

(3.85 g.) which upon cooling in the presence of petroleum ether (b. p. 60–68°) produced a solid product (2.70 g.; m. p. 50–65°), was obtained. Crystallization of the solid material from a mixture of ether and alcohol yielded a pure compound (m. p. 71–72°), which gave a dark purple color with a ferric chloride solution.

Anal. Calcd. for $C_{26}H_{31}NO_4$: C, 74.07; H, 7.42; N, 3.33. Found: C, 73.94; H, 7.44; N, 3.38.

The Hydrolysis of Ethyl β -Di-*n*-propylamino- α,γ -dibenzoylcrotonate was carried out as follows. The dibenzoylated amine (1.0 g.), dissolved in acetic acid (10 ml.), was boiled for ten minutes. After cooling, water was added, and a precipitate (0.51 g.) was obtained. Crystallization from a mixture of benzene and petroleum ether produced the pure product (m. p. 147–147.5°).

Anal. Calcd. for $C_{24}H_{29}NO_3$: C, 76.76; H, 6.71; N, 3.73. Found: C, 77.08; H, 6.66; N, 3.87.

Synthesis of 3-Benzoyl-4-di-*n*-propylamino-6-phenylpyrone.—This synthesis was conducted in the manner described above for the preparation of the corresponding diethylamino compound. The melting point (147–147.5°) of the synthetic specimen was unchanged by the addition of the compound produced by the acid treatment of the ethyl β -di-*n*-propylamino- α,γ -dibenzoylcrotonate.

Summary

It was found that benzylation of ethyl β -diethylaminocrotonate and of ethyl β -di-*n*-propylaminocrotonate yields α,γ -dibenzoyl derivatives. These dibenzoylation products undergo ring closure to produce substituted pyrones, which were synthesized.

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

Electric Moments of Inorganic Halides in Dioxane. I. Phosphorus, Arsenic and Antimony Trihalides¹

BY P. A. McCUSKER AND B. COLUMBA CURRAN

Molecular complexes of inorganic halides with donor compounds are commonly interpreted as resulting from the formation of coördinate bonds between the acceptor and donor molecules. Studies of the dielectric properties of solutions of coördination complexes enable the persistence of coördination in solution to be detected and an estimate of the extent of coördination to be made. In the majority of previous investigations² of this kind, solutions of crystalline complexes in non-polar solvents were studied. Electric moments calculated from such data are of significance for only those complexes which are not dissociated in non-polar solvents. This work has thus been limited to those halides in which the central atoms form strong bonds with donor molecules.

Complexes of inorganic halides with dioxane are not subject to this limitation. Dioxane has, among ordinarily available solvents, the unique characteristic of being a donor compound and at the same time non-polar. This latter character permits the use of the Debye equation in calculating the electric moments of dioxanates in dioxane solution, and in estimating therefrom the extent of coördination. A knowledge of the extent of coördination affords a means of comparing the relative tendencies of certain elements to use

available bond orbitals in forming coördinate linkages with donor compounds.

Halides were chosen in this series of investigations because in these compounds the residual positive charge on the central atoms promotes coördination. Electric moments of some trihalides of members of the nitrogen family are reported in this first paper. The saturated character of nitrogen in its trihalides and the low solubility of bismuth halides in dioxane have limited the compounds investigated to the phosphorus, arsenic and antimony halides.

Incidental to the main purpose of the present work, but confirming the conclusions as to the formation of molecular coördination compounds between the halides studied and dioxane, definite crystalline compounds of dioxane with certain of these halides were isolated. Further studies on these crystalline dioxanates are being carried out and will be reported in a later paper.

Experimental

Preparation and Purification of Compounds.—Phosphorus trichloride, phosphorus tribromide and arsenic trichloride were purified by fractional distillation of the c. p. liquids directly into weighing bottles under moisture-free conditions in an all glass system.

Arsenic tribromide, an Eastman Kodak Co. product, was fractionally distilled, a middle fraction being used in sample preparation.

(1) The material in this paper was presented in part at the Detroit meeting of the American Chemical Society, September, 1940.

(2) Ulich and Nespital, *Z. angew. Chem.*, **44**, 750 (1931).

Arsenic triiodide was prepared by a standard method³ and purified by recrystallization from benzene. Analysis for iodine was used to check the purity.

Antimony trichloride, a Baker C. P. product, was added to anhydrous dioxane; the dioxanate formed was purified by several recrystallizations from dioxane and excess solvent removed in a vacuum desiccator. The composition of the dioxanate was determined by analysis for chlorine and the dioxanate used directly in sample preparation.

