

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MARYLAND]

The Dipole Moments of Diethyl Sulfite, Triethyl Phosphate and Tetraethyl Silicate<sup>1</sup>

BY W. J. SVIRBELY AND JOHN J. LANDER

The dipole moments of diethyl sulfite, triethyl phosphate and tetraethyl silicate were determined in benzene with the hope that the data would lead to some conclusions concerning the structures of those compounds.

## Materials and Experimental Procedure

**Benzene.**—The purification and storing of the benzene used in the measurements already has been described.<sup>2</sup>

**Diethyl Sulfite.**—Material was prepared<sup>3</sup> by causing thionyl chloride to react with absolute alcohol. The reaction product was fractionated under anhydrous conditions. The boiling point of  $(C_2H_5O)_2SO$  was 158–158.2°,  $n_D^{25}$  was 1.4118.

**Triethyl Phosphate.**—Material was prepared<sup>3</sup> by causing phosphorus oxychloride to react with sodium ethylate. The reaction product was fractionated under anhydrous conditions. The boiling point of  $(C_2H_5O)_3PO$  was 216–217°.

**Tetraethyl Silicate.**—Material was prepared<sup>3</sup> by causing silicon tetrachloride to react with absolute alcohol. Fractionation of the reaction product under anhydrous conditions gave a material boiling at 168–168.5°;  $n_D^{25}$  was 1.3829.

All the above compounds were kept in sealed tubes until measured.

**Procedure.**—The measurements were made by the heterodyne beat apparatus using the methods previously described.<sup>2,4</sup> Index of refraction measurements were made at room temperature using an Abbe refractometer.

## Experimental Results

The dielectric constants  $\epsilon$ , the densities  $d$  of the benzene solutions containing mole fractions  $N_2$  of the solute, the polarization  $P_2$  of the various solutions and the extrapolated value of  $P_\infty$  for the solute are given in Table I. The values of  $MRD$  in Table II were determined from the data in the present paper and from data in the literature.<sup>5</sup> The values for  $P_E + P_A$  used in the calculation of the dipole moments were taken equal to 1.05  $MRD$ . The dipole moments calculated in the usual fashion along with their probable errors are given in the third column of Table II.

(1) This paper was presented in part at the spring meeting of the Washington Section of the American Chemical Society held at the University of Maryland, College Park, Maryland, May, 1945.

(2) Lander and Svirbely, *THIS JOURNAL*, **66**, 235 (1944).

(3) Biltz, Hall and Blanchard, "Laboratory Methods of Inorganic Chemistry," 2nd Edition, John Wiley and Sons, Inc., New York, N. Y.

(4) Davis, Bridge and Svirbely, *THIS JOURNAL*, **65**, 857 (1943).

(5) (a) Diethyl sulfite,  $d^{25}_4$  1.0772, Walden, *Z. physik. Chem.*, **55**, 224 (1906); (b) triethyl phosphate,  $d^{25}_4$  1.074, Sugden, Reed and Williams, *J. Chem. Soc.*, **127**, 1525 (1925);  $n_D^{20}$  1.4057, Zecchini, *Gazz. chim. ital.*, [1] **24**, 37 (1894); (c) tetraethyl silicate,  $d^{25}_4$  0.933; Ebelmen, *Ann.*, **57**, 334 (1846).

Check runs were made where sufficient material was available. The  $P_\infty$  values only are given in Table I for these runs.

TABLE I  
SUMMARY OF DATA IN BENZENE

| $N_2 \times 10^3$                     | $d$       | $\epsilon$ | $P_2$            |
|---------------------------------------|-----------|------------|------------------|
| sym-Diethyl sulfite at 24.18°         |           |            |                  |
| 0.0000                                | 0.87241   | 2.2695     | $P_\infty = 216$ |
| 3.5149                                | (.87350)  | 2.3120     | 214              |
| 8.0489                                | (.87478)  | 2.3683     | 216              |
| 18.5592                               | .87788    | 2.4992     | 212              |
| 26.6345                               | (.87992)  | 2.6051     | 213              |
| 40.4105                               | .88365    | 2.7707     | 205              |
| Run no. 2, $P_\infty = 218$ at 25.42° |           |            |                  |
| Triethyl phosphate at 24.30°          |           |            |                  |
| 0.0000                                | 0.87243   | 2.2697     | $P_\infty = 235$ |
| 1.5442                                | (.87301)  | 2.2880     | 235              |
| 2.8966                                | (.87356)  | 2.3055     | 236              |
| 5.0993                                | .87448    | 2.3336     | 235              |
| 6.6745                                | (.87505)  | 2.3534     | 234              |
| 10.9409                               | .87677    | 2.4094     | 235              |
| Run no. 2, $P_\infty = 243$           |           |            |                  |
| Tetraethyl silicate at 32°            |           |            |                  |
| 0.0000                                | (0.86491) | 2.2553     | $P_\infty = 113$ |
| 0.9266                                | .86504    | 2.2582     | 114              |
| 1.9204                                | (.86518)  | 2.2612     | 112              |
| 4.2524                                | (.86550)  | 2.2679     | 112              |
| 9.5374                                | .86625    | 2.2862     | 115              |

Data in parentheses have been picked off a mole fraction plot.

