4. *The Compound of Boron Trichloride with Dioxan.*

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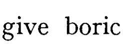
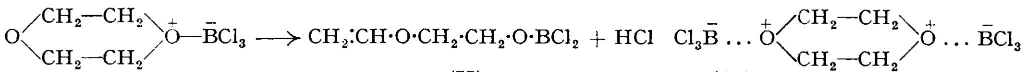
Boron trichloride reacts with dioxan at 20° to give an equimolecular compound $BCl_3,C_4H_8O_2$. The compound $2BCl_3,C_4H_8O_2$ cannot be prepared by allowing an excess of boron trichloride to react with either dioxan or the 1 : 1-compound.


(I)

Few compounds in which boron trichloride is directly co-ordinated to a carbon-linked oxygen atom have been isolated. The formation of compounds $>CO,BCl_3$ has been assumed in some cases, especially if the corresponding trifluoride has been identified, but immediate breakdown occurs with evolution of hydrogen chloride and formation of complex mixtures of products (Martin, *Chem. Reviews*, 1944, **34**, 468). Co-ordination compounds of the type (I) appear to be rather more stable when R = R′ = Me or Et; *e.g.*, boron trichloride–dimethyl ether is formed by direct reaction at −80° but decomposes at higher temperatures to give boric oxide, methyl chloride, and methyl dichloroborate (Wiberg and Sütterlin, *Z. anorg. Chem.*, 1931, **202**, 1, 22, 31, 37). The diethyl ether compound (I; R = R′ = Et) is also prepared by direct reaction and is relatively stable in dry air

(Nespital, *Z. physikal. Chem.*, 1932, *B*, **16**, 173). When R′ = H, isolation of compounds ROH,BCl_3 has not been possible, because these lose hydrogen chloride to yield successively the esters $BCl_2{\cdot}OR$, $BCl(OR)_2$, and $B(OR)_3$ (R = Me, Et) (Wiberg and Sütterlin, *loc. cit.*; Wiberg and Smedsund, *Z. anorg. Chem.*, 1935, **225**, 204; Wiberg and Ruschmann, *Ber.*, 1937, **70**, 1393).

Lane, McCusker, and Curran (*J. Amer. Chem. Soc.*, 1942, **64**, 2076) measured electric moments of boron trichloride in dioxan as solvent. Comparison of the observed dipole moment with that of (I; R = R′ = Et) suggested that co-ordination to give a 1 : 1-compound was almost complete in solution, but the compound was not isolated. We have found that slow reaction of boron trichloride with dioxan in a vacuum at 20° yields colourless hexagonal crystals with composition and molecular weight corresponding to $C_4H_8O_2,BCl_3$. This substance is stable in dry air, but reacts instantaneously with water to yield boric acid; it is soluble in dioxan and in dibenzyl ether, sparingly soluble in benzene and carbon tetrachloride, and insoluble in *cyclo*hexane. When heated *in vacuo*, it darkens, and becomes blue at 75°. At 78·5°, it melts to a deep blue liquid and this change is accompanied by an abrupt discontinuity in the vapour pressure–temperature curve. Further heating at 78·5° causes an increase in vapour pressure; when the system is cooled and the products fractionated, there remains a non-volatile tarry solid containing boron and chlorine. The volatile products are hydrogen chloride and a viscous liquid which finally crystallises to give a white solid. The latter reacts with moist air, evolving hydrogen chloride; it attacks tap grease readily and is rather unstable. Analysis for boron and chlorine gives values in agreement with those required for 2-vinyloxyethyl dichloroborate (II), but the substance is too unstable to permit determination of its molecular weight. The thermal decomposition of boron trichloride–dioxan can then be represented as



(II) (III)

the breakdown being similar to that observed with boron trichloride–ether compounds.

