of trimethylamine upon either borine carbonyl or diborane. The behavior of ammonia toward diborane and toward borine carbonyl is quite different from that of trimethylamine toward these reagents.

CHICAGO, ILLINOIS RECEIVED FEBRUARY 10, 1937

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE]

Principal Optical and Physical Properties of the Carbon Tetrachloride Solvate of Rotenone

BY ERNEST L. GOODEN AND CHARLES M. SMITH

For several years chemists and manufacturers working with rotenone have been familiar with the carbon tetrachloride solvate, in which one molecule of rotenone is combined with one molecule of carbon tetrachloride of crystallization ($C_{23}H_{22}O_6 \cdot CCl_4$).[1] Since this solvate is of great practical importance, especially in the analysis of derris and cubé, it was considered necessary to determine its principal optical and physical properties.

The material used for the study was a sample of rotenone that had been recrystallized several times and subjected to microdetermination of carbon and hydrogen to gain assurance of purity.[2] A portion of this analyzed sample was recrystallized from carbon tetrachloride to form the carbon tetrachloride solvate.

Optical Crystallographic Properties

The optical properties investigated were such as are determinable by the use of the petrographic microscope. The solvate crystals were colorless, with a typical elongated, somewhat flattened prismatic shape (Fig. 1). The crystals were found to be biaxial with the following refractive indices (white light): $\alpha = 1.563$, $\beta = 1.612$, $\gamma = 1.631$. The indication of negative optical character obtained by the selenite plate is fairly distinct, and the observed value of β is so much nearer γ than α as to allow no doubt that the character is truly negative. In all cases observed the elongation is negative, the long edges of the crystal lying in the vibration direction for α. Extinction is sensibly parallel at all stages of rotation about the axis of crystal length, which is the vibration direction for α. It is concluded that the crystal belongs in the orthorhombic system.

Density

The density of the crystals was measured with a pycnometer, with water as the displaced liquid. In view of the volatility of the solvate, the accuracy attainable under the conditions of the experiment is considered as extending to two decimal places only. The observed value is 1.40 g. per cc. at 30°. A comparison of the density of the solvate with the densities of rotenone and carbon tetrachloride indicates that practically no volume change accompanies the combination.

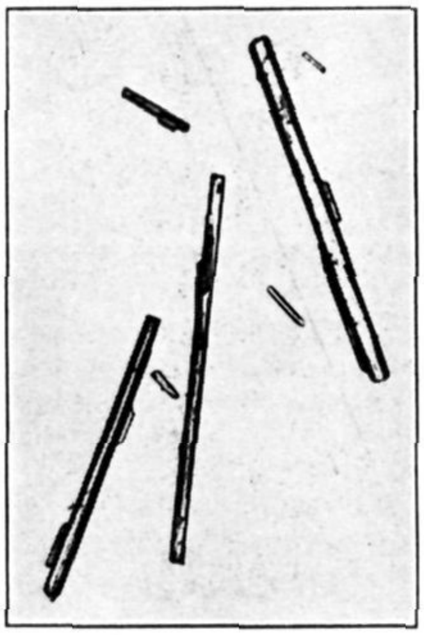

Fig. 1.—Carbon tetrachloride solvate of rotenone (× 175).

Dissociation Pressure

The dissociation pressure was investigated by the static method of vapor pressure measurement.[3] The source of controlled heating for the sample was the vapor above a boiling bath of a pure liquid, acetone, carbon tetrachloride and trichloroethylene being used separately for observations at their respective boiling points.

---

(1) H. A. Jones, *This Journal*, **53**, 2738 (1931).

(2) This is the sample referred to by Gooden and Smith, *ibid.*, **57**, 2116 (1935), as having been analyzed by J. R. Spies.

(3) The apparatus used was one constructed by O. A. Nelson, a modification of the apparatus described by Nelson and Senseman, *J. Ind. Eng. Chem.*, **14**, 58 (1922).

