[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Electric Moments of Some Organomercuric Halides in Dioxane[1]

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Practically all of the available experimental evidence indicates that the configuration of dicovalent mercury compounds is linear both in the vapor and solid states. This is in accord with the postulate that *sp* bonds have a maximum strength when the bond angle is 180°.

The determination of the configuration of mercury compounds in solution by measurement of their electric moments has been hindered by the very low solubility of many of these compounds in non-polar liquids. By working at 142° Hampson[2] obtained the moments of some symmetrical mercury diaryls in decalin. These moments differed from zero, being as large as 1.1 *D* for mercury di-*p*-chlorophenyl. His results indicated that the mercury valence angle in these compounds was less than 180°, and that it varied somewhat with different substituents. He concluded that the moment of the carbon-to-mercury linkage was small, probably about 0.5, with the negative pole toward the mercury.

The electric moments of the mercuric halides were determined in this Laboratory[3] in dioxane, the only non-polar liquid of sufficient solvent power. As the moment obtained for mercury diphenyl in dioxane, 0.42, checked the value obtained by Hampson in benzene and decalin, the authors concluded that the oxygen of dioxane does not form a coördinate link with mercury, and that dioxane is therefore a suitable solvent for determining dielectric properties of mercury compounds. The moments obtained for the halides were interpreted as revealing a non-linear configuration. At about the same time, Braune and Linke[4] reported zero moments for the mercuric halides in the vapor state.

Crenshaw, Cope and co-workers[5] concluded from vapor pressure measurements that the mercuric halides form dioxanates in dioxane solution. Analyses of the crystallized dioxanates revealed that one molecule of halide combined with one molecule of dioxane. They claimed that our conclusion with regard to the lack of coördination between dioxane and mercury compounds was questionable, and that the electric moments of the halides determined in dioxane solution were of "doubtful significance."

As a continuation of the investigation of dielectric properties of mercury compounds in dioxane solution, the moments of phenylmercuric bromide, *p*-tolylmercuric bromide, *p*-chlorophenylmercuric bromide, butylmercuric bromide, and amylmercuric chloride have been determined. The low solubility of phenylmercuric bromide in dioxane made it necessary to work at 50° with this compound.

Experimental

Preparation and Purification of Compounds.—The organomercuric bromides were prepared by the method of Hilpert and Grüttner,[6] adding mercuric bromide to the organomagnesium bromides in ether. The products were washed with alcohol and ether, subjected to repeated crystallizations from benzene and dioxane, and dried for a few hours in a stream of dry air at about 75°; melting points: phenylmercuric bromide 276°, *p*-tolylmercuric bromide 236°, *p*-chlorophenylmercuric bromide 239°, butylmercuric bromide 130°. Amylmercuric chloride was prepared by adding mercuric chloride to amylmagnesium chloride in ether and purified in the same manner as the bromides; m. p. 125°.

Commercial chlorobenzene was distilled through a column one meter in length packed with glass helices. Fractions having the same index of refraction were used in preparing solutions; n^{25}_D 1.5217, d^{25}_4 1.1012.

Merck reagent grade benzene was dried by refluxing over sodium and distilled in an all-glass still. Commercial dioxane was purified in a similar manner.

Measurements and Calculations.—The measurement of dielectric constants and densities, and the calculation of the solute polarization at infinite dilution have been described previously.[7] The molar refractions were calculated from the values for the mercuric halides reported by Fajans,[8] the value for mercury diphenyl reported by Hampson,[2] and the value for mercury diethyl reported by Bergmann and Schutz.[9] Atomic polarizations were neglected in calculating electric moments.

Discussion of Results

The small difference between the moments of amylmercuric chloride in dioxane and benzene is

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[1] Presented before the Physical and Inorganic Division at the Cincinnati meeting of the American Chemical Society, April, 1940.

[2] Hampson, *Trans. Faraday Soc.*, **30**, 877 (1934).

[3] (a) Curran and Wenzke, THIS JOURNAL, **57**, 2162 (1935); (b) these moments have recently been recalculated, using more accurate values of the electronic polarizations, Curran, *ibid.*, **63**, 1470 (1941).

[4] Braune and Linke, *Z. physik. Chem.*, **31B**, 12 (1935).

[5] Crenshaw, Cope, Finkelstein and Rogan, THIS JOURNAL, **60**, 2308 (1938).

[6] Hilpert and Grüttner, *Ber.*, **46**, 1686 (1913).

