Electric Moments of Inorganic Halides in Dioxane. II. Chlorides of Boron, Aluminum, Iron, Silicon, Germanium and Tin[1]

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In the first paper[2] of this series, the degree of coördination of phosphorus, arsenic and antimony halides with dioxane was estimated from electric moment data. Further similar studies on the chlorides of some other trivalent elements and some of the tetravalent elements of Group IV B have been made. The number of compounds suitable for such study was limited either by low solubility in dioxane or by the occurrence of reactions other than coördination between the halide and dioxane. Whereas the chlorides of boron and aluminum caused no decomposition of dioxane, the corresponding bromides were found to react with this solvent to form decomposition products, the reaction with boron bromide taking place violently. In the case of titanium tetrachloride electric moment data of sufficient accuracy were unobtainable due to the low solubility of the dioxanate in dioxane.

Experimental

Preparation and Purification of Compounds.—Boron chloride was prepared from boron fluoride and aluminum chloride by the method of Gamble, Gilmont and Stiff.[3] The product was purified by several distillations and was finally absorbed in weighed amounts of cold dioxane, the composition of each solution being checked by analysis for chlorine. All manipulations were carried out under conditions which effectively prevented absorption of moisture.

Anhydrous aluminum chloride, a Baker c. p. product, was resublimed three times in a current of carbon dioxide, using an all-glass apparatus. The final product was sublimed directly into weighing bottles and anhydrous dioxane added.

Anhydrous ferric chloride was prepared by passing dry chlorine over heated standard iron wire in an all-glass apparatus. The apparatus was so designed that the product could be sublimed in an atmosphere of chlorine, without removal from the apparatus, through two glass wool plugs in series directly into weighing bottles. The chlorine atmosphere in the receivers was replaced by drawing a slow current of dry air over the sublimate. Analysis for chlorine indicated a purity of 99.8% for the product. Samples were prepared by direct addition of dioxane.

Silicon tetrachloride was prepared and purified by a standard method.[4] The product was fractionally distilled

and a middle fraction boiling at 57° was used in sample preparation.

Germanium tetrachloride was obtained by the purification of a sample furnished through the courtesy of the Eagle–Picher Lead Company. Dissolved chlorine was removed by treatment with mercury and the chlorine-free liquid fractionally distilled through a glass-helix packed column. The middle fraction, boiling at 83.6° at 751 mm., was used in sample preparation. Analysis of this fraction for chlorine by the method of Baxter and Cooper[5] indicated a purity above 99%.

Anhydrous stannic chloride, a Baker c. p. product, was fractionally distilled several times in an atmosphere of carbon dioxide and a sample of the distillate sealed off in a glass tube. Absorption of moisture was prevented by opening the glass tube and making up the dioxane solutions in a dry-atmosphere chamber fitted with long-sleeved rubber gloves.

Dioxane for all purposes was purified by refluxing the commercial product over sodium for twenty-four hours and fractionally distilling.

Measurements and Calculations.—Densities and dielectric constants were measured as previously described.[2] The solute polarizations at infinite dilution were calculated by the method of Hedestrand.[6] The $\Delta\epsilon/C_2$ ratio for the dioxane solutions of boron chloride, germanium tetrachloride and stannic chloride showed a slight variation with concentration. The average value of this ratio, rather than an extrapolated value, was used in calculating the total polarization of each compound. The difference in the moments calculated from the average ratio and from that for the most dilute solution is in every case within the limit of accuracy indicated in Table II.

The distortion polarizations listed in Table II were determined in the following manner. The value for germanium tetrachloride is the polarization of the pure liquid.[7] The values for boron chloride and stannic chloride are the total polarizations at infinite dilution in benzene solution.[8] The value for silicon tetrachloride is the molar refraction for the sodium D line in the vapor state,[9] plus ten per cent. The values for aluminum chloride and ferric chloride are the molar refractions for the sodium D line determined in water solution,[10] plus ten per cent.

Attempts to measure the dielectric constants of dioxane solution of boron bromide gave values which changed continuously with time. That decomposition of dioxane results from its interaction with boron bromide was shown by the incomplete precipitation of bromine, as silver bromide, from the hydrolyzed solutions.

Dielectric constants and densities are listed in Table I.

(1) Presented in part at the Atlantic City meeting of the American Chemical Society, September, 1941.

