The Formation of Sulfur Compounds in the Radiolysis of a Toluene Solution of Sulfur*

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In a previous investigation of the radiolysis of a benzene solution of sulfur,[1] the formations of mercaptan, disulfide and a few minor products have been observed, and it has been suggested that the reaction passes through the initial formation of a phenyl radial, which eventually reacts with sulfur to give the final products.

The treatment of hydrocarbon with ionizing radiation usually results in the formation of a variety of fragmentation products.[2] These radicals attack the S–S bond of elemental sulfur, thus:

$$\mathrm{RH} \xrightarrow{\gamma} \mathrm{R} + \mathrm{H}$$

$$\mathrm{R} + \mathrm{S_8} \rightarrow \mathrm{RS_8} \rightarrow \mathrm{RS}$$

Consistent with this view, the reaction of sulfur with cyclohexane under the ionizing radiation with gamma rays has also been shown by Barzynski and Hummel[3] to proceed via the initial formation of a cyclohexyl radical which cleaves the S–S bond of sulfur in the following step.

However, in the case of toluene, the free radical that formed initially would be benzyl which is remarkably more stable than the phenyl or cyclohexyl radical, and which hence might show somewhat different reaction patterns. In fact, the formation of dimerization products is the main path for the thermal reaction of toluene with sulfur,[4] while the similar reaction of cyclohexane undergoes dehydrogenation to benzene[5] and that of benzene leads to the formation of benzenethiol and its derivatives.

Thus, the study of the radiolysis of a toluene solution of sulfur would provide further insight into the nature of the radiolysis process of hydrocarbons in the presence of sulfur.

In the radiolysis of a toluene solution of sulfur, benzyl mercaptan was found to be formed by the cleavage of the S–S bond with the benzyl radical. Hydrogen and hydrogen sulfide were observed to evolve during the runs. This paper will describe a detailed study of the mechanism of the radiation-induced reaction of toluene with sulfur.

Experimental

Reagents.—Toluene was purified by fractional distillation just before use. The sulfur used in this

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

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

[2] A. J. Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, Oxford (1960).

[3] H. Barzynski and D. Hummels, *Z. physik. Chem. N. F.*, **33**, 352 (1962).

[4] A. W. Horton, *J. Org. Chem.*, **14**, 761 (1949).

[5] A. S. Brown and B. V. Ioffee, *Nauk. Byull. Leningrod. Gosudarst Univ.*, **20**, 11 (1948); *Chem. Abstr.*, **43**, 5376e (1949).

work was of an exceptionally high purity, as in the previous experiment.[1]

The preparation of the samples and the techniques of irradiation by cobalt-60 gamma rays have been described in a previous paper.[1]

Product Handling and Analysis.—After irradiation, the ampoules were broken in an evacuated system. All the volatile products formed were vacuum-transferred into a trap cooled with liquid nitrogen and carefully degassed by repeated warming and cooling. Then, non-condensable gases were vacuum-transferred to another trap by pumping. The major portion of the non-condensable gases at the temperature of liquid nitrogen, e.g., hydrogen and methane, were pumped into calibrated glass tubing with a Töpeler pump, and the pressure was measured. From this pressure measurement, *G*-values for the hydrogen gases were calculated.

The procedures for the determination of the mercaptan and hydrogen sulfide were almost identical with those described in the previous paper.[1]

Results and Discussion

Effects on Radiation on the Toluene-Sulfur System.—The irradiation of toluene with sulfur at room temperature gave benzyl mercaptan, hydrogen and hydrogen sulfide as the main products. The results of several illustrative runs are shown in Table I. In the experimental results, the following features are observed; 1) The *G*-value of the formation of the mercaptan depends on the concentration of sulfur. 2) The *G*-value for the formation of hydrogen is almost identical with that of hydrogen formation in the radiolysis of toluene alone, increasing slightly with the increase in sulfur concentration.

TABLE I. IRRADIATION OF TOLUENE WITH SULFUR

Sulur concn.	*G*-Value of product		
g./100 ml.	$C_6H_5CH_2SH$	H_2	H_2S
0.25	0.068	0.14	0.008
0.5	0.088	0.15	0.011
1.0	0.107	0.17	0.014
1.5	0.123	0.18	0.017

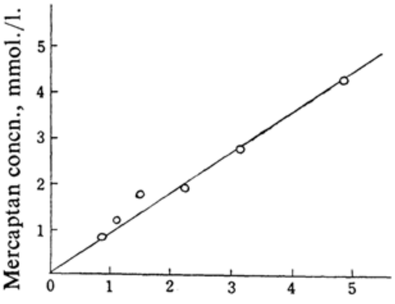

Fig. 1. Formation of benzyl mercaptan in radiolysis of toluene with sulfur (1.0 g. sulfur per 100 ml. of toluene).

