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"ONIUM" BASE BOROHYDRIDES—I

TRIMETHYL SULPHONIUM BOROHYDRIDE

H. G. HEAL
Chemistry Department, Queen's University, Belfast

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Abstract—The new compound trimethyl sulphonium borohydride has been prepared. It decomposes above 90° to methane and the co-ordination compound dimethyl sulphide-borine.

BANUS *et al.*⁽¹⁾ have described the preparation of three quaternary ammonium borohydrides. They are stable substances. Even ammonium borohydride itself, which is, as expected, relatively unstable, has been isolated in crystalline form.⁽²⁾ These observations suggest that many borohydrides of organic "onium" bases, especially the strong fully alkylated or arylated bases, should be easy to make. Apart from those just mentioned, none have been reported, though some tetraphenylborates of "onium" bases are described in the literature.⁽³,⁴,⁵⁾

The thermal decomposition of "onium" borohydrides is interesting as a possible route to the co-ordination compounds of BH_3 with phosphines, thioethers, etc. Some reactions of this type are known, e.g.

$$[(CH_3)_4N]^+[BH_4]^- \xrightarrow[-250^\circ]{150^\circ} CH_4 + (CH_3)_3N{:}BH_3 \qquad (1)$$

Decomposition at higher temperatures, or in presence of catalysts,⁽⁶⁾ might be expected in certain cases to yield cyclic boron compounds containing the central atom of the cation in the ring, as in the known reaction

$$3[NH_4]^+[BH_4]^- \rightarrow B_3N_3H_6 + 9H_2 \qquad (2)$$

The investigation reported here is the first of a series with the object of making representative new "onium" borohydrides, and studying their thermal decomposition.

EXPERIMENTAL METHODS AND RESULTS

The previously unreported compound trimethyl sulphonium borohydride was obtained by the reaction

$$[(CH_3)_3S]^+F^- + Na^+[BH_4]^- \rightarrow NaF\downarrow + [(CH_3)_3S]^+[BH_4]^-$$

in water or ethanol solution. Sodium fluoride is less soluble in ethanol than in water, so that the reaction goes more nearly to completion in ethanol, but this advantage is outweighed by the fact that

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(1) M. D. BANUS, R. W. BRAGDON and T. R. P. GIBB, *J. Amer. Chem. Soc.* **74**, 2346 (1952).
(2) R. W. PARRY, D. R. SCHULTZ and P. R. GIRARDOT, *J. Amer. Chem. Soc.* **80**, 1 (1958).
(3) G. WITTIG and P. RAFF, *Liebigs Ann.* **573**, 195 (1951).
(4) G. A. RAZUVAYEV and T. G. BRILKINA, *Dokl. Akad. Nauk SSSR* **85**, 815 (1952).
(5) L. C. HOWICK and R. T. PFLAUM, *Anal. Chim. Acta.* **19**, 342 (1958).
(6) H. J. EMELEUS and G. J. VIDELA, *Proc. Chem. Soc.* 288 (1957); *J. Chem. Soc.* 1306 (1959).

the sodium fluoride precipitated from ethanol is gummy and hard to filter, whereas that from water is crystalline. The following procedure worked well:

Starting with dimethyl sulphide and methyl iodide, trimethyl sulphonium iodide (5·7 g, 28 millimoles) was made(7) and converted by treatment with silver oxide and water to a solution of the base. The base was added to 26·6 milliequivalents of hydrofluoric acid. The excess base made the solution alkaline, which helped to prevent the decomposition of borohydride ion. The solution was concentrated to 4 ml by evaporation at room temperature in a vacuum desiccator. Commercial sodium borohydride was assayed for BH_4^- by the iodate method.(8) A quantity of it containing 28 millimoles of BH_4^- was dissolved in the minimum of water. One drop of the solution was added to the trimethyl sulphonium fluoride solution. This completed the precipitation of traces of silver left in the solution from the silver oxide treatment; it was thought advisable to remove this silver in case it catalytically decomposed the borohydride in the final stages of preparation. The solution was filtered, filtrate and washings totalling 8 ml. The remaining sodium borohydride solution was added, at 17°C. Without filtering off the precipitated sodium fluoride, the mixture was evaporated to dryness over conc. sulphuric acid in a vacuum desiccator, which was continuously exhausted by a rotary pump to remove some gas evolved from the mixture. The residue was extracted at 25°C with three portions of absolute ethanol, totalling 18 ml. This was filtered, and the filtrate cooled to −10°C. Most of the trimethyl sulphonium borohydride crystallized out. It was filtered by suction on a sintered glass crucible, washed quickly with two small portions of cold ethanol, and transferred in the crucible to a desiccator containing sulphuric acid, which was immediately evacuated. The dry product weighed 1·3 g (50 per cent yield). Its identity was confirmed by an I.R. spectrum, taken by the KBr disk method with a Perkin–Elmer Model 21 Spectrometer. The spectrum was almost identical with the superposed spectra of $(CH_3)_3SI$ and $NaBH_4$. Analysis for BH_4^- by the iodate method(8) and the gasometric method(9) showed that it contained 98·5 per cent of the theoretical amount of this ion. Found: C, 38·0; H, 13·9; Calc. C, 39·1; H, 14·3%).

