[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF CHICAGO]

# The Reduction of Iron(III) Chloride with Lithium Aluminohydride and Lithium Borohydride: Iron(II) Borohydride[1]

BY GEORGE W. SCHAEFFER, JOHN S. ROSCOE[2] AND ALBERT C. STEWART[3]

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Lithium aluminohydride in excess reacts with $FeCl_3$ in diethyl ether to give as ultimate products aluminum, Fe·2Al, LiCl and hydrogen. The first step of the reaction is probably the reduction of $FeCl_3$ to $FeCl_2$ and the formation of $AlH_3$. If $FeCl_3$ is in excess, it is reduced to $FeCl_2$ by the $AlH_3$ thus formed, but if the aluminohydride is in excess, metathesis occurs and an iron aluminohydride is formed. This intermediate aluminohydride has not been isolated because it rapidly decomposes, producing hydrogen, but the behavior of the system can be most satisfactorily explained by postulating its formation. In the presence of the finely divided metal produced by the decomposition of the aluminohydride, the $AlH_3$ obtained in the first step decomposes into the metal and hydrogen. Analogous to the aluminohydride reaction, $LiBH_4$ reduces $FeCl_3$, the products being $B_2H_6$ and $Fe(BH_4)_2$. The $Fe(BH_4)_2$ thus obtained is a white, non-volatile solid, fairly soluble in ether. It decomposes slowly at −10° and rapidly at 0° into diborane, hydrogen and a pyrophoric residue containing iron and boron.

Borohydrides and aluminohydrides react with anhydrous metal halides in several ways: (a) the reactants may undergo simple metathesis as in the reaction of lithium chloride with sodium borohydride[4] to give lithium borohydride; (b) the metal halide may be reduced to the metal: for example thallium(III) chloride[5] with lithium aluminohydride gives thallium and aluminum hydride; (cs the halide may be converted to the hydride, a) when copper(II) chloride[6] reacts with lithium borohydride to give copper(I) hydride, hydrogen and diborane; (d) finally, a boride or aluminide may be obtained as, for example, when cobalt(II) bromide[6] reacts with lithium aluminohydride to give cobalt dialuminide. The investigation of the reaction of iron(III) chloride with lithium borohydride and lithium aluminohydride described herein was initiated as part of a detailed study of these reactions with particular emphasis upon the isolation and characterization of the unusual intermediates obtained, and upon the factors that determine the course of the reaction.

If an excess of lithium aluminohydride and iron(III) chloride are brought together in ether solution in the absence of water and air, there is an immediate exothermic reaction which produces hydrogen and yields a black, finely divided, ether-insoluble substance. This precipitate contains all the iron, between two and three moles of aluminum per mole of iron, the amount of which increases as the time increases between the initiation of the reaction and the separation of the precipitate. The precipitate also contains nearly all the chloride (most probably as lithium chloride), and a variable amount of hydrogen. The black precipitate, whether separated or not from the reaction mixture, exhibits a sharp decrease in the rate of loss of hydrogen after three equivalents but continues to evolve the gas for an extended period at a greatly reduced rate until all of it is lost. The process may be summarized by the equation

$$FeCl_3 + 3LiAlH_4 = 3LiCl + Fe \cdot 3Al + 6H_2 \quad (1)$$

The precipitate, Fe·3Al, is pyrophoric, reacts violently with water and rapidly but smoothly with methyl alcohol. This latter reaction gives hydrogen in the amount expected for the formation of aluminum methylate from aluminum

$$Fe \cdot 3Al + 9CH_3OH = Fe + 3Al(OCH_3)_3 + 4^1/_2H_2 \quad (2)$$

The variation with time, already noted, of the aluminum content of the precipitate, suggests that the precipitate as initially formed contains two moles of aluminum and that the third mole of aluminum is precipitated by a slow secondary reaction. This behavior is most easily explained by assuming that the iron(III) chloride is first reduced to iron(II) chloride with the production of a mole of aluminum hydride

$$FeCl_3 + LiAlH_4 = FeCl_2 + AlH_3 + LiCl + {}^1/_2H_2 \quad (3)$$

The iron(II) chloride so produced could undergo metathesis with the excess lithium aluminohydride to give iron(II) aluminohydride which then precipitates from solution

$$FeCl_2 + 2LiAlH_4 = 2LiCl + Fe(AlH_4)_2 \quad (4)$$

The aluminum hydride formed in reaction 3 would gradually polymerize, a behavior known of the substance,[7,8] and precipitate along with the iron(II) aluminohydride.

