SOME REACTIONS OF TETRA(DIMETHYLAMINO)-DIBORON

A. G. MASSEY and N. R. THOMPSON University Chemical Laboratory, Lensfield Road, Cambridge

(Received 22 June 1962; in revised form 16 July 1962)

Abstract—The reactions of tetra(dimethylamino)diboron, $B_2[N(CH_3)_2]_4$, with oxygen, hydrogen, ethylene, nitric oxide and various chlorinating and fluorinating agents are described.

DIBORON compounds as simple sources of boron-boron bonds, have received active interest in the last two decades⁽¹⁾. The halides are difficult to prepare but recently it has proved possible to isolate tetra(dimethylamino)diboron, $B_2[N(CH_3)_2]_4$, in high yield by the Wurtz-type reaction.⁽²⁾

$$2XB[N(CH_3)_2]_2 + 2Na \rightarrow 2NaX + B_2[N(CH_3)_2]_4$$

X = Chlorine or bromine.

Tetra(dimethylamino)diboron, a colourless, slightly volatile liquid, is extremely sensitive to traces of moisture with which it produces dimethylamine and sub-boric acid. Previous workers had noted its high thermal stability; we restudied the thermal decomposition hoping to prepare such compounds as $[BN(CH_3)_2]_x$ analogous to the boron chlorides, B_4Cl_4 , B_8Cl_8 and $(BCl)_x$:

$$xB_2[N(CH_3)_2]_4 \rightarrow xB[N(CH_3)_2]_3 + [BN(CH_3)_2]_x$$

Table 1 shows that even after many days at 300° only about 20 per cent of the boronboron bonds had been broken. The decomposition, though producing tri(dimethylamino)borane, B[N(CH₃)₂]₃, as one product was obviously not straight-forward since methane was obtained in significant yield indicating parallel fission of the carbonnitrogen bonds. Furthermore, infra-red studies on the liquid product also indicated traces of a compound containing boron-hydrogen links although the yield of this compound was so small as to preclude its isolation. (Its presence will of course affect

 TABLE 1.—THERMAL DECOMPOSITION OF TETRA(DIMETHYLAMINO)DIBORON.

 (Quantities expressed in mmoles)

Experiment No.	1	2	3	4
$B_2(NMe_2)_4$ used	0.84	0.92	0.84	0.92
Temperature (°C)	200	300	300	300
Time (days)	4	4	16	24
Hydrogen removed	0.01	0.06	trace	0.00
Methane removed	0.01	0.01	0.12	0.17
Dimethylamine removed	0.03	0.11	0.03	0.02
Hydrogen on alkaline hydrolysis of liquid residue	0.76	0.76	0.67	
Recovery of B-B bonds (%)	92	83	80	

⁽¹⁾ A. K. HOLLIDAY and A. G. MASSEY, Chem. Revs. 62 (1962).

⁽²⁾ R. J. BROTHERTON, A. L. MCCLOSKEY and H. STEINBERG, J. Amer. Chem. Soc. 82, 6242 (1960).

the estimation, by alkaline hydrolysis, of boron-boron bonds in the decomposition products though to a negligible extent).

It has been reported that tetra(dimethylamino)diboron is not attacked by $oxygen^{(2)}$, but on repeating the work under more quantitative and more vigorous conditions we found a complex reaction. In some experiments dimethylaminoboroxole, [BON(CH₃)₂]₃, and tri(dimethylamino)borane were formed as might be expected from previous work using the tetra-alkoxydiborons.⁽³⁾

$$B_2[N(CH_3)_2]_4 + \frac{1}{2}O_2 \rightarrow B[N(CH_3)_2]_3 + \frac{1}{3}[BON(CH_3)_2]_3$$

However, only when the tetra(dimethylamino)diboron was in a large excess (Expt. 8, Table 2) were reaction ratios obtained which approximated to those demanded by the equation but even then side reactions also produced methane, hydrogen and dimethylamine. Though the simultaneous presence of amines and carbon dioxide in some experiments caused difficulty in obtaining accurate volume data the results clearly showed amounts of free amine which could not be explained away by adventitious hydrolysis of the starting material by water occluded in the glass walls of the reaction vessel; cf. the small amounts of amine isolated in the decomposition experiments. The presence of hydrogen in the gaseous products suggested the amine may have arisen from a reaction of the type:

$$B - N + H_2 \rightarrow B - H + (CH_3)_2 NH$$

but subsequent experiments showed hydrogen did not react with tetra(dimethylamino)diboron under these conditions; cf. the reaction of diboron tetrachloride and hydrogen.⁽¹⁾ The reaction products, carbon monoxide and carbon dioxide, indicated that oxidation of the organic material was taking place:

$$-CH_3 + O_2 \rightarrow CO + CO_2 + H_2O_2$$

Water formed in this way would certainly explain the isolation of dimethylamine:

$$B - N(CH_3)_2 + H_2O \rightarrow B - OH + HN(CH_3)_2$$

but the mechanism by which ammonia and mono-methylamine appear as products remains obscure.

