[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

# Preparation of Diborane from Lithium Hydride and Boron Trihalide Ether Complexes[1]

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The preparation of diborane from lithium hydride and boron trihalide etherates under different conditions is described and secondary reactions are discussed. The reaction between lithium hydride and boron trifluoride in ethyl ether has been shown to proceed by two different courses. If ether-soluble, active hydrogen-containing promoters are present, or if pressure is used to force the reaction between lithium hydride and diborane, the hydride is converted completely to lithium borohydride and lithium fluoride before diborane is evolved. In the absence of soluble promoters, diborane escapes continually from the solution, lithium borofluoride is formed and lithium borohydride does not accumulate. If less than a specified ratio of borohydride to hydride exists in the ether solution, the borohydride is consumed in the continuing reaction, and diborane is evolved. In tetrahydrofuran, a promoter is not required for the conversion of lithium hydride to lithium borohydride. Since the solubility of diborane is relatively high in tetrahydrofuran, conditions favor the production of borohydride by reaction of diborane with lithium hydride, as in the pressure reaction with ether as solvent.

## Introduction

The preparation of diborane from lithium hydride and the ethyl ether complex of boron trifluoride was discovered and investigated by Schlesinger and Brown.[2,3] They have also prepared diborane by the reaction of boron fluoride with alkali metal borohydrides and methoxyborohydrides.[2]

The Naval Research Laboratory has reported that in the presence of methyl borate, higher yields of diborane are obtained from the lithium hydride, boron fluoride reaction in ether.[4] Lithalloys Corporation[5] reported a "surge" method in which a portion of the boron trifluoride etherate was added to a lithium hydride suspension and allowed to stand until a vigorous reaction occurred; subsequent addition of the boron trifluoride etherate produced good yields of diborane. Lithalloys also reported that at lower temperatures the chief reaction product was lithium borohydride. There was no explanation for variations in the reaction under different conditions.

Attempts to apply the available data to a semi-pilot plant operation in our laboratory led to erratic results involving induction periods and variable yields. Therefore, a study of the reaction between lithium hydride and boron trifluoride ethyl etherate was conducted in the laboratory under controlled conditions. The reactions were found to be reproducible and free from induction periods if carried out under strictly anhydrous conditions.

## Results

The reaction between lithium hydride and boron trifluoride in ethyl ether was found to proceed by two distinct stoichiometric patterns dependent on reaction conditions.

$$6LiH + 8BF_3 \xrightarrow[\text{ether}]{} B_2H_6 + 6LiBF_4 \quad (1)$$

$$6LiH + 2BF_3 \xrightarrow[\text{ether}]{\text{promoter}} B_2H_6 + 6LiF \quad (2)$$

Equation (1) describes the exothermic reaction in ether at room temperature. Diborane was continuously evolved at a mole rate approximately one-eighth that of boron fluoride addition,[6] and the chief product was lithium borofluoride.

The course of reaction was altered to equation (2) by small amounts of the ether-soluble, active hydrogen-containing promoters, lithium borohydride and lithium trimethoxyborohydride. In the presence of sufficient promoter, the reaction proceeded in two distinct stages, represented by equations (3) and (4)

$$6LiH + 1.5BF_3 \xrightarrow[\text{ether}]{\text{Promoter}} 1.5LiBH_4 + 4.5LiF \quad (3)$$

$$1.5LiBH_4 + 0.5BF_3 \xrightarrow[\text{ether}]{} B_2H_6 + 1.5LiF \quad (4)$$

In the first stage, lithium hydride was converted almost quantitatively to lithium borohydride in an exothermic reaction.[7] In the second stage, diborane was evolved in an endothermic reaction at a mole rate almost exactly twice that of boron fluoride addition.

The reaction of lithium hydride and boron trichloride in ethyl ether proceeded according to equation (2), even in the absence of promoter. In tetrahydrofuran as a solvent, lithium hydride and boron trifluoride also reacted by the stoichiometry of equation (2), with or without added promoter. In both cases, the two-stage process occurred.

In the reaction with boron fluoride in ethyl ether, the minimum amount of promoter required to obtain the stoichiometry of equation (2) was 3.5 to 5 mole per cent. of the initial lithium hydride. With less added promoter, diborane evolution commenced immediately and followed the general pattern of equation (1).

Lithium trimethoxyborohydride promotion was always initiated by addition of methyl borate to the lithium hydride suspension in ether. Lithium borohydride and methyl borate were effective in promoting equation (2) when present at the beginning of a run. Attempts were made to activate lithium hydride at intermediate stages of equation (1) by addition of promoters to a partially reacted mixture containing excess lithium

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[1] This work was done on Army Ordnance Contract TUI-2000.

[2] H. I. Schlesinger, H. C. Brown, *et al.*, Final Report on Contracts OEM sr-117 and OEM sr-368 (1943).

[3] H. I. Schlesinger and H. C. Brown, U. S. Patent No. 2,543,511 (1951), assigned to U.S.A.

[4] D. S. Burgess, *et al.*, Naval Research Laboratory Report No. P-2571, July 16, 1945.

[5] See Reference (4).

[6] Boron halides were generally added as ether complexes.

