*The Radiation-induced Reactions of Benzene with Sulfur and Sulfur Compounds**

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(Received December 27, 1962)

The radiolysis of the aqueous benzene solution has been studied extensively and is known to give phenol and other minor products[1]. The formation of phenol is known to be increased by the introduction of oxygen into the system. The radiation-induced reaction of benzene has also been studied by many workers[2-6]. According to the reaction mechanisms hitherto suggested, the process of phenol formation involves the initial formation of a hydrogen atom and of a phenyl radical which reacts immediately with dissolved oxygen. We have extended a similar study in the hope of getting thiophenol and other sulfur-containing compounds, since sulfur is also quite an effective radical scavenger[7-9]. Since mercaptans are readily oxidized to their corresponding disulfides under irradiation with X-, beta-, or gamma-rays[10-11], one would expect diphenyl disulfide and hydrogen among the products formed. The present paper deals with the radiation-induced reaction of benzene with sulfur, together with the chemical behavior of thiophenol and hydrogen sulfide in benzene under the irradiation of gamma-rays.

Experimental

Chemicals.—*Benzene.*—Reagent-grade thiophene-free benzene was purified by three successive distillations.

Sulfur.—The sulfur employed was C. P.-grade, large, rhombic crystals, formed from carbon disulfide. The sulfur was again recrystallized from hot, reagent-grade benzene to obtain small, granular, rhombic crystals.

Thiophenol.—C. P.-grade thiophenol was purified by repeated distillations in a nitrogen atmosphere and was vacuum-distilled shortly before use.

The Preparation of the Samples.—Exactly 40 ml. of a benzene solution containing an aliquot amount of sulfur was sealed under vacuum in an ampoule with a glass break-off tip. Air was degassed by freezing and pumping.

The irradiation was carried out with 3800-curie cobalt-60 gamma rays at room temperature. The dosimetry was based on a Fricke dosimeter. The dose rate was approximately 5×10^5 r/hr.

Analysis.—All the analyses of the irradiated samples containing sulfur or thiophenol in benzene were carried out as described below. First, gases were collected from the irradiated samples by the usual repeated freezing evacuation and melting technique[12]. The collected gases were then passed through liquid nitrogen traps. The uncondensed gas was identified as hydrogen, and the gas which passed through a series of dry-ice acetone trap and was condensed at the liquid nitrogen temperature was identified as hydrogen sulfide.

Hydrogen sulfide was absorbed into a solution containing 5% of zinc acetate and 1% sodium acetate. Then, 25 ml. of 10% ammonium molybdate and 5 ml. of phosphoric acid were added to the solution. It was diluted to 50 ml., and the absorption at 670 mμ was observed after one or two days[13].

Thiophenol, which was distilled from irradiated benzene and sulfur at 50°C into a trap cooled by a dry-ice acetone bath, was allowed to react with p,p'-dinitrodiphenyl disulfide; then, the amount of p-nitrobenzenethiol formed was determined by spectrophotometry following the method of Ellman[14]. For each run, 5 ml. of a 0.1 M phosphate buffer at pH 8 and 5 ml. of a saturated acetone solution of p,p'-dinitrodiphenyl disulfide were added into 20 ml. of the sample and the whole solution was diluted to 100 ml. with acetone. The absorbancy at 470 mμ was measured within one minute after the disulfide had been added.

When a benzene solution of thiophenol was irradiated, both the initial and final amounts of thiophenol was determined by titrating the solution with a solution of silver nitrate in isopropyl

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* Presented at the 5th Symposium of Radiation Chemistry, Tokyo, November, 1962.

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alcohol[15]. The break in the potentiometric curve was found to be between approximately −325 and −175 mV. vs. SCE. The amounts of decreased thiophenol were calculated by subtracting the final values from the initial ones.

Results and Discussion

The Radiolysis of a Benzene Solution of Sulfur.—An aliquot amount of sulfur was dissolved in benzene and was irradiated with gamma-rays. The vacuum technique was employed throughout. The thiophenol and hydrogen sulfide formed were measured. The results obtained at varying concentrations of sulfur and radiation doses are shown in Tables I and II.

TABLE I. THE FORMATION OF THIOPHENOL AT VARIOUS SULFUR CONCENTRATIONS

Sulfur concentration	*G*-Value of thiophenol formed Irradiation dose		
g./100 ml.	1.1×10⁷ r	2.5×10⁷ r	3.6×10⁷ r
2.0	0.056	0.039	0.041
1.5	0.027	0.039	0.037
0.8	0.041	—	0.030
0.25	0.017	0.017	0.013

Dose rate: 5×10^5 r/hr.

