

### Summary

The absorption, characteristic of the presence of the OH group and in the region of its first vibrational overtone, has been measured quantitatively for certain ortho substituted phenols and the results have been presented as curves of the

molal absorption coefficient against position in the spectrum.

The results have been discussed in the light of Pauling's recent interpretation of this type of spectra. For the most part the correspondence is remarkably close.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## The Heat of Fusion and Vapor Pressure of Stannic Iodide

By GEORGE R. NEGISHI

The investigations of Hildebrand and co-workers<sup>1</sup> in this Laboratory during recent years upon the subject of intermolecular forces and solubility have included a study of tetrahalides as examples of molecules having widely differing volumes and intermolecular fields but with a common highly symmetrical structure. Stannic iodide is one of the substances concerning which a considerable body of solubility data has been accumulated; however, its evaluation has been unsatisfactory on account of lack of accurate knowledge of its heat of fusion and vaporization. The work herein described has been carried out in order to fill this gap.

**Preparation and Purification of Stannic Iodide.**—This compound was prepared and purified by the method described by Dorfman and Hildebrand,<sup>1</sup> followed by two fractional distillations under high vacuum ( $10^{-6}$  mm.). The purity of the final product was undoubtedly high, as indicated by sharp breaks in the cooling curve, and by the absence of premelting in the heat of fusion determinations.

**The Melting Point.**—The sample was distilled under high vacuum into a Pyrex tube, in the center of which extended a narrow Pyrex tube almost to the bottom. The temperature of the freezing mixture was measured by means of an alumel-chromel thermocouple inserted into the central narrow tube. The couple was calibrated against the melting points of water and tin, the boiling point of water and the transition point of sodium sulfate decahydrate. The thermoelectric current was measured by means of a Leeds and Northrup Student Type potentiometer. A change in temperature of  $0.1^\circ$  could be detected. The sample was heated in a copper cylinder 20 cm. high, 5 cm. in diameter and 9 mm. thick, provided with a heating coil and thermally insulated with Sil-o-cel. The temperature was regulated by means of a rheostat. During the measurements the temperature of the furnace was lowered rather rapidly to the freezing point of the

stannic iodide, after that at about  $0.05^\circ$  per minute. The apparatus was shaken continuously on a rocker except when the readings were taken. The melting point was determined from the "break" in the cooling curve. The plot of the curve is shown in Fig. 1. The melting point thus determined was  $144.5^\circ$ . This value is to be compared with the values of  $143.5$ ,<sup>1</sup>  $145.3$ <sup>2</sup> and  $146.2$ ,<sup>3</sup> from other sources.

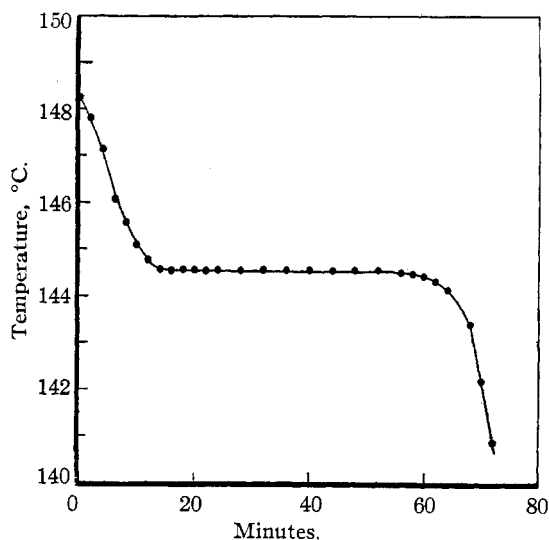


Fig. 1.

The vapor pressure was determined by means of a glass click gage as described by Smith and Taylor.<sup>4</sup> The click constant was determined at the pressures and temperatures of the actual runs. The constant increased with both increasing pressure and temperature up to a point where a permanent change set in. The "click-in" constant was found to be more reliable than that of "click-out," so only the former was calibrated. The space above the click gage (the manometer side) was evacuated to  $10^{-2}$  mm. before each "click-in" was made. This was not necessary at lower temperatures, but above  $200^\circ$  it was essential.

