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

Crystalline Complexes of Arsenic, Antimony and Bismuth Trihalides with Dioxane

BY C. J. KELLEY[1] AND P. A. MCCUSKER

Dioxane readily coördinates with many inorganic halides to form well-defined crystalline solids. Various workers[2,3,4] have reported the formation of dioxanates of inorganic halides, in most cases only the composition and method of preparation being described. A systematic study of these molecular compounds would be of value in extending our understanding of the variation of the acceptor properties of elements. Since well-defined crystalline complexes appear to be formed readily between dioxane and those inorganic halides with some degree of covalent character, comparison of the stabilities of various dioxanates should give a measure of the relative strengths of the donor–acceptor bonds in these complexes. Measurement of the dissociation pressures affords a convenient means of determining relative stabilities. Such a study has been reported for the dioxanates of the mercuric halides.[5]

In a recent communication[6] from these laboratories the degree of coördination between dioxane and the Group VB trihalides in dioxane solution was estimated from electric moment data. The present paper[7] is concerned with the characterization of these coördination complexes in the solid state. The dioxanate of arsenic trichloride has been reported previously.[8]

Experimental

Preparation and Purification of Compounds.—The preparation and purification of most of the materials have been described previously.[6] Arsenic trifluoride was prepared and purified by a method similar to that described by Russell, Rundle and Yost.[9] A clear, water-white product, b. p. 57.8° at 746 mm., was obtained. Bismuth trichloride was purified by subliming a C. P. Mallinckrodt product in a stream of carbon dioxide. Purity was checked by analysis for chlorine. Calcd. for $BiCl_3$: Cl, 34.0. Found: Cl, 33.8. Purified dioxane was freshly distilled over sodium before use.

All dioxanates were prepared by direct addition of the halides to anhydrous dioxane. The white crystalline complexes separated immediately and were purified by several recrystallizations from dioxane. After filtration of the mixture on a Büchner funnel two procedures were followed. In procedure I, the solvent-free crystals were kept in a vacuum desiccator at a pressure of 15 mm. for three to four hours and then quickly transferred to weighing bottles for analysis. In procedure II, the crystals were pressed between filter papers and let stand in air for several minutes until they appeared to be solvent-free and then transferred to weighing bottles.

Methods of Analysis.—Gravimetric analyses for halogen were made on all dioxanates except the arsenic fluoride complex which was analyzed for arsenic by titration with standard iodine solution. The arsenic trihalide dioxanates dissolved readily in water. The antimony trihalide complexes were dissolved in water containing tartaric acid to prevent precipitation of antimony oxychloride. The bismuth chloride and its dioxanate were dissolved in 3 *N* nitric acid solution.

Measurement of Dissociation Pressures.—Dissociation pressures were measured by a static method using a vacuum-line technique. Solvent was distilled from mixtures of the crystalline complex and solution. Pressures were measured at temperatures controlled to ±0.02°. When sudden changes in pressure were observed the crystals were removed from the apparatus and analyzed. Dissociation pressures were checked by placing crystals of known composition in the vacuum apparatus and measuring the pressure directly.

TABLE I

ANALYTICAL DATA AND MELTING RANGES FOR DIOXANATES

Compound	% Halogen Calcd.	% Halogen Found	Melting range, °C.
$2AsCl_3 \cdot 3C_4H_8O_2$[a]	33.9	33.8	75–81
$2AsBr_3 \cdot 3C_4H_8O_2$	53.7	53.8	60–64
$AsF_3 \cdot C_4H_8O_2$[b]	. .	. .	66–72
$2SbCl_3 \cdot 3C_4H_6O_2$	29.8	29.7	129–132
$SbCl_3 \cdot 2C_4H_8O_2$	26.4	26.5	. . . . .
$2SbBr_3 \cdot 3C_4H_8O_2$	48.4	48.3	155–164
$2BiCl_3 \cdot 3C_4H_8O_2$	23.7	23.8	221–226

[a] Previously reported[8]; included for comparison.

[b] Analyzed for As. Calcd.: As, 34.0. Found: As, 34.0.

Of the trihalides of this group of elements studied only the triiodides of arsenic and antimony failed to yield coördination complexes with dioxane. These iodides are very slightly soluble in dioxane. The remaining compounds yield crystalline solvates of the general formula $2MX_3 \cdot 3C_4H_8O_2$ with the exception of arsenic trifluoride which gives a dioxanate having a 1:1 ratio of halide to dioxane. Antimony trichloride gave in addition to the complex corresponding to the general formula a second complex of higher dioxane content and appreciable dissociation pressure.

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(2) Rheinboldt and Boy, *J. prakt. Chem.*, **129**, 273 (1931).

(3) Rheinboldt, Luyken and Schmittmann, *ibid.*, **148**, 81 (1937), **149**, 30 (1937).

