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Intermediates in the Thiohydrolysis of Lithium Borohydride

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MANY investigators have studied the hydrolysis of metal borohydrides and have postulated and searched for boron–hydrogen-containing intermediates.[1] Only recently, however, have reports of experimental evidence been offered in support of two unstable intermediates, an $HOBH_3^-$ anion[2] and an aquated BH_2^+ species.[3] We have been investigating the analogous thiohydrolysis (reaction with hydrogen sulphide) of metal borohydrides, and report the experimental observation of two intermediates, thus offering mechanistic information of interest to compare with the hydrolysis reaction.

The reaction of lithium borohydride with hydrogen sulphide in tetrahydrofuran solution was investigated under oxygen and moisture-free conditions using high-vacuum line techniques. At −22°, in the presence of an excess of hydrogen sulphide, the hydrogen evolution rate slowed considerably after the evolution of one mole of hydrogen per mole of lithium borohydride. At this point, rapid removal of the excess of hydrogen sulphide (quantitatively recovered) left a colourless solution of composition $LiHSBH_3$ which, at −22°, was stable towards further evolution of hydrogen. Upon warming to 0°, a slow evolution of hydrogen was initiated.

The ^{11}B n.m.r. spectrum of the solution of composition $LiHSBH_3$ was obtained (32·1 Mc./sec.) at a temperature slightly below 0° and exhibited a very large, well resolved 1 : 3 : 3 : 1 quartet at +25·0 p.p.m. relative to boron trifluoride etherate* with an ^{11}B–proton coupling constant of 94 c./sec. Also displayed but with much less intensity relative to the quartet were two other well resolved multiplets; a 1 : 4 : 6 : 4 : 1 quintet at +32·2 p.p.m. which is attributable to the borohydride ion by comparison with the published spectra,[4] and a 1 : 2 : 1 triplet at +14·5 p.p.m. with a coupling constant of 114 c./sec. The high-field position of both the quartet and triplet is indicative of tetraco-ordinate boron rather than trico-ordinate boron.[5] The relative intensities within the multiplets as well as the ^{11}B–proton coupling constants are consistent with the formulation of the quartet as originating from a species containing the borane (BH_3) group and the triplet from a BH_2-containing species.[5]

Bonding of borane to solvent tetrahydrofuran can be eliminated since the chemical shift of tetrahydrofuran borane is reproduced[6] to be +0·9 p.p.m., compared to +25·0 p.p.m. observed here for the borane group. The observation of both a borane group and borohydride ion presented the possible existence in solution of the $B_2H_7^-$ anion. Association of borane with lithium borohydride to form LiB_2H_7 has been suggested to occur in tetrahydrofuran solution.[7] In a study by Gaines,[8] the ^{11}B n.m.r. spectrum of NaB_2H_7 (in monoglyme solution with excess of borohydride) displayed a 1 : 3 : 3 : 1 quartet with a similar chemical shift (+23·5 ± 0·3 p.p.m.) and coupling

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* All subsequent chemical shifts are reported relative to boron trifluoride etherate.

constant (102±2 c./sec.) observed for the quartet in the thiohydrolysis solution. However, the quartet observed by Gaines was broadened[9] while the quartet displayed by the thiohydrolysis solution was sharp and well resolved. To provide additional information, a solution proposed to contain LiB_2H_7[7] in tetrahydrofuran (with excess of borohydride) was prepared and the ^{11}B n.m.r. spectrum taken. The spectrum exhibited a broadened quartet very similar to that observed for NaB_2H_7 by Gaines, but with a somewhat different chemical shift of $+21{\cdot}7$ p.p.m. and coupling constant of 104 ± 2 c./sec. Thus, in view of the above observed differences in the quartet signal, a $B_2H_7^-$ anion does not appear to be present in the thiohydrolysis solution in any observable concentration.

