Composition of Complex Aluminum Hydrides and Borohydrides, as Inferred from Conductance, Molecular Association, and Spectroscopic Studies

E. C. Ashby,*[1a] Frank R. Dobbs,[1a] and Harry P. Hopkins, Jr.[1b]

Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, and the Department of Chemistry, Georgia State University, Atlanta, Georgia 30303. *Received September 7, 1972*

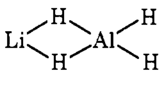
Abstract: The equivalent conductance of THF solutions of $LiAlH_4$, $NaAlH_4$, Bu_4NAlH_4, and $LiBH_4$ were obtained over a wide concentration range, *i.e.*, 0.5 to 1×10^{-7} *M*. The data are consistent with the presence of free ions and ion pairs in dilute solution and the formation of triple ions as the concentration is increased. The application of the Fuoss treatment to the data, where only free ions and ion pairs are encountered, permits the evaluation of the infinite dilution equivalent conductance (Λ_0) and the ion-pair dissociation constant (K_a) for each hydride. Utilizing a sphere in a continuum model, the center-to-center distances between the ions in the ion pair calculated from the experimental K_a values indicate that the ion pairs of Bu_4NAlH_4 and $LiBH_4$ are in intimate contact, whereas the $LiAlH_4$ and $NaAlH_4$ species are solvent-separated ion pairs. Thermodynamic parameters also suggest that $LiAlH_4$ ion pairs are predominantly solvent separated, whereas a substantial fraction of the $NaAlH_4$ ion pairs are are in intimate contact at 25°. The Λ_0 values obtained for these hydrides also support these conclusions. In the region where ion pairs and triple ions are encountered, the triple ion dissociation constants (K_t) have been evaluated from the data using the Fuoss method. Combining the K_a and K_t values, the fraction of each species present at any concentration below 0.1 *M* has been calculated. When these data are used to calculate association *i* values, good agreement is found between the observed ebullioscopic *i* values and those calculated from the conductance results. Nmr studies indicate the formation of a 4:1 THF solvate with $LiAlH_4$, LiI, and $LiClO_4$ and the formation of a 2:1 THF solvent with $LiBH_4$. Similar studies show no interaction for Bu_4NAlH_4. The appearance of infrared bands near 420 cm^{-1} (attributed to the vibration of the lithium ion in a solvent cage) are found for $LiAlH_4$, $LiClO_4$, LiI, and LiBr, but well-defined bands are absent for $LiBH_4$ in THF.

Since the discovery of lithium aluminum hydride and lithium borohydride by Schlesinger[2] and coworkers, thousands of reports[3] concerning the use of these compounds as reducing agents in organic synthesis have appeared in the literature. The availability of these ether-soluble reducing reagents has provided the organic chemist with a means of performing selective reductions on organic substrates, which prior to this time were not possible. Although there has been considerable mechanistic speculation concerning the mechanism of complex metal hydride reduction of organic substrates, definitive mechanistic studies in this area are sparse indeed. The major obstacle to exact mechanistic descriptions of complex metal hydride reductions has been the lack of precise information concerning the exact nature of the solute species describing complex metal hydrides in ether solvents. Thus, in spite of the fact that reduction of ketones and other organic functional compounds by $LiAlH_4$ represents one of the most fundamental reactions in all of organic chemistry, it has been impossible to describe the mechanism of these reactions with any degree of certainty. Consequently, it appears that information concerning the nature of the solute species present in ether solutions of complex metal hydrides, such as $LiAlH_4$, is crucial before a precise description of the mechanism of these reductions can be described.

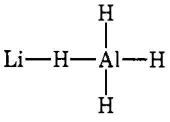
The crystal structures[4] of $LiAlH_4$ and $LiBH_4$ have been determined from X-ray studies, and the tetrahedral symmetry[5] of the AlH_4^- and BH_4^- is well established. In solution, the presence of ionic species (I) or covalent species (II, III) has not been definitely established, even though both types have been proposed to exist in diethyl ether and THF. Previous molecular weight and conductance studies have suggested that some form of association of the solute occurs in solution. Wiberg and Graf[6] performed crude molecular weight measurements on $LiAlH_4$ in diethyl ether and found that the solute was extensively associated. Extensive association of $LiBH_4$ was also observed in diethyl ether by Nöth.[7] It has been proposed that the observed association of $LiAlH_4$ is due to the formation of hydrogen bridge species (IV).

$Li^+AlH_4^-$

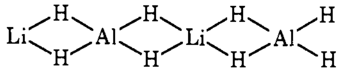
I



II



III



IV

Four Raman and two infrared bands were observed by Lippincott[8] for $LiAlH_4$ in diethyl ether. The coincidence of the infrared bands with the Raman bands is consistent with the tetrahedral model for the AlH_4^-

---

(1) (a) Georgia Institute of Technology; (b) Georgia State University.

(2) A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 1199 (1947).

(3) N. G. Gaylord, "Reductions with Complex Metal Hydrides," Interscience, New York, N. Y., 1956.

(4) (a) N. Sklar and B. Post, *Inorg. Chem.*, **6**, 669 (1967); (b) S. Abrahams and J. Kalnojs, *J. Chem. Phys.*, **22**, 434 (1954).

(5) K. Nakamota, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

(6) E. Wiberg and H. Graf, diploma work of H. Graf, University of Munich, 1953.

(7) H. Nöth, *Angew. Chem.*, **73**, 371 (1961).

(8) E. R. Lippincott, *J. Chem. Phys.*, **17**, 1351 (1949).

