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The Dipole Moments of Some Mercaptans and Sulfides

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The dipole moments of thianthrene, two thioethers and two mercaptans are measured and compared with values in the literature. The differences in moment of corresponding oxygen and sulfur compounds are attributed to inherent

differences in the H-O, C-O, H-S and C-S moments and to the greater polarizability of sulfur as compared to oxygen. In contrast to the oxygen ethers, the thioethers show as much intermolecular action as the mercaptans.

THIS investigation was undertaken some time ago with the object of comparing the mercaptans and sulfides, for certain of which approximate moments had been calculated previously,¹ with the corresponding oxygen compounds, which had shown unusual dielectric behavior.² Hunter and Partington, who determined the dipole moments of ethyl mercaptan and ethyl sulfide some little time ago,³ have just published values for thiophenol, two alkyl mercaptans, and three more sulfides,⁴ and have given an interesting discussion of their results. Although their values for the sulfides are in excellent agreement with those in the present paper, as will shortly be seen, there is a marked discrepancy in the values for the mercaptans, which are difficult to obtain in a very pure state. On this account an unusually detailed description of the criteria of purity of the two mercaptans here measured seems desirable.

PURIFICATION OF MATERIALS

Benzene

Mallinckrodt's (Thiophene Free) analytical reagent grade benzene was treated as in earlier work.⁵

¹ C. P. Smyth, *J. Am. Chem. Soc.* **46**, 2151 (1924).

² C. P. Smyth and W. N. Stoops, *J. Am. Chem. Soc.* **51**, 3312, 3330 (1929).

³ E. C. E. Hunter and J. R. Partington, *J. Chem. Soc.* **1931**, 2062.

⁴ E. C. E. Hunter and J. R. Partington, *J. Chem. Soc.* **1932**, 2812, 2819.

⁵ C. P. Smyth and W. S. Walls, *J. Am. Chem. Soc.* **54**, 1854 (1932).

Thianthrene

Material very kindly loaned by Professor Gregg Dougherty (m.p. 156.5–157.5°) was fractionally crystallized nine times from pure dry benzene and dried in an evacuated desiccator. This material was odorless and concentrated solutions in benzene showed no coloration; m.p., 157.5–157.8°. Bergmann and Tschudnowsky report⁶ their material to melt at 154°.

Ethyl sulfide

Material from the Eastman Kodak Company was extracted with sodium hydroxide solution, washed several times with water, shaken with mercury (no decoloration), dried for several days with anhydrous sodium sulfate, decanted and twice fractionally distilled; b.p., 91.8° (756 mm); n_D^{20} 1.44265; n_D^{25} 1.4400.

n-Amyl sulfide

Material from the Eastman Kodak Company was treated in the same way as the ethyl sulfide and twice fractionally distilled under reduced pressure; b.p., 103–103.5° (13 mm); n_D^{20} 1.45547; n_D^{25} 1.45377.

n-Butyl mercaptan

Material from the Eastman Kodak Company was dried for several days with anhydrous sodium sulfate and fractionally distilled in an apparatus filled with nitrogen. The boiling point was constant at 97.5° (760 mm) during the collection of the first three fractions, after which it rose 0.1°. A 240 cc sample was collected in seven fractions

⁶ E. Bergmann and M. Tschudnowsky, *Ber.* **65**, 457 (1932).

in the quantities given below with the following refractive indices: (1) 50 cc, n_D^{20} 1.4381; (2) 40 cc, n_D^{20} 1.4381, n_D^{25} 1.4356; (3) 35 cc, n_D^{20} 1.4381; (4) 50 cc, n_D^{20} 1.4387; (5) 25 cc, n_D^{20} 1.4402; (6) 20 cc, n_D^{20} 1.4416. The second fraction, which was used for preliminary dielectric constant and density measurements, had an index considerably lower than the value 1.4411 found by Hunter and Partington and a density, 0.8377, obtained by extrapolation to 20°, also lower than the value 0.8397 found by Hunter and Partington and the value 0.8412 obtained from the specific volume determined by Bingham and Fornwalt.⁷ The density of this second fraction was, however, slightly higher than the value 0.836 given in *International Critical Tables* and its boiling point 97.5° was between the value 98° given by *International Critical Tables* and the value 97.2° found by Hunter and Partington.