Other diboron compounds show remarkable activity towards nitric oxide.⁽¹⁾ However, tetra(dimethylamino)diboron reacted only sluggishly, and incompletely, at 200° to produce nitrous oxide, dimethylamino boroxole and tri(dimethylamino)borane, presumably according to the equation:

$$B_2[N(CH_3)_2]_4 + 2NO \rightarrow N_2O + \frac{1}{3}[BON(CH_3)_2]_3 + B[N(CH_3)_2]_3$$

The incompleteness of the reaction and the extreme volatility of the nitric oxide precluded a quantitative study of the system.

Ethylene reacts smoothly at low temperatures with the diboron tetrahalides⁽¹⁾ to produce 1,2 bis(dihaloboryl)ethanes, $X_2BC_2H_4BX_2$, X = Cl or F. Ethylene did not react with tetra(dimethylamino)diboron at 200°; nor did the two react at room

⁽³⁾ R. J. BROTHERTON, A. L. MCCLOSKEY, J. L. BOONE and H. M. MANASEVIT, J. Amer. Chem. Soc. 82, 6245 (1960).

temperature in the presence of boron trichloride. The decreased reactivity of tetra(dimethylamino)diboron towards the π -bonded donor molecules oxygen, nitric oxide and ethylene (as compared to the diboron halides) is no doubt due to substantial "backdonation" of electrons from the nitrogen atoms into the vacant 2*p*-orbitals of the two boron atoms. Such an effect would inhibit a reaction involving an intermediate of the

$$X = X$$

 $B \leftarrow Z$
 Z
 $B \leftarrow Y$
 $X = X$
 $X = X$
 $X = X$

nitric oxide with diboron tetrachloride.⁽¹⁾

The attempted fluorination or chlorination of tetra(dimethylamino)diboron using phosphorus (III) chloride, antimony (III) fluoride, iodine pentafluoride and tin (IV) chloride gave involatile, moisture sensitive solids and liquids but no volatile compounds. When excess of sulphur chloride pentafluoride, SF_5CI , was used boron trifluoride was produced, chlorine and sulphur tetrafluoride being isolated as by-products.

Although transamination reactions occur with several amines including monoethylamine,⁽²⁾ little or no exchange occurred between tetra(dimethylamino)diboron and ammonia even at room temperature thus allowing studies to be made on the diboron compound in liquid ammonia. However, the hope that useful substitution reagents, such as $KB[N(CH_3)_2]_2$, might be made was short-lived; potassium or sodium did not cleave the boron-boron bond in liquid ammonia -78° .

EXPERIMENTAL

Volatile compounds were handled in conventional vacuum systems; products which were moisture sensitive were handled in a dry-box. Quantities given below are expressed in mmoles. unless otherwise stated.

We thank Borax Consolidated Ltd. for the sample of tetra(dimethylamino)diboron. On hydrolysis with 10 per cent caustic soda at 100° 235·1 mg of the tetra(dimethylamino)diboron (1·188) produced 1·036 mmole of hydrogen in 5·5 hr, 1·182 mmole in 10·5 hr and 1·188 mmole at the end of 15·5 hr.

Hydrolysis of the tetra(dimethylamino)diboron sometimes produced small amounts of ammonia mixed with the dimethylamine; the infra-red spectrum of tetra(dimethylamino)diboron showed no N—H bonds whilst analysis showed its purity approached 100 per cent. A further unexplained fact noted in the hydrolysis was that more vigorous conditions (15 hr at 100–120°) were required to produce the quantitative amount of hydrogen on fission of the boron-boron bond with 10 per cent caustic soda when compared to diboron tetrachloride, which required 3 hr at 70°. Both compounds initially produce sub-boric acid which is then oxidised to boric acid:

$$B_2(OH)_4 + 2H_2O \xrightarrow{OH^-} 2B(OH)_3 + H_2$$

Reaction with hydrogen

Tetra(dimethylamino)diboron (0.71) and hydrogen (1.29) were heated in a sealed tube at 200° for 48 hr. The volatile products were hydrogen (1.30) and dimethylamine (0.04). An infra-red study of the remaining liquid showed it to be pure tetra(dimethylamino)diboron.

