Structural Investigations of Alkyl Mercury Sulphide, Alkyl Mercury Oxide and Alkyl Mercury Selenide by Dipole Moment Method

M. Kesler

Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia, Yugoslavia

These structural investigations by the dipole moment method follow earlier reported papers.[1,2] On the basis of the influence of bond length, valence angles and electronegativity differences on the dipole moment, we expected to get some structural informations on these compounds. Dipole moment values with some experimental data are given in Table I.

TABLE I

Compound	Dipole moment	$x_2 \cdot 10^3$	ε	$x_2 \cdot 10^3$	n	$x_2 \cdot 10^3$	v
$(CH_3Hg)_2O$	3.34 D	0.00	2.2725	0.00	1.49756	0.00	1.1469
		0.44	2.2741	0.35	1.49766	0.35	1.1457
		0.50	2.2743	0.65	1.49774	0.50	1.1454
		0.67	2.2749	0.80	1.49778	0.80	1.1446
		0.97	2.2759	1.05	1.49779	1.05	1.1438
$(CH_3Hg)_2S$	1.78 D	0.00	2.2725	0.00	1.49725	0.00	1.1463
		0.41	2.2729	0.43	1.49730	0.26	1.1461
		0.52	2.2731	0.82	1.49735	0.41	1.1460
		0.70	2.2733	1.04	1.49738	0.83	1.1457
		0.83	2.2734	1.22	1.49740	1.04	1.1454
$(CH_3Hg)_2Se$	2.21 D	0.00	2.2725	0.00	1.49750	0.00	1.1459
		0.30	2.2730	0.30	1.49757	0.26	1.1456
		0.32	2.2731	0.43	1.49759	0.38	1.1455
		0.46	2.2733	0.68	1.49764	0.08	1.1451
		0.71	2.2737	0.86	1.49769	0.95	1.1447

x_2 = molar concentration, ε = dielectric constant, v = specific volume, n = refractive index.

It has been observed that the dipole moment value in methyl mercury derivatives investigated shows an interesting change on substituting oxygen with sulphur and selenium. The oxygen derivative has the highest value of the dipole moment, as expected from the oxygen atom electronegativity. Likewise,

the dipole moment value of sulphur and selenium derivatives should decrease. However, a distinct minimum for sulphur derivative has been found. This lower value may be attributed to the following three tendencies: 1) decrease of the electronegativity from oxygen to sulphur, 2) increase of the bond length with respect to selenium, 3) change of the valence angle. If it is supposed that electronegativity has not decreased much from sulphur to selenium, with the increase of the bond length at the same time, than the increase of the dipole moment from sulphur to selenium can be understood.

According to the Pauling electronegativity scale[3] for oxygen, sulphur, selenium and mercury, and taking into account the interatomic distances from oxide[4], sulphide[4] and selenide[4] (calculated from the unit cell dimensions) the figures collected in the Table II. are obtained.

TABLE II

	Hg — O	Hg — S	Hg — Se
Electronegativity difference	1.6	0.6	0.5
Bond length (Å)	2.03	2.53	2.62

Precise calculations of the dipole moment in these molecules could be performed only if the exact values for bond length and bond angles were available. It is not justified to use simply the distances obtained from mercuric oxide, sulphide and selenide. However, on the basis of the experimental values of the dipole moments it is possible to discuss the bond length $Hg — X$ ($X = O$, S, Se), the bond angles $Hg — X — Hg$ and the effective differences of electronegativity in these compounds. It has been shown previously that the bond angle $Hg — S — Hg$ in methyl mercury sulphide amounts to $\varphi = 105°$. The possible bond angle change in oxide and selenide may explain the change of the dipole moment.

We can suppose that the following factors are of influence in these considerations: bond moment $CH_3 — Hg$, the bond moment $Hg — X$ and the bond angle $Hg — X — Hg$. Assuming that the bond moment $Hg — X$ is proportional to the bond length (r) and electronegativity difference (e),

$$\mu_{(Hg-X)} = k \cdot r \cdot e,$$

it follows

$$y = k \cdot r \cdot e + y_0,$$

where y = bond moment $CH_3 — Hg — X$
y_0 = bond moment CH_3Hg
k = constant

The bond moment $CH_3 — Hg — X$ (y) depends on the total dipole moment and valence angle $Hg — X — Hg$. Assuming that the valence angles are the same for all the compounds ($\varphi = 105°$) and using r and e from Table II, we obtain three points in the diagram representing

