

# A DRY SYNTHESIS OF AROMATIC SULFIDES: PHENYLENE SULFIDE RESINS

A. DOUGLAS MACALLUM

*Received September 15, 1947*

Up to the present several of the simpler aromatic sulfide derivatives, such as phenyl sulfide, the disulfide, hexasulfide, and thianthrene, have been prepared directly from benzene by action of sulfur or sulfur chloride in the presence of aluminum chloride or iodine (1, 2). Other definitely oriented aromatic sulfides have been made from the corresponding sulfonates by roundabout methods (3) or through the hydrocarbon halides by way of the organometallic compounds (4).

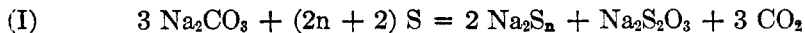
There are a number of rather labile haloaromatic compounds, such as chloronitronaphthalenes (5), chloronaphthols (6), or dibromoanthracene (7), which react easily enough with alcoholic solutions of the alkali metal sulfides and polysulfides. However, this is exceptional and most aromatic chloro compounds, including the chlorobenzenes, are comparatively inert, and have been made to react with alkali sulfides and polysulfides only in the presence of water at high pressures, and temperatures of 300–350° (8, 9).

The technique of preparing aromatic sulfide and polysulfide derivatives has been much simplified by the method described here, which hinges on an observation that aromatic chloro compounds, though generally unaffected by dry metal sulfides, can be made to react with them in a dry way by the addition of quite small amounts of free sulfur. The reaction goes under pressure in the liquid-solid phases at temperatures of 275–360°, best at about 300°.

By a further simplification, which gives satisfactory results in many cases, the metal sulfides are not used as such, the chloro hydrocarbons being reacted with nascent metal sulfide as it is formed under the above conditions from mixtures of sulfur with a number of oxides, carbonates, or borates of the alkali or alkaline earth metals.

The two methods are of use in preparing simple bicyclic sulfides, such as phenyl sulfide or thianthrene, or aromatic sulfide polymers, such as the phenylene sulfide resins dealt with in this paper. These dry methods decrease considerably the difficulties due to corrosion and pressure, as well as to side reactions involving hydrolysis or reduction, which are encountered when the reactions are carried out in the presence of water.

The formation of alkali metal sulfides and polysulfides from the alkali carbonates and sulfur has been studied by Pearson and Robinson (10), the reaction being reported as going slowly at 200°, but with increasing speed at higher temperatures. At 350° the reaction followed mainly equation (I), at 640° mainly equation (II), some sulfite being produced along with the sulfate formed.



Actually, however, when such a mixture, in some excess, is heated at 300–340° with *p*-dichlorobenzene in order to produce a sulfide derivative, the soluble by-products are found to include both thiosulfate and sulfate. It would thus appear that the formation of a polyphenylene sulfide resin, which is obtained under the above conditions, involves at least two reactions (equations III and IV).

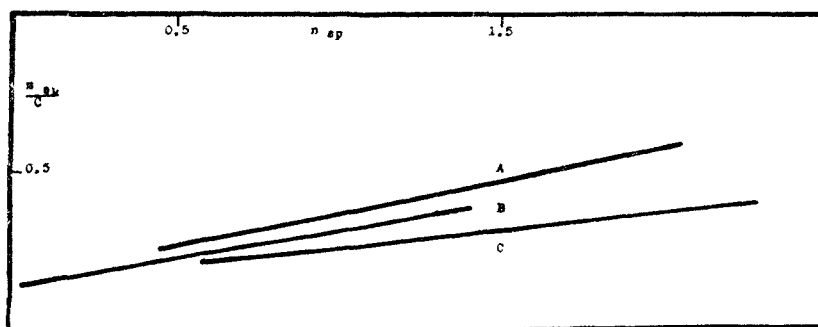
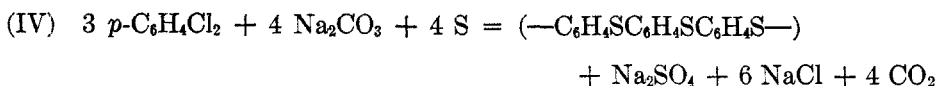
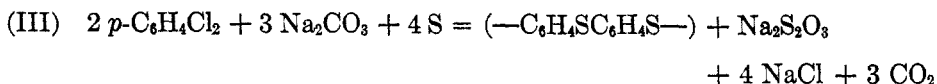