(4) Brand and Türck, *C. A.*, **31**, 212 (1937).

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

(6) McCusker and Curran, *ibid.*, **64**, 614 (1942).

(7) The authors thank Mr. T. A. Schmidt for assistance in some of the experimental work.

(8) Doak, *J. Am. Pharm. Assoc.*, **23**, 541 (1934).

(9) Russell, Rundle and Yost, THIS JOURNAL, **63**, 2825 (1941).

The dioxanates of arsenic trichloride, arsenic tribromide, antimony tribromide and bismuth trichloride whether obtained by procedure I or II described in the experimental part gave analytical results indicating a constant and unvarying composition. From this behavior it may be concluded that the crystals of the above complexes existing in equilibrium with the solvent have relatively low dissociation pressures, since they are unchanged on standing in a vacuum desiccator. Confirmatory studies on the vacuum line showed that the above dioxanates have at 20° dissociation pressures of the order of one to four mm. Because of the slowness with which these crystals come to equilibrium, precise determinations of these dissociation pressures were not made. The stability of these solvates is further indicated by the observation that exposure for periods of ten to fifteen minutes to normal atmosphere caused no detectable change in appearance or composition. The strong hygroscopic character of the unsolvated compounds is well known; the crystalline solvates are at most only slightly hygroscopic.

The dioxanate of arsenic trifluoride is considerably less stable. When procedure II was followed crystals of constant composition $AsF_3 \cdot C_4H_8O_2$ were obtained. Procedure I, however, gave mixtures of varying composition resulting from decomposition in the vacuum desiccator. The high dissociation pressure of the arsenic trifluoride complex causes loss of both dioxane and arsenic trifluoride from the crystals in the vacuum desiccator.

The higher dioxanate of antimony trichloride was obtained when procedure II was followed. This indicates that the crystals in equilibrium with dioxane are of composition $SbCl_3 \cdot 2C_4H_8O_2$ and lose dioxane in the vacuum desiccator to form $2SbCl_3 \cdot 3C_4H_8O_2$. Further studies on the vacuum line of the system $SbCl_3$–dioxane by determination of the equilibrium pressures at varying compositions gave the results shown in Fig. 1. Analyses of the solid were made when the sudden changes in pressure occurred as dioxane was removed from or added to the system. The constant pressure line in Fig. 1 corresponds to the vapor pressure of the saturated solution, 27 mm. at 20°, and the equilibrium pressure of mixtures of the two dioxanates, 23.2 mm. at 20°. This latter pressure is the dissociation pressure of the higher dioxanate. The equilibrium pressure of the lower dioxanate and unsolvated antimony trichloride mixture was not determined precisely due to slowness in reaching equilibrium. Variation of the dissociation pressure of $SbCl_3 \cdot 2C_4H_8O_2$ in the range 0 to 20° was determined as described in the experimental part and is shown in Fig. 2.

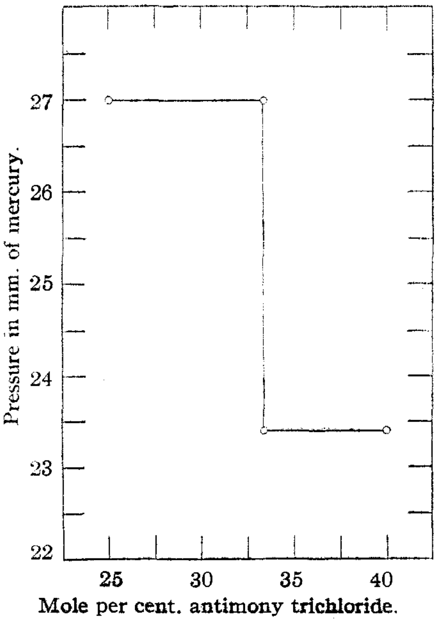

Fig. 1.—Pressure–composition isotherm for a portion of the system antimony trichloride–dioxane at 20°.

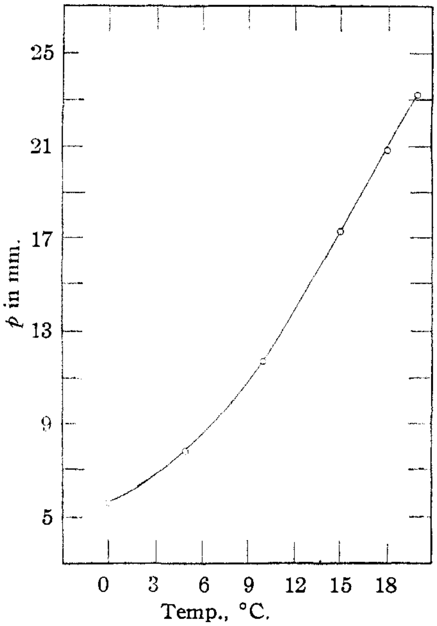

Fig. 2.—Dissociation pressure–temperature curve for $SbCl_3 \cdot 2C_4H_8O_2$.

