*Decomposition and Energy Transfer in the Radiolysis of Sulfur Compounds in Toluene**

By Wataru ANDO, Ken'ichi SUGIMOTO and Shigeru OAE

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One of the most interesting problems in the radiation chemistry of organic compounds is that of energy transfer from excited solvent molecules to reacting solute molecules. Energy transfer has been used to explain the nonlinear dependence of product yields upon the electron fraction of a two-componet system. In the typical example of the cyclohexane-benzene system,1) the yield of the hydrogen formed was found to be always less than that to be expected from the decomposition of two components.

Much evidence on the energy transfer has been obtained recently. For example, unusually high G-values have been found for the nitrate decomposition in alkali halide,2) and for the radical formation in a benzene solution of organic disulfide.3) Gusynin and Tal'roze4) have found that, for terphenyl in dioxane, the quenching cross section for an alcohol is proportional to the number of carbon atoms in the alcohol, suggesting that energy can be transferred readily along the $-CH_2-$ chain to the OH group. The compounds, 1, 1-dicyclohexyldodecane, 1, 1-diphenyldodecane, 1-phenyl-1-cyclohexyldodecane, cyclohexane, and benzene, were irradiated while frozen at $-120°C$, and their radical yields and ESR spectra were measured.5) The results have suggested a possible intramolecular transfer of energy to the benzene ring. Intermolecular transfer also occurs, but with a lower efficiency.

The recent study of energy transfer in the benzene - thiophenol system6) has shown that most of the energy of the excited benzene molecule is transferred to thiophenol. Furthermore, in the toluene - sulfur - cyclohexane or the toluene - sulfur - carbon disulfide system,7) hydrogen formation is consistent with the interpretation that toluene is protected by carbon disulfide because the latter compound has a lower excitation, or that cyclohexane is protected by toluene because the latter has lower excitation and ionization potentials.

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* The Study of the Radiation Chemistry of Organic Sulfur Compounds, III.

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2) A. B. Jones, *J. Chem. Phys.*, **35**, 751 (1961).

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The present investigation was undertaken in order to obtain some direct information about the energy transfer in the free radical formation from a toluene solution of sulfur compounds under irradiation.

Experimental

Material.—Toluene was purified by the usual fractional distillation, and its purity was checked by gas chromatography. All the disulfides were purchased from Tokyo Kasei and were used after recrystallization from 96% ethanol. Purified products with a melting point range of less than 1.0 deg. were used. Diphenyl sulfide was obtained by the reaction of benzene with sulfur in the presence of aluminum chloride, and it was purified by vacuum distillation[8] (b. p. 126°C at 3 mmHg.).

Procedure.—The free radical yields in the decomposition of the sulfur compounds were determined by scavenging the radicals with diphenyl picryl hydrazyl (DPPH). The disappearance of the scavenger was followed by measuring the decrease in the optical density at $530\,\mathrm{m}\mu$ with the absorption coefficient of $1.2\times10^4\,\mathrm{mol}^{-1}\,\mathrm{l.\,cm}^{-1}$, where the absorption of the yellow scavenged product is insignificant.

The concentration of DPPH in toluene was kept constant within the range of 1×10^{-3} and 4×10^{-4} mol./l. during the run. The observed optical densities were corrected against the relaltive background absorption of the solution of DPPH in toluene without sulfur compounds which would be formed during the irradiation. The solution of DPPH in pure toluene was irradiated under the same conditions as those used for the solution ncotaining the sulfur compound, and the differenec between the absorbances of DPPH in the two solutions was taken as the consumption of DPPH reacting with radicals derived from the sulfur compounds.

All the samples were thoroughly degassed by twice freezing and thrawing them in a vacuum. Irradiation was carried out with a 1000-curie Co-60 source at room temperature, and the dose rate was 1.6×10^4 r.

Results and Discussion

The irradiation of the sulfur compounds in toluene at room temperature produced a significant change in the optical density of DPPH, presumably by means of the formation of radicals from the decomposition of the sulfur compounds. The overall reaction of DPPH with free radicals is complicated by secondary reactions.[9,10] However, it may safely be assumed that the free radicals formed by the decomposition of the sulfur compounds in the primary step react with two DPPH molecules to form inactive products, and that, therefore, the amount of the decomposition of a sulfur compound is just a half of that of the disappearance of DPPH.