The reduction implied above is consistent with two additional observations: first, if the reaction is carried out at −45°, an equivalent of hydrogen as required by equation 3 is obtained at the rate of mixing and additional hydrogen is produced at a markedly reduced rate. Second, if a large excess of iron(III) chloride is taken, iron(II) chloride is obtained by a reaction which can be represented by the equation

$$4FeCl_3 + LiAlH_4 = LiCl + AlCl_3 + 4FeCl_2 + 2H_2 \quad (5)$$

To account for the change in rate of hydrogen formation observed at three equivalents (the first equivalent is produced by the reduction of iron-

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[3] Taken in part from a thesis presented to the Graduate School of St. Louis University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1951. Part of the experimental work (that on the reaction between lithium borohydride and iron(III) chloride) was completed at the University of Chicago during the year 1948–1949.

[4] H. I. Schlesinger, H. C. Brown and E. K. Hyde, THIS JOURNAL, **75**, 209 (1953).

[5] E. Wiberg and M. Schmidt, *Z. Naturforsch.*, **6b**, 334 (1951).

[6] A. C. Stewart, Ph.D. Thesis, St. Louis University, June, 1951.

[7] O. Stecher and E. Wiberg, *Ber.*, **75**, 2003 (1942).

[8] E. Wiberg and M. Schmidt, *Z. Naturforsch.*, **6b**, 333 (1951).

(III)), the iron(II) aluminum hydride must decompose into a fairly stable iron–aluminum–hydrogen composition containing six atoms of hydrogen for each of iron

$$FeAl_2H_8 = FeAl_2H_6 + H_2 \qquad (6)$$

and this material decomposes slowly

$$FeAl_2H_6 = Fe{\cdot}2Al + 3H_2 \qquad (7)$$

In presence of finely divided metal,[9,10] aluminum hydride is reported to decompose into the metal and hydrogen

$$AlH_3 = Al + 1^1/_2H_2 \qquad (8)$$

The sum of the processes represented by equations 3, 4, 6, 7 and 8 give equation 1, the extended room temperature reaction.

Although the iron(II) aluminohydride, equation 4, has not been isolated, the behavior of the system is consistent with its intermediate existence and further, its postulation has been made more plausible by the isolation of iron(II) borohydride in the analogous lithium borohydride–iron(III) chloride system which is described below.

Lithium borohydride, in excess, undergoes a stepwise reaction with iron(II) chloride at room temperature to give hydrogen, diborane and a precipitate with properties like those described above for that obtained with lithium aluminohydride

$$3LiBH_4 + FeCl_3 = 3LiCl + 4^1/_2H_2 + {}^1/_2B_2H_6 + Fe{\cdot}2B \qquad (9)$$

The principal difference between the aluminohydride reaction and borohydride reaction results from the difference in properties of the two hydrides; the boron hydride, being volatile, is removed from the scene of reaction, but the aluminum hydride can participate as previously described.

If the reaction is carried out at −45°, hydrogen corresponding to the reduction of iron(III) to iron(II) (one equivalent), a precipitate consisting solely of lithium chloride, and one-half mole of diborane are obtained. After separation of the lithium chloride and upon evaporation of the filtrate, a white to tan, non-volatile solid is obtained. The analysis of this residue is consistent with iron(II) borohydride

$$FeCl_3 + 3LiBH_4 = 3LiCl + {}^1/_2H_2 + {}^1/_2B_2H_6 + Fe(BH_4)_2 \qquad (10)$$

Iron(II) borohydride is stable below −10° but rapidly decomposes above 0°, producing hydrogen and diborane, and leaving a black, pyrophoric residue. Although the ratio of iron to boron in the residue is variable, it is to be noted, Table III, that the total boron, the sum obtained as diborane and found in the residue, is always, within experimental error, twice the iron. Such results may be interpreted to mean that the iron(II) borohydride may decompose in either of two ways

$$Fe(BH_4)_2 = Fe + H_2 + B_2H_6 \qquad (11)$$

$$Fe(BH_4)_2 = Fe{\cdot}2B + 4H_2 \qquad (12)$$

All of the hydrogen required by equations 10 and 11 is not obtained if the decomposition is allowed to occur after as much as possible of the ether has been removed, unless fresh ether is returned to the black solid. Ray and Sahai[11] have reported the existence of an iron hydride, $FeH_2$, which, according to them, is catalytically decomposed by water or alcohol. Such a hydride might conceivably be formed in this case and be catalytically decomposed by ether. An alternate and more probable explanation is the displacement of the hydrogen absorbed on the solid by the ether. Failure to obtain reproducible results strengthens the latter interpretation.