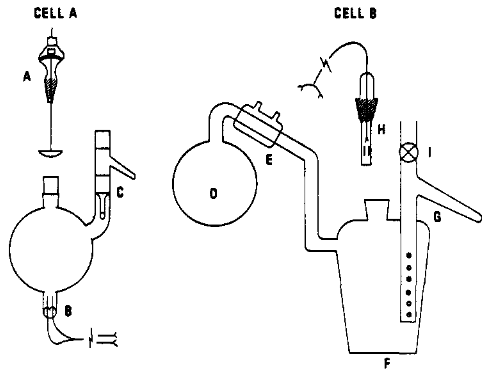


Figure 1. Description of conductance cells A and B.

ion in solution. This conclusion has also been substantiated by the infrared studies of D'Or and Fuger.[9] A similar conclusion was arrived at by Haraguchi and Fujiwara,[10] who observed that the ^{27}Al chemical shift and line width for $LiAlH_4$ in diethyl ether was similar to other aluminum compounds known to possess tetrahedral symmetry.

A distorted tetrahedral symmetry for the AlH_4^- ion has been suggested by several other investigators.[11,12] A shift to lower frequency is observed for the Al-H stretching band of $LiAlH_4$ in diethyl ether (1740 cm^{-1}) and THF solutions (1698 cm^{-1}) compared with that found in the solid (1798 cm^{-1}). A shift is also found for the THF-benzene solutions of $LiAlH_4$ where the ratio of $LiAlH_4$ to THF is 3:1 (1724 cm^{-1}) and 8:1 (1674 cm^{-1}). The Al-H stretching frequency for $LiAlH_4$ in diethyl ether, on the other hand, is independent of concentration even though the association increases with increasing concentration.

Conductance data on solutions of complex metal hydrides are indeed meager owing to the extreme reactivity of the hydrides with trace amounts of water. The only available data are limited to concentrations above 0.05 *m*. The conductances of diethyl ether solutions of $LiAlH_4$ and $LiBH_4$ have been reported by several investigators[7,13-15] to be extremely independent of concentration, whereas the conductance of THF solutions of $LiAlH_4$, $NaAlH_4$, and $LiBH_4$ are reported[7,16] to be substantially larger and concentration dependent. It has been suggested that the conductance is due to the presence of ionic species in these solutions.

The limited association data support the concept of the hydrogen-bridged species (IV), whereas the spectral and conductance data suggest that the tetrahedral symmetry of the AlH_4^- ion is retained in solution, *i.e.*, ionic species (I). Before this question can be resolved and kinetic data unambiguously interpreted, the exact nature of the solute species present in solution must be determined. The studies reported here provide extensive conductance (0.5 to 1 × 10^{-7} *M*) and ebullioscopic data (0.05 *m* to 0.5 *m*) on lithium aluminum hydride, sodium aluminum hydride, tetrabutylammonium aluminum hydride, and lithium borohydride. From these data as well as data obtained from nmr and infrared studies, an exact description of the solution species present in THF solution has been developed.

Experimental Section

Conductance Measurements. The conductances of the solutions were measured on a Beckman Model RC-18A conductivity bridge, which has a reported accuracy of ±0.05% of the decade resistance reading over the range 500-50,000 ohms. A Sargent constant-temperature water bath (Model S-82055) was employed to regulate temperatures between 0 and 25°, using a thermometer calibrated against a NBS standard to determine the temperature of the solution to the nearest 0.02°. For temperatures below 0°, an isopropyl alcohol-carbon dioxide slush bath containing appropriate amounts of water was employed with an iron-constantan thermocouple (±1.0°) to determine the temperature of the bath.

A high-vacuum system was designed to obtain reproducible conductance data below 3 × 10^{-3} *M*, where it is essential to remove all traces of oxygen and water, if hydrolysis is to be avoided. Two types of cells were employed and are shown in Figure 1. Cell A consisted of a 1-l. flask with a (A) vacuum magnetic stirrer (Scientific Glass No. JS-3085, 24/40), a (B) Beckman conductivity cell (Model Cel-A001-Y87) sealed to the bottom, and a (C) side arm for storage and introduction of the hydride samples. This cell was attached to a standard high-vacuum system and flamed until the pressure was below 5 × 10^{-5} Torr. Sealed ampoules containing the hydrides were then moved from the side arm into the flask and broken by means of a Teflon-coated magnetic stirring bar. Known amounts of THF were transferred from a storage flask on the high-vacuum rack through a buret with a vacuum stopcock. The storage flask contained a saturated solution of $LiAlH_4$ in THF. With this arrangement, reproducible conductance data were obtained down to 5 × 10^{-5} *M* hydride.

In order to obtain data below 5 × 10^{-5} *M* it was necessary to employ cell B. This cell consisted of a storage bulb (D), a condenser (E), an oblong conductance flask (F) with calibration marks on the side for volume determinations, a side arm (G) for sample bulb storage and introduction, and a 24/40 joint to insert an unmodified Beckman conductivity cell (H) into the flask, and a Teflon high-vacuum stopcock (I). This cell was attached to the main vacuum system and the THF introduced by the method described earlier. After removing the cell from the vacuum system with stopcock I closed, a sample of hydride was introduced into the cell and allowed to react with any water present. When the conductance was constant, this solution was poured into the storage bulb (D) and THF distilled back into the cell to wash out any remaining hydride. This solution was poured back into bulb D and the distillation repeated. When the conductance of the distilled THF was 0.4 × 10^{-6} mhos or less, a new sample bulb was broken. To obtain lower concentrations, an appropriate amount of solution was poured into bulb D and pure THF distilled back into the cell to effect the desired dilution. With this procedure conductance data were obtained on each hydride down to 2 × 10^{-7} *M*. Even with this procedure it was difficult to determine accurately the conductance of the solutions of $LiAlH_4$ below 1 × 10^{-6} *M*.

The cell constants for both cells A and B were determined from the measured conductivity of a 0.01 demal KCl solution.[17] The constants are 0.00958 ± 0.00001 cm^{-1} for both cells A and B. In order to check the entire apparatus, the conductances of aqueous acetic acid solutions were measured between 10^{-5} and 10^{-4} *M* and found to agree within 0.1% of the published data.[18]

Concentrated solutions of $LiAlH_4$, $NaAlH_4$, and $LiBH_4$, in THF were prepared from commerically available materials. The THF was distilled from $LiAlH_4$ under a nitrogen atmosphere. The solutions were filtered in a drybox[19,20] in order to remove excess solids and stored in a flask in the drybox. Analyses for lithium and sodium by flame emission, aluminum by EDTA titra-

---

[9] L. D'Or and J. Fuger, *Bull. Soc. Roy. Sci. Liege.*, **25**, 14 (1956).

