

## The Lewis Acidity of Trialkoxyboranes: A Reinvestigation

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A reinvestigation into the Lewis acidity of trialkoxyboranes  $B(OR)_3$ , has shown that contrary to earlier reports none of these compounds forms Lewis acid-base adducts with nitrogen bases. However they do form 'onium' salts in which the anion is a tetra-alkoxyborate complex. The thermodynamic stability of these salts is discussed and is shown to be critically dependent upon the crystal lattice energy and temperature. Triphenoxyborane forms the piperidine adduct and corresponding piperidinium salt.

THE literature on the Lewis acidity of trialkoxyboranes is not large. The only compound considered to show Lewis acid behaviour is the methyl derivative. Goubeau, *et al.*<sup>1,2</sup> have reported its adducts with ammonia and the methylamines. Gould, *et al.*<sup>3,4</sup> have reported interactions of various degrees between trimethoxyborane and numerous amines. They observed that some of the addition reactions are strongly catalysed by lower aliphatic alcohols but were unable to propose a mechanism for the catalysis. No solid compounds were obtained on mixing amines with triethoxyborane, tri-*n*-butyloxyborane or tri-*n*-pentyloxyborane, although considerable heat evolution was noted with triethoxyborane. Landesman and Williams<sup>5</sup> however, observed poorly characterised solids from trimethoxyborane, triethoxyborane, and triallyloxyborane with several amines. Young and Anderson<sup>6</sup> reacted trimethoxyborane with various amines in the presence of different solvents and rationalised their findings in terms of inclusion compounds.

Triaryloxyboranes give well defined adducts with a variety of amines.<sup>7,8</sup>

In order to obtain quantitative physical data on trialkoxyborane adducts attempts were made to make some of the reported solid adducts of trimethoxyborane.

### RESULTS AND DISCUSSION

On addition of equimolar amounts of piperidine or ethylenediamine to trimethoxyborane no visible reaction was observed. Addition of catalytic amounts of methanol resulted in the immediate production of white crystalline material. Further addition of methanol produced a vigorous exothermic reaction and the reaction mixture solidified. Analysis showed the products to have the empirical formulae:  $C_5H_{11}N \cdot$

<sup>1</sup> J. Goubeau and U. Böhm, *Z. anorg. Chem.*, 1951, **266**, 161.

<sup>2</sup> J. Goubeau and R. Link, *Z. anorg. Chem.*, 1951, **267**, 27.

<sup>3</sup> E. S. Gould and S. V. Urs, *J. Amer. Chem. Soc.*, 1952, **74**, 2948.

<sup>4</sup> E. S. Gould and H. Hom, *J. Amer. Chem. Soc.*, 1956, **78**, 5772.

<sup>5</sup> H. Landesman and R. E. Williams, *J. Amer. Chem. Soc.*, 1961, **83**, 2663.

$B(OMe)_3 \cdot MeOH$  and  $NH_2CH_2CH_2NH_2 \cdot B(OMe)_3 \cdot MeOH$ . The piperidine compound sublimed unchanged. It had the same m.p. (Table I) as Gould's piperidine adduct.

TABLE I

The melting points<sup>a</sup> of the compounds  $Base \cdot B(OR)_3 \cdot ROH$

Base	R		
	Me	Et	Pr <sup>l</sup>
Piperidine	74.5	18	<i>b</i>
$\frac{1}{2}$ (Ethylenediamine)	81—82	17.5	—24
Diethylamine	52	15	<i>b</i>
Cyclohexylamine	41.5	8	—13
Triethylamine	<i>b</i>	<i>b</i>	<i>b</i>
Pyridine	<i>b</i>	<i>b</i>	<i>b</i>

<sup>a</sup> In sealed tubes. <sup>b</sup> No solid compound produced at temperatures above  $-60^\circ$ .

The ethylenediamine compound did not melt but decomposed over a wide range and on sublimation yielded white crystals with the empirical formula  $NH_2CH_2CH_2NH_2 \cdot 2B(OMe)_3 \cdot 2MeOH$  and the same m.p. as Gould's ethylenediamine adduct. The composition of this compound was confirmed by direct synthesis from the stoichiometric amounts of reactants. After characterisation of these two systems the direct preparation of other similar amine-trialkoxylborane-alcohol systems was attempted. The results are summarised in Table I. In all cases where solid products were produced, they were not obtained until the alcohol was added. All were white crystalline compounds.

These compounds can be formulated as either the Lewis acid-base adducts solvated with one mole of alcohol (I) or as the substituted ammonium ('onium') salts (II) of the unstable acids  $HB(OR)_4$  whose metal salts are well known.<sup>9,10</sup>

<sup>6</sup> D. M. Young and C. D. Anderson, *Canad. J. Chem.*, 1962, **40**, 1805.