In order to remove possible butyl alcohol, fractions 1 and 4 combined were washed five times with distilled water, dried with anhydrous sodium sulfate, further dried with phosphorus pentoxide for a few hours, decanted, and fractionally distilled as before; b.p., 97.9° (755 mm); n_D^{20} 1.44275; n_D^{25} 1.44025; d_4^{20} 0.8415. These constants are in excellent agreement with those recently published by Ellis and Reid.⁸

As this sample appeared to be purer than the first material measured, it was used to obtain the data given in this paper. The dipole moment obtained for it was 0.04×10^{-18} lower than that found for the first sample.

***n*-Amyl mercaptan**

Material from the Eastman Kodak Company was dried for several days with anhydrous sodium sulfate, decanted, and fractionally distilled three times; b.p., 123.7–124.0° (756 mm); n_D^{20} 1.4459; n_D^{25} 1.44386. The density, 0.8418, obtained by extrapolation to 20°, is in excellent agreement with the value 0.8415 of Bingham and Fornwalt, but much lower than the value 0.857 in *International Critical Tables*, which gives a somewhat lower refractive index, 1.4437, and a higher boiling point 126°. Our values are in agreement

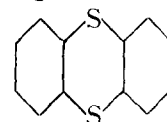
with the values d_4^{25} 0.8375 and n_D^{25} 1.4440 obtained by Ellis and Reid.

EXPERIMENTAL RESULTS

The densities d and dielectric constants ϵ of the polar substances of mole fraction c_2 in solution in benzene were measured with the apparatus and methods previously employed,⁹ a wave-length of 1000 meters being used in the dielectric constant determinations. The results are shown in Table I, in which the values opposite $c_2=0$ for the benzene-thianthrene mixtures are for the pure benzene used in all the measurements. $P_2 = (\epsilon - 1)M/(\epsilon + 2)d$ has been extrapolated to $c_2=0$ in the usual manner to obtain P_∞ , from which, together with the molar refraction MR_D , the moment is calculated as $\mu = 0.0127 \times 10^{-18}[(P_\infty - MR_D)T]^{1/2}$. The values are summarized in Table II, and the moments of the mercaptans and sulfides are shown in Table III marked "W. and S." together with the values of Hunter and Partington in the column marked "H. and P."

DISCUSSION OF RESULTS

The moment, 1.41×10^{-18} , found for thianthrene is decidedly lower than the value, 1.68×10^{-18} , just published by Bergmann and Tschudnowsky⁶ but surprisingly high for the structure, indicating, as Bergmann and Tschudnowsky conclude, that the rings do not lie in the same plane. Indeed, a considerable folding of the structure about the two sulfurs must occur in order to give such a moment, for the C–S valences must act at such angles as partially to oppose one another's moments. The reason for the discrepancies in the values for thianthrene and the mercaptans is presumably the difficulty of purification, but it is believed that the materials finally used in the present investigation are reliable as to purity. Impurity should account for the difference found by Hunter and Partington between the higher mercaptan and the ethyl compound, the value for which is nearer than the others to the values found in the present work for the higher compounds.



⁷ E. C. Bingham and H. J. Fornwalt, *J. Rheology* **1**, 372 (1930).

⁸ L. M. Ellis, Jr., and E. E. Reid, *J. Am. Chem. Soc.* **54**, 1674 (1932).

⁹ C. P. Smyth and W. S. Walls, *J. Am. Chem. Soc.* **53**, 527 (1931).

TABLE III. *Dipole moments of sulfides and mercaptans*
($\times 10^{18}$).

| Hydrogen sulfide | | 0.93* | |
|------------------|-----------|----------------|-----------|
| <i>Mercaptan</i> | | <i>Sulfide</i> | |
| W. and S. | H. and P. | W. and S. | H. and P. |
| Methyl | | | 1.40 |
| Ethyl | 1.39 | 1.58 | 1.57 |
| Propyl | 1.33 | | 1.55 |
| Butyl | 1.48 | | 1.57 |
| Amyl | 1.50 | 1.58 | |

