Chemical Behavior of Intermediates Produced in Sulfuric Acid Glass by Gamma Irradiation. I. Reactivities of Mobile Electrons with Inorganic Ions

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The yield of the trapped hydrogen atom, H_t, produced in the 6 M sulfuric acid matrix at 77 K was decreased by the presence of an electron scavenger. Based on the competition reaction kinetics, the reactivities of mobile electrons, e_m^-, with metallic and oxygen-containing ions were determined from the decrease in the H_t yield. It was found that e_m^- is scavenged most efficiently with the TeO_4^{2-} ion. The relative reaction rates of e_m^- with oxyanions were generally larger than those of the corresponding e_{aq}^- reactions. On the other hand, a good accordance in the reaction rates for both forms of electrons was observed in the cases of the reactions with metallic ions. An interpretation was given to the discrepancy in the observed reaction rates that e_m^- in the epithermal energy region goes over the Coulomb barrier, which is too high for e_{aq}^- to pass through, and thus reacts more efficiently with anionic species than does e_{aq}^-. Some unstable intermediates produced at 77 K polymerized with the solute during the thermal annealing. The ESR and optical spectra of the polymerized cadmium and molybdenum are shown, together with those of the primarily-produced species.

It is well recognized that e_m^- in an acidic matrix is converted into H_t:[1)]

$$e_m^- + P \longrightarrow H_t \tag{1}$$

where P is a reaction partner of e_m^-, such as an H^+ or HSO_4^- ion. The addition of an electron scavenger, S, depresses the H_t formation:

$$e_m^- + S \longrightarrow S^- \tag{2}$$

From competition reaction kinetics applied to the e_m^- concentration, the following equation is obtained:[2)]

$$G_0(H_t)/G(H_t) = 1 + k_s[S]/k_p[P] \tag{3}$$

where $G_0(H_t)$ and $G(H_t)$ are the G values of H_t in the absence and in the presence of the electron scavenger, and where k_s and k_p are the rate constants for the reaction of e_m^- with S and P respectively.

Kevan[2)] has reported on the reactivities of e_m^- in the acidic matrix and concluded that the relative rates, except that of the reaction of e_m^- with the H^+ ion, were approximately proportional to those of e_{aq}^- at room temperature. However, similar studies using the other matrices[3,4)] showed some deviations from the results which would be expected from the corresponding e_{aq}^- reactions. The disagreement might arise from a difference in the experimental method; Kevan employed acidic matrices with a low H_t yield ($G(H_t)=$ 0.14—0.27),[5)] while the latter authors directly measured the disappearance of trapped electrons, e_t^-, in the matrices of high e_t^- yields ($G(e_t^-)=2.8$).[4)]

Recently, Steen and Kongshaug[6)] found, by employing an ethylene glycol-water matrix, that the relative scavenging efficiency of such anionic solutes as NO_3^- and $ClCH_2COO^-$ ions diminished with a decrease in the energy of the electron, *i.e.*, in the order of the dry electron, e^-, e_m^-, and the stabilized electron, e_s^-, produced in an ethylene glycol-water matrix at 77 K. We ourselves have also reported[4)] that the relative rates of the e_m^- reactions in the same matrix are not always in accordance with those of the e_{aq}^- reactions, and that larger relative e_m^- rates were obtained, especially in the reaction with polynegative complex ions.

For the e_m^- reactions in sulfuric acid glass, Brown and Dainton[7)] have studied the reactivities with Ag^+, Cd^{2+}, and In^{3+} ions by means of spectrophotometry. However, no correlation with the reactivity has been derived from their data.

The H_t yield in the frozen solution of 6M sulfuric acid is comparatively large ($G(H_t)=1.3$ at 77 K[8)]) and the matrix becomes homogeneously glassy upon rapid freezing, which is convenient for the estimation of the reactivity of e_m^- from the decrease in the H_t yield. In the present paper, the relative rates of the e_m^- reactions in the acidic matrix were determined for 18 inorganic ions. Though it is qualitative, a distinct difference in the reactivity was observed between the e_m^- and e_{aq}^- reactions. This discrepancy seems to arise from an essential difference in the average kinetic energy possessed by the two entities at the time of the scavenging reaction rather than from the difference in the matrix or phase employed.

