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A NEW METHYLAMINOBORANE POLYMER

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Abstract—Dimethylaminoborane underwent transamination with methylamine in the vapour phase to give a new methylaminoborane polymer. In tetrahydrofuran and in cyclohexane solution the main reaction was a disproportionation. A similar disproportionation also occurred in liquid methylamine and an unstable compound considered to be bismethylaminoborane was isolated.

INTRODUCTION

Methylaminoborane is an exception among simple aminoboranes in that two isomeric forms of the cyclic trimer, $(MeNHBH_2)_3$, are the only reported forms.(1,2) In contrast, dimethylaminoborane usually occurs as a monomer-dimer equilibrium mixture,(3,4) may be transformed with difficulty into a very stable trimer,(5,6) by heating with a pentaborane or higher borane catalyst, or into a linear polymer(7) by treatment at 3000 atm and 150°. The parent aminoborane, NH_2BH_2, also exists in a variety of forms of which the trimer(8,9) is the most well characterized but dimer, pentamer, and higher polymers also appear to exist.(10) Other aminoboranes(11) are usually monomeric and/or dimeric.

As a route to methylaminoborane, the reaction of dimethylaminoborane with methylamine, previously unreported, was of interest to us initially because of the possibility that transamination according to:

$$Me_2NBH_2 + MeNH_2 \rightarrow MeNHBH_2 + Me_2NH$$

would be followed by association of the monomeric $MeNHBH_2$, at least in part, with Me_2NBH_2 to give mixed compounds. In particular, a synthesis of the cyclic compound $\underline{Me_2NBH_2\cdot MeNHBH_2\cdot MeNHBH_2}$ was sought. However, from our study of the reaction under various conditions we found that transamination appeared to be the major process only when the reaction was carried out in the vapour phase at slightly

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(11) M. F. Lappert, in *Developments in Inorganic Polymer Chemistry* (Edited by M. F. Lappert and G. J. Leigh), p. 22. Elsevier, Amsterdam (1962).

elevated temperatures (~60°). Moreover, the only identifiable product, under these conditions, was a novel form of methylaminoborane, produced in yields of 50–75 per cent, as a thin and initially transparent film on the surface of the glass reaction vessel.

Direct measurement of the degree of association of this product was not possible because of its insolubility, but a relatively high degree of association, implying the linear polymeric structure (I), seems probable.

$$\text{—NH(Me)} \rightarrow \mathrm{BH_2}\text{—NH(Me)} \rightarrow \mathrm{BH_2}\text{—} \qquad \text{(I)}$$

The highly involatile and insoluble nature of this new polymer of $\mathrm{MeNHBH_2}$ renders cyclic structures $(\mathrm{MeNHBH_2})_n$, where n is a low number such as 2, 4 or even 5, or a mixture of such low cyclic structures, unlikely. It is involatile *in vacuo* at temperatures of up to 160°, at which temperature decomposition commences, whereas the sym- and unsym-forms of trimeric $\mathrm{MeNHBH_2}$ sublime unchanged(2) *in vacuo* at 70° and 50°, respectively. Other cyclic aminoboranes of similar type are also volatile *in vacuo*, e.g. $(\mathrm{NH_2BH_2})_3$ sublimes(8) at 100° and $(\mathrm{Me_2NBH_2})_3$ sublimes(5) at 35°; and cyclic dimers are usually even more volatile. Further, cyclic compounds such as those mentioned above are invariably soluble in polar solvents such as tetrahydrofuran, whereas the methylaminoborane polymer is completely insoluble in this and other common solvents.

The i.r. spectrum of the product has several features in common with that of the sym-isomer of the cyclic trimer. Both spectra show single N–H stretching bands, at 3276 $\mathrm{cm^{-1}}$ for the polymer and at 3240 $\mathrm{cm^{-1}}$ for the trimer, and similar broad and ill-resolved absorptions between about 2300–2400 $\mathrm{cm^{-1}}$ characteristic of $\mathrm{BH_2}$ (or $\mathrm{BH_3}$) stretching vibrations.(12) In the 650–1500 $\mathrm{cm^{-1}}$ region, the spectra although distinct, show broadly the same pattern of absorptions, in particular, a strong band at 1273 $\mathrm{cm^{-1}}$ for the trimer shifted to 1236 $\mathrm{cm^{-1}}$ for the polymer, intense absorptions between 1100 and 1200 $\mathrm{cm^{-1}}$ ascribed at least in part to $\mathrm{BH_2}$ deformation modes,(12) and three medium to strong absorption bands in the region 900–1100 $\mathrm{cm^{-1}}$. The polymer, unlike the trimer, has a strong absorption band at 875 $\mathrm{cm^{-1}}$.

