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Structural Investigations of Alkyl Mercury Bromides and Alkyl Mercury Sulphides by Dipole Moment Method

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Dipole moments of some alkyl mercury bromides and sulphides have been determined. A discussion of experimental data is given with relation to structural considerations of compounds examined. It has been concluded that the change of the dipole moment in the alkyl mercury sulphide and alkyl mercury bromide series is caused mainly by a change of alkyl-mercury bond dipole.

INTRODUCTION

For structural investigations of alkyl mercury sulphides by dipole moment measurements the bond dipoles R—Hg and Hg—S have to be known. It is very difficult to estimate sulphur valence angle without some knowledge of these bond dipoles. In an earlier paper[1] it has been shown that in case the dipole moments of two symmetric and an asymmetric alkyl mercury sulphides are known, one can obtain the sulphur valence angle. Investigations on alkyl mercury bromides[2] supply sufficient informations that a similar discussion can be extended on the sulphides series. In this work a discussion of the results of dipole moment investigation of methyl, ethyl, *n*-propyl, and *n*-butyl mercury bromides is presented. Dipole moments for ethyl and *n*-butyl derivatives only have been reported earlier[3]. This work includes also the results and a discussion of dipole moment investigation of methyl, ethyl, and *n*-propyl mercury sulphides, none of which has been previously investigated.

EXPERIMENTAL

Alkyl Mercury Bromides

These compounds are synthetized by a method described by Slotta and Jacobi[4]. Mercury bromides used for dielectric constant measurements have been grinded into a fine powder and dried *in vacuo* in presence of P_2O_5 to a constant weight.

Alkyl Mercury Sulphides

First in the series, methyl mercury sulphide, was prepared by Frankland[5] in 1853, but no description of the compound was given. Hilpert and Ditmar[6] said something more on preparation and of its properties. They obtained it by an action of hydrogen sulphide on methyl mercury chloride, and mentioned very unpleasant smell of the substance, but no melting point. Later, Perret and Perrot[7] have described it more fully. Alkyl mercury sulphides used in this work were obtained by introducing hydrogen sulphide in saturated alcohol solution of alkyl mercury bromides[1,2].

Determination of Dipole Moments

The dipole moments of mentioned alkyl mercury bromides and sulphides were determined by a method described by Halverstadt and Kumler[8]. The instrument used for dielectric constant measurements has been described already[9]. Measurements of specific volume and of refractive index have been performed by standard techniques. All experiments have been carried out at room temperature (25°C). Benzene used as a solvent has been previously refined several times by recrystallization. To so obtained benzene P_2O_5 has been added (10 grams/litre) and the flask firmly closed. Immediately before the measurements took place, the benzene was distilled in a dry air stream, and used for the preparation of solutions.

RESULTS

Experimental results are given in Table I. The results for methyl mercury bromide only are also given in figures 1 — 3, as an illustration. Fig. 1 illustrates