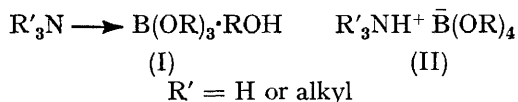
<sup>7</sup> M. F. Lappert, *Chem. Rev.*, 1956, **56**, 959.

<sup>8</sup> R. C. Mehrotra and G. Srivastava, *J. Indian Chem. Soc.*, 1962, **39**, 526.

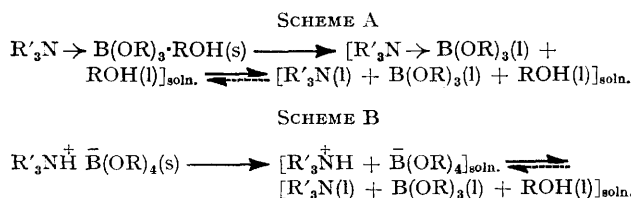
<sup>9</sup> E. Wiberg and R. Hartwimmer, *Z. Naturforsch.*, 1955, **10b**, 290.

<sup>10</sup> H. C. Brown and E. J. Mead, *J. Amer. Chem. Soc.*, 1956, **78**, 3614.

The  $^{11}\text{B}$  n.m.r. spectra of the trimethoxyborane derivatives in benzene and nitrobenzene and of the neat liquid



triethoxyborane and tri-isopropoxyborane systems showed a single resonance in the range  $-18.0 \pm 0.3$  p.p.m. from external boron trifluoride etherate. This shift is identical to that observed for the pure trialkoxyboranes<sup>11</sup> and indicates that in an inert solvent or in the liquid state the compounds completely dissociate to starting materials. The only compounds studied in this work which are solids above room temperature are the methyl derivatives. The expected steps in the dissociation of (I) and (II) in solution are given in Schemes A and B.



If the solvent is inert, then both schemes give the same final product. However if the solvent is the alcohol ROH, then the equilibrium in Scheme A should still be completely over to the right whereas in Scheme B it should be driven to the left. When the methyl derivatives were dissolved in methanol the single  $^{11}\text{B}$  resonance absorption shifted toward the high field value of  $-2.9$  p.p.m. observed for lithium tetramethoxyborate.<sup>12</sup> The magnitude of the upfield shift is a function of amine and to a slight extent, concentration. For the methyl compounds listed in Table 1 the resonance appeared in the range  $-10$  to  $-6$  p.p.m. The single absorption indicates that the boron atom is undergoing rapid exchange between the trigonal and tetrahedral environments. These observations are consistent with structure (II).

TABLE 2

Compound	Conductivity $\Omega^{-1} \text{cm}^{-1}$	
	Methanol <sup>a</sup>	Nitrobenzene <sup>b</sup>
PipH <sup>+</sup> B(OMe) <sub>4</sub> <sup>-</sup>	$1.61 \times 10^{-3}$	$1.69 \times 10^{-6}$
enH <sup>+</sup> B(OMe) <sub>4</sub> <sup>-</sup>	$1.24 \times 10^{-3}$	$1.60 \times 10^{-3}$
enH <sub>2</sub> <sup>2+</sup> [B(OMe) <sub>4</sub> ] <sub>2</sub> <sup>-</sup>	$1.63 \times 10^{-3}$	$1.78 \times 10^{-3}$

<sup>a</sup> 0.05M solutions. <sup>b</sup> Because of the low solubility of the compounds in nitrobenzene at room temperature (17°) these values are for saturated solutions (approximately 0.03M).

Conductivity measurements on the piperidine and two ethylenediamine compounds of trimethoxyborane

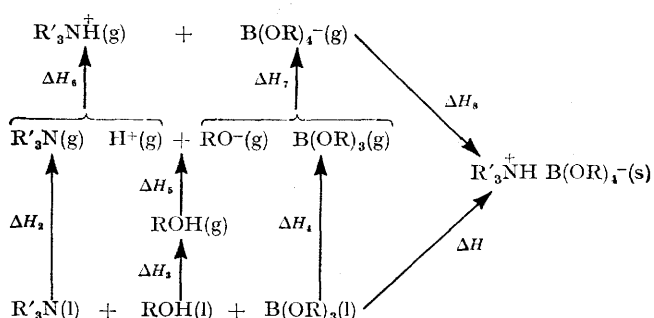
<sup>11</sup> E. F. Mooney, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 272.  
<sup>12</sup> T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, 1959, **63**, 1533.

<sup>13</sup> J. A. Riddick and W. B. Bunger, 'Techniques of Chemistry,' vol. 2, 'Organic Solvents,' 3rd edn., Interscience, New York, 1970.

