[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

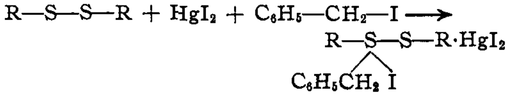
The Formation of Sulfonium Compounds from Benzyl Iodide and Organic Disulfides

BY OTTO HAAS AND GREGG DOUGHERTY

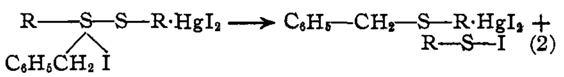
Steinkopf and Müller[1] found that sulfonium salts were formed when alkyl disulfides are heated with alkyl halides. Since their experiments were carried out at 100° in sealed tubes for thirty hours, it seemed possible that the products resulted from rather profound decompositions. It was of interest therefore to study this reaction under mild conditions which would favor greater stability of the primary products, and possibly lead to a surer knowledge of the mechanism by which the products were formed.

Using mercuric iodide or ferric chloride as catalysts, it has now been found that benzyl iodide reacting on organic disulfides in acetone solution, forms the sulfonium salts of the monosulfides at room temperature. The compounds are isolated in the form of the addition complex with the salt used as a catalyst. (In this way the following have been prepared: tribenzylsulfonium iodide-mercuric iodide, dibenzylethylsulfonium iodide-mercuric iodide, dibenzylbutylsulfonium iodide-mercuric iodide, tribenzylsulfonium iodide-ferric chloride.) Unlike the results obtained by Hilditch and Smiles, who worked with ethyl iodide, diethyl disulfide and mercuric iodide, no disulfide sulfonium salts could be isolated.[2]

These reactions may be explained by a mechanism similar to that proposed by Steinkopf and Müller



$$\mathrm{R{-}S{-}S{-}R + HgI_2 + C_6H_5{-}CH_2{-}I \longrightarrow R{-}\underset{C_6H_5CH_2\ \ I}{\overset{}{S}}{-}S{-}R\cdot HgI_2} \quad (1)$$



$$\mathrm{R{-}\underset{C_6H_5CH_2\ \ I}{S}{-}S{-}R\cdot HgI_2 \longrightarrow C_6H_5{-}CH_2{-}S{-}R\cdot HgI_2 + R{-}S{-}I} \quad (2)$$

$$\mathrm{C_6H_5{-}CH_2{-}S{-}R\cdot HgI_2 + C_6H_5{-}CH_2{-}I \longrightarrow (C_6H_5CH_2)_2RS{-}I\cdot HgI_2} \quad (3)$$

$$\mathrm{R{-}S{-}I + C_6H_5{-}CH_2{-}I \longrightarrow C_6H_5{-}CH_2{-}S{-}R\cdot I_2} \quad (4)$$

$$\mathrm{C_6H_5{-}CH_2{-}S{-}R\cdot I_2 + HgI_2 \longrightarrow C_6H_5{-}CH_2{-}S{-}R\cdot HgI_2 + I_2} \quad (5)$$

$$\mathrm{C_6H_5{-}CH_2{-}S{-}R\cdot HgI_2 + C_6H_5{-}CH_2{-}I \longrightarrow (C_6H_5CH_2)_2R{-}S{-}I\cdot HgI_2} \quad (6)$$

Summing up these reactions in one equation:

$$\mathrm{R{-}S{-}S{-}R + 4C_6H_5{-}CH_2{-}I + 2HgI_2 \longrightarrow 2(C_6H_5{-}CH_2)_2RS{-}I\cdot HgI_2 + I_2} \quad (7)$$

Positive evidence for the above mechanism is that iodine is liberated in approximately the calculated amount and that, excepting iodine, only one product is formed. It is found in the theoretically required amounts when the reactants are present in the proportions represented in equation 7. Also the reactions 3 and 4 are known to occur. Reaction 5 was tested by first forming a sulfide diiodide, then adding mercuric iodide and determining the quantity of free iodine present.

Experimental

Tribenzylsulfonium Iodide-Mercuric Iodide.—Two and five-tenths grams of dibenzyl disulfide, 8.8 g. of benzyl iodide, and 9.2 g. of mercuric iodide were added to 20 cc. of acetone. The mercuric iodide dissolved after the mixture had stood for five minutes at room temperature. Ether was added to precipitate the product which melted at 136–137° after one recrystallization from an ether-acetone solution. The yield was 17.2 g. or 95.5%. Calculated for $C_{21}H_{21}S\cdot HgI_3$: S, 3.61; I, 43.0. Found: S, 3.58; I, 42.5. This is a new compound. The filtrates from the above were titrated with 0.1181 *N* sodium thiosulfate solution; 152 cc. was required and this accounts for 89% of the free iodine indicated in equation 7.

Dibenzylethylsulfonium Iodide-Mercuric Iodide.—This compound was prepared in the same way from 1.25 g. of diethyl disulfide, 8.8 g. of benzyl iodide, and 9.2 g. of mercuric iodide. The melting point was 115–116°, as reported in the literature, and the yield was 16 g. Calculated for $C_{16}H_{19}S\cdot HgI_3$: S, 3.88. Found: S, 3.73.

Dibenzylbutylsulfonium Iodide-Mercuric Iodide.—This compound was prepared in an analogous manner from 1.8 g. of di-*n*-butyl disulfide, 8.8 g. of benzyl iodide and 9.2 g. of mercuric iodide. The melting point was 84–85° as reported in the literature and the yield was 16.4 g. Calculated for $C_{18}H_{22}S\cdot HgI_3$: S, 3.76. Found: S, 3.73.

