3. With a constant concentration of the acid, the reaction rate sinks with rising concentration of the menthone. If the menthone concentration is lower than the acid concentration, the retarding effect of the menthone is more pronounced than with menthone concentrations higher than those of the acid.

4. The temperature coefficient of the reaction was determined at intervals between 20 and 50°. The heat of activation is 6200 cal.

5. The rotation of the equilibrium mixture depends on the concentration of the trichloroacetic acid for two reasons. The acid affects the specific rotation of the components of the equilibrium mixture, and, with higher concentration of the acid, the equilibrium shifts in favor of the *d*-isomenthone.

6. The analysis of the kinetic results shows that the inversion takes place by interaction of a binary acid–menthone complex with a further molecule of the monomeric acid. Equivalent to this assumption would be the spontaneous rearrangement of a complex of one molecule of menthone with two molecules of monomeric acid.

7. Freezing-point determinations were carried out on benzene solutions of menthone and trichloroacetic acid to determine the constant of the complex formation between menthone and acid, and the association constant of the acid.

8. By comparison of the reaction rate of "Rechtsmenthon," *l*-menthone and *d*-isomenthone, it was confirmed that "Rechtsmenthon" is a mixture of *l*-menthone and *d*-isomenthone.

ROCHESTER, N. Y. RECEIVED AUGUST 14, 1942

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[CONTRIBUTION FROM THE DEPARTMENT OF BACTERIOLOGY, THE SCHOOL OF MEDICINE, UNIVERSITY OF PENNSYLVANIA]

# Properties of *p*-Hydroxylaminobenzenesulfonamide and a Related Molecular Complex[1]

BY M. G. SEVAG

Mayer[2] reported a crystalline substance melting at 161° but did not give either its preparation or analysis. Bratton, White and Marshall[3] obtained a product melting at 139.5–141.5° and having the composition $C_6H_8N_2SO_3$ which they regarded as *p*-hydroxylaminobenzenesulfonamide. Thorpe and Williams[4] confirmed the work of Bratton, *et al.* Burton, *et al.*,[5] obtained a substance melting at 163–164°, the analysis of which did not fully agree with that required by $C_6H_8N_2SO_3$. Burton[6] reported two substances, one melting at 139–140° and the other at 160–161°. He did not give their analyses but considered them to be dimorphic forms. Sevag and Shelburne[7] obtained two forms of hydroxylaminobenzenesulfonamide, one melting at 139–141° and the other at 161.5°. In view of the above conflicting results, a detailed study of the properties and the nature of these substances was considered necessary.

The present study confirms the findings of Bratton, White and Marshall regarding the nature of the substance melting at 141.5°. On the other hand, the substance melting at 161.5° is found to differ from it in C, H and N analyses, salt-forming and solubility properties and in the volume of oxygen they consume.

According to the findings of Bamberger[8] hydroxylamine on oxidation yields one mole of nitrosobenzene and one mole of hydrogen peroxide. One mole of nitrosobenzene is then combined with one mole of hydroxylamine forming azoxybenzene and water. The oxidation of *p*-hydroxylaminobenzenesulfonamide seems to follow the same course. The substance melting at 141.5° consumed a volume of oxygen corresponding to 92.4%, and that consumed by the substance melting at 161.5° to only 64% of the theoretical value (Fig. 1). It was evident that the latter substance contained 36% a non-oxidizable substance. The analysis of the products in the reaction mixture revealed the presence of 35% sulfanilamide (Table I, compare columns 1, 5 and 8). These results show that the substance melt-

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(1) This work started under a grant from The Commonwealth Fund, and was continued under grants from The Josiah Macy, Jr. Foundation, and Merck and Co.

(2) R. L. Mayer, *Bull. acad. med.*, **117**, 727 (1937); *Biol. med. Paris* (Suppl.), **27**, 45, 75 (1937).

(3) A. C. Bratton, H. J. White and E. K. Marshall, Jr., *Proc. Soc. Exp. Biol. Med.*, **42**, 847 (1939).

(4) W. V. Thorpe and R. T. Williams, *Biochem. J.*, **35**, 61 (1941).

(5) H. Burton, J. W. McLeod, T. S. McLeod and A. Mayr-Harting, *Brit. J. Exptl. Path.*, **21**, 292 (1940).