FIG. 1. Showing curves based on specific viscosity data for several *p*-phenylene polysulfide polymer resins in sulfur at 132° (over boiling chlorobenzene). The polymers were obtained from *p*-dichlorobenzene by reaction with mixtures of anhydrous sodium carbonate and sulfur as described in the text. The curves A, B, and C are for resins of 47.8, 56.2, and 68.2% sulfur respectively. The monosulfide resins, containing about 30% sulfur, are too sparingly soluble to affect the viscosity of sulfur appreciably at 132°. The concentrations here have been in terms of g. resin per 100 cc. sulfur solution at 132°.

From the curves, the intrinsic viscosities of the resins are figured at about 0.15 by the method of Huggins, *Ind. Eng. Chem.*, **35**, 980 (1943).

One high-molecular form of *p*-phenylene disulfide, ( $\text{C}_6\text{H}_4\text{S}_2$ ), was obtained by Leuckart (11) and by Parekh and Guha (3) through the chemical oxidation of dithiohydroquinone. This substance has been described as an amorphous powder, insoluble in all common solvents and not melting at 300°. However, products of this type, prepared by the methods described here using mixtures of *p*-dichlorobenzene with sulfur and sodium carbonate, are quite different in physical properties. They are all either fusible or thermoplastic, the di- and poly-sulfide compounds dissolving in molten sulfur and having an intrinsic viscosity in the neighborhood of 0.15 in this solvent (Figure 1). Molecular weights on these compounds are difficult to determine by conventional methods owing to a dearth of suitable solvents. However, some initial data, obtained by isothermal distillation of the sulfur solutions, would indicate a probable weight figure in excess of 9000 (Table I).

When the resins are purified and subjected to thorough elementary analysis, they correspond closely to an empirical composition of  $(C_6H_4S_x)$ , where  $x$  stands for one or more atoms of sulfur. They are practically insoluble in sodium sulfide solutions and have so far exhibited no dyeing properties. They would thus differ, in properties as well as in composition, from the sulfur dyes having an empirical composition of  $(C_3HS_2)$  or  $(C_6H_2S_4)$ , which have been obtained in the dehydrogenation of gaseous benzene or toluene by means of sulfur at ordinary pressure and at elevated temperatures, generally in excess of  $360^\circ$  (12).

Much of the experimental work on this subject has been carried out using stationary charges heated in sealed glass pressure tubes. However, for the preparation of plastic resins, having regard for the viscous nature of the mixtures during the reaction, more uniform products are to be obtained where the charges are steadily rotated during the heating. In this way, and by a proportioning of the mixtures and control of the temperature at close to  $300^\circ$ , it has been possible to build up phenylene sulfide polymers of considerably improved toughness and strength. The flexural and tensile strengths of these resins, which can run at 5000–7000 lb. per sq. in. in the unplasticized state, would be in agreement with a reasonably high degree of polymerization, maybe 100–200, if analogy with cellulose derivatives is to be accepted in this respect (15).

Otherwise the phenylene sulfide resins obtained by the present method can be described as light colored, cream to canary yellow in the powder state, and as having a high thermal stability. Their chemical stability is generally high also, except toward strong oxidizing agents, such as nitric acid. After fusing or pressing, they take on the character of glasses, but with rise in temperature become resilient and finally pass into a plastic state. Some of the resins exist in a tough but vitreous or resilient condition over a wide temperature range. When plasticized by sulfur, the phenylene di- and poly-sulfide resins are mostly rubber-like in properties; they also readily dissolve on heating with organic disulfides, such as phenyl disulfide or tetramethylthiuram disulfide, but evidently undergo a disproportionation in doing so, causing little change in viscosity but a large depression of the freezing point of the solvent.