A further complication in the reaction at −45° is illustrated by experiment 5 of Table II. Here, as in the decomposition of iron(II) borohydride, the diborane is less than that required by equation 10 and the hydrogen is increased by an equivalent amount. Two possible processes can account for this result: either the diborane produced could react with the unreacted iron(III) chloride

$$3FeCl_3 + {}^1/_2B_2H_6 = BCl_3 + 3FeCl_2 + 1^1/_2H_2 \qquad (13)$$

or the borohydride could react with the iron(III) chloride by another process

$$FeCl_3 + LiBH_4 = FeCl_2 + LiCl + B + 2H_2 \qquad (14)$$

The stoichiometry would allow both processes, but in exact accord with equation 13. Reactions such as that represented by equation 13 have been observed in other systems[12] which seems to be the more satisfactory explanation.

Finally, it should be pointed out that there are no data to indicate whether the black solids obtained in these reactions are compounds or mixtures of the elements. Several observations, however, may be noted: (a) treatment of the solids with water or methyl alcohol gives products characteristic of reactions of the elements: iron as the element, boron as boric acid or methyl borate, and aluminum as aluminum hydroxide or aluminum methylate. (b) The iron–aluminum–hydrogen combination as separated from the reaction product is not ferromagnetic, but exhibits this property when the hydrogen content has been reduced to about one atom of hydrogen per atom of metal. (c) Extensive treatment of the iron–aluminum–hydrogen combination fails to remove more than the one mole of aluminum hydride formed by the initial reaction. It is thus improbable that the product contains additional $AlH_3$ units. (d) Preliminary study of the hydrogen decomposition pressures of the iron–aluminum–hydrogen combinations has failed to reveal any composition-independent regions and the existence of an iron hydride phase of definite composition is considered unlikely.

## Experimental

The experimental difficulties attendant upon the measurement of the volatile products of reaction, the sensitivity of reactants and products to moisture, and the pyrophoricity of the solid products made the use of a high vacuum apparatus necessary for all experiments. The apparatus is adequately described by Stock[13] and by Sanderson.[14]

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[9] E. Wiberg, R. Bauer, M. Schmidt and R. Uson *Z. Naturforsch.*, **6b**, 393 (1951).

[10] E. Wiberg and W. Henle, *ibid.*, **7b**, 250 (1952).

[11] R. C. Ray and R. B. N. Sahai, *J. Indian Chem. Soc.*, **23**, 67 (1946).

[12] R. H. Toeniskoetter, Master's Thesis, St. Louis University, January, 1956. Diborane reacts with copper(I) chloride in the presence of ether to give copper and boron trichloride. The reaction is favored by low temperatures and high partial pressures of diborane.

[13] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[14] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

**A. Materials. 1. Lithium Borohydride.**—Lithium borohydride was purified by recrystallization from diethyl ether. The purified material was pumped free of ether at 90 to 100°; a two-hour period was usually allowed. Purity was determined by hydrolysis with dilute acid titration for boron in the usual manner. A typical determination on a 0.0391-g. sample gave 153.5 cc. of hydrogen,[15] 40.1 cc. of boron, and a hydrogen to boron ratio of 3.83.

**2. Iron(III) Chloride.**—Iron(III) chloride was prepared by heating pure iron in a stream of dry chlorine.[16] The resublimed crystals of iron(III) chloride were sealed in glass tubes under a nitrogen atmosphere. Immediately after a tube was opened, it was stored in a nitrogen-filled dry box, and the material was transferred to the reaction flask in the dry box whenever possible. Purity was established by analysis for chloride: calculated, 65.6%; found 65.6% (67.0%).

**3. Lithium Aluminohydride.**—Weighed quantities of concentrated solution of lithium aluminohydride were dispersed from a storage vessel under nitrogen. The concentration of the stock solution was determined from time to time by determination of active hydrogen.

**B. Reaction of Iron(III) Chloride with Lithium Aluminohydride at Room Temperature: The Extended Reaction. 1. Hydrogen Produced.**—Iron(III) chloride, 0.91 mmole (0.62 mmole), was treated with an excess of lithium aluminohydride solution. Although it was necessary to moderate the initial reaction by cooling, it required several days before all the hydrogen, 5.48 mmoles (3.79 mmoles), was evolved. The ratio of hydrogen to iron(III) chloride, 6.02 (6.06), is in accord with equation 1.