[7] Subsequent to submission of this paper for publication, the reaction of lithium aluminum hydride with boron trifluoride to yield diborane was reported to proceed in two stages. Lithium borohydride was postulated as the product of the first stage. I. Shapiro, *et al.*, THIS JOURNAL, **74**, 901 (1952).

hydride and lithium borofluoride. Lithium borohydride produced a small additional yield of diborane, but methyl borate was completely inert. Mixtures of fresh lithium hydride and lithium borofluoride were successfully activated by both methyl borate and lithium borohydride.

Lithium borohydride promotion was accomplished by several methods: (a) the borohydride was added as such; (b) diborane was passed into the lithium hydride slurry to form borohydride *in situ*[2,8]; (c) the early stage of the lithium hydride-boron fluoride reaction was carried out under an autogenous pressure of diborane; (d) approximately one-fourth the boron fluoride was added to the lithium hydride suspension at 0–10°. When the mixture had warmed to 20°, rapid diborane evolution occurred in a "surge" reaction. Lithium borohydride remained in solution, after the surge, in amounts sufficient for promotion of equation (2).

In general, promotion by methods (a), (b) and (c) resulted in essentially complete conversion of lithium hydride to borohydride before evolution of diborane. In method (d), diborane was evolved continuously subsequent to the surge.

The use of diborane as described in (b) was also effective in preventing induction periods caused by surface contamination of lithium hydride. In larger scale reactions in steel equipment, a combination of (b) and (c) was very effective in controlling the reaction and rendering it completely reproducible.

The over-all reactions which have been discussed in stoichiometric terms do not indicate the complexity of the system. Some of the competing reactions which must occur are listed below and are described briefly.

$$2\mathrm{LiH} + \mathrm{B_2H_6} \longrightarrow 2\mathrm{LiBH_4} \qquad (5)$$

$$3\mathrm{LiBH_4} + \mathrm{BF_3{:}O(C_2H_5)_2} \longrightarrow 2\mathrm{B_2H_6} + 3\mathrm{LiF} + \mathrm{(C_2H_5)_2O} \qquad (6)$$

$$3\mathrm{LiBH_4} + \mathrm{LiBF_4} \longrightarrow 2\mathrm{B_2H_6} + 4\mathrm{LiF} \qquad (7)$$

$$6\mathrm{LiH} + 2\mathrm{LiBF_4} \xrightarrow{\text{promoter}} \mathrm{B_2H_6} + 8\mathrm{LiF} \qquad (8)$$

$$\mathrm{LiH} + \mathrm{B(OCH_3)_3} \longrightarrow \mathrm{Li(CH_3O)_3BH} \qquad (9)$$

$$6\mathrm{Li(CH_3O)_3BH} + 2\mathrm{BF_3{:}O(C_2H_5)_2} \longrightarrow \mathrm{B_2H_6} + 6\mathrm{LiF} + 6\mathrm{B(OCH_3)_3} + 2\mathrm{(C_2H_5)_2O} \qquad (10)$$

$$6\mathrm{Li(CH_3O)_3BH} + 2\mathrm{LiBF_4} \xrightarrow{?} \mathrm{B_2H_6} + 8\mathrm{LiF} + 6\mathrm{B(OCH_3)_3} \qquad (11)$$

$$\mathrm{LiF} + \mathrm{BF_3{:}O(C_2H_5)_5} \longrightarrow \mathrm{LiBF_4} + \mathrm{(C_2H_5)_2O} \qquad (12)$$

Reactions (5), (6) and (7) proceeded smoothly and rapidly in ethyl ether at room temperature and above. The rate of reaction of lithium borohydride with boron trifluoride ethyl etherate at 0° was approximately one-fourth that at 25°; with lithium borofluoride, the rate at 0° was very slow.

Lithium hydride and lithium borofluoride in ether appeared unreactive at 25° in the absence of a promoter. However, the addition of a small amount of either lithium borohydride or methyl borate initiated a reaction which subsequently produced 85% of the diborane calculated from equation (8).

It has been reported[2] that methyl borate adds to lithium hydride in ether to give lithium trimethoxyborohydride (equation 9); the latter compound has also been reported[2,4,9] to react smoothly with boron trifluoride etherate at 35° to give diborane in good yields (equation 10). The reaction of lithium trimethoxyborohydride with lithium borofluoride has not been studied, but is assumed to proceed according to equation (11) to give diborane; the promoting effect of methyl borate in reaction (8) could then depend on a series of steps including (9), (11) and possibly (5).

Lithium fluoride did not add readily to boron trifluoride ethyl etherate (equation 12) in dilute ether solution, but could be quantitatively converted to lithium borofluoride if boron trifluoride gas were passed continuously into the reaction mixture. Under these conditions, the solvent was actually boron trifluoride ethyl etherate.

Several of the subsidiary reactions were also examined in tetrahydrofuran, with results similar to those observed in ether. Lithium hydride and lithium borofluoride showed no evidence of reaction at either room temperature or 65°. Lithium borohydride reacted readily with the tetrahydrofuran complex of boron trifluoride and with lithium borofluoride at reflux temperature, but yields of diborane were much lower than from equivalent reactions in ether.