The tendency toward formation of plastic sulfide resins is not confined to the metathesis reactions of *p*-dichlorobenzene but has been observed as well with *m*-dichlorobenzene, with mixed dichlorobenzenes and other dihalogenated aromatic compounds, including diphenyl, diphenyl ether, terphenyl, and naphthalene derivatives. The resins are generally sparingly soluble in organic solvents except where the reaction mixtures started with include some monochloride along with the dichloride. Such mixtures tend to yield low-melting, soluble resins of low viscosity and molecular weight.

Polychlorinated benzenes, such as 1,2,4-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, or hexachlorobenzene, react under like conditions but lead to practically insoluble, yellow to green pigments, which do not fuse at temperatures up to  $450^\circ$ . They do not seem to have any dyeing effects.

TABLE I

SHOWING MOLECULAR WEIGHT DATA ON A RELATIVELY HIGH-MOLECULAR *p*-PHENYLENE POLYSULFIDE RESIN (H) AS DETERMINED BY ISOTHERMAL DISTILLATION IN SULFUR AT 295-305° IN BALANCE WITH A SIMILAR MIXED SULFIDE RESIN (L) OF KNOWN MOLECULAR WEIGHT

RESIN	WT. G.	SOL'N., G.	MOLES/KG.	WT. CHANGE, G.	M. WT.
L	0.0695	1.1505	0.04	+0.009	1500
H	.377	1.0425	below	-.0145	above 9000
L	.0286	0.978	0.0195	-.038	1500
H	.0985	.29	above	+.0375	below 17,000

The resin (H) had a sulfur content of 47.8% and was obtained from *p*-dichlorobenzene by reaction with a mixture of anhydrous sodium carbonate and sulfur at 300-340°. It was sealed up, after evacuating, in one arm of an inverted "Y"-tube in balance with a low-molecular, carbon disulfide-soluble resin (L) obtained similarly, starting with a mixture of monochloro- and *p*-dichloro-benzene, as described in the last example in the text. Before use, both resins were freed as far as possible of volatile materials by prolonged vacuum-distillation at 300-340° in sealed tubular stills.

TABLE II

SHOWING RECOVERY BALANCE OF SOLUBLE BYPRODUCTS WHEN 3.3 G. OF *p*-DICHLORO-BENZENE WAS HEATED FOR 20 HOURS AT 300-340° WITH 3.9 G. OF SODIUM CARBONATE AND 3 G. OF SULFUR

The procedure of Shereshevskii (13) and Paessler (14) for analysis of inorganic sulfide mixtures was followed here for the most part.

BY-PRODUCT	ANALYSIS YIELD, G.	RECOVERY % ON	
		Na <sub>2</sub> CO <sub>3</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>
Na <sub>2</sub> S	0.0214	0.7	—
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	.75	12.8	—
Na <sub>2</sub> SO <sub>4</sub>	.442	8.4	—
Na <sub>2</sub> CO <sub>3</sub>	.553	14.1	—
NaCl	2.495	58.0	95.1

The aqueous extracts from the phenylene polysulfide resin were here diluted to a fixed volume, 125 cc., and 5- or 10-cc. samples used for the different analyses. Thiosulfate was determined by iodine titration after precipitating sulfide and polysulfide with zinc sulfate; sulfide and thiosulfate together by treatment with excess acid iodine solution; carbonate and sulfide together by acid titration with phenolphthalein as indicator; sulfate by boiling with dilute hydrochloric acid to eliminate sulfur dioxide, filtering from liberated sulfur and treating with barium chloride; chloride by evaporating over steam in a crucible, burning the residue with a 1:3 mixture of potassium nitrate and sodium carbonate, then working up for chloride in the usual way, acidifying with nitric acid and treating with silver nitrate; total extracted salts by fuming down several times with excess sulfuric acid and weighing as sodium sulfate.

The sulfur liberated in the sulfate determination corresponded to an analysis yield of 0.16 g. as against 0.1519 g. calc'd for the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> found; the extracted salts, converted to sulfate, were equivalent to 5.0882 g. Na<sub>2</sub>SO<sub>4</sub> or a 97.3% recovery on the Na<sub>2</sub>CO<sub>3</sub> used.