(6) H. Burton, *Chemistry & Industry*, **60**, 449 (1941).

(7) M. G. Sevag and M. Shelburne, *J. Bact.*, **43**, 411, 421, 447 (1942).

(8) E. Bamberger, *Ber.*, **33**, 113 (1900).

TABLE I

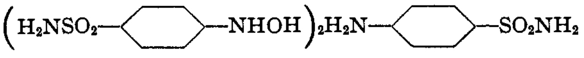
THE SULFANILAMIDE CONTENT OF THE SUBSTANCE MELTING AT 161.5°

HONHR = $p$-hydroxylaminobenzenesulfonamide.

| Sulfanilamide (SA) | | HONHR m. p. 141.5° | | HONHR m. p. 141.5° | | Substance m. p. 161.5° | | |
|---|---|---|---|---|---|---|---|---|
| Mg./10 cc. | Reading[a] | Mg./10 cc. | Reading[a] | To which was added Mg. of SA/10 cc. | Reading[a] | Mg./10 cc. | Mg. SA calcd. | Reading[a] |
| (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) |
| 0.02 | 15 | 0.13 | 6 | 0.034 | 27 | 0.112 | 0.04 | 32 |
| .05 | 37 | .26 | 8 | .068 | 56 | .224 | .09 | 71 |
| .12 | 79 | .39 | 11 | .102 | 80 | .336 | .135 | 106 |
| .15 | 108 | .52 | 13 | .136 | 106 | .448 | .18 | 142 |
| .20 | 143 | | | | | | | |
| .71 | 453 | | | | | | | |

[a] Photoelectric colorimetric readings.

ing at 161.5° is a trimolecular complex having the composition of



$(H_2NSO_2—C_6H_4—NHOH)_2H_2N—C_6H_4—SO_2NH_2$

The properties of two substances are given in Table II.

TABLE II

PROPERTIES OF THE TWO SUBSTANCES

| | Substance m. p. 141.5° | Substance m. p. 161.5° |
|---|---|---|
| Solubility, g./100 cc. of absolute ethyl ether | 0.276 | 0.115 |
| Solubility, g./100 cc. of 0.016 $N$ HCl | 1.33 | Insoluble |
| $O_2$ consumed, per cent. of the calcd. for $C_6H_8N_2SO_3$ | 92.40 | 64 |
| Sulfanilamide content, per cent. | None | 35 |
| Formation of ether insoluble sulfate | None | Forms |
| Formation of ether insoluble hydrochloride | Forms | Forms |
| Carbon, % | 38.51 | 39.98 |
| Hydrogen, % | 4.65 | 4.56 |
| Nitrogen, % | 14.52 | 15.60 |

The determination of the molecular weight of the substance melting at 161.5° using the Rast method was unsuccessful because of decomposition at elevated temperatures. Camphor, pinene hydrochloride and camphene were tried as solvents. The cryoscopic method was not applicable because of its insolubility in benzene or acetic acid. Its oxidizability with relative ease and sparing solubility did not encourage the use of other methods.

## Experimental

**$p$-Hydroxylaminobenzenesulfonamide.**—The method of preparation of this substance is an adaptation[8] of Bamberger's method[9] of preparing $\beta$-phenylhydroxylamine. Five grams of $p$-nitrobenzenesulfonamide was added to 125 cc. of water solution containing 2.5 g. of ammonium chloride. Zinc dust (3.5 g.) was then added gradually while the mixture was stirred mechanically. The mixture