TABLE II. THE FORMATION OF HYDROGEN SULFIDE AT VARIOUS SULFUR CONCENTRATIONS

Sulfur concentration	*G*-Value of hydrogen sulfide irradiation dose		
g./100 ml.	1.1×10⁷ r	2.5×10⁷ r	3.6×10⁷ r
2.0	0.047	0.049	0.049
1.5	0.058	0.049	0.040
0.8	0.040	0.040	0.026
0.25	0.003	0.011	0.008

Dose rate: 5×10^5 r/hr.

The formation of thiophenol and hydrogen sulfide showed nearly identical *G*-values, and both are independent of the sulfur concentration and the radiation dose except at an extremely low concentration of sulfur. This means that sulfur cleavage is not the initial step in the formation of these substances and that sulfur reacts at a secondary step of the overall reaction. It appears that the formation of the phenyl radical and of hydrogen atoms from a benzene solution and the reactions of these species with sulfur to form thiophenol and hydrogen sulfide follow.

However, thiophenol, being a very strong hydrogen donor, does not remain unchanged in the solution; rather, a portion is oxidized to diphenyl disulfide. Table II shows a little higher *G*-value of hydrogen sulfide formation than that of thiophenol formation. This seems to suggest that hydrogen sulfide is also produced by the radiolysis of thiophenol, along with the reaction of hydrogen atoms and sulfur.

Radiolysis of Thiophenol in Benzene.—The radiolysis of thiophenol in a benzene solution was carried out under various conditions. Figure 1 shows the relation between the *G*-values and the radiation doses.

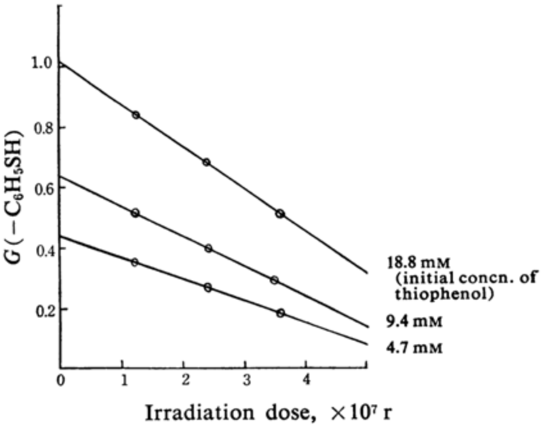

Fig. 1. Relation of *G*-value of decreased thiophenol and irradiation dose on radiolysis of thiophenol in benzene.

The decrease in thiophenol by irradiation was proportional to the initial concentration of thiophenol. This suggests that thiophenol is more susceptible to gamma irradaition than benzene. Therefore, the *G*-value for thiophenol decomposition in benzene could be calculated from the remaining thiophenol concentration.

The variation in *G*-values for different radiation doses and for initial concentrations of thiophenol seems to be caused by the regeneration of thiophenol from the radiolysis of diphenyl disulfide[16], which was found to be the main product in the radiolysis of thiophenol in benzene. In fact, we found that thiophenol was formed by the radiolysis of diphenyl disulfide, as Table III shows.

TABLE III. RADIOLYSIS OF DIPHENYL DISULFIDE IN BENZENE

Disulfide	50 mmol./l.
Irradiation dose	2.8×10⁷ r
Found	*G*-Value
Thiophenol	0.024 mM
Hydrogen sulfide	0.001 mM

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[15] M. W. Tamele and L. B. Ryland, *Ind. Eng. Chem., Anal. Ed.*, **8**, 16 (1936).

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[17] E. C. Truesdale and S. C. Lind, ibid., **54**, 516 (1932).

The formation of hydrogen sulfide increases with an increase in the radiation dose, but at a high radiation dose, the formation of hydrogen sulfide became steady or decreased. This can be explained if one assumes that hydrogen sulfide is slowly decomposed in benzene with an increase in the radiation dose[17].

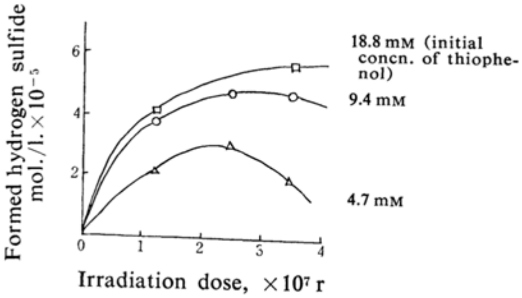

Fig. 2. Relation of hydrogen sulfide formed and irradiation dose on radiolysis of thiophenol in benzene.

