222. *The Reactions of Boron Chlorides with Acetone.*

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Acetone and boron trichloride react rapidly at −78° to form a white solid of variable composition, which decomposes above −15° with evolution of hydrogen chloride. All three chlorine atoms of the boron trichloride can be lost as hydrogen chloride. Acetone and diboron tetrachloride react in a molar ratio of 2 : 1 or *ca.* 1 : 1 at −78° according to the conditions. Two moles of hydrogen chloride are evolved per mole of diboron tetrachloride when the mixture is heated to 100°; 2-chloropropane and t-butyl chloride are also formed. At 150° the amount of hydrogen chloride evolved decreases.

GREENWOOD and PERKINS,[1] when attempting to measure the heat of solution of boron trichloride in acetone, noted that the expected 1 : 1 addition compound could not be isolated owing to its rapid decomposition to hydrogen chloride and resin. This reaction has now been studied more closely. Reaction was rapid at temperatures between −78° and −35° to form white solids which always contained acetone in excess of the amount required for 1 : 1 addition even when boron trichloride was used in excess. Increasing the temperature of reaction to 0° decreased the quantity of acetone associated with each mole of boron trichloride but side-reactions involving the elimination of hydrogen chloride then proceeded to a considerable extent, making it impossible to obtain the 1 : 1 addition compound pure. When the solid product was warmed to room temperature (22°) it rapidly melted to deep red liquid which evolved hydrogen chloride vigorously; the liquid, at room temperature or when heated, gradually solidified to a dark red polymer.

Three generalisations can be made about the thermal decomposition of the solid: (i) All three chlorine atoms of the original boron trichloride could be recovered as hydrogen chloride, provided sufficient acetone was present. (ii) More than two moles of hydrogen chloride were evolved per original mole of acetone at 135°. (iii) No alkyl chlorides were detected in any of the experiments.

Reaction of Acetone with Diboron Tetrachloride.—With excess of acetone, diboron tetrachloride formed a white adduct $2COMe_2,B_2Cl_4$ between −78° and −23° which slowly lost acetone on increase of temperature to 0°, the loss being accompanied by the formation of small quantities of hydrogen chloride. With diboron tetrachloride in excess, ratios approaching 1 : 1 could be achieved at −45°. The adducts so formed only slowly evolved hydrogen chloride at room temperature, forming red solids. On decomposition of the 2 : 1 adduct at temperatures up to 100°, two moles of hydrogen chloride were evolved per mole of diboron tetrachloride used. Ratios based on hydrogen chloride formed in reactions involving the boron chlorides are necessarily somewhat approximate owing to side reactions with water outgassed from the reaction vessel walls during the experiment; in this case, the maximum deviation was *ca.* 5%.

In contrast to the boron trichloride experiments, several alkyl chlorides were isolated among the decomposition products, those in the greatest yield being 2-chloropropane and t-butyl chloride. Increasing the decomposition temperature to 150° caused the ratio $HCl : B_2Cl_4$ to fall well below the 2 : 1 value noted above, indicating a secondary reaction between the polymeric residue and the hydrogen chloride initially evolved. Methylboron dichloride, $CH_3{\cdot}BCl_2$, could also be isolated in small yield during the decomposition of adducts containing a deficiency of acetone from the 2 : 1 ratio. This probably indicated the presence of boron–carbon bonds in the residues, since it is known that compounds such as B_2X_4,C_2H_4 ($X =$ halogen) evolve alkylboron dihalides on pyrolysis.[2,3]

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[1] Greenwood and Perkins, *J.*, 1960, 356.

[2] Holliday and Massey, *J.*, 1960, 2075.

[3] Ceron, Finch, Frey, Kerrigan, Parsons, Urry, and Schlesinger, *J. Amer. Chem. Soc.*, 1959, **81**, 6388.

EXPERIMENTAL

The materials were handled in a conventional high-vacuum apparatus equipped with mercury-float valves. Acetone was purified *via* its sodium iodide complex,[4] which was allowed to dissociate under vacuum: v. p. 67 mm. at 0°, 175 mm. at 20°. The preparation of diboron tetrachloride has been described previously.[5] Boron trichloride was fractionated through baths held at −78° and −112°; v. p. 476 mm. at 0°. Unless otherwise stated all the quantities recorded below are in terms of mmoles or mequivs.