Figure 1 shows that the amount of mercaptan formed increases linearly with the increase of the dose.

The increasing formation of the mercaptan appears to suggest that the reaction proceeds through the initial opening of the S_8 ring by γ-ray irradiation to form an open-chain sulfur radical which subsequently abstracts the hydrogen of the methyl group of toluene, producing the benzyl radical and the HS_x radical:

$$S_8 \xrightarrow{\gamma} S_x$$

$$C_6H_5CH_3 + S_x \rightarrow C_6H_5CH_2 + HS_x$$

$$C_6H_5CH_2 + S_x \rightarrow C_6H_5CH_2S_x \rightarrow C_6H_5CH_2S$$

However, the fact that the *G*-value of the hydrogen formation in this reaction system is nearly identical with that of the radiolysis of toluene alone[6] seems to suggest that the first step of this reaction is the radiolysis of toluene, forming hydrogen and the benzyl radical, which then opens the S_8 ring to form the mercaptan.

The radiolysis of toluene can be represented by the equation:

$$C_6H_5CH_3 \xrightarrow{\gamma} C_6H_5CH_2 + H \qquad (1)$$

The benzyl radical thus formed can react by any one of the following paths:

$$C_6H_5CH_2 + H \rightarrow C_6H_5CH_3 \qquad (2)$$

$$2C_6H_5CH_2 \rightarrow C_6H_5CH_2CH_2C_6H_5 \qquad (3)$$

$$C_6H_5CH_2 + S_8 \rightarrow C_6H_5CH_2S_8 \rightarrow C_6H_5CH_2S \qquad (4)$$

The formation of the mercaptan can be considered to result from reaction 4, and the mercapto radical thus formed would abstract hydrogen from the methyl group of toluene:

$$C_6H_5CH_2S + C_6H_5CH_3 \rightarrow C_6H_5CH_2SH + C_6H_5CH_2 \qquad (5)$$

while the hydrogen atom formed in the initial radiolysis of toluene is expected to react as in the following scheme:

$$H + C_6H_5CH_3 \rightarrow H_2 + C_6H_5CH_2 \qquad (6)$$

$$H + S_8 \rightarrow HS_8 \rightarrow HS \qquad (7)$$

The benzyl-hydrogen atom is undoubtedly more readily abstracted than phenyl hydrogen.

As can be seen from Table I, the *G*-values of hydrogen formation are considerably larger than those of hydrogen sulfide but are not much

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[6] L. H. Gale, B. E. Gordon, G. Steiberg and C. D. Wagner, *J. Phys. Chem.*, **66**, 1538 (1962).

larger than that of toluene alone ($G_{H_2}=0.13$). The hydrogen atom, once formed, will react either with toluene to give a hydrogen molecule or with sulfur to form hydrogen sulfide, and the results suggest that the former reaction is more favorable. The increasing *G*-values of hydrogen formation with the increasing sulfur concentration could be interpreted as resulting from the additional formation of hydrogen in the secondary reaction of the decomposition of mercaptan to form the disulfide and the hydrogen molecule.

The *G*-value of the formation of hydrogen sulfide varies remarkably when the hydrocarbon in the reaction system is changed.

The relative ratios of the *G*-values of hydrogen and of hydrogen sulfide for the benzene system are far less than those for the toluene system.

The Toluene-Sulfur-Carbon Disulfide System.—In order to clarify the nature of the radiolysis of toluene and sulfur, radiolysis was studied for a mixed solution of carbon disulfide and toluene, with a constant concentration of sulfur dissolved in it. In this mixture, the fate of the radical or atom formed could be altered by the presence of the other component. However, if the initial step of the reaction process is the cleavage of the sulfur ring, the formation of the sulfur biradical must depend on the irradiation dose, and the *G*-value of formation of mercaptan is constant when the irradiation was applied to solutions containing enough toluene and a constant concentration of sulfur, because the formation of mercaptan depends on the number of sulfur biradicals formed—toluene is merely a hydrogen donor in such a reaction process.