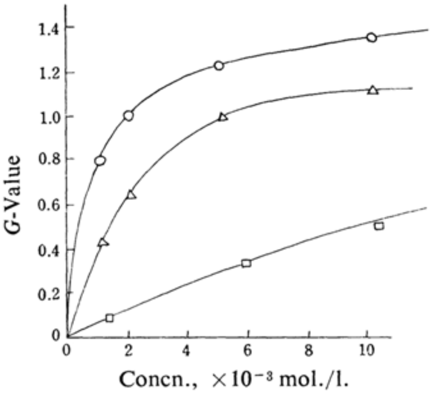

Fig. 1. Comparison of *G*-value on the decomposition of benzyl sulfur compounds in toluene solution.
○ Benzyl mercaptan
△ Benzyl disulfide
□ Benzyl sulfide

From Fig. 1, it is quite obvious that the amount of the decomposition of a sulfur compound depends on the initial concentration of the sulfur compounds. Assuming that the ionizing radiation directly effects the decomposition of the sulfur compound, the apparently higher *G*-values can be calculated on the basis of the direct effect; thus, the *G*-values are calculated to be nearly 700 for the disulfide, 200 for the sulfide, and 25000 for the mercaptan.

When one considers their bond dissociation energies, these *G*-values are much higher than the maximum *G*-values to be expected from the complete consumption of the direct energy absorbed. A better interpretation would be that the excited toluene formed by the irradiation transfers energy relatively easily to the sulfur compounds, resulting in dissociation into free radicals. Figure 2 shows the linearity of the relationship of the benzyl disulfide decomposition against the irradiation dose.

Now, let us assume that most of the energy is absorbed by toluene and that the amount of energy absorbed directly by the small amount of a sulfur compound is presumably small enough to be disregarded, since the absorption of energy is essentially independent of the nature of the component.

$$C_6H_5CH_3 \xrightarrow{I} C_6H_5CH_3^* \tag{1}$$

Therefore, excited toluene molecules in the system would usually lose their energy by the

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[10] J. Russel, *J. Phys. Chem.*, **58**, 437 (1954).

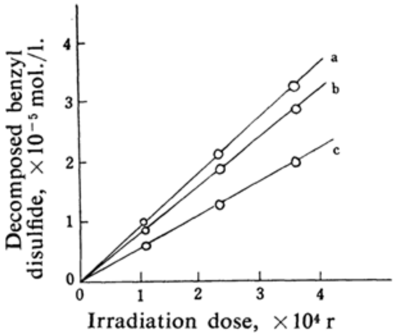


Fig. 2. Decomposition of benzyl disulfide in toluene solution under irradiation.
a 10 mmol./l. b 5 mmol./l. c 2 mmol./l.

following two processes:

Deactivation $C_6H_5CH_3^* \xrightarrow{k_1} C_6H_5CH_3$ (2)

Transfer of energy

$C_6H_5CH_3^*$ + Sulfur compd.

$\xrightarrow{k_2} C_6H_5CH_3$ + Sulfur compd.* (3)

Each sulfur compound, when sufficiently excited, produces at leasts two radicals by the decomposition. A part of the excited sulfur compound may lose its energy by collision without decomposition.

Decomposition

Sulfur compd.* $\xrightarrow{k_3}$ 2 Radicals (4)

Deactivation

Sulfur compd.* $\xrightarrow{k_4}$ Sulfur compd. (5)

Recombination

2 Radicals $\xrightarrow{k_5}$ Sulfur compd. (6)

Radicals formed according to Eq. 4 will be trapped by DPPH, which is present in a high concentration.

Product Radical + DPPH $\xrightarrow{k_6}$ Product (7)

Using the steady state equation, the *G*-value of the decomposition of a sulfur compound is obtained from this expression, which is based on a relatively small value of k_2:

$$G=\frac{k_3\cdot k_2\cdot I\cdot C}{(k_3+k_4)(k_1+k_2\cdot C)}$$

In the above equation *I* represents the number of molecules excited by 100 eV. of gamma rays, where *C* is the concentration of the sulfur compound. The above relation may be rewritten in the following convenient form, since k_3 would be much larger than k_4:

$$\frac{1}{G}=\frac{1}{I}\left(1+\frac{k_1}{k_2\cdot C}\right)$$

The relations of $1/G$ and $1/C$ for the benzyl sulfur compounds are shown in Fig. 3.