[10] H. Haraguchi and S. Fujiwara, *J. Phys. Chem.*, 73, 3467 (1969).

[11] R. Dautel and W. Zeil, *Z. Elektrochem.*, **64**, 1234 (1960).

[12] R. Ehrlich, A. Young, G. Rice, J. Dvorak, P. Shapiro, and H. F. Smith, *J. Amer. Chem. Soc.*, **88**, 858 (1966).

[13] M. F. Paddock, *Nature (London)*, **167**, 1070 (1951).

[14] G. G. Evans, J. K. Kennedy, and F. P. DeGeco, *J. Inorg. Nucl. Chem.*, 4, 40 (1957).

[15] G. Jarder and K. Draffezyth, *Z. Anorg. Allg. Chem.*, **283**, 27 (1956).

[16] N. M. Alpatova, T. N. Dymava, Y. M. Kessler, and O. R. Osepov, *Russ. Chem. Rev.*, 37, 99 (1968).

[17] G. Jones and B. Bradshaw, *J. Amer. Chem. Soc.*, **55**, 1780 (1933).

[18] D. M. Maciner and T. J. Shedlovsky, *ibid.*, **54**, 1429 (1932).

[19] T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instrum.*, 33, 491 (1962).

[20] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

tion, and hydrogen by gas measurement techniques were used to determine the concentrations of the stock solutions. These solutions were used to prepare samples of the hydrides in sealed ampoules for the conductance measurements. A 10–500-mg sample of an approximately 1.0 *M* stock solution was transferred by means of a syringe in the drybox to an ampoule sealed to a 10/18 joint. The exact weight of the sample was determined by difference. After the second weighing of the ampoule and joint, the lower portion of the ampoule was immersed in liquid nitrogen and the ampoule sealed and removed from the joint with a torch.

The benzene and THF solutions of tetrabutylammonium aluminum hydride (Bu_4NAlH_4) were prepared according to the procedure of Ehrlich and coworkers.[21] Analysis for aluminum and bromine showed that the formation of the hydride from Bu_4NBr was complete in less than 5 days. The residual concentration of bromine was less than 0.5%. For the conductance measurements the Bu_4NAlH_4 samples were prepared in sealed ampoules.

Ebullioscopic Measurements. A detailed description of the apparatus and procedure for the ebullioscopic determination of apparent molecular weights is described elsewhere.[22] The measurements were performed in THF and diethyl ether at a pressure of 740 Torr.

Spectral Measurements. A Varian Model A-60A, 60-Hz, nuclear magnetic resonance spectrometer was used for recording all spectra. Tetramethylsilane was used as an internal standard for all measurements. Frequencies were measured by the side band technique with a Hewlett-Packard oscillator (Model 2000D) and frequency counter (Model 5512A) and were reproducible to within ±0.2 Hz. Solutions were prepared in a drybox or on a bench top using Schlenk-type techniques,[20] and spectra were run immediately after preparation of the solutions.

A Beckman IR-12 spectrometer and potassium bromide matched cells (0.5 mm) were used for recording of the infrared spectra.

Calculations. All pertinent calculations were performed on the RCA Spectra-70 computer.

Results

Conductance. When free ions are present in equilibrium with ion pairs and triple ions, Fuoss[23] has shown that the equivalent conductance of the solution is adequately represented by eq 1 or 2, where K_a is the

$$\Lambda = \Lambda_0/(K_aC)^{1/2} + \lambda_0C^{1/2}/K_t(K_a)^{1/2} \tag{1}$$

$$\Lambda = AC^{-1/2} + BC^{1/2} \tag{2}$$

ion pair dissociation constant, Λ_0 is the limiting equivalent conductance, λ_0 is the limiting equivalent conductance of the triple ion, *C* is the molar concentration of the solute, and K_t is the triple ion dissociation constant. Consequently, a plot of log Λ *vs.* log *C* should be linear with a slope of −0.5, if only ion pairs are present in the dilute solution region. The equivalent conductances of the THF solutions of the hydrides studied are presented in Table I. For each hydride studied a concentration was found below which the log Λ *vs.* log *C* plot was linear with a slope of approximately −0.5. These data are listed in the left-hand column below each hydride in Table I. The Fuoss conductance equation (eq 3), which describes the equivalent conductance of

$$F/\Lambda = 1/\Lambda_0 + \gamma_\pm{}^2C\Lambda/FK_a\Lambda_0{}^2 \tag{3}$$

ionic solutions when only ion pairs and free ions are present, was applied to the data in the left-hand columns for each hydride. An initial approximation of Λ_0 was made from the literature values of λ_0^+ for the cation and λ_0^- for chloride, and an iterative procedure was employed to give the best least-squares fit of the data to eq 3.

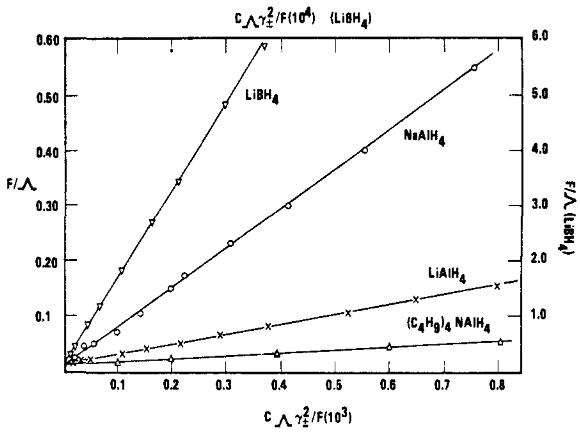


Figure 2. Fuoss plots for $LiAlH_4$, $NaAlH_4$, $LiBH_4$, and Bu_4NAlH_4 in THF at 25°. The coordinates for $LiBH_4$ are above and to the right.

