9. *Diboron Tetrachloride–Olefin Compounds. Part I. Some Properties of Diboron Tetrachloride–Ethylene.*

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Diboron tetrachloride–ethylene forms a stable 1 : 2 adduct with trimethylamine, and this further adds hydrogen chloride without decomposition. With ammonia and methylamine, substances $[B_2(NR)_4,C_2H_4]_n$ (R = Me or H) are formed; dimethylamine reacts incompletely, to give $B_2[NMe_2)_4,C_2H_4$. Hydrolysis yields $B_2(OH)_4,C_2H_4$, which loses water when heated, giving B_2O_2,C_2H_4. Oxidation produces variable amounts of ethylene, boron trichloride, hydrogen chloride, and a solid residue; a mechanism involving initial formation of $>$B–O–O linkages is suggested.

Schlesinger and his co-workers[1] found that diboron tetrachloride and ethylene formed a volatile 1 : 1 addition compound B_2Cl_4,C_2H_4, whose structure[2] contained a B–C–C–B bond system (I). The chlorine atoms are replaceable by alkyl or alkoxy-groups,[1] but no reactions involving the boron–carbon bonds have been reported. We report now some further reactions of diboron tetrachloride-ethylene primarily with regard to their stoicheiometry, the products not having been studied in detail.

(I) $Cl_2B\cdot CH_2\cdot CH_2\cdot BCl_2$ $\quad$ $Me_3\overset{+}{N}-\overset{-}{B}Cl_2\cdot CH_2\cdot CH_2\cdot \overset{-}{B}Cl_2-\overset{+}{N}Me_3$ (II)

From the structure (I) either or both of the boron atoms might act as acceptor atoms. Further, the B–Cl bonds should be attacked by donor molecules containing reactive hydrogen atoms (*e.g.*, H_2O, NH_3) with elimination of hydrogen chloride, as is observed with boron trichloride. If the B–C bonds resemble those in alkylborons they should suffer hydrolysis but might be cleaved by pyrolysis or oxidation. These expectations have been fulfilled.

Diboron tetrachloride–ethylene reacted with trimethylamine in a 1 : 2 ratio, giving a white solid, which was thermally stable and not oxidised or hydrolysed at room temperature. Structure (II) would account for this stability since in compounds such as $Me_3N^+–BCl_3^-$ and $Me_3N^+–BMe_3^-$ co-ordinative saturation of the boron precludes attack by other molecules.[3] However, hydrogen chloride might be expected to remove the trimethylamine and liberate the parent compound: hydrogen chloride in fact reacted with the trimethylamine adduct in the expected 2 : 1 ratio, but no diboron tetrachloride–ethylene was liberated and no other volatile products were formed; the solid product appeared to be stable. This certainly suggests the formation of a diboron hexachloride–ethylene anion, *i.e.*, $[Me_3NH]_2^+[Cl_3B\cdot C_2H_4\cdot BCl_3]^{2-}$. If this is correct, the anion is formed under less specific conditions than the simple borochloride ion BCl_4^- and is possibly more stable.

With ammonia or monomethylamine diboron tetrachloride–ethylene reacted according to the equation (R = Me or H):

$$nB_2Cl_4,C_2H_4 + 6nR\cdot NH_2 \longrightarrow 4nR\cdot NH_3Cl + [B_2(NR)_4,C_2H_4]_n$$

Presumably the initial step was co-ordination of two ammonia or amine molecules and was followed by removal of hydrogen chloride as the quaternary salt. The salt could be removed from the other product by sublimation; the polymeric nature of the remaining boron compound is inferred from its non-volatility and high thermal stability (no volatile products were evolved below the melting point of glass).

With dimethylamine, the reaction expected was:

$$B_2Cl_4,C_2H_4 + 8Me_2NH \longrightarrow 4Me_2NHCl + B_2(NMe_2)_4,C_2H_4,$$

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[1] Urry, Kerrigan, Parsons, and Schlesinger, *J. Amer. Chem. Soc.*, 1954, **76**, 5299.

[2] Moore and Lipscomb, *Acta Cryst.*, 1956, **9**, 668.

[3] Wiberg and Sütterlin, *Z. anorg. Chem.*, 1931, **202**, 35.

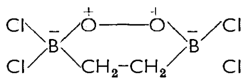
requiring a reaction ratio of 1 : 8. In fact, a ratio of 1 : 7·5 was the best that could be achieved even after prolonged reaction. The monomeric character of the product was indicated by its volatility; it was distilled from the quaternary chloride, but could not be separated from unchanged diboron tetrachloride–ethylene.