A postulated reaction path for the transamination involves initial formation of the weak methylamine complex (II), migration of a proton to give the dimethylamine complex (III) dissociation of which would give monomeric methylaminoborane.

$$\mathrm{Me_2NBH_2} + \mathrm{MeNH_2} \rightleftharpoons \underset{\text{(II)}}{\mathrm{Me_2NBH_2{\cdot}MeNH_2}} \rightleftharpoons$$

$$\underset{\text{(III)}}{\mathrm{Me_2NH{\cdot}BH_2MeNH}} \rightleftharpoons \mathrm{Me_2NH} + \mathrm{MeNHBH_2}$$

A similar complex of dimethylaminoborane with trimethylamine has previously been postulated(4) although more recent work(13) suggests that this complex, if formed, is less stable than had hitherto been supposed. However, with the stronger Lewis acid $\mathrm{Me_2NBCl_2}$, complex formation with trimethylamine has definitely been observed.(14)

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(14) C. A. BROWN and R. C. OSTHOFF, *J. Am. chem. Soc.* **74**, 2340 (1952).

Either the monomer or the complex (III) may be the reacting species giving polymer, or possibly both may directly participate in polymer formation:

$$n\mathrm{MeNHBH_2} \rightarrow (\mathrm{MeNHBH_2})_n$$

$$n\mathrm{Me_2NH{\cdot}BH_2MeNH} \rightarrow (\mathrm{MeNHBH_2})_n + n\mathrm{Me_2NH}$$

However, irrespective of the nature of the reacting species, it seems very likely that polymer chains of the type $\mathrm{Me_2NH} \rightarrow (\mathrm{BH_2{-}NHMe} \rightarrow)_n\mathrm{BH_2{-}NHMe}$ are built up since free amine is present throughout the reaction. Co-ordinative saturation, or blocking, of the end boron by a dimethylamine group could account for formation, under favourable conditions, of linear polymer rather than cyclic trimer. Similar stabilization of linear polymeric phosphinoboranes has previously been reported.(15)

Although the polymer is stable *in vacuo* below temperatures of about 140–160°, in the presence of only a trace of dimethylamine at 55–75° for about 12 hr, it transforms to the extent of about 50 per cent to cyclic trimer. Presumably reorganization of the methylaminoborane units occurs via nucleophilic attack at the boron atoms by free base. The polymer appears to be thermodynamically unstable with respect to cyclic trimer. A similar situation exists with polymeric $\mathrm{Me_2NBH_2}$, produced at high pressure, since this polymer is stated to undergo depolymerization giving dimer, merely on being kept at room temperature for several months.(7)

When the reaction between dimethylaminoborane and methylamine was carried out in solvents, no insoluble polymer formation was observed, instead disproportionation, of a type similar to that reported for dimethylaminoborane and trimethylamine,(4,13) appeared to be the main reaction.

$$2\mathrm{Me_2NBH_2} + \mathrm{MeNH_2} \rightarrow \mathrm{Me_2NH{\cdot}BH_3} + (\mathrm{Me_2N})(\mathrm{MeNH})\mathrm{BH}$$

From reactions in tetrahydrofuran and in cyclohexane, dimethylamine-borane was obtained together with a volatile boron-containing compound, presumed to be a bisaminoborane, in the solvent fraction. From reactions in liquid methylamine at room temperature, methylamine-borane was obtained. This is explained on the basis of the following equilibrium being

$$\mathrm{Me_2NH{\cdot}BH_3} + \mathrm{MeNH_2} \rightarrow \mathrm{Me_2NH} + \mathrm{MeNH_2{\cdot}BH_3}$$

forced to the right, despite the stronger donor character of dimethylamine, by the large excess of methylamine. The bisaminoborane fraction in this case was isolated and appeared to be a mixture of the compounds $(\mathrm{Me_2N})(\mathrm{MeNH})\mathrm{BH}$ and $(\mathrm{MeNH})_2\mathrm{BH}$, and on further treatment with liquid methylamine, what is considered to be an almost pure sample of bismethylaminoborane, unstable at room temperature, was obtained.