TABLE I

	$x_2 \times 10^3$	ε	$x_2 \times 10^3$	n	$x_2 \times 10^3$	v
Methyl mercuric bromide	0.00	2.2725	0.00	1.49758	0.00	1.1463
	0.63	2.2743	0.63	1.49768	0.65	1.1456
	0.69	2.3743	0.65	1.49770	0,87	1.1463
	0.87	2.2748	0.69	1.49771	1.03	1.1452
	1.11	2.2755	0.87	1.49775	1.11	1.1451
Ethyl mercuric bromide	0.00	2.2725	0.00	1.49772	0.00	1.1463
	0.44	2.2738	0.21	1.49775	0.44	1.1459
	0.57	2.2743	0.44	1.49779	0.70	1.1456
$\mu = 2.80$ D	0.83	2.2752	0.57	1.49780	0.93	1.1454
	1.16	2.2762	1.16	1.49789	1.16	1.1450
n-Propyl mercuric bromide	0.00	2.2725	0.00	1.49737	0.00	1.1480
	0.34	2.2739	0.34	1.49740	0.56	1.1475
	0.56	2.2747	0.63	1.49743	0.69	1.1472
$\mu = 3.28$ D	0,69	2.2752	0.69	1.49744	0.91	1.1471
	1.07	2.2766	0.88	1.49745	1.07	1.1469
n-Butyl mercuric bromide	0.00	2.2725	0.00	1.49737	0.00	1.1480
	0.36	2.2741	0.40	1.49740	0.40	1.1478
	0.45	2.2744	0.61	1.49741	0.61	1.1475
$\mu = 3.57$ D	0.54	2.2747	0.90	1.49744	0.90	1.1472
	0.61	2.2752	1.10	1.49744	1.20	1.1471
Methyl mercuric sulphide	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
$\mu = 1.78$ D	0.70	2.2733	1.04	1.49738	0.83	1.1457
	0.83	2.2734	1.22	1.49740	1.04	1.1454
Ethyl mercuric sulphide	0.00	2.2725	0.00	1.49775	0.00	1.1465
	0.70	2.2740	0.30	1.49780	0.30	1.1462
	0.94	2.2743	0.70	1.49785	0.70	1.1459
$\mu = 2.78$ D	1.31	2.2752	0.94	1.49790	0.94	1.1452
	1.42	2.2756	1.42	1.49795	1.10	1.1455
n-Propyl mercuric sulphide	0.00	2.2725	0.00	1.49753	0.00	1.1463
	0.83	2.2741	0.83	1.49760	0.83	1.1454
	1.16	2.2747	1.16	1.49761	1.16	1.1451
	1.44	2.2753	1.44	1.49762	1.44	1.1447
$\mu = 2.84$ D	2.22	2.2768	2.22	1.49767	2.22	1.1439

the relation of a dielectric constant of a solution ε against a concentration x_2 of the solution. The relation of a specific volume of the solution v against a concentration x_2 is presented in Fig. 2, while Fig. 3 presents a relation between a refractive index n and a concentration x_2. All the three relations are linear, with α, β and γ being coefficients giving the slope of these straight lines respectively. The lines are obtained by applying the least square method.

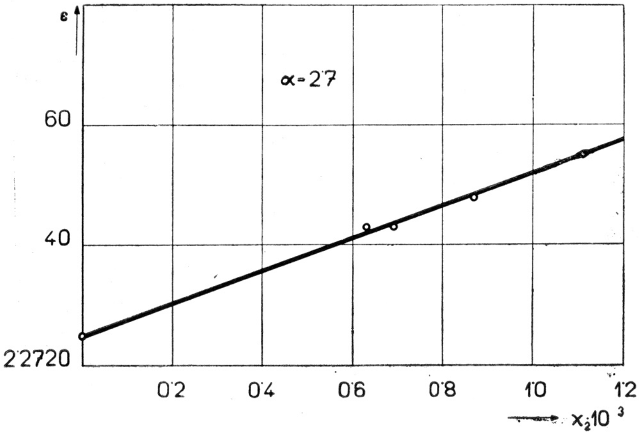

Fig. 1. $\varepsilon = f(x_2)$ for a solution of methyl mercury bromide in benzene (25°C).

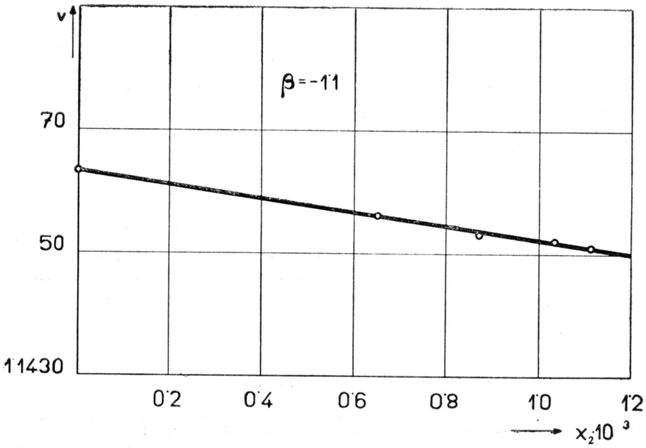

Fig. 2. $v = f(x_2)$ for a solution of methyl mercury bromide in benzene (25°C).