The temperature readings were corrected by the established correction curve for the individual thermometer, and the manometer readings were corrected for temperaure of the mercury. With each bath liquid the rise in pressure in the space above the sample was observed repeatedly and the gas was released (for the elimination of air) between successive sets of observations, until a sufficiently precise determination of limiting pressure for given temperature was obtained. Two observed values of limiting pressure were obtained with each of the three baths, giving six points for determination of the vapor pressure curve. When these points were plotted as log pressure (in millimeters of mercury) against reciprocal of absolute temperature, they were found to lie almost exactly in a straight line. The best fitting straight line was calculated,[4] and is expressed by the equation

$$\log P = 9.308 - (2313/T)$$

where P is the pressure in millimeters of mercury and T is the temperature on the absolute (Kelvin) scale. The six points and the calculated line are shown in Fig. 2.

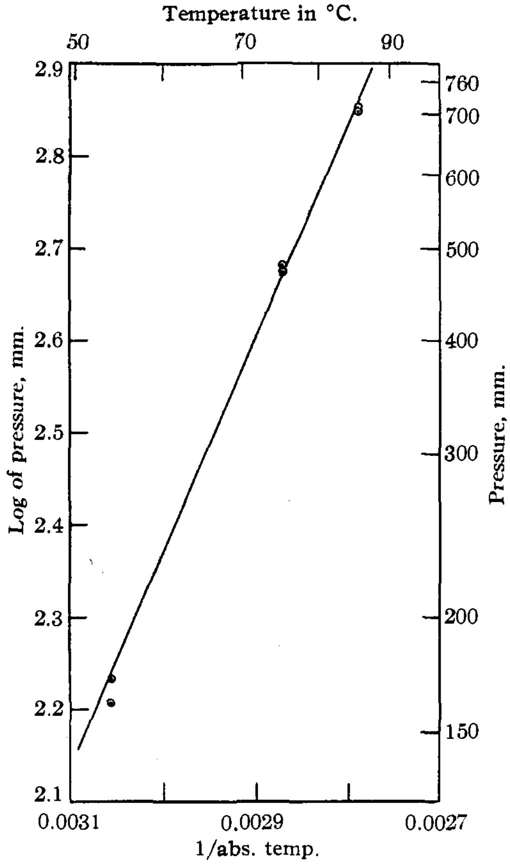

Fig. 2.—Dissociation pressure of the carbon tetrachloride solvate of rotenone (pressure of CCl_4 vapor over $C_{23}H_{22}O_6 + C_{23}H_{22}O_6 \cdot CCl_4$).

This equation leads to a value of 87° for what may be termed the "decomposition temperature" of the solvate, in the sense of the temperature at which the carbon tetrachloride vapor reaches normal atmospheric pressure. The heat of dissociation–vaporization as calculated on the basis of the same equation is 69 cal. per gram of carbon tetrachloride, which is approximately 23 cal. per gram in excess of the heat of vaporization of carbon tetrachloride at the same temperature. These results indicate that the solvate is so unstable as to require careful sealing for storage.

Additional Comparisons and Checks

It is interesting and worth while to compare the optical properties of the carbon tetrachloride solvate of rotenone with those of rotenone itself in the common (m. p. 163°) form. The indices β and γ of the solvate nearly coincide, respectively, with α and β of rotenone (α = 1.616, β = 1.635, γ = 1.662); the maximum birefringence, however, is one and one-half times as great in the solvate as in rotenone. The specific refraction is conspicuously lower in the solvate, as would be expected from the fact that the specific refraction of carbon tetrachloride is approximately 36% lower than that of rotenone. The calculated molecular refraction cannot be arrived at precisely because of the complex structure of rotenone. The various calculated values for the molecular refraction of the solvate are all very close to 129 (cubic centimeters per mole, according to Lorentz–Lorenz formula), if no allowance is made for a linkage refraction for the combination of the rotenone molecule with the carbon tetrachloride molecule. The observed molecular refraction is 134, this value being nearly equal to the sum of the observed molecular refraction (107) for rotenone and the observed value (26.45) for carbon tetrachloride.

