

benzoic acid gave an immediate precipitate from hot dilute acid. This salt was extremely insoluble, and analysis showed it to be the di-(S-benzylthiuronium) *o*-sulfobenzoate. The *p*-sulfobenzoic acid gave a derivative which was more soluble, crystallizing slowly from cold dilute acid. Analysis shows this to be the acid salt, S-benzylthiuronium hydrogen *p*-sulfobenzoate. The difference in solubilities of these three salts gives a convenient method of identification of the three acids. A solution of the free acid, or a solution of a salt of the acid which has been acidified with a few drops of concentrated hydrochloric acid, is heated to boiling and the calculated quantity of a 10% solution of S-benzylthiuronium chloride is added. An immediate precipitate indicates *o*-sulfobenzoic acid. A precipitate which crystallizes slowly on cooling indicates *p*-sulfobenzoic acid, and if no precipitate, or an oil, is obtained, the acid is *m*-sulfobenzoic acid.

### Experimental

***p*-Sulfobenzoic Acid.**—Two grams of *p*-toluenesulfonic acid was oxidized with 5 g. of potassium permanganate in basic solution. The precipitated manganese dioxide was filtered off, and hydrochloric acid was added until the solution became acidic. The addition of barium chloride caused an immediate precipitate of white flakes of the barium salt of *p*-sulfobenzoic acid, which was soluble in base and reprecipitated by acid. One gram of this salt was digested in 30 ml. of hot water with excess sodium sulfate and 1 ml. of concentrated hydrochloric acid. The precipitate of barium sulfate was removed, and 10 ml. of 10% S-benzylthiuronium chloride was added. The clear solution, on cooling, gave flat plates of S-benzylthiuronium hydrogen *p*-sulfobenzoate which were recrystallized with difficulty from ethyl alcohol, m. p. 212.6–214.4° (cor.).

*Anal.* Calcd. for  $C_{15}H_{13}N_2O_6S_2$ : N, 7.61; Found: N, 7.80.

***m*-Sulfobenzoic Acid.**—This acid was prepared in the usual manner by sulfonating benzoic acid in 30% fuming sulfuric acid and salting out the acid sodium salt. One gram of this salt was dissolved in 20 ml. of distilled water containing 1 ml. of concentrated hydrochloric acid and 10 ml. of 10% S-benzylthiuronium chloride was added. No precipitate formed on cooling. At freezing temperatures an emulsion formed which redissolved as it warmed to room temperature. No further attempt was made to isolate this salt.

***o*-Sulfobenzoic Acid.**—The acid ammonium salt of this acid was prepared from saccharin according to the method of Clarke and Dreger.<sup>6</sup> One gram of the crude salt was dissolved in 30 ml. of hot water, 1 ml. of concentrated hydrochloric acid and 10 ml. of 10% S-benzylthiuronium chloride were added. An immediate precipitate was formed in the hot solution. After cooling, the di-(S-

benzylthiuronium) *o*-sulfobenzoate was recrystallized from 70% alcohol as fine white needles, m. p. 205.5–206.5° (cor.). When mixed with the derivative from *p*-sulfobenzoic acid the melting point was 194–196°.

*Anal.* Calcd. for  $C_{23}H_{21}N_4O_6S_3$ : N, 10.25. Found: N, 10.35.

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## The Formation of Insoluble Sulfur in the Presence of Gases Other than Sulfur Dioxide

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The work of Smith and Holmes<sup>1</sup> and, more recently, of Das and Ghosh<sup>2</sup> would indicate that the plasticity and insolubility of certain forms of sulfur are dependent upon the presence of at least a trace of sulfur dioxide. The former investigators considered the presence of this compound an essential condition for the formation of plastic sulfur; the latter believe that all insoluble forms of the element owe their distinctive property to the presence of an insulating film of sulfur dioxide about the minute crystallites. On the other hand, suggestions have been made by various investigators, notably Deines<sup>3</sup> and Meyer,<sup>4</sup> that possibly other foreign substances might also be capable of causing the formation of insoluble forms of sulfur.

In order to decide between these two conflicting points of view, an improved quenching method was devised in this Laboratory for the preparation of insoluble, plastic sulfur in a closed system which permitted contact with any desired gas while eliminating all possibility of contact with air. Under these conditions the formation of traces of sulfur dioxide by aerial contact is avoided, and it becomes possible to ascribe the various effects to their true causes.

It was found that while air and sulfur dioxide gave the expected results, yielding clear, amber, plastic masses analyzing about 36% insoluble sulfur after 6 days, and while nitrogen and ammonia gave opaque, yellow, brittle masses analyzing less than 4% insoluble sulfur, both hydrogen chloride and hydrogen sulfide were capable of producing clear, amber, plastic masses analyzing 36% and 8% insoluble sulfur, respectively. The plasticity of these latter forms was, it is true, rela-

(1) Smith and Holmes, *Z. physik. Chem.*, **42**, 469 (1903); *This Journal*, **27**, 979 (1905).

(2) Das and Ghosh, *Indian J. Phys.*, **13**, 91 (1939).