Reaction of Boron Trichloride with Acetone.—Acetone and boron trichloride (excess) were condensed into a reaction vessel at −196°, and the mixture was warmed to −78° (or −35°); a rapid reaction ensued, forming a white solid. The excess of boron trichloride was then removed, purified from traces of hydrogen chloride by fractionation at −126°, and measured. In a typical experiment boron trichloride (1·73) and acetone (1·06) were allowed to react for 2 hr. at −78°; 1·19 mmoles of boron trichloride and 0·06 mmole of hydrogen chloride were the sole volatile products. Hence $COMe_2 : BCl_3 = 1{\cdot}96 : 1$. On warming the white solids formed at −78° or −35°, rapid coloration started at −6°, −8° to −9°, and −9° in three independent experiments, the coloration being accompanied by evolution of hydrogen chloride. Very slow coloration was also noted in a sample of solid held at −15° for long periods. The decomposition of the solid at higher temperatures was studied by allowing the acetone and boron trichloride to react as above at −78°, the reaction tube was then sealed and held at the required temperature for some arbitrary time. When the tube, cooled to −196°, was opened to the vacuum apparatus, any non-condensable gases present were removed by the Töpler pump and identified by combustion analysis. The material volatile at −126° was shown to be hydrogen chloride by vapour-density and vapour-pressure determinations. The remaining volatile material was identified by its infrared spectrum, any boron trichloride present being estimated by hydrolysing a sample with distilled water and titrating the resulting hydrochloric and boric acids. Two experiments are summarised below: (1) Acetone (1·80) and boron trichloride (0·84) after reaction at −78° were held at 23° for 14 hr.; hydrogen chloride (1·75) and boron trichloride (0·03) were the only volatile products. Heating for 4 hr. at 90° produced hydrogen chloride (0·49) and boron trichloride (0·07). Hence, total hydrogen chloride produced = 2·24, boron trichloride used = 0·74. Thus the ratio $HCl : BCl_3 = 3{\cdot}03 : 1$. (ii) Acetone (0·85) and boron trichloride (1·65) were heated at 100° for 7 hr. Hydrogen chloride (1·63) and boron trichloride (0·87) were recovered. Acetone : HCl = 1 : 1·91. Heating the mixture at 135° for a further 12 hr. produced more hydrogen chloride (0·15) and boron trichloride (0·05). Ratio, acetone : HCl = 1 : 2·11. The boron and chlorine remaining in the residues were readily titratable after hydrolysis with distilled water at room temperature.

Reaction of Acetone with Diboron Tetrachloride.—The experiments were conducted similarly to those with boron trichloride and acetone. Acetone (3·13) and diboron tetrachloride (0·86) were allowed to react at −78° for one hr., 1·36 mmoles of acetone then being recovered; ratio $COMe_2 : B_2Cl_4 = 2{\cdot}06 : 1$. In an experiment employing an excess of diboron tetrachloride (0·83) over acetone (0·72), 0·22 mmole of diboron tetrachloride was removed after 10 min. at −45°; ratio, $COMe_2 : B_2Cl_4 = 1{\cdot}18 : 1$.

The decomposition of the 2 : 1 adduct was studied by allowing measured quantities of diboron tetrachloride and acetone to react at −78°, the white adduct being rapidly formed. The reaction tube was then sealed and held at the required temperature as in the boron trichloride experiments. The hydrogen chloride isolated from these experiments contained *ca.* 2% of an impurity which, from its volatility at −126° and the fact that it absorbed in the C–H region of the infrared spectrum, was assumed to be a lower alkane but was not positively identified. Owing to its presence, the quantity of hydrogen chloride in the −126° volatile material had to be estimated by titration. In the experiments with boron trichloride the same impurity was present but in amounts much less than the experimental error involved in the measurement of the vapour density or volume of the hydrogen chloride; hence its presence could be neglected. A summary of several experiments conducted under various conditions of temperature, time, and concentration of reactants is shown in the Table; methylboron dichloride was isolated in those experiments marked by an asterisk. Fraction X

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[4] Vogel, " Practical Organic Chemistry," Longmans, Green and Co., 1954, p. 170.

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

contained several alkyl chlorides, mainly 2-chloropropane and t-butyl chloride; in experiments 3 and 7 the fraction also contained small quantities of excess of acetone.

Decomposition of the acetone–diboron tetrachloride adduct.

Expt. No.	1*	2*	3	4*	5	6	7	8*	9
B_2Cl_4 added	0·86	0·46	0·82	1·00	0·83	0·89	0·65	0·91	0·93
Acetone added	1·77	0·72	3·37	1·77	1·84	1·76	3·02	1·44	0·96
Reaction time, hr.	2	1	3	3	10	10	6	16	19
Reaction temp.	90°	100°	100°	100°	100°	100°	150°	150°	150°
Reaction products: H_2	—	—	0·03	—	—	trace	0·20	—	—
CH_4	1·80	0·76	1·72	2·08	1·73	1·82	1·04	1·60	1·22
BCl_3	0·20	0·35	0·00	0·11	0·12	0·18	0·00	0·35	0·58
X			0·50	0·09	0·17	0·12	1·13	0·18	0·44
Residues: Hydrolysis H_2	—	—	0·34	—	0·07	0·05	0·26	—	—
Cl^-	—	0·30	0·88	1·05	0·90	0·85	0·35	0·36	0·35
B	—	—	—	1·36	1·70	1·54	—	1·10	0·72
Ratio B_2Cl_4 : HCl	1 : 2·09	1 : 1·65	1 : 2·10	1 : 2·08	1 : 2·08	1 : 2·05	1 : 1·60	1 : 1·76	1 : 1·31

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