovered with a Toepler pump. The gas analyses were performed with a Yanagimoto G-8-type gas chromatograph, and the yield was determined absolutely by comparison with a standard volume of pure H_2 gas.

Results

The bright brown color due to the SO_4^- radical was not observed for the irradiated samples containing a large amount of the cationic solute.

The ESR spectrum of the irradiated sulfuric acid glass consisted of a doublet splitting by 510 G and a singlet centered at 3288 G. These have been ascribed to the H_t and SO_4^- radicals respectively.[8] A power saturation of the H_t signal in the samples containing a paramagnetic cation was observed to begin at approximately 3×10^{-2} mW. This observation agrees with the results obtained previously for H_t power saturations in the sulfuric acid glasses.[9] The intensity ratios of the low-field line to the high-field line in the H_t signal were measured for the following systems; 6M sulfuric acid glass and the glasses containing the 0.04 M Co^{2+} ion and the 0.5 M Co^{2+} ion. For all

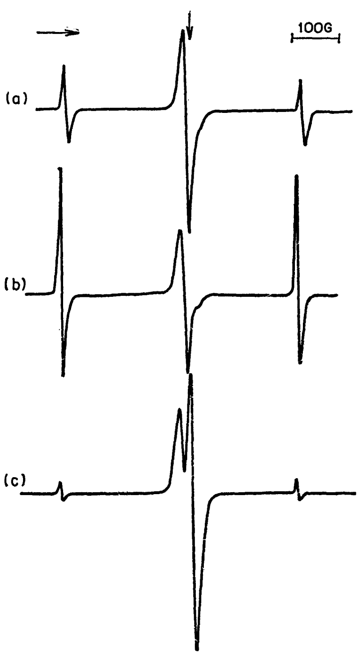

Fig. 1. ESR spectra of the samples irradiated at 77 K. A vertical arrow indicates a signal position of DPPH radical.
(a) 6M sulfuric acid glass.
(b) 6M sulfuric acid glass containing 5×10^{-2} M Ni^{2+} ion.
(c) 6M sulfuric acid glass containing 5×10^{-2} M Ni^{2+} and 0.1 M TeO_4^{2-} ions.

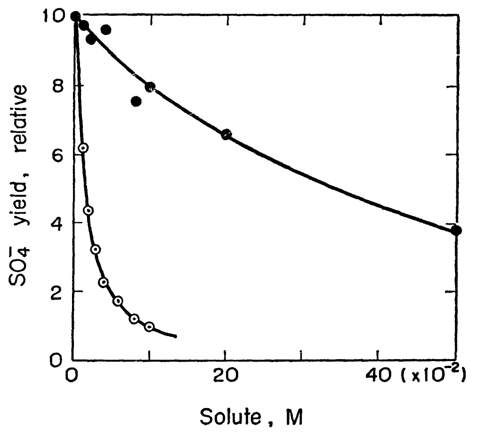

Fig. 2. Positive hole scavenging in the 6 M sulfuric acid glass by Ni^{2+} and Fe^{2+} ions.
●: Ni^{2+}, ⊙: Fe^{2+}

the above systems, the ratios were 1.1±0.1 under the microwave power employed.

The addition of the Ni^{2+} ion resulted in an abrupt increase in the H_t yield, as is shown in Fig. 1(b). As the intense H_t signal declines in the presence of a strong electron scavenger, TeO_4^{2-}, as may be seen in Fig. 1(c), it is considered that a mobile electron contributes to a reaction of the H_t formation. On the other hand, the SO_4^- yield decreases upon the addition of the cationic solute. The details for the systems containing Fe^{2+} and Ni^{2+} ions are shown in Fig. 2. For the other systems, it was difficult to obtain analogous scavenger curves because of the complexity in the central part of the ESR spectra. The decrease in the SO_4^- yield has been also previously observed for the system containing the Fe^{2+} ion and ascribed to a hole scavenging by the solute.[10] The present monotonous decreases suggest that the G value for initial ionic processes is almost constant, even in the presence of the solutes.

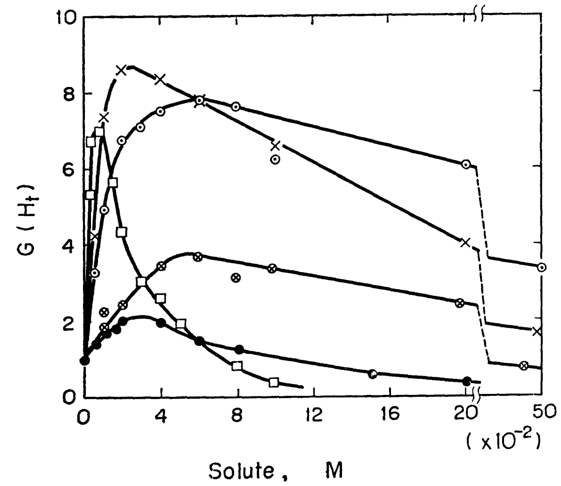

Fig. 3. $G(H_t)$ for the 6 M sulfuric acid glass containing various kinds of cationic solute.
●: VO^{2+}, ⊗: Ni^{2+}, ⊙: Fe^{2+}, ×: Co^{2+}, □: Mn^{2+}