Table II presents the values of electric dipole moments of alkyl mercury bromides. We note a regular increase of the dipole by the increase of the chain of alkyl radical. For a comparison dipole moments of alkyl bromides are included[3] and it can be seen that there is no change of the dipole after the second member of the series. Also, the magnitude of the dipole is larger in mercury bromide series.

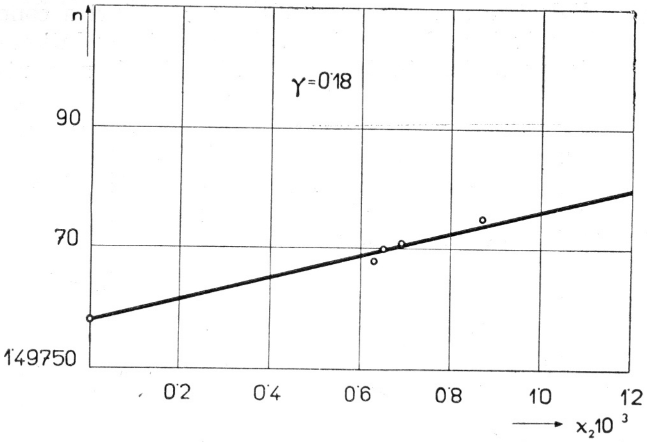

Fig. 3. $n = f(x_2)$ for a solution of methyl mercury bromide in benzene (25^0C).

TABLE II

	Methyl-	Ethyl-	*n*-Propyl-	*n*-Butyl-
Mercury bromide	2.42	2.80	3.28	3.57
Bromide	1.78	1.99	2.19	1.98

Table III gives the dipole moments of sulphur derivatives. The presence of an alkyl group in mercury sulphides causes a dipole of the same direction as in mercury bromides. An increase of the dipole is pronounced only from methyl to ethyl mercury sulphide.

TABLE III

	$(CH_3Hg)_2S$	$(C_2H_5Hg)_2S$	$(C_3H_7Hg)_2S$	
μ	1.78	2.78	2.84	

DISCUSSION

The increase of the dipole moment for a single CH_2 group in alkyl mercury bromide series is 0.38, 0.48, and 0.29 until a saturation is reached after *n*-butyl mercury bromide[10]. This increase of the dipole moment with the size of the alkyl chain might be interpreted either by an increase of the opposite charges on mercury and bromine atoms, or, by a spread of the positive charge over all, or a significant part of mercury alkyl group. In case that the positive charge is localized predominantly on the mercury atom one can speak of a gradual change of the character of Hg-Br bond on passing from methyl to butyl derivative. In other words Hg-Br bond dipole would be responsible for the increase of the dipole moment of a molecule. This means that the ionic character of Hg-Br bond is increasing along the series.

The other possibility is that the positive charge is distributed over alkyl radical, or at least that part of it, close to mercury atom. This assumption seems to be more probable. As is known, the presence of an alkyl group in the molecule is manifested by the inductive effect. This results in a polarization of the molecule in the direction of the alkyl group. The effect will be more pronounced when a mercury atom is present, and it would be interesting to investigate the same effect in compounds when other metal atoms are involved. On the other side, in organic molecules with alkyl group a hiperconjugative effect is established which is manifested as a mesomeric effect along a tautomeric mechanism. It is likely that such an effect may play some importance in this case (as a second order hiporconjugation[11], since no double bonds are present in these molecules).

