366. *The Reaction of Diboron Tetrachloride with Ethylene Oxide.*

By A. G. Massey and A. K. Holliday.

Diboron tetrachloride reacts rapidly with ethylene oxide at −78° to form the liquid tetra-(2-chloroethoxy)diboron, which reacts slowly with oxygen and trimethylamine. Cold aqueous hydrolysis gives 2-chloroethanol and sub-boric acid; hydrolysis by strong alkalis at 90° breaks the boron–boron bond to give hydrogen. Pyrolysis up to 135° produces tri-(2-chloroethoxy)-boron; and at 240° causes complete decomposition to ethylene, dioxan, 1,2-dichloroethane, and ethyl chloride.

Ethylene oxide might be expected to form stable co-ordination complexes with tervalent boron compounds, *e.g.*, $R_3\overset{-}{B}-\overset{+}{O}(CH_2)_2$. However, Edwards, Gerrard, and Lappert[1] have shown that excess of ethylene oxide reacted with boron trichloride at −78° to form tri-(2-chloroethoxy)boron:

$$BCl_3 + 3(CH_2)_2O \longrightarrow B(O{\cdot}CH_2{\cdot}CH_2Cl)_3$$

In this work diboron tetrachloride reacted rapidly with more than 4 moles of ethylene oxide at −78° to give a viscous liquid. Freezing the product in liquid nitrogen produced a glass which had no definite melting point; increasing the temperature slowly decreased the viscosity until at 100° the liquid was quite mobile. There were no volatile products, and alkaline hydrolysis of the residue produced up to 90% of the hydrogen expected if there was no fission of the boron–boron bonds. The probable product of the reaction is therefore tetra-(2-chloroethoxy)diboron:

$$B_2Cl_4 + 4(CH_2)_2O \longrightarrow B_2(O{\cdot}CH_2{\cdot}CH_2Cl)_4$$

As in all reactions of diboron tetrachloride, some decomposition to boron trichloride occurred, accounting for the incomplete recovery of hydrogen on hydrolysis. Moreover, polymerisation of ethylene oxide is readily initiated by boron trichloride[1] and by other boron compounds,[2] and the ethylene oxide used in excess of the 4 moles required was therefore probably polymerised. Presence of this polymer may account for the viscous nature

---

[1] Edwards, Gerrard, and Lappert, *J.*, 1957, 348.

[2] Worsfold and Eastham, *J. Amer. Chem. Soc.*, 1957, **79**, 901.

of the product, since compounds analogous to tetra-(2-chloroethoxy)diboron, *e.g.*, tetramethoxydiboron[3] and tri-(2-chloroethoxy)boron[4] are not viscous liquids at ordinary temperatures.

Separation of pure tetra-(2-chloroethoxy)diboron from the polymeric contaminant could not be achieved, but hydrolysis gave further evidence of its presence as 80—90% of the reaction product. Hydrolysis by cold water gave 2-chloroethanol as the only volatile product, with only a trace of hydrogen and hydrochloric acid, indicating the reaction

$$B_2(O{\cdot}CH_2{\cdot}CH_2Cl)_4 + 4H_2O \longrightarrow 4CH_2Cl{\cdot}CH_2{\cdot}OH + B_2(OH)_4$$

and confirming the virtual absence of boron-chlorine bonds. The solution had strong reducing properties, as expected for sub-boric acid; the latter gave boric acid and hydrogen when hydrolysed with alkali. Prolonged alkaline hydrolysis was necessary to release chloride ion from the original product.

When mixed with oxygen, the product did not inflame even when heated. A slow reaction occurred; B–B bonding disappeared after 22 hr. at ordinary temperature, and 0·5 mole of oxygen was used for each mole of diboron tetrachloride reacting. The products were white boric oxide and an involatile liquid shown by infrared and nuclear magnetic resonance spectra to be tri-(2-chloroethoxy)boron. The reaction is therefore similar to that of oxygen and diboron tetrachloride,[5] *viz.*,

$$6B_2(O{\cdot}CH_2{\cdot}CH_2Cl)_4 + 3O_2 \longrightarrow 2B_2O_3 + 8B(O{\cdot}CH_2{\cdot}CH_2Cl)_3$$

and a similar mechanism[6] involving initial co-ordination of an oxygen molecule across the B–B bond may well operate.