Table I. Equivalent Conductances of Complex Metal Hydrides in THF at 25°

Concn, 10^6 *M*	Λ	Concn, 10^4 *M*	Λ	Concn, 10^6 *M*	Λ	Concn, 10^4 *M*	Λ
	LiAlH$_4$				NaAlH$_4$		
						7.37	1.53
0.157	71.6	4.90	3.68	0.174	64.4	11.5	1.19
0.320	57.5	7.11	3.54	0.523	49.5	24.9	0.85
1.02	44.2	7.91	3.37	2.14	21.3	39.5	0.68
4.16	31.3	8.90	3.22	3.70	19.7	73.9	0.45
6.05	24.9	10.2	3.03	5.76	13.0	98.2	0.41
9.96	23.0	11.9	2.82	10.0	12.5	122	0.44
12.1	20.3	14.2	2.63	17.9	8.72	146	0.46
16.4	16.0	17.8	2.39	25.0	8.31	169	0.47
34.8	12.6	21.1	2.22	30.2	7.69	192	0.48
66.2	9.09	24.9	2.07	31.9	7.03	215	0.49
71.0	8.93	30.0	1.94	43.5	5.81	248	0.52
81.7	8.37	35.6	1.82	78.9	4.13	253	0.54
93.0	7.86	43.8	1.69	80.9	4.03	279	0.57
112.0	7.27	51.8	1.59	133	3.41	316	0.59
135.0	6.91	63.3	1.51	139	3.29	364	0.61
169.0	6.01	81.4	1.43	156	3.13	431	0.64
193	5.69	114	1.26	211	2.69	526	0.70
225	5.27	229	1.27	227	2.59	611	0.74
257	4.97	263	1.29	290	2.35	729	0.82
300	4.63	305	1.35	383	1.98	861	0.90
346	4.31	338	1.36	550	1.71		
416	3.94	397	1.42				
	LiBH$_4$				Bu$_4$NAlH$_4$		
0.25	4.98	7.50	0.082	0.13	81.1	7.5	5.49
1.00	2.49	8.39	0.069	0.52	66.3	8.75	5.11
2.06	1.66	8.95	0.053	1.97	59.4	10.0	4.75
2.25	1.49	9.18	0.039	5.06	43.6	25.0	4.29
2.77	1.39	10.1	0.038	11.1	32.5	50.0	4.00
4.09	1.24	15.0	0.029	25.0	25.5	62.5	3.83
9.14	0.83	24.8	0.026	56.3	17.5	75.0	3.70
20.7	0.55	39.3	0.023	121.1	12.2	87.0	3.60
50.4	0.36	58.2	0.022	260	8.65	100	3.50
77.8	0.29	80.1	0.016	634	5.92	235	3.30
143	0.21	192	0.017				
222	0.16	287	0.019				
420	0.12	546	0.024				
648	0.10	658	0.027				
		762	0.029				
		998					

The values obtained in the last iteration are plotted in Figure 2 as *F*/Λ *vs.* $C\Lambda\gamma_\pm{}^2/F$. From the intercept and slope determined from the least-squares calculations, Λ_0 and K_a were evaluated. The Λ_0 and K_a values extracted in this manner from the conductance data are tabulated in Table II. Considerable uncertainty exists

---

[21] R. Erhlich, A. Young, and D. Perry, *Inorg. Chem.*, 4, 758 (1965).

[22] F. W. Walker and E. C. Ashby, *J. Chem. Educ.*, 45, 654 (1968).

[23] R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience, New York, N. Y., 1959.

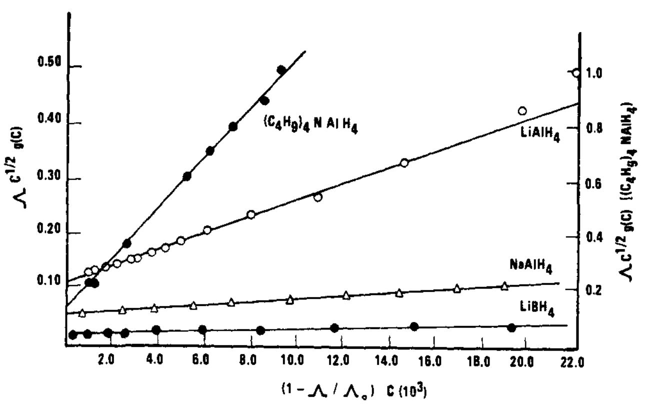


Figure 3. A plot of the data in the region of the minimum as $\Lambda C^{1/2}g(C)$ *vs.* $(1 - \Lambda/\Lambda_0)C$ for $LiAlH_4$, $NaAlH_4$, Bu_4NAlH_4, and $LiBH_4$ in THF at 25°.

Table II. Limiting Conductances and Equilibrium Constants for Dissociation of Complex Metal Hydrides in Tetrahydrofuran at 25°

Compound	Λ_0	K_a	K_t[a]
$LiAlH_4$	90	0.69×10^{-6}	1.77×10^{-3}
$NaAlH_4$	81	0.21×10^{-6}	3.76×10^{-3}
Bu_4NAlH_4	97	0.18×10^{-5}	1.40×10^{-3}
$LiBH_4$[b]	80	1.0×10^{-9}	8.15×10^{-3}

[a] The Fuoss treatment employed for the determination of K_t from conductance data assumes that the formation constants for the two types of triple ions are equal. [b] Since the conductances of $LiBH_4$ solutions are low even at 10^{-7} *M*, the values obtained for this salt are not as reliable as the other K_a's in the table.

for the intercepts and thus the Λ_0 and K_a values are uncertain by at least ±10%. However, Szwarc[24] and coworkers have shown that the λ_0^+ values for Li^+, Na^+, and Bu_4N^+ are approximately the same in THF; therefore, the Λ_0 values of the aluminum hydride salts studied here should be approximately the same. Since this is observed for all the salts studied, these results are consistent with previous investigations.