[7] McCusker and Curran, THIS JOURNAL, **64**, 614 (1942).

[8] Fajans, *Z. Elektrochem.*, **34**, 517 (1928).

[9] Bergmann and Schutz, *Z. physik. Chem.*, **19B**, 401 (1932).

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS

c_2	ϵ	d
Dioxane–Phenylmercuric Bromide 50°		
0.00000	2.182	1.0002
.00677	2.270	1.0193
.00711	2.274	1.0200
.00715	2.276	1.0201
Dioxane–*p*-Tolylmercuric Bromide 50°		
0.00000	2.190	1.0007
.00802	2.314	1.0221
.00944	2.338	1.0258
.01026	2.349	1.0280
Dioxane–*p*-Tolylmercuric Bromide 25°		
0.00000	2.225	1.0274
.00880	2.381	1.0523
.00981	2.401	1.0548
Dioxane–*p*-Chlorophenylmercuric Bromide 25°		
0.00000	2.225	1.0274
.00602	2.254	1.0450
.00822	2.265	1.0529
.00955	2.271	1.0564
Dioxane–Butylmercuric Bromide 25°		
0.00000	2.221	1.0265
.00940	2.386	1.0500
.01008	2.396	1.0514
.01355	2.456	....
Dioxane–Amylmercuric Chloride 25°		
0.00000	2.228	1.0257
.00854	2.385	1.0429
.01038	2.417	1.0464
.01147	2.438	1.0492
Benzene–Amylmercuric Chloride 25°		
0.00000	2.276	0.8737
.00835	2.420	0.8922
.00884	2.429	0.8932
Dioxane–Chlorobenzene 25°		
0.00000	2.218	1.0270
.02061	2.299	1.0288
.02887	2.330	1.0296
.03829	2.366	1.0305
Benzene–Chlorobenzene 25°		
0.00000	2.276	0.8734
.02210	2.347	0.8791
.03011	2.384	0.8809
.04285	2.427	0.8845

TABLE II

POLARIZATIONS AND ELECTRIC MOMENTS

	$P_{2\infty}$	MR_D	μ
Phenylmercuric bromide (50°)	227.9	47.7	3.06
p-Tolylmercuric bromide (50°)	273.5	52.3	3.39
p-Tolylmercuric bromide (25°)	292.1	52.3	3.39
p-Chlorophenylmercuric bromide	104.1	52.8	1.57
Butylmercuric bromide	288.9	40.7	3.45
Amylmercuric chloride (dioxane)	301.8	41.7	3.53
Amylmercuric chloride (benzene)	292.1	41.7	3.47
Chlorobenzene (dioxane)	85.4	31.1	1.62
Chlorobenzene (benzene)	82.5	31.1	1.57

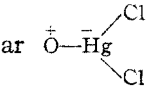
about the same as the variation in moment exhibited by chlorobenzene in these two solvents. This indicates that the specific solvent effect of dioxane on the moments of the organomercuric halides is small, and that dioxane does not coördinate in solution with these compounds.

The moments reported by Hampson[2] for the mercury diaryls suggest the strong contribution of such structures as $^+C_6H_5{=}Hg^-{-}C_6H_5$ and $^+Cl{=}C_6H_4{=}Hg^-{-}C_6H_4Cl$ to these molecules. A comparison of the moments of butylmercuric bromide and phenylmercuric bromide, however, shows that these highly polar structures do not contribute appreciably to the arylmercuric halides. The increase in moment obtained by substituting a butyl for a phenyl group in phenylmercuric bromide is 0.4, exactly what would be expected in the absence of any double bond character for the phenyl carbon-to-mercury bond. This reluctance of dicovalent mercury to use its two unoccupied 6*p* orbitals is further evidence that the heavier elements do not readily form double bonds.

The moments of the arylmercuric bromides listed in Table II reveal that these compounds are not linear. In order to calculate the mercury valence angles it is necessary to assign a value to the C–Hg bond moment. The moments of di-*p*-tolyl mercury and diphenyl mercury show that in the latter compound mercury is certainly more negative with respect to carbon than are the para hydrogen atoms. It is not possible to accurately evaluate the difference between the C–H and C–Hg moments, but if the H–C dipole is taken as 0.3 the C–Hg moment is probably close to zero. In the alkylmercuric halides mercury is definitely negative with respect to carbon.