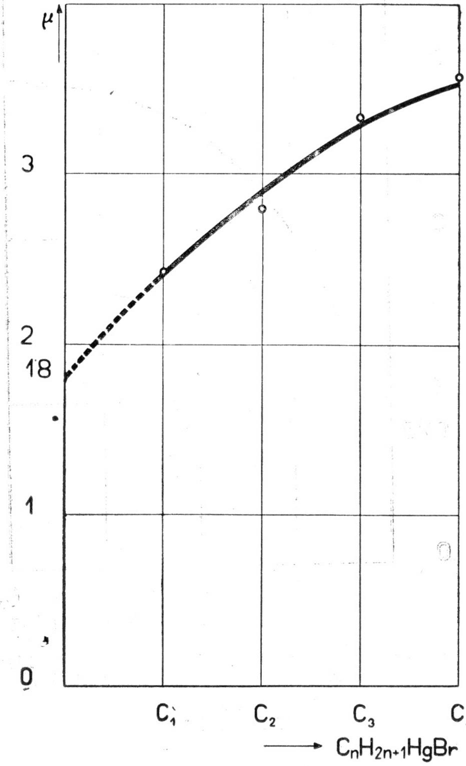

Fig. 4. The variation of dipole moments of alkyl mercury bromides on an increase of the number of carbon atoms in the chain.

A similar discussion for alkyl mercury sulphides follows. The different behaviour of sulphides, *i. e.* the constant value of the dipole after ethyl derivative, is probably due to smaller electronegativity of sulphur relative to bromine. Therefore the negative charge is »saturated« by inductive effect already in methyl derivative. No further increase of the dipole is caused therefore by a presence of additional CH_2 group. Besides, there are two alkyl groups present in these compounds, with a result of a double inductive contribution.

It is not simple to extend the discussion of bond dipoles on these molecules. A large change of the dipole moment from methyl to ethyl mercury sulphide ($\Delta\mu = 1.00$) indicates that it is difficult to speak of a single value, with the

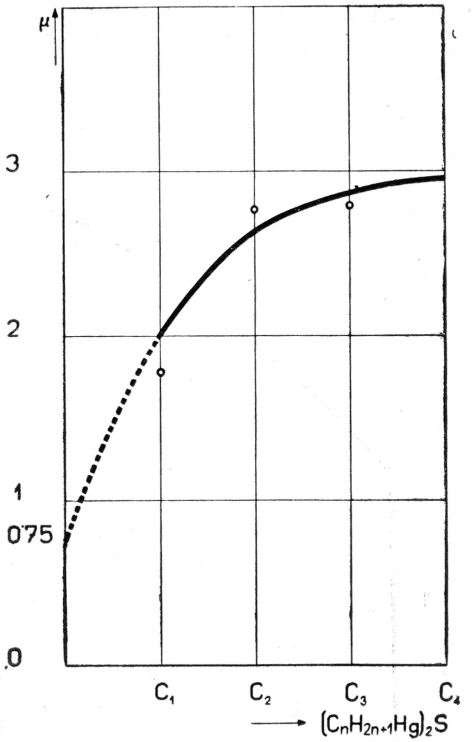

Fig. 5. The variation of dipole moments of alkyl mercury sulphides on an increase of the number of carbon atoms in the chain.

TABLE IV

	CH_3 — Hg	C_2H_5 — Hg	C_3H_7 — Hg
Alkyl HgS	0.46	1.16	1.19
Alkyl HgBr	0.62	1.00	1.48
Mean	0.54	1.08	1.33