When the plots of log Λ *vs.* log *C* are no longer linear, higher aggregates such as triple ions probably begin to form. Fuoss[23] has developed eq 4 to describe the

$$\Lambda C^{1/2}g(C) = \Lambda_0 K_a + (\lambda_0 K_a^{1/2}/K_t)(1 - \Lambda/\Lambda_0)C \quad (4)$$

equivalent conductance of ionic solutions when triple ion aggregates and ion pairs are encountered. From this equation the triple ion dissociation constant, K_t, can be estimated.

The data for each salt studied have been fitted to eq 4 in the concentration region where both triple ions and ion pairs are encountered (right-hand column of data for each salt in Table I). In Figure 3, $\Lambda C^{1/2}g(C)$ *vs.* $(1 - \Lambda/\Lambda_0)C$ is plotted for each salt. Since the plots are all straight lines with a correlation coefficient of at least 0.99, it appears that eq 4 adequately describes the data and that triple ions are forming in the solutions of all the salts studied.

In order to calculate K_t from the slope of the line, a value of λ_0 is needed. An approximate value[23] for this quantity is taken to be $^1/_3$ of Λ_0 because the triple ion is a cluster of three ions. The K_t values determined in this manner are listed in Table II. For all the hydrides, except $LiBH_4$, the K_t's are nearly equal.

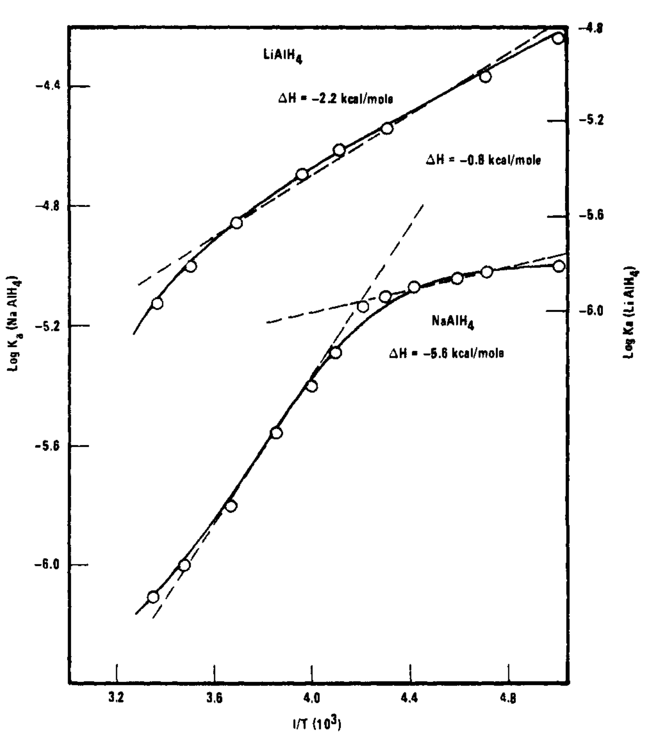


Figure 4. A plot of log K_a *vs.* $1/T$ for $LiAlH_4$ and $NaAlH_4$ in THF.

A minimum is observed in the equivalent conductance values for all the salts studied. Above the minimum the data show a positive deviation from eq 4. As the concentration is increased the conductance value for all the salts increases to a maximum at about 1 *M*.

Temperature-dependence studies were performed on a separate set of $LiAlH_4$ and $NaAlH_4$ solutions between 25 and −70°. The Fuoss equations were applied to the data to obtain a consistent set of K_a and K_t values at each temperature. The values of the density, viscosity, and dielectric constant for THF needed to apply the Fuoss equation to the data were obtained from the work of Hogen-Esch and Smid.[25] A plot of log K_a *vs.* $1/T$ for both salts is shown in Figure 4. The points for $LiAlH_4$ can be fitted to a straight line and the enthalpy of dissociation is estimated to be −2.20 kcal/mol. In the plot for $NaAlH_4$, considerable curvature is observed but the curve can be resolved into two component lines giving $\Delta H°$ values of −0.6 and −5.6 kcal/mol. The variations found for the K_t values were approximately zero indicating that the enthalpy of dissociation for the triple ions is small but slightly exothermic.

Ebullioscopic. The apparent molecular weights of the complex metal hydrides in THF were determined near the boiling point of the solvent between 0.05 and 0.6 *m*. The observed *i* values defined as the ratio of the apparent molecular weight to the formula weight are plotted *vs.* the concentration in Figure 5. Over the entire range of concentrations studied the lithium and sodium salts have nearly identical *i* values. At 0.05 *m* concentration an *i* value of approximately 1.0 is predicted from the conductance results, which

---

(24) D. N. Bhattacharyra, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).

(25) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 318 (1966).

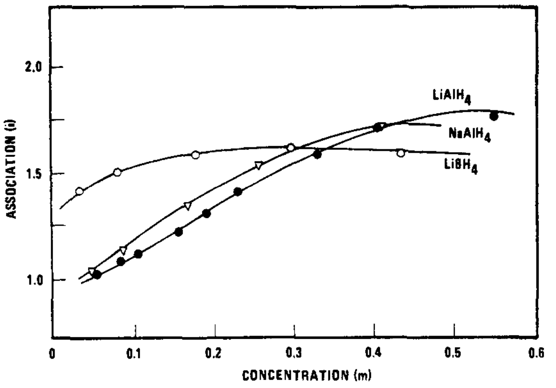


Figure 5. The association of $LiAlH_4$, $NaAlH_4$, and $LiBH_4$ in THF.

is in good agreement with the observed values. At higher concentrations the conductance data indicate that triple ions are the predominant species in solution; *i.e.*, the *i* values should approach a limiting value of 1.5. For $LiBH_4$, the conductance results show that this salt is considerably more associated than the other salts studied and the calculated *i* value from the conductance data is 1.0 at 0.05 *m*. Since the conductance and ebullioscopic results are consistent at 0.05 *m*, it is unlikely that any species other than ion pairs and triple ions are present at this concentration. However, activity coefficients have been taken into account only in the conductance data calculations and predicted *i* values. Since it is impossible at this time to correct the ebullioscopic results above 0.1 *m* for activity coefficients, higher aggregates cannot be completely ruled out as a possibility above 0.1 *m*.