## Discussion

The role of promoters on the lithium hydride, boron trifluoride reaction in ethyl ether has not been clearly defined because of the complexity of the system. The observed reactions suggest that the promoters aid in maintaining a clean lithium hydride surface. In the unpromoted reaction, the first step is probably addition of boron fluoride to lithium hydride, resulting in surface contamination of the hydride. Further reaction of this complex lithium salt with boron trifluoride would produce lithium borofluoride. The inability of methyl borate to activate lithium hydride in an intermediate reaction stage suggests that the methyl borate did not have free access to the lithium hydride.

Lithium borohydride is known to be highly reactive toward both boron fluoride and lithium borofluoride. Boron fluoride may react preferentially with lithium borohydride (or trimethoxyborohydride) rather than with lithium hydride, thereby preventing accumulation of relatively insoluble intermediate salts on the hydride surface, and permitting ready access of dissolved diborane to lithium hydride. Furthermore, lithium borofluoride cannot accumulate in the system if the proper balance of borohydride is maintained.

With boron chloride, equation (1) is not probable because of the instability of the boron tetrachloride ion. In tetrahydrofuran, surface contamination of lithium hydride by intermediate salts is improbable because of the high solubility of the complex lithium salts in this system.[10] The unusually high solubility of diborane in tetrahydro-

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(8) H. I. Schlesinger and H. C. Brown, U. S. Patent 2,545,633 (1951), assigned to U.S.A.

(9) H. I. Schlesinger and H. C. Brown, Final Report on Contracts Nos. N173 S-9058 and N173 S-9820 (1945).

(10) J. R. Elliott, *et al.*, This Journal, **74**, 5211 (1952).

furan[10] should also promote its addition to lithium hydride, in a manner comparable to the reaction in ether under diborane pressure.

The lower measured yield of diborane in reactions carried out in tetrahydrofuran, as compared to ethyl ether, may be due to the high solubility of diborane in tetrahydrofuran. With good fractionation, yields of diborane may be equivalent in the two systems.

## Experimental

Storage and handling of reagents was carried out in a dry-box flushed with nitrogen gas dried over activated alumina to a dew point below −50°. All reagents prepared or purified outside the dry-box were protected from the atmosphere by a stream of dry nitrogen.

**Reagents.**—Commercial anhydrous ether was dried by refluxing over sodium metal or lithium hydride until hydrogen evolution ceased. After drying, the ether was distilled in a nitrogen blanketed system into a container so fitted that the ether could be forced directly into the dry-box by means of dry nitrogen.

Commercial tetrahydrofuran was refluxed for 12 hours over lithium hydride, then distilled under nitrogen. The center cut, b.p. 66°, was stored in the dry-box for subsequent work.

Lithium hydride from the Maywood Chemical Company was received in the form of 4–8 mesh lumps. The hydride was transferred into a brass rod mill mounted inside the dry-box and was ground for a 24-hour period in 200-g. batches. The powder assayed 95–100% as measured by hydrogen evolution on hydrolysis.

Boron trihalide etherates were prepared by passing commercial boron trifluoride or boron trichloride gas into ethyl ether or tetrahydrofuran contained in an ice-cooled flask equipped with stirrer and reflux condenser. Boron trihalide feed was stopped when a steady stream of the fuming gas appeared at the nitrogen-protected outlet. Boron trifluoride–ethyl ether complex was assayed by boiling with excess sodium fluoride and determining increase in weight of the dried salts. Boron trifluoride content ranged from 99–101%. The boron trichloride–ethyl ether complex containing excess ether was analyzed for etherate content by titration of hydrolyzable chlorine with standard alkali. The crude boron trifluoride tetrahydrofuran complex after distillation (b.p. 95–97.5° (18 mm.)) was faintly yellow with a penetrating but pleasant organic odor; it did not fume in air as does the ethyl ether complex.

Lithium borohydride was prepared by passing diborane into a lithium hydride–ether slurry. The solution was either filtered in the dry-box and stored as the saturated solution, or was evapoated to dryness in a vacuum. Minimum purity of the dry salt was 95% as measured by hydrogen evolution from a cobaltous chloride-catalyzed hydrolysis.[11]

Lithium borofluoride was prepared by saturating with boron fluoride gas a suspension of 450 g. of lithium fluoride in 1500 cc. of ether. The supernatant liquid was decanted from the solid, and the precipitate washed repeatedly with ether until the decanted washings were colorless. The solid was filtered by suction and dried in a vacuum desiccator, then heated for four hours at 100°. The borofluoride was analyzed by decomposition of the salt to lithium fluoride and boron trifluoride on ignition to the melting point of lithium fluoride; molecular ratio of $LiF/BF_3$, 0.99.

Methyl borate was prepared by continuous distillation of methyl alcohol–boric acid mixtures. The azeotrope was separated by shaking with concentrated sulfuric acid. Methyl borate (b.p. 63°) was distilled as required.

**Apparatus.**—The reactions were carried out in a three-necked, 1-liter flask provided with a mercury sealed stirrer, dropping funnel and reflux condenser leading to scrubbers and traps. Collection traps were arranged in parallel so that the yield of diborane during any portion of a run could be measured and analyzed. All material transfer was performed in the dry-box and all equipment was dried by baking or by long exposure to dry nitrogen before a run. Reactions were carried out under a slow stream of nitrogen.

