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Reaction Intermediates in γ-Irradiated Mercaptans at 77°K

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Elementary processes in the radiolysis of ethyl mercaptan has been investigated by both spectrophotometric and electron spin resonance (ESR) methods. Ethyl mercaptan (C_2H_5SH) forms a glassy solid at 77°K, and when irradiated with γ-rays from Co-60, it develops a deep orange color; this color fades upon illumination with visible light, leaving a clear yellow color. The ESR spectrum of γ-irradiated C_2H_5SH at 77°K consists of two components; one is a complex spectrum which has been identified with the spectrum of $C_2H_5S\cdot$, while the other is a photobleachable broad singlet which has been assigned to the ionic species. The $C_2H_5S\cdot$ radical shows an absorption spectrum with $\lambda_{max}=405$ nm. The G-values for the formation of the radicals and the ionic species were 0.5 and 2.9 respectively. Studies of 2-methyltetrahydrofuran and butyl chloride solutions of C_2H_5SH were performed to identify these ionic species. Some significant elementary processes will be discussed on the basis of these results.

The reaction intermediates in the radiolysis of organic compounds have recently been studied in order to elucidate the elementary processes in the radiation chemistry using spectrophotometric and ESR methods. Much information about the ionic species and radicals produced by the γ-irradiation of organic glasses has been given by these techniques.

Ethyl mercaptan forms a clear glass at 77°K, so it is easy to measure the reaction intermediates by an optical method. In the case of sulfur-containing compounds, molecular ions have been expected as intermediates of γ-radiolysis.[1-3] Hitherto, there have been only a few ESR studies of the intermediates in the radiolysis of mercaptans and other organic compounds containing sulfur atoms in the solid state.[4-9] The assignment of free radicals has been established in these studies, while the broad ESR singlet observed in ethyl mercaptan has been attributed to ionic species without conclusive evidence.[5,8,9]

In the present study, the ionic intermediates and radicals produced by the γ-irradiation of pure ethyl mercaptan and by those in 2-methyltetrahydrofuran (MTHF) or butyl chloride glasses at 77°K have been investigated in detail by both spectrophoto-

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1) F. K. Truby, D. C. Wallace and J. E. Hesse, *J. Chem. Phys.*, **42**, 3845 (1965).

2) S. B. Milliken, K. Morgan and R. H. Johnson, *J. Phys. Chem.*, **71**, 3238 (1967).

3) T. Shida, *ibid.*, **72**, 2597 (1968).

4) C. F. Luck and W. Gordy, *J. Amer. Chem. Soc.*, **78**, 3240 (1956).

5) K. Akasaka, S. Ohnishi and H. Hatano, *Kogyo Kagaku Zasshi*, **68**, 1548 (1965).

6) H. Shields and W. Gordy, *J. Phys. Chem.*, **62**, 789 (1958).

7) Y. Kurita and W. Gordy, *J. Chem. Phys.*, **34**, 282 (1961).

8) J. J. Myron and R. H. Johnson, *J. Phys. Chem.*, **70**, 2951 (1966).

9) S. B. Milliken, K. Morgan and R. H. Johnson, *ibid.*, **71**, 3238 (1967).

metric and ESR methods. Studies of several alkyl mercaptans have also been performed.

Experimental

Materials. Extra-pure-grade ethyl, *n*-propyl, isopropyl, and *n*-butyl mercaptans were distilled several times on a vacuum line and then stored in a vessel containing calcium hydride. MTHF (supplied by K & K Co.) was purified by passing it through an alumina column after having been fractionally distilled and dried with calcium hydride. Butyl chloride was purified by passing it through a silica gel column, after which it was distilled under vacuum and stored in a vessel containing calcium hydride.

Procedure. Sample tubes for ESR measurements were 4 mm in i.d. and were made of high-purity quartz; the quartz cells with a rectangular cross-section (1×1×4 cm) were used for spectrophotometric measurements. The degassing of the purified samples was accomplished by repeated freeze-pump-thaw cycles. Irradiations were made with γ-rays from Co-60 at 77°K, and in most cases at a dose rate of 6.3×10^{18} eV/g·hr. After γ-irradiation, ESR and optical absorption spectra measurements were carried out at 77°K on a Japan Electron JES-3BX spectrometer and a Hitachi EPU-2-type or Hitachi-Perkin Elmer 139 type spectrophotometer respectively.