Consistent with both the ^{11}B n.m.r. and reaction stoicheiometry, it is postulated that the quartet is due to an $HSBH_3^-$ anion,[10] which is formed according to equation (1) and is the predominant species in solution.

$$LiBH_4 + H_2S \rightarrow LiHSBH_3 + H_2 \qquad (1)$$

A shift of 7·2 p.p.m. downfield from the borohydride ion is compatible with the replacement of a hydride by the more electron-withdrawing SH^-.

The BH_2-containing species observed in the spectrum may be formulated as an $(HS)_2BH_2^-$ anion resulting from further reaction of $HSBH_3^-$ with hydrogen sulphide according to equation (2)

$$LiHSBH_3 + H_2S \rightarrow Li(HS)_2BH_2 + H_2 \qquad (2)$$

Thus, since the reaction only slows at −22° after the evolution of one mole of hydrogen per mole of lithium borohydride, if the reaction is quenched by rapid removal of hydrogen sulphide after the evolution of one mole of hydrogen (per mole of borohydride), the presence of small concentrations of unreacted borohydride and the suggested $(HS)_2BH_2^-$ is not unexpected. Further evidence supporting a tetraco-ordinate boron anion such as $(HS)_2BH_2^-$ comes from comparison of the ^{11}B n.m.r. data found for $C_2H_5SBH_2$ trimer[11] (BH_2 units connected by bridging sulphurs). A triplet with chemical shift of $+14{\cdot}5$ p.p.m. and coupling constant of 116 c./sec. was found, compared to $+14{\cdot}5$ p.p.m. and coupling constant of 114 c./sec. observed for the suggested $(HS)_2BH_2^-$.

However, there is some evidence to indicate borohydride and the $(HS)_2BH_2^-$ species may also be formed by a disproportionation of $HSBH_3^-$ according to equation (3)

$$2LiHSBH_3 \rightarrow LiBH_4 + Li(HS)_2BH_2 \qquad (3)$$

Thus upon warming the solution to 30°, the ^{11}B spectrum shows a rapid increase in intensity of both triplet and quintet signals and decrease of the quartet signal. Although decomposition of $HSBH_3^-$ *via* loss of hydrogen and formation of new BH_2-containing species would be expected to increase the triplet intensity, an increase in the quintet signal suggests an accompanying disproportionation.

At 30°, the increase in triplet intensity is also accompanied by significant broadening of the signal. Loss of hydrogen from $HSBH_3^-$ would give a species of empirical formula SBH_2^-. However, the chemical shift and coupling constant of the triplet do not change, indicating the maintenance of tetraco-ordinate boron and a very similar chemical environment for the new BH_2-containing species. Thus, dimers, trimers, and polymers of SBH_2^- may be formed. Absence of bridge hydrogen absorption in the infrared spectrum indicates that the BH_2 units are connected by sulphur bridges rather than hydrogen bridges.

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[1] R. M. Adams, "Boron, Metallo-Boron Compounds and Boranes" ed. R. M. Adams, Interscience, New York, 1964, p. 404.

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[6] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 4496.

[7] H. Nöth, *Angew. Chem.*, 1961, **73**, 373.

[8] D. F. Gaines, *Inorg. Chem.*, 1963, **2**, 523.

[9] The broad signal obtained for the quartet was suggested by Gaines to result from unresolved coupling with the single bridge hydrogen postulated for $B_2H_7^-$ (ref. 8).

[10] $LiHSBH_3$ has been claimed to be an intermediate compound in the reaction of lithium borohydride with sulphur in ether solution (H. Nöth and G. Mikulashek, *Z. anorg. Chem.*, 1961, **311**, 241). It was isolated at −50° as a very unstable yellow substance and was characterized by elemental analysis. By contrast, if the solvent is removed at −22° from the thiohydrolysis solution of composition $LiHSBH_3$, a white solid remains which is stable towards hydrogen evolution at that temperature.

[11] D. J. Pasto, C. C. Cumbo, and P. Balasubramanian, *J. Amer. Chem. Soc.*, 1966, **88**, 2187, quoting results obtained by private communication from R. Schaeffer.