

(8) or else the hypothesis that chlorophyll acts as a donor of hydrogen in photosynthesis should be abandoned.

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#### Summary

1. The formation of chlorophyll containing T could not be detected during photosynthesis of

*Chlorella pyrenoidosa* in HTO + H<sub>2</sub>O.

2. No (<5%) thermal exchange was observed between purified chlorophyll and 80% ethanol containing HTO.

3. The implications of these results for the theory that chlorophyll acts as a hydrogen donor in photosynthesis are discussed.

4. It is pointed out that repetition of the experiments herein described using 100% D<sub>2</sub>O would avoid the question of isotope separation and make possible an unequivocal conclusion regarding the role of chlorophyll.

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## NOTES

### Characteristics of $\beta$ -[2,5-Dimethoxyphenyl]- $\beta$ -hydroxyisopropylamine Hydrochloride

BY RICHARD BALTZLY AND JOHANNES S. BUCK

This compound was reported recently<sup>1</sup>; subsequent investigation makes it evident that the substance to which that formula was attributed is actually  $\beta$ -[2,5-dimethoxyphenyl]- $\beta$ -oxoisopropylamine hydrochloride. This could have been anticipated<sup>2</sup> but was not at the time. The error arose partly from the difficulty of interpreting small absorptions of hydrogen when using a catalyst (palladized charcoal) that itself binds relatively large amounts of hydrogen and partly from adverse conditions over which the analyst had no control.

The substance previously obtained (m. p. 176° dec.) when dissolved in water and reduced with hydrogen and platinum-black absorbed 1 mole of hydrogen. A new hydrochloride was isolated melting at 215°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>18</sub>O<sub>2</sub>N: C, 53.31; H, 7.33. Found: C, 53.43; H, 7.53.

When the corresponding base was acetylated with acetic anhydride a diacetyl derivative was formed melting at 120° and crystallizing from ethyl acetate-hexane in parallelogrammatic plates.

*Anal.* Calcd. for C<sub>15</sub>H<sub>21</sub>O<sub>5</sub>N: C, 60.98; H, 7.17. Calcd. for C<sub>18</sub>H<sub>17</sub>O<sub>4</sub>N: C, 62.12; H, 6.83. Found: C, 61.09; H, 7.30.

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(1) Baltzly and Buck, *THIS JOURNAL*, **62**, 164 (1940).

(2) Cf. Hartung, *ibid.*, **53**, 4149 (1931).

### Identification of *o*- and *p*-Sulfobenzoic Acids<sup>1</sup> as their S-Benzylthiuronium Salts

BY E. CAMPAIGNE<sup>2</sup> AND C. M. SUTER<sup>3</sup>

The structure of the alkylated benzenesulfonic acids may be partially clarified by oxidation to the sulfobenzoic acids. The identity of the *o*-, *m*- and *p*-sulfobenzoic acids may be determined by conversion to the acid chlorides and to the amides.<sup>4</sup> This involves separation and drying of the salts of the sulfobenzoic acids, and the somewhat tedious conversion to the chlorides with a phosphorus halide. The use of S-benzylthiuronium chloride as an analytical reagent for sulfonic acids<sup>5</sup> has recently been reported. Since the benzylthiuronium derivatives are prepared in water solutions, the use of this reagent should give a quick and easy method for the identification of the oxidation products of alkylbenzenesulfonic acids and related compounds.

The S-benzylthiuronium salts of *o*- and *p*-sulfobenzoic acid were obtained in good yield from water solutions of the acid sodium or ammonium salts, but the derivative of the *m*-sulfobenzoic acid was found to be quite soluble in water, and could not be isolated conveniently. The *o*-sulfo-

(1) This investigation was supported by a grant from the Abbott Fund of Northwestern University.

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(4) Beilstein's "Handbuch," 4th ed., Vol. XI, p. 369.

(5) Chambers and Watt, *J. Org. Chem.*, **6**, 376 (1941).

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  $C_{16}H_{16}N_2O_6S_2$ : 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  $C_{22}H_{22}N_4O_6S_2$ : 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

By EDWARD A. FEHREL

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.