Tribenzylsulfonium Iodide-Ferric Chloride.—One and one-quarter grams of dibenzyl disulfide, 4.4 g. of benzyl iodide, and 1.7 g. of anhydrous ferric chloride were added to 20 cc. of absolute ether. After standing for two hours at room temperature, the fine brown needles which had collected at the bottom of the flask were removed by filtration and washed with ether. The melting point was 142°. Qualitative tests for iron were positive. Calculated for $C_{21}H_{21}SIFeCl_3$: S, 5.39; Cl, 17.9. Found: S, 5.37; Cl, 18.0. This is a new compound. Addition of mercuric iodide to an alcohol solution of the new compound converted it to tribenzylsulfonium iodide-mercuric iodide.

The reaction indicated by equation 5 was tested in the following way: equivalent amounts of dibenzyl sulfide (0.5 g.) and iodine (0.65 g.) were added to 10 cc. of acetone. To this was added an equivalent quantity of mercuric iodide. The resulting solution was titrated with 0.1181 *N* sodium thiosulfate; 48.7 cc. was required to decolorize

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(1) Steinkopf and Müller, *Ber.*, **56**, 1926 (1923).

(2) Hilditch and Smiles, *J. Chem. Soc.*, **91**, 1394 (1907).

the solution and this corresponds to 96.6% of the iodine originally added.

Summary

The reaction of benzyl iodide with three organic disulfides, in the presence of mercuric iodide or ferric chloride, has been studied.

Four sulfonium compounds, in the form of the addition complex with the metallic halide, were prepared. Two of these are new compounds.

A mechanism for the reaction has been proposed.

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Reactions of Sulfur and Vapors of Organic Compounds at Different Temperatures[1]

BY GEO. D. PALMER, S. J. LLOYD, W. P. MCLURE, NORMAN LEMAISTRE, W. S. WARING AND L. W. BACHMAN

The preparation of a new series of sulfur dyes by a vapor method using benzene and other organic compounds in contact with molten sulfur at temperatures *above* 300° has been reported.[2] With similar apparatus, we are now able to report the preparation of two new classes of sulfur organic compounds prepared at temperatures *below* 300°.

Experimental

Preparation of New Sulfur Organic Compounds.—We find that the vapors of many organic substances, including benzene, toluene, aniline, phenol, etc., when passed through molten sulfur at 240–260° form resinous sulfur dyes (A) which are in some cases rubber-like after purification, whereas at 260–300° non-resinous sulfur organic compounds (B) which are not dyes result. These are brown to black powdery solids, insoluble in sodium sulfide and carbon bisulfide. Hydrogen sulfide is a by-product, much more being evolved in preparation of A than B. The yields of A are much better than those of B and are comparable to the yields of compounds prepared above 300° (C).[2]

Purification and Analyses.—Eighteen samples were purified with carbon bisulfide, acetone, benzene, and water for 525 hours in large-scale Soxhlet extractors. Analyses for sulfur were made at intervals until the percentage of sulfur in each substance became constant.

Discussion

All sulfur dyes prepared by this vapor method and producing intense colors contain 50 to 83% sulfur. A few aliphatic substances which have yielded small amounts of low-sulfur-content dyes have produced much less intense colors on cotton and rayon.

It appears that the higher the sulfur content of the dye, the less the sodium sulfide (in aqueous solution) required to dissolve it. It also appears that the higher the sulfur content, the more resinous is the material. The resinous property of the chlorobenzene product (A) is lost when it is dissolved in aqueous sodium sulfide, but is regained by precipitation with a mineral acid.

TABLE I

COMPOSITION OF PURIFIED SULFUR ORGANIC SUBSTANCES PREPARED BELOW 300°

Compd. reacting with sulfur	Opt. temp. for prepn., °C.	S, %	N, %	Cl, %
Benzene	260–300	30.95		
Aniline	260–300	30.96	9.63	
Chlorobenzene	240–260	83.44		1.08

TABLE II

PROPERTIES OF DYES PREPARED FROM CHLOROBENZENE AND SULFUR ABOVE AND BELOW 300°

Opt. temp., for prepn., °C.	Phys. form	Color of solid	Soly. in CS_2	Soly. in aq. Na_2S	Color on cot. and rayon
360–444.6	Powd.	Red	Insol.	Sl.	Red-brown
240–260	Res. matl.	Gray-black	Sl.	Fairly	Dark-brown

TABLE III

COMPOSITION OF PURIFIED SULFUR DYES PREPARED AT 360–444.6°

Sample	Compound reacting with sulfur	C, %	H, %	S, %	N, %	O, %
1	Benzene	34.54	0.92	62.46		
2	Toluene	36.17	0.93	62.68		
3	Phenol	34.95	1.97	55.15		7.93
4	Aniline	37.88	1.23	53.38	6.56	

Empirical formulas have been calculated for dyes 1 and 2 in Table III, and a constancy of $C_3H_1S_2$ is indicated. The grouping in these high sulfur content organic substances prepared from hydrocarbons and sulfur at 360–444.6 is apparently similar to the recurrent grouping in the formula of thiokol[3] in that in each case *one* hydro-

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[1] Presented at the Baltimore meeting of the American Chemical Society, April, 1939.

[2] Geo. D. Palmer and S. J. Lloyd, THIS JOURNAL, **52**, 3388 (1930).

[3] J. C. Patrick, *Modern Plastics*, [2] **14**, 46 (1936).