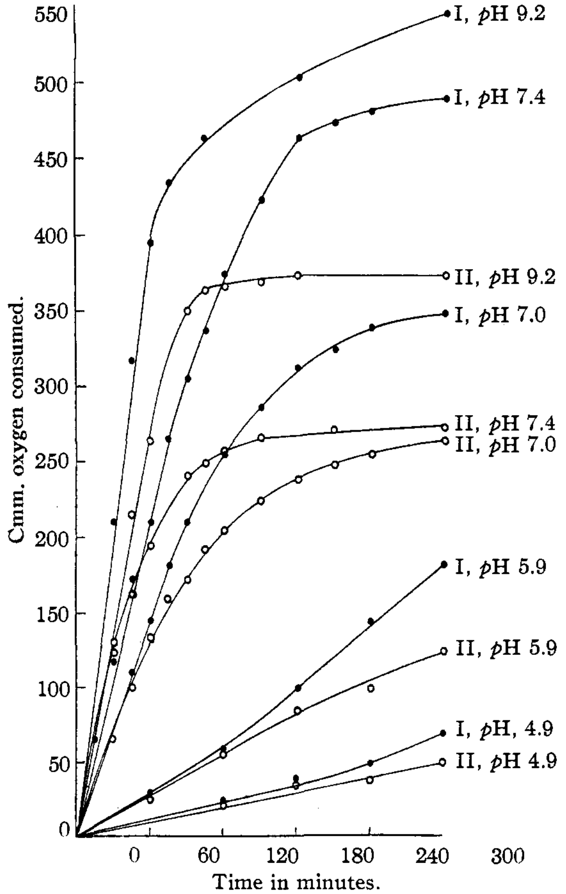


Fig. 1.—Oxygen uptake of $p$-hydroxylaminobenzenesulfonamides: I, m. p. 141.5°; II, m. p. 161.5°.

was then filtered by suction; the filtrate was saturated with sodium chloride (33 g. per 100 cc.), evacuated to remove oxygen, stoppered and cooled. The resulting precipitate was filtered quickly and dried in a desiccator. The dry material was then extracted a few times by refluxing on water-bath with 200 to 400 cc. of absolute ethyl ether each time. The ether extracts were filtered into equal volumes of petroleum ether. The resulting crystalline precipitates were filtered into a Gooch filter, dried *in vacuo* and studied. The filtrates of precipitates on concentration *in vacuo* yielded considerably more substance. A total of 1.57 g. of substance (34% yield) was obtained.

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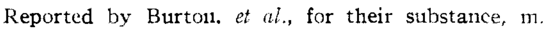
(9) E. Bamberger, *Ber.*, **27**, 1548 (1894); **28**, 245 (1895).

The fractions obtained as above melted either at 141.5°, or at 161.5°. Fractions melting within the range 145 to 155° were likewise obtained, which were further purified by the above method.

The reduction of the nitro derivative was carried out at 0, 25 and 65°. At lower temperature a period of one hour is allowed for the addition of zinc dust, at the higher temperature about twenty minutes.

*Anal.* Calcd. for $C_6H_8N_2SO_3$: C, 38.29; H, 4.28; N, 14.89; S, 17.04. Substance m. p. 141.5°. Found: C, 38.51; H, 4.65; N, 14.52. Reported by Bratton, *et al.*: C, 38.08; H, 4.37; N, 14.40; S, 16.84. Calcd. for  $(H_2NSO_2C_6H_4NHOH)_2H_2NC_6H_4SO_2NH_2$ as the substance melting at 161.5°. Calcd.: C, 39.42; H, 4.41; N, 15.33. Found: C, 39.98; H, 4.56; N, 15.60. Reported by Burton, *et al.*, for their substance, m. p. 163–164°: C, 38.5; H, 4.5; N, 15.3.

**Crystalline Forms.**—A polarizing microscopic examination of the several preparations of the substance melting at 141.5° showed homogeneous eight-sided platelets and occasionally uniform needle-shaped crystals. The substance melting at 161.5° appeared as rhomboidal and four-sided crystals. This substance was observed also to crystallize in needle forms. The needle-shaped crystals melting at 141.5 or at 161.5° are indistinguishable under the microscope. Ethyl ether solutions of either of the two substances filtered into an equal volume of petroleum ether may yield needle forms; on centrifuging and drying the sediment *in vacuo* over sulfuric acid the dry substance may still be seen in needle form or may appear as eight-sided platelets (m. p. 141.5°) or rhomboidal or tetrahedral platelets (m. p. 161.5°).