(1) M. E. Dorfman and J. H. Hildebrand, *THIS JOURNAL*, **49**, 729 (1927); Miriam E. Dice and J. H. Hildebrand, *ibid.*, **50**, 3023 (1928); J. H. Hildebrand and J. M. Carter, *ibid.*, **54**, 3592 (1932); J. H. Hildebrand, *ibid.*, **57**, 866 (1935).

(2) M. G. Raeder, *Z. anorg. allgem. Chem.*, **130**, 325 (1923).

(3) W. Biltz, *ibid.*, **203**, 277 (1932).

(4) D. F. Smith and N. W. Taylor, *THIS JOURNAL*, **46**, 1393 (1924).

The click gage used seemed to have experienced fatigue above 200°.

A tube containing the sample was broken off in an atmosphere of nitrogen, inside of a box dried with phosphorus pentoxide, and some of the solid was transferred to the apparatus. After evacuating it down to  $10^{-5}$  mm. the side pieces were sealed off. The lower half of the apparatus was wrapped in a thin copper sheet. The apparatus up to 3.8 cm. from the stopcock was then placed in a furnace, which was similar to the one described above except that the height of the copper cylinder was 35.5 cm. The temperature of the sample was measured with a mercury thermometer inserted in the cylinder next to the bulb of the apparatus. All the thermometers used were calibrated against the Bureau of Standards calibrated mercury thermometers. The mercury columns in the manometer were read by means of a cathetometer which was graduated to 0.1 mm. The readings were reduced to 0°.

The temperature was kept within  $\pm 0.05^\circ$  for at least thirty minutes before runs were made. Usually it required from one and one-half to two hours to complete a series of three to five runs at a given temperature. Two complete sets of determinations were made over the range of temperature, one ascending, the other descending. The readings agreed within 0.1 mm. in most cases.

The results of the measurements are shown in Table I.

TABLE I

VAPOR PRESSURE OF STANNIC IODIDE FROM 160 TO 250°

Temp., °C.	Obsd. P, mm.	Calcd.
160.22	6.00	6.04
170.07	8.76	8.62
185.35	14.25	14.38
200.86	23.52	23.53
225.75	48.52	48.52
250.35	93.59	92.33

The last column of the table is calculated from the equation

$$\log P_{\text{mm.}} = 7.6571 - \frac{2971.36}{T} - \frac{3689.1}{T^2} \quad (1)$$

empirically derived from the experimental data. The influence of the term in  $1/T^2$  is very small. The extrapolated value of the boiling point is

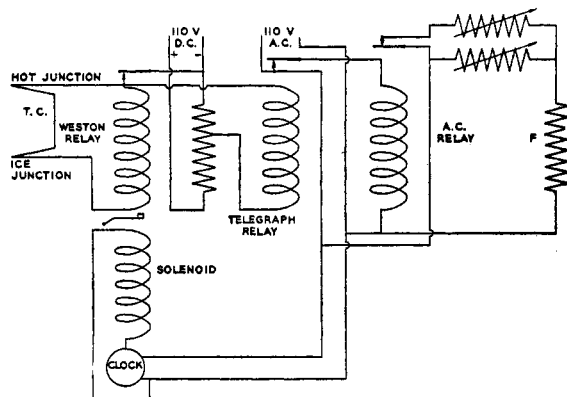


Fig. 2.—Temperature regulation circuit.

found to be  $348^\circ$  in comparison with  $340^\circ$  and  $346^\circ$  found elsewhere. The last two values are of unknown reliability since no experimental details are given and no special precautions to exclude oxygen and water vapor are mentioned, although stannic iodide decomposes readily in the presence of even slight amounts of oxygen or water vapor in the neighborhood of its boiling point. In our case, although the vapor pressure measurements made within the temperature range are reliable, the extrapolation beyond the range was so large that the uncertainty in the value of the boiling point might be appreciable. The heat of vaporization, calculated from equation 1, is 13,700 cal. per mole at  $25^\circ$  and 13,650 at the boiling point.