**2. Composition of the Precipitate.**—$FeCl_3$, 1.11 mmoles (0.62 mmole), was treated with an excess of $LiAlH_4$, as described above. The black precipitate was washed free of excess $LiAlH_4$ with ether and the total ether-insoluble material was analyzed for iron and aluminum; 1.05 mmoles (0.60 mmole) of iron and 3.12 mmoles (1.61 mmoles) of aluminum, a ratio of 1 to 2.98 (2.7), were obtained. The precipitate, therefore, contains all the iron and three atoms of aluminum for each atom of iron as required by equation 1. The sample derived from 0.62 mmole of $FeCl_3$ was further analyzed for chloride; of the 1.86 mmoles expected, 1.82 mmoles were obtained; the loss can be accounted for by the slight solubility of LiCl in ether.

**3. Behavior of the Precipitate,** $Fe{\cdot}3Al$.—The black precipitate is pyrophoric, inflames on treatment with water and reacts rapidly but smoothly with methyl alcohol. This latter reaction produces iron and $Al(OCH_3)_3$. A sample of $Fe{\cdot}3Al$ derived from 0.62 mmole of $FeCl_3$ was treated with an excess of $CH_3OH$. 2.80 mmoles of hydrogen was produced, a ratio of hydrogen to $Fe{\cdot}3Al$ of 4.5. In a second experiment, a sample of $Fe{\cdot}3Al$ derived from 0.35 mmole of $Fe{\cdot}Cl_3$ gave 1.49 mmoles of hydrogen, a ratio of 4.3, the amount expected, equation 3, if the aluminum had reacted to give aluminum methylate. After the reaction with methyl alcohol was complete, there remained a black precipitate, presumably iron. In one experiment this precipitate, derived from 0.30 mmole of $FeCl_3$, was treated with dilute hydrochloric acid and 0.30 mmole of hydrogen was obtained, exactly the amount expected if the precipitate was elemental iron.

**4. Examination of the Ether-soluble Material.**—The combined ether washings from one experiment in which 11.88 mmoles of $LiAlH_4$ was treated with 1.12 mmoles of $FeCl_3$ were analyzed for aluminum and hydrogen, 8.75 mmoles and 35.0 mmoles, a ratio of 3.96, being obtained. This corresponds to 8.75 mmoles of unreacted $LiAlH_4$ or 3.14 mmoles of $LiAlH_4$ being treated with the $FeCl_3$. The ratio of iron to hydride reacting is 2.8, reasonably close to the 3.0 expected.

**C. Reaction with Lithium Aluminohydride at Room Temperature. The Intermediate Reactions. 1. Hydrogen Produced.**—As already described, upon extended reaction at room temperature with $LiAlH_4$ in excess, six moles of hydrogen per mole of $FeCl_3$ taken is obtained. At first the rate of evolution is very rapid, but it quickly subsides and becomes very slow after 4.5 mmoles per mole of $FeCl_3$ is produced. Because it was nearly impossible to reproduce experimental conditions, precise data could not be obtained, but in a typical series of experiments for each mole of $FeCl_3$ taken about 1.5 mmoles (three equivalents) is produced at the rate of mixing; between 2.2 and 2.7 mmoles is produced in 1 to 2 hours; 3.0 to 3.6 mmoles in 3 hours; 3.4 to 4.0 mmoles in 5 hours; and 4.0 to 4.7 mmoles in one to five days. From these data it is seen that the process represented by equation 1 is not simple, and an intermediate hydrogen-containing compound, such as that represented by equation 6, is produced.

**2. Composition of the Precipitate.**—If the precipitate is separated from the reaction mixture after the evolution of hydrogen is complete, the aluminum to iron ratio is three, but if separated earlier, it contains all of the iron and between two and three moles of aluminum per mole of iron, the amount increasing as the time between initiation of the reaction and separation of the precipitate increases. Data obtained in a series of such experiments are given in Table I.

TABLE I

EFFECT OF TIME ON THE COMPOSITION OF THE RESIDUE

| | Reactants | | Residue | | |
|---|---|---|---|---|---|
| Time, hr. | $FeCl_3$, mmole | $LiAlH_4$, mmole | Fe, mmole | Al, mmole | Al/Fe |
| 1 | 1.05 | 4.87 | 0.70[a] | 1.43 | 2.05 |
| 2 | 1.28 | 5.25 | 1.23 | 2.68 | 2.18 |
| 3 | 0.90 | 2.84 | 0.89 | 2.09 | 2.35 |
| 4 | 0.66 | 6.23 | 0.425[a] | 1.04 | 2.45 |
| 9 | 2.02 | 6.15 | 2.02 | 5.33 | 2.69 |
| 7 days | 2.82 | 8.65 | 2.82 | 8.50 | 3.01 |

[a] In these experiments only portions of the residue were taken for analysis.