Tetra-(2-chloroethoxy)diboron reacted very slowly with trimethylamine at room temperature or above, but not to the extent required for donation to both boron atoms. The reaction was so slow that some thermal decomposition inevitably proceeded to a considerable extent, making any interpretation of the results difficult. Tri-(2-chloroethoxy)boron also reacted very slowly with trimethylamine to form a similar white solid adduct.

Tetra-(2-chloroethoxy)diboron had greater thermal stability than diboron tetrachloride. The only major indication of decomposition at moderate temperatures was the slow disappearance of the boron–boron bonds; thus a 22% loss occurred after 6 days at 20°, or a 71% loss after 22 hr. at 135°. The infrared spectrum of the involatile liquid residue indicated the presence in it of tri-(2-chloroethoxy)boron; the only volatile products were traces of dioxan and 1,2-dichloroethane. However, at 240° the decomposition was rapid and accompanied by extensive charring, and the evolution of ethylene, dioxan, ethyl chloride, and 1,2-dichloroethane; the residues from pyrolyses at 240° gave no ionisable chlorine on hydrolysis with distilled water at room temperature. This indicated that no boron-chlorine bonds had re-formed during the decomposition; however, some boron–carbon bonds were obviously present in the residues because the boron was not all titratable as boric acid after alkaline hydrolysis. The absence of any solid products of pyrolysis below 135° precludes the possibility of the type of disproportionation previously suggested for diboron tetra-alkoxides,[7] *viz.*,

$$3B_2(O{\cdot}CH_2{\cdot}CH_2Cl)_4 \longrightarrow 2B + 4B(O{\cdot}CH_2{\cdot}CH_2Cl)_3$$

A more probable mechanism is analogous to that obtained in the case of diboron tetrachloride:[3]

$$nB_2Cl_4 \longrightarrow nBCl_3 + (BCl)_n$$

$$nB_2(O{\cdot}CH_2{\cdot}CH_2Cl)_4 \longrightarrow nB(O{\cdot}CH_2{\cdot}CH_2Cl)_3 + (CH_2Cl{\cdot}CH_2{\cdot}OB)_n \quad (I)$$

---

[3] Schlesinger, Wartik, Moore, and Urry, *J. Amer. Chem. Soc.*, 1954, **76**, 5293.

[4] Jones, Thomas, Pritchard, and Bowden, *J.*, 1946, 824.

[5] Apple and Wartik, *J. Amer. Chem. Soc.*, 1958, **80**, 6153.

[6] Holliday and Massey, *J. Inorg. Nuclear Chem.*, 1961, in the press.

[7] Wiberg and Ruschmann, *Ber.*, 1937, **70**, 1393.

A chloroethylboroxole (I; $n = 3$) would contain boron–carbon as well as boron–oxygen bonds.

The slow reactions of tetra-(2-chloroethoxy)diboron with oxygen and trimethylamine are to be expected if, as in $B(OR)_3$ compounds, there is a considerable degree of double bonding between the boron and oxygen atoms, with the consequent filling of the vacant boron orbitals, which would cause a reduction in the acceptor powers of the boron atoms. It is of interest that this also enhanced the stability of tetra-(2-chloroethoxy)diboron with respect to disproportionation, thus supporting the hypothesis[8] that the instability of B_2X_4 compounds is due, not to an inherent weakness of the boron–boron bond, but to a tendency to internal co-ordination with subsequent rupture of the boron–boron bond.

EXPERIMENTAL

The preparation of diboron tetrachloride has been described previously.[9] Ethylene oxide was purified by passage through a trap held at −78°; the material volatile at −78° was distilled at reduced pressure, and the middle fraction retained: v. p. at 0°, 494 mm.

Reaction of Diboron Tetrachloride with Ethylene Oxide.—The results are summarised in Table 1; quantities are expressed in mmoles unless otherwise stated. In Experiment 1, reaction was vigorous at −78° to give a colourless liquid; no change was noted on warming the system to 40° when the excess of ethylene oxide was removed. Hydrolysis here was with concentrated sodium hydroxide solution at 90° for 2 hr.

In expt. 2, low acidity and hydrogen values were obtained after hydrolysis with a large excess of distilled water at 0° for 1 hr.; this produced an oil. The acidity of the hydrolysate slowly rose to 0·07 mequiv. after 12 hr. The boric acid was estimated only after addition of concentrated alkali and boiling, followed by acidification.

In expt. 3, hydrolysis was again controlled, 3·66 mmoles of water being used at 20° for 1 hr.

TABLE 1.

