The Radiation-induced Reaction of Benzyl Mercaptan and p-Tolyl Mercaptan in Various Organic Solvents[*]

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The radiation chemistry of hydrocarbon has been widely investigated. However, the effect of a minute amount of solute in the radiolysis of hydrocarbon has to date received very little attention.[1,2] When a solute is dissolved in a large excess of hydrocarbon, the direct effect of irradiation on the solute is rather unimportant. However, when the solute is involved in the reaction, additional effects occur; the solute is attacked by active species formed from the hydrocarbon, or excited energy is transferred to it from the hydrocarbon. Williams and Hamill[3] have previously shown that the irradiation of cyclohexane containing methyl iodide at the concentration of 1 mol.% results in a considerable dissociation of the methyl iodide. The effect has been ascribed to the dissociative capture of free electrons by methyl iodide. Furthermore, Hughes[4] has pointed out, in the radiolysis of iodine cyanide as a scavenger in liquid benzene, that energy from benzene is transferred, leading to the dissociation of the iodine cyanide, which in turn results in the production of iodine.

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[*] The Study of the Radiation Chemistry of Organic Sulfur Compounds, IV.

[1] R. H. Schuler, *J. Phys. Chem.*, **61**, 1472 (1957).

[2] M. Burton and S. Lipsky, ibid., **61**, 1461 (1957).

[3] R. R. Williams and W. H. Hamill, *Radiation Research*, **1**, 158 (1954).

[4] G. Hughes, *J. Phys. Chem.*, **65**, 2160 (1961).

It has been observed in previous investigations[5,6] the radiolysis of hydrocarbon solutions of sulfur compounds that they are all appreciably reactive and that the efficiency of energy absorption from hydrocarbon is usually very high.[7,8] The effect of thiophenol in the radiolysis of benzene has already been investigated.[5]

It is the purpose of the present investigation to extend these studies to other organic solvents. It is well known that six electrons of the aromatic molecule are loosely coupled to form a π-bond and that these π-electrons are non-localized and are thus free to move around in the molecule. Therefore, a π-electron system is expected to possess many excited levels, with lower excited energies. When an electron collides with a hydrocarbon which has a π-electron system, the non-localized electrons are expected to interact with the incident electron rather strongly, either dissociating themselves to form two active species or absorbing the energy. Meanwhile, the yields of free radicals from hydrocarbons have been shown to be related to the sensitivities of the hydrocarbons to radiation.[9]

In this work, the effects of the solvents on the decomposition of benzyl mercaptn and *p*-tolyl mercaptan will be investigated using a wider variety of solvents.

The solvents are divided into radiation-sensitive and -insensitive molecules from the magnitudes of the *G*-values of the radical formations, as is shown below:[10]

RELATIVELY RADIATION-INSENSITIVE MOLECULES

Solvent	*G*-value for radical yield
Carbon disulfide	0.85
Benzene	1.8
Toluene	3.1
Nitrobenzene	4.5

RELATIVELY RADIATION-SENSITIVE MOLECULES

Solvent	*G*-value for radical yield
Hexane	7.6
Cyclohexane	14.3
Acetone	50.0
Methanol	24.0
Dioxane	20.0

This paper will also discuss the reaction mechanism on the basis of a good set of experimental data on the effect of solvents.

Experimental

Experimental details are similar to those outlined in an earlier paper.[5] All the solvents used were purified by ordinary distillations. Benzyl mercaptan and *p*-tolyl mercaptan were purchased from Tokyo Kasei and were distilled in a vacuum under a nitrogen atmosphere before use. A solution of mercaptan was made by weighing, and also the concentration was checked by potentiometric titration with silver nitrate. Each sample was composed of a 20 ml. solution and was degassed in a vacuum line by repeating a cycle of freezing, pumping and melting at least three times. The degassed samples were sealed in irradiation tubes 200 mm. long and 20 mm. in diameter and irradiated.

After irradiation the samples were placed in a beaker, and the amount of mercaptan present was determined by potentiometric titration with silver nitrate. Irradiations were carried out at room temperature with a 5000 curie Co-60 source at a dose rate of 2×10^5 r/hr. The relative values for the decompositions were expressed by the difference between the mercaptan concentrations before and after the irradiation of 100 eV. absorbed into the solution.