## EXPERIMENTAL

*Thianthrene.* A mixture of 4 g. of dry, U.S.P. calcium sulfide (63.7% sulfide conc'n), 0.283 g. of sulfur, and 4 g. of *o*-dichlorobenzene, is sealed up in a glass tube at about 25 mm. pressure and heated undisturbed for about 20 hours at 300–340°. (Ordinary Pyrex tubes of 14–15 mm. diameter and 14–16 inches long serve well enough here if heated within a capped steel nipple or pipe, perforated by a few touch-holes.) The product is isolated by direct distillation at about 250° (25 mm.) or by extraction with hot benzene. It is purified by redistilling over about half its weight of copper powder. It comprises colorless crystals of thianthrene; m.p. 158.8–159°. The yield is 75% or more on the dichlorobenzene.

*Anal.* Calc'd for  $C_{12}H_8S_2$ : S, 29.6; mol. wt. 216.

Found: S (Asbóth method), 29.0; mol. wt. (Rast), 207–214.

When dry calcium sulfide is heated under the same conditions with *o*-dichlorobenzene alone, no separable thianthrene is formed, the starting materials being recovered practically unchanged.

*Phenyl sulfide and disulfide.* A mixture of 2.5 g. of calcium oxide powder (calcined slaked lime), 1.43 g. of sulfur, and 4.52 g. of chlorobenzene, is sealed up in an evacuated tube and heated 20 hours at 295–305°. The product can be isolated from the mixture by direct distillation under reduced pressure, or by extraction with carbon tetrachloride. It comprises a mixture of phenyl sulfide and disulfide boiling at 290–315°, the yield being 75% or more on the chlorobenzene. Redistilled over copper powder, the phenyl sulfide boils at 290–296° and has a specific gravity of 1.118 at 16°.

*Phenylene sulfide polymers.* A mixture of 3 g. of sulfur, 3.9 g. of low-density sodium carbonate (obtained by heating sodium bicarbonate at 250–300°) is pulverized together and added to 3.3 g. of *p*-dichlorobenzene. After evacuating and sealing, the tube is heated 20 hours at 300–340° in a nearly horizontal position. The reaction develops a high pressure, the effluent gases, on cautious opening of the tube, being practically odorless. After pulverizing, extracting with water, and drying, the crude product, 4.1 g., is a sulfur-colored resin containing 56.2% total S (by modified Liebig method), 9–10% labile S [by Parker's method (16) modified by carrying out in presence of toluene].

The crude material is purified for analysis by continuous extraction with acetone and toluene in succession and dried at 140–150° under reduced pressure. The purified resin is 50–51% of the crude. It is straw-colored and brittle cold, resilient at 80–180°, plastic from this temperature up to above 350°. It corresponds in empirical composition to  $(C_6H_4S_{2.3})$ .

*Anal.* Calc'd: C, 48.1; H, 2.67; S, 49.2.

Found: C(micro), 47.9–48.1; H(micro), 2.5–2.7; S(total), 48.2–48.6; also 1–2% labile S; 0.3% ash; less than 0.4% Cl.

The reaction by-products here comprised mainly sodium chloride along with lesser amounts of thiosulfate, sulfate, and unchanged sodium carbonate, very little unreacted sodium sulfide (Table II).

When *p*-dichlorobenzene has been heated with either sodium carbonate or sulfur alone under the above conditions, practically no inorganic chloride or resin has been obtained.

A resin approaching in composition a phenylene monosulfide polymer is obtained as follows: A mixture of 1.2 g. of sulfur, 4 g. of anhydrous sodium carbonate, and 3.3 g. of *p*-dichlorobenzene is heated as above, giving 2.4 g. of pale yellow crude resin, which is purified by continuous extraction in the same way. After drying, the recovery amounts to 87–88% of the crude. It comprises a white powder, brittle cold, fusing fairly sharply at 255°. The analysis corresponds to an empirical composition of  $(C_6H_4S_{1.2})$ .

*Anal.* Calc'd: C, 62.9; H, 3.5; S, 33.6.