**Analysis of Reaction Mixtures.**—The amounts of lithium hydride, lithium borohydride, lithium fluoride and lithium borofluoride in the ether suspension after partial reaction of lithium hydride and boron trifluoride were analyzed by a method based on hydrolysis of the salts.

Ether and any unreacted boron trifluoride–ether complex were removed from the suspension of salts by distillation to dryness in vacuum. The solid residue was ground and thoroughly mixed in the dry-box. Five to ten grams of the solid salt mixture was added slowly to 100 cc. of water–ice mixture in a nitrogen atmosphere.

Lithium hydride and borohydride hydrolyze readily to give hydrogen and water-soluble products

$$\text{(a)}\quad LiH + H_2O \longrightarrow H_2 + LiOH$$

$$\text{(b)}\quad LiBH_4 + 4H_2O \longrightarrow 4H_2 + LiOH + H_3BO_3$$

Lithium borofluoride dissolves in the alkaline solution. Lithium fluoride is insoluble and was isolated by filtration. Combined lithium hydride and borohydride were determined as lithium hydroxide by titration of the filtrate with acid. A further potentiometric titration of the neutralized solution, after mannitol addition, determined the amount of boric acid derived from lithium borohydride. Since rate of hydrolysis of the borofluoride ion is low in alkaline solution[12] (less than 1% in three hours), lithium borofluoride does not interfere with the determination of lithium borohydride. Analysis for total boron[13] in another aliquot, gave combined amounts of lithium borofluoride and lithium borohydride.

Combined lithium hydride and lithium borohydride were also determined by measurement of active hydrogen. The theoretical amount of hydrogen described by equations (a) and (b) is evolved rapidly in the presence of traces of cobaltous chloride.[11]

The analysis of a synthetic mixture of salts is given in Table I.

TABLE I

ANALYSIS OF SYNTHETIC MIXTURE OF SALTS

| Compound | Purity of source | Weighed sample, g. | Found in mixture, g. |
|---|---|---|---|
| LiH | 95.5% | 4.0 | 3.7 |
| $LiBH_4$ | 95% (minimum) | 1.1 | 1.1 |
| LiF | C.P. reagent | 7.8 | 7.4 |
| $LiBF_4$ | 96–100% | 14.2 | 13.6 |

Duplicate analyses on solid reaction mixtures checked closely, and analyses from equivalent runs also gave good checks. Material balances were usually about 10% low, probably because of difficulty in removing the last portion of solvent.

**General Comments.**—Diborane is a highly inflammable gas. When pure, it does not ignite spontaneously in air, but it is believed that highly reactive by-products or decomposition products can cause its ignition. Solid diborane may be highly reactive toward oxygen, and such a mixture should be considered a violent explosive until proved otherwise. Ether suspensions of lithium hydride and hydrogen-containing intermediates are hazardous if exposed to water; heat of reaction may be high enough to ignite the hydrogen-enriched ether vapor.

Lithium hydride, which is very insoluble, was handled as a finely divided suspension of the solid in ether: maximum amount of hydride used in a single experiment was 48 g. in 350 cc. of solvent. The addition of 5 cc. of boron trifluoride etherate to the hydride suspension produced a rise in temperature in the reaction mixture within a few minutes. If the exothermic reaction did not start immediately, final yield of diborane was unpredictable. Induction periods never occurred when reagents were pure. Purity of diborane was 99–100% except when otherwise indicated. Amount of hydrogen liberated in the reactions was negligible.

**Lithium Hydride and** Boron **Trifluoride Etherates.** Non-promoted **Reaction.**—Boron trifluoride–ethyl ether complex (2 moles) was added slowly to 6 moles of powdered lithium hydride suspended in 350 cc. of ethyl ether at room temperature. An exothermic reaction started immediately; temperature of the ether rose rapidly to 34° and diborane evolution commenced. During the major portion of the

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(11) H. I. Schlesinger, Report on Contract W3434, sc-174 (1944).

(12) I. G. Ryss and M. M. Slutskaya, *J. Phys. Chem.* (*U.S.S.R.*), **21**, 549–561 (1947).

(13) C. F. Swinehart, A. R. Bumblis and H. F. Flisek, *Ind. Eng. Chem., Anal. Ed.*, **19**, 31 (1947).

reaction, moles of collected diborane were approximately $^{1}/_{8}$ the moles of added boron fluoride. The yield of diborane was essentially reproducible, varying in ten experiments from 21 to 28% based on lithium hydride (equation 2). Increased rate of addition of the boron trifluoride complex did not affect diborane yield.

The products from a reaction between 2 moles of lithium hydride and 0.87 mole of boron trifluoride complex in 150 cc. of ether were analyzed: Found $B_2H_6$, 0.09 mole; LiH, 1.27 moles; $LiBF_4$, 0.41 mole; LiF, 0.18 mole; $LiBH_4$, 0.02 mole.

Reagents were also mixed in the stoichiometry of equation (1): (lithium hydride, 1.06 moles; boron fluoride etherate, 1.42 moles; ether, 100 cc.). Temperature of the reaction mixture was still maintaining itself at 33.5° one hour after boron fluoride addition had been completed, and diborane was still collecting slowly when the apparatus was dismantled. Yield of diborane at this point was 75% based on equation (1). Addition of 1.2 moles of powdered lithium fluoride to an ether suspension of 3 moles of lithium hydride had no influence on the reaction.