TABLE 1. MAXIMUM $G(H_t)$ IN 6M SULFURIC ACID GLASS CONTAINING VARIOUS KINDS OF CATIONIC SOLUTE

Solute	Max. $G(H_t)$	Solute concentration $\times10^{-2}$ M
none	1.0	—
VO^{2+}	2.1	2.5
Ni^{2+}	3.7	5.5
Fe^{2+}	7.8	6.0
Co^{2+}	8.7	2.5
Mn^{2+}	6.5	0.8

Figure 3 shows the curves of the H_t yield in the systems containing the cationic solute. The curves have two principal characteristics. The first is a remarkable increase in the H_t yields, followed by a slow decrease. Especially in the system containing the Co^{2+} ion, the maximum G value amounts to 8.7, which is much larger than yield of H_t in the pure matrix ($G(H_t)=1.0$). At the higher solute concentration, the $G(H_t)$ becomes less than 1.0 because of Reaction (1). It is noteworthy that these cationic solutes can scavenge mobile electrons as well as positive holes. The second is that the slope of the increasing curve and the maximum H_t concentration depend on a kind of solute. The maximum $G(H_t)$ are summarized in Table 1, together with the solute concentrations. In all the systems, the G value reaches its maximum at the solute concentrations of $0.8\times10^{-2}-6\times10^{-2}$ M.

The decreases at the higher solute concentrations suggest that the excited states of the solute also participate in the H_t formation, as has been observed in the photochemical production.[3] To confirm this presumption the second solute effect on the H_t formation

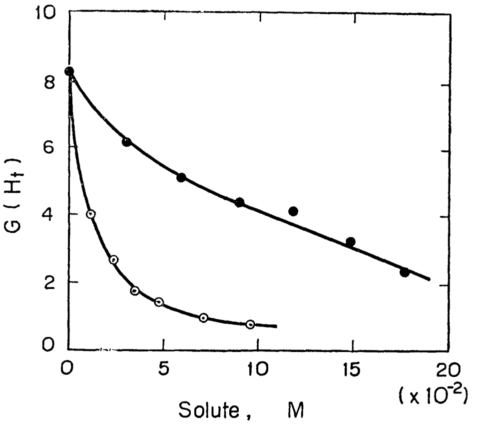

Fig. 4. Second solute effect on the H_t formation in the 6 M sulfuric acid glass containing 4×10^{-2} Co^{2+} ion. ●: Ni^{2+}, ⊙: TeO_4^{2-}

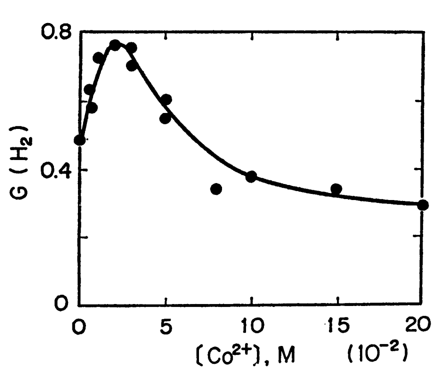

Fig. 5. $G(H_2)$ values determined after melting the irradiated 6 M sulfuric acid glass containing Co^{2+} ion.

was studied. Monotonous decreases in the H_t yield with an increase in the solute concentration were observed; the results are shown in Fig. 4. The depression of the H_t formation seems to be easily attained by the addition of the TeO_4^{2-} ion, which acts not only as an electron scavenger but also probably as a quencher for excited states of the Co^{2+} ion.

The $G(H_2)$ value for the pure matrix was determined to be 0.48 which is almost a half of the H_t yield. The H_2 yield for the system containing the Co^{2+} ion is shown in Fig. 5. Although the yield increases about 1.5 times upon the addition of 2.5×10^{-2} M of the Co^{2+} ion, the absolute value is incompatible with the results of the H_t yield. This discrepancy may arise from the complex reactions during the melting procedures.

Discussion

The primary processes in the radiation effects on matter are ionization and the formation of various excited states of the matrix molecule:

$$S \longrightarrow S^+ + e^- \text{ (or } e_m^-) \qquad (2)$$

$$S \longrightarrow S^* \qquad (3)$$

According to the following reactions, the mobile electron in the 6 M sulfuric acid glass produces H_t at almost the same rates:[7,11]

$$e_m^- + H^+ \longrightarrow H\ (\rightarrow H_t) \qquad (4)$$

$$e_m^- + HSO_4^- \longrightarrow H\ (\rightarrow H_t) + SO_4^{2-} \qquad (5)$$

Assuming that H in the acidic glasses is produced only through Reactions (4) and (5), the yield could not exceed $G\simeq4$, which is the ultimate yield of the ionic processes in the aqueous solution at 293 K.[12]