<sup>14</sup> E. M. Arnett, F. M. Jones, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 4724.

confirmed that structure (II) is correct. The conductivities of the compounds in methanol ( $\kappa = 6.60 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ ) and nitrobenzene ( $\kappa = 1.00 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ ) are shown in Table 2. The considerable increase in conductivity of the methanol solutions confirms the presence of ions derived from the compounds with structure (II).

A large negative entropy change is likely to accompany these reactions. Therefore the enthalpy change and possibly the temperature at which the reaction is carried out are critical. The enthalpy change can be sub-divided according to the following cycle:



For each trialkoxyborane, and its corresponding alcohol,  $\Delta H_3$ ,  $\Delta H_4$ ,  $\Delta H_5$ , and  $\Delta H_7$  are constant. For change of amine the variables are the enthalpy of vaporisation,  $\Delta H_2$ , the negative value of the proton affinity,  $\Delta H_6$ , and the crystal lattice energy  $\Delta H_8$ . The enthalpies of vaporisation of the amines used in this work lie in the range 32 to 47 kJ mol<sup>-1</sup>.<sup>13</sup> Likewise their proton affinities<sup>14-17</sup> lie in the range 945 to 985 kJ mol<sup>-1</sup> and it is seen that pyridine is as strong a base in the gas phase as the alkylamines, and that triethylamine has the highest value. It appears therefore that the magnitude of the crystal lattice energy  $\Delta H_8$  is the critical factor in determining the exothermicity of  $\Delta H_1$  and hence the thermodynamic stability of the salt. *Ceteris paribus* the magnitude of the crystal lattice energies is a function of the size and shape of the two ions forming the lattice. The non-existence of the pyridinium and triethylammonium salts and the piperidinium and diethylammonium salts of tetra-isopropoxyborate is therefore attributed to a low crystal lattice energy brought about by large differences in the sizes of the ions involved and/or crystal packing effects. The fact that triethylammonium tetraphenoxyborate is a stable compound supports these ideas.<sup>18</sup>

Since the tetraethoxyborate and tetraisopropoxyborate salts totally dissociate on melting the 'sublimation' of the tetramethoxyborate salts is considered to be a thermal dissociation and recombination process analogous to the behaviour of the ammonium halides.

<sup>15</sup> D. H. Auc, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, 1972, **94**, 4726.

<sup>16</sup> W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, J. L. Beauchamp, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 4728.

<sup>17</sup> J. P. Briggs, R. Yamdagni, and P. Kebarle, *J. Amer. Chem. Soc.*, 1972, **94**, 5128.

<sup>18</sup> K. Jones and E. F. Mooney, unpublished work reported in ref. 11, p. 230.

It is interesting that, whereas the trialkoxyboranes only form complexes with the strongly basic alkoxide ions the triaryloxyboranes form complexes with numerous nitrogen donors.<sup>7,8</sup> However only weak adduct formation takes place with triethylamine.<sup>19</sup> This is probably due to steric strain, which is observed when trimethylborane is the acid.<sup>20</sup> Triethylammonium tetraphenoxyborate is the only 'onium' salt of the tetraphenoxyborate anion so far reported.<sup>18</sup> It was of interest therefore to find a system where both the Lewis adduct and the corresponding 'onium' tetraphenoxyborate salt are stable. This was achieved with piperidine.

#### EXPERIMENTAL

All amines, except ethylenediamine, were dried over potassium hydroxide for 48 h, heated under reflux, and fractionally distilled through a 15 theoretical plate column. Ethylenediamine was dried over sodium wire for 24 h, heated under reflux, and distilled. Methanol (AnalaR) was dried by the dimethyl phthalate method and stored in the dry-box. Nitrobenzene (AnalaR) was heated under reflux over phosphorus pentoxide and fractionally distilled. Phenol (AnalaR) was distilled before use.

Trimethoxyborane was made according to Schlesinger.<sup>21</sup> The azeotrope was split using lithium chloride and the pure ester was distilled twice, the first and last 10% being rejected each time, b.p. 68.4°, 754 mmHg. Triethoxyborane and tri-isopropoxyborane were prepared from boric acid by the benzene ternary azeotrope method. After fractional distillation the products had b.p. 119.6°, 762 mmHg, and 142.1°, 762 mmHg respectively. Triphenoxyborane was made from tri-isopropoxyborane by the trans-esterification<sup>8</sup> procedure m.p. 92.5—93.5°.