(2) McCusker and Curran, THIS JOURNAL, **64**, 614 (1942).

(3) Gamble, Gilmont and Stiff, *ibid.*, **62**, 1257 (1940).

(4) Biltz, Hall and Blanchard, "Laboratory Methods of Inorganic Chemistry," 2nd ed., John Wiley and Sons. Inc., New York, N. Y., 1928, p. 80.

(5) Baxter and Cooper, *J. Phys. Chem.*, **28**, 1049 (1924).

(6) Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

(7) Miller, THIS JOURNAL, **56**, 2630 (1934).

(8) Ulich and Nespital, *Z. Elektrochem.*, **37**, 559 (1931).

(9) Goldschmidt and Holemann, *Z. physik. Chem.*, **B24**, 199 (1934).

(10) Limann, *Z. Physik*, **8**, 13 (1922).

The calculated polarizations and electric moments are listed in Table II. Electric moments are expressed in Debye units.

TABLE I

D̊IELECTRIC CONSTANTS AND DENSITIES OF DIOXANE SOLUTIONS AT 25°

c_2	ϵ	d
Boron Chloride		
0.00000	2.211	1.0279
.01158	2.599	1.0355
.01342	2.674	1.0368
.01880	2.880	1.0408
Aluminum Chloride		
0.00000	2.211	1.0280
.00805	2.264	1.0352
.01045	2.284	1.0373
.01291	2.297	1.0395
.01510	2.309	1.0414
Ferric Chloride		
0.00000	2.211	1.0279
.00556	2.232	1.0350
.01378	2.257	1.0452
.01601	2.267	1.0479
Silicon Tetrachloride		
.00000	2.223	1.0279
.01618	2.228	1.0369
.02242	2.230	1.0430
Germanium Tetrachloride		
0.00000	2.213	1.0280
.01031	2.224	1.0394
.01930	2.228	1.0494
.02530	2.231	1.0567
Stannic Chloride		
0.00000	2.214	1.0279
.00504	2.337	1.0391
.00646	2.358	1.0419
.00654	2.360	1.0425
.00859	2.394	1.0471

TABLE II

POLARIZATIONS AND ELECTRIC MOMENTS

	$P_{2\infty}$	P_{E+A}	μ
Boron chloride	517	24.5	4.86 ± 0.07
Aluminum chloride	112	27.0	2.02 ± .05
Ferric chloride	67	33.0	1.27 ± .05
Silicon tetrachloride	30	31.9	0.0
Germanium tetrachloride	47	37.1	0.67 ± .08
Stannic chloride	345	42.5	3.82 ± .15

Discussion

The symmetrical planar configuration of boron chloride in inert solvents, as evidenced by its zero moment in benzene,[8] gives way to a tetrahedral complex in donor solvents. The value obtained by Ulich and Nespital[8] for the moment of the etherate of boron chloride, $(C_2H_5)_2O \cdot BCl_3$, is 5.98 D. Assuming that the ether moment vector,

1.2, makes an angle of 125° with the $^+O\text{-}B^-$ bond, the sum of the $^+O\text{-}B^-$ bond moment and the resultant of the three B–Cl dipoles is 5.2. This value should be equal to the moment of the dioxanate of boron chloride, $C_4H_8O_2 \cdot BCl_3$. Comparison of the observed moment of boron chloride in dioxane, 4.86, and the moment calculated for the complex, 5.2, indicates that coördination of boron chloride with dioxane is almost complete.

A similar calculation for aluminum chloride from the moment of its etherate,[8] 6.54, yields a value of 5.6 for the moment of $C_4H_8O_2 \cdot AlCl_3$. The observed moment of aluminum chloride in dioxane is 2.02. This low moment indicates either that the extent of coördination is small, or that in a large number of the complexes two dioxane molecules coördinate with each aluminum atom to form trigonal bipyramids having the three chlorine atoms in the equatorial plane. Such complexes would have zero moments. Since aluminum chloride may be expected to exist as a dimer in completely inert solvents, indications of interaction were sought in cryoscopic measurements on the solutions listed in Table I. These measurements indicated that aluminum chloride is monomolecularly dispersed in dioxane solution. It is difficult to understand how dioxane could break up the aluminum chloride dimers without at the same time forming coördinate bonds with aluminum.