On the other hand, the behavior of the excited states of the water molecule in an aqueous solution is scarcely known, while triplet formation through energy transfer from the excited matrix molecule to the solute have been observed in several organic systems[13] and energy-transfer processes in scintillator systems have been well established.[14] In the liquid water, the probability of energy transfer from the excited states to the solute would be very small, because the excited singlets are quenched in the time of a single vibration, 10^{-13} s, and the excited triplets are unknown.[15] However, in the vapor phase, isotope exchange experiments gave $G\simeq12$ for the total activated water[16] and $G\simeq8$ for the total H-atom formation.[17] Moreover, in the frozen system of an ethylene glycol-water mixture containing a small amount of triptophane, Steen has obtained $G\simeq10$ for the total light emission from its singlet and triplet states.[18] Because the $G(e_t^-)$ has been determined to be approximately 3,[19] the last observation indicates that an excitation energy is efficiently transferred from the excited matrix molecule to the solute. Moorthy *et al.*[3] have elucidated that the excited states of the solute bring about the H_t production by exposing an acidic frozen solution containing the Fe^{2+} ion or the I^- ion to 2537 Å light. In these cases, the H_t yield increases with an increase in the solute concentration and reaches maximum at $[I^-]\simeq0.01$ M for the polycrystalline specimen and at $[Fe^{2+}]\simeq0.2$ M for the glassy specimen. For these observation, a mechanism was proposed that a primary process is a direct excitation of the solute, followed by electron detachment from the excited state, which causes the H_t production by means of Reactions (4) and (5).

As regards the present results, it seems impossible to interpret the large $G(H_t)$ on the basis of the ionic processes alone. Though more direct evidence on the reaction processes is necessary, the following mechanism would, however, account for the yield curves in Fig. 3.

In the present systems, it may be considered that the excitation energy of the matrix molecule is efficiently transferred to the solute, which is consequently excited to its metastable states. The energy of the lowest electronic excited state of the isolated water molecule is *ca.* 7.5 eV, while its ionization energy is 12.6 eV.[20] On the other hand, as regards the solute, *e.g.*, the Fe^{2+} ion, the lowest charge-transfer energy in the rigid matrix is 4.7 eV.[21] These data indicate that the excited states of the water molecule can be converted to those of the Fe^{2+} ion. Hydration ligands surrounding the Fe^{2+} ion and hydrogen bondings probably facilitate energy transfer:

$$S^* + Fe^{2+} \longrightarrow S + Fe^{2+*} \qquad (6)$$

Because the energy transferred exceeds its ionization energy, the Fe^{2+*} ion undergoes ionization or, in some cases, is competitively deactivated by light emissions and radiationless transitions:

$$\mathrm{Fe^{2+*}} \longrightarrow \mathrm{Fe^{3+}} + \mathrm{e^-}\ (\text{or } \mathrm{e_m^-}) \qquad (7)$$

$$\mathrm{Fe^{2+*}} \longrightarrow \mathrm{Fe^{2+}} \qquad (8)$$

The resulting mobile electron is converted to H_t through Reactions (4) and (5). There is no difference in the physicochemical properties of the mobile electrons formed through the two reactions, (2) and (7).

At lower solute concentrations the mechanism described above predicts the promotion of the H_t formation with a decrease in the ionization energy of the solute. As is listed in Table 2, the initial increase in the rate of the H_t formation, *i.e.*, $dG(H_t)/d[S]$ is closely related to the decline in the charge transfer energy, E_{ct}, of the solute. Especially, the excitation energy is most efficiently utilized for the H_t formation in the system containing the Co^{2+} ion, and the maximum $G(H_t)$ amounts to 8.7.

TABLE 2. EFFICIENCIES OF THE H_t FORMATION IN THE SULFURIC ACID GLASS CONTAINING CATIONIC SOLUTE

Solute	$dG(H_t)/d[S]$[a) $\times 10^{-2}\ M^{-1}$	E_{ct}[b) eV	Ref.
VO^{2+}	0.68	5.2	22)
Ni^{2+}	0.85	5.2	23)
Fe^{2+}	3.9	4.7	21)
Co^{2+}	6.5	4.6	24)
Mn^{2+}	17.1	4.5	23)

a) The values were taken from the initial slopes in Fig. 3.
b) E_{ct} denotes an absorption edge of charge transfer band in the optical spectrum and was taken from the UV spectrum in the rigid matrix.

On the other hand, the decrease in the H yield at higher solute concentrations must be due to Reaction (1) and the deactivation of the excited states. The latter process may be caused by a resonance energy transfer between the excited and the ground states of the solute, as is found in the system of the liquid scintillator.[25)

Here, it is worthwhile to interpret on the basis of the present mechanism the results obtained at 77 K by Dainton *et al.*[5) They have observed the hyper-reduced ion in the gamma-irradiated sulfuric acid glasses containing transition-metal ions. The solute concentrations were 0.12 M Mn^{2+} and 0.5 M Ni^{2+} ions where the $G(H_t)$ were less than 1.0, as is seen in Fig. 3. Therefore, the observations may be attributed to a predominant contribution from Reaction (1). On the contrary, they could not observe the reduced form in the system containing the 0.01 M Fe^{2+} ion. This may be due not only to the hole scavenging by the solute, but also to the predominance of Reaction (7) over the competitive reaction (1) at that solute concentration where $G(H_t)$ amounts to 5.0. This presumption is also consistent with their results, which have revealed the absence of the reduced species.

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