**3. Isolation and Characterization of $AlH_3$.**—The above observation is explained by postulating that $AlH_3$ is formed in the initial reaction and that this polymerizes and slowly precipitates. That $AlH_3$ is formed is demonstrated by treating the reaction product with $(CH_3)_3N$ and distilling the compound,[17] $(CH_3)_3N{:}AlH_3$, from the other reaction products. In a typical experiment, 1.94 mmoles of $FeCl_3$ was treated with an excess of $LiAlH_4$; $(CH_3)_3N$ was distilled onto the reaction products and the mixture allowed to stand. The volatile materials were removed, and after repeated fractionation through a trap maintained at −45°, a homogeneous crystalline material was obtained. Analysis of this substance gave $Al_{1.76}H_{5.14}[(CH_3)_3N]_{1.82}$ which corresponds closely to the expected 1.94 mmoles of the aluminohydride adduct. To eliminate the possibility that the $AlH_3$ could be derived from the excess $LiAlH_4$, a sample of the pure substance was repeatedly treated[18] with $(CH_3)_3N$ but no $AlH_3$ could be obtained.

If the reaction products were allowed to age before treatment with $(CH_3)_3N$, the $AlH_3$ obtained was less than the one mole, but the total aluminum in the product was always 3 moles per mole of iron as illustrated by the following extreme experiments: $FeCl_3$, 1.06 mmoles, was treated with an excess of $LiAlH_4$, 2.52 mmoles of Al was found in the precipitate and, by the techniques just described, 0.44 mmoles of $AlH_3$ was obtained. Thus for each mole of iron taken, a total of 2.89 moles of aluminum reacted. In a second experiment, 1.63 mmoles of $FeCl_3$ was treated with an excess of $LiAlH_4$; 3.26 mmoles of aluminum was found in the precipitate and 1.62 mmoles of $AlH_3$ was recovered, or a total of 2.99 moles of aluminum for each mole of iron taken, had reacted.

**4. Examination of the Ether-soluble Material. Stoichiometry of the Reaction.**—In several experiments, even though lengthy and complex manipulations were involved. complete analytical data were obtained on a single sample, thus providing direct support for the stoichiometry of the reaction implied by equations 3 and 4. For example, 1.94 mmoles of $FeCl_3$ was treated with 9.83 mmoles of $LiAlH_4$, the solution filtered and the $AlH_3$ removed with $(CH_3)_3N$. The precipitate contained 1.94 mmoles of iron and 3.80 mmoles of

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(15) Where cc. is given as a unit of the quantity of a material, the quantity has been converted to normal gas equivalents. Milliliters are consistently used for liquid measure and for volumes of glass apparatus.

(16) B. R. Tarr, *Inorg. Syntheses*, **3**, 191 (1950).

(17) E. Wiberg, H. Graf, M. Schmidt and R. Uson, *Z. Naturforsch.*., **7b**, 578 (1952).

(18) In the course of these experiments it was observed that the addition compound $LiAlH_4{\cdot}N(CH_3)_3$ is stable at −64°. It dissociates into its components rapidly at room temperature and is insoluble in ether.

aluminum; the filtrate, 4.22 mmoles $LiAlH_4$ and 1.76 mmoles of $AlH_3$, was removed with the trimethylamine. Thus all the iron taken was recovered from the precipitate and 9.78 mmoles of aluminum was recovered, compared to the 9.83 mmoles taken. That the aluminum found in the filtrate was $LiAlH_4$ was confirmed by determination of hydrolyzable hydrogen, 16.70 mmoles or 3.97 mmoles per mmole of aluminum being obtained, in satisfactory agreement with the one to four ratio required by $LiAlH_4$.