Results

Pure Ethyl Mercaptan. Ethyl mercaptan is a glassy solid at 77°K; when irradiated with γ-rays, it develops a deep orange color and gives the ESR spectrum shown in Fig. 1a. This spectrum consists of two components. When γ-irradiated ethyl mercaptan glass is photobleached with visible light ($\lambda>325$ nm), the broad singlet ($\Delta H_{\mathrm{msl}}=30$ gauss) centered at $g=2.010$ gradually decreases and there remains a complicated radical spectrum (Fig. 1c).

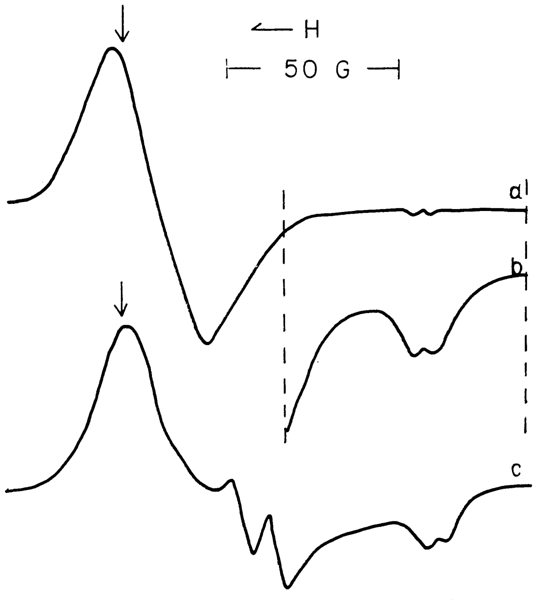

Fig. 1. ESR spectra of γ-irradiated ethyl mercaptan at 77°K.
a: before photobleaching (40db), b: the same spectrum with a greater sensitivity (80db), c: after photobleaching with light of $\lambda>325$ nm (80db) irradiation dose: 3.7×10^{19} eV/g

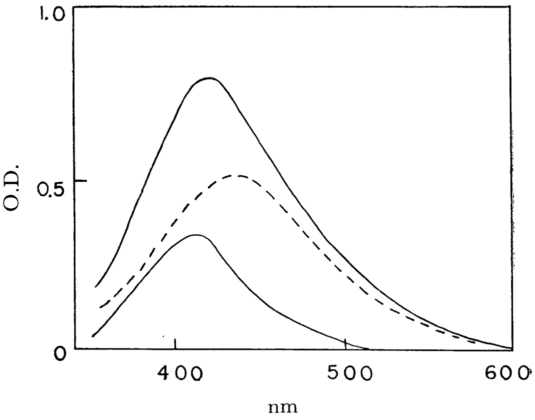

Fig. 2. Absorption spectra of γ-irradiated ethyl mercaptan at 77°K.
a: before photobleaching, b: after photobleaching with light of $\lambda>325$ nm, c: photobleached species, irradiation dose: 2.5×10^{18} eV/g

The absorption spectrum of a glassy ethyl mercaptan at 77°K is shown in Fig. 2. γ-Irradiation produces a broad band centered about 430 nm. This band is bleached with visible light and is responsible for the deep orange color. When bleached with visible light, there remains a band centered at 405 nm which is responsible for the yellow color.

When pure ethyl mercaptan is irradiated with light from a low-pressure mercury lamp at 77°K, it develops a clear yellow color and gives an absorption spectrum with $\lambda_{\max}=405$ nm (Fig. 3). The ESR spectrum of UV-irradiated pure ethyl mercaptan is shown in Fig. 4. This spectrum is identical with that in Fig. 1c and is assigned to the $C_2H_5S\cdot$ radical, because its g-tensor agrees with

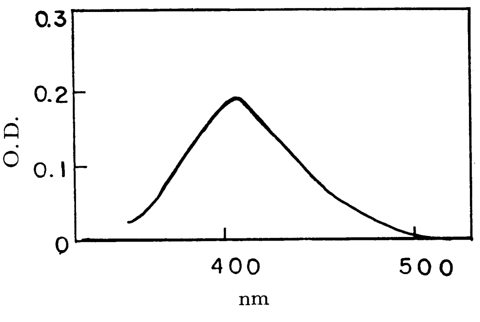

Fig. 3. Absorption spectrum of UV-irradiated ethyl mercaptan at 77°K.

