Composition of Lithium Aluminum Hydride, Lithium Borohydride, and Their Alkoxy Derivatives in Ether Solvents as Determined by Molecular Association and Conductance Studies

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Abstract: Ebullioscopic molecular weight and conductance measurements were carried out on $LiAlH_4$, $LiBH_4$, and several alkoxy derivatives of these hydrides in tetrahydrofuran and diethyl ether. The results in tetrahydrofuran are consistent with the formation of ion pairs and triple ions for $LiAlH_4$, $NaAlH_4$, $LiBH_4$, and for the larger substituent alkoxy derivatives of $LiAlH_4$ and $LiBH_4$. When the complex metal hydride contains a methoxy substituent, there is evidence that linear aggregates are formed via oxygen bridge bonds. Larger aggregates than the triple ion appear to be formed for $LiAlH_4$ and $LiBH_4$ in diethyl ether. The higher stereoselectivity of $LiAlH_4$ in the reduction of cyclic ketones is postulated to be due to the formation of a complex between lithium and the carbonyl group as the initial step in the reduction process.

Since the discovery of $LiAlH_4$ and $LiBH_4$ by Schlesinger[1] and coworkers, thousands of reports concerning the use of these compounds as reducing agents in organic synthesis have appeared in the literature.[2] 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. The lack of precise information concerning the nature of the solute species in ethereal solvents has been the major obstacle in providing an exact description of the mechanisms of complex metal hydride reduction of organic substrates. Thus, in spite of the fact that the 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 not been possible to describe the mechanism of this reaction in any detail. Consequently, it would appear that precise information concerning the nature of the solute species present in ethereal solutions of complex metal hydrides, such as $LiAlH_4$, is crucial before precise mechanisms of reduction can be described.

Recently, we have provided detailed information concerning the composition of $LiAlH_4$ in tetrahydrofuran deduced primarily from conductance studies.[3] The predominant species in solution at 0.01 *M* and 25° is the solvent-separated ion pair; in dilute solution, solvated lithium ions and tetrahydridoaluminate ions are formed, while triple ions of the type $[LiAlH_4Li]^+$ or $[AlH_4LiAlH_4]^-$ are formed at higher concentrations.

Information concerning molecular association of complex metal hydrides in ether solvents is very sparse. Molecular weight and conductance studies by Nöth on $LiBH_4$ indicate that extensive association of the solute occurs in diethyl ether.[4] In addition, unpublished molecular weight studies by Wiberg[5] on $LiAlH_4$ in diethyl ether indicate that the solute is extensively associated in solution.

To provide additional information on the nature of the solute species, ebullioscopic measurements were obtained for a wide variety of complex metal hydrides and their alkoxy derivatives in THF and diethyl ether over a wide concentration range, i.e., from 0.05 to 0.6 *m*. Conductance measurements over the same concentration range were also obtained for several of the hydrides in both solvents to supplement the ebullioscopic results.

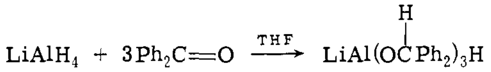
Experimental Section

Tetrahydrofuran and diethyl ether were purified by distillation from $LiAlH_4$ under a nitrogen atmosphere. Methanol was purified by distillation from magnesium turnings. *tert*-Butyl alcohol was purified by distillation from sodium. Benzophenone was purified by fractional distillation.

Hydride solutions were prepared by stirring slurries of the solid hydride in ethereal solvent for several days followed by removal of the solids by filtration in a drybox. The drybox used in these studies was equipped with a recirculating system in order to remove oxygen and moisture.[6] Bench top transfers[7] were accomplished via syringe under fast nitrogen purge through T-bore stopcocks.

