Co-ordination Compounds of Boron Trihalides. Part II. Boron Trichloride–Cyclic Ethers.*

By Joan Grimley and A. K. Holliday.

[Reprint Order No. 4771.]

Boron trichloride forms 1 : 1 compounds with ethylene oxide, propylene oxide, tetrahydrofuran, and tetrahydropyran. Ethylene oxide–boron trichloride dissociates reversibly on heating; the other 1 : 1 compounds yield boron trichloride and hydrogen chloride in amounts depending upon the ring size.

In Part I * the compound of boron trichloride with dioxan was described, and we now report the preparation and properties of some cyclic ether–boron trichloride co-ordination compounds.

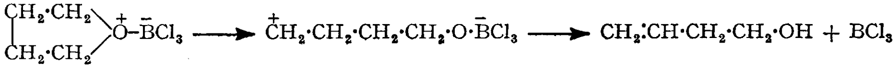
The 1 : 1 compounds of boron trichloride with ethylene oxide, propylene oxide, tetrahydrofuran, and tetrahydropyran fume strongly in moist air and react spontaneously with water, forming boric acid and liberating hydrogen chloride. When these compounds are heated they may decompose in one or more of three ways, *viz.*: (*a*) by simple breaking of the boron–oxygen bond, *i.e.*, dissociation; (*b*) by ring fission followed by loss of boron trichloride; (*c*) by ring fission followed by loss of hydrogen chloride. Ethylene oxide–boron trichloride decomposes reversibly by process (*a*) only. This compound appears to be dimeric in the vapour state at low temperatures, dissociating into monomer and thence into ethylene oxide and boron trichloride at higher temperatures. Propylene oxide–boron trichloride decomposes irreversibly on heating, and at 100° the decomposition products include boron trichloride and hydrogen chloride in the molar ratio 3 : 1, a colourless volatile liquid of empirical formula $(C_3H_6O)_2BCl_3$, and a non-volatile residue containing boron and chlorine (B : Cl = 1 : 0·77). With the reasonable assumption that $(C_3H_6O)_2BCl_3$ is the molecular formula of the liquid condensate, the primary decomposition is then by mechanism (*a*), *e.g.*, $2C_3H_6\overset{+}{O}{-}\overset{-}{B}Cl_3 \longrightarrow (C_3H_6O)_2BCl_3 + BCl_3$; some secondary decomposition by mechanisms (*b*) and (*c*) must also take place. The compound $(C_3H_6O)_2BCl_3$ reacted vigorously with water to yield hydrogen chloride and boric acid in solution, but was not investigated further. This compound could also be formulated as the chloroboronate $[CH_2Cl{\cdot}CH(CH_3)O]_2BCl$. Martin and Mako (*J. Amer. Chem. Soc.*, 1951, **73**, 2674) have shown that β-substitution by chlorine for hydrogen in chloroboronates would be expected to weaken the boron–oxygen bond.

Tetrahydrofuran–boron trichloride decomposes irreversibly between 38° and 52°; at 87° boron trichloride and hydrogen chloride are recovered in the molar ratio 4·8 : 1,

---

* The paper by Holliday and Sowler, *J.*, 1952, **11**, is regarded as Part I of this series.

together with a colourless volatile liquid which contains effectively no boron or chlorine and behaves as a pure substance, b. p. 112°/760 mm. (by extrapolation). If mechanism (*b*) is postulated for the primary decomposition, then a plausible scheme is



forming but-3-enol (b. p. 112·5—113·5°). Saturated alcohols react readily with boron trichloride to form boric esters (Wiberg and Sütterlin, *Z. anorg. Chem.*, 1931, **202**, 1; Gerrard and Lappert, *J.*, 1951, 2545), but unsaturated alcohols have not been investigated. The only other C_4H_8O compound having b. p. ~112° is 2-methylallyl alcohol (b. p. 114°).