Reaction with oxygen

The experiments, conducted at $200-300^{\circ}$ in sealed tubes, are summarized in Table 2. Combustion and infra-red analyses showed the non-condensable products to be hydrogen, methane and, sometimes, carbon monoxide. The material volatile at -78° was mainly dimethylamine; varying proportions

of monomethylamine and ammonia were also present. If a large excess of oxygen was used (Experiments 12 and 13) carbon dioxide and nitrous oxide could also be detected in the -78° volatile fraction.

When oxygen:tetra(dimethylamino)diboron ratios of about 1:1 were used, large colourless crystals, identified by their volatility and infra-red spectrum as dimethylamino boroxole $[BON(CH_3)_2]_3$, formed on cooling the tubes to room temperature; infra-red spectra of the liquid residues also revealed the presence of tri(dimethylamino)borane. Reaction ratios greater than 1:1 produced non-volatile tar-like materials indicating extensive oxidation of the organic material.

 TABLE 2.—REACTION OF TETRA(DIMETHYLAMINO)DIBORON WITH OXYGEN (Quantities expressed in mmoles)

				and a design of the local division of the lo					
Experiment No.	5	6	7	8	9	10	11	12	13
$B_2[N(CH_3)_2]_4$ taken	0.59	1.03	0.83	1.39	1.08	0.92	0.66	0.44	0.36
Temperature (°C)	200	200	200	300	300	300	300	300	200
Time (days)	3	4	16	1	1	1	6	1	10
Oxygen added	1.13	0.90	1.06	0.45	0.83	1.03	1.25	2.19	1.94
Oxygen recovered	0.74	0.00	0.00	0.00	0.00	0.00	0.00	0.25	0.15
Non-condensable gas removed	0.00	0.04	0.08	0.11	0.13	0.06	0.13	0.38	0.19
-78° Volatile material removed	0.36		1.30		1.18	<u> </u>	1.19	0.95	0.43
Hydrogen on alkaline									
hydrolysis of liquid residues	0.00	0.00	<u> </u>	0.61	0.00	0.00	0.00	0.00	
Ratio O_2 : $B_2[N(C\dot{H}_3)_2]_4$	0.66:1	0.87:1	1.3:1	0.58:1	0.77:1	1.1:1	1.9:1	4·0:1	5.0:1

Reaction with nitric oxide

Tetra(dimethylamino)diboron (0.86) and nitric oxide (1.01) were held at 200° for 48 hr. Nitric and nitrous oxides (0.86) were recovered; alkaline hydrolysis of the liquid residue indicated that 0.65 mmoles of tetra(dimethylamino)diboron remained unchanged. Other similar experiments showed the presence of small amounts of dimethylaminoboroxole and tri(dimethylamino)borane in the reaction products.

Reaction with ethylene

Ethylene was recovered in over 99 per cent yield when heated with tetra(dimethylamino)diboron at 200° for 48 hr; no ethylene take-up was detected when the two were held at room temperature in the presence of boron trichloride for three days.

Reaction with ammonia

Tetra(dimethylamino) diboron (1.00) and ammonia (7.32) were held at room temperature for ten days in a sealed tube. At the end of this time 7.36 mmole of ammonia, containing only a trace of dimethylamine, were recovered. Micro- and infra-red analyses of the remaining liquid residue showed it to be unchanged tetra(dimethylamino)diboron.

Reaction with sulphur chloride pentafluoride

Sulphur chloride pentafluoride (0.70) and tetra(dimethylamino)diboron (1.14) were allowed to warm up slowly from -196° . Just below room temperature a vigorous reaction produced an involatile liquid and a little thionyl fluoride, SOF₂. Alkaline hydrolysis at 100° for 10 hr produced 0.32 mmole of hydrogen showing that extensive cleavage of the boron-boron bond had occurred. Experiments conducted at room temperature with an excess of sulphur chloride pentafluoride produced boron trifluoride, sulphur tetrafluoride and chlorine as the products volatile at -112° ; traces of sulphur dioxide where retained by the -112° trap. The involatile liquid residues contained no boronboron bonds. The lack of boron trichloride in the volatile products prompted a study of the system, boron trichloride-sulphur chloride pentafluoride; no reaction occurred at room temperature.

Acknowledgement—We thank the Imperial Chemical Industries and British Titan Products for Fellowships.