Aluminum was determined by EDTA titration, lithium and sodium by flame photometry, and active hydride by measuring the evolved hydrogen from a hydrolyzed sample. A detailed description of the apparatus and procedure for the ebullioscopic determination of apparent molecular weights of air-sensitive materials is described elsewhere.[8] The ebullioscopic studies were performed in THF and diethyl ether at a pressure of 740 mmHg. Conductance measurements were carried out under a nitrogen atmosphere at 25° in cells previously described.[3]

The alkoxy derivatives of $LiAlH_4$ and $LiBH_4$ were prepared in THF by the addition of precise stoichiometric amounts of alcohol or ketone to a known quantity of hydride at 0° (eq 1 and 2). The



$$\mathrm{LiAlH_4 + 3Ph_2C{=}O \xrightarrow{THF} LiAl(O\overset{H}{\overset{|}{C}}Ph_2)_3H} \qquad (1)$$

$$\mathrm{LiBH_4 + \mathit{t}\text{-}BuOH \xrightarrow{THF} LiB(O\text{-}\mathit{t}\text{-}Bu)H_3 + H_2} \qquad (2)$$

reactions were found to be quantitative in that no unreacted alcohol or ketone could be detected by ir or GLC. All of the alkoxy derivatives of $LiAlH_4$ except $LiAl(OCH_3)_3H$ gave clear, colorless solutions without the formation of a precipitate. After approximately 24 hr at 25°, a white solid having a low hydridic activity (H/Al = 0.29) precipitated from the $LiAl(OCH_3)_3H$ solution (1.0 *M*), but the solution still retained a high degree of hydridic activity (H/Al = 1.88). Apparently, $LiAl(OCH_3)_3H$ disproportionates slowly according to eq 3.

$$\mathrm{2LiAl(OCH_3)_3H \rightleftharpoons LiAl(OCH_3)_4\!\downarrow + LiAl(OCH_3)_2H_2} \qquad (3)$$

The preparation of the alkoxy derivatives of $LiBH_4$ in THF required longer reaction times; $LiB(O\text{-}t\text{-}Bu)H_3$ and $LiB(O\text{-}t\text{-}Bu)_3H$ were prepared by the reaction of $LiBH_4$ and *tert*-butyl alcohol in THF at reflux temperature after 6 and 43 days, respectively. The other derivatives were prepared at 25°. As found with $LiAl(OCH_3)_3H$, $LiB(OCH_3)_3H$ undergoes disproportionation to $LiB(OCH_3)_2H_2$ (solution H/Li = 2.5) and $LiB(OCH_3)_4$ (solid H/Li = 0.12) after 10 hr at 25° (1.0 *M*). Elemental analysis of the hy-

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Table I. Infrared (in THF) and Elemental Analysis of Complex Metal Hydrides

Compd	Sample weight, mg	Active hydride, mmol	Aluminum, mmol	H:Al	$\nu_{\mathrm{Al-H}}$, cm^{-1}	$\delta_{\mathrm{Al-H}}$, cm^{-1}
$LiAlH_4$	350.0	2.44	0.606	4.02	1690	765
$LiAl(OCH_3)H_3$	559.2	3.20	1.08	3.09	1690	785, 755, 720
$LiAl(OCH_3)_2H_2$	485.4	0.674	0.737	1.88		
$LiAl(OCH_3)_3H$	506.0	0.670	0.642	1.01	1690	755
$LiAl(OCH_3)_4$	80.1	0.926	3.16	0.29		
$LiAl(O\text{-}t\text{-}Bu)H_3$	609.2	2.38	0.793	3.01	1760, 1705	795, 775, 738
$LiAl(O\text{-}t\text{-}Bu)_3H$	550.2	0.640	0.608	1.05	1760	788, 772
$LiAl(OCHPh_2)H_3$	792.6	2.90	0.963	3.02	1690	760
$LiAl(OCHPh_2)_3H$	2257.8	1.96	2.05	0.96	1800	775, 738
$LiBH_4$	323.0	1.86	0.463	4.04	2220	
$LiB(OCH_3)H_3$	486.0	2.07	0.668	3.10	2220	
$LiB(OCH_3)_2H_2$	778.6	1.02	0.405	2.54	2210	
$LiB(OCH_3)_3H$	980.3	0.630	0.651	0.97	2210	
$LiB(OCH_3)_4$	163.5	0.778	5.91	0.13		
$LiB(O\text{-}t\text{-}Bu)H_3$	452.9	1.50	0.482	3.11	2220	
$LiB(O\text{-}t\text{-}Bu)_3H$	711.1	0.825	0.639	1.26	2260	
$LiB(OCHPh_2)H_3$	857.4	1.67	0.536	3.11	2220	
$LiB(OCHPh_2)_3H$	1052.9	0.516	0.537	0.96	2220	