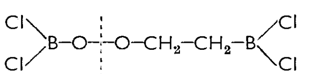
Diboron tetrachloride, on hydrolysis, gives the tetrahydroxy-compound $B_2(OH_4)$ which readily loses water to give boron suboxide.[4] Diboron tetrachloride–ethylene reacted similarly, and there was no evidence of rupture of B–C bonds at temperatures up to 100°. The product, $B_2(OH)_4,C_2H_4$ was a white solid, sparingly soluble in water to give a very weakly acidic solution. Adding mannitol enhanced the monobasic acidity, but titration with alkali did not give a sharp end-point. Heating to 130° caused loss of water and gave a glass, B_2O_2,C_2H_4, which re-absorbed water on cooling whilst the solid assumed its original powdery appearance. The oxide B_2O_2,C_2H_4 could be heated to 300° without any apparent decomposition; it did not show the peculiar thermal transformation noted[4] for the suboxide BO formed by dehydration of $B_2(OH)_4$.

Diboron tetrachloride–ethylene appeared to be slowly oxidised in dry air; in pure oxygen a violent exothermic reaction, with a green flash, occurred at temperatures down to $-3°$. Below this, the oxidation proceeded rapidly but quietly. A complex mixture of products was obtained (Table, p. 46), but the following facts permit some interpretation of the oxidation mechanism: (*a*) The reaction ratio $B_2Cl_4,C_2H_4 : O_2$ was 1 : 1 where no ignition occurred, 1 : >1 when ignition was observed. (*b*) Ethylene was produced in varying amounts, *e.g.*, at $-23°$ nearly half that available was found, at $-78°$ only a trace. At higher temperatures, ignition probably reduced the ethylene yield, and combustion products (carbon monoxide and dioxide) appeared, with traces of methane and hydrogen (probably pyrolysis products). The other combustion product, water, would react with any boron trichloride and give boric acid and hydrogen chloride; hence, in runs at the higher temperature, the amount of these two products increased while that of boron trichloride decreased. (*c*) Taking into account the formation of boron trichloride and hydrogen chloride as the only volatile products containing boron or chlorine shows that some of the boron and chlorine remaining in the solid residue was not brought into titratable form (as boric acid or chlorine ion) by hydrolysis. There was no evidence for peroxide in the hydrolysate.

A 1 : 1 reaction ratio between oxygen and a trialkylboron R_3B has been interpreted[5] in terms of initial co-ordination of the oxygen molecule to the boron atom, followed by rearrangement to give first the peroxy-compound $R_2BO{\cdot}OR$ and then the dialkoxide $R{\cdot}B(OR)_2$. With diboron tetrachloride–ethylene, the same initial co-ordination to one boron atom can be assumed, and this might then be followed by further co-ordination,

(III)





(IV)

by the same O_2 molecule, to the second boron atom (as in III) or by re-arrangement (to IV). It is suggested that both these products are formed and give rise to the observed products. If product (III) is assumed to give ethylene, the entity left is $Cl_2B{\cdot}O{\cdot}O{\cdot}BCl_2$. Now other simple π-bonded molecules can, like ethylene, add to diboron tetrachloride in a 1 : 1 ratio.[6] Hence, oxygen might add initially to diboron tetrachloride to give the same peroxide as is left after loss of ethylene from (III). However, oxidation of diboron tetrachloride in fact yields boric oxide and boron trichloride at low temperatures, with chlorine additionally at higher temperatures.[7] We have confirmed this observation, and have not been able to isolate the peroxide $Cl_2B{\cdot}O{\cdot}O{\cdot}BCl_2$. Hence product (III) seems likely to appear finally as ethylene, boric acid (appearing as " titratable " boron in the residue),

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[4] Apple and Wartik, *J. Amer. Chem. Soc.*, 1955, **77**, 6400.

[5] Petry and Verhoek, *ibid.*, 1956, **78**, 6416.

[6] Holliday and Massey, unpublished work.

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

boron trichloride, and possibly chlorine. If product (IV) undergoes fission at the point indicated, dimerisation of the $Cl_2BO\cdot$ fragment would give the peroxide already discussed, and hence ultimately the same products. Re-arrangement of the other fragment might occur in more than one way. One possibility is the formation of an aldehyde $Cl_2B{\cdot}CH_2{\cdot}CHO$, in which the B–C bond is retained. Retention of this bond implies presence of non-titratable boron in the hydrolysed residue. The aldehydic oxygen would, however, react further with any boron trichloride present, since carbon-attached oxygen almost invariably acts as donor to boron trichloride; and this would inevitably be followed by evolution of hydrogen chloride, leaving a non-volatile residue. The observed evolution of hydrogen chloride can be explained in this way. The fate of any chlorine evolved in the decomposition of the peroxide $Cl_2B{\cdot}O{\cdot}O{\cdot}BCl_2$ is uncertain; no free chlorine or chlorinated hydrocarbons were observed in the volatile products. Attack on the fragment $O{\cdot}CH_2{\cdot}CH_2{\cdot}BCl_2$ might give an alkoxychloro-compound such as $Cl{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl_2$; this again would probably interact further with boron trichloride, but the carbon-attached chlorine would not be expected to appear as chloride ion in the hydrolysate.