Expt. No.	1	2	3
B_2Cl_4 used	0·71	0·81	0·89
C_2H_4O added	4·90	4·48	4·95
C_2H_4O recovered	1·54	0·93	0·59
Reaction temp.	−78° to 40°	−78° to 22°	−78°
Hydrolysis products:			
H_2	0·64	0·01	0·74
Cl^-	2·88	—	—
$B(OH)_3$	1·38	1·62	—
H^+	—	0·03	—

TABLE 2.

Expt. No.	4	5	6	7	8	9
B_2Cl_4 used	0·79	0·71	0·81	0·75	0·84	0·79
C_2H_4O used	3·57	3·49	3·81	3·60	3·78	3·44
Decomposition temp.	22°	40°	90°	135°	240°	240°
Time of decomposition, hr.	144	0·5	21	22	19	44
Volatile products: H_2	—	—	—	—	0·03	0·02
CH_4	—	—	—	—	—	trace
C_2H_6	—	—	—	—	0·01	0·01
C_2H_4	—	—	—	—	0·03	0·25
X	—	—	0·01	0·03	0·23	0·23
Hydrogen on hydrolysis of residue	0·62	0·64	0·55	0·22	0·00	—
% recovery of B–B bond	78	90	69	29	0	—

The small amount of oily product was distilled off and identified as 2-chloroethanol by its infra-red spectrum and by its reaction with potassium hydroxide, which gave water and ethylene oxide. The hydrogen was obtained after further hydrolysis of the solid residue by strong alkali.

Decomposition of the reaction product. The experiments are summarised in Table 2. In

---

[8] Feeney, Holliday, and Marsden, *J.*, 1961, 356.

[9] Holliday and Massey, *J.*, 1960, 43.

expts. 4 and 5 there were no volatile products. Fraction X in expt. 6 was pure dioxan, and in 7, fraction X contained a trace of 1,2-dichloroethane in addition to dioxan. Considerable charring of the product was noted in expts. 8 and 9; fraction X now contained relatively large amounts of dioxan, 1,2-dichloroethane, and ethyl chloride. The residue in expt. 8 was hydrolysed with concentrated caustic alkali at 90° but no hydrogen was produced; titration of the hydrolysate gave chloride 2·83, and boric acid 1·41 mequivs.: B : Cl = 1 : 2·01. In expt. 9, the residue was hydrolysed with a large excess of distilled water; no hydrogen and very little acidity (0·01 mequiv.) could be detected.

Reaction product–oxygen reactions. Diboron tetrachloride (0·79) and ethylene oxide (4·65) were held at $-78°$ for 30 min.; 1·22 mmoles of oxide were recovered. 1·30 mmoles of pure, dry oxygen were added to the product at $-196°$; warming cautiously to $-78°$ produced no apparent reaction. On warming to 22° there still appeared to be no reaction; after 22 hr. at 22°, 0·90 mmole of oxygen was removed: ratio $O_2 : B_2Cl_4 = 0{\cdot}40 : 0{\cdot}79$. No hydrogen was evolved on hydrolysis of the colourless residue by concentrated alkali. Other mixtures of oxygen and the reaction product failed to ignite when brought rapidly to room temperature (or above) from $-196°$ (cf. the reaction of diboron tetrachloride with oxygen [5]). Boric oxide was apparent in the reaction vessels as a faint white precipitate. The involatile liquid product gave the infrared and nuclear magnetic resonance spectra of $B(O{\cdot}CH_2{\cdot}CH_2Cl)_3$.

Reaction product–trimethylamine reactions. Diboron tetrachloride (0·78 mmole) reacted with ethylene oxide (3·42 mmoles) at $-78°$. Trimethylamine (2·12) was added to the product and the vessel kept at 22° for 1 hr. A small quantity of white solid was produced and 0·37 mmole of amine was absorbed; after 2 days at 22°, 1·43 mmoles of amine were recovered; amine reacted = 0·69 mmole. Alkaline hydrolysis of the residue (a mixture of liquid and solid) produced 0·65 mmole of hydrogen. Similar reactions with tri-(2-chloroethoxy)boron showed that trimethylamine was again slowly absorbed but not in stoicheiometric quantities.

We thank the Department of Scientific and Industrial Research for a maintenance grant (to A. G. M.), and Dr. L. H. Sutcliffe, who carried out the proton magnetic resonance studies.

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

[*Received, July 25th,* 1960.]