Results

The Decomposition of Benzyl Mercaptan in Relatively Radiation-sensitive Solvents.—The radiolysis of benzyl mercaptan in the solvents which are relatively sensitive to the irradiation leads the mercaptan to the disulfide quite readily. The results obtained in cyclohexane, dioxane, methanol, acetone and hexane solutions are shown in Table I. The results indicate that in all the runs high degrees of the decomposition of the mercaptan (over 50~80% at 9.0×10^6 r) were observed.

TABLE I. THE DECOMPOSITION OF BENZYL MERCAPTAN IN THE SOLVENTS

Solvent	% Decomposition of 0.047 mol./l. of solvent at 9.0×10^6 r
Hexane	79
Acetone	64
Methanol	63
Cyclohexane	57
Dioxane	56

Although the initial mercaptan concentration varied from about 10 to 50 mmol./l., the *G*-values apparently depend on the concentration of the mercaptan.

The kinetics of the decomposition of the mercaptan are summarized in Fig. 1.

The decomposition of the mercaptan appears to be of the first order with respect to its concentration at the beginning, but it then rapidly levels off as soon as an equilibrium is

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[5] W. Ando, K. Sugimoto and S. Oae, This Bulletin, **36**, 893 (1963).

[6] W. Ando, K. Sugimoto and S. Oae, ibid., **37**, 353 (1964).

[7] W. Ando, K. Sugimoto and S. Oae, ibid,, **37**, 357 (1964).

[8] V. A. Krongang, and Kh. S. Bagadasaryan, *Doklady. Akad. Nauk. S.S.S.R.*, **132**, 1136 (1960).

[9] M. Inokuti, *Isotope and Radiation*, **1**, 82 (1958).

[10] A. Prevost-Bernas, *Discussions Faraday Soc.*, **12**, 88 (1958).

TABLE II. THE EFFECT OF CONCENTRATION ON THE DECOMPOSITION OF BENZYL MERCAPTAN IN SOLVENTS

Solvent	Initial concentration mol./l.	*G*-Value of decomposition of mercaptan at 9.0×10^6 r
Hexane	0.047	6.1
	0.035	4.5
	0.024	3.0
	0.0096	1.0
Acetone	0.047	4.1
	0.035	2.8
	0.024	2.5
	0.0096	0.8
Methanol	0.048	4.2
	0.036	3.3
	0.024	2.5
	0.0096	0.64
Cyclohexane	0.042	3.4
	0.031	3.1
	0.024	2.2
	0.0084	1.0
Dioxane	0.043	3.3
	0.032	2.7
	0.024	2.3
	0.0084	0.75

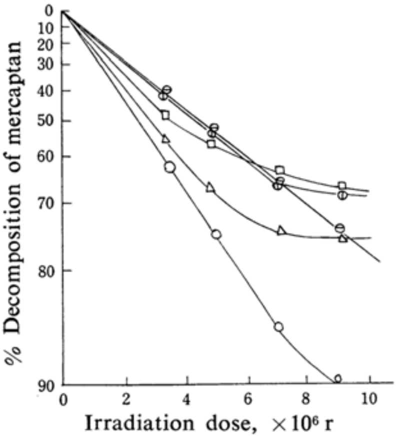

Fig. 1. The decomposition of benzyl mercaptan in various solvents at room temperature.
△ hexane ⦶ cyclohexane ○ dioxane
⊖ acetone □ methanol

attained by the reversal hydrogen-abstraction reaction of the mercapto radical from the solvents.

The Decomposition of *p*-Tolyl Mercaptan in Relatively Radiation-sensitive Solvents. — The radiolysis of *p*-tolyl mercaptan in hexane, cyclohexane, dioxane, methanol and acetone follows a course very similar to that of benzyl mercaptan in relatively radiation-sensitive solvents; the conversion of the mercaptan with radiation dose was nearly of the first order with respect to its concentration, but it is gradually accelerated as the decomposition of the mercaptan proceeds further. Table III and Fig. 2 show the results of these experiments.