EXPERIMENTAL

I.R. spectra were recorded on Unicam SP 200 and Perkin–Elmer 125 Spectrometers.

Reactants and solvents. Methylamine, dried with sodium hydroxide and lithium, was distilled *in vacuo.* Tetrahydrofuran and cyclohexane were dried with lithium aluminium hydride and were distilled. Dimethylaminoborane, prepared by heating dimethylamine-borane at 120–140° under nitrogen,(3,4) was purified by fractionation on a vacuum line and had v.p. 8 mm/20°.

Vapour phase reactions. In a typical reaction, dimethylaminoborane (1·551 g, 27·3 m-mole) and methylamine (17·5 m-mole) were sealed into a reaction vessel of about 1100 ml capacity and were

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(15) R. I. Wagner and F. F. Caserio, *J. inorg. nucl. Chem.* **11**, 259 (1959).

heated in a water-bath at 60–65° for 1·5 hr. During this period only a trace of white solid and colourless liquid could be seen in the bottom of the vessel, but on removal from the water-bath, a colourless condensate which soon crystallized appeared on the walls of the vessel. As the volatile deposit on the walls of the vessel was removed, the residual film beneath was observable. Addition of tetrahydrofuran (~25 ml) to the flask completely detached the film to give a suspension of small fragments. The polymeric product (0·331 g) (Found: C, 28·1; H, 14·1; B, 24·9; N, 31·7. CH_6BN requires C, 28·0; H, 14·1; B, 25·2; N, 32·7%) was collected by filtration, washed with solvent and dried *in vacuo* first at room temperature and then at 100°. Evaporation of tetrahydrofuran from the filtrate gave only a small amount (0·154 g) of unidentified viscous oil.

The volatile material consisted of permanent gas (0·05 m-mole), presumably hydrogen, dimethylaminoborane (0·803 g, 14·1 m-mole) and a mixture (16·7 m-mole by volume) of dimethylamine with a little methylamine (all identified by volatility characteristics and i.r. spectra).

Based on the dimethylaminoborane consumed (0·748 g, 13·1 m-mole), the yield of polymeric $MeNHBH_2$ was 59 per cent. In other similar reactions, yields of polymer were usually between 50 and 75 per cent but decreased markedly when the temperature was raised even a few degrees. The i.r. spectra of polymer samples from several runs were indistinguishable and exhibited the following absorption maxima (cm^{-1}): 758 w, 875 s, 910 m, 998 m, 1050 m, 1109 w, 1123 m, 1147 s, 1173 vs, 1191 w, 1236 vs, 1363 w, 1380 m, 1419 w, 1456 w, 1476 w, 1595 w, 2305 s, 2400 s, 2897 w, 2953 w, 2987 m, and 3276 m (nujol mulls and KBr discs).

Since the film of polymer was transparent, it was not certain at first whether the polymer was formed during the period of heating, or whether it was formed, together with the readily observable crystalline deposit, on removal of the vessel from the water-bath. To settle this point a reaction was carried out in modified apparatus. Before removing the vessel from the water-bath, the volatile materials were quickly transferred by rupture of a break-seal, to a trap at −196°. Polymer was subsequently recovered in the usual way from the sides of the reaction vessel proving that formation of the polymeric film was independent of the deposition of crystalline material.

Liquid phase reactions. These were carried out in small sealed ampoules each fitted with a break-seal. In all cases only insignificant amounts of non-condensable gas were formed.

Reaction in tetrahydrofuran. Dimethylaminoborane (0·882 g, 15·5 m-mole) and methylamine (11·7 m-mole) in tetrahydrofuran (~5 ml) were heated at 65° for 1 hr after which time the readily volatile contents were removed. The residue was warmed to 40–50° when fairly pure dimethylamine-borane (0·164 g, 2·8 m-mole), identified by its i.r. spectrum, transferred *in vacuo* to a cooled U-trap leaving behind a small amount (~0·1 g) of unidentified viscous liquid. Fractionation of the volatile materials gave unreacted dimethylaminoborane (0·439 g, 7·7 m-mole) and a fraction containing several components which could not be completely separated but which according to i.r. examination appeared to contain, in addition to tetrahydrofuran, methylamine and dimethylamine, a substance, thought to be a bisaminoborane, with absorptions at 2480 and 1540 cm^{-1}.