EXPERIMENTAL

Diboron tetrachloride was prepared by passage of a high-tension discharge through boron trichloride vapour, the method being based on that used by Urry *et al.*[8] and by Apple and Wartik.[9] Improvement in the yield due to use of a direct-current discharge has been reported;[10] later it was found that an equal yield was obtained by using an alternating-current arc with a high current. Yields of up to 0·2 g./hr. were obtained by using a triple-jet diffusion pump to circulate boron trichloride vapour, free from hydrogen chloride, from a trap at −78° through a water-cooled quartz H-shaped discharge cell with mercury electrodes and back to the trap. The discharge was supplied from a source giving 4 kv and 0·5 ampere. After fractionation from unused trichloride, the product had v. p. 44—46 mm. at 0°.

Complete separation from the trichloride was unnecessary in preparing the compound with ethylene; excess of the latter was added to the partly purified tetrachloride, and unused ethylene and boron trichloride were removed by fractionation. The final product had v. p. 5 mm. at 23° (Found: B, 11·6; Cl, 73·6. Calc. for B_2Cl_4,C_2H_4: B, 11·5; Cl, 74·0%).

The fractionations required above, and those for purification of starting materials, were carried out in an all-glass high-vacuum apparatus provided with float-valves. The methods used to study the reactions in this apparatus, and the analytical methods, have been described previously.[11]

Reaction with Trimethylamine.—Excess (4·03 mmoles) of trimethylamine was condensed on to 0·60 mmole of diboron tetrachloride-ethylene at −196°, and the mixture warmed to 20° and then to ~50° for 1 min. in a closed vessel. After cooling, the only volatile material was trimethylamine (2·82 mmole); hence 1·21 mmole had reacted. The solid *product* was purified by sublimation, and did not melt below 220° (Found: Cl, 46·1. $2Me_3N,B_2Cl_4,C_2H_4$ requires Cl, 45·8%). Samples treated for 2 hr. with excess of methyl alcohol, water, and hydrogen chloride severally at 20° gave quantitative recovery of these reagents; but when 0·66 mmole of product was warmed with 5·17 mmoles of hydrogen chloride in a sealed tube only 3·86 mmoles of hydrogen chloride were recovered; no other volatile product and no diboron tetrachloride-ethylene was obtained.

Reaction with Ammonia and Mono- and Di-methylamine.—Excess (6·80 mmoles) of ammonia was condensed on to 0·68 mmole of diboron tetrachloride-ethylene at −196°, and the whole was warmed to 20° in a sealed tube and left for 3 days. 2·74 mmoles of ammonia were recovered, but no other volatile product. Heating the solid residue gave a sublimate of ammonium chloride (2·73 mmoles). Hence the reaction ratio (product : NH_3 : NH_4Cl) was 1 : 5·98 : 4·02. Reactions with mono- and di-methylamine were carried out similarly, except that with dimethylamine other conditions were also investigated. Typical ratios obtained for product : amine : hydrochloride were 1 : 6·18 : 4·12 for monomethylamine and 1 : 7·1 : 3·8 for dimethylamine.

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

[9] Apple and Wartik, personal communication.

[10] Holliday and Massey, *J. Amer. Chem. Soc.*, 1958, **80**, 4744.

[11] Holliday *et al.*, *J.*, 1952, 11; 1953, 530; 1956, 4653.

Hydrolysis.—Condensing an excess of water on 0·98 mmole of diboron tetrachloride-ethylene gave no volatile products other than hydrochloric acid; titration gave 3·83 milliequivalents of chloride ion. In another experiment, the whole excess of water and the hydrogen chloride were removed by prolonged distillation and pumping; 1·92 mmoles of diboron tetrachloride-ethylene then yielded 229 mg. of a white solid [1·92 mmoles $B_2(OH)_4,C_2H_4$ weighs 225 mg.], 0·66 mmole of which when heated evolved 1·29 mmoles of water; further heating, to 300°, gave no volatile product and no visible change.

Oxidation.—Details of the runs are tabulated; units are mmoles unless otherwise stated. Excess of oxygen was condensed on to diboron tetrachloride-ethylene at −196°, and the sealed reaction vessel was warmed to the temperature indicated; excess of oxygen and other non-condensable gases was then removed, followed by the volatile products, the tube being warmed to effect complete removal of the latter. The residue was then hydrolysed and titrated for boron and chloride.

Temp.	−78°	−23°	−3·5°	20°
B_2Cl_4,C_2H_4 used	0·97	1·21	1·34	0·81
O_2 used	0·96	1·20	1·53	1·50
Products: CO	—	—	0·20	0·50
CO_2	—	—	0·10	0·12
C_2H_4	0·02	0·48	0·27	0·14
CH_4	—	—	—	Trace
H_2	—	—	—	Trace
HCl	0·71	0·65	1·48	1·56
BCl_3	0·73	0·75	0·56	0·17
Residue: Cl^- milliequiv.	0·27	0·60	0·70	0·54
B (titrn.) milliequiv.	0·98	1·47	1·56	1·32

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