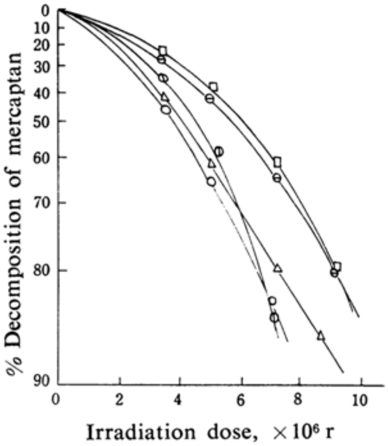

Fig. 2. The decomposition of *p*-tolyl mercaptan in various solvents at room temperature.
△ hexane ○ cyclohexane ⦶ dioxane
□ acetone ⊖ methanol

TABLE III. THE EFFECT OF CONCENTRATION ON THE DECOMPOSITION OF *p*-TOLYL MERCAPTAN IN SOLVENTS

Solvent	*G*-Value of the decomposition of the mercaptan at 9.0×10^6 r Initial concn., mol./l.			
	0.048	0.036	0.024	0.010
Hexane	4.6	4.4	3.5	1.5
Acetone	3.7	3.2	2.5	1.2
Methanol	2.7	2.7	2.6	1.1
Cyclohexane	4.2	3.8	3.3	1.4
Dioxane	2.2	2.1	2.3	0.6

This evidence leads to the following conclusion. The mercapto radical formed in the radiolysis of the mercaptan may usually abstract hydrogen from hydrocarbon, as was discussed in the previous section. However, the mercapto radical formed by the decomposition of *p*-tolyl mercaptan would be substantially resonance-stabilized, and hydrogen abstraction by this mercapto radical is not favored. In this case, probably some radicals formed by the dissociation of solvent molecules leads the decomposition of *p*-tolyl mercaptan.

The Decomposition of Benzyl Mercaptan and *p*-Tolyl Mercaptan in Relatively Radiation-insensitive Solvents.—Carbon disulfide, benzene, toluene and nitrobenzene were investigated as solvents for the decomposition of benzyl mercaptan and *p*-tolyl mercaptan (Tables IV and V). It was found that the amount of the decomposition of the mercaptans in these solvents was much less than that in radiation-sensitive solvents, and that the G-values of the decomposition of the mercaptans were of the same order of magnitude in all four cases.

TABLE IV. THE EFFECT OF THE CONCENTRATION ON THE DECOMPOSITION OF BENZYL MERCAPTAN IN RELATIVELY RADIATION-INSENSITIVE SOLVENTS

Solvent	The G-value of decomposed mercaptan at 9.0×10^6 r Initial concn., mol./l.			
	0.048	0.036	0.024	0.0096
Carbon disulfide	0.78	—	0.58	0.35
Benzene	1.9	1.7	1.5	0.8
Toluene	2.1	1.8	1.7	0.8
Nitrobenzene	1.3	1.1	0.9	0.36

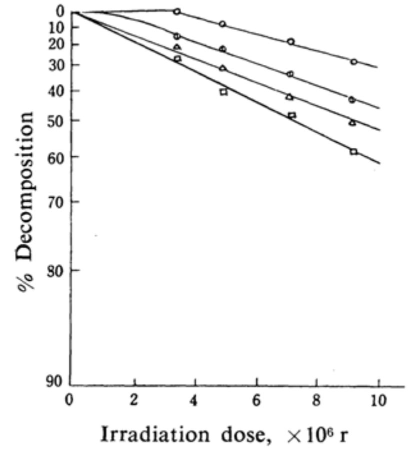

Fig. 3. The decomposition of benzyl mercaptan in aromatic hydrocarbon at room temperature.
○ carbon disulfide △ benzene □ toluene
① nitrobenzene

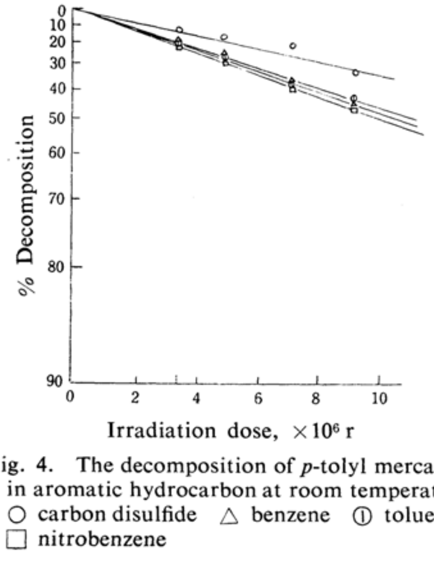

Fig. 4. The decomposition of p-tolyl mercaptan in aromatic hydrocarbon at room temperature.
○ carbon disulfide △ benzene ① toluene
□ nitrobenzene