**Oxygen Uptake by *p*-Hydroxylaminobenzenesulfonamide.**—The oxygen uptake was measured by a Barcroft–Warburg set-up at 37.5°. The flasks contained 1.0 cc. of $M/15$ phosphate buffer of desired *p*H and 1.8 cc. of water. Ten mg. of substance was introduced into the side-arm of the flask in dry form. After attaching the flask to the manometer and the equilibration of temperature the substance was tipped into the phosphate solutions. The completed reactions were treated with 0.3 cc. of water clear catalase to decompose and measure the hydrogen peroxide formed. Of the volumes of oxygen consumed by the substances melting at 141.5 and at 161.5°, 93.6 and 95.8%, respectively, were recovered as hydrogen peroxide.

**Determination of *p*-Aminobenzenesulfonamide Content of the Trimolecular Complex Melting at 161.5°.**—A satisfactory method to determine sulfanilamide in the presence of *p*-hydroxylaminobenzenesulfonamide has been lacking. The following method has been worked out during this study. It is based on the known fact that dimethylaminobenzaldehyde combining with amino compounds yields colored solutions. Both the *p*-hydroxylamino- and *p*-amino-benzenesulfonamide[10] give a yellow solution with this reagent. In order to estimate the amount of sulfanilamide the solution of the substance melting at 161.5° was freed from *p*-hydroxylaminobenzenesulfonamide by oxidation and filtering the resulting product; the filtrate was then analyzed for sulfanilamide as described below. For control, the solution of pure sulfanilamide in the presence and absence of *p*-hydroxylaminobenzenesulfanamide (m. p. 141.5°) was treated identically.

**Test Solutions.**—(1) 10.3 mg. of *p*-hydroxylaminobenzenesulfonamide (m. p. 141.5°); (2) 7.5 mg. of the substance as in (1) + 3.4 mg. of sulfanilamide, and (3) 11.2 mg. of the substance melting at 161.5°. Each of these was dissolved in 10 cc. of $M/15$ phosphate of *p*H 9.2 to which 0.2 cc. of normal sodium hydroxide solution was added. The solutions heated in a 56° water-bath for three hours turned yellow as a result of oxidation. They were made acid to litmus and the resulting precipitates were centrifuged and discarded. The supernatants were made up to a volume of 20 cc. with water.

From 0.1 to 0.8 cc. of the above solutions was treated in standard 10 cc. tubes with 0.2 cc. of 1.5% solution of dimethylaminobenzaldehyde (containing 20 cc. of concd. hydrochloric acid/100 cc. reagent) and made up to 10 cc. with water. A yellow color developed immediately and was measured after ten minutes in a Klett–Summerson photoelectric colorimeter using no. 42 filter (blue). A control which contained all the reagents was run with each experiment and the necessary corrections made. The colorimeter was calibrated with a solution of pure sulfanilamide. The readings between 0 and 450 corresponding up to 0.7 mg. of sulfanilamide formed a straight line. The results are given in Table I.

**Sulfate and Hydrochloride of *p*-Hydroxylaminobenzenesulfonamide.**—A clear solution of 534 mg. of the higher melting (161.5°) substance in 90 cc. of absolute ethyl ether (containing 15 cc. of absolute ethyl alcohol) treated with 0.3 cc. of 25% sulfuric acid solution immediately yielded a flocculent precipitate. After washing the centrifuged precipitate twice with petroleum ether and drying *in vacuo*, it weighed 115 mg. Under the polarizing microscope it appeared to be granular in form. It contained 11.95% nitrogen.

In contrast the substance melting at 141.5° did not yield an insoluble sulfate salt.

A solution of 450 mg. of the substance melting at 161.5° in 240 cc. of absolute ethyl ether (containing 30 cc. of absolute ethyl alcohol) treated with 1 cc. of concd. hydrochloric acid immediately assumed a milky appearance. After being chilled for three hours it was filtered into a weighed Gooch, washed with petroleum ether and dried *in vacuo*. The dry weight of the hydrochloride was 450 mg. It was of chalky appearance and granular in form under a polarizing microscope. It contained 12.26% nitrogen.

An ether–alcohol solution of 450 mg. of the substance melting at 141.5° treated identically as above did not readily yield a precipitate. However, in a few minutes crystals of salt began to form gradually. After chilling for three hours it was filtered and dried as above. Dry weight of the hydrochloride was 388.4 mg. Unlike the granular chalky hydrochloride of the higher melting (161.5°) substance, the dry substance under the polarizing microscope consisted of many-sided platelets and also of needles. It contained 12.5% nitrogen in comparison to 12.4% nitrogen calculated for the hydrochloride (1:1 molecular ratio).