Experiments with tetrahydrofuran as solvent are summarized in Table II.

Table II

| Run no. | LiH, moles | $BF_3$: $C_4H_8O$, moles | $LiBH_4$, mole | $C_4H_8O$, cc. | Temp., °C. | $B_2H_6$, mole | $B_2H_6$, % yield |
|---|---|---|---|---|---|---|---|
| 60 | 2.0 | 0.72 | .. | 155 | 35–50 | 0 | 0 |
| 63 | 2.95 | 0.80 | .. | 150 | 35–40 | Uncontrolled reaction | |
| 66 | 3.0 | 1.44 | .. | 140 | 68–75 | 0.345 | 69.0 |
| 67 | 3.0 | 1.16 | 0.05 | 150 | 68–75 | 0.368 | 67.6 |

In runs 60 and 63, temperature of the reaction was controlled with an ice-bath. In run 60, the highly exothermic reaction ceased after $^{3}/_{4}$ of the boron trifluoride had been added: further addition of boron trifluoride resulted in a drop in temperature, but no yield of diborane, although gas appeared to be dissolved in the condensate from the Dry Ice–acetone cooled reflux condenser. Run 63 was a repetition of 60, carried out with the intention of refluxing the reaction mixture after all the boron fluoride complex had been added. The reaction was maintained at 40° or less by an ice-bath until 80% of the boron trifluoride had been added; at this point, the reaction could not be controlled, the temperature rose rapidly, and the contents of the flask boiled out of the various safety devices.

In run 66, the suspension was maintained at reflux throughout the entire reaction. During the addition of $^{3}/_{4}$ of the boron fluoride complex, the reaction was exothermic, and no diborane was evolved. The temperature then dropped sharply, and diborane was collected, in 69% yield. The addition of lithium borohydride in run 67 had no apparent effect on the course of reaction or final yield of diborane.

**Promoted Reactions in Ethyl Ether.**—Promoter was usually introduced into a lithium hydride–ether slurry at room temperature before addition of the boron trifluoride complex.

Table III

Production of Diborane in Promoted Reactions

| Run no. | LiH, moles | $BF_3:OEt_2$, moles | Ether, cc. | Promoter | Mole %$^c$ promoter | Mole $B_2H_6$$^b$ before prom. addition | Total moles $B_2H_6$ | Yield, %$^d$ $B_2H_6$ |
|---|---|---|---|---|---|---|---|---|
| 11 | 6.00$^a$ | 2.31 | 320 | $LiBH_4$ | 5.5 | .. | 1.03 | 83 |
| 17 | 6.10$^a$ | 2.30 | 300 | $LiBH_4$ | 3.6 | .. | 0.98 | 84 |
| 18 | 6.00$^a$ | 2.18 | 315 | $(CH_3O)_3B$ | 8.3 | .. | .85 | 85 |
| 31 | 3.00$^a$ | 1.14 | 200 | $(CH_3O)_3B$ | 4.0 | .. | .44 | 88 |
| 34 | 3.04$^a$ | 1.15 | 200 | $(CH_3O)_3B$ | 1.1 | .. | .16 | 33 |
| 33 | 3.04$^a$ | 1.14 | 200 | $(CH_3O)_3B$ | 0.1 | .. | .13 | 26 |
| 47 | 2.02$^b$ | 0.75 | 275 | $LiBH_4$ | 5.9 | 0.10 | .24 | 49 |
| 45 | 3.10$^b$ | 1.10 | 200 | $LiBH_4$ | 3.2 | .14 | .29 | 43 |
| 30 | 3.00$^b$ | 1.10 | 200 | $LiBH_4$ | 1.3 | .13 | .17 | 29 |
| 44 | 3.04$^b$ | 1.11 | 225 | $(CH_3O)_3B$ | 15.8 | .13 | .14 | 25 |

[a] Promoter added before addition of boron fluoride etherate. [b] Promoter added after addition of boron fluoride etherate. [c] Based on initial lithium hydride. [d] From lithium hydride according to equation (2); yield corrected for diborane produced from added promoter.

The first six runs listed in Table III illustrate the influence of catalyst added before introduction of boron trifluoride. In the presence of 3.6 to 5.5 mole per cent. (based on initial lithium hydride) of either lithium borohydride or methyl borate, slow addition of the boron trifluoride etherate resulted in an immediate exothermic reaction which continued until the mole ratio of added boron fluoride to initial lithium hydride was 1.5/6. Amounts of diborane collected up to this point were from 0–15% of theoretical according to equation (2). The products at this $^{3}/_{4}$ stage in a methyl borate-catalyzed reaction are listed in Table IV.

Further addition of boron trifluoride caused a sudden drop in solution temperature accompanied by rapid evolution of diborane. One mole per cent. methyl borate did not produce the two-stage reaction, but did result in slightly better yields of diborane than were obtained in the absence of promoter.

The last four runs listed in Table III illustrate the effect of catalyst added to the ether suspension of salts remaining after completion of a non-promoted reaction. Methyl borate was ineffective; its addition to the final suspension did not result in an exothermic reaction and did not produce any appreciable further amount of diborane in 1.75 hours. The addition of lithium borohydride produced a short exothermic reaction accompanied by diborane evolution. The diborane collected in this second promoted reaction was in excess of the amount which could be produced from the added borohydride.