TABLE V. THE EFFECT OF THE CONCENTRATION ON THE DECOMPOSITION OF p-TOLYL MERCAPTAN IN RELATIVELY RADIATION-INSENSITIVE SOLVENTS

Solvent	The G-value of Decomposition of mercaptan at 9.0×10^6 r Initial concn., mol./l.			
	0.048	0.036	0.024	0.0096
Carbon disulfide	0.96	0.76	0.65	0.33
Benzene	1.7	1.5	1.3	0.5
Toluene	1.9	1.7	1.1	0.5
Nitrobenzene	1.1	1.1	1.0	0.5

Figures 3 and 4 indicate that the decomposition of both benzyl mercaptan and p-tolyl mercaptan is of the first order with respect to the mercaptans and that there is no deviation from the first order kinetics, unlike in radiation-sensitive solvents.

The results indicate that either the mercapto radicals formed by the decomposition of the mercaptans do not abstract hydrogen from these solvents, or the induced decomposition of the mercaptans by the solvent radicals is much less than that in radiation-sensitive solvents.

Discussion

A General Examination of the Reaction Mechanism for the Decomposition of Mercaptan. —Our original intention was to estimate the extent of the radiation-induced decomposition of mercaptan. For this purpose it is, however, necessary to identify the liquid decomposition products. Even so, a few suggestions can be made on the basis of our previous observations and of the present findings on the decomposition of the mercaptans.

Haines, Cook and Ball,[11] in studying the photochemical decomposition of sulfur compounds, have indicated that the decomposition of mercaptan involves primarily the cleavage of RS-H linkage, as can be formulated in the following equations:

$$\mathrm{RSH} \rightarrow \mathrm{RS} + \mathrm{H} \tag{1}$$

$$\mathrm{H} + \mathrm{RSH} \rightarrow \mathrm{RS} + \mathrm{H_2} \tag{2}$$

$$2\mathrm{RS} \rightarrow \mathrm{RS\text{-}SR} \tag{3}$$

This mechanism can be adopted similarly for the interpretation of the observation made in the radiolytic decomposition of benzyl mercaptan. In order to get a clear picture of the decomposition of the mercaptan in the solvents, it is desirable to obtain the G-values of the decomposition of the mercaptan alone without solvents.

The results obtained are shown in Table VI.

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[11] W. E. Haines, G. L. Cook and J. S. Ball, *J. Am. Chem. Soc.*, **78**, 5213 (1956).

TABLE VI. BENZYL MERCAPTAN DECOMPOSITION UNDER GAMMA-RAY IRRADIATION

Irradiation	1.8×10^7 r
Sample	5.290 g.
$G(H_2)$	0.95
$G(-C_6H_5CH_2SH)$	1.9, assuming $G(-SH) = 2G(H_2)$

Now that the *G*-value of the mercaptan decomposition can be compared with those in solvents, one can draw the following conclusions concerning the general nature of the decomposition processes of mercaptan. (1) The reaction presumably proceeds through the process of transferring energy from the solvents to mercaptan. (2) The intermediate radicals from solvents are hydrogen acceptors of mercaptan.

It may be seen from the data in radiation-insensitive solvents that the concentration of mercaptan appears to effect the decomposition of mercaptan, and that the *G*-value of mercaptan decomposition is nearly identical with that of mercaptan alone. One can, therefore, assume that the radiation energy from the gamma rays effects the mercaptan decomposition either by a direct or an indirect process.

First the energy of irradiation is absorbed by then solvent; then it forms some radicals so formed attack the S–H bond of the mercaptan as illustrated below:

$$S \rightsquigarrow S^* \tag{4}$$

$$S^* \rightarrow S\cdot \tag{5}$$

$$S\cdot + RSH \rightarrow SH + RS\cdot \tag{6}$$

where S is the solvent.