Nmr Studies. The chemical shift of the α-methylene hydrogens of THF was monitered as a function of the mole ratio of THF to lithium salt dissolved in diethyl ether (Figure 6). In the absence of salt, the chemical shift of THF remained constant at 218.5 Hz over the range of concentration of THF in diethyl ether used in this study. In the presence of $LiAlH_4$, a change in the chemical shift of the α-methylene protons of THF was observed, while the chemical shifts due to the hydrogens of diethyl ether remained constant. The chemical shift decreased as the mole ratio of THF to salt increased until the chemical shift approached that value found in pure THF. At a mole ratio of THF to $LiAlH_4$ of 4:1, a change in the slope was observed indicating the existence of a stable four-coordinate species, *i.e.*, $LiAlH_4 \cdot 4THF$ (Figure 7). A similar result was obtained for lithium perchlorate and iodide. However, the tetrabutylammonium aluminum hydride salt did not cause a chemical shift of the α-methylene hydrogens of THF. Consequently, the chemical shift changes observed for $LiAlH_4$ must be attributed to solvation at the lithium ion exclusively. A similar experiment for $LiBH_4$ in THF–diethyl ether mixtures did not show a break at a mole ratio of THF to lithium of 4:1, as was found with $LiAlH_4$, but rather a plateau at a mole ratio of 2:1 with a gradual change in chemical shift thereafter. Apparently, there is less specific solvation of the lithium ion by THF. This is consistent with the low conductance and higher association values found for $LiBH_4$ in THF. The most reasonable explanation for these results is to view the lithium ion in THF as specifically solvated by four moles of THF which are tightly bound to the lithium ion. $NaAlH_4$ does not have appreciable solubility in diethyl ether; therefore, it was impossible to perform corresponding experiments on sodium salts. Previous workers have performed similar experiments with lithium salts in ace-

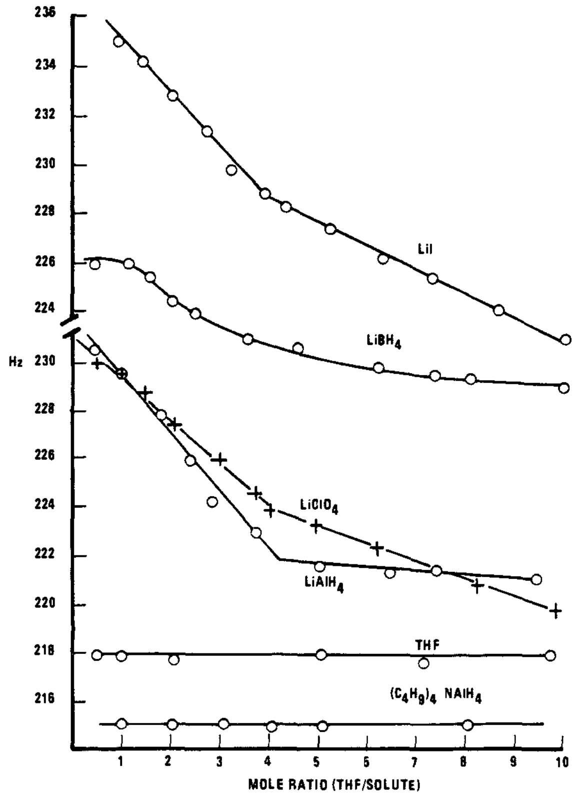


Figure 6. Chemical shifts of the α-methylene protons of THF plotted as a function of the mole ratio of added THF to salt.

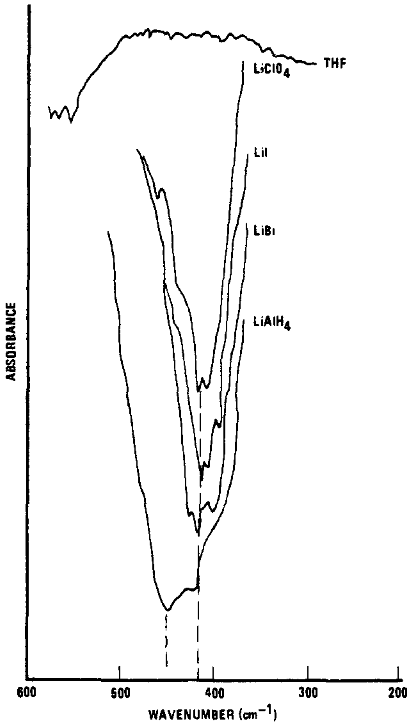


Figure 7. Infrared spectra of several lithium salts in THF.

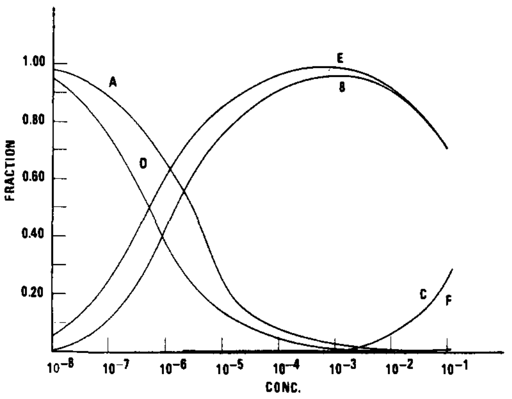


Figure 8. The fraction of hydride present as free ions, ion pairs, or triple ions for $LiAlH_4$ and $NaAlH_4$. Curves A, B, and C represent these fractions for $LiAlH_4$, whereas curves D, E, and F correspond to $NaAlH_4$.

tone–nitromethane mixtures,[26] dimethylformamide–dioxane mixtures,[27] and 2-pyridine–dioxane mixtures.[28] In each case, the carbonyl oxygen formed a four-to-one solvate with the lithium ion. Apparently, four ligands are the maximum number which can be placed in the first coordination sphere of the lithium ion.