The apparent lack of coördination between ferric chloride and dioxane, as evidenced by the low moment, 1.27, is surprising. The structure of the isolated ferric chloride molecule is not known. The magnetic moment of this compound in the solid state[11] indicates five unpaired electrons. The most probable bond types for a ferric chloride molecule with five unpaired electrons are sp^2 and dsp, the former resulting in a trigonal planar structure having a zero moment, and the latter in an unsymmetrical planar structure having a low moment. Coördination complexes of ferric chloride and dioxane having various configurations are possible, most of which would have large moments. It appears from the observed low moment that only a small percentage of ferric chloride molecules coördinate with dioxane in solution.

The complete lack of coördination between dioxane and silicon tetrachloride, as evidenced by

(11) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 107.

the zero moment of this compound in dioxane, is of importance in connection with the mechanism of the hydrolysis of silicon tetrachloride. This reaction has been interpreted[12] as resulting from the formation of $^{+}O\text{-Si}^{-}$ bonds with the subsequent splitting off of hydrogen chloride. A mechanism involving the formation of Cl–H bonds would appear more probable unless the smaller size of the water molecule, compared to dioxane, makes the formation of an $^{+}O\text{-Si}^{-}$ bond possible in this special case.

The low moment of germanium tetrachloride in dioxane reveals that only a small amount of interaction takes place between these compounds in solution. Efforts to isolate a solid dioxanate of germanium tetrachloride have been unsuccessful and this confirms the view that very little tendency exists for germanium to expand its valence shell in forming coördinate bonds with dioxane. A comparison of the behavior of germanium and titanium tetrachlorides toward dioxane is of interest. While the solubility of the complex of titanium tetrachloride in dioxane is too small to permit determination of its moment in dioxane, the existence of the crystalline complex indicates that coördination readily occurs, at least in the solid state. The greater size of the titanium atom is probably responsible for the difference in the behavior of titanium and germanium tetrachlorides.

The effect of atomic radius is further shown in the case of stannic chloride. A solid coördina-

(12) Sidgwick, J. Chem. Soc., **125**, 2672 (1924).

tion complex having the composition $SnCl_4 \cdot 2C_4H_8O_2$ has previously been reported.[13] That coördination persists in solution is evident from a comparison of the zero moment obtained for stannic chloride in benzene[8] with the value, 3.82, in dioxane. The values[14] reported for $(C_2H_5)_2O \cdot SnCl_4$ and $2(CH_3)_2CO \cdot SnCl_4$ are 3.60 and 7.7, respectively. The possible arrangements of the chlorine atoms and dioxane molecules in the octahedral complexes would permit various configurations having moments ranging from 0 to about 6. For this reason it is not possible to estimate from the data the degree of coördination of stannic chloride with dioxane, but it is evident that dioxane coördinates to a greater extent with stannic chloride than with germanium tetrachloride.

Summary

Electric moments have been determined for boron chloride, aluminum chloride, ferric chloride, silicon tetrachloride, germanium tetrachloride and stannic chloride in dioxane. Coördination between dioxane and boron chloride in solution is almost complete. Ferric chloride appears to interact only slightly with dioxane. The extent of coördination of the group IV B elements increases with increasing size of the central atom, silicon tetrachloride having a zero moment and stannic chloride a moment of 3.8 in dioxane.

(13) Rheinboldt and Boy, J. prakt. Chem., **129**, 268 (1931).
(14) Ulich, Hertel and Nespital, Z. physik. Chem., **B17**, 21 (1932).

The Effect of Temperature on the Surface Tension and Density of Some Halogen Substituted Acetic Acids

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In a recent investigation carried out in this Laboratory, accurate surface tension–temperature data were required for the comparison of certain physico-chemical properties of the halogen substituted acetic acids. Search of the literature revealed the apparent unavailability of such data for most of the compounds involved. To supply this deficiency, the surface tension–temperature data for monobromoacetic acid and monoiodoacetic acid were determined over an appreciable temperature range in their molten states.

Experimental

Materials.—The compounds were Eastman Kodak Company reagent quality. The melting point of the monobromoacetic acid was 49.7° and that of monoiodoacetic acid 81.9°. No decomposition of the latter was observed below 130° during the measurements. The decomposition of this compound below its boiling point is believed to be dependent upon traces of mineral acids and moisture present[1]; therefore, great care was used to prevent traces of those impurities from reaching the molten monoiodoacetic acid.

(1) Eastman Kodak Company, private communication.