**D. Reaction with Lithium Aluminohydride at −45°. Hydrogen Produced.**—At −45° the rate of hydrogen production is markedly decreased and it is possible to observe another sharp break in this rate at 0.5 mole, corresponding to the reduction of $FeCl_3$ to $FeCl_2$ with the production of $AlH_3$. In one experiment, 1.13 mmoles of iron(III) chloride was added slowly to a large excess of lithium aluminohydride in diethyl ether and 0.463 mmole of hydrogen was evolved over a 25-minute period or at the same rate as the addition of the $FeCl_3$. Following this, additional hydrogen was evolved at a reduced and approximately constant rate (0.635 mmole in 335 minutes). Thus, a pronounced break occurs in the rate of hydrogen evolution at a hydrogen to iron ratio of 0.41. In a second experiment, 3.36 mmoles of $FeCl_3$ was added to a large excess of $LiAlH_4$ and a similar break was observed at a hydrogen to iron ratio of 0.508.

**E. Reaction at Room Temperature with Excess** Iron(III) **Chloride.**—If an excess of $FeCl_3$ is taken, and if the reactants are mixed so that no local excess of $LiAlH_4$ occurs, then two moles of hydrogen per mole of $LiAlH_4$ is obtained as illustrated by the following experiments, the results of which may be represented by equation 5.

In the first experiment, an ether solution containing 1.85 mmoles of lithium aluminohydride was treated with an ether solution containing 11.51 mmoles of iron(III) chloride; 3.60 mmoles of hydrogen, or 1.95 mmoles of hydrogen for each mmole of lithium aluminohydride, was produced at the rate of mixing. A yellowish-green ether-insoluble precipitate was obtained, which, except for a few small black particles, was completely soluble in water without the production of additional gas. The material is undoubtedly iron(II) chloride with admixed lithium chloride. In a second experiment, 1.20 mmoles of lithium aluminohydride was treated with 10.01 mmoles of iron(III) chloride; 2.41 mmoles of hydrogen, 2.00 mmoles per mmole of lithium aluminohydride, was obtained. The ether-insoluble material behaved as in the previous experiment.

**F. Reaction with Lithium Borohydride. 1. Reaction at Room Temperature. The Volatile Products.**—Iron(III) chloride, 0.65 mmole, was treated with 2.16 mmoles of lithium borohydride in diethyl ether at room temperature. A white precipitate, probably lithium chloride, was immediately formed. This slowly was replaced by a black substance, which appeared to be the final product. After four hours, the reaction was complete, as indicated by the cessation of the production of hydrogen. The reaction mixture was allowed to stand overnight but only a small additional amount of hydrogen was obtained, the total being 3.04 mmoles or 4.7 moles per mole of iron(III) chloride.

In a second experiment, 1.80 mmoles of iron(III) chloride was treated with 5.34 mmoles of lithium borohydride and 7.95 mmoles (4.42 moles per mole of iron) of hydrogen was produced. The volatile products were fractionated and 20.6 cc. of diborane (identified by its vapor pressure, 223 mm. at −112°) was recovered from the ether, an amount equivalent to 0.51 mole per mole of iron(III) chloride taken. The quantities of hydrogen and diborane produced are in accord with equation 9.

**2. Reaction at −45°. The Volatile Products.**—Upon treating lithium borohydride and iron(III) chloride in the mole ratio of three to one in ether solution at −45° a white precipitate is formed, the brown coloration of iron(III) chloride is slowly discharged, and hydrogen and diborane are evolved. The reaction requires 15 to 20 hours for completion. At the completion of the reaction, the reactor was cooled with liquid nitrogen and the hydrogen removed and measured. The reaction products were filtered[19] at −80°, the volatile products were distilled (the residue being maintained at −45°) from the filtrate and separated by fractional condensation into ether and diborane. There was usually obtained from the filtrate a non-volatile white residue, but on several occasions this material was observed to have a blue to blue-green color as the ether solution was concentrated, becoming white as the last trace of ether was removed.

It was difficult to remove all the solvent ether from the non-volatile reaction products at the low temperature necessarily employed (to avoid decomposition of the product) and some diborane always remained in the viscous solution. The difficulty was circumvented by returning fresh ether to the reactor and again distilling from the residue at −45°. After several repetitions of this process no additional diborane could be removed. The data obtained in this step of the reaction are summarized in Table II and equation 10.