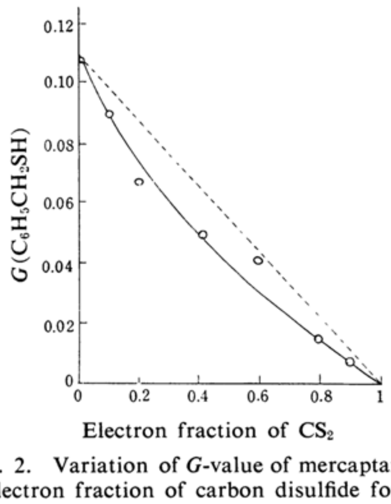

Fig. 2. Variation of *G*-value of mercaptan with electron fraction of carbon disulfide for toluene-carbon disulfide-sulfur system. (2.0 g. sulfur per 100 ml. of solution, irradiation dose was 4.8×10^7 r.).

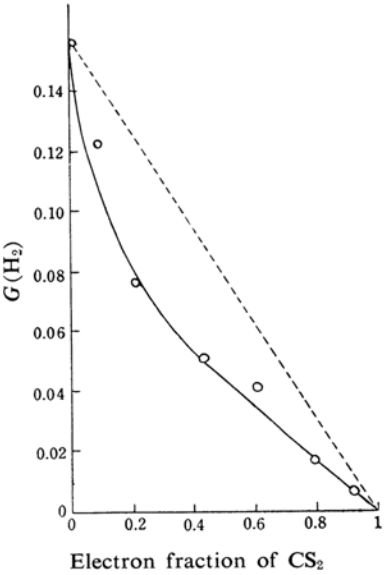

Fig. 3. Variation of *G*-value of hydrogen with electron fraction of carbon disulfide for toluene-carbon disulfide-sulfur system: (2.0 g. of sulfur per 100 ml. of solution, irradiation dose was 4.8×10^7).

Figures 2 and 3 give the *G*-values for the formation of benzyl mercaptan and hydrogen as a function of the electron fraction of a toluene-carbon disulfide mixture. The *G*-values of the formation of mercaptan and hydrogen are proportional to the electron fraction of toluene. The actual curves obtained show a substantial departure from the dotted lines, which represent the yields that are expected in an average absorption of energy into the system.

The results could, therefore, be explained on the basis of an energy transfer mechanism in which the initial step is the decomposition of the toluene molecule. Here again, the formation of hydrogen and mercaptan should result from the initial radiolysis of toluene.

The Interaction of Hydrogen Atom and Elemental Sulfur.—It has been shown in a previous paper[1] that the hydrogen atom formed by the radiolysis of benzene could be used for the formation of hydrogen sulfide by reacting it with sulfur and that this reaction between hydrogen and the sulfur molecule takes place more readily than the reaction between hydrogen and benzene. In the radiolysis of a toluene solution of sulfur, however, the *G*-value of the formation of hydrogen is higher than that of hydrogen sulfide. In order to compare the reactivity of various types of hydrocarbons, the radiolysis of a toluene-cyclohexane mixture dissolving sulfur of a definite concentration were carried out. Data on the hydrogen and

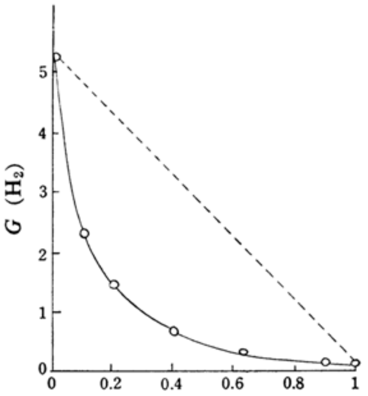

Fig. 4. Variation of *G*-value of hydrogen with electron fraction of toluene for cyclohexane-toluene-sulfur system (0.2 g. sulfur per 100 ml. of solution).

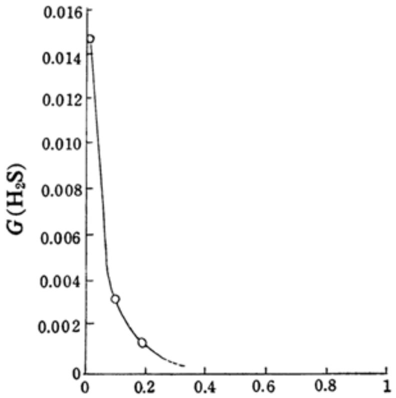

Fig. 5. Formation of hydrogen sulfide with electron fraction of mixture for toluene-cyclohexane-sulfur system (0.2 g. sulfur per 100 ml. of solution).

hydrogen sulfide yields are shown in Figs. 4 and 5.