The behavior on melting of all the dioxanates studied was similar and normal for molecular compounds containing a volatile constituent. Closed capillary tube determinations gave in all cases melting ranges whose values were reproducible within a few degrees. The melting ranges observed are listed in Table I.

Complete dissociation in the vapor phase of the arsenic trichloride dioxanate was shown by subjecting the compound to a distillation through a short Vigreux column. During the first stages of the distillation dioxane came over quite free of arsenic trichloride. The middle fraction solidified in the condenser as $2AsCl_3 \cdot 3C_4H_8O_2$ and the last fraction consisted of arsenic trichloride. These results indicate that complete dissociation of this complex takes place on vaporization and fractionation of the two volatile constituents follows.

In dilute benzene solution all the dioxanates of the Group VB trihalides undergo complete dissociation. Cryoscopic determinations give apparent molecular weights agreeing quite closely with those calculated for complete dissociation of the complex into trihalide and dioxane.

Summary

1. Crystalline dioxanates of some Group VB trihalides have been prepared and characterized.

2. Dissociation pressures of these dioxanates at 20° have been measured and the dissociation pressure of $SbCl_3 \cdot 2C_4H_8O_2$ was measured from 0 to 20°.

3. Complete dissociation of the arsenic trichloride complex in the vapor state and of all the dioxanates in benzene solution occurs.

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The Aldol Condensation. I. Detection of Carbonyl Groups in Aldols by Use of Raman Spectra

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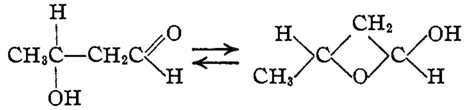
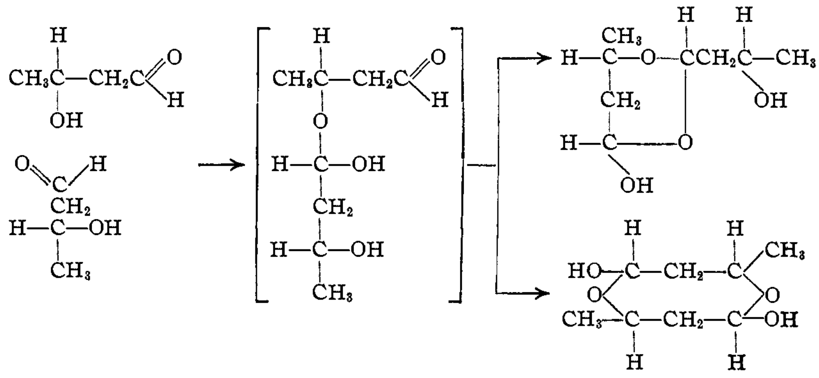
The aldols are a group of relatively unstable compounds whose structures are designated classically by β-hydroxyaldehyde formulas. The chemical reactions and physical properties of these substances indicate that such a formulation may not be entirely correct; and almost since their discovery by Wurtz[1] in 1872, investigations have been carried on which have left the structures of the aldols and their polymerization products still unsettled.[2-7]

Acetaldol has been studied most extensively, probably because it was the aldol most easily obtained. Also, it may be considered as one of the elementary sugars and from this standpoint its structure is of theoretical interest. Hurd and Abernethy[5] believe that acetaldol exists in the open chain aldehyde form in agreement with classical structures since the methylation products were all straight chain compounds. In the opinion of others,[2,4] this compound is more correctly represented by a monomeric inner hemiacetal which is in equilibrium with a small amount of the true aldehyde form. Apparently no stable derivatives of this cyclic form have been prepared. The two forms of the acetaldol in equilibrium are shown in the equation



As acetaldol ages it becomes progressively more and more viscous and finally solidifies. The solid is known as paraldol and, according to an earlier idea, its formation is due to physical interactions and involves no new chemical bonds.[8] Later researches indicate the formation of six-[6] or eight-membered,[3,7] ring compounds from two molecules of the classical aldol. This dimerization is shown below.



Spectrographic investigations of acetaldol occasionally have been reported. Backès,[4] using ultraviolet absorption spectra, found no trace of a carbonyl group in anhydrous acetaldol, but in aqueous solutions a carbonyl maximum could be observed which was intensified in the presence of hydrochloric acid. Using infrared absorption with a benzene solution of acetaldol he reported that a band at 10,000 cm.$^{-1}$, generally ascribed to tertiary OH, disappeared on standing. Hilbert,

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(2) Bergmann and Kann, *Ann.*, **438**, 278 (1924).

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(5) Hurd and Abernethy, THIS JOURNAL, **63**, 1966 (1941).

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