This reaction of hydrogen sulfide in a benzene solution will give thiophenol again as a result of the attack of the phenyl radical on hydrogen sulfide. However, this reaction is of minor importance. Therefore, the formation of hydrogen sulfide can probably best be explained as a result of the direct decomposition of thiophenol.

The radiolysis of benzene saturated with hydrogen sulfide was also carried out; the results are shown in Table IV. The amounts of thiophenol formed were similar at various radiation doses, suggesting that more than a certain amount of thiophenol was always converted to diphenyl disulfide.

TABLE IV. RADIOLYSIS OF BENZENE SATURATED WITH HYDROGEN SULFIDE

Irradiation dose	Thiophenol formed	*G*-Value
1.2×10^7 r	0.46 mmol./l.	0.046
2.6×10^7 r	0.41 mmol./l.	0.020
3.6×10^7 r	0.42 mmol./l.	0.014

Proposed Mechanisms.—*The Radiolysis of a Benzene Solution of Sulfur.*—The mechanism for the radiolysis of benzene has recently been shown in a number of publications[2-6]. In the formation of the phenyl radical and the hydrogen atom under the irradiation of benzene, they further react with benzene to form polymers :

$$C_6H_6 \xrightarrow{\gamma} C_6H_6{}^* \qquad (1)$$

$$C_6H_6{}^* \rightarrow C_6H_5 + H \qquad (2)$$

However, when elemental sulfur is dissolved in benzene, the phenyl radical and the hydrogen atom formed in the primary step of the radiolysis of benzene react with sulfur to form thiophenol and hydrogen sulfide, as can be seen from the data in Tables I and II.

Since the overall stoichiometry of the *G*-values of the thiophenol and hydrogen sulfide formed is independent both of the radiation dose and the relative concentration of sulfur, the following reaction scheme may be considered :

$$C_6H_5 + S_8 \rightarrow C_6H_5\text{-}S_8 \rightarrow C_6H_5S + S_x \qquad (3)$$

$$H + S_8 \rightarrow HS_8 \rightarrow HS + S_x \qquad (4)$$

In this case, benzene and sulfur compete for reaction with the phenyl and hydrogen radicals formed in reaction 2. As elemental sulfur is an effective radical scavenger, the phenyl radical and hydrogen atom attack the S-S bonds of sulfur and the open S_8 ring rather than reacting with benzene. Therefore, reactions 3 and 4 take place more readily than the polymer formation.

The incipient open chain polysulfides radicals are quite unstable and immediately decompose to give phenyl, sulfenyl and sulfhydryl radicals[18-20]. These sulfenyl radicals then react with free hydrogen to form the thiophenol. Similarly, the formation of hydrogen sulfide can be written as in reaction 6. Some sulfenyl radicals also recombine to form diphenyl disulfide :

$$C_6H_5S + H \rightarrow C_6H_5SH \qquad (5)$$

$$SH + H \rightarrow H_2S \qquad (6)$$

$$2C_6H_5S \rightarrow C_6H_5S\text{-}SC_6H_5 \qquad (7)$$

The Radiolysis of Thiophenol in Benzene.—The rate of the disappearance of thiophenol was found to depend on the initial concentration of thiophenol and on the radiation dose. This indicates that the main path for the disappearance of thiophenol is not through the following reaction :

$$C_6H_6{}^* \rightarrow C_6H_5 + H \qquad (2)$$

$$C_6H_5 + C_6H_5SH \rightarrow C_6H_6 + C_6H_5S \qquad (8)$$

$$2\ C_6H_5S \rightarrow C_6H_5S\text{-}SC_6H_5 \qquad (7)$$

Although most of the radiation energy is absorbed into the benzene, the energy absorbed is transferred to thiophenol, which upon the absorption of energy splits into the sulfenyl radical and the hydrogen atom.

$$C_6H_6{}^* + C_6H_5SH \rightarrow C_6H_6 + C_6H_5SH^* \qquad (9)$$

$$C_6H_5SH^* \rightarrow C_6H_5S + H \qquad (10)$$

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The sulfenyl radicals thus formed mainly recombine, forming diphenyl disulfide, as is shown by 7. Another reaction for the decomposition of thiophenol may be proposed from the formation of hydrogen sulfide[21-23] as follows:

$$C_6H_5SH^* \rightarrow C_6H_5 + SH \qquad (11)$$

$$SH + C_6H_5SH \rightarrow C_6H_5S + H_2S \qquad (12)$$

$$SH + H \rightarrow H_2S \qquad (6)$$

By comparing the yield of hydrogen sulfide with the amount of the decomposition of thiophenol, the relative bond stability of S–H and C–S under the irradiation may be calculated, as is shown in Table V. From these calculations, one finds that reactions 10 and 11 occur in the ratio of about 200 to 1.