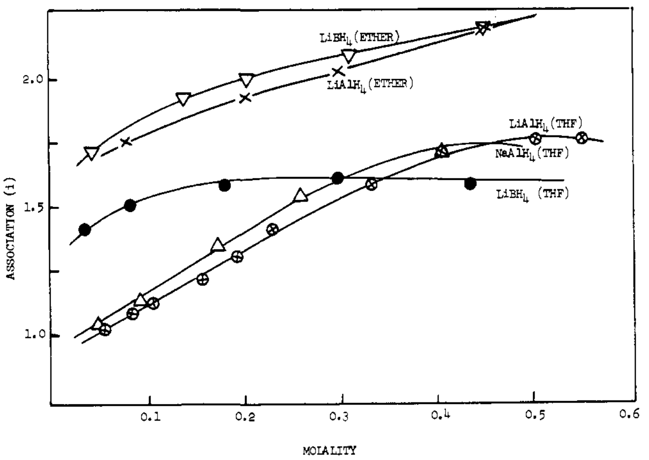


Figure 1. The molecular association of $LiAlH_4$. $NaAlH_4$. and $LiBH_4$ in ethereal solvents as determined by ebullioscopic molecular weight studies.

drides prepared for this work and the Al-H or B-H infrared vibrational frequencies are recorded in Table I.

Ebullioscopic Results

The molecular weights of the complex metal hydrides were determined near the boiling point of the solvent between 0.05 and 0.6 *m*. The calculated "*i* values" defined as the ratio of the experimentally determined molecular weight and the formula weight are shown in Figures 1-3 as a function of concentration.

The association curves for $LiAlH_4$, $NaAlH_4$, and $LiBH_4$ are shown in Figure 1. In THF, both $LiAlH_4$ and $NaAlH_4$ have *i* values of 1.0 in dilute solution, increasing with increasing concentration to a limiting value of ~1.8. In diethyl ether, $LiAlH_4$ has significantly higher *i* values over the same concentration range. $NaAlH_4$ is insoluble in diethyl ether, therefore ebullioscopic data could not be obtained. The *i* values for $LiBH_4$ in THF are approximately constant at 1.5 over the entire concentration range. In diethyl ether, the *i* values of $LiBH_4$ are higher at all concentrations, increasing from 1.7 in dilute solution to 2.3 at the highest concentration. It is interesting that the association behavior of $LiAlH_4$ and $LiBH_4$ in diethyl ether is so similar.

$LiAl(OCH_3)H_3$ in THF (Figure 2) has an association curve which is almost identical with that found for $LiAlH_4$. $LiAl(O\text{-}t\text{-}Bu)H_3$ and $LiAl(OCHPh_2)H_3$ have identical association curves with *i* values varying from 1.0 to 1.3. The trisubstituted derivatives, $LiAl(O\text{-}t\text{-}Bu)_3H$ and $LiAl(OCHPh_2)_3H$, have a relatively constant *i* value of 1.0 from 0.05 to 0.4 *m* showing a slight decrease in association at the higher concentrations. The association curves for $LiAl(OCH_3)_2H_2$ and $LiAl(OCH_3)_3H$ are substantially different from the curves found for the other hydrides shown in Figures 1 and 2. At the most dilute concentrations, the *i* values are 1.0 and 1.5, respectively, rising sharply to 2.5 and 2.8 at the higher concentrations.