The heat of fusion was determined by the method of mixtures. The furnace was made of a heat-insulated solid copper block 12 cm. in diameter and 33 cm. long. In the center of the block to two-thirds of the way up from the bottom, was drilled a 1.5-cm. hole, which was 1 mm. larger than the diameter of the tube containing the sample. The tube was supported in the furnace by the wire inserted at the side of the block. Two holes of small diameter were drilled down from the top, one of them as closely as possible to the central bore. A No. 20 chromel–alumel calibrated thermocouple cased in a 5-mm. thin Pyrex tubing was inserted into this in order to measure the temperature of the furnace. A similar thermocouple for regulating the temperature of the furnace was inserted into the other. The block was heated electrically. The central bore was extended 3 cm. beyond the bottom with a monel tube of the same bore closed with a brass cap.

The calorimeter was made of a half-pint (210-cc.) silvered Dewar flask with a tightly fitting copper cover consisting of two copper sheets at 1 cm. apart. A "basket" of copper gauze was suspended from the cover near the bottom of the flask to catch the tube of stannic iodide as it dropped in from the furnace above. The heat capacity of the calorimeter was determined by the aid of a copper rod weighing 55 g. The rise in the temperature of the water was measured with a 6-junction (No. 32 copper–No. 26 advance) thermocouple whose junctions were cased in a thin 6-mm. Pyrex tube filled with pure naphthalene. The thermocouple was calibrated against the melting point of ice and the transition point of sodium sulfate decahydrate. The heat content of the Pyrex tubing used was determined at several temperatures.

The temperature of the furnace was regulated with a regulator built by Mr. Abrams of this Department. A diagram of it is shown in Fig. 2, which is self-explanatory except, perhaps, for the clock. This was so connected that it made a contact with the magnetic hammer every minute, which tapped the Weston relay in order to keep the fine wire of the relay from "sticking" to the contact. By means of this regulator, the temperature of the furnace was kept within  $\pm 0.05^\circ$  without any difficulty.

(5) "Int. Crit. Tables," Vol. I, 1926, p. 163.

**Measurements.**—The tube containing the distilled sample of stannic iodide was heated in the furnace at a given temperature (within  $\pm 0.05^\circ$ ) for at least one and one-half hours before it was dropped into the calorimeter, which contained a measured quantity of water at approximately the thermostat temperature,  $25 \pm 0.02^\circ$ . The calorimeter was placed in the water thermostat; part of the copper cover was immersed in the water of the thermostat in order to keep its temperature uniform. The stirrer was then connected to the motor and the thermocouple was inserted into the calorimeter. The temperatures of both the water in the calorimeter and the furnace were read on the Leeds and Northrup type  $K_2$  potentiometer, which was graduated to 0.5 microvolt, and it could be estimated easily to 0.1 microvolt. The potentiometer was connected to a sensitive galvanometer. With this set-up temperature changes of  $0.001^\circ$  in the calorimeter and of  $0.01^\circ$  in the furnace could be detected. Readings were made every two minutes until the rate of the change in the temperature of the water became uniform, then the sample tube was dropped into the calorimeter. About one minute elapsed between the time the stirrer was stopped and started again. The temperature change was recorded every two minutes until a uniform cooling rate was obtained. A complete run required from twenty-five to thirty-five minutes. The rate of heating due to stirring was on the average  $0.001^\circ$  per minute, and the rate of cooling was from  $0.001$  to  $0.0012^\circ$  per minute. The total temperature change in the calorimeter was from  $0.6$  to  $2^\circ$ .

**Results and Discussion.**—The value of the total heat capacity of the calorimeters used including 325 cc. of water, was approximately 340 cal., with the largest deviation amounting to 1.6 cal. for the first calorimeter and 0.15 cal. for the second. The specific heat of the Pyrex glass used could be expressed within  $\pm 0.1\%$  from the measured values by  $C_p = 0.1141 + 0.00025323T$ . The total heat of the copper rod used was derived from its specific heat equation

$$C_p = 0.09202 + 0.0000136T - \frac{452}{T}$$

determined empirically by Bronson, Chisholm, and Dockerty<sup>6</sup> from the results of their measurements.

