420. *Diboron Tetrachloride–Olefin Compounds. Part II.*[1] *The Decomposition of Diboron Tetrachloride–Ethylene.*

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

Diboron tetrachloride–ethylene is partly decomposed by several days' heating at 200°; boron trichloride is the major volatile product. At 500° decomposition is complete in a few hours, and hydrogen, methane, ethane, boron trichloride, and polymer $(BCl)_n$ are obtained. Further heating at 500° gives more methane and ethane, probably by hydrogenation of residual $ClB{\cdot}CH_2{\cdot}CH_2{\cdot}BCl$ groups. Decomposition in a silent discharge gives hydrogen as the major decomposition product.

In Part I[1] some properties of diboron tetrachloride–ethylene were described; the B–Cl bonds showed typical reactivity, whereas the B–C–C–B bond system was relatively unreactive, although easily disrupted by oxidation to give ethylene and other products. B–Cl bonds (*e.g.*, in boron trichloride) are difficult to pyrolyse, and the same stability is shown by the B–C bonds in, *e.g.*, trimethylboron, which must be heated to 400—600° to decompose it to form polymers containing (BCH_2), (BCH), and (BC) units.[2] The alkylboron chlorides also appear to be thermally stable, apart from disproportionation equilibria which may be set up.[3] However, diboron tetrachloride readily disproportionates at ordinary temperatures to give boron trichloride and $(BCl)_n$, and tetramethyldiboron–ethylene decomposes at 100° thus:[4]

$$3B_2Me_4,C_2H_4 \longrightarrow 4BMe_3 + B_2(C_2H_4)_3$$

It is therefore difficult to predict the behaviour to heat of diboron tetrachloride–ethylene, although the elimination of boron trichloride might reasonably be expected.

Wartik and Rosenberg[5] have investigated the effect of a silent discharge on boron trichloride, diboron tetrachloride, and mixtures of these with carbon monoxide, and have observed the formation of polymers $(BCl_3,2CO)_n$. Hydrocarbons in the silent discharge lose hydrogen; it was therefore hoped that with diboron tetrachloride–ethylene in the discharge the breaking of B–Cl and B–C bonds might not occur, but that hydrogen might be lost to give compounds such as diboron tetrachloride–acetylene.

We report here results for the decomposition of diboron tetrachloride–ethylene at 200° and 500°, and in a 15 kv discharge at ordinary temperature.

Experimental

The methods of preparation, identification and analysis have been described previously.[1] Thermal decompositions were carried out in sealed tubes; volatile products were then removed, fractionated, and identified. The residues were hydrolysed, evolved gases were removed, and the hydrolysates titrated for boron and chlorine. The discharge was set up between concentric zinc-foil electrodes, separated by a simple cylindrical cell.

Results and Discussion

Thermal Decompositions.—The results are given in Table 1; units are mmoles unless otherwise stated; the analytical values for boron and chloride ion in the residues represent only titratable material. The fraction X had a vapour pressure near to that of boron trichloride, but the latter could not be separated from it by fractionation. The observed molecular weights and B : Cl ratios of the hydrolysis products suggest that boron trichloride

---

[1] Part I, Holliday and Massey, *J.*, 1960, **43**.
[2] Goubeau and Epple, *Chem. Ber.*, 1957, **90**, 171.
[3] McCusker, Hennion, and Ashby, *J. Amer. Chem. Soc.*, 1957, **79**, 5192.
[4] Urry, Kerrigan, Parsons, and Schlesinger, *J. Amer. Chem. Soc.*, 1954, **76**, 5299.
[5] Wartik and Rosenberg, *J. Inorg. Nuclear Chem.*, 1957, **3**, 388.

was the predominant constituent of fraction X, but that small amounts of other constituents $RBCl_2$ might be present. A mixture of boron trichloride (95%) and trimethylboron (5%) heated at 400° for 12 hr. had an infrared spectrum very similar to that of fraction X, suggesting that R = Me (BCl_3; *M*, 117·5. $MeBCl_2$; *M*, 96). However,

TABLE 1.