Infrared Spectra. New absorption bands appear in the infrared spectra of the THF solutions (0.1 *M*) of $LiClO_4$, LiI, LiBr, and $LiAlH_4$ near 420 cm^{-1}, which are not present in pure THF. These spectra are shown in Figure 7. Two closely spaced absorptions are evident for $LiClO_4$, LiI, and LiBr near 420 cm^{-1}. $LiAlH_4$ has a much broader absorption in this region with three peaks clearly evident. The most intense band occurs at 450 cm^{-1} for $LiAlH_4$, but the two bands near 420 cm^{-1} are also present in solutions containing this salt. Previous workers[29] have found similar bands for LiI, LiBr, and LiCl in THF at 373, 378, and 387 cm^{-1}, respectively, which have been attributed to a vibration of the lithium ion in its solvent cage. The new bands that appear in this study can also be attributed to a vibration of the lithium ion against the four THF molecules that are specifically solvated, which is consistent with the nmr results. Extreme care was taken to remove trace quantities of water and the concentrations of the salts are much larger than the estimated concentration of water (0.001 *M*). In the case of $LiAlH_4$ solutions, it is unlikely that any water is present. Two of the bands found in $LiAlH_4$ agree with those for the other salts. Consequently, it is possible that the 50-cm^{-1} difference between the results shown in Figure 7 and the results of the previous workers is mainly due to their solutions containing appreciable quantities of water. This conclusion is further substantiated by the work of Dautel and Zeil[11] who report bands for $LiAlH_4$ in THF at 426 and 416 cm^{-1}. The higher frequency band at 450 cm^{-1}, observed only for $LiAlH_4$, is possibly due to the interaction of the AlH_4^- hydrogens with the oxygens of the THF solvate molecules. At 0.5 *M* the spectrum of $LiAlH_4$ in THF consists of two bands of approximately equal intensity at 455 and 440 cm^{-1} with a shoulder near 420 cm^{-1}. The conductance and ebullioscopic results indicate that the major species present at 0.1 and 0.5 *M* changes from an ion pair to a triple ion and it is not surprising that spectral changes accompany this transformation.

Spectral studies were also performed on THF solutions containing lithium salts of the bromide and perchlorate with acetone and benzophenone present at various mole ratios with respect to the lithium salt. As the ratio of the lithium salt to the carbonyl compound increased, the carbonyl band of both acetone and benzophenone shifted to lower wave numbers. At a ratio of 14:1 and a carbonyl compound concentration of 0.02 *M*, the shift reached a maximum of 7 cm^{-1}. This indicates that the THF solvate molecules can readily be replaced in the coordination sphere by carbonyl compounds.

Discussion

The results of the conductance studies on the complex metal hydrides indicate the presence of free ions and ion pairs in dilute solution, whereas at higher concentrations the data indicate the formation of triple ions. From K_a and K_t values derived from the conductance data, the fraction of each species present at a particular concentration can be calculated from the equilibrium expressions, the mass balance requirement, and the extended Debye–Hückel relationship for the activity coefficients of the ions. This has been done for the region below 0.1 *M* for $LiAlH_4$ and $NaAlH_4$ with the results plotted in Figure 8 as smooth curves representing the fraction of each species present *vs.* the concentration of the hydride. From these values an *i* value is obtained for each hydride that agrees within experimental error with those found in the ebullioscopic experiments at 0.05 *m*.

The simplest model of an electrolyte solution assumes the ions to be charged spheres, with radii equal to that found in the crystal, distributed in a solvent continuum characterized by the macroscopic dielectric constant and viscosity. Using this model, Fuoss[23] demonstrated that K_a for ion pairs is best represented by eq 5, where

$$K_a = (3000/4\pi N r^3)\exp(-e^2/rDkT) \qquad (5)$$

D is the macroscopic dielectric constant, *r* is the center-to-center distance between the ions, and the remaining symbols have their usual meaning. Using the measured K_a values and the dielectric constant at 25°, eq 5 was solved numerically to give a value for the center-to-center distance between the ions in the ion pairs.

The center-to-center distances for each ion pair derived from eq 5 are presented in Table III in comparison with the values estimated from crystallographic parameters and the Dreiding models proposed for the ion pair. It was assumed that the four THF solvate molecules are tetrahedrally arranged around the lithium ion in the model. The closest distance of approach of the complex metal hydride to the solvated lithium ion or sodium ion was found to be *via* attachment of one of the hydrogens to an oxygen of a THF molecule. This conclusion is supported by the appearance of a band at 450 cm^{-1} in the infrared spectrum of a THF solution of $LiAlH_4$, which did not occur in the spectra of other lithium salts. For $LiAlH_4$, this model

---

(26) M. K. Wong, W. J. McKinney, and A. Popov, *J. Phys. Chem.*, 75, 56 (1971).

(27) C. Lassigne and P. Baine, *ibid.*, 75, 3188 (1971).

(28) J. Wuepper and A. Popov, *J. Amer. Chem. Soc.*, 91, 4352 (1969).

(29) W. Edgell, J. Lyford, R. Wright, W. Resin, and A. Watts, *ibid.*, **92**, 2240 (1970).