**Surge Reaction in Ethyl Ether.**—Ten to forty per cent. of the theoretical boron trifluoride complex calculated according to equation (2) was added to an ice-cooled suspension of lithium hydride in ether. Temperature was controlled at 0–7° during the addition and was then held at 1-2° for two to three hours. When the ice-bath was removed, temperature of the solution rose to the boiling point of ether and diborane was evolved rapidly in a "surge" after which the ether cooled slowly to room temperature. Further addition of boron trifluoride produced a steady evolution of diborane. A series of surge reactions are enumerated in Table V. The rate of diborane evolution following the 9.8% surge was characteristic of a non-promoted reaction. After the 11.5% surge, rate of diborane production was in the mole ratio boron trifluoride/diborane = 2/1 until 60% of the theoretical boron trifluoride had been added (equation (2)).

Table IV

Analysis of Reaction Mixture at Three-quarter Point

| | Reactants, moles | Product, moles Found | Product, moles Calculated from eq. (3) |
|---|---|---|---|
| LiH | 3.04 | 0.09 | 0.08 |
| $BF_3:O(C_2H_5)_2$ | 0.74 | .. | .. |
| $(CH_3O)_3B$ (volatile) | .12 | .. | .. |
| $LiBH_4$ | .. | 0.73 | 0.74 |
| LiF | .. | 2.23 | 2.22 |
| $B_2H_6$ | .. | 0 | 0 |

Diborane evolution then slowed down to a rate about $^1/_7$ that of added boron trifluoride.

TABLE V

SURGE REACTIONS

| Moles LiH | Total moles $BF_3$:O-$(C_2H_5)_2$ | Ether, cc. | Etherate added at 0°C. | | Mole $B_2H_6$ from surge | Final mole $B_2H_6$ |
|---|---|---|---|---|---|---|
| | | | Amount | % Theoretical | | |
| 6.0 | 2.3 | 345 | 0.760 | 38.0 | 0.24 | 0.84 |
| 6.1 | 2.1 | 340 | .428 | 21.0 | .16 | .83 |
| 6.0 | 2.2 | 345 | .23 | 11.5 | .08 | .58 |
| 6.1 | 2.2 | 330 | .198 | 9.8 | .02 | .31 |

The products of the reaction of 3 moles of lithium hydride and 1 mole of boron trifluoride etherate in 175 cc. of ether at 2–5° were analyzed after 2.25 hours standing at this temperature. No diborane had been evolved. The solution was filtered rapidly in the dry-box and the solids were dried in a vacuum desiccator. The solids contained: $LiBH_4$, 0.14 mole; LiH, 1.38 moles; $LiBF_4$, 0.39 mole; LiF, 0.90 mole. The filtrate, which was not analyzed, fumed in air, had a density of 0.76 g./cc., and deposited crystalline material on standing.

The compounds present at the end of a 34% surge were also analyzed. Boron trifluoride etherate (0.23 mole) was added to 2 moles of lithium hydride suspended in 140 cc. of ether at 4°. After 1 hour at 3–5°, the solution was allowed to warm and surge. Found: LiH, 1.26 moles; $LiBH_4$, 0.09 mole; $LiBF_4$, 0.03 mole; LiF, 0.55 mole; $B_2H_6$, 0.03 mole.

**Pressure Reactions.**—In coöperation with the Chemical Engineering section of the laboratory, diborane was prepared in one-pound quantities in metal equipment designed for operation under pressure.

After addition of a small amount of boron trifluoride etherate, diborane pressure rose rapidly to 5–15 p.s.i. and then remained constant in the closed system until three-fourths of the theoretical etherate based on equation (2) had been added. At this point, the exothermic reaction changed to endothermic. Diborane gas was allowed to escape into a collection trap until pressure had been reduced to atmospheric. During addition of the remaining etherate at atmospheric pressure, diborane was evolved according to equation (4). Temperature of the reaction kettle was controlled at 30–35° throughout the entire process. If a 20% excess of etherate was used, one pound of diborane could be prepared in 2.5 to 3 hours in a 95–96% yield, based on equation (2). In the metal reactor, induction periods of 15 to 60 minutes often occurred due to difficulty in maintaining anhydrous conditions in the larger scale equipment. The induction period was completely eliminated by addition of 2–10 wt. % of diborane to the lithium hydride slurry prior to introduction of etherate.

**Lithium Borohydride and Boron Trifluoride Etherates.**—At room temperature, 0.118 mole of $BF_3:O(C_2H_5)_2$ was added to a saturated ether solution of lithium borohydride (202 cc.; calcd. mole, 0.335). During the 20-minute addition period, temperature of the solution dropped from 25 to 18° and diborane evolved rapidly. Solution temperature then rose to 24°, while diborane evolution continued slowly. After a total reaction time of one hour, yield of diborane was 0.220 mole; after five hours, 0.224 mole; calculated yield, 0.223 mole. A similar reaction was carried out at reflux temperature with 0.332 mole of lithium borohydride and 0.134 mole $BF_3:O(C_2H_5)_2$. Yield of diborane in 45 minutes was 0.212 mole; in 1.25 hours, 0.221 mole; calculated yield, 0.221 mole. The same experiment was repeated at 2° with 0.335 mole of lithium borohydride and 0.118 mole of boron trifluoride etherate. The yield of diborane after 70 minutes was 0.047 mole; calculated yield, 0.223 mole. After removal of the ice-bath, temperature rose slowly to 22° and diborane was collected for two hours; final yield 0.220 mole.