Assuming a value of 0.3 for the over-all $H\text{-}C_6H_4\text{-}Hg$ moment, 0.4 for the $CH_3\text{-}C_6H_5$ moment, and 1.6 as the difference between the C-Cl and C-H dipoles, the mercury valence angles in *p*-tolylmercuric bromide and *p*-chlorophenylmercuric bromide have been calculated by comparing the moments of these compounds with that of phenylmercuric bromide. These calculations give 140 and 167° for the mercury valence angles, indicating that in the arylmercuric halides, as in the mercury diaryls, the valence angle depends on the nature of the aryl group. The identical value obtained for the moment of *p*-tolylmercuric bromide at 50 and 25° indicates that the average mercury valence angle in this compound does not vary appreciably over this temperature range.

The average moment calculated for the Hg-Br bond in the arylmercuric bromides is 2.75. The small difference between the moments of amylmercuric chloride and butylmercuric bromide indicates that the Hg-Cl moment is about 0.1 greater than the Hg-Br moment. Oesper and Smyth have recently reported[10] the value 3.0 for the Hg-Cl moment in benzylmercuric chloride, calculated on the assumptions of an 180° mercury bond angle and a zero moment for the C-Hg bond in this compound.

The large moments of the mercury-to-halogen bonds, compared to the small moments obtained for the mercuric halides in dioxane, disprove the contention of Crenshaw, Cope and co-workers[5] that dioxane coördinates with the mercuric halides in solution. Such coördination would result in a co-planar  $\overset{+}{\mathrm{O}}-\overset{-}{\mathrm{Hg}}\begin{smallmatrix}\diagup \mathrm{Cl}\\ \diagdown \mathrm{Cl}\end{smallmatrix}$ configuration for the mercuric chloride dioxanate, with 120° valence angles. This complex would have a moment greater than 5.0. The bromide and iodide dioxanates would have slightly smaller moments. The experimental values for the moments of mercuric chloride, bromide and iodide are 1.43, 1.53 and 1.67.[3b]

It appears to the author that the dioxanates of the mercuric halides result from the formation of O---Hg dipole-dipole bonds, similar to the H_2O---M^+ ion-dipole bonds in hydrated cations of many transitional elements. This interpretation is consistent with the increase in moment from the chloride to the iodide, as the formation of the O---Hg bonds would probably result in steric repulsion between the halogen atoms and the methylene groups in dioxane, forcing the mercury to assume a valence angle less than 180°. This steric effect is greatest for mercuric iodide; this molecule would be expected to have the smallest valence angle and therefore possibly the largest moment. The calculation of these mercury valence angles from steric considerations is necessarily an approximation because of the unknown O---Hg distance. Assuming this internuclear distance to be 2.5 Å. (the sum of the O^{--} and the Hg^{++} radii), the mercury valence angles required to prevent contact between the halogen atoms and the methylene groups have been measured from diagrams constructed with the aid of the mercury–halogen internuclear distances reported from electron diffraction measurements,[11] the van der Waals radii listed by Pauling,[12] and the oxygen valence angle in dioxane, 110°, reported by Branch and Calvin.[13] These angles are 166°, 158° and 153° for mercuric chloride, bromide and iodide. The mercury valence angles calculated from the moments of mercuric chloride and mercuric bromide, taking the mercury-to-halogen bond moments as 2.9 and 2.8, and assuming that the formation of the O---Hg dipole-dipole bond introduces no appreciable moment,[14] are 152° for mercuric chloride and 148° for mercuric bromide.

The proposal of dipole-dipole bonds between oxygen and mercury in the dioxanates of the mercuric halides is consistent with the instability of the solid chloride and iodide dioxanates in air, and with their heats of formation, about 5 kcal. per mole,[5] which are similar to the heats of formation of hydrogen bonds.

Summary

1. Dielectric constants and densities are reported for dioxane solutions of phenylmercuric bromide and *p*-tolylmercuric bromide at 50°, for dioxane solutions of *p*-tolylmercuric bromide, *p*-chlorophenylmercuric bromide, butylmercuric bromide, amylmercuric chloride, and chlorobenzene at 25°, and for benzene solutions of amylmercuric chloride and chlorobenzene at 25°.

2. An analysis of the electric moments of the arylmercuric bromides shows that these compounds are not linear.

3. A comparison of the moments of the arylmercuric bromides with those of the alkylmercuric halides indicates that the phenyl carbon-to-mercury bond has practically no double bond character.

4. The electric moments of the mercuric halides and the organomercuric halides in dioxane show conclusively that dioxane does not form coördinate bonds with these compounds in solution.