Antimony tribromide was prepared from antimony powder and bromine in carbon disulfide. The product was recrystallized from carbon disulfide and converted to a crystalline dioxanate by reaction with dry dioxane. The dioxanate was further purified by recrystallization from dioxane and excess solvent removed in a vacuum desiccator. The composition of the dioxanate was determined by analysis for bromine and the crystalline product used in sample preparation.

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

Measurements and Calculations.—Densities were measured with an Ostwald-Sprengel pycnometer having a volume of 5 ml. Dielectric constants were determined by the method of Otto and Wenzke⁴ using similar apparatus. The polarizations at infinite dilution were calculated by the method of Hedestrand.⁵ In the absence of solute association and other abnormalities, the dielectric constant-concentration curve for solutions of a polar solute in a non-polar solvent is a straight line up to solute mole fractions of about 0.05. Designating $\epsilon_{12} - \epsilon_1$ as $\Delta\epsilon$, the $\Delta\epsilon/C_2$ ratio is a constant for these solutions. This constancy permits the calculation of the solute polarization at infinite dilution from the dielectric constants and densities of the pure solvent and one solution.

It is evident from the curves in Fig. 1 that the $\Delta\epsilon/C_2$ ratios are not constant for the dioxane solutions of the phosphorus trihalides. Accurate values of the electric moments of these compounds cannot be calculated from the data of Table I. The moments of phosphorus trichloride and phosphorus tribromide listed in Table II were calculated and reported in order to give an approximate picture of the decrease in polarity of these dioxanates with increasing concentration.

An analysis of the data listed in Table I indicates that the $\Delta\epsilon/C_2$ ratios are constant, within the limits of experimental error, for dioxane solutions of the arsenic and antimony trihalides. The low solubility of arsenic triiodide in dioxane, together with the small changes in dielectric constant at the concentrations listed, limits the accuracy of the moment calculated for this compound to ≈ 0.1 .

The distortion polarizations of arsenic tribromide, arsenic triiodide, antimony trichloride and antimony tribromide listed in Table II are the values reported by Malone and Ferguson.⁶ They were determined by measuring the dielectric constants and densities of the solids. The electronic polarizations of phosphorus trichloride and arsenic trichloride are the molar refractions for the sodium

D line determined by Smith.⁷ The electronic polarization listed for phosphorus tribromide was calculated from the value for phosphorus trichloride.

TABLE I
DIELECTRIC CONSTANTS AND DENSITIES OF DIOXANE SOLUTIONS OF PHOSPHORUS, ARSENIC AND ANTIMONY HALIDES AT 25°

C_2	ϵ	d
Phosphorus Trichloride		
0.00000	2.215	1.0279
.01014	2.268	1.0339
.01483	2.289
.01862	2.295	1.0388
.02006	2.298	1.0398
.02844	2.316	1.0445
.03819	2.340	1.0507
.05636	2.356	1.0598
.07467	2.398	1.0708
Phosphorus Tribromide		
0.00000	2.216	1.0278
.01142	2.264	1.0510
.01371	2.271	1.0555
.02505	2.297	1.0786
.03350	2.324
.03572	2.332	1.1000
.06591	2.405	1.1604
Arsenic Trichloride		
0.00000	2.226	1.0262
.01375	2.425	1.0435
.01920	2.507	1.0503
.02691	2.623	1.0598
Arsenic Tribromide		
0.00000	2.225	1.0273
.00749	2.323	1.0472
.01288	2.393	1.0617
.02280	2.521	1.0878
Arsenic Triiodide		
0.00000	2.225	1.0273
.00425	2.254	1.0445
.00446	2.255	1.0452
.00448	2.255	1.0451
Antimony Trichloride		
0.00000	2.225	1.0273
.00742	2.520	1.0412
.00840	2.552	1.0426
.00903	2.590	1.0442
.01030	2.633	1.0459
Antimony Tribromide		
0.00000	2.207	1.0279
.00469	2.383	1.0431
.00570	2.421	1.0463
.00621	2.439	1.0479

Discussion of Results

The solutions of phosphorus trichloride and phosphorus tribromide are the only dioxane solu-

(7) Smith, *Proc. Roy. Soc. (London)*, **136**, 256 (1932).

(3) Booth, "Inorganic Syntheses," McGraw-Hill Book Company, New York, N. Y., 1939, p. 103.

(4) Otto and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **6**, 187 (1934).

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

(6) Malone and Ferguson, *J. Chem. Phys.*, **2**, 101 (1931).