**Differences in Solubilities.**—The solubilities of the two substances were compared in absolute ethyl ether since they are more resistant to oxidation in this solvent than any other. The saturated ethyl ether solution obtained by

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(10) M. M. Hartman, *J. Lab. Clin. Med.*, **26**, 401 (1940).

refluxing the substance melting at 141.5° contained 0.276% solids, while that of the substance melting at 161.5° contained 0.115% total solids. Two hundred mg. of the substance melting at 141.5° dissolved completely in 15 cc. of $N/60$ hydrochloric acid solution. In contrast 180 mg. of the substance melting at 161.5° did not dissolve in the same solvent after prolonged stirring. Warming at 56° for thirty minutes caused the solution of the latter mixture, but neutralization with sodium bicarbonate and cooling caused it to flocculate. Sodium bicarbonate did not show this effect on the solution of the substance melting at 141.5°.

## Summary

*p*-Hydroxylaminobenzenesulfonamide melting sharply at 141.5° and a related substance melting sharply at 161.5° have been studied.

The higher melting substance is a crystalline trimolecular complex composed of two molecules of *p*-hydroxylaminobenzenesulfonamide and one molecule of *p*-aminobenzenesulfonamide. This has been shown by chemical analyses, oxidation and quantitative determination of sulfanilamide in the presence of *p*-hydroxylaminobenzenesulfonamide.

PHILADELPHIA, PA. RECEIVED MAY 29, 1942

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[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC.]

# Surface Area of Oxide Coated Cathodes by Adsorption of Gas at Low Pressures[1]

BY L. A. WOOTEN AND CALLAWAY BROWN

## Introduction

The high thermionic emission obtainable with the oxide-coated cathode has been generally attributed to a film of free barium adsorbed on the surface of the alkaline earth oxide coating.[1a,2,3,4] The influence of surface area on the electron emission, however, has not been determined and no direct measurements of the surface area of oxide-coated cathodes have been reported. The present paper describes a new method for the measurement of relatively small surface areas and its application to oxide coated cathodes, activated and aged under conditions closely appproximating those obtaining in commercial vacuum tubes.

The method developed represents an extension of the method of Emmett and Brunauer,[5] which depends on physical adsorption of gases at temperatures near their boiling points. A comprehensive theory of adsorption in multimolecular layers has been developed[6,7] which makes it possible to deduce the quantity of gas in a monomolecular adsorbed layer from adsorption isotherms covering a range of pressures from 0.05–0.30 $p_0$, where $p_0$ is the vapor pressure of the gas at the temperature of the isotherm. Previous applications of the method have used temperatures near the boiling point of the gas so that adsorption measurements at pressures up to several hundred mm. were necessary. Thus butane at 0° ($p_0 = 770$ mm.) has been used as an adsorption reagent to measure the surface area of silica gel.[6] The theory[6,7] indicates that butane at $-116°$ ($p_0 = 0.17$ mm.) should be equally suitable with adsorption measurements necessary only at pressures less than 0.05 mm. Since it is possible to measure much smaller quantities of adsorbed gas at low pressures, use of the relatively low temperature greatly increases the sensitivity of the surface area measurements. In the present work, adsorption isotherms obtained for butane at $-116°$ and ethylene at $-183$ and $-196°$, at pressures less than 0.01 mm. in the case of ethylene, are found to resemble closely isotherms of gases near their boiling points and to allow measurement of the surfaces of oxide coated cathodes with areas of the order of 100 square centimeters. The ethylene isotherms on alkaline earth oxides are of interest from an adsorption standpoint in that they exhibit a very abrupt reversible rise in adsorption in the pressure region 0.25–0.30 $p_0$.

## Experimental

**Experimental Cathode.**—The cathode, of the indirectly heated type, consisted of a nickel tube coated with a mixture of barium and strontium oxides—38 mole per cent. of barium. A thick suspension of the carbonate mixture in amyl acetate containing 2% pyroxylin was ball milled with flint pebbles for forty-eight hours. The suspension was

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(1) Original manuscript received March 10, 1942.

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