65° to, perhaps, 140°. Because of the fact that the effects upon one another of the different moments in the molecule may not be wholly negligible, as well as because of the experimental error, the oxygen valence angle in the diphenyl ethers cannot positively be taken as 121°. However, the previously advanced reasons for deciding these effects to be small are sufficient to warrant the conclusion that the angle is correct to within ±5°. It is evident that the 90° angle calculated by the wave mechanics[14] may be much altered by the groups with which the oxygen combines.

Summary

The electric moments of para-substituted diphenyl ethers and a sulfide, an anisole, a phenetole and heterocyclic compounds have been determined and used, together with other moments taken from the literature, to study the angles between the valences in the oxygen and sulfur atoms.

The oxygen valence angle in the diphenyl ethers is found to be 121 ± 5°. The results for the anisoles and phenetoles, which are more complex, do not give dependable values for the oxygen angle, although they may be explained in terms of an oxygen angle not far from 135°. Limited data give for the sulfur valence angle in the diphenyl sulfides a value of about 146°, which may be too high. The oxygen valence angles in various heterocyclic compounds calculated from the interatomic distances vary from 65 to about 140° and the moments are in excellent qualitative agreement with predictions based on the size of the angles. The behavior of thiophene is strictly analogous to that of the corresponding oxygen compound.

[14] Slater, *Phys. Rev.*, **37**, 481 (1931); *ibid.*, **38**, 1109 (1931): Pauling, THIS JOURNAL, **53**, 1367 (1931).

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE ACTION OF HYDRIODIC ACID ON STANNIC OXIDE

BY EARLE R. CALEY

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The recent note of Laubengayer and Brandt[1] on a method for the preparation of germanium tetraiodide by the action of hydriodic acid on germanium dioxide leads me to mention an analogous reaction that I first observed some months ago and to which I can find no reference in the chemical literature.

It is a well-known fact that stannic oxide, especially ignited stannic oxide, is very resistant toward the usual chemical reagents. It was found, however, that concentrated hydriodic acid acts readily on stannic oxide, converting the latter into stannic iodide. With constant boiling hydriodic acid the reaction commences at about 90–95° and takes place quite

[1] Laubengayer and Brandt, THIS JOURNAL, **54**, 621 (1932).

rapidly at the boiling point of the acid. The conversion is never quite complete with fixed amounts of the reactants in a closed system but successive additions of hydriodic acid to a heated reaction mixture will effect the complete transposition of the stannic oxide. With slightly diluted acid the reaction is slower and less complete, while dilute hydriodic acid has no effect. Stannic oxide prepared by different methods and ignited at various elevated temperatures gives the same reaction. Even the natural oxide, when powdered, reacts readily with concentrated hydriodic acid in the manner described.

The following experiments were performed to establish the course of the reaction.

A. On heating a weighed amount of stannic oxide with hydriodic acid, the increase in weight, after allowing for the amount of oxide not acted upon and after removal of the excess acid, was found to correspond closely to the calculated increment for the formation of stannic iodide alone. In a typical experiment 0.1553 g. of pure stannic oxide, prepared by igniting the metastannic acid derived from a specimen of Kahlbaum's pure tin, was placed in a weighed glass dish together with 3.0 cc. of pure constant boiling hydriodic acid. After heating the covered vessel for fifteen minutes on a steam-bath the dish was placed in a desiccator charged with calcium chloride, potassium hydroxide and metallic copper to remove water, excess acid and iodine formed by the oxidation of the hydriodic acid. Simple evaporation of the excess hydriodic acid by heating was found to be an impossible procedure for exact work, due to the volatility of the stannic iodide under these conditions. After reaching constant weight, the contents of the dish were found to weigh 0.5672 g. The tin iodide in the mixture was dissolved out with pure benzene, leaving a residue of unchanged stannic oxide weighing 0.0249 g. From these data it follows that 0.1304 g. of oxide was converted into 0.5423 g. of iodide. This agrees well with the calculated value of 5420 g. based upon the conversion of the stated amount of oxide into stannic iodide alone.

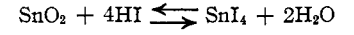
B. Analysis of the salt obtained by evaporation of the benzene extracts from experiments like the one just described indicated that stannic iodide was the sole compound present.

Anal. Sample taken, 0.4857 g.: SnO_2 found, 0.1175 g.; AgI found, 0.7283 g.; Sn, 19.06%; I, 81.06%; total, 100.12%. Another specimen was analyzed for tin by an alternative method: sample taken, 0.2594 g.; SnO_2 found, 0.0626 g.; Sn, 19.01%. Calculated for SnI_4: Sn, 18.95%; I, 81.05%.