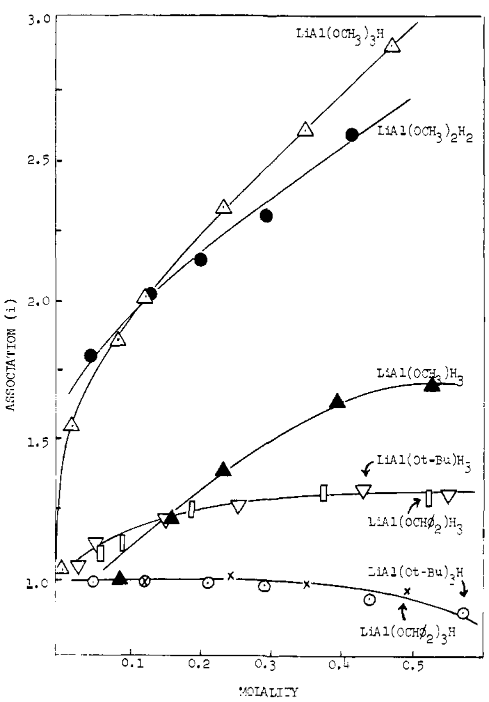


Figure 2. The molecular association of alkoxy derivatives of $LiAlH_4$ in THF as determined by ebullioscopic molecular weight studies.

The association curves for the corresponding alkoxy derivatives of $LiBH_4$ in THF are presented in Figure 3. The methoxy derivatives of $LiBH_4$ exhibit association curves which are similar to those found for the methoxy derivatives of $LiAlH_4$. For the remaining derivatives of $LiBH_4$, the *i* values are close to 1.0 and almost constant in the concentration range studied.

All of the alkoxy derivatives of $LiAlH_4$ and $LiBH_4$ are insoluble in diethyl ether; therefore ebullioscopic data could not be obtained in that solvent.

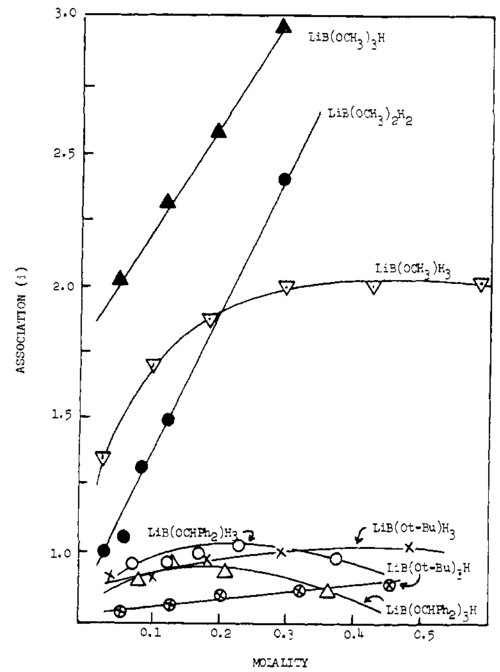


Figure 3. The molecular association of alkoxy derivatives of $LiBH_4$ in THF as determined by ebullioscopic molecular weight studies.

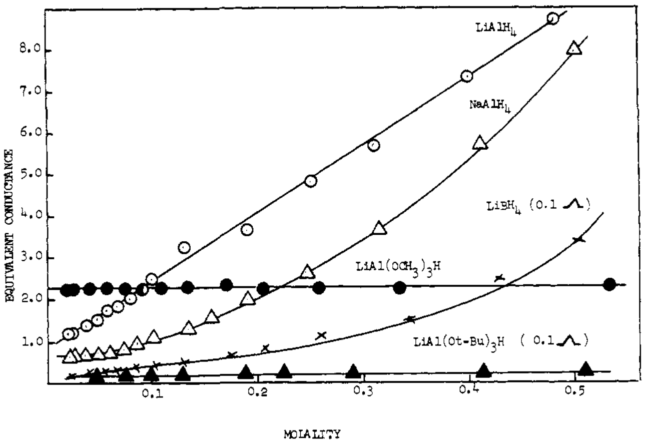


Figure 4. The equivalent conductance curves above 0.1 *M* for $LiAlH_4$. $NaAlH_4$. $LiBH_4$. $LiAl(OCH_3)_3H$. and $LiAl(O\text{-}t\text{-}Bu)_3H$ in THF at 25°.