The heat content of the solid with a mean deviation of  $\pm 20$  cal. in the temperature interval between  $25$  and  $144.5^\circ$  is given by

$$C_p = 19.4 + 0.036T$$

where  $C_p$  is the molal heat capacity of the solid. The average deviation of the measured values from this equation is  $\pm 0.8\%$  with the maximum deviation  $1.5\%$ . The curve for the total heat content of the liquid is a straight line, giving  $40.1 \pm 0.5$  cal. per mole for the molal heat capacity in the range of temperature from  $144.5$  to

$170^\circ$ . We get  $4600 \pm 20$  cal. for the molal heat of fusion. Hildebrand<sup>7</sup> estimated the value of  $\Delta H_m$  from the entropy of fusion of other tetrahalides (chlorides and bromides) of the fourth group and from the solubility of stannic iodide in carbon disulfide, and obtained the value 3850 cal. per mole. This value is, of course, only an approximation and it is likely to be too small. If the melting and boiling points, the entropy of fusion and other physical properties of the halogens (except fluorine) are plotted, it is seen that changes from bromine to iodine are always greater than those from chlorine to bromine. A similar state of affairs results when the melting and boiling points of the tetrahalides of the fourth group are plotted. This indicates that the intermolecular forces are determined to a large extent by those halogen atoms surrounding the central atom and independent of it.<sup>8</sup> Moreover, these curves are roughly parallel to those of the halogens, but not coincident with them. This is to be expected from the fact that the molecular size and bond energies of these tetrahalides have some effect on their intermolecular forces and orientations in the liquid state.<sup>9</sup> Since the entropy of fusion of iodine is much greater than those of bromine and chlorine, we may assume that the entropy of fusion of stannic iodide should be greater than those of tetrachlorides and bromides.

If intermolecular forces of tetrahalides are determined largely by the halogen atoms surrounding the central atom, we should expect the solubility of stannic iodide in iodine and also that of iodine in stannic iodide<sup>10</sup> to obey closely the ideal law. This corresponds to the facts. The slope of the former solubility curve gives  $\Delta H_m$  approximately equal to 4250. This value is lower than ours, but it is within their experimental accuracy.

Parks and Dodd<sup>11</sup> obtained  $\Delta H_m = 4110$  cal. per mole from their rough experimental measurements employing also the method of mixtures. However, they have stated that there was a considerable amount of premelting near the melting point of the solid and so their results were not very reliable. We shall, therefore, take  $\Delta H_m = 4600$  as the heat of fusion of stannic iodide at its melting point.

(7) J. H. Hildebrand, *THIS JOURNAL*, **51**, 66 (1929).

(8) W. M. Latimer, *ibid.*, **44**, 90 (1922).

(9) A. Peterlin, *Physik. Z.*, **37**, 43 (1936).

(10) (a) Van Klooster, *Z. anorg. Chem.*, **79**, 223 (1912); (b) W. Reinders and S. de Lange, *ibid.*, **79**, 230 (1912).

(11) Parks and Dodd, personal communication.

(6) H. L. Bronson, H. M. Chisholm and S. M. Dockerty, *Can. J. Research*, **8**, 282 (1933).

**Acknowledgment.**—I wish to thank Professor Hildebrand for his valuable suggestions and helpfulness during the course of this investigation, and Mr. John Lyman for his assistance in making the heat of fusion determinations.

### Summary

The melting point of stannic iodide has been determined by the cooling method, and the value obtained was  $144.5 \pm 0.1^\circ$ .

The vapor pressure of stannic iodide from its melting point to  $250^\circ$  has been determined by

means of a glass click gage. The molal heat of vaporization calculated from the vapor pressure is  $13,750 \pm 50$  cal. per mole at  $25^\circ$  and varies but little with temperature.