Experiment		1	2	3	4	5	6	7
Temp.		200°	550°	500°	500°	500°	500°	500°
Time (hr.)		117	4·5	5·0	9·0	9·0	48	168
B_2Cl_4,C_2H_4, added		1·10	0·87	0·99	0·93	1·15	1·04	1·41
,, found		0·47	0·00	0·00	0·00	0·00	0·00	0·00
Reaction products	H_2	0·01	0·18	0·19	0·13	0·20	0·10	0·03
	HCl	0·23	0·07	0·05	0·17	0·07	0·08	0·01
	CH_4	trace	0·15	0·16	0·35	0·48	0·60	0·99
	C_2H_6	0·00	0·07	0·11	0·05	0·08	0·07	0·04
	X	0·34	1·15	1·15	1·04	1·46	1·21	1·71
X, mol. wt.		—	—	112	115	111	116	115
Hydrolysis products of " X "	H_2	0·00	—	—	0·02	0·07	0·03	0·03
	Cl^-	—	2·90	2·94	2·89	3·94	3·41	4·76
	B	—	1·11	1·12	1·05	1·42	1·20	1·63
	Cl^- : B	—	2·63	2·63	2·74	2·77	2·84	2·82
Residue	Cl^-	0·64	—	0·36	0·31	0·29	0·40	0·61
	B	0·40	—	0·33	0·39	0·44	0·49	0·67

Table 1 shows that hydrolysis of fraction X yielded small amounts of hydrogen and it is difficult to account for this except by assuming the presence of dichloroborane ($HBCl_2$; *M*, 82). This substance is in fact formed by reaction of hydrogen and boron trichloride at high temperatures[6] and this reaction could well have occurred here, the other reaction product being hydrogen chloride, also found in small amounts. If X is assumed to contain about 90% of boron trichloride approximately 1 mol. of boron trichloride was formed from diboron tetrachloride–ethylene in the high-temperature decompositions.

Expt. 1 is typical of several at 200° and shows that decomposition was then very slow. The large amount of hydrogen chloride may have been due in part to hydrolysis by traces of water desorbed from the reaction vessel during the prolonged reaction period. The only other important volatile product was impure boron trichloride. Separation of unchanged diboron tetrachloride–ethylene from the non-volatile products was very difficult in these low-temperature experiments.

In experiments at 500° decomposition was complete in a few hours and dark-coloured residues were obtained. Analysis of the products of hydrolysis of these suggested the presence of $(BCl)_n$ polymers. In expt. 2, the residue was again heated at 300° after removal of the volatile product and a yellow sublimate obtained; hydrolysis indicated this to be $(BCl)_n$: a similar yellow polymer is obtained during the preparation of diboron tetrachloride. In expt. 5 the residue was heated for many hours at 500° after removal of volatile products, but did not yield any further appreciable amounts of volatile material. These experiments suggest that some $(BCl)_n$ was present as such in the residues, and that further loss of volatile material in expts. 6 and 7 was due to interaction of the residue with gases already present.

No ethylene was found in the hydrocarbons evolved at 500°; Table 1 shows that these were methane and ethane with some hydrogen also; the methane content increased at the expense of the hydrogen with increasing time of heating. An experiment in which ethylene alone (0·96 mmole) was heated for 5 hr. at 500° in a sealed tube gave only 0·05 mmole of methane, 0·14 mmole of ethane, and 0·02 mmole of hydrogen; hence it is unlikely that ethylene was a primary product of the decomposition process. This seems to preclude the possibility of a decomposition

$$nB_2Cl_4,C_2H_4 \longrightarrow nBCl_3 + (BCl)_n + nC_2H_4$$

---

[6] Lynds and Stern, *J. Amer. Chem. Soc.*, 1959, **81**, 5006.