Tetrahydropyran–boron trichloride melts with decomposition at 52°. A sample heated at 90° for several hours yields only hydrogen chloride and an unidentified liquid containing boron and chlorine in the ratio 1 : 2. The amount of hydrogen chloride recovered corresponded to the loss of one chlorine atom from three molecules of the 1 : 1 compound. This suggests decomposition by mechanism (*c*), *i.e.*, $C_5H_{10}\overset{+}{O}-\overset{-}{B}Cl_3 \longrightarrow C_5H_9O\cdot BCl_2 + HCl$, but the condensate is too low in boron and chlorine to be the chloroboronite, $C_5H_9O\cdot BCl_2$.

It is observed that as the ring size of the donor molecule increases, (i) the temperature of decomposition rises, and (ii) the amount of boron trichloride isolated after thermal decomposition falls, and the amount of hydrogen chloride increases. Again, α-substitution in the ethylene oxide ring by a methyl group for a carbon-attached hydrogen, or replacement of a ring CH_2 group in tetrahydropyran by an oxygen atom has the same effects as an increase in ring size; *e.g.*, dioxan–boron trichloride melts with decomposition at 78°, and at 80°, 0·97 mmole of hydrogen chloride is recovered from each mmole of the 1 : 1 compound (Part I, *loc. cit.*). Although it is not possible to determine unequivocally an order of stability for the boron trichloride–cyclic ethers, the tentative orders ethylene oxide>propylene oxide, and dioxan>tetrahydropyran>tetrahydrofuran are proposed, based on the temperature of initial decomposition of the 1 : 1 compounds and on the nature of the thermal decomposition products. These orders may be compared with the electron-donor abilities of cyclic ethers in hydrogen bonding, determined by Searles, Tamres, and Lippincott (*J. Amer. Chem. Soc.*, 1953, **75**, 2775). They measured the heats of mixing of ethylene oxide, propylene oxide, tetrahydrofuran, and tetrahydropyran with chloroform, and found an order propylene oxide>ethylene oxide, and tetrahydrofuran>tetrahydropyran>ethylene oxide. Hamilton, McBeth, Bekebrede, and Sisler (*ibid.*, p. 2881) also found an order of stability, dioxan>(tetrahydrofuran, tetrahydropyran) for 1 : 1 compounds of these donors with titanium tetrachloride.

Tetrahydropyran–boron trichloride and dioxan–boron trichloride both react with equimolar amounts of hydrogen chloride at low temperatures; the resulting compounds can be given the ionic formulations $[C_5H_{10}\cdot OH]^+[BCl_4]^-$ and $[O<(CH_2\cdot CH_2)_2>OH]^+[BCl_4]^-$. There is some evidence that other 1 : 1 addition compounds of boron trichloride do add on hydrogen chloride to form ionic borochlorides (Hewitt and Holliday, *J.*, 1953, 530).

EXPERIMENTAL

The addition compounds were prepared in a general-purpose high-vacuum apparatus similar to that described by Sanderson ("Vacuum Manipulation of Volatile Compounds," Wiley, New York, 1948). Transfers of non-volatile, moisture-sensitive materials were made in a dry box. The methods used for the analysis of boron and chlorine, and the apparatus used to determine molecular weights in solution, were as described in Part I (*loc. cit.*). Vapour-pressure measurements were made by means of Stock and Küss's isoteniscope method (*Ber.*, 1914, **47**, 3115). Volatile starting materials were purified by fractionation in the high-vacuum apparatus; less volatile materials were dried and then fractionally distilled.