## Vectorial Derivation of Equations Involving Free Rotation

**Acknowledgment.**—We acknowledge our indebtedness to Dr. John Richardson, of the Bell Telephone Laboratories, for the following vectorial derivation of Eq. 1.

Consider the case of two vectors of equal magnitude ( $m$ ), which make the same angle ( $\alpha$ ) with their respective axes of rotation which axes are at an angle ( $\beta$ ) with each other as illustrated in Fig. 1. The total instantaneous moment is

$$\vec{\mu} = \vec{\mu}_1 + \vec{\mu}_2$$

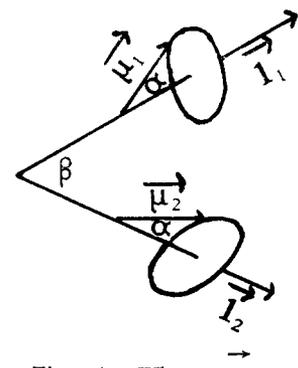


Fig. 1.—Where  $|\mu_1| = |\mu_2| = m$ , and where  $l_1$  and  $l_2$  are unit vectors.

furthermore

$$\overline{\mu^2} = \overline{\mu \cdot \mu} = \overline{\mu_1^2} + 2\overline{\mu_1 \cdot \mu_2} + \overline{\mu_2^2}$$

$$\overline{\mu_1^2} = \overline{\mu_2^2} = m^2$$

but

$$\overline{\mu_1 \cdot \mu_2} = \overline{\mu_1} \cdot \overline{\mu_2}$$

since  $\overline{\mu_1}$  and  $\overline{\mu_2}$  are independent. Assuming free rotation

$$\overline{\mu_1} = l_1 m \cos \alpha \text{ and } \overline{\mu_2} = l_2 m \cos \alpha$$

therefore

$$\overline{\mu^2} = 2m^2(1 + \overline{l_1 \cdot l_2} \cos^2 \alpha)$$

$$\overline{\mu^2} = 2m^2(1 + \cos \beta \cos^2 \alpha) \quad (1)$$

Equation 1 is general for molecules containing two identical groups which have a fixed angle between their axes of rotation. It is easily extended to include molecules where the groups are different, resulting in vectors of different magnitude having different angles  $\alpha_1$  and  $\alpha_2$  with their axes of rotation, namely

$$\overline{\mu^2} = m_1^2 + m_2^2 + 2m_1 m_2 \cos \beta \cos \alpha_1 \cos \alpha_2 \quad (2)$$

If  $\beta$  is equal to  $180^\circ$  then equation 1 reduces to

$$\overline{\mu^2} = 2m^2 \sin^2 \alpha \quad (3)$$

If  $\overline{\mu^2}$  is replaced by  $\overline{\mu^2}$ , then equation 2 reduces to the equations developed by Fuchs and Wolf<sup>6</sup> on application of the free rotation principle to the ortho, meta and para isomers of benzene derivatives.

If the same replacement is made in Eqn. 3, one obtains the Williams<sup>7</sup> equation for free rotation in a molecule like ethylene dichloride.

If the two different cases of three and four rotating groups are considered, then proceeding by the above vector method, one obtains Eqns. 4 and 5, respectively.

$$\overline{\mu^2} = \overline{\mu_1^2} + \overline{\mu_2^2} + \overline{\mu_3^2} + 2(\overline{\mu_1 \cdot \mu_2} + \overline{\mu_1 \cdot \mu_3} + \overline{\mu_2 \cdot \mu_3}) \quad (4)$$

$$\overline{\mu^2} = \overline{\mu_1^2} + \overline{\mu_2^2} + \overline{\mu_3^2} + \overline{\mu_4^2} + 2(\overline{\mu_1 \cdot \mu_2} + \overline{\mu_1 \cdot \mu_3} + \overline{\mu_1 \cdot \mu_4} + \overline{\mu_2 \cdot \mu_3} + \overline{\mu_2 \cdot \mu_4} + \overline{\mu_3 \cdot \mu_4}) \quad (5)$$

If vectors of equal magnitude ( $m$ ), which make the same angle  $\alpha$  with their respective axes of rotation, and these axes make the same angle  $\beta$  with each other, are considered, then Eqns. 4 and 5 become equations 6 and 7, respectively

$$\overline{\mu^2} = 3m^2(1 + 2\cos \beta \cos^2 \alpha) \quad (6)$$

$$\overline{\mu^2} = 4m^2(1 + 3\cos \beta \cos^2 \alpha) \quad (7)$$

Equation 5, if expressed in words, would have the same meaning as a relation previously derived by Eyring<sup>8</sup> (his Eqn. 6) using matrix algebra.