Conductance Results

The equivalent conductance curves above 0.05 *M* for $LiAlH_4$, $NaAlH_4$, and $LiBH_4$ in THF at 25° are shown in Figure 4. The equivalent conductance increases with increasing concentration for these hydrides. At 0.1 *M*. $LiAlH_4$ is 2.5 times more conducting than $NaAlH_4$ and 50 times more conducting than $LiBH_4$. The equivalent conductance of $LiAl(OCH_3)_3H$ and $LiAl(O\text{-}t\text{-}Bu)_3H$ is independent of concentration over the same concentration range. The equivalent conductances of diethyl ether solutions of $LiAlH_4$ and $LiBH_4$ are extremely small and concentration independent.

Discussion

The alkoxy-substituted hydrides reported herein were considered to be stable to disproportionation in solution as evidenced by a comparison of the infrared spectra of the desired compound to the expected disproportionation products. For example, the Al-H deformation bands (δ Al-H) for $LiAl(OCH_3)H_3$ are different from the expected disproportionation products: $LiAlH_4$, $LiAl(OCH_3)_2H_2$, and $LiAl(OCH_3)_3H$. In addition, the expected disproportionation products [$LiAl(OR)_4$ and $LiB(OR)_4$] are insoluble in THF

$$LiAl(OCH_3)H_3 \not\rightleftharpoons LiAlH_4 + LiAl(OCH_3)_nH_{4-n} \quad (4)$$
$$\text{where } n = 2,\ 3 \text{ or } 4$$

and therefore would be expected to precipitate from solution if disproportionation is taking place. Only in the case of $LiAl(OCH_3)_3H$ and $LiB(OCH_3)_3H$ did precipitation take place after several hours standing; therefore, association and conductance data were collected immediately after preparation of the compounds and before precipitation took place. Previous studies by Eliel and Brown[9] indicate that $LiAl(OR)_nH_{4-n}$ compounds are stable to disproportionation in solution except when the alkoxy group is secondary (e.g., O-*i*-Pr).

The molecular association curves for $LiAlH_4$ and $NaAlH_4$ in THF (Figure 1) are virtually identical and are consistent with the presence of ion pairs at the lower concentrations (0.1 *m*) and triple ion aggregates at the higher concentrations (0.4 *m*). A limiting *i* value of ~1.5 at the higher concentrations is consistent with equal amounts of the two possible triple ions being present in solution. An analysis of conductance data for these hydrides obtained at 10^{-6} *M* concentration[3] indicates that free ions represent an appreciable fraction of the total concentration only at the most dilute concentrations, with ion pairs and triple ions being formed as the concentration is increased (eq 1). Furthermore, the conductance data in THF indicate that $LiAlH_4$ ion pairs exist predominantly as the solvent sepa-

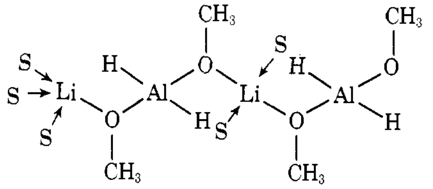
$$3Li^+ + AlH_4^- \rightleftharpoons 3[Li^+AlH_4^-] \rightleftharpoons [Li^+AlH_4^-Li^+] + [AlH_4^-Li^+AlH_4^-] \quad (5)$$

rated species, whereas $NaAlH_4$ ion pairs exist in equilibrium between solvent-separated and contact species.[3]