TABLE V. THE RATIO OF THE NUMBERS OF BROKEN BONDS S–H/C–S

Irradiation dose	Initial concentration of thiophenol		
	18.8 mM	9.4 mM	4.7 mM
1.2×10^7 r	217	133	189
2.4×10^7 r	—	167	200
3.6×10^7 r	285	175	217
Average	192 S–H/C–S		

The Radiolysis of Diphenyl Disulfide in Benzene.—Sulfenyl radicals are produced from the radiolysis of diphenyl disulfide; these radicals are then converted into thiophenol by reaction with free hydrogen from the radiolysis of benzene:

$$C_6H_5S\text{–}SC_6H_5 \rightarrow 2\ C_6H_5S \qquad (13)$$

$$C_6H_5S + H \rightarrow C_6H_5SH \qquad (5)$$

The Energy Transfer of Excited Benzene in the Decomposition of Thiophenol.—The *G*-value of decomposition of thiophenol apparently depends on the concentration of thiophenol, the value ranging anywhere 200 to 600 when it is calculated on the basis of the concentration of thiophenol.

The available bond dissociation energy is less than 70 kcal. per mol. for the S–H bond of thiophenol. This means that the *G*-value for the thiophenol decomposition is much larger than the maximum *G*-value obtained when the absorbed energy is used completely for the decomposition of thiophenol.

By assuming the energy transfer from benzene to thiophenol, the overall kinetics for the only favorable conditions of thiophenol decomposition in benzene can be developed by the steady-state approach. Since one may reasonably assume that the direct excitation of thiophenol by gamma rays and the recombination of the sulfenyl radical and the hydrogen atom are small, the *G*-value of the decomposition of thiophenol may be given by the following equation:

$$G(-C_6H_5SH)=\frac{2k_4k_3(M)I}{(k_2+k_4)(k_1+k_3(M))}$$

which may be written in the following convenient form, since k_4 is much larger than k_2:

$$\frac{1}{G}=\frac{1}{2I}\left(1+\frac{k_1}{k_3(M)}\right)$$

where I represents the rate constant for the formation of benzene molecules excited by 100 eV.; k_1 and k_2, the rate constants for the deactivation of excited benzene and thiophenol; k_3 and k_4, the rate constants for Eqs. 9 and 10, and M, the initial concentration of thiophenol.

This equation can be used only for lower concentrations of thoiphenol; at higher concentrations, the direct decomposition of thiophenol by gamma irradiation becomes so large as to obscure the overall assumptions for setting up the equation.

Figure 3 illustrates the relation between the *G*-values at the minimum radiation dose obtained from Fig. 1 and the initial concentrations of thiophenol.

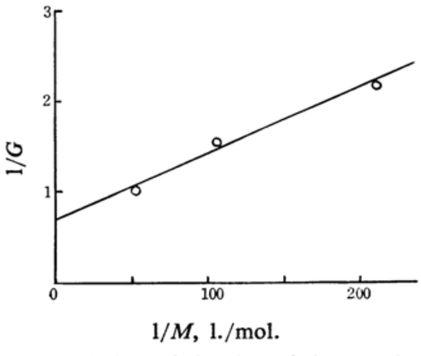

Fig. 3. Relation of *G*-value of decreased thiophenol and its initial concentration on radiolysis thiophenol in benzene.

From Fig. 3, (I) can be obtained by intersecting the slope with the vertical line, and k_1/k_3, from the slope of the line.

The calculation indicates that about 0.7 molecule of excited benzene is formed per 100 eV. of gamma irradiation, and that the ratio of the energy transfer to thiophenol from excited benzene to the deactivation of excited benzene itself is about 100 to 1.

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Summary

The irradiation of a benzene solution of sulfur gave thiophenol, diphenyl disulfide, diphenyl sulfide, hydrogen sulfide, hydrogen and some polymers. The formation of thiophenol and of hydrogen sulfide is considered to be initiated by the radiolysis of benzene, which gives phenyl and hydrogen radicals, which in turn combine with sulfur in succeeding steps.

However, the thiophenol formed is oxidized to the disulfide as the radiation energy absorbed in benzene transfers to thiophenol. The effect of the initial concentration of thiophenol and of the radiation dose has been measured. The relative stability of the S–H and C–S bond for radiation was about 1 : 200. The radiolysis of diphenyl disulfide or hydrogen sulfide in benzene were found to form thiophenol. In a kinetical study of the decomposition of thiophenol in benzene, 0.7 benzene molecule is excited by the 100 eV. of gamma rays absorbed, while the ratio between the energy transfer to thiophenol from excited benzene and the deactivation of excited benzene itself is about 100 to 1.

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