which would have accounted for the observed amount of boron trichloride formed; the amount of $(BCl)_n$ was however much less than that expected from this equation. It therefore seems better to postulate loss of boron trichloride by an intermolecular process as the initial step in decomposition:

$$nCl_2B\cdot CH_2\cdot CH_2\cdot BCl_2 \longrightarrow (ClB\cdot CH_2\cdot CH_2)_n + nBCl_3$$

The resulting non-volatile material presumably does not undergo further breakdown to any extent at 200°, although some rearrangement may occur whereby the boron becomes partly hydrolysable; the chlorine atoms would be recovered as chloride on hydrolysis if they remained attached to boron atoms.

At 500° the further process occurring is clearly loss of hydrogen and this increases with increasing time of heating, although the form in which the hydrogen appears changes with time. Since compounds containing $\colon B\cdot CH\colon CH\cdot B\colon$ and $\colon B\cdot C\colon C\cdot B\colon$ groups are known,[7] loss of hydrogen as such can occur without simultaneous rupture of B–C or C–C bonds; but the appearance of $(BCl)_n$ must mean that some B–C bonds have broken. Moreover, the amount of titratable chlorine diminishes at 500° indicating transfer of chlorine atoms from boron to carbon. Nevertheless the important initial effect at 500° is loss of hydrogen as such. Later, the methane concentration becomes appreciable; but this methane cannot come from unchanged diboron tetrachloride–ethylene (which has all decomposed) or from the non-volatile products directly since these on further heating evolve no more volatile material. It therefore seems probable that methane (and ethane) is formed by reaction of the residual $ClB\cdot CH_2\cdot CH_2$ groups which have not lost hydrogen with the hydrogen already formed, *e.g.*

$$(ClB\cdot CH_2\cdot CH_2)_n + 2nH_2 \longrightarrow (BCl)_n + 2nCH_4$$

or

$$(ClB\cdot CH_2CH_2)_n + nH_2 \longrightarrow (BCl)_n + nC_2H_6$$

The amount of $(BCl)_n$ increases with time, but not so much as might be expected by this argument; it is possible that slow disproportionation may be occurring giving boron trichloride and elemental boron. Ultimately a residue containing mainly boron and carbon is obtained.

Decompositions in the Discharge.—The results of a typical experiment are given in Table 2 (units are mmoles):

TABLE 2.

	B_2Cl_4,C_2H_4		Products					Residue	
Time (hr.)	added	found	H_2	HCl	CH_4	C_2H_6	BCl_3	Cl^-	B
4·0	1·05	0·05	0·50	0·14	trace	0·00	0·27	2·67	1·13

The boron trichloride obtained was pure, suggesting that the impurities found in the previous experiments may have been due to secondary reactions of the boron trichloride originally produced, at the high temperatures used. The residue was a mixture of a solid with some viscous liquid; hydrolysis gave a trace of hydrogen, but the product was not completely soluble and recovery of boron and chlorine was not complete. Experiments over longer periods gave similar results except that the yield of hydrogen was increased.

The results suggest that processes similar to those observed in the early stages of the thermal decompositions are occurring except that here loss of hydrogen is more rapid than elimination of boron trichloride. There was no evidence for the formation of compounds such as $Cl_2B\cdot CH\colon CH\cdot BCl_2$, although the viscous liquid product may have contained units of this formula linked through C–C bonds; the solid product may then have contained units $ClB\cdot CH_2\cdot CH_2$ as found in the thermal experiments.

---

[7] Hartmann and Birr, *Z. anorg. Chem.*, 1959, **299**, 174.

These studies suggest that the high reactivity of the B–Cl bonds in diboron tetrachloride–ethylene is likely to interfere with studies of the B–C–C–B bond system; hence replacement of the chlorine atoms by entities giving less reactive bonds to boron may be necessary for further fruitful studies.

One of us (A. G. M.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

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

[*Received, November 26th,* 1959.]