TABLE II
POLARIZATIONS AND ELECTRIC MOMENTS OF PHOSPHORUS,
ARSENIC AND ANTIMONY HALIDES

Compound	$P_{2\infty}$	P_E	P_{E+A}	μ
Phosphorus trichloride	C_2 0.01014	(100.2)	26.15	(1.89)
	C_2 0.03819	(72.0)		(1.49)
Phosphorus tribromide	C_2 0.01142	(88.2)	32.2	(1.65)
	C_2 0.03572	(74.3)		(1.33)
Arsenic trichloride	232	32		3.11
Arsenic tribromide	212		37.6	2.90
Arsenic triiodide	128		59	1.83
Antimony trichloride	594		44	5.16
Antimony tribromide	504		50	5.01

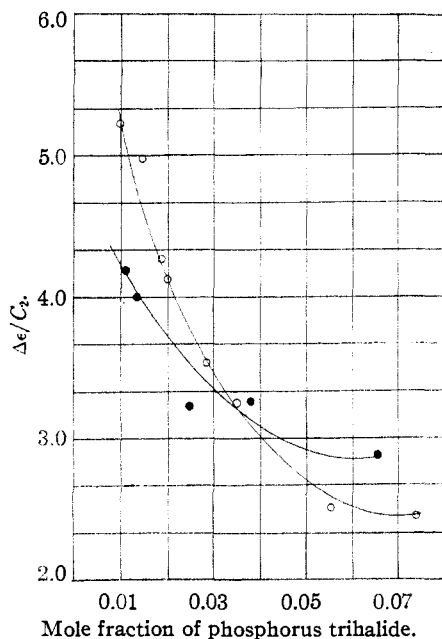


Fig. 1.—Variation of $\Delta\epsilon/C_2$ with concentration of phosphorus trihalides in dioxane: O, PCl_3 ; ●, PBr_3 .

tions known to the authors in which the $\Delta\epsilon/C_2$ ratios decrease with increasing concentration in the dilute region. We are unaware of the cause of this phenomenon. The variation in $\Delta\epsilon/C_2$ for phosphorus trichloride was checked by using a new sample of dioxane having a slightly different dielectric constant. The freezing points determined for both the chloride and bromide solutions indicate that the solutes are not associated at any of the concentrations listed in Table I.

The electric moments obtained by Bergmann and Engel⁸ for phosphorus trichloride and tribromide in carbon tetrachloride are 0.8 and 0.6. A comparison of these values with those listed in Table II indicates that dioxane coordinates with the phosphorus trihalides, as this solvation would result in an increase in moment.

The moments of the arsenic and antimony halides in dioxane may be analyzed by comparing

(8) Bergmann and Engel, *Physik. Z.*, **32**, 507 (1931).

them with values obtained by other investigators in carbon tetrachloride and carbon disulfide. These values are listed in Table III.

TABLE III
ELECTRIC MOMENTS IN DEBYE UNITS OF ARSENIC AND
ANTIMONY TRIHALIDES IN VARIOUS SOLVENTS

	CS_2	CCl_4	Dioxane	$\Delta\mu$
$AsCl_3$..	1.97	3.11	1.1
$AsBr_3$	1.60	1.66	2.90	1.3
AsI_3	0.96	..	1.83	0.9
$SbCl_3$	3.12	..	5.16	2.0
$SbBr_3$	2.47	..	5.01	2.5

These data indicate that dioxane coordinates with the arsenic and antimony trihalides. It is not possible to estimate the extent of coordination between dioxane and antimony at the present time because the moment of the O^+-Sb^- bond is not known. The only moment known to the authors for a coordinate bond with no double bond character is the value reported by Linton⁹ for the N^+-O^- bond in trimethylamine oxide, 4.4. That this value is larger than the moments of most O^+-M^- bonds is evident from an analysis of the moments determined by Ulich and Nesipal² for complexes of donor compounds with beryllium, boron and aluminum halides. The exact values of the O^+-M^- bond moments in these complexes cannot be calculated because the central atom-to-halogen bond moments are not known.¹⁰ By comparison with the C-Cl moment a minimum value of 1.8 may be assigned to the B-Cl bond in the $(C_2H_5)_2O \cdot BCl_3$ complex. Assuming this moment, the value calculated for the O^+-B^- moment is 3.4. This represents a maximum value; the actual moment is probably appreciably lower than 3.4.

The relatively low moment of the O^+-B^- bond in this complex suggests that an O^+-M^- bond results from resonance between a dipole-dipole bond and a purely covalent bond in which two oxygen electrons are equally shared by the oxygen and acceptor atoms. The extent to which the latter structure contributes to the O^+-M^- bond, and therefore the polarity of the bond, should depend on the relative electronegativities of the joined atoms, the specific donor properties of the donor atom, and the unsaturated character of the acceptor atom in the dipole-dipole structure.