C. On heating the two reacting substances under an atmosphere of carbon dioxide no iodine was found to be liberated from the reaction, thus indicating absence of valence change.

D. The salt obtained from the reaction hydrolyzed slowly on the addition of water in accordance with the known behavior of stannic iodide.

On the basis of these experiments it follows that the reaction may be represented by the simple equation



$$SnO_2 + 4HI \rightleftharpoons SnI_4 + 2H_2O$$

This reaction is therefore quite analogous to the one between germanium dioxide and hydriodic acid and it differs from the general one between this acid and most higher metallic oxides.

In contrast to the chemical action of hydrobromic acid on germanium dioxide as recorded by Laubengayer and Brandt,[1] stannic oxide is apparently not affected by hot concentrated hydrobromic acid. Several experiments in which different specimens of stannic oxide were heated with many times their weight of constant boiling hydrobromic acid yielded no evidence of any action between the two substances. In a typical quantitative experiment, for example, 0.2170 g. of pure ignited stannic oxide treated with 10 cc. of hydrobromic acid at the steam-bath temperature for an hour left a residue of stannic oxide weighing 0.2169 g. after evaporation of the acid. There is, therefore, an interesting and distinct difference in the behavior of these two related oxides toward hydrobromic and hydriodic acids.

The formation of red stannic iodide in the manner described is a rather distinctive reaction for stannic oxide and can serve to differentiate readily this latter substance from other highly insoluble compounds encountered in qualitative analysis. It also suggests itself as a convenient means for identifying the natural oxide, cassiterite. If pure constant boiling hydriodic acid is employed in making the test, however, liberation of iodine is often so excessive that the reaction is obscured unless it is performed under a carbon dioxide atmosphere. It is much preferable for this purpose to use the concentrated acid that has been stabilized by the addition of 1–2% of hypophosphorous acid. A reagent of this composition behaves like the pure acid toward stannic oxide, can be kept without decomposition, and permits the performance of the test in air since liberation of iodine is slight even at the boiling point. In making the test it is sufficient to treat the powdered sample with a few cc. of the above reagent and boil the mixture gently in a test-tube for two or three minutes. In the presence of stannic oxide the orange-red stannic iodide is formed in the reaction mixture and on the cooler parts of the vessel it appears as a yellow to orange sublimate. With proper manipulation amounts of oxide as small as one milligram can be readily identified.

Summary

1. Concentrated hydriodic acid readily reacts with stannic oxide forming stannic iodide and water.

2. Concentrated hydrobromic acid does not react with stannic oxide under similar conditions.

3. The reaction described can be used as a qualitative test for natural or artificial stannic oxide.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, IN COÖPERATION WITH THE UNIVERSITY OF CALIFORNIA]

AN EQUATION FOR THE REPRESENTATION OF HIGH-TEMPERATURE HEAT CONTENT DATA[1]

BY CHAS. G. MAIER[2] AND K. K. KELLEY[3]

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High temperature heat content data have commonly been represented by the empirical equation

$$Q_{273.1}^{T} = \left[aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 + \ldots\right]_{273.1}^{T} \quad (1)$$

because the manipulation of such power series is easy and rapid. However, it is well known that this form of equation is not particularly satisfactory for the purpose. A reasonable number of terms often cannot be made to fit the data with sufficient accuracy; moreover, the resulting derived equation for specific heat

$$C_p = a + bT + cT^2 + \ldots\ldots \quad (2)$$

may have a maximum in the temperature range under consideration due to the signs and magnitudes of the coefficients, but such a maximum does not correspond to known physical facts. These difficulties are most apparent where the specific heats are still far below the Dulong and Petit equipartition value of 6 calories per gram atom at 0°. Obviously, a better form of equation is desirable, but the choice is limited by several conditions: namely, (1) the equation selected should be usable in conjunction with conventionally accepted methods in thermodynamic calculations, (2) differentiation and integration under the conditions imposed by thermodynamic calculations should be analytic and reasonably easy to perform, and (3) derived values should be consistent with the available facts.

The Pacific Experiment Station of the United States Bureau of Mines is interested in the correlation of high temperature thermal data on metallurgically important elements and compounds, and has investigated several forms of equations for the representation of these data. It is apparent that at high temperatures specific heats of normally behaving substances

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