$BF_3:OC_4H_8$ (0.22 mole) was added slowly to a 25° solution of lithium borohydride (0.250 mole) in 88 cc. of tetrahydrofuran. Solution temperature rose immediately to 33°, then dropped slowly to 25° during addition of the remaining complex. There was no evidence of diborane evolution until the reaction mixture was heated to reflux; yield of diborane, 32% after one hour of reflux.

**Lithium Borohydride and Lithium Borofluoride.**—At room temperature a saturated ether solution of lithium borohydride (177 cc., calculated moles, 0.294) was added over a one-hour period to 0.133 mole of lithium borofluoride in 200 cc. of ether. A small amount of lithium borohydride was lost through crystallization in the dropping funnel. Solution temperature slowly dropped from 25 to 22° and remained steady at that temperature during the addition of borohydride. The yield of diborane after 1.5 hours was 0.173 mole; after 2.5 hours, 0.178 mole; calculated yield, 0.196 mole. The same experiment was repeated at 2° with 0.264 mole of lithium borohydride in 219 cc. of ether and 0.106 mole of lithium borofluoride in 115 cc. of ether. At the end of two hours, the yield was 0.0176 mole; calculated yield, 0.176 mole. The ice-bath was removed, the solution warmed to 22°, and after 2 hours yield of diborane was 0.163 mole.

In tetrahydrofuran, the reaction was carried out in equipment of approximately one-tenth the usual capacity. Gaseous product was collected in a liquid nitrogen-cooled trap and was fractionated on a low temperature Podbielniak still. Diborane was identified on the mass spectrograph. A mixture of lithium borohydride (0.109 mole) and lithium borofluoride (0.037 mole) in 35 cc. of tetrahydrofuran produced 651 cc. (S.T.P.), of diborane gas (40% yield) after five hours refluxing.

**Lithium Hydride and Lithium Borofluoride.**—A suspension of 1.9 moles of lithium hydride and 0.66 mole of lithium borofluoride in 225 cc. of ethyl ether produced a maximum of 0.001 mole of diborane after four hours at room temperature. When a saturated solution of lithium borohydride (0.08 mole in 50 cc. of ether) was added to the suspension, the temperature rose rapidly to reflux, then dropped to 24° after 15 minutes. A total of 0.308 mole of diborane was collected within 1.5 hours after addition of the borohydride. Diborane produced from lithium hydride, corrected for lithium borohydride, was 0.258 mole; calculated, 0.32 mole.

Methyl borate also catalyzed the reaction between lithium hydride and lithium borofluoride in ether. A mixture of 2.0 moles of lithium hydride, 0.78 mole of lithium borofluoride, 0.17 mole of methyl borate and 225 cc. of ether maintained itself at reflux temperature for 2.5 hours, with no diborane evolution. Temperature then dropped rapidly to 18° and 0.252 mole of diborane was collected in 45 minutes; calculated yield, 0.33 mole.

A mixture of lithium hydride and lithium borofluoride in tetrahydrofuran showed no evidence of reaction after 3.5 hours at 63–69°.

**Lithium Fluoride and Boron Trifluoride.**—Lithium borofluoride can be prepared quantitatively from lithium fluoride and the boron trifluoride–ethyl ether complex if the boron trifluoride concentration is maintained at the saturation point, as described in the section on reagents. The reaction does not appear to go to completion in less concentrated solution. Equimolar portions of lithium fluoride and the boron trifluoride etherate were allowed to stand for one hour at room temperature and the suspension was then heated with an infrared lamp to remove ether. The mushy solid was heated further at 160° for six hours until it appeared dry. The weight increase of the solid indicated 80% conversion to lithium borofluoride.

Our analytical laboratory[14] has reported that at room temperature the density of boron trifluoride etherate is decreased by shaking with powdered lithium fluoride, but conversion to borofluoride is in the order of 20%, based on solution density measurements. Presumably, a coating of lithium borofluoride on the lithium fluoride surfaces prevents further reaction with boron trifluoride.

**Lithium Hydride and Boron Trichloride.**—Boron trichloride–ethyl ether complex (207.3 g. of ether solution, containing 1.08 moles of boron trichloride by analysis) was added slowly to 3.1 moles of lithium hydride in 200 cc. of ether. An exothermic reaction started immediately, the solution temperature maintaining itself at 30 to 35° during addition of 0.64 mole of etherate. During this time, 0.08 mole of condensable gas was collected, analyzing to 6% diborane. Further addition of boron trichloride etherate produced a drop in solution temperature to 25°, and was accompanied by evolution of diborane. The next 0.134 mole of diborane was 88.6% pure; remaining portions of diborane analyzed to 98.6–99.8%. The total yield of diborane, corrected for impurities, was 0.362 mole, or 72% of theoretical for equation (2).