The mercapto radicals formed will then lead to reaction 3. However, the kinetic data which follow the first order with respect to the mercaptan are not in accord with this process. The other possibility is that the radiation energy initially absorbed by the solvent is transferred very rapidly to the mercaptan. Such a direct transfer of radiation-excited energy is well known in liquid solutions.[12] It is possible that this process of energy transfer is responsible for the decomposition of mercaptan. In addition to the excitation process of the solvent in reaction 4, the energy transfer to the mercaptan can be represented by:

$$S^* + RSH \rightarrow S + RSH^* \tag{7}$$

Excited mercaptan would then be led to dissociation into two radicals according to reaction 1. The decomposition of the mercaptan can thus be correlated with the experimental observations, especially in the case of the decomposition in radiation-insensitive solvents.

However, since mercaptan is quite sensitive to radical attack, one cannot be absolutely certain that this process alone is responsible for the decomposition of mercaptan. The results obtained in this work to indicate, however, that energy can be absorbed readily into the solvent and that the process of energy transfer to the solute (reaction 7) is in competition with the process of forming their own radicals from the excited solvent molecules (reaction 5).

Evidence of Solvent-Mercaptan Interaction.—As can be seen in Figs. 1 and 2, the two different mercaptans follow different courses in the decompositions in relatively radiation-sensitive solvents. The decomposition of benzyl mercaptan initially increases linearly with the increase in the radiation dose, then it rapidly levels off from the linear relationship. This could be interpreted as being caused by the equilibration, arising from the hydrogen abstraction by the mercapto radicals in order to reverse the reaction, since the solvents are generally thought to function as hydrogen donors.[13]

$$RS\cdot + RH \rightleftarrows RSH + R\cdot \tag{8}$$

However, the results for the decomposition of the mercaptan in radiation-insensitive solvents indicate that it is difficult for the above process to occur, as can be seen in Figs. 3 and 4, since the bond energy of the C–H linkage of the radiation-insensitive solvents is much higher than that of the sensitive solvents; hence, the radiation-insensitive solvents can not be good hydrogen donors. Meanwhile, the decomposition of *p*-tolyl mercaptan in radiation-sensitive solvents initially shows a linear relationship with the dose; it is rapidly accelerated as the decomposition proceeds, thus suggesting that the reaction is promoted by some process as the decomposition of the mercaptan proceeds further.

This is not surprising, since the mercapto radical from *p*-tolyl mercaptan is substantially resonance-stabilized; thus the radicals, formed by the radiolysis of solvents, may easily abstract hydrogen from *p*-tolyl mercaptan, accelerating the decomposition of the mercaptan as the reaction proceeds.

The Solvent Effect on the Decomposition of Mercaptan.—The results of the decomposition of mercaptan in various solvents may be summarized thus. (1) The radiation-sensitive solvents are easily attacked by the benzyl mercapto

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[12] J. P. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952).

[13] C. Walling and R. Rabinowitch, *J. Am. Chem. Soc.*, **81**, 1137 (1959).

radical and function as hydrogen donors. (2) When the resulting mercapto radicals are fairly stabilized by resonance such as that of the tolyl mercapto radical obtained from tolyl mercaptan, solvent radicals from the radiolysis of solvents will abstract hydrogen from mercaptan. This will cause the additional decomposition of mercaptan which is seen in *p*-tolyl mercaptan in solvents. (3) The decomposition of the mercaptan in radiation-insensitive solvents show relatively lower *G*-values than those in radiation-sensitive solvents. When a radiation-insensitive solvent has an aromatic π-electron system, the radiation energy absorbed will be dissipated quite readily through the electronic excitation to lower levels of the solvent molecules; therefore, the proportion of energy transferred to the solute became very small, thus reducing the decomposition of the mercaptan.

Summary

The decomposition of benzyl mercaptan and *p*-tolyl mercaptan in various organic solvents has been studied, and the following conclusions have been obtained. 1) A radiation-sensitive solvent such as hexane is readily attacked by the benzyl mercapto radical. 2) When the resulting mercapto radicals are stabilized substantially by resonance, solvent radicals from the radiolysis of solvents will abstract hydrogen from the mercaptan. 3) The *G*-values of mercaptan decomposition in such solvents as hexane, cyclohexane, acetone, methanol and dioxane are relatively higher than those in carbon disulfide, benzene, toluene and nitrobenzene. The reaction presumably proceeds through the energy transfer process from solvent to mercaptan. When an aromatic π-electron system is present in any solvent, the radiation energy absorbed will be dissipated quite readily through electronic excitation to lower-energy levels of the solvent molecule.

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