(6) Fuchs and Wolf, "Hand- und Jahrbuch der chemischen Physik," Vol. 6, I, Akad. Verlags, Leipzig, 1935, p. 398.

(7) Williams, *Z. physik. Chem.*, **138A**, 75 (1928).

(8) Eyring, *Phys. Rev.*, **39**, 746 (1932).

## Discussion of Data

The moments of diethyl sulfite and triethyl phosphate given in Table II are in good agreement with the value of 2.90  $D$  reported<sup>9</sup> for dimethyl sulfite and with the average value of 3.05  $D$  reported<sup>10</sup> for alkyl phosphates. The moment for tetraethyl silicate varies considerably from the value of 1.1  $D$  reported<sup>11</sup> for ethyl orthocarbonate with which, on the basis of apparent similarity of structure, it should be comparable.

TABLE II

| Compound            | MRD   | $\mu \times 10^{18}$<br>(exp.) | $\mu \times 10^{18}$<br>(calcd.) |
|---------------------|-------|--------------------------------|----------------------------------|
| Diethyl sulfite     | 31.98 | 2.96 $\pm$ 0.02                | 3.08                             |
| Triethyl phosphate  | 41.23 | 3.07 $\pm$ .03                 | 3.03                             |
| Tetraethyl silicate | 52.07 | 1.70 $\pm$ .02                 | 1.78                             |

In an attempt to correlate the measured moments with the possible structure of these compounds, free rotation of the ethoxy groups was assumed. The potential energies of the dipoles and their effect on the oscillation of the dipoles, variable inductive effects on one another and steric effects were not considered. After calculation of  $\overline{\mu^2}$  by means of one of the appropriate equations given above, the assumption was made that the mean moment due to free rotation was equal to the square root of the mean square moment. In making the calculations, the value of  $m$ , the link moment of  $C_2H_5-O$  bond, was taken to be 1.1  $D$ ;  $\alpha$  was taken to be  $70^\circ$  (assuming the C-O-C valency angle to be  $110^\circ$ );  $\beta$ , the angle between the axes of rotation was taken as  $110^\circ$  in the case of O-Si-O, O-P-O, O-C-O valency angles (tetrahedral structure) and as  $103^\circ$  in the case of the O-S-O valency angle.<sup>12</sup> Each case will be considered briefly. Results are given in Table II.

Tetraethyl silicate was assumed to be a tetrahedron with Si at the center. The mean moment, due to free rotation of the ethoxy groups, was calculated by Eqn. 7 to be 1.78  $D$ . Since the four Si-O link moments will cancel out due to symmetry, this value should be equal to the measured value.

Triethyl phosphate was assumed to have a tetrahedral structure. The mean moment, due to free rotation of the three ethoxy groups, was calculated by Eqn. 6 to be 1.66  $D$ . This mean moment, due to symmetry, should be acting in the direction of P to the unattached O atom. Based on the electronegativity values,<sup>13</sup> the P-O single bond link moment should be 1.4  $D$ . The sum of the vertical components of the three P-O single bond link moments should act in the opposite direction to the mean moment of the rotating ethoxy

(9) Hunter and Partington, *J. Chem. Soc.*, 309 (1933).

(10) Costello and Curran, Abstracts of Papers of the Division of Physical and Inorganic Chemistry, presented at Cleveland, Ohio, April, 1944.

(11) Ebert, Eisenschitz and V. Hartel, *Z. physik. Chem.*, **B1**, 94 (1928).

(12) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 227.

(13) Ref. 12, p. 64.

groups and is equal to 1.43  $D$ . Using a value<sup>14,15</sup> of 2.8  $D$  for the semipolar P-O bond acting from P to the unattached oxygen, one obtains on adding up vectorially the three different vertical components, a value of 3.03  $D$  for the molecule.

Diethyl sulfite was assumed to have a pyramidal structure by analogy to thionyl chloride.<sup>16</sup> The mean moment due to the free rotation of the two ethoxy groups was calculated by Eqn. 1 to be 1.42  $D$ . A value<sup>13</sup> of 1.0  $D$ , based on electronegativities, was used for the S-O single link moment and a value<sup>15</sup> of 3.0  $D$  was used for the semipolar S-O bond. A value<sup>16</sup> of 1.45 for the S-O bond distance was assumed for evaluation of other desired data in the pyramid. Following a procedure similar in principle to the one used in the triethyl phosphate calculation, one calculates the value 3.08  $D$  for the molecule.