Reaction in cyclohexane. Dimethylaminoborane (0·798 g, 14·0 m-mole) and methylamine (9·6 m-mole) in cyclohexane (~8 ml) at 60° for 3 hr also gave dimethylamine-borane (0·275 g, 4·7 m-mole) and a similar mixture of volatile products. Further sublimation of the residue, however, gave in addition, a small amount (0·050 g) of the sym-isomer of $(MeNHBH_2)_3$.

Reaction in liquid methylamine. Dimethylaminoborane (1·153 g, 20·3 m-mole) was allowed to react with liquid methylamine (8 ml) at room temperature for 10 days. After removal of the volatile contents of the reaction vessel, fractional sublimation of the residue at 30–50° gave methylamine-borane (0·133 g, 3·0 m-mole) identified by its i.r. spectrum. Recovery of this product was low because of difficulty in separating it from an unidentified liquid of somewhat greater volatility. Repeated fractionation of the volatile materials gave only an amine fraction, trapped at −196°, and a small amount of a colourless liquid (0·458 g) trapped but still slightly volatile at −84°. Its v.p. at 0° (3·0–3·4 cm) was somewhat variable and suggested a mixture. Its i.r. spectrum (gas phase) was more complex than, but still strikingly similar to, that of bisdimethylaminoborane,(16) in particular it exhibited a single sharp absorption at 2480 cm^{-1}, characteristic of the B–H grouping, and a band at 1540 cm^{-1}. Unlike bisdimethylaminoborane, however, it absorbed at 3470 cm^{-1} indicating the presence of N–H. Consistent with these observations would be a mixture of the bisaminoboranes $(MeNH)_2BH$ and $(MeNH)(Me_2N)BH$.

In handling a previous sample of this mixture it was observed that after only a few days at room

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(16) G. F. CLARK and A. K. HOLLIDAY. Personal communication.

temperature, extensive decomposition occurred giving amine, hydrogen and a viscous oil but it was noticed that decomposition was virtually inhibited by liquid methylamine. Hence the above mixture was treated with this liquid for a period of 3 weeks at room temperature and on fractionation, a sample of what appeared to be almost pure bismethylaminoborane (0·171 g, 2·4 m-mole) (Found: B, 14·18. $C_2H_9N_2B$ requires B, 15·0%), with v.p. 3·55 cm/0°, was obtained. Nitrogen micro-analyses gave irreproducible results. Its i.r. spectrum exhibited fewer absorptions than that of the parent mixture, but those at 3470, 2480, and 1540 cm^{-1} were still present. Further examination of it was difficult because of its instability but its PMR spectrum (56·4 Mc/s) contained only one observable and very broad band.

Action of heat on polymeric methylaminoborane. When heated *in vacuo* the polymer did not undergo decomposition below temperatures of 140–160°. The precise decomposition point appeared to depend on the particular batch of polymer. In addition to hydrogen, a complex mixture of products appeared to be formed from which only methylamine-borane was isolated (by sublimation) and identified.

When the polymer (0·078 g) was heated with a trace of dimethylamine (2 ml at N.T.P.) for about 12 hr at a temperature of 55° increasing to 75°, and the products subjected to sublimation, trimeric $(MeNHBH_2)_3$ (sym-isomer) (0·041 g, 53 per cent yield) was obtained together with traces of unidentified products of somewhat greater volatility. The residue (0·016 g) was unchanged polymer.

Sym-isomer of trimeric methylaminoborane. Approximately equimolar amounts of methylamine and triethylamine-borane were heated at 100° for 2–3 hr in a sealed bulb. Sublimation(2) of the crude product at about 80° gave the desired compound (Found: C, 28·0; H, 14·2; B, 25·2; N, 32·8%). Its i.r. spectrum (nujol mull and KBr disc) had the following absorption maxima (cm^{-1}): 812 w, 916 m, 967 m, 1024 s, 1135 w, 1151 m, 1175 s, 1194 vs, 1273 s, 1375 s, 1400 w, 1422 m, 1466 m, 2285 s, 2400 vs, 2880 w, 2930 w, 2975 m, and 3240 m.

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