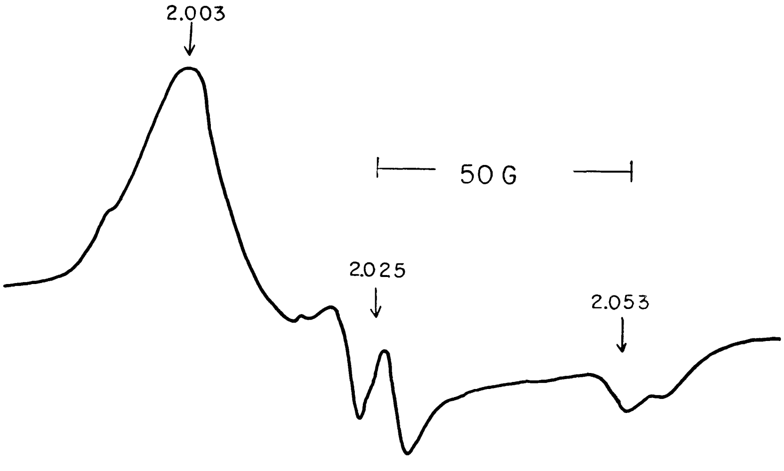

Fig. 4. ESR spectrum of UV-irradiated ethyl mercaptan at 77°K.

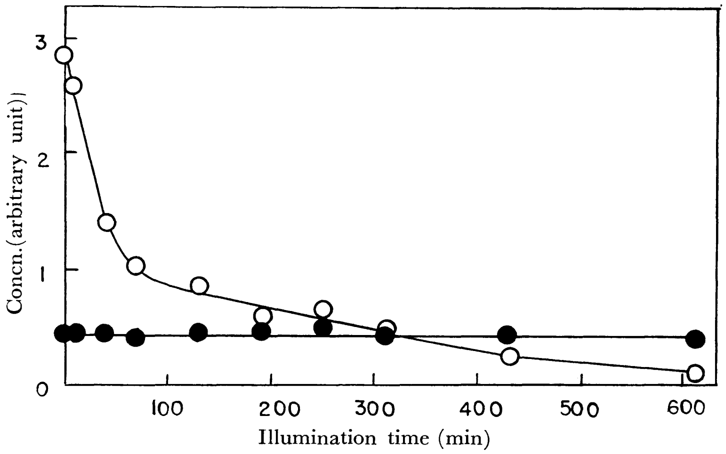

Fig. 5. Photobleaching of ionic species in γ-irradiated ethyl mercaptan at 77°K.
○: ionic species, ●: $C_2H_5S\cdot$ radicals

that of the cystein radical,[4] $HOOC(NH_2)CHCH_2S\cdot$.

The broad singlet which gives $\lambda_{max}=430$ nm is tentatively assigned to an ionic species, and the complicated ESR spectrum which gives $\lambda_{max}=405$ nm is assigned to the $C_2H_5S\cdot$ radical.

The effect of the time of photobleaching on the ionic species and the radicals is shown in Fig. 5. The ionic species decayed rapidly in the initial period and then slowly at 77°K, while the amounts of $C_2H_5S\cdot$ radicals did not change significantly between before and after photobleaching. It was also confirmed that the ionic species decayed relatively rapidly in the initial stage and then very slowly at 77°K in the dark, and no increase was observed in the quantity of $C_2H_5S\cdot$ radicals.

The concentrations of ionic species and of $C_2H_5S\cdot$ radicals increases with an increase in the irradiation dose in the range studied.

The G-values for the formation of the ionic species and the radicals were 2.9 and 0.5 respectively. The latter value agrees with the radical yield of hexyl mercaptan, $G(\text{radical})=0.4$ at $-150°C$,[10] within the limits of experimental error.

Ethyl Mercaptan in MTHF. When a MTHF solution containing 5 mol% of ethyl mercaptan is irradiated at 77°K with γ-rays, it develops a yellowish green color. The ESR spectrum is shown in Fig. 6, superimposed on the seven-line spectrum due to the MTHF radical. This broad singlet spectrum is the same as that observed in γ-irradiated pure ethyl mercaptan. Small amounts of the ethyl radical are also seen in Fig. 6. The narrow singlet due to the trapped electron of MTHF was not observed in this case.