(14) Lister and Sutton, *Trans. Faraday Soc.*, **35**, 495 (1939). These authors quote this value from unpublished work of J. S. Hunter and argue in its favor because of similarity to the C-O and S-O bonds.

(15) Smyth, Lewis, Grossman and Jennings, *THIS JOURNAL*, **62**, 1223 (1940). These authors assign a value of 3.5  $D$  to the P-O semi-polar bond. This value would lead to a calculated moment of 3.73  $D$  for the molecule.

(16) Palmer, *THIS JOURNAL*, **60**, 2360 (1938).

Reference to Table II will show that the agreement between experiment and theory, assuming free rotation, is as good as can be reasonably expected, considering the assumptions made. Reference to atomic models indicates the possibility of a large amount of rotation before steric hindrance becomes important. In the case of ethyl orthocarbonate, steric hindrance is much more important than in the case of tetraethyl silicate and thus the moments of these compounds will differ from one another regardless of apparent similarity in structure.

### Summary

1. The dipole moments of diethyl sulfite, triethyl phosphate and tetraethyl silicate were determined in benzene and were found to be 2.96, 3.07 and 1.70  $D$ , respectively.

2. Vectorial derivations of equations assuming free rotation of groups in a molecule are given.

3. The measured moments are in reasonably good agreement with those calculated assuming free rotation.

COLLEGE PARK, MARYLAND

RECEIVED JULY 29, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

## Cleavage of the Carbon-Sulfur Bond. The Action of Acid Catalysts, Especially Aluminum Bromide, on Benzyl Phenyl Sulfide

BY DONALD P. HARNISH<sup>1</sup> AND D. S. TARBELL

In spite of the increasing importance of sulfur compounds in organic chemistry and in biological processes, there is little definite information available about many fundamental aspects of the chemistry of the carbon-sulfur bond. A survey of the literature dealing with cleavage of the carbon-sulfur bond in sulfides, which was carried out in connection with some projected syntheses, disclosed a number of qualitative observations,<sup>2</sup> indicating that the carbon-sulfur bond is cleaved by acidic reagents much more slowly than the corresponding carbon-oxygen bond, but no systematic quantitative information was found.<sup>3</sup>

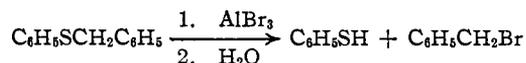
The present paper reports a quantitative study of the cleavage of the carbon-sulfur bond in benzyl phenyl sulfide (BPS) by acidic substances,

(1) Beaunit Mills Fellow, 1947-1948; present address, Department of Chemistry, Columbia University, New York, N. Y.

(2) Auwers and Arndt, *Ber.*, **42**, 537 (1909); Arndt, Loewe and Ozansoy, *ibid.*, **72**, 1860 (1939); Stevens and Gustus, *THIS JOURNAL*, **55**, 378 (1933).

(3) The usefulness of the reductive cleavage of S-benzyl groups by sodium and liquid ammonia (Sifferd and du Vigneaud, *J. Biol. Chem.*, **108**, 757 (1935), and later papers) and of the Raney nickel desulfuration reaction (Mozingo, Wolf, Harris and Folkers, *THIS JOURNAL*, **65**, 1013 (1943)) has been abundantly demonstrated. The cleavage of sulfides by chlorine is described by Zincke and Rose, *Ann.*, **406**, 127 (1914); Lee and Dougherty, *J. Org. Chem.*, **5**, 81 (1940), and Baker, Dodson and Riegel, *THIS JOURNAL*, **68**, 2636 (1946), among others.

principally aluminum bromide, according to the equation



Numerous preliminary experiments, some of which are given in Table I, showed that aqueous halogen acids did not produce any thiophenol from BPS, although complete decomposition sometimes occurred. This behavior is in striking contrast to the facile cleavage of analogous oxygen ethers. Glacial acetic acid containing hydrogen bromide (about 30%) was studied in detail as a cleavage agent<sup>4</sup>; it was found that under optimum conditions about 15% of free thiophenol was formed, and about an equal amount of phenyl thiolacetate ( $\text{C}_6\text{H}_5\text{SCOCH}_3$ ) formed by the reaction of acetic acid with thiophenol. The evidence all indicated that a maximum of 30-35% of thiophenol, free and esterified, could be formed by cleavage of BPS with acetic acid-hydrogen bromide. Analysis of a reaction mixture obtained by heating 1.0 g. of BPS with 4 cc. of acetic acid-hydrogen bromide at 100° for twenty-four hours gave 14.2% thiophenol, 17.8% phenyl thiolacetate and 76.2%

(4) Cf. Pinck and Hilbert, *ibid.*, **68**, 751 (1946).