Hunter and Partington have based a fairly satisfactory calculation of the moments of the sulfides and the mercaptans upon the assumption of a 90° sulfur valence angle. A fairly satisfactory result is also obtained by using the 146° valence angle and the high $m_{C-H} + m_{C-S}$ moment, 2.5×10^{-18} , calculated by Smyth and Walls.¹⁰ The moment, 1.46×10^{-18} , thus calculated for the sulfides is very close to the experimentally determined values in Table III. However, as pointed out by Smyth and Walls, this large sulfur valence angle and surprisingly high C-S moment are dependent upon a somewhat inaccurate value in the literature for the moment of $p\text{-ClC}_6\text{H}_4\text{SC}_6\text{H}_5$ and upon the assumption that the moment of the para-substituted group is approximately independent of the other moments in the molecule. The differences between the moments of para-substituted phenols, anisoles, etc.,¹⁰ make it appear probable that this assumption is not generally justifiable in the case of the ethers and thioethers, thus leaving the question of the sulfur valence angle open as far as dipole moments are concerned.

Hunter and Partington have explained the differences between the moments of corresponding oxygen and sulfur compounds largely in terms of the considerable difference in polarizability of oxygen and sulfur, as was done roughly for water and hydrogen sulfide by Smyth.¹ A C-S moment inherently larger than the H-S and a C-O inherently smaller than the H-O, both of which probable facts are influenced by the sulfur and oxygen polarizabilities, can account for the differences in moment. Not only the increase in moment from the hydrogen halides to the

TABLE II. *Refractions, orientation polarizations and dipole moments.*

| | MR_D | $P_\infty - MR_D$ | | $\mu \times 10^{18}$ | |
|---------------------------|--------|-------------------|------|----------------------|------|
| | | 25° | 50° | 25° | 50° |
| Thianthrene | 65.9 | 41 | 38 | 1.41 | 1.41 |
| Ethyl sulfide | 28.57 | 51.7 | 48.2 | 1.58 | 1.58 |
| <i>n</i> -Amyl sulfide | 56.44 | 51.9 | 48.8 | 1.58 | 1.59 |
| <i>n</i> -Butyl mercaptan | 28.40 | 45.4 | 42.8 | 1.48 | 1.49 |
| <i>n</i> -Amyl mercaptan | 33.03 | 47 | 44 | 1.50 | 1.51 |

corresponding methyl halides, but, to a smaller extent, also the increase of the methyl halide to the corresponding ethyl compound increases with increasing polarizability of the halogen. It thus appears reasonable that, although the C-O moment is smaller than the H-O, the C-S moment should be larger than the H-S, which gives the mercaptans higher moments than H_2S and the sulfides higher moments than the mercaptans.

A surprising effect is apparent in the dependence of the observed polarization of the sulfide upon concentration. The highly associated alcohols show a strong and complicated dependence of apparent polarization upon concentration because of the strong effects of the H-O dipoles upon one another,¹¹ while the ethers show a polarization independent of concentration, presumably because the alkyl groups screen the C-O dipoles in adjacent molecules from one another. As would be expected, the supposedly unassociated mercaptans show (see Table I) a

change of only 10 to 15 units of observed polarization between the pure liquid and the substance at infinite dilution, the difference from the behavior of the alcohols presumably being due to the partial screening of the H-S dipole by the structure of the sulfur atom. The sulfides in Table I, however, show a dependence of polarization upon concentration which, when the difference in molecular size is taken into account, is as great as that of the mercaptans. Thus, the ethyl sulfide molecule, which is approximately the same size as that of butyl mercaptan, increases in apparent polarization from the pure liquid to infinite dilution, 14.0 at 25° and 11.3 at 50°, while butyl mercaptan increases 12.6 at 25° and 10.8 at 50°. It appears possible that the larger size of the sulfur atom as compared to the oxygen prevents complete screening of the C-S dipoles by the alkyl groups so as to permit a larger external field than in the case of the oxygen ethers and consequently some molecular interaction. The larger moments of the sulfides are also a factor, possibly, helping to make the intermolecular action of the sulfides as large as that of the mercaptans.

¹¹ C. P. Smyth, *Dielectric Constant and Molecular Structure*, p. 180, The Chemical Catalog Company, Inc., New York, 1931.