The optical absorption spectrum of the MTHF solution of ethyl mercaptan is essentially the same as that of Fig. 2, although some shift in λ_{max} is

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[10] V. I. Trofimov, I. I. Chkheidze, L. I. Bellen'kii and N. Ya. Buben, *Kinetika i Katalyz*, **7**, 540 (1966).

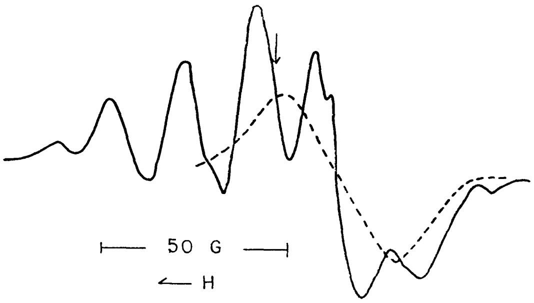

Fig. 6. ESR spectra of γ-irradiated MTHF solutions containing 5 mol% of ethyl mercaptan at 77°K.
irradiation dose: 8.7×10^{18} eV/g

seen in this case. Upon the illumination of this sample with light of $\lambda > 325$ nm, the band centered at 410 nm was bleached. This band is also reduced by the addition of carbon tetrachloride as an electron scavenger.

Ethyl Mercaptan in Butyl Chloride. The ESR spectrum of γ-irradiated butyl chloride containing 5 mol% of ethyl mercaptan consists of two components; one is assigned to the butyl radicals, and the other is the same broad singlet as that observed in γ-irradiated pure ethyl mercaptan.

The general features of the optical absorption spectrum of γ-irradiated BuCl solution of ethyl mercaptan are like those of γ-irradiated pure ethyl mercaptan.

Other Alkyl Mercaptans in MTHF. The optical absorption spectra of γ-irradiated MTHF solutions of *n*-propyl, isopropyl, and *n*-butyl mercaptans give broad bands centered at about 410 nm and develop a deep orange color. They are also photobleached with visible light ($\lambda > 325$ nm) leaving a yellow color.

Discussion

The species responsible for the ESR singlet and the 430 nm band observed in γ-irradiated ethyl mercaptan may be attributable to ionic species, because they can be photobleached and considerably reduced in the presence of iodine.

Truby *et al.*[1] have extensively studied the intermediates in the solid state radiolysis of disulfides and have concluded that electron ejected by the radiation are captured by the sulfur group of disulfide, that positive charges are also localized at the sulfur group, and that these processes do not lead to molecular dissociation. In the case of the solid state radiolysis of ethyl mercaptan, it also seems reasonable to consider that the mercaptan positive ion remains in the form of $C_2H_5SH^+$ and that ejected electrons are captured to form a molecular anion, $C_2H_5SH^-$. The results obtained from the ESR and optical absorption spectra of γ-irradiated ethyl mercaptan in MTHF solutions essentially coincide with those of γ-irradiated pure ethyl mercaptan. The bond dissociation energy of C_2H_5–SH (69 ± 5 kcal/mol) is greater than its electron affinity (60 kcal/mol); the dissociative electron capture, $C_2H_5SH + e^- \rightarrow C_2H_5\cdot + SH^-$, can, therefore, not be expected in this case. These facts indicate that $C_2H_5SH^-$ is involved in the spectrum of γ-irradiated pure ethyl mercaptan.

The ethyl radicals observed in γ-irradiated ethyl mercaptan in MTHF solutions may arise from the decomposition of directly excited C_2H_5SH. The fact that the ethyl radical was not observed in an appreciable amount in pure ethyl mercaptan can be explained by assuming that the $C_2H_5\cdot + C_2H_5SH \rightarrow C_2H_6 + C_2H_5S\cdot$ reaction takes place in this case, although the activation energy of this reaction has not been established. This assumption seems reasonable, because diethyl disulfide has been found among the radiolysis products of liquid ethyl mercaptan.[8]

The following interpretations of the broad ESR singlet and the optical absorption band in the 430 nm region observed in γ-irradiated ethyl mercaptan in BuCl glasses may be derived from the experimental results:

It is well known that butyl chloride forms a glass at 77°K and that radiation ejected electrons in the chloride are scavenged by the matrix itself,

$$\mathrm{BuCl} + e^- \rightarrow \mathrm{Bu}\cdot + \mathrm{Cl}^{-\,11)} \qquad (1)$$

The positive hole is mobile at an early stage but is then trapped by the matrix, giving rise to a broad band at 400—600 nm.