TABLE II

REACTION OF IRON(III) CHLORIDE AND LITHIUM BOROHYDRIDE AT −45°

| Expt. | $FeCl_3$, mmoles | $LiBH_4$, mmoles | $H_2$, mmoles | $H_2$/ $FeCl_3$ | $B_2H_6$, mmoles | $B_2H_6$/ $FeCl_3$ |
|---|---|---|---|---|---|---|
| 1 | 1.75 | 5.27 | 0.87 | 0.50 | 0.86 | 0.49 |
| 2 | 1.52 | 4.66 | 0.76 | .50 | 0.74 | .49 |
| 3 | 2.43 | 4.96 | 1.21 | .50 | 1.01 | .42 |
| 4 | 1.85 | 8.05 | 1.50 | .81 | 0.74 | .40 |

In experiment 3, the ratio of lithium borohydride to iron(III) chloride was two instead of three. The reaction was much slower; the time required for the evolution of the hydrogen was 48 hours and, as indicated in the table, only 83% of the expected diborane was obtained, which indicates that the reaction had not actually gone to completion.

In experiment 4, an excess of lithium borohydride was employed, the volume of hydrogen was greater than that expected, while the diborane obtained was less than the anticipated amount. Several reactions may be postulated to explain this low diborane and high hydrogen but the ratio of the diborane deficiency (0.18) to the hydrogen excess (0.58) is just that required by equation 13. It should be noted, however, that the hydrogen content of the hydrogen–diborane mixture still bears the relation of four atoms of hydrogen to one atom of iron(III) chloride and it is probable that reaction involving reduction of iron below iron(II) is responsible for the observation.

**3. Isolation and Decomposition of** Iron(II) **Borohydride.**—If the previously described operations were carried out carefully, a white to tan residue remained in the reaction flask. Part of this residue was ether soluble, and by careful manipulation at −45° it was possible to separate the non-volatile reaction products into an ether soluble fraction and an ether-insoluble fraction. The ether-insoluble fraction contained all of the chloride and none of the iron or boron, except those small amounts which resulted from the inadvertent decomposition of the ether-soluble products.

The residue obtained by evaporation of the filtrate decomposes upon raising the temperature between −10 and 0°. Hydrogen and diborane are liberated and a black, highly pyrophoric residue, quite like that obtained in the room temperature reaction described above, remains. The volatile products were measured and the residue was taken up in water and analyzed for iron and boron. The data are displayed in Table III. The ratio of iron to boron to hydrogen obtained from these analyses is exactly that expected for iron(II) borohydride, and serves to establish the formula of that substance to verify equations 11 and 12. It should be noted that the reaction of the residue remaining after the decomposition with water resulted in conversion of the boron to boric acid, leaving all the iron as the element.

TABLE III

DECOMPOSITION OF IRON(II) BOROHYDRIDE

| Fe in solid, mmole | $H_2$, mmole | $B_2H_6$, mmole | B in solid, mmole | Total H, mmole | Total B, mmole | Ratio Fe:B:H |
|---|---|---|---|---|---|---|
| 1.40 | 4.55 | 0.29 | 2.15 | 10.8 | 2.73 | 1:1.94:7.72 |
| 1.23 | 3.18 | .38 | 1.74 | 8.64 | 2.50 | 1:2.04:7.02 |
| 0.63 | 1.53 | .20 | 0.88 | 2.24 | 1.28 | 1:2.00:6.68 |

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(19) Details of the experimental procedure are found in reference 6.

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ST. LOUIS 4, MISSOURI

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[CONTRIBUTION FROM THE RICHARD BENBRIDGE WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

# The Effect of the Solvent on the Polarographic Reduction of Cations[1]

BY DOUGLAS B. BRUSS AND THOMAS DE VRIES

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The effect of the solvent on the reduction of metal ions was investigated at a dropping mercury electrode with a silver-silver chloride electrode as reference. Nine cations were studied in water, ethylene glycol, formamide, dimethylformamide, pyridine, the normal alcohols through pentanol and isopropyl alcohol. The half-wave potentials were found to vary in a regular manner with the dielectric constant of the solvent, usually becoming more positive as the dielectric constant decreased. A correlation was found between the shift in half-wave potential per dielectric constant unit and the quotient of the magnetic susceptibility of the ion divided by the ionic radius. The variation of the diffusion current with the square root of the fluidity of the solvent demonstrated that, for the majority of the ions, viscosity was not the only factor affecting the diffusion coefficients.

The increasing importance and use of organic and other non-aqueous solvents in polarography has led to the need of a greater clarification of the factors affecting the reduction characteristics in such media. Hence, the principal objective in this investigation was the study of cations in organic solvents selected with a wide range of dielectric constants. There was definite correlation between the variation of the half-wave potential and the dielectric constant. The variation of the diffusion current with the viscosity of the media was related to the solvation of the ions.