Summary

The carbon tetrachloride solvate of rotenone, $C_{23}H_{22}O_6 \cdot CCl_4$, has been studied with respect to refractive indices, density and dissociation pressure,

---

[4] One of the six points, the lowest, showed an appreciable departure from a straight line, and was therefore disregarded; the line was calculated from the other five points by the method of least squares.

The principal results of the optical determinations are: $\alpha = 1.563$; $\beta = 1.612$; $\gamma = 1.631$; optical character, negative; elongation, commonly negative; system, orthorhombic.

The density at 30° is 1.40 g. per cc.

The dissociation pressure in the range 60 to 90° is expressed by the equation $\log P_{\text{mm.}} = 9.308 - (2313/T_K)$. The "decomposition temperature" is consequently 87°, and the heat of dissociation–vaporization 69 calories per gram of carbon tetrachloride.

WASHINGTON, D. C. RECEIVED FEBRUARY 17, 1937

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 584, AND THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Crystal Structure of Selenium Dioxide

BY JAMES D. MCCULLOUGH

Quoting measurements made by C. F. Rammelsburg, Groth[1] describes selenium dioxide as monoclinic prisms with $a:b:c = 1.292:1:1.067$. He states that the measurements were only approximate, however, due to the extreme hygroscopic nature of the crystals, which made rapid work necessary. All crystals examined in the present work were found to be tetragonal needles with the axial ratio $a:c = 1:0.6047$.

Method of Preparation.—Pure selenium dioxide was dried at approximately 200° in a stream of oxygen which had been passed first through a tube containing phosphorus pentoxide. After drying for several hours, the Pyrex tube containing the selenium dioxide was sealed off at both ends and the substance was sublimed very slowly in an electric furnace. The atmosphere of oxygen prevented the decomposition which sometimes accompanies sublimation of the oxide in the open. The tube was opened inside a moisture-free box and selected crystals were mounted in moisture-proofed gelatine capsules. Except when being photographed they were kept in a desiccator. These precautions were found necessary in order to preserve the crystal faces and prevent lines due to selenious acid appearing on the photographs.

The crystals were transparent, colorless needles about 2–10 mm. long and 0.2–0.5 mm. thick with (100), (110) and (111) principally developed.

The Unit Cell and Space-Group

Laue photographs prepared with the incident beam perpendicular to a (100) face showed a vertical as well as a horizontal plane of symmetry as did the photographs normal to a (110) face. The tetragonal nature of the crystals was established by noting that a rotation of 90° about the needle axis gave a Laue photograph indistinguishable from the original one. Further evidence was furnished by the fact that the photographs prepared with the x-ray beam parallel to the needle axis showed a fourfold axis and four planes of symmetry at 45° intervals. The Laue symmetry thus indicated is that of D_{4h}.

A complete set of 15° oscillation photographs was prepared using unfiltered copper radiation with a 5-cm. camera. The oscillation was about the c-axis. One 30° oscillation photograph was prepared using [110] as an axis but was not very satisfactory for intensity considerations due to the shape of the crystal. Attempts to cleave the crystals across the needle or c-axis were unsuccessful and resulted in shattering.

From these photographs the unit edges $a_0 = 8.353 \pm 0.005$ Å. and $c_0 = 5.051 \pm 0.010$ Å. were calculated. Using these dimensions, values of $n\lambda$ were calculated for a completely indexed Laue photograph in which the x-ray beam made an angle of about 2° with the a-axis. The smallest value thus found was $n\lambda = 0.245$ Å. from (810), the short wave length limit being 0.24 Å.

The oscillation photographs and the first order reflections on the indexed Laue photograph showed all varieties of (hkl) and ($hk0$) reflections. The lattice is accordingly simple. Reflections of the type (hhl) were not observed for l odd although many such planes were in position to reflect, especially on the oscillation photograph about [110]. Further, ($h0l$) was not observed for h odd. These conditions indicate $D_{4h}^{13} - P4/mbc$ or $C_{4v}^{8} - C4cb$ as probable space groups. Attempts to detect a pyroelectric effect failed, but this may have been due to the hygroscopic

---

(1) P. Groth, "Chemische Kristallographie," Vol. I, 1906, p. 93.