In the case of the γ-irradiated ethyl mercaptan in BuCl glasses, the BuCl cation band disappeared. The 430 nm band is similar to that of the anion band in its position, but considering the efficient scavenging reaction (1), this species may be attributable to the $C_2H_5SH^+$ produced instead of $BuCl^+$.

Another possible species is $C_2H_5SH^-$, which is produced by the competivie reaction between (1) and

$$C_2H_5SH + e^- \longrightarrow C_2H_5SH^- \qquad (2)$$

for the following reasons: 1) The rate constants of hydrated electrons at room temperature are of the order of $\sim 5 \times 10^{18}\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$ for butyl chloride and of $\sim 2 \times 10^{10}\mathrm{M}^{-1}$ for methyl mercaptan. The efficiency of the electron capture of mercaptan in an aqueous solution is roughly 40 times that of BuCl, so the competition between (1) and (2) seems conceivable under the present experimental conditions (the concentration of ethyl mercaptan in BuCl is 5 mol% in this case) and 2) The fact that $C_2H_5SH^+$ and $C_2H_5SH^-$ have the same posi-

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[11] a) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 4372 (1966). b) *J. Amer. Chem. Soc.*, **88**, 3683 (1966). c) *Ibid.*, **88**, 5371 (1966). d) *Ibid.*, **88**, 5376 (1966).

tion in λ_{max} is not acceptable in view of the general features of the optical absorption measurements of many other linear organic compounds.

If the 430 nm band or the broad ESR singlet is assigned to an anionic species, $C_2H_5SH^+$ should be found, because the BuCl cation band disappears upon the addition of ethyl mercaptan.

The cationic species of disulfides have been found to have absorption maxima between 700—900 nm.[3,12] The absorption spectra of ethyl mercaptan in the BuCl matrix and the 3-methylpentane matrix were measured over the range of 700—1000 nm in order to identify $C_2H_5SH^+$. However, no species other than the 430 nm band was found in this case. This fact seems to indicate that $C_2H_5SH^+$ has an absorption maximum at a wavelength longer than 1000 nm or that the extinction coefficient of $C_2H_5SH^+$ band is too small to be found in the visible region of the absorption spectrum under the present experimental conditions. Another possibility is that the 430 nm band includes some cationic species other than $C_2H_5SH^+$.

It is difficult to identify the 430 nm band in the BuCl matrix with either cationic or anionic ones. Further study is required to establish the assignment of this band.

The following elementary processes for γ-irradiated ethyl mercaptan can be considered on the basis of these results, although cationic species have not yet been clearly identified:

$$C_2H_5SH \rightsquigarrow \begin{cases} C_2H_5SH^+ + e^- \\ C_2H_5SH^* \end{cases}$$

$$C_2H_5SH + e^- \longrightarrow C_2H_5SH^-$$

$$C_2H_5SH^* \longrightarrow C_2H_5S\cdot + H$$

$$\searrow \text{ or } C_2H_5\cdot + \cdot SH$$

$$C_2H_5\cdot + C_2H_5SH \longrightarrow C_2H_6 + C_2H_5S\cdot$$

Photobleaching

$$C_2H_5SH^- \longrightarrow C_2H_5SH + e^-$$

$$C_2H_5SH^+ + e^- \longrightarrow C_2H_5SH$$

The optical absorption spectra of γ-irradiated MTHF solutions of *n*-propyl, isopropyl, and *n*-butyl mercaptans give broad bands centered about 410 nm and develop a deep orange color. They are also photobleached with visible light ($\lambda > 325$ nm) leaving a yellow color. The photobleachable species may be attributable to a molecular anion, RSH^-, and unbleachable parts, to the radicals, $RS\cdot$.

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[12] J. Wendenburg, H. Mockel, A. Granzow and A. Henglein, *Z. Naturforsch.*, **21b**, 632 (1966).