A variety of organic solvents have been used by previous investigators in the polarographic reduction of selected cations. A study of the alkali metal ions was made by Peracchio and Meloche[2] in water solutions of hydroxy compounds such as methanol and trimethylene glycol. Zlotowski and Kolthoff[3] investigated the reduction of some alkali ions in 50 to 80% ethanol. The fact that they found the half-wave potentials constant with drop-time indicated that the reductions were reversible. Matyas[4] studied the variation of half-wave potential of bivalent metal ions in a variety of alcohols. He attributed a shift to more negative potentials because of the adsorption of the solvent on the mercury drops while a shift to more positive potentials in methanol and ethanol indicated that these are not adsorbed. Univalent ions were not affected. The influence of the viscosity of the solvent on the magnitude of the diffusion currents has been studied in water-ethylene glycol media,[5] in water-ethanol mixtures[6] and other non-aqueous solvents,[7] and apparently the viscosity of the solvent was not the only factor which affected the diffusion current.

## Experimental

**Reagents.**—The organic solvents were dried over the appropriate drying agents such as metallic sodium or calcium hydride and distilled or fractionated in all glass systems equipped with drying tubes. However, it was soon found that the addition of up to 1% water did not appreciably affect the reduction characteristics. The solvents which were selected because of their wide range in dielectric constants are listed in Table I together with their properties. The viscosities there given were determined with Fenske-type glass viscometers for 0.2 *M* LiCl solutions.

All of the metal salts used were chlorides and were reagent grade. The anhydrous chlorides of bismuth, iron(II), lead and zinc were available and were used as such. The hydrated chloride of cadmium was rendered anhydrous by heating at 110°. Chromic chloride hexahydrate was obtained as a special preparation in the department. Cobaltous chloride hexahydrate, cupric chloride dihydrate and manganous chloride tetrahydrate were used as such. Nickel chloride hexahydrate was heated under reduced pressure to constant weight. The lithium chloride for the supporting electrolyte was oven dried at 110° for 24 hours.

The most suitable maximum suppressor was ethyl cellulose, but methyl red and gelatin were also used when water was the solvent.

**Apparatus.**—A silver-silver chloride electrode was used as anode, thus avoiding complications from liquid boundary potentials. It was prepared from 8 cm. of No. 22 platinum wire, wound into a tight spiral, which was then silver plated and anodized.[8] The same capillary was used for the dropping mercury electrode throughout this investigation. In a 0.2 *M* solution of LiCl in water on open circuit it had a drop time of 3.77 seconds and a capillary constant of 2.00 mg.$^{2/3}$ sec.$^{-1/2}$.

A Leeds and Northrup Type E Electrochemograph was used to record the polarograms. A Rubicon potentiometer was used to check the half-wave potentials to one millivolt. The cell resistances which are listed in Table I were determined for 0.2 *M* LiCl solutions at 1000 cycles using a General Radio Co. Amplifier and Null Detector in a conventional

TABLE I

SOLVENTS USED AND THEIR PROPERTIES

| | | Dielectric constant | Viscosity, poise | Fluidity$^{1/2}$ | Cell resistance |
|---|---|---|---|---|---|
| 1 | Formamide | 109.5 | 0.03532 | 5.33 | 510 |
| 2 | Water | 78.5 | .00917 | 10.44 | 170 |
| 3 | Ethylene glycol | 37.7 | .1854 | 2.32 | 2,300 |
| 4 | Dimethylformamide | 36.7 | .00931 | 10.38 | 3,000 |
| 5 | Methanol | 31.5 | .00626 | 12.62 | 350 |
| 6 | Ethanol | 24.3 | .01333 | 8.66 | 1,050 |
| 7 | Propanol | 20.1 | .02478 | 6.36 | 2,200 |
| 8 | Isopropyl alc | 18.0 | .02624 | 6.19 | 6,400 |
| 9 | Butanol | 18.0 | .03304 | 5.77 | 7,200 |
| 10 | Pentanol | 15.8 | .04370 | 4.79 | 20,000 |

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(1) Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, February, 1955. From the Ph.D. thesis of D. B. Bruss, Purdue University, June, 1954.

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(3) I. Zlotowski and I. M. Kolthoff, *ibid.*, **64**, 1297 (1942).

(4) M. Matyas, *Chem. Listy*, **46**, 65 (1952).

(5) C. H. R. Gentry, *Nature*, **157**, 479 (1946).

(6) G. Matsuyama, Ph.D. Thesis, University of Minnesota, 1948.

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(8) A. S. Brown, THIS JOURNAL, **56**, 646 (1934).