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[14] E. H. Winslow and G. S. Poellmitz, unpublished work.

In a similar experiment methyl borate (8 mole per cent. based on lithium hydride) was added to the lithium hydride before addition of boron trichloride etherate. Reaction characteristics were almost identical with the above reaction in which no catalyst was used. The first diborane collected was of low purity. The final yield was 77%.

Boron trichloride gas was also passed directly into a lithium hydride–ether slurry. In a reaction between 3.1 moles of lithium hydride in 325 cc. of ether and 1.01 moles of boron chloride, exothermic reaction changed to endothermic when 0.65 mole of boron trichloride had been added. The 0.055 mole of diborane collected during the exothermic reaction was 93% pure. Remaining diborane analyzed to 100%; total yield of diborane, 0.384 mole; calculated, 0.517 mole.

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

# Stability of Metal Chelates. I. Iminodiacetic and Iminodipropionic Acids

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Acid dissociation constants of iminodiacetic acid and iminodipropionic acid, and the chelate stability constants of the corresponding anions with cupric, nickelous, cobaltous, zinc and cadmium ions are reported for a temperature of 30° and 0.1 ionic strength. The replacement of acetate groups by β-propionate groups in the ligand results in a considerable decrease in the stability of the chelate.

This is the first of a series of publications describing the effect of structure of the ligand on the stability of aqueous metal complexes. The chelating agents to be described are amino acids, soluble in water in the form of their salts, which have more or less ability to combine with the more basic metal ions, such as the alkaline earth metals, and having appreciable affinity for transition metals and other "heavy metal" ions. Thus all the compounds in this series may be classified as sequestering agents. A guiding principle in our investigation involves the selection of the two most useful sequestering agents known—ethylenediaminetetraacetic acid and nitrilotriacetic acid—as having more or less optimum structures. By changing these basic structures with respect to (1) variation of the number of acetic acid groups, and (2) replacement of these by other groups, it may be possible to draw logical conclusions concerning the basis of metal ion affinity in these compounds. Thus a quantitative study of the stabilities of the corresponding metal chelates may lead to a better understanding of the method of function of sequestering agents, and to the development of superior sequestering agents.

Iminodiacetic acid, $NH(CH_2COOH)_2$, and iminodipropionic acid, $NH(CH_2CH_2COOH)_2$, have not been investigated previously, with the exception of the former, for which dissociation constants and approximate stability constants with calcium and magnesium have been published. In the present paper, the dissociation constants and chelate stability constants with a number of metal ions of the first transition series are reported.

The structures of these complexing agents differ from that of the parent compound, nitrilotriacetic acid, $N(CH_2COOH)_3$, in that in the first an acetic acid group is replaced by a hydrogen, and in the second, both remaining acetic acid groups are replaced by β-propionic acid groups. In accordance with the now accepted theories[2] concerning the structure of aminopolycarboxylic acid–metal chelates, nitrilotriacetic acid is probably tetradentate. Hence the removal of an acetic acid group would be expected to render the resulting structure tridentate, and the stability of the chelate would thus be lowered. Indeed, the differences in calcium and magnesium formation constants for nitrilotriacetic acid and iminodiacetic acid reported by Schwarzenbach[3a,b] indicated a very dramatic drop in stability. The logarithms of the stability constants of the calcium and magnesium nitrilotriacetate ions, $Ca{\cdot}N(CH_2COO)_3^{-1}$ and $Mg{\cdot}N(CH_2COO^-)_3^{-1}$ were found by Schwarzenbach to be 6.41 and 5.41, respectively. On the other hand, the corresponding values for the iminodiacetic acid chelates, $Ca{\cdot}NH(CH_2COO)_2$, and $Mg{\cdot}NH(CH_2COO)_2$ were found to be only 3.41 and 3.66.

There is little quantitative information on the effect of replacement of an acetic acid group by propionic acid. Schwarzenbach[3a] found the logarithm of the stability constant of calcium with β-alanine-N,N-diacetic acid, $Ca{\cdot}OOCCH_2CH_2N(CH_2COO)_2^{-1}$, to be 5.04. This shows a drop of 1.37 log *K* units when compared to that of nitrilotriacetic acid.

## Experimental

The experimental method consisted of potentiometric titration of the amino acid in the absence of and in the presence of the metal ion being investigated. The ionic strength was maintained constant by using 0.1 *M* KCl as a supporting electrolyte and by employing relatively very low concentrations of metal and amino acid. The titrations were carried out using both 1:1 and 2:1 ratios for amino acid to metal ion concentration. All measurements were carried out at 30 ± 0.02°.

**Apparatus.**—The titration assembly consisted of a Beckman model G *p*H meter with extension electrodes, and a glass reaction flask of about 250-ml. capacity. The titration vessel was fitted with a mercury seal stirrer and contained 9 necks sealed into the periphery to accommodate the microburet, glass and calomel electrodes, gas inlet and outlet, and a number of hydrogen and silver–silver chloride electrodes. The platinum (hydrogen) electrodes were of

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[2] Calvin and Martell, "The Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, chapter 4.

[3] (a) G. Schwarzenbach, H. Ackermann and P. Ruckstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949); (b) G. Schwarzenbach, E. Kampitsch and R. Steiner, *ibid.*, **28**, 1133 (1945).