Experimental

Materials. The water was redistilled, and the ethylene glycol was fractionally distilled. As matrices, a 67 vol % ethylene glycol-water solution was used in the case of the e_m^- reaction with the H^+ ion, while in the other cases 6M sulfuric acid was employed.

Sulfates or alkali metal salts were generally used for the reactivity determinations of e_m^-. In the case of the reaction with the Ag^+ ion, silver nitrate was used as a solute. Since the NO_3^- ion itself is a strong e_m^- scavenger, the reaction rate was estimated from the summation of the efficiencies for Ag^+ and NO_3^- ions. All of the chemicals tabulated in Tables 1 and 2 were of an analytical reagent grade and were used without further purification.

Irradiation and Measurement. The samples which were made into a glassy state without any degassing treatment were exposed to gamma rays from a ^{60}Co source for 2 hr at 77 K. The dose rate was 4×10^{18} eV g^{-1} hr^{-1}. The ESR measurements were performed at 77 K in the absence of power saturation, and the optical measurements were carried out as has previously been described.[4)] The H_t yield was determined from the ESR signal intensity in the higher magnetic field, while the estimation of the e_t^- yield was based

TABLE 1. RELATIVE RATES OF e_m^- AND e_{aq}^- REACTIONS WITH METALLIC IONS

Ion (S)	Compound	Relative rates $k(e_m^-+S)$ at 77K	 $k(e_{aq}^-+S)$ at 300K[a]
Mg^{2+}	$MgSO_4 \cdot 7H_2O$	0.15	—
Al^{3+}	$KAl(SO_4)_2 \cdot 12H_2O$	0.09	0.07
Cr^{3+}	$Cr_2(SO_4)_3 \cdot 15H_2O$	1.0	1.5
Fe^{3+}	$Fe_2(SO_4)_3 \cdot 10H_2O$	3.0	—
Cu^{2+}	$CuSO_4 \cdot 6H_2O$	1.0	1.1
Ag^+	$AgNO_3$	2.2	1.0
Cd^{2+}	$CdSO_4 \cdot 2.7H_2O$	1.0	1.0
Ce^{4+}	$Ce(SO_4)_2 \cdot 6H_2O$	0.65	—
Hg^{2+}	$HgCl_2$	2.9	—
Tl^+	Tl_2SO_4	0.72	0.98

a) The data were cited from the table compiled by Anbar and Neta.[13]

TABLE 2. RELATIVE RATES OF e_m^- AND e_{aq}^- REACTIONS WITH OXYGEN CONTAINING IONS

Ion (S)	Compound	Relative rates $k(e_m^-+S)$ at 77K	 $k(e_{aq}^-+S)$ at 300K[a]
$B_4O_7^{2-}$	$Na_2B_4O_7 \cdot 10H_2O$	<0.03	—
NO_3^-	KNO_3	1.9	0.35
HSO_4^-[b]	H_2SO_4	0.95[b]	—
$Cr_2O_7^{2-}$	$K_2Cr_2O_7$	4.2	1.1
MnO_4^-	$KMnO_4$	0.58	0.71
MoO_4^{2-}	$Na_2MoO_4 \cdot 2H_2O$	1.1	—
TeO_4^{2-}	$H_2TeO_4 \cdot 2H_2O$	4.4	0.52
UO_2^{2+}	$UO_2SO_4 \cdot 3H_2O$	1.4	2.4 (pH ?)

a) The data were cited from the table compiled by Anbar and Neta.[13] b) Activity coefficient of HSO_4^- ion was assumed to be 0.34.

on the method which will be described in the following section.