All preparations of complexes and their subsequent manipulation were carried out in a dry-box or on a conventional vacuum line due to their moisture sensitivity. Conductivity measurements were carried out in a dry-box using a Wayne-Kerr B221 Bridge and dip type cell with a constant of 1.504 cm<sup>-1</sup>. <sup>11</sup>B n.m.r. spectra were run on a Perkin-Elmer R 10 instrument using boron trifluoride-diethyl ether as external reference.

*Piperidinium Tetramethoxyborate.*—Piperidine (5.49 g, 64.5 mmol) was added to trimethoxyborane (6.70 g, 64.5 mmol). No visible reaction took place on cooling to -60°. Methanol (2.06 g, 64.5 mmol) was added slowly. An immediate and vigorous exothermic reaction took place and the mixture solidified as a white crystalline mass with a

moist appearance. The crystals were dried by pumping (vacuum pump at 1.0 mmHg, ½ h). Their vapour pressure was such that approximately one third of the material was removed by this procedure leaving well formed, dry crystals. These were further purified by slow vacuum sublimation at 40°, m.p. 74.5° (B, 4.9; C<sub>5</sub>H<sub>11</sub>N, 38.7. C<sub>9</sub>H<sub>24</sub>BNO<sub>4</sub> requires B, 4.9; C<sub>5</sub>H<sub>11</sub>N, 38.5%).

*2-Aminoethylammonium Tetramethoxyborate.*—Ethylenediamine (3.60 g, 60 mmol) was added to trimethoxyborane (6.24 g, 60 mmol) followed by the dropwise addition of methanol (1.90 g, 60 mmol). An immediate reaction took place and the system solidified. The product was pumped in a similar fashion to the piperidinium salt to yield well formed crystals which decomposed over the range 65—73° (B, 5.8; C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>, 27.4. C<sub>6</sub>H<sub>21</sub>BN<sub>2</sub>O<sub>4</sub> requires B, 5.5; C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>, 30.6%). On sublimation these crystals yielded a different product, m.p. 81—82° (B, 6.2; C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>, 18.5. C<sub>10</sub>H<sub>34</sub>B<sub>2</sub>N<sub>2</sub>O<sub>8</sub> requires B, 6.5; C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>, 18.1%). This product was confirmed as ethylenediammonium ditetramethoxyborate by direct synthesis from the stoichiometric quantities of reactants.

*The Piperidine-Triphenoxyborane Adduct.*—Triphenoxyborane (9.42 g, 32.5 mmol) was dissolved in anhydrous benzene (100 ml) and piperidine (2.77 g, 32.5 mmol) added. The solution became warm and a white crystalline precipitate was obtained on cooling. The crystals were filtered off, washed with benzene, and then pumped free of volatile material on a vacuum line (10<sup>-3</sup> mmHg) at 30°, m.p. 159.5—160.5° (B, 2.8; C<sub>5</sub>H<sub>11</sub>N, 22.0. C<sub>23</sub>H<sub>26</sub>BNO<sub>3</sub> requires B, 2.88; C<sub>5</sub>H<sub>11</sub>N, 22.7%). <sup>11</sup>B N.m.r. (nitrobenzene) -2.3 p.p.m. compared to -3.0 p.p.m. for the 4-methylpyridine adduct in benzene.<sup>22</sup>

*Piperidinium Tetraphenoxyborate.*—Triphenoxyborane (6.65 g, 22.9 mmol) and phenol (2.16 g, 22.9 mmol) were dissolved in anhydrous benzene (100 ml) and piperidine (1.95 g, 22.9 mmol) was added. Immediate precipitation took place. The white crystals were filtered, washed twice with benzene, and pumped free of volatiles at 30°, m.p. 172—173 (decomp) (B, 2.3; C<sub>5</sub>H<sub>11</sub>N, 18.1. C<sub>29</sub>H<sub>32</sub>BNO<sub>4</sub> requires B, 2.3; C<sub>5</sub>H<sub>11</sub>N, 18.15%). <sup>11</sup>B N.m.r. (tetrahydrofuran) -2.6 p.p.m. All other compounds were made by mixing the stoichiometric amounts of the acid, base, and alcohol and where solid compounds were obtained (Table I) these were purified by fractional crystallisation.

The assistance of Dr. N. M. D. Brown with the <sup>11</sup>B n.m.r. measurements is gratefully acknowledged.

[2/2716 Received, 30th November, 1972]

<sup>19</sup> T. Colclough, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 1955, 907; 1956, 3006.

<sup>20</sup> H. C. Brown, *J. Chem. Soc.*, 1956, 1248.

<sup>21</sup> H. I. Schlesinger, H. C. Brown, D. L. Mayfield, and J. R. Gilbraith, *J. Amer. Chem. Soc.*, 1953, 75, 213.

<sup>22</sup> J. T. F. Fenwick and J. W. Wilson, to be published.