The *G*-value of the formation of hydrogen sulfide which may be formed from the initial reaction of the hydrogen atom with sulfur clearly depends on the concentration of toluene. At a high concentration of cyclohexane, hydrogen is the major product, and the reaction between sulfur and the hydrogen atom is apparently of minor importance. Therefore, the hydrogen atom, once formed, seems to abstract hydrogen from cyclohexane preferentially, to form a hydrogen molecule rather than to react with sulfur.

A General Scheme for the Radiolysis of Hydrocarbon Solutions of Elemental Sulfur.—In a series of the related reactions of hydrocarbons with sulfur, the primary reaction involving C–H bond rupture may be schematically written as:

$$\mathrm{RH} \xrightarrow{\gamma} \mathrm{R} + \mathrm{H}$$

Here, the reaction undoubtedly depends on the bond energy of the C–H bond from which the hydrogen atom is cleaved in the reaction. Hydrocarbon-free radicals which escape the recombination reaction will react with sulfur to form mercapto radicals, which eventually give rise to mercaptan or disulfide.

$$\mathrm{R} + \mathrm{S}_8 \rightarrow \mathrm{RS}_8 \rightarrow \mathrm{RS}$$

In benzene or cyclohexane, the formation of orgnic sulfur compounds does not depend on the concentration of sulfur, but it does on that of toluene, probably because the benzyl radical is cosiderably stabilized by the resonance, and the reaction of sulfur with the benzyl radical apppears to be the product-determining step.

In the case of toluene and cyclohexane mixtures, the hydrogen atom probably abstracts hydrogen from the hydrocarbons a little faster than it reacts with sulfur to form hydrogen sulfide, thus lowering the yield of hydrogen sulfide. Only in benzene would the reaction of the hydrogen atom with sulfur be favored, and thus the yield of hydrogen sulfide is more than that of hydrogen molecules.

A General Examination of the Energy Transfer of the Radiolysis of the Toluene Solution System.—The formations of both the hydrogen molecule and the mercaptan are initiated by the prior decomposition of toluene. In the mixture of toluene and carbon disulfide, carbon disulfide is considered to behave only as an energy-absorbing solvent which absorbs the radiation energy of gamma rays and transfers the energy to reacting molecules to form excited molecules, since carbon disulfide does not seem to react to give the related products.

The deviation from linearity in Figs. 2 and 3 can be considered to be derived from the energy transfer from toluene to carbon disulfide. Probably the contribution of the ionization transfer mechanism is unimportant, for the ionization potential of toluene is lower than that of carbon disulfide. Consequently, the overall reaction may proceed via energy transfer only through excitation. As has been stated by Inokuti,7) it might be that carbon disulfide has a large cross section value for the excitation of electrons, and that it is easily excited to lower excited levels. The energy stored in the lower excited levels of carbon disulfide is then transferred to toluene molecules, which eventually undergo a series of radiolysis reactions.

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7) M. Inokuti, *Isotope and Radiation*, 1, 82 (1958).

The Cyclohexane-Toluene System. — As has been stated by Manion and Burton, the formation of hydrogen in Fig. 4 clearly shows that energy transfer is taking place from cyclohexane to toluene; this is consistent with the interpretation that toluene protects cyclohexane because it has both lower ionization and lower excitation potentials.

Summary

The radiolysis of a toluene solution of sulfur has been investigated. The formations of benzyl mercaptan, hydrogen, and hydrogen sulfide have been observed, and their amounts determined under various considerations. The amounts of mercaptan formed increase linearly with the concentration of sulfur, and the reactions seem to proceed through the initial decomposition of toluene to form the benzyl radical, which then opens the S_8 ring molecule to form the mercaptan. The *G*-value of hydrogen formation is considerably larger than that of hydrogen sulfide. Similar studies were made of the systems of toluene - cyclohexane - sulfur and of toluene - carbon disulfide - surfur in order to clarify the nature of the radiolysis of toluene and sulfur.

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