5. Dielectric data are shown to be consist-

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[10] Oesper and Smyth, THIS JOURNAL, **64**, 173 (1942).

[11] Gregg, Hampson, Jenkins, Jones and Sutton, *Trans. Faraday Soc.*, **33**, 859 (1937).

[12] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 189.

[13] Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 122.

[14] The formation of the hydrogen bond, which is similar in character to the proposed dipole-dipole bond, probably does not produce an appreciable moment in most instances. The electric moments of water, alcohols and carboxylic acids in dioxane are very nearly equal to the moments obtained for these compounds in the gaseous state.

ent with the postulate of dipole-dipole bonds between oxygen and mercury in dioxane solutions of the mercuric halides.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Anomalous Electroreduction of Water at the Dropping Mercury Electrode in Relatively Concentrated Salt Solutions[1]

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In an investigation of the electroreduction of iodate and bromate ions, the results of which will be communicated in a subsequent paper, we found a marked increase in the "apparent" diffusion currents with increasing concentration of potassium chloride, when the concentration of this salt was greater than 0.5 *M*. A similar effect of the concentration of potassium chloride on the "apparent" diffusion current of other reducible ions was found. Further investigations showed that these, and some related, effects were due to an anomalous electroreduction of water molecules. By an electroreduction of a water molecule we mean the introduction of an electron directly into a water molecule to produce a hydrogen atom and an hydroxyl ion. The current resulting from this reduction process is called the "water current" and its characteristics and partial interpretation are discussed in this paper.

Experimental

The manual apparatus described in a previous communication[3] was used. All experiments were carried out in a thermostat at 25 ± 0.02°. Solutions were made up using reagent quality salts and conductivity water. The current measurements were precise to ± 1 %, and the diffusion currents reported in this paper have been corrected for the residual current. Unless otherwise stated, the characteristics of the capillary used were: m = 1.80 mg./sec and t = 3.50 seconds at −0.6 v. (*vs.* S. C. E.) in 0.1 *M* potassium chloride. All potentials are based on the S. C. E. at 25° as a reference electrode.

The Anomalous c. v. Curve of Thallous Chloride in 4 *M* Potassium Chloride Solution.—In Fig. 1. the c. v. curves obtained with 0.001 *M* thallous chloride in air-free 0.1 and 4 *M* potassium chloride solutions are shown. The residual current in 4 *M* potassium chloride is almost identical with that found in 0.1 *M* potassium chloride. Curve 2 has a normal appearance and the slight decrease in the diffusion current with increasing negative potential is due to a decrease in the quantity $m^{2/3}t^{1/6}$ with increasing negative potential.[3,4] It is evident that practically the same diffusion current of thallium is found in 0.1 and 4 *M* potassium chloride solutions. In curve 3, however, the current begins to rise at −0.9 v. and increases with increasing negative potential until a maximum value is reached at a potential of the order of −1.35 v. When the potential is made more negative than −1.4 v., the current decreases and the decrease is much greater than that corresponding

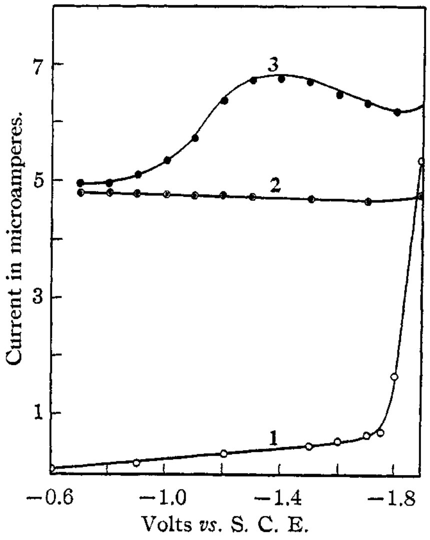

Fig. 1.—Current–voltage curves of thallous chloride in potassium chloride solutions: Curve 1 is the residual current in 4 *M* potassium chloride; Curve 2, 0.001 *M* thallous chloride in 0.1 *M* potassium chloride; Curve 3, 0.001 *M* thallous chloride in 4 *M* potassium chloride. Curves 2 and 3 have been corrected for the residual current.

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[1] From a thesis submitted by Edwin F. Orlemann to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941.

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[3] J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939).

[4] I. M. Kolthoff and E. F. Orlemann, *ibid.*, **63**, 2085 (1941).