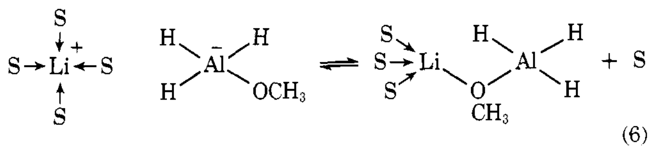
The association curves for the diethyl ether solutions of $LiAlH_4$ and $LiBH_4$ and the THF solution of $LiBH_4$ are similar indicating that these solutions contain similar solute species. Preliminary conductance studies on $LiBH_4$ in THF reveals a slight up-turn in the equivalent conductance curve in the 10^{-6} *M* concentration range. When the Fuoss treatment is applied to the data, an estimate of the ion-pair dissociation constant predicts the ion pair to be of the contact type.[3] A similar increase in the equivalent conductance for diethyl ether solutions of $LiAlH_4$ and $LiBH_4$ below 1×10^{-3} *M* is not found. The higher *i* values which are found even at low concentrations and the conductance data indicate that the ion aggregates in these solutions contain the ions in intimate contact. The conclusion then is that the ion pairs of $LiAlH_4$ in THF are solvent separated, $NaAlH_4$ in THF is a mixture of contact and solvent-separated ion pairs, whereas $LiAlH_4$ in diethyl ether and $LiBH_4$ in diethyl ether and THF are contact ion pairs. The fact that $LiBH_4$ is solvated by only two molecules of THF, whereas $LiAlH_4$ is solvated by four,[3] is further evidence that $LiAlH_4$ in THF exists as solvent-separated ion pairs, whereas $LiBH_4$ in THF exists as contact ion pairs.

More extensive association is observed for $LiAlH_4$ and $LiBH_4$ in diethyl ether than in THF because of the much lower dielectric constant (4.34 vs. 7.60) and the reduced solvating power of the oxygen of diethyl ether. The addition of stoichiometric amounts of THF to a diethyl ether solution of $LiAlH_4$ results in an increase in conductivity; either the solute species becomes more conducting, or the number of ionic species is increased. A plot of the equivalent conductance vs. the mole ratio of THF/$LiAlH_4$ (Figure 5) suggests that specific solvation by THF occurs in the mixed solvent. A change in the slope of the curve occurs primarily between the mole ratio of 2 and 6, thus supporting the presence of $LiAlH_4 \cdot 4THF$ species suggested earlier by ourselves from spectroscopic evidence. NMR experiments[3] and infrared studies showed that THF readily displaces diethyl ether attached to the lithium ion in $LiAlH_4$, forming the more stable four-coordinated lithium solvate. The increased solvating tendency of THF is, therefore, partly responsible for the formation of the solvent-separated ion pair of $LiAlH_4$. On the other hand, the increased stability of the contact species of $LiBH_4$ in THF could be due to the fact that the ionic radius of the BH_4^- ion is smaller than the ionic radius of the AlH_4^- ion thus enhancing the electrostatic forces and shortening the lithium-boron bond distance.

Figure 2 reveals that the association of methoxy derivatives of $LiAlH_4$ increases as the number of methoxy groups increase. This is apparently due to the ability of the oxygen of the methoxy group to coordinate the lithium ion and displace solvent molecules. When methoxy substituents are present, chain-like structures (I) are possible, involving methoxy bridge bonds or mixed methoxy-hydrogen bridge bonds. The unique shape of the association curves of the di- and tri-substituted methoxy derivatives of both $LiAlH_4$ and $LiBH_4$ (Figure 3) in THF indicates that linear chains joined by methoxy bridge bonds are occurring. Association of this type would account for the insolubility of the tetramethoxy derivatives, and the apparent disproportionation of the trimethoxy derivatives. $LiAl(OCH_3)H_3$ and $LiB(OCH_3)H_3$ in THF exhibit association phenomena similar to $LiAlH_4$ and $LiBH_4$, respectively in THF, and therefore similar solute species in solution are suggested. However, since the methoxy group is such a good bridging group, it is possible that monomethoxy derivatives also exist partially as bridged species (eq 6). Obviously the more methoxy groups present, the more bridging species would be expected (I). On the other hand, replacement of the methoxy substituent with the larger *tert*-butoxy or diphenylmethylcarbinyloxy substituent in both $LiAlH_4$ and $LiBH_4$ derivatives apparently inhibits further association of $LiAl(OR)_3H$ and $LiB(OR)_3H$ compounds for reasons of steric hindrance ($i \sim 1.0$ at 0.5 m concentration).