The thermal treatments above 77 K were done by using a variable-temperature accessory. The sample vessel was composed of double tubes of Pyrex glass which were covered with adiabatic material. An inner tube, 20 cm long and 1.5 cm in *i.d.*, was covered with paraffin wax, and a heating coil was wound on the outside of the wall. This tube was then inserted into a larger Pyrex tube covered with asbestos. The vessel was dipped in liquid N_2. The temperature of the sample was measured with a platinum resistance thermometer and held within ±1 °C with a Chino E501 temperature controller.

Results and Discussion

Electron-scavenging Efficiency of Sulfuric Acid. The total scavenging efficiency of sulfuric acid for e_m^- was estimated from the decrease in the e_t^- concentration. On exposure to gamma rays, the ethylene glycol-water glass acidified with sulfuric acid develops a deep blue color which arise from the e_t^-. The color completely disappears above the acidic concentration of *ca.* 0.5 M or upon photobleaching with a light of wavelengths $\lambda \geq 390$ nm. The SO_4^- radical, which is characterized by its bright yellow color, is not observed in the region of sulfuric-acid concentrations employed.

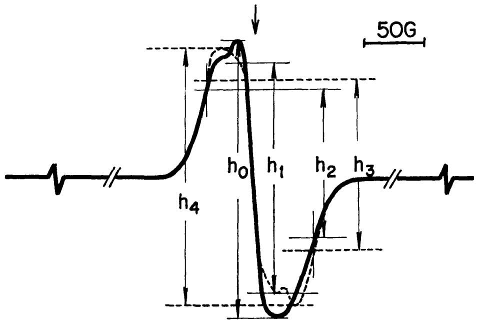

Fig. 1. ESR spectra of gamma-irradiated 67 vol % ethylene glycol-water glass containing 5×10^{-2}M sulfuric acid.
———— before photobleaching
------------ after bleaching by light of tungsten lamp

The ESR spectra (the 1st differential) of the gamma-irradiated sample are shown in Fig. 1. The shapes are essentially the same as those reported previously.[4] After photobleaching, the central singlet which mainly arises from e_t^- disappears and the triplet which is probably due to the ethylene glycol radical increases, as may be seen in Fig. 1. The H_t yield is dependent upon neither the photobleaching procedure nor the concentration of sulfuric acid.

The absolute e_t^- concentration is proportional to the difference in the intensity of the integrated ESR spectra at the e_t^- position before and after photobleaching. In the preliminary examinations, however, the following simple method was confirmed to give a reliable estimate of the relative e_t^- concentration. By photobleaching, the singlet spectrum of e_t^- is probably converted to the triplet spectrum of the ethylene glycol radical.[9] Consequently, the contribution of the triplet at the e_t^- position increases by h_1h_3/h_2, where h_1 is the signal intensity of the triplet at the e_t^- position and where h_2 and h_3 are the intensities of the triplet before and after photobleaching respectively. Therefore, the relative e_t^- concentration, $C(e_t^-)$, is approximately given as follows:

$$C(e_t^-) \simeq (h_0 - h_1h_3/h_2)/h_4 \qquad (4)$$

where h_0 is the signal intensity at the e_t^- position before photobleaching. A normalization factor, h_4, is the total intensity of the ethylene glycol radical, regardless of the concentration of sulfuric acid employed. These notations are also presented in Fig. 1.

Based on the competition reaction kinetics described previously,[4] the value of $[C_0(e_t^-)/C(e_t^-)-1]$, where $C_0(e_t^-)$ is the relative e_t^- concentration in the absence of sulfuric acid, is plotted against the acidic concentration in Fig. 2. The total scavenging efficiency of 8.0 M^{-1} obtained for sulfuric acid is 0.21 of that for the NO_3^- ion in the same matrix. The chemical species which can scavenge e_m^- in the sulfuric acid matrix are H^+ and HSO_4^- ions.[1,10] Because the reaction rate of e_m^- with the H^+ ion was given as 0.12 $k(e_m^- + NO_3^-)$ in the experiment using chloric acid,[3] the rate with the HSO_4^- ion is estimated as follows:

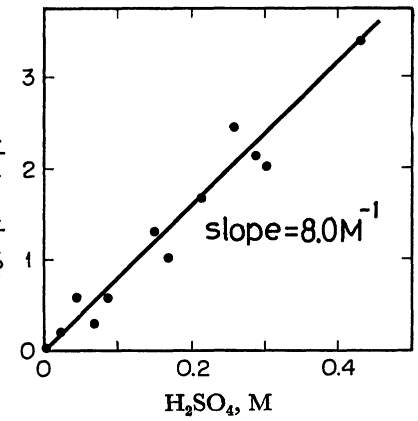

Fig. 2. Relationship between $[C_0(e_t^-)/C(e_t^-)-1]$ and sulfuric acid concentration.

$$k(e_m^- + HSO_4^-) = k(\text{total}) - k(e_m^- + H^+)$$
$$= (0.21/a - 0.12) \times k(e_m^- + NO_3^-) \quad (5)$$

where a is an activity coefficient of the HSO_4^- ion in the medium. Assuming that the coefficient is the same as that in the 0.1 M solution at 0 °C, *i.e.*, 0.34, the reaction rate of e_m^- with the HSO_4^- ion is found to be equal to 0.50 $k(e_m^- + NO_3^-)$.

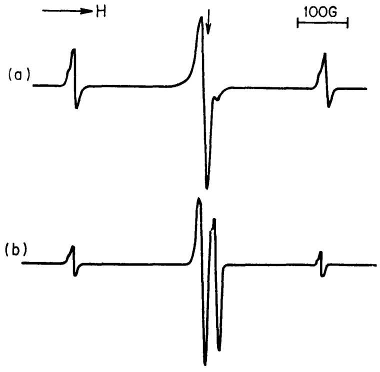

Fig. 3. ESR spectra of gamma-irradiated specimens.
(a) 6M sulfuric acid glass immediately after the irradiation.
(b) 6M sulfuric acid glass containing 1×10^{-2}M Cd^{2+}.

Electron-scavenging Efficiencies of Inorganic Ions. The ESR spectra of the gamma-irradiated samples which contained the Cd^{2+} ion are displayed in Fig. 3. The spectrum of the 6 M sulfuric acid glass is also shown for purposes of comparison. The doublet pattern of H_t is diminished efficiently by the presence of the Cd^{2+} ion. Because the reduction of the Cd^{2+} ion with e_{eq}^- is very fast ($k < 5.2\times10^{10}$ M^{-1} s^{-1}),[11] whereas that of the Cd^{2+} ion with the hydrogen atom is negligibly slow at room temperature ($k = 10^5$ M^{-1} s^{-1}),[12] the above observation implies that the reaction partner of the Cd^{2+} ion is not the hydrogen atom, but e_m^-. This finding allows us to estimate the reactivity of e_m^- from the decrease in the H_t yield.

Frohlinde *et al.* have reported that the H_t in the 6 M sulfuric acid glass is subject to thermal decay, even at 77 K.[14] This was confirmed in the present study; the rate was increased by the addition of the electron scavenger. The fraction decaying in the first 2 hr amounted to 18% for the pure matrix and 27% for the matrix containing 5×10^{-2} M Cu^{2+} ions respectively. Therefore, the precise H_t yields were obtained by correcting the thermal decay at 77 K.

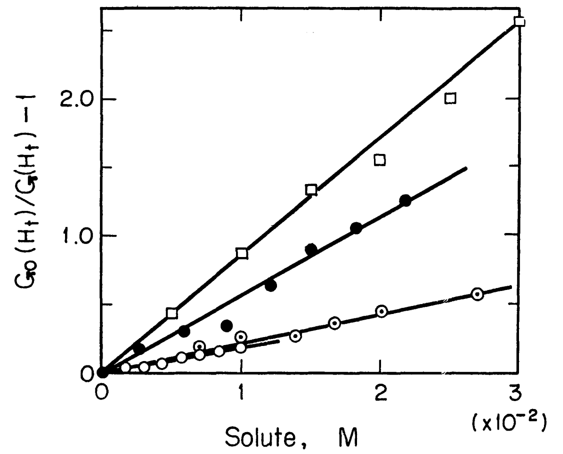

Fig. 4. Relationships between $[G_0(H_t)/G(H_t)-1]$ and solute concentration.
○: Cd^{2+}, ●: Fe^{3+}, ⊙: MoO_4^{2-}, □: TeO_4^{2-}.

Based on Eq. (3), the relative rates of the e_m^- reaction can be determined from the slope of the straight line obtained by plotting $[G_0(H_t)/G(H_t)-1]$ against $[S]$. Some of the plottings are shown in Fig. 4. The relative reaction rates are summarized in Tables 1 and 2. The corresponding data known about the reactivities of e_{aq}^- in neutral solution are also presented. All the values normalized to unity for the reaction of $(e_m^- + Cd^{2+})$ or $(e_{aq}^- + Cd^{2+})$. As may be seen in the tables, the most effective e_m^- scavengers are the Fe^{2+} ion in the cationic solutes and the TeO_4^{2-} ion in the anionic solutes.

In the reaction of the Cr^{3+} ion with e_m^-, the relative rate is less than that which would be expected from the corresponding e_{aq}^- reaction, while in the case of the Ag^+ ion the reactivity amounts to 2.2 times the expected value. At present, it is impossible to give a reasonable interpretation of this irregularity. In the cases of the other metallic ions, the relative rates of the e_m^- reaction are roughly proportional to those of the e_{aq}^- reaction. These results are consistent with the previous observations for e_m^- in the ethylene glycol-water matrix.[4] On the other hand, in the cases of the oxyanions listed in Table 2 the reactivities of e_m^- seem to be independent of those of e_{aq}^-, and they are mostly larger than those of the e_{aq}^- reaction. This discrepancy seems to be closely related to the difference in the kinetic energy at the time of the scavenging reaction. The maximum concentration of e_t^- in alkaline glass has been determined to be 5.4×10^{17} g^{-1}, *viz.*, 2.4×10^{-2} M.[15] Assuming a homogeneous spatial distribution, the e_t^-'s are estimated to be 41 Å distant from each other. Furthermore, the e_t^- yield is reduced to 50% by the addition of 2.5×10^{-2} M acrylamide, an effective electron scavenger.[16] After all, the e_m^- in the acidic glass is also expected to travel a distance of over 20.5 Å before it is captured by the solute. Therefore, the electron in the system containing a sufficient amount of the scavenger may encounter the solute a few times during the slowing-down processes. It is probable that the e_m^- in the epithermal energy region goes over the Coulomb barrier, which is too high for e_{aq}^- to pass through, and thus reacts more efficiently with the anionic species. In other words, the present results suggest that the electron can be scavenged even in the somewhat higher-energy region before slowing down to the thermal energy. This postulation is supported by the results of a previous experiment,[4] where the relative rates of the e_m^- reaction with polynegative cyano and oxalato complex ions are also larger than those which would be expected from the e_{aq}^- reaction.

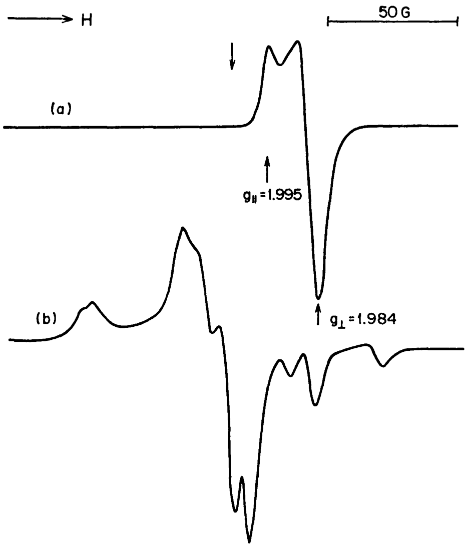

Fig. 5. ESR spectra of gamma-irradiated 6M sulfuric acid glasses containing 1×10^{-2}M Cd^{2+}.
(a) difference spectrum; Figs. 3(b)—(a)
(b) after thermal annealing at 152 K

