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Determination of the Bond Angle of Sulphur in Alkyl Mercuric Sulphides by Dipole Moment Method

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The question of the bond angle in sulphur is still of interest, although large experimental evidence is available, obtained by different methods. However, these data are scarce in cases where sulphur is bound on electropositive atoms, as for example in alkyl mercuric sulphides. This paper gives a determination of sulphur bond angle, based on experimental data obtained from dipole moment measurements of symmetrical and asymmetrical alkyl mercuric sulphides.[1]

The knowledge of the total dipole moment value of an alkyl mercuric sulphide molecule is not sufficient for determination of the bond angle, as the dipole moments of the C-Hg and Hg-S bonds are not known. It will be shown that the bond angle Hg-S-Hg can be determined on the basis of the following three dipole moments: the moments of symmetrical molecules R'Hg-S-HgR' and R''Hg-S-HgR'' and the dipole moment of asymmetrical molecule R'Hg-S-HgR'', with R' and R'' as in the first two molecules; supposing that the bond angles in these three molecules are equal or approximately identical. It is also necessary to assume that the moments for R'HgS (μ') and R''HgS (μ'') do not differ in symmetrical and asymmetrical alkyl mercuric sulphides and that the total dipole moment depends only upon the bond moment and bond angle. Using the symbols μ_1, μ_2 and $\mu_{1,2}$ for the dipole moments of the molecules $(R'Hg)_2S$, $(R''Hg)_2S$ and R'HgSHgR'', respectively, the following sequence of equations is obtained,

$$\mu_1^2 = 2\,\mu'^2\,(1 + \cos\varphi) \tag{1}$$

$$\mu_2^2 = 2\,\mu''^2\,(1 + \cos\varphi) \tag{2}$$

$$\mu_{1,2} = \mu'^2 + \mu''^2 + 2\,\mu'\,\mu''\cos\varphi \tag{3}$$

where φ is the bond angle Hg-S-Hg in all the three molecules. It follows further that

$$\mu_{1,2} = \frac{\mu_1^2}{2\,(1 + \cos\varphi)} + \frac{\mu_2^2}{2\,(1 + \cos\varphi)} + \frac{\mu_1\,\mu_2\cos\varphi}{1 + \cos\varphi} \tag{4}$$

or

$$\cos\varphi = \frac{\mu_1^2\,\mu_2^2 - 2\,\mu_{1,2}}{2\,\mu_{1,2} - 2\,\mu_1\,\mu_2} \tag{5}$$

This means that by measuring the dipole moment of three different related sulphides, the bond angle can be determined.

The measurements have been carried out for methyl (R′), ethyl (R″) and methyl-ethyl derivatives:

$$(CH_3Hg)_2S \quad \mu_1 = 1.78\ D$$
$$(C_2H_5Hg)_2S \quad \mu_2 = 2.78\ D$$
$$CH_3HgSHgC_2H_5 \quad \mu_{1,2} = 2.37\ D$$

By substituting these dipole moment values in equation (5) the angle Hg-S-Hg $\varphi = 105^0$ is obtained.

It has to be pointed out that the value for Hg-S-Hg angle given here is the first one obtained by the dipole moment method.

EXPERIMENTAL

Methyl- and ethyl-mercuric sulphides have been prepared by introducing hydrogen sulphide into a saturated alcoholic solution of alkyl mercuric bromide at room temperature.

$$2\ RHgBr + H_2S \rightarrow (RHg)_2S + 2\ HBr$$

Hydrobromic acid obtained may be neutralized with sodium hydroxide (0.3 g per 100 ml) or with dimethylaniline (0.5 g per 100 ml). If this neutralization is not performed, the yield of alkyl mercuric sulphide is somewhat lower (5—10%).

Alkyl mercuric sulphide was obtained in form of a white precipitate, which gradually darkens in air. After filtration the precipitate was washed with small amount of water and alcohol and recrystallized from benzene.

Methyl- and ethyl-mercuric sulphides were prepared according to the method of M. Dadić and D. Grdenić.[2]

Methyl mercuric sulphide. Dipole moment $\mu_1 = 1.78$ D was determined on the basis of data given in Table I.

TABLE I

x_2	ε	x_2	v	x_2	n
0.00	2.2725	0.00	1.1463	0.00	1.49725
$0.41 \cdot 10^{-3}$	2.2729	$0.26 \cdot 10^{-3}$	1.1461	$0.43 \cdot 10^{-3}$	1.49730
$0.52 \cdot 10^{-3}$	2.2731	$0.41 \cdot 10^{-3}$	1.1460	$0.82 \cdot 10^{-3}$	1.49735
$0.70 \cdot 10^{-3}$	2.2733	$0.83 \cdot 10^{-3}$	1.1457	$1.04 \cdot 10^{-3}$	1.49738
$0.83 \cdot 10^{-3}$	2.2734	$1.04 \cdot 10^{-3}$	1.1454	$1.22 \cdot 10^{-3}$	1.49740

x_2 — molar concentration
ε — dielectric constant
v — specific volume
n — refractive index

Ethyl mercuric sulphide. Dipole moment $\mu_2 = 2.78$ D was determined on the basis of data given in Table II.

Methyl mercuri-ethyl mercuric sulphide. Dipole moment $\mu_{1,2} = 2.37$ D was determined on the basis of data given in Table III.

All the physical measurements have been carried out at 25°C.

TABLE II

x_2	ε	x_2	n	x_2	v
0.00	2.2725	0.00	1.49775	0.00	1.1465
$0.70 \cdot 10^{-3}$	2.2740	$0.30 \cdot 10^{-3}$	1.49780	$0.30 \cdot 10^{-3}$	1.1462
$0.94 \cdot 10^{-3}$	2.2743	$0.70 \cdot 10^{-3}$	1.49785	$0.70 \cdot 10^{-3}$	1.1459
$1.31 \cdot 10^{-3}$	2.2752	$0.94 \cdot 10^{-3}$	1.49790	$0.94 \cdot 10^{-3}$	1.1452
$1.42 \cdot 10^{-3}$	2.2756	$1.42 \cdot 10^{-3}$	1.49795	$1.10 \cdot 10^{-3}$	1.1455

TABLE III

x_2	ε	x_2	n	x_2	v
0.00	2.2725	00.0	1.49840	0.00	1.1463
$0.51 \cdot 10^{-3}$	2.2733	$0.51 \cdot 10^{-3}$	1.49847	$0.51 \cdot 10^{-3}$	1.1458
$0.67 \cdot 10^{-3}$	2.2737	$0.67 \cdot 10^{-3}$	1.49849	$0.67 \cdot 10^{-3}$	1.1456
$0.82 \cdot 10^{-3}$	2.2739	$0.89 \cdot 10^{-3}$	1.49852	$0.89 \cdot 10^{-3}$	1.1454
$1.00 \cdot 10^{-3}$	2.2742	$1.09 \cdot 10^{-3}$	1.49856	$1.12 \cdot 10^{-3}$	1.1451

DISCUSSION

The stereochemistry of sulphur is similar to the stereochemistry of oxygen, being determined by the configuration of valence electrons $ns^2\ n(p_x, p_y, p_z)^2$, where $n = 2$ and $n = 3$ for oxygen and sulphur, respectively. However, as the valence electrons of sulphur are in the $n = 3$ electron shell, some difference in behaviour of sulphur is observed on comparison with oxygen atoms. By using 3 *d* orbitals, sulphur can increase the number of electrons in the outer shell. In addition, *d* electrons may influence the final shape of hybridized bond orbitals, causing for that reason some difference from oxygen, which can use only *s* and *p* electrons. Burrus and Gordy[3] considered this in calculating the sulphur bond angle. According to Abrahams[4] the values of sulphur bond angle does not exceed 109.5°, with exception of sulphur dioxide with an angle of 119°. The majority of bond angle values are over 100°, except in cyclic compounds. The angle is slightly below 100° only in the case of hydrogen sulphide and mercaptans. It has been expected that the Hg-S-Hg angle in our compounds would not be much different from the value in thioethers, *i.e.* from 105° to 109°. The result obtained on the basis of dipole moment measurements is 105°.

The value of 105°, obtained as above, shows that it is possible to determine accurately enough a bond angle by dipole moment determination. The equation (5) may be applied in other analogous cases.

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IZVOD

Određivanje valentnog kuta sumpora u živinim alkil sulfidima mjerenjem dipolnog momenta

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Određen je valentni kut sumpora mjerenjem dipolnog momenta jednog nesimetričnog i dvaju simetričnih živinih alkil sulfida. Vrijednost kuta $\varphi = 105^0$. Izneseni su matematički izrazi za izračunavanje valentnog kuta ovom metodom, kao i kratka diskusija stereokemije sumpora.

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