(3) Deines, *Z. anorg. allgem. Chem.*, **213**, 183 (1933).

(4) Meyer, *Trans. Faraday Soc.*, **32**, 148 (1936).

(6) Clarke and Dreger, "Organic Syntheses," Coll. Vol. I, p. 13.

tively short-lived, lasting about twenty minutes in the case of the HCl-produced material and only two minutes in the case of the H<sub>2</sub>S-produced material. Nevertheless, the plastic state was observed to exist, and in contrast to the immediate solidification of the material formed in the presence of the inert gases nitrogen and ammonia, its life in this state was quite appreciable. The corresponding increases in the proportion of insoluble sulfur present in the hardened samples is also indicative of the ability of hydrogen chloride and hydrogen sulfide to act similarly to sulfur dioxide in the formation of the plastic and insoluble modifications.

Thus, theories postulating the indispensability of sulfur dioxide in the formation of plastic sulfur or for the maintenance of insolubility in the hardened mass appear, on the basis of these facts, to be untenable. The suggestions by Deines and by Meyer that foreign substances other than sulfur dioxide might be effective in causing similar results are upheld by the experimental evidence.

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### Preparation of Germanium Tetrachloride, GeCl<sub>4</sub>

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When germanium dioxide, GeO<sub>2</sub>, is boiled with hydrochloric acid, germanium tetrachloride, GeCl<sub>4</sub>, volatilizes if the concentration of hydrogen chloride approaches 6 *N*.<sup>1</sup> It has been observed in this Laboratory and elsewhere, however, that if the concentration of hydrogen chloride is too high, germanium tetrachloride vapor is carried uncondensed through a water cooled condenser.<sup>2</sup> The loss of germanium is readily explained. When the acid concentration is high, germanium tetrachloride is not hydrolyzed and, in addition, is not very soluble in such acid solutions. Its vapor pressure, furthermore, is quite high at the temperature of the cooling water in the condenser. When 6 *N* hydrochloric acid, approximately the constant boiling mixture, is used, both the acid and the germanium tetrachloride are completely condensed; when mixtures with higher concentrations of hydrogen chloride are boiled, however,

gaseous hydrogen chloride passes through the condenser and carries considerable germanium tetrachloride along with it.

Aitkenhead and Middleton<sup>2b</sup> took advantage of this phenomenon in the analysis of minerals for small amounts of germanium; germanium tetrachloride was distilled in a stream of hydrogen chloride gas, thus removing the germanium completely from the rest of the dissolved sample. The gases which escaped from the top of a reflux condenser were absorbed in a small volume of water and the germanium content readily determined.

At very low temperatures (−72°) no complexes form between germanium tetrachloride and hydrogen chloride<sup>3</sup> so that it is possible to separate the two by judicious cooling. It has been found that if the vapors which emerge from the top of a reflux condenser, after being dried, are cooled in a "dry-ice"-isopropyl alcohol mixture, the hydrogen chloride (b. p. −85°) escapes uncondensed and the germanium tetrachloride freezes out as a pure white solid (m. p. −49.5°). The method has the added advantage that the germanium dioxide is more readily dissolved in the boiling flask when the concentration of hydrogen chloride is kept high.

**Procedure.**—Germanium oxide is suspended in 6 *N* hydrochloric acid and the suspension is boiled gently under a reflux condenser. Hydrogen chloride is passed into the flask at a rapid rate at first so that some of it escapes slowly through a sulfuric acid trap at the end of the train. Later, when the absorption in the boiling flask nears completion, the rate of flow is reduced. As the gases pass through the reflux condenser, condensed germanium tetrachloride and constant boiling hydrochloric acid return to the flask, but the gases escaping through the condenser carry a high percentage of germanium tetrachloride and gradually all of it is volatilized. The gas mixture, having been cooled to the dew point of the germanium tetrachloride at the temperature of the cooling water, will be unsaturated at room temperature and will not deposit liquid germanium tetrachloride in the calcium chloride tower used to remove residual moisture. When passed through the tube cooled by means of dry-ice, however, the germanium tetrachloride is completely removed and entrains very little hydrogen chloride. An all glass apparatus is preferable, but no difficulties are encountered if rubber connections are used. By this procedure 5 to 10 g. of GeO<sub>2</sub> may be converted to the tetrachloride within an hour. Residual hydrogen chloride may be removed by allowing the product to stand over sodium carbonate, filtering and distilling in dry apparatus.<sup>1b</sup>

CONTRIBUTION FROM THE  
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(1) (a) Dennis and Johnson, *THIS JOURNAL*, **45**, 1380 (1923); (b) Tabern, Orndorff and Dennis, *ibid.*, **47**, 2040 (1925); (c) Pugh and Thomas, *J. Chem. Soc.*, 1052 (1926).

(2) (a) H. Lundin, *Trans. Am. Electrochem. Soc.*, **63**, 149 (1933); (b) W. C. Aitkenhead and A. R. Middleton, *Ind. Eng. Chem., Anal. Ed.*, **10**, 633 (1938).

(3) R. Schwarz and H. Giese, *Ber.*, **63**, 2429 (1930).