Table III. Comparison of Center-to-Center Distances between the Ions

Compound	Calcd from cryst data,[c] Å	Calcd from eq 5, Å	Estimated from Dreiding model, Å
$LiAlH_4$	3.35[3]	4.9	5.0[a]
$NaAlH_4$	3.65	4.4	5.5[a]
$LiBH_4$	3.10[d]	3.3	4.8[a]
Bu_4NAlH_4		5.2	5.0[b]

[a] The cation is specifically solvated by four molecules of THF with the anion at the point of closest approach. [b] The cation is not specifically solvated by THF with the anion at the point of closest approach. [c] L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960. [d] P. Ford and R. Richards, *Discuss. Faraday Soc.*, No. **19**, 230 (1955).

for the ion pair is in perfect agreement with the center-to-center distance derived from K_a *via* eq 5. With the corresponding sodium salt, the value predicted by the model does not exactly agree with the derived radius but is reasonably close. Consequently this comparison strongly suggests that the ion pairs for the sodium and lithium salts at 25° are solvent separated species. This conclusion is consistent with the nmr studies and the infrared spectral interpretation of the new bands in THF solutions. When the radius calculated from the Dreiding model of the ion pair of tetrabutylammonium aluminum hydride with the two ions placed as close as possible to each other is compared to the value derived from the K_a, almost perfect agreement is obtained. The center-to-center distance predicted from the crystal radii is very close to the value found for $LiBH_4$. It is to be expected that Bu_4NAlH_4 would exist as a contact ion pair in THF solution since no specific solvation is observed by nmr. Since solvation of the lithium ion should occur for $LiBH_4$ as well as $LiAlH_4$, some forces must exist in the contact species of $LiBH_4$ that compensate for the loss of the solvation energy of the lithium ion. It is possible that the $LiBH_4$ ion pair has appreciable covalent character, since the difference observed between $LiBH_4$ and $LiAlH_4$ cannot be due to slight changes in the anion sizes.

An analysis of the available thermodynamic data for the dissociation of ion pairs in THF by Hogen-Esch and Smid[25] has established that the enthalpy of dissociation for the contact ion pair is approximately −8 to −10 kcal/mol for a salt with a cation, like lithium, which is specifically solvated. On the other hand, the enthalpy of dissociation for a solvent-separated ion pair should be −1 to −2 kcal/mol. Furthermore, if little specific solvation occurs upon dissociation of the ion pair, the enthalpy of dissociation ($\Delta H_d°$) will be represented by expression 6 derived from the continuum model.

$$\Delta H_d° = (Ne^2/rD)[1 + d \ln D/d \ln T] \qquad (6)$$

Since $d \ln D/d \ln T$ is calculated from the temperature dependence of the dielectric constant to be −1.20 at 25°, the $\Delta H_d°$ predicted by the continuum model for $LiAlH_4$ is −0.8 kcal/mol. This is in reasonable agreement with the observed value and further substantiates the conclusion that $LiAlH_4$ is a solvent-separated ion pair.

Since the plot of log K_a *vs.* $1/T$ is nonlinear, it is not possible unambiguously to derive an enthalpy of dissociation for the ion pair of $NaAlH_4$. The pronounced curvature of this plot can be interpreted as indicative of the presence of both contact- and solvent-separated ion pairs in equilibrium with the free ions. Between −30 and −70° the points can be fitted to a least-squares line with a slope corresponding to a $\Delta H_d° = -0.6$ kcal/mol. This value is consistent with the presence of predominantly solvent separated ion pairs. As the temperature is increased, the contact species are favored by the increase of the kinetic energy of the solvent molecules, causing the equilibrium between the two types to shift toward the contact species. Consequently, the $\Delta H_d° = -5.6$ kcal/mol, derived from the slope of the curve between 25 and −15°, suggests that an appreciable portion of the $NaAlH_4$ ion pairs exists in solution as contact species. When the contact ion pair dissociates, the cation must add at least one more THF molecule to its inner solvation sphere, leading to the evolution of the extra quantity of energy not observed for the solvent-separated dissociation process.

The difference in the log K_a *vs.* $1/T$ plot observed between $LiAlH_4$ and $NaAlH_4$ parallels that seen in the comparison of the center-to-center distances for the ion pairs at 25° contained in Table II. The fact that the radius derived from the experimental K_a is midway between the values calculated from the crystal radii and the proposed model further substantiates the presence of both types of ion pairs in THF solutions of $NaAlH_4$.

The entropies of dissociation for the $LiAlH_4$ ion pair is calculated to be −36 and −34 cal/(mol deg), at 25 and −70°, respectively. The corresponding $\Delta S_d°$ parameters for $NaAlH_4$ at 25 and −70° are −44 and −25 cal/(mol deg). The large negative values observed are consistent with the $\Delta S_d°$ values found by previous workers for systems containing solvent-separated ion pairs. At −70°, the $\Delta S_d°$ for $NaAlH_4$ increased by 50% over that at 25° indicating that the dissociation process at −70° occurs with less change in the orientation of the solvent around the ions.

The formation of triple ions in this system is to be expected, since it is well established[30] that in solvents of dielectric constant less than 12 triple ions usually occur. However, from the conductance data it is impossible to distinguish between the two possible triple ions, *e.g.*, $[LiAlH_4Li]^+$ and $[AlH_4LiAlH_4]^-$. For $LiAlH_4$, $LiBH_4$, and $NaAlH_4$ the i values reach a limiting plateau at 1.5. This would indicate that these complex metal hydrides exist at the higher concentrations in equal proportions of the two types of triple ions.

It would appear from these results that the reduction of ketones by complex metal hydrides such as $LiAlH_4$ could take place by the initial displacement of ether solvent (THF) from the coordination sphere of the alkali metal ion (Li). The carbonyl group could then be attached by the AlH_4 group either by a four- or six-center process depending on whether the complex metal hydride is a solvent separated or tight ion pair. We are presently engaged in a mechanistic study of the reduction of ketones by complex metal hydrides using the composition description of the complex metal hydride in solution generated by the study described herein.

Acknowledgment. We are grateful for support of this work by the Petroleum Research Fund, administered by the American Chemical Society.

---

(30) Charles A. Kraus, *J. Chem. Educ.*, **35**, 324 (1958).