Reaction of Boron Trichloride and Ethylene Oxide.—Equivalent amounts (2·34 mmoles) of ethylene oxide (v. p. 3·5 mm. at −78·5°) and boron trichloride (v. p. 3—4 mm. at —78·5°) were mixed at −78·5°. Reaction was spontaneous, and a colourless liquid containing a small amount of white solid was formed. Distillation *in vacuo* at 20° gave 0·158 g. (0·98 mmole) of liquid, *ethylene oxide–boron trichloride* (Found: B, 6·4; Cl, 65·1%; *M*, 165. C_2H_4O,BCl_3 requires B, 6·8; Cl, 66·0%; *M*, 161). The only other products were 0·67 mmole of boron trichloride and 0·14 mmole of hydrogen chloride. The highly viscous non-volatile residue contained ethylene oxide and boron trichloride in the ratio 1·97 : 1, but was not dioxan–boron trichloride, m. p. 78°. Ascending and descending vapour-pressure readings for 10° increments between 0° and 90° were coincident, indicating that no irreversible decomposition had taken place over this range. Saturated vapour-pressure data are given by $\log p + 1263/T = 5{\cdot}90$, hence the apparent boiling point is 146° at 760 mm. (extrap.), the molar latent heat (20—90°) is 5·78 kcal./mole, and Trouton's constant is 13·8. Vapour densities over the range 18—118° were determined by measuring the pressure exerted by a known weight of the compound in a high-temperature bulb (Sanderson *loc. cit.*); the results are given below:

Temp.	18·0°	37·3°	44·1°	56·1°	68·0°	81·3°	98·0°	118·0°
V.d.	153·5	124·2	112·2	90·0	79·2	73·5	71·5	69·5

The calculated vapour density for C_2H_4O,BCl_3 is 80·7.

Reaction of Boron Trichloride and Propylene Oxide.—Propylene oxide (4·75 mmoles, v. p. 183 mm. at 0°) and boron trichloride (4·80 mmoles) were mixed at −78·5°. A colourless liquid was formed which became yellow when warmed to room temperature; distillation *in vacuo* at 20° yielded 0·696 g. (3·98 mmoles) of *propylene oxide–boron trichloride* as a colourless liquid (Found: B, 5·88; Cl, 61·1%; *M*, 177. C_3H_6O,BCl_3 requires B, 6·16; Cl, 60·7%; *M*, 175). The only other volatile product was hydrogen chloride (0·22 mmole), and the non-volatile residue contained propylene oxide and boron trichloride in the ratio 1·0 : 1·07. Non-reproducibility of saturated vapour-pressure readings between 0° and 60° indicated that irreversible decomposition had taken place throughout this temperature range. A freshly distilled sample (3·97 mmoles) was heated at 102° for 1 hr.; 0·59 mmole of hydrogen chloride and 1·16 mmoles of boron trichloride were formed, together with 0·1 g. of a colourless liquid which condensed out at −78·5° [Found: B, 4·30; Cl, 45·2. $(C_3H_6O)_2BCl_3$ requires B, 4·64; Cl, 45·8%] and 0·07 g. of a brown, non-volatile residue (Found: B, 11·4; Cl, 28·6%).

Reaction of Boron Trichloride and Tetrahydrofuran.—When the liquid reactants were mixed at −78·5°, the reaction was strongly exothermic and gave an ill-defined product. The 1 : 1 compound was isolated, however, when equivalent amounts (10·4 mmoles) of tetrahydrofuran (b. p. 65·2—66°/760 mm.) and boron trichloride were condensed separately into the limbs *A* and *B* of a reaction vessel, and the whole was immersed in a bath at −78·5° for 12 hr. Volatile products at 20° were then condensed into *B*, and tube *A*, which contained a white solid, was sealed off from *B* and later opened in the dry box and analysed (Found: B, 5·80; Cl, 54·4%; *M*, 185. C_4H_8O,BCl_3 requires B, 5·72; Cl, 56·2%; *M*, 189). Thus, 10 mmoles of *tetrahydrofuran–boron trichloride* were formed in *A*. The volatile products in *B* were identified as tetrahydrofuran (0·18 mmole) and hydrogen chloride (0·69 mmole). Saturated vapour-pressure measurements were made on a sample of the 1 : 1 compound prepared directly in the isoteniscope. The compound melted slowly, with decomposition, between 38° and 52°; an abrupt discontinuity in the vapour pressure–temperature curve occurred at the latter temperature, and a clear cherry-red liquid was seen in the isoteniscope. On cooling below 52°, no solid separated and vapour-pressure values remained high, *i.e.*, irreversible decomposition had occurred. A freshly prepared sample was heated for 2 hr. at 60° and then for a further 2 hr. at 87°; the decomposition products included boron trichloride, hydrogen chloride, and a colourless liquid which condensed at −78·5° and contained only traces of boron and chlorine. Saturated vapour pressures of the latter compound followed the equation $\log p + 1720/T = 7{\cdot}35$, giving b. p. = 112° at 760 mm. (extrapolated).