Trimethyl sulphonium borohydride is a light, white, well crystallized solid. It can be kept for long periods if dry, though it always smells of dimethyl sulphide, perhaps owing to slow decomposition by the reaction about to be described. It is very hygroscopic and very soluble in water. It is easily soluble in ethanol, with a large temperature coefficient of solubility, and is easily recrystallized from that solvent, without much decomposition, if the temperature is kept below 25°C.

Samples obtained from several preparations in water solution, and one from a preparation in ethanol (subsequently recrystallized from ethanol) all contained between 98 and 100 per cent of the theoretical amount of borohydride ion.

When heated quickly in a melting capillary, the substance melted at 120°–124°C, with decomposition. Larger samples, heated more slowly *in vacuo*, decomposed suddenly at temperatures from 90°C upwards. A sample of 0·6 g exploded mildly at about 90°. The products of thermal decomposition were investigated as follows. Samples weighing 0·3–0·7 g were placed in an L-shaped tube fitting by means of a ground joint into a reaction vessel, which in turn communicated by wide tubing with a large trap. With the system coupled to the vacuum line and evacuated, the trap was cooled in liquid nitrogen and the reaction vessel heated to 110°. By rotating the L-tube on its ground joint, the sample was dropped in small portions into the reaction vessel, allowing each portion to decompose before adding the next. The chief decomposition products were *methane* and the *compound* $(CH_3)_2S:BH_3$. The methane was identified by means of its infra-red spectrum (taken at 93 mm pressure in a 10 cm gas cell), which was identical with the published spectrum of methane.(10) On cooling

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(7) H. J. Emeleus and H. G. Heal, *J. Chem. Soc.* 1126 (1946).

(8) D. A. Lyttle, E. H. Jensen and W. A. Struck, *Analyt. Chem.* **24**, 1843, (1952).

(9) W. D. Davis, L. S. Mason and G. Stegeman, *J. Amer. Chem. Soc.* **71**, 2775 (1949).

(10) *Catalogue of Infra-red Spectral Data of the American Petroleum Institute* (1956).

to the temperature of liquid nitrogen, its pressure fell to about 15 mm, slightly higher than the published vapour pressure of methane (10 mm) perhaps because of the presence of a little hydrogen. The other product, which condensed entirely in the cold trap during preparation, was a colourless liquid at room temperature. It was identified as the known compound $(CH_3)_2S{:}BH_3$(11) by the following evidence.

(a) Its I.R. spectrum in the vapour state was identical with that of a specimen of $(CH_3)_2S{:}BH_3$ made up by mixing $(CH_3)_2S$ and B_2H_6 in the mole ratio 2 : 1. The spectrum showed all the stronger bands of $(CH_3)_2S$ and B_2H_6, since the compound is largely dissociated in the vapour:(11) in addition, there were strong, narrow bands peaking at 1102 cm^{-1} and 2420 cm^{-1}, which must be attributed to the compound itself.

(b) The vapour pressures agreed approximately with those given for $(CH_3)_2S{:}BH_3$ by Burg and Wagner.(11)

Temperature °C	Our product	$(CH_3)_2S{:}BH_3$
23·0	21·4 mm	19·5 mm
13·0	11·4	10·5
6·5	6·7	6·8

(c) The vapour density indicated a mean molecular weight of 58 at 15° and 10 mm pressure. This figure agrees approximately with the published value(11) and implies considerable dissociation in the vapour.

Our product, however, melted at —27°, whereas Burg and Wagner reported —38; for $(CH_3)_2S{:}BH_3$.(11)

Measurement of the volume of methane evolved and the weight of $(CH_3)_2S{:}BH_3$ formed showed that the decomposition had gone mainly (apparently over 90 per cent) according to the equation

$$[(CH_3)_3S]^+[BH_4]^- \rightarrow CH_4 + (CH_3)_2S{:}BH_3$$

though an exact material balance was not attempted, in view of the tendency of particles of the starting material to get blown out of the reaction vessel by the violence of the decomposition.

A small quantity of white solid, infusible up to 340°C and soluble in water, was left behind in the reaction vessel. Its I.R. spectrum resembled published spectra of sodium borates.(12)

DISCUSSION

The ease of preparation and stability of trimethyl sulphonium borohydride lead to the expectation that many other "onium" borohydrides will be made. Its decomposition by elimination of methane parallels the reported modes of decomposition of ammonium borohydride, the substituted ammonium borohydrides, and the

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(11) A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.* **76**, 3307 (1954).

(12) F. A. Miller and C. H. Wilkins, *Analyt. Chem.* **24**, 1253, (1952).

tetraphenyl borates, and probably takes place via a nucleophilic displacement of dimethyl sulphide from the cation by the anion.

$$\mathrm{BH_4^-} \overset{\curvearrowright}{+} \mathrm{CH_3^+}\ldots\ldots\mathrm{S(CH_3)_2} \rightarrow \mathrm{BH_3} + \mathrm{CH_4} + \mathrm{S(CH_3)_2}$$

followed by

$$\mathrm{BH_3} + \mathrm{S(CH_3)_2} \rightarrow \mathrm{(CH_3)_2S{:}BH_3}$$

However, there is no way of knowing, from our work, to what extent diborane may be formed as an intermediate, subsequently reacting with the dimethyl sulphide.