(9) Linton, *THIS JOURNAL*, **62**, 1945 (1940).

(10) Moments of some tin halide complexes have been determined, and the value of the Sn-Cl bond moment is known, but the various possible arrangements of the groups in these bipyramidal and octahedral configurations prevent a calculation of the O^+-Sn^- moment from these data.

We hope to be able to evaluate the moments of some O^+-M^- bonds after further investigations in this series.

The arsenic and antimony valence angles in the trihalides are approximately 100° . The halogen atoms are thus very nearly in contact with one another, leaving a portion of the central atom exposed. Coördination with dioxane probably occurs in such a manner as to form trigonal bipyramids or octahedra (depending on whether one or two dioxane molecules coördinate with one halide molecule) in which the unshared electrons occupy one of the corners and the three chlorines are adjacent to one another. These configurations would have maximum moments, and the $SbCl_3 \cdot 2C_4H_8O_2$ complex should have a larger moment than the $SbCl_3 \cdot C_4H_8O_2$ molecule. The moments of the arsenic and antimony trihalides should, therefore, increase with increasing degree of solvation. The freezing points obtained for dioxane solutions of arsenic and antimony trichloride indicate that the solutes are monomolecularly dispersed, ruling out the presence of complexes in which one molecule of dioxane coördinates with two molecules of solute.

The O^+-As^- moment should be slightly greater than the O^+-Sb^- moment because of the greater electron attraction of the arsenic atom. Solvation with dioxane should bring about a greater increase in moments for the arsenic trihalides

than for the corresponding antimony compounds. The data of Table III reveal that this increase is actually smaller for the arsenic halides, indicating that dioxane coördinates less completely with the arsenic halides than with the antimony halides. This is probably due to the smaller size of the arsenic atom.

It may be objected that the moments calculated for these halides in dioxane are of questionable accuracy, as these molecules are solvated. It can be demonstrated that the difference in moment calculated for the solute as MX_3 and as $MX_3 \cdot C_4H_8O_2$ is small. The moment of antimony chloride listed in Table II is 5.16. The value calculated for the solute as $SbCl_3 \cdot C_4H_8O_2$ is 5.15.

Summary

1. Dielectric constants and densities are reported for dioxane solutions of phosphorus trichloride, phosphorus tribromide, arsenic trichloride, arsenic tribromide, arsenic triiodide, antimony trichloride, and antimony tribromide.

2. The $\Delta\epsilon/C_2$ ratios for the dioxane solutions of the phosphorus trihalides decrease with increasing solute concentration.

3. The electric moments determined for the arsenic and antimony trihalides indicate that coördination in dioxane solution occurs to a greater extent with antimony than with arsenic.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Heat Capacities of Red and Yellow Lead Monoxides at High Temperatures

BY HUGH M. SPENCER AND W. MONROE SPICER¹

The individuality and allotropy of the red tetragonal and yellow orthorhombic forms of lead monoxide have been the subject of numerous papers in recent years. References to most of these are given in a paper by one of the authors² in which the free energies of formation of the red and yellow forms are shown to be $-45,101$ and $-44,956$ cal., respectively, at 25° .

In order to round out our knowledge of the thermodynamic properties of the two oxides, their ΔH 's of formation and their heat capacities

(1) Phillip Francis du Pont Research Fellow, 1935-1936; present address, Department of Chemistry, Georgia School of Technology, Atlanta, Georgia.

(2) Hugh M. Spencer and John H. Mote, *THIS JOURNAL*, **54**, 4618 (1932).

TABLE I
HEAT CAPACITY OF LEAD MONOXIDE

Form	Temp., °C.	Mean sp. ht. cal. deg. ⁻¹ g. ⁻¹	Investigator
"Crystalline" ^a	22-98	0.05118	Regnault ³
Fused oxide ^a	22-98	.05089	Regnault ³
Crystalline powder ^b	19-50	.0553	Kopp ⁴
Commercial product ^c	17-99	.05078	Magnus ⁵
Commercial product ^c	19-268	.0523	Magnus ⁵

^a The fused oxide was prepared from red lead and was probably the yellow form, but no reference as to the color of the crystalline sample was made. ^b Larger particles of litharge freed from finer ones by sieving. ^c No reference to color or crystalline form.

(3) H. V. Regnault, *Ann. chim. phys.*, [3] **1**, 129 (1841).

(4) H. Kopp, *Liebig's Ann. Suppl.*, **3**, 1, 289 (1865).

(5) A. Magnus, *Physik. Z.*, **14**, 5 (1913).