Found: C, 62.7–62.9; H, 3.4–3.5; S, 30.8–30.9; ash, 0.4; Cl, 0.8.

(The figures for carbon and hydrogen quoted above were obtained in the laboratory of Dr. C. Tiedeke in New York.)

The physical character of such a resin can be much improved by closer control of the reaction conditions. Thus when such a mixture as the last is rotated continuously during

the heating and the temperature kept at 300°, the resin obtained molds very well between aluminum plates at 260–280°, forming tough, glassy sheets which become resilient from the softening point, about 100°, to about 210°, when the material becomes workable. The resins obtained in this manner show the most promise as regards physical strength. The toughness can be still further increased by use of somewhat less sulfur in the reaction mixtures. However, inclusion of even small amounts of water in the mixtures has been observed to lower the strength of the resins obtained.

*Soluble mixed sulfide resin.* A mixture of 3 g. of sulfur, 3.9 g. of anhydrous sodium carbonate, 3 g. of *p*-dichlorobenzene, and 0.5 g. of chlorobenzene, is heated 20 hours in a sealed, evacuated tube at 300–325°, and the cooled mixture extracted with water after releasing the gas generated in the reaction. The dried product, 4.3 g., contains 54.8% S and is a yellow, brittle resin, softening at 30°, becoming moderately fluid at 70°. It is easily soluble in carbon disulfide and is recovered by evaporating the solvent (finally at 140–180° under reduced pressure) as a clear, yellow, low-melting glass. The molecular weight is about 1500 (1480 found in balance with olein by the Barger method).

#### SUMMARY

A convenient process has been devised for preparing aromatic sulfide and polysulfide compounds in a dry way by heating the aromatic chloro compounds with certain metal sulfides in presence of some free sulfur. Mixtures of sulfur with a number of oxides or salts of metals of groups I and II of the periodic table can also be substituted for the preformed metal sulfides.

By this method the aromatic dichloro compounds give condensation products, mostly in the form of sparingly soluble, high-melting, plastic resins, some of moderately high apparent molecular weight. The physical strength of some of the resins is satisfactory. Mixed sulfide resins which are both soluble and low-melting can also be made this way.

LONDON, ONTARIO, CANADA

#### REFERENCES

- (1) DOUGHERTY AND HAMMOND, *J. Am. Chem. Soc.*, **57**, 117 (1935).
- (2) ONUFROVITCH, *Ber.*, **23**, 3369 (1890).
- (3) PAREKH AND GUHA, *J. Indian Chem. Soc.*, **11**, 95 (1934).
- (4) RUNGE, "Organomagnesiumverbindungen," Stuttgart, **1932**, 261.
- (5) HODGSON AND LEIGH, *J. Chem. Soc.*, 126 (1939).
- (6) RINGEISSEN, *Compt. rend.*, **198**, 2180 (1934).
- (7) COOKE, HEILBRON, AND WALKER, *J. Chem. Soc.*, **127**, 2250 (1925).
- (8) VOROZHTZOV AND MITZENGENDLER, *Org. Chem. Ind. (U. S. S. R.)*, **21**, 457 (1936).
- (9) PATRICK, U. S. Patent, 2,195,380 (1940); 2,278,172 (1942).
- (10) PEARSON AND ROBINSON, *J. Chem. Soc.*, 413, 1304, 1473 (1931).
- (11) LEUCKART, *J. prakt. Chem.*, (2), **41**, 206 (1890).
- (12) PALMER, LLOYD, McCURE, LEMAISTRE, WARING, AND BACHMAN, *J. Am. Chem. Soc.*, **52**, 3388 (1930); **62**, 1005 (1940); U. S. Patent, 1,884,762 (1932).
- (13) SHERESHEVSKII, *Z. anal. Chem.*, **105**, 110 (1936).
- (14) PAESSLER, *Chem. Abstr.*, **23**, 3187 (1929).
- (15) OTT, "Advancing Fronts in Chemistry," Vol. I, High Polymers, New York, **1945**, 87.
- (16) PARKER, *India-Rubber J.*, **108**, 387 (1945).