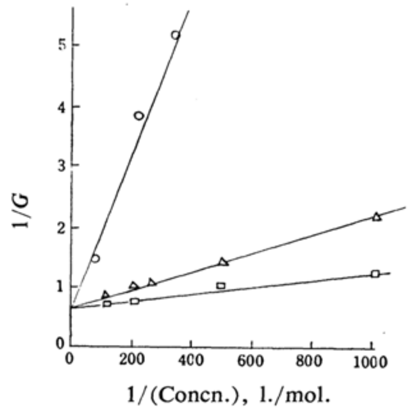


Fig. 3. Relation of $1/G$ and $1/C$ of sulfur compounds.
□ Benzyl mercaptan
△ Benzyl disulfide
○ Benzyl sulfide

The intercept of a straight line in Fig. 3 presumably gives the value of $1/I$, in which *I* represents the number of excited toluene molecules formed by 100 eV. of gamma rays. From the slope of the lines, one can get the relation of k_1 and k_2, which may represent the efficiency of the energy transfer from excited toluene to the sulfur compounds. Table I shows the relative energy transfer and the *G*-value at 5 mmol. of the sulfur compounds.

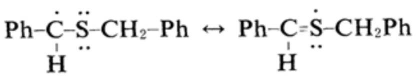
TABLE I. RADIOLYSIS OF SULFUR COMPOUNDS IN TOLUENE

Compound	I	k_2/k_1	*G*-Value at 5 mmol./l.
Benzyl mercaptan	1.4	1160	1.22
Benzyl disulfide	1.4	470	1.0
Benzyl sulfide	1.4	45	0.26
Diphenyl disulfide	1.4	660	1.1
p-Tolyl disulfide	1.4	660	1.1
Diphenyl sulfide	1.4	3.5	0.01
p-Tolyl sulfide	1.4	1.4	0.025

The largest energy transfer from toluene was observed in the decomposition of benzyl mercaptan. The lower value of decomposition for the disulfides shows that the disulfides can absorb energy from the excited toluene less than half as effectively as does the mercaptan.

As compared to the mercaptans or the disulfides, benzyl sulfide is less effective in energy absorption. This means that the C–S bond is relatively insensitive to radiation compared to the –S–H or –S–S– bond. However, the C–S bond in dibenzyl sulfide is relatively more sensitive to the radiation than that in diphenyl sulfide.

In dibenzyl sulfide, not only the cleavage of C–S bond but also that of the C–H bond of methylene linkage could take place, since the latter cleavage would be facilitated by the stabilization through the following electron-sharing 3d-orbital resonance with a sulfur atom:[11,12]



$$\mathrm{Ph{-}\underset{H}{\overset{\cdot}{C}}{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}{-}CH_2{-}Ph} \leftrightarrow \mathrm{Ph{-}\underset{H}{C}{=}\underset{\cdot\cdot}{\overset{\cdot}{S}}{-}CH_2Ph}$$

Particularly important are the findings that the S–H bond is very effective in energy absorption from the solvent and that the S–S bond is similarly quite effective in energy absorption from the solvent.

An interesting implication from these data is that a similar process may be involved in the radiation protection in the biological system by such mercapto compounds as cystein or cysteamine.[13-15] Here, too, mercaptans are more effective in protecting radiation than disulfides, which in turn are better radiation-protecting compounds than sulfides.

Summary

The decomposition yields of organosulfur compounds in toluene have been studied using DPPH as a radical scavenger. The effect of the concentration of sulfur compound is quite marked, and the irradiation energy absorbed in the solution of toluene seemed to be transferred to the sulfur compound. The largest energy transfer from toluene has been observed in the decompostion of benzyl mercaptan, while the disulfide has been shown to absorb the energy from the excited toluene less than half as effectively as does the mercaptan. As compared to the mercaptan or the disulfide, benzyl sulfide is far less effective in energy absorption.

Department of Chemistry
Radiation Center of Osaka Prefecture
Sakai, Osaka. (W. A. & K. S.)

Department of Applied Chemistry
Faculty of Engineering
Osaka City University
Kita-ku, Osaka (S. O.)

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