TABLE V

	CH_3	C_2H_5	C_3H_7
Hg — S	0.67	0.83	0.61
Hg — Br	1.88	1.72	1.95

additivity properties, for C-Hg and Hg-S bond dipole, at least for the first members of this series. From the experimental values, assuming the sulphur valence angle[1] of 105° it follows; $\mu(CH_3Hg\text{-}S) = 1.21$ D, $\mu(C_2H_5Hg\text{-}S) = 1.91$ D, and $\mu(C_3H_7Hg\text{-}S) = 1.94$ D. The only estimated value for C-Hg bond dipole is 0.5 D given by Hampson[11] and based on dipole moments of some aryl mercury derivatives. This value, however, cannot be transfered to alkyl mercury compounds, as will be shown. For example, starting with the dipole moments of phenyl and ethyl mercury bromides: $\mu = 2.88$ D and $\mu = 2.80$ D respectively, it follows[2] that $\mu(C_6H_5Hg) \sim \mu(C_2H_5Hg) \sim 0.5$ D. From this we obtain the moment of Hg-S as a difference: $\mu(Hg\text{-}S) = \mu(C_2H_5Hg\text{-}S) - \mu(C_2H_5Hg\text{-}) = (1.91 - 0.5)\,D = 1.41$ D. This result is however not in agreement with the value of the dipole for methyl mercury sulphide $\mu = 1.21$ D. Therefore we conclude that the value of the bond dipole $\mu(C\text{-}Hg) = 0.5$ D is too low.

Better results are obtained by extrapolating the values of dipole moments in the alkyl mercury bromides and sulphides series. Figures 4 and 5 illustrate the dependence of the dipole against the number of carbon atoms present in the alkyl chain. From the graphs it follows: $\mu\,(Hg\text{-}Br) = 1.80$ D and $\mu\,(Hg\text{-}S) = 0.75$ D. Assuming these values for the bond moments we can obtain alkylmercury bond dipoles. The results should not be considerably different when calculated from bromine or sulphur series. The small differences may be caused by inaccurate values of Hg-S and Hg-Br bond dipole, and also due to a fact that these bond moments vary slightly along the alkyl series. In Table IV the values of alkyl mercury bond dipoles are listed assuming the above values of the dipoles for Hg-S and Hg-Br bonds. From these results it follows that the positive charge is distributed over the alkyl-mercury part of the molecules, as the centre of the charge is shifted off mercury atom. The mean values of dipoles for bromine and sulphur compounds given in Table IV correspond to hypothetical alkyl mercury radical. These values may now be used to investigate the change of a character of Hg-S and Hg-Br bonds in alkyl derivatives. As can be seen from Table V which lists the values of dipole moments of these bonds the variations are very small, and inside the precision of the method. Therefore we can conclude that the change of the dipole moment in the alkyl mercury sulphide and alkyl mercury bromide series is caused mainly by a change of alkyl-mercury bond dipole.

REFERENCES

1. M. Kesler, *Croat. Chem. Acta* **34** (1962) 123.
2. M. Kesler, *Thesis*, Faculty of Science, University of Zagreb, 1958.
3. J. Kadomtzeff, *Bull. Soc. Chim.* France **1949**, D 394.
4. K. H. Slotta and K. R. Jacobi, *J. prakt. Chem.* **119** (1928) 249.
5. E. Frankland, *Ann. Chem.* **85** (1853) 361.
6. S. Hilpert and M. Ditmar, *Ber.* **46** (1913) 3740.
7. A. Perret and R. Perrot, *Helv. Chim. Acta* **16** (1933) 848.
8. I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.* **64** (1942) 2988
9. M. Kesler and A. Pregernik, *Arhiv kem.* **27** (1955) 37
10. A. E. Remick, *Electronic Interpretation of Organic Chemistry,* 2nd Ed., New York 1950.
11. G. C. Hampson, *Trans. Faraday Soc.* **30** (1934) 877.

IZVOD

Strukturna istraživanja alkilmerkuri bromida i alkilmerkuri sulfida metodom dipolnog momenta

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Određeni su dipolni momenti slijedećih alkil merkuri bromida i sulfida: CH_3HgBr, C_2H_5HgBr, $n\text{-}C_3H_7HgBr$, $n\text{-}C_4H_9HgBr$, $(CH_3Hg)_2S$, $(C_2H_5Hg)_2S$ i $(n\text{-}C_3H_7Hg)_2S$. Provedena je diskusija dipolnih momenata veza pa je nađeno da se promjena dipolnog momenta kod ovih spojeva može tumačiti uglavnom promjenom dipola veze R-Hg, dok je dipol veze Hg-Br i veze Hg-S približno konstantan.

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