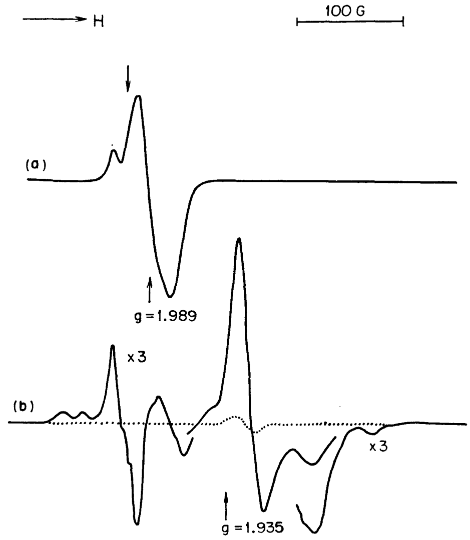

Fig. 6. ESR spectra of gamma-irradiated 6M sulfuric acid glasses containing
(a) 3×10^{-2}M TeO_4^{2-}. The sample has been annealed at 152 K.
(b) 4×10^{-2}M MoO_4^{2-}. The sample has been annealed at 154 K.

Spectra of the Reaction Products. Several fine spectra of the reaction intermediates could be obtained by thermal annealing at *ca.* 150 K, where the SO_4^- radical completely disappears. A difference spectrum (Figs. 3(b)—(a)) and a spectrum after thermal annealing for the samples containing the Cd^{2+} ion, both of which have axially symmetric *g*-factors, are shown in Fig. 5. The spectrum in Fig. 5(a) has a line shape attributable to the Cd^{1+} ion primarily formed.[17,18] The most intense signal in Fig. 5(b), which is complicated by the superposition of the Cd^{1+} ion, is assigned to a diatomic cation, *i.e.*, the Cd_2^{3+} ion found previously at 233 K.[18] These observations indicate that even in the solid phase, the migration of the Cd^{1+} ion takes precedence over the electron transfer from the Cd^{1+} ion to the SO_4^- radical.

Figure 6(a) shows the irradiated specimen containing the TeO_4^{2-} ion. The tellurium of the 5-valency state has an unpaired electron in its 4d shell, and it is expected to give rise to an intense singlet with a weak doublet due to ^{125}Te (6.99%, $I=1/2$). Therefore, the spectral pattern in Fig. 6(a) may be attributed to Te(V), *i.e.*, the TeO_4^{3-} ion. However, this assignment remains somewhat tentative, because no information is known about the spectral characteristics of the Te(V) species.

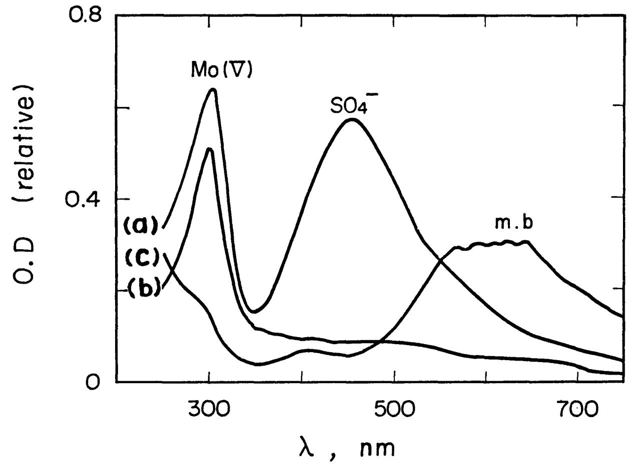

Fig. 7. Optical spectra of gamma-irradiated 6 M sulfuric acid glasses containing 4×10^{-2}M MoO_4^{2-}.
(a) after irradiated at 77 K
(b) after thermal annealing at 154 K
(c) after thermal annealing at 250 K