$$y = f(e, r)$$

We can then fit the most probable straight line D, shown in Fig. 1.
The deviations from this line and the calculated values are relatively large.
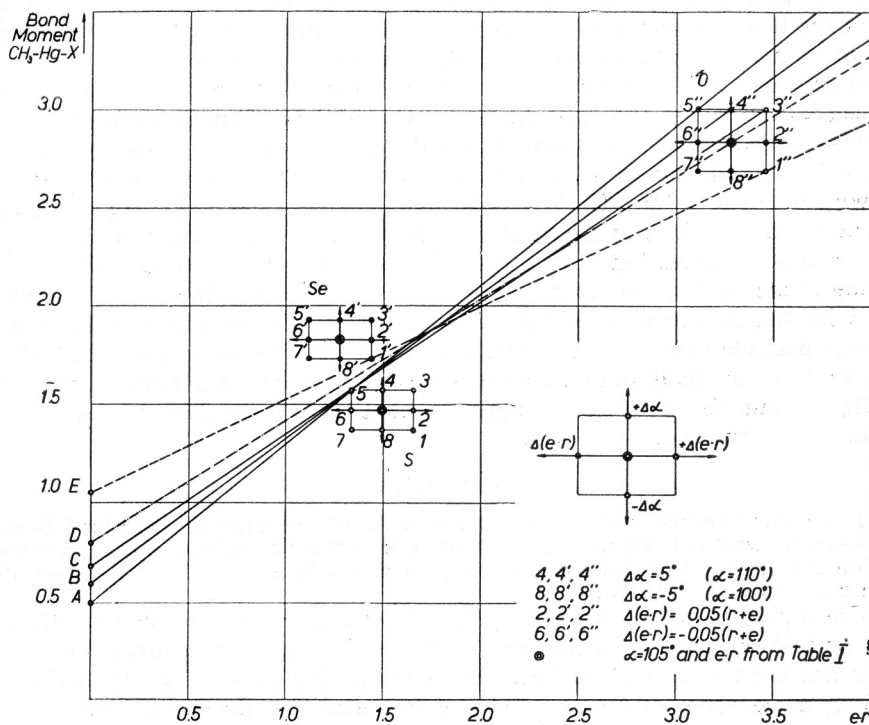
The bond angle difference between oxide and selenide causes the change
in the CH_3—Hg—X bond. If the effective angle in the oxide and selenide
molecule is smaller or larger than 105^0 by $\varphi = \pm 5^0$, the bond moment values
are modified and this can be followed in the diagram. Points 4' and 4" are
obtained with the bond moment values for the valence angle $\varphi = 110^0$, and
points 8' and 8" for the valence angle $\varphi = 100^0$. A similar discussion is possible
for the change of the product

$$\Delta (e \cdot r) = \Delta e \cdot r + \Delta r \cdot e$$

If, for example, the effective difference for electronegativity and interatomic
distances deviate for 0.05 from the values given in Table I. points 2, 2' and 2"
for positive and 6, 6' and 6" for negative deviations of (e. r) are obtained.

It has been already mentioned that the standard deviations from D are
relatively large. Much smaller deviations from the most probable straight line
D could be obtained by drawing this line between points 6, 1' and 5" (line A).
In this case it is necessary to assume that the valence angle Hg—Se—Hg is
smaller than 105^0, being approximately 100^0. A larger value for r Hg—Se and a
smaller one for Hg—S than found in mercury selenide and sulphide is also
expected. An increase, or a decrease of the effective difference of the electro-
negativity may perhaps be expected too. Based on the line A for oxygen, a
bond angle change from 105^0 to 110^0 is to be expected.

Satisfactory results may be obtained taking into account points 4'' and 3'' (lines B and C) and therefore a detailed discussion of Hg—O bond change cannot be performed. From the diagram it is obvious that only points 6 and 1' give small deviations from the most probable line D. All the other combinations of points for sulphide and selenide give larger deviations.

In this whole discussion a bond angle Hg—S—Hg amounting to $\varphi = 105^0$ was considered. From the lines A, B and C the bond moment values CH_3—Hg (y_0) between 0.5 and 0.7 D were obtained. We get the largest deviation from the line by taking into account points 2, 5' and 1'' (line E) with the corresponding bond moment value 1,05. The bond moment value for CH_3—Hg is between 0.5 and 0.7 D, which is in agreement with our earlier investigations.[2]

The above discussion shows that the dipole moment values allow some considerations of the structural characteristics of the compounds examined. Following the argument according to which the calculated points must show the least possible deviation from the line A, the conclusion is plausible that the bond angle in selenide and oxide amounts to about 100^0 and 110^0, respectively. For Hg—S and Hg—Se a bond length of about 2.47 Å and 2.67 Å, respectively, is also to be expected.

EXPERIMENTAL

The methyl mercury oxide and sulphide were prepared as described before.[7] The selenide was not known before and was prepared by introducing hydrogen selenide into an alcoholic solution of methyl mercury bromide.[8] It is a light sensitive white substance, m. p. 128⁰ C.

The dipole moments were determined by a method described by Halverstadt and Kumler.[5] The instrument used for the dielectric constant measurements has been described earlier.[6] All the experiments have been carried out at 25⁰ C, in benzene solutions, following the technique already given.[1,2]

REFERENCES

1. M. Kesler, Croat. Chem. Acta 34 (1962) 123.
2. idem. ibidum., 35 (1963) 101.
3. L. Pauling, Nature of the Chemical Bond, Cornell University Press, N. Y., 1961.
4. A. F. Wells, Structural Inorganic Chemistry, Oxford University Press, 1961.
5. I. F. Halverstadt and W. D. Kumler, J. Am. Chem. Soc. 64 (1942) 2988.
6. M. Kesler and A. Pregernik, Arhiv Kem. 27 (1955) 37.
7. D. Grdenić i F. Zado, Croat. Chem. Acta 29 (1957) 425.
8. M. Kesler, Thesis, Faculty of Science, University of Zagreb, 1958.

IZVOD

Strukturna istraživanja alkilmerkuri sulfida, alkilmerkuri oksida i alkilmerkuri selenida metodom dipolnoga momenta

M. Kesler

Određeni su dipolni momenti alkilmerkuri oksida, sulfida i selenida i njihove vrijednosti diskutirane na bazi duljine veze, valentnog kuta i razlike elektronegativnosti između žive i kisika, sumpora, te selena. Diskusijom je prikazano kako se vrijednosti dipolnih momenata ovih molekula mogu dovesti u vezu s veličinom kuta i duljinom veze Hg — O, Hg — S i Hg — Se, odnosno kako se iz dipolnih momenata mogu izvesti strukturni parametri ispitivanih molekula.

ZAVOD ZA OPĆU I ANORGANSKU KEMIJU
PRIRODOSLOVNO-MATEMATIČKI FAKULTET
ZAGREB