The heat of fusion of stannic iodide was found to be  $4600 \pm 20$  cal. per mole at the melting point. The molal heat capacity of the solid can be expressed within 0.8% of the measured values in the temperature range  $25^\circ$  to the melting point by  $C_p = 19.4 + 0.036T$ , while that of the liquid, from the melting point to  $170^\circ$  is  $40.1 \pm 0.5$  cal. per mole.

BERKELEY, CALIFORNIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

## The Ultraviolet Absorption Spectra of Substituted Biphenyls<sup>1</sup>

BY LUCY W. PICKETT, GERTRUDE F. WALTER AND HELEN FRANCE

Investigations by Adams and others<sup>2</sup> have shown that those unsymmetrical derivatives of biphenyl which have substituents above a certain limiting size in the positions adjacent to the bond joining the two benzene nuclei may be resolved into stereoisomers. This phenomenon is explained as a result of the restriction of the rotation of the two benzene rings by the interference of the substituting groups. Some absorption spectra measurements made in a study of the physical properties of biphenyl derivatives showed unexpected differences in absorption which led to further investigation.

Methyl and chloro derivatives of biphenyl were chosen for the comparison because these groups do not show selective absorption in the region under investigation and are known to introduce comparatively slight modifications in the spectrum of benzene. Furthermore, these groups are sufficiently large to restrict the rotation of the benzene nuclei when they are in the 2,2',6,6'-positions. The spectroscopic study was made with the simplest compounds available which had the above characteristics.

### Experimental

**Preparation of Compounds.**—After purification the compounds were in each case crystallized from the optically pure solvent used in the measurements. After the absorption spectrum had been photographed, the material from

which the sample was taken was further distilled or crystallized and photographs again taken. The second results agreed with the first in all cases except one as noted below in the discussion of the source and treatment of individual substances.

**Biphenyl**, m. p.  $69-69.5^\circ$ , obtained from Eastman Kodak Co., was purified by vacuum distillation and repeated crystallization from alcohol.

**3,3'-Bitolyl**,<sup>3</sup> b. p.  $154^\circ$  at 14 mm., was prepared by the condensation of *p*-iodotoluene with activated copper bronze and purified by two vacuum distillations. Although the product boiled constantly, a photograph taken at this time indicated slightly different absorption from that which was obtained from material distilled a third time. A fourth distillation yielded material identical with the latter.

**4,4'-Bitolyl**, m. p.  $119.5-120^\circ$ , was prepared by the condensation of *p*-bromotoluene and purified by vacuum distillation and crystallization from alcohol.

**Bimesityl**, m. p.  $100-100.5^\circ$ , was prepared from bromomesitylene by the method described by Moyer and Adams<sup>4</sup> and crystallized repeatedly from alcohol.

**4,4'-Dichlorobiphenyl**, m. p.  $146.5-147^\circ$ , was obtained from Eastman Kodak Co. and purified by recrystallization from alcohol.

**2,4,6,2',4',6'-Hexachlorobiphenyl**, m. p.  $111.5-112^\circ$ , was prepared from trichloriodobenzene by condensation with copper bronze and recrystallized from alcohol. The trichloriodobenzene was obtained from diazotization of trichloroaniline.

*o*-, *m*- and *p*-diphenylbenzenes, m. p.  $58, 87, 211.5^\circ$ , were obtained from Eastman Kodak Co., and recrystallized repeatedly from benzene and alcohol.

**Mesitylene**, b. p.  $66.4^\circ$  at 24.5 mm., was obtained from Eastman Kodak Co., and vacuum distilled.

**Absorption Spectra Measurements.**—The absorption measurements were made with a Hilger quartz spectro-

(3) This compound was prepared and photographed by Mary Dunlap.

(4) Moyer and Adams, *THIS JOURNAL*, **51**, 630 (1929).

(1) This paper was presented at the New York meeting of the American Chemical Society, in April, 1935.

(2) An extensive review of this subject is given by Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).