After the thermal annealing at 154 K, the irradiated glass containing the MoO_4^{2-} ion remained bright yellow, but it turned dark blue above *ca.* 190 K. The optical absorption spectra are displayed in Fig. 7. The spectrum of the blue species is assigned to molybedenum blue,[19] which is a nonstoichiometric polymolybdate composed of the Mo(V) and the Mo(VI) oxides.[20] The ESR pattern of the bright yellow species is shown in Fig. 6(b). There are two magnetic isotopes of molybdenum in natural abundance, ^{95}Mo (15.7%, $I=5/2$) and ^{97}Mo (9.45%, $I=5/2$). The molybdenum of the 5-valency state has unpaired electron in the 4d shell. Hence, we may assign the sixtet splitting to the hyperfine coupling of ^{95}Mo and ^{97}Mo, which is overlapped with a stronger central singlet due to the nonmagnetic molybednum nuclei.

From these observations it may be concluded that the Mo(V) species primarily produced polymerize with some MoO_4^{2-} ions during the thermal annealing as in the case of the Cd^{1+} ion. By performing thermal-annealing experiments on the frozen specimen, much information would be obtained on the inorganic polymerized species, which are hard to be detected at room temperature.

References

1) L. Kevan, P. N. Moorthy, and J. J. Weiss, *J. Amer. Chem. Soc.*, **86**, 771 (1964); L. Kevan, *Progr. Solid State Chem.*, **2**, 304 (1965); S. Ohno, T. Sasaki, and M. Koike, This Bulletin, **45**, 2383 (1972).

2) L. Kevan, *J. Amer. Chem. Soc.*, **89**, 4238 (1967); "Radiation Chemistry of Aqueous Systems", ed. by G. Stein, Weizmann Science Press, Israel (1968), p. 62.

3) H. B. Steen, O. Kaalhus, and M. Kongshaug, *J. Phys. Chem.*, **75**, 1941 (1971).

4) T. Sasaki and S. Ohno, This Bulletin, **44**, 2626 (1971).

5) L. Kevan and C. Fine, *J. Amer. Chem. Soc.*, **88**, 869 (1966).

6) H. B. Steen and M. Kongshaug, *J. Phys. Chem.*, **76**, 2217 (1972).

7) D. M. Brown and F. S. Dainton, *Trans. Faraday Soc.*, **62**, 1139 (1966).

8) R. Livingston and A. J. Weinberger, *J. Chem. Phys.*, **33**, 499 (1960).

9) J. Moan, *Int. J. Radiat. Phys. Chem.*, **5**, 293 (1973).

10) B. G. Ershov and A. K. Pikaev, *Radiat. Res. Rev.*, **2**, 66 (1969).

11) J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Proc. Royal Soc., Ser. A*, **286**, 320 (1965).

12) E. Hayon and M. Moreau, *J. Chim. Phys.*, 391 (1965).

13) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, **18**, 493 (1967).

14) W. Kohnlein and D.S. Frohlinde. *Radiat. Res.*, **38**, 173 (1969).

15) H. Hase and L. Kevan, *J. Phys. Chem.*, **73**, 3290 (1969).

16) W. A. Seddon and D. R. Smith, *Can. J. Chem.*, **45**, 3083 (1967).

17) P. N. Moorthy and J. J. Weiss, *Nature*, **201**, 1318 (1964).

18) R. S. Eachus and M. C. R. Symons, *J. Chem. Soc. A*, **1970**, 3080.

19) F. L. Conde and L. Prat, *Anal. Chim. Acta*, **16**, 473 (1957).

20) "Advanced Inorganic Chemistry", ed. by P. J. Durrant and B. Durrant, Longmans, London (1962), p. 1001.