NOTES

*The Radiation-induced Reaction of Sulfur in Various Solvents**

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Previous papers have described studies of the radiolysis of both benzene and toluene solutions of sulfur.[1-2] The reaction products reported have included such substances as mercaptan, disulfide, sulfide, hydrogen sulfide, hydrogen and other hydrocarbons. Among these products, quantitative determination is possible for mercaptan, hydrogen and hydrogen sulfide.

The radiolysis of solvent hydrocarbon produces free radicals which attack sulfur at room temperature; mercaptan is then formed in this manner:

$$RH \xrightarrow{I} R + H \quad (1)$$

$$R + S_8 \rightarrow RS_8 \rightarrow RS \quad (2)$$

The formation of mercaptan depends mainly on the bond dissociation energy of C–H in the solvent, because the formation of mercaptan through Eq. 3

$$RS + H \rightarrow RSH \quad (3)$$

$$RS + RH \rightarrow RSH + R \quad (4)$$

is rare, even though the reaction in benzene shows very little tendency to undergo radical displacement (reaction 4).

In the reaction with toluene, the benzyl mercapto radical would abstract hydrogen from the methyl group of toluene since its C–H bond is known to be quite weak.

In this investigation, *G*-values for the formation of various mercaptans and hydrogen in the radiolysis of various hydrocarbon solutions of sulfur will be determined, and the *G*-value of hydrogen formation will be compared with these of the corresponding hydrocarbons with the hope of obtaining some direct infomation on the effect of hydrocarbons as solvents on the radiolysis of hydrocarbon solutions of sulfur.

Experimental

The experimental details are similar to those outlined in an earlier paper.[1] The sulfur used in this work was a portion of an exceptionally pure sample previously employed. The solvents were purified by conventional fractional distillations. A solution of sulfur in a solvent was made by weighing and then degassing it by freezing, pumping and thrawing in vacuo. After irradiation, each ampoule was attached to a vacuum line in order to analyze the hydrogen formation. The amount of mercaptan was determined by a potentiometric titration with silver nitrate.[3]

Results and Discussion

The data in Table I on the radiolysis of sulfur in various hydrocarbons indicates that the *G*-values of the formations of mercaptans were of similar magnitudes, with only a little difference caused by the differences in the stabilities of the mercaptans formed.

TABLE I. THE FORMATION OF MERCAPTANS IN THE RADIOLYSIS OF SULFUR WITH HYDROCARBONS AS SOLVENTS (THE CONCENTRATION OF SULFUR IS 0.2 g. PER 50 ml. OF SOLVENT)

Solvent	*G*-value for the mercaptan formation
Hexane	0.06
Cyclohexane	0.07
Mesitylene	0.06
Ethylbenzene	0.06
p-Xylene	0.05
Toluene	0.09
Diphenylmethane	0.013

The interesting feature of Table I is that the radicals formed in the radiolysis of these hydrocarbons as solvents showed similar reactivities toward sulfur. The formation mercaptan is considered to depend on the concentration of sulfur and on the stability of the

* The Study of the Radiation Chemistry of Organic Sulfur Compounds. Part V.

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

2) W. Ando, K. Sugimoto and S. Oae, ibid., in press.

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

radical formed.

In a diphenylmethane solution of sulfur, the *G*-value for the mercaptan formation is about one-fifth that of the other solvents. Probably the radical, formed in the radiolysis of diphenyl methane, is substantially resonance-stabilized and is, therefore, not reactive enough to open the sulfur ring as do the other solvents.

The Effects of Sulfur on the Formation of Hydrogen from Solvents. — The *G*-value of hydrogen formation observed for various solvent solutions of sulfur are given in Table II, together with those from hydrocarbons without sulfur.

The *G*-values of hydrogen formation in both hexane and cyclohexane solutions of sulfur are appreciably decreased by the presence of sulfur. A similar decrease in hydrogen formation has been reported in other cyclohexane solutions with other solutes dissolved in them.[7] Therefore, these decreases do not seem to be due to any specific chemical nature of the added solute but merely to the introduction of some new physical impurities into the system. The *G*-values of hydrogen formation for mesitylene, ethylbenzene, *p*-xylene and toluene do not change regardless of the presence or absence of sulfur in the hydrocarbons. Here the formation of hydrogen is mainly due to the following reaction:

$$H + RH \rightarrow H_2 + R$$

It is, therefore, not affected by the presence of sulfur. A similar observation on the lack of the effect of the hydrogen atom in the formation of hydrogen sulfide has been reported previously in the system of toluene and sulfur.

TABLE II. THE *G*-VALUE OF HYDROGEN FORMATION IN THE RADIOLYSIS OF HYDROCARBONS

Solvent	In the presence of sulfur	Without sulfur
Hexane	1.6	5.0
Cyclohexane	3.05	5.85[4]
Mesitylene	0.25	0.24[5]
Ethylbenzene	0.19	0.18[6]
p-Xylene	0.17	0.22
Toluene	0.12	0.13[6]
Diphenylmethane	0.026	0.027

4) M. Burton, J. Chang, S. Lipsky and M. P. Reddy, *Rad. Res.*, **8**, 203 (1958).
5) R. R. Hentzad and M. Burton, *J. Am. Chem. Soc.*, **73**, 532 (1951).
6) T. J. Sworski and M. Burton, ibid., **73**, 3970 (1951).
7) R. H. Schuler, *J. Phys. Chem.*, **61**, 1474 (1957).

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