Attempts to prepare di(boron trichloride)–dioxan were unsuccessful. Treatment of dioxan with a large excess of boron trichloride, or of boron trichloride–dioxan with boron trichloride at pressures greater than atmospheric and at temperatures up to 70°, yielded only the 1 : 1-compound. If the boron–oxygen link in the 1 : 1-compound is covalent, it is difficult to see how formation of this link can greatly affect the ability of the second dioxan oxygen atom to co-ordinate with another molecule of boron trichloride, especially as the two oxygen atoms are not linked by a conjugated ring or other potentially resonating system. However, Coates (*J.*, 1951, 2003) has suggested that co-ordination compounds of oxygen differ from those of other donor atoms in that the binding is primarily electrostatic rather than covalent, the oxygen being held by attraction between its negatively charged lone pairs and the positive centre of the acceptor. McCusker and Curran (*J. Amer. Chem. Soc.*, 1942, **64**, 614) have noted the relatively small moment of the $\overset{-}{B}$–$\overset{+}{O}$ link (in Et_2O,BCl_3) compared with that of other co-ordinate linkages; this is to be expected if the oxygen–boron linkage is electrostatic rather than covalent. Moreover, compounds of the form A_2D (where A is an acceptor molecule and D is dioxan) have not been isolated, and Lane, McCusker, and Curran (*loc. cit.*) found no evidence for the existence of such compounds in dioxan solutions. Since the formation of one electrostatic oxygen–boron link gives a compound of limited stability, formation of a second link as in (III), involving two positively charged oxygen atoms in the same saturated ring, cannot be expected to occur at a temperature above the m. p. of dioxan.

EXPERIMENTAL

Apparatus and Materials.—A high-vacuum apparatus of conventional type was used in the preparative work, with a vessel through which known volumes of boron trichloride vapour could be passed. Reaction products were fractionated in U-traps on the main vacuum line.

Transfers of moisture-sensitive materials to and from the reaction vessel were made in a dry box. Boron trichloride was purified by fractional condensation in a vacuum apparatus of the Stock type to avoid excessive attack of tap grease; the material used had a vapour pressure of 3—4 mm. at −78°. Dioxan was refluxed over sodium for 6 hours, and the fraction of b. p. 101—101·3°/760 mm. collected.

Reaction of Boron Trichloride and Dioxan.—In a typical experiment, excess of dioxan (60 mmols.) was frozen in the reaction vessel, the apparatus evacuated, and the temperature brought to 20°. Boron trichloride (15 mmols.) was bubbled slowly through the dioxan (rapid bubbling gave a violent reaction). Volatile material was then removed, condensed in liquid nitrogen, and fractionated; a small amount of hydrogen chloride (0·71 mmol.) and dioxan were the only constituents. The remaining *addition compound* was purified by sublimation *in vacuo* below 50°; the yield was 80%.

Analysis for chlorine and boron. Complete hydrolysis of the product without loss of hydrogen chloride was attained either by sealing a weighed sample into a capillary-tipped tube and breaking the capillary under potassium hydroxide solution, or by condensing water on to the sample in an evacuated tube at a low temperature and allowing the whole to warm slowly. Boron was then determined volumetrically in presence of mannitol, and chlorine gravimetrically as silver chloride in solutions sufficiently acid to retain silver borate in solution (Found : Cl, 50·8; B, 5·2. $C_4H_8O_2,BCl_3$ requires Cl, 51·8; B, 5·3%). A specimen exposed to air and allowed to attain constant weight gave Cl, 0; B, 16·5% (Calc. for H_3BO_3 : B, 17·7%).

Molecular weight. A cryoscopic method was used with dioxan as solvent in an apparatus similar to that of Zeffert and Hormatz (*Anal. Chem.*, 1949, **21**, 1420), and adapted to exclude water vapour. Temperatures were measured with a type F2311/300 thermistor (Standard Telephone and Cables, Ltd.), the resistance being determined to ±1 ohm by an ordinary bridge circuit. The apparatus was calibrated by using solutions of naphthalene in dioxan. Resistance of the thermistor at the freezing point of dioxan was 2336Ω, and at this temperature a resistance change of $\pm 1\Omega$ corresponded to $\mp 0{\cdot}008°$. The cryoscopic constant for dioxan was taken as 4710/100 g. of solvent (Found : *M*, 203 ± 4. $C_4H_8O_2,BCl_3$ requires *M*, 205).

Vapour Pressure and Thermal Decomposition.—Vapour pressure–temperature curves were determined between 17° and 156°, Stock and Küss's isoteniscope method (*Ber.*, 1914, **47**, 3115) being used. Heating and cooling curves did not coincide, and at 78·5° the discontinuity in the v.p.–*T* curve was observed. Prolonged heating at this temperature resulted in a marked increase in vapour pressure, the magnitude depending on the amount of material present. Thermal decomposition was therefore studied by placing the compound in a tube attached to the vacuum line and keeping it at 78·5—82° for about 5 hours; the volatile products were condensed in liquid nitrogen and fractionated. Hydrogen chloride was identified (v.p. at −112°, 122 mm.), and a viscous liquid which gave Cl, 45; B, 6·2% (2-*vinyloxyethyl dichloroborate*, $C_4H_7O_2Cl_2B$, requires Cl, 42·0; B, 6·4%).

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