Reaction of Boron Trichloride and Tetrahydropyran.—Boron trichloride (15·8 mmoles) was bubbled through excess of tetrahydropyran (b. p. 87—87·8°/760 mm.) at −40°. Volatile products were distilled off at 20°, and tetrahydropyran alone was isolated. The white solid remaining in the reaction vessel was sublimed *in vacuo* below 52°; needle-shaped crystals separated and were identified as *tetrahydropyran–boron trichloride* (14·2 mmoles) (Found: B, 5·50; Cl, 52·1%; *M*, 203. $C_5H_{10}O,BCl_3$ requires B, 5·40; Cl, 52·3%; *M*, 203·5). It melts slowly, with decomposition, between 49° and 52°, and at the latter temperature there is a marked discontinuity in the saturated v. p.–temperature curve, and, on cooling, vapour-pressure values are not reproduced, indicating irreversible decomposition. Freshly prepared samples were therefore heated in sealed tubes at 90° for different periods of time. The only products isolated were hydrogen chloride and a colourless liquid condensate at −78·5° (Found:

B, 3·0; Cl, 18·9%). The following table shows the effect of the time of heating on the amount of hydrogen chloride produced.

Time of heating, hr.	3	5	25
$C_5H_{10}O,BCl_3$: HCl	1 : 0·19	1 : 0·29	1 : 0·33

Reaction of Tetrahydropyran–Boron Trichloride with Hydrogen Chloride.—Excess of dry hydrogen chloride (41·0 mmoles) was condensed on solid, freshly-prepared tetrahydropyran–boron trichloride (5·47 mmoles) at −196°, and the temperature allowed to rise to −112°. The tube was shaken vigorously, and reaction allowed to take place for 2 hr.; the 1 : 1-compound dissolved when shaken. Unchanged hydrogen chloride was then distilled off (at −112°) until the vapour pressure fell from 122 mm. (for hydrogen chloride) to a persistently low value of 66 mm.; 35·3 mmoles of hydrogen chloride were then recovered. On warming to 20°, the remaining 5·70 mmoles of hydrogen chloride were evolved. Hence, if the compound $C_5H_{10}O,BCl_3,HCl$ is formed at −112°, it dissociates completely above this temperature into hydrogen chloride and tetrahydropyran–boron trichloride.

Reaction of Dioxan–Boron Trichloride with Hydrogen Chloride.—Excess of dry hydrogen chloride (46·1 mmoles) was condensed on solid dioxan–boron trichloride (7·97 mmoles) at −196°, and the temperature allowed to rise to −112°. The solid did not dissolve at this temperature, even after vigorous shaking. After 2 hours' reaction at −112°, 40·3 mmoles of hydrogen chloride were recovered, and the vapour pressure above the solid fell to 31 mm. On warming to 20°, the remaining 5·80 mmoles of hydrogen chloride were recovered. Thus, if a compound is formed between hydrogen chloride and dioxan–boron trichloride at −112°, it dissociates completely above this temperature.

DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY,
THE UNIVERSITY OF LIVERPOOL.

[*Received, November* 6*th*, 1953.]