$[LiAl(OCH_3)_2H_2]_2$
(I)
S = solvent



(6)

Support for representation of $LiAl(OCH_3)_3H$ and $LiAl(O\text{-}t\text{-}Bu)_3H$ as alkoxy bridge structure is given by the conductance data shown in Figure 4 and in ref 3. Whereas the conductance of hydrides that do not contain alkoxy groups ($LiAlH_4$, $NaAlH_4$, and $LiBH_4$) varies with concentration, the conductance of alkoxy-substituted hydrides is independent of concentration. Such behavior is expected of alkoxy-substituted hydrides that are held together by bridge bonds rather than by electrostatic attraction.

At the concentrations usually employed in reductions of organic compounds by $LiAlH_4$, $NaAlH_4$, and $LiBH_4$ in THF and diethyl ether, the fraction present as free ions is very small. However, due to expected differences in reactivity between free ions and ion pairs, it should be possible for either to be the reactive species. Furthermore, ion-pair solute species may be solvent separated, in intimate contact, or may be mixtures of solvent-separated and contact species.[3]

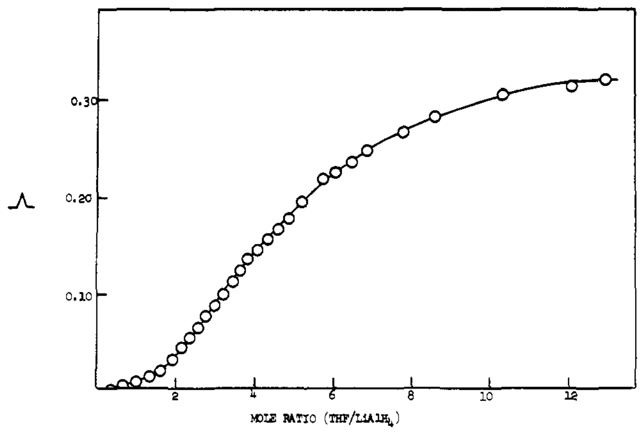


Figure 5. A plot of equivalent conductance vs. mole ratio ($THF\text{-}LiAlH_4$) at 0.257 M $LiAlH_4$.

NMR and infrared studies[10] have shown that specific solvation by four molecules of acetone occurs at the lithium ion for lithium iodide and lithium perchlorate in acetone-nitromethane mixtures. Furthermore, conductance data[11] are consistent with the presence of solvent-separated ion pairs for these salts in acetone. Specific solvation[9] by four molecules of THF at the lithium ion is also observed for these salts in THF-diethyl ether mixtures. Ketones, such as acetone and 3,3,5-trimethylcyclohexanone, are also observed to coordinate preferentially with lithium ions in THF and diethyl ether. Consequently, it appears that specific solvation occurs at the lithium ion in the solvent-separated ion pairs by coordination with the oxygen having the greatest solvating power.

Since the $LiAlH_4$ ion pair is a solvent-separated ion pair in THF, it is probable that the initial step in the reaction with a ketone is the complexation of a carbonyl oxygen by the lithium ion, followed by hydride transfer. The specific solvation of the sodium ion is usually less than that found for the lithium ion because of its larger size. Since the conductance data for $NaAlH_4$ is consistent with the presence of both solvent-separated and contact solute species, initial complexation of the carbonyl oxygen by the sodium ion is less likely to occur. Therefore, it is reasonable to expect that a difference in the selectivity of $NaAlH_4$ and $LiAlH_4$ in THF will occur.

The stereoselectivities of reduction of 3,3,5-trimethylcyclohexanone with $LiAlH_4$ and $NaAlH_4$ in THF[12] are both concentration dependent; the stereoselectivity, as measured by the formation of the less stable axial alcohol in the product, increases with decreasing concentration, i.e., from 0.5 to 0.001 M. Although the selectivity of $LiAlH_4$ is significantly greater than that found for $NaAlH_4$ at the higher concentrations, the selectivities of $LiAlH_4$ and $NaAlH_4$ are comparable at the most dilute concentration studied indicating solvent-separated ion pairs as the reactive species in both cases at the lower concentration. Evidently the ion pair is the active reducing species in these solutions, and the solvent-separated ion pair appears to give the greatest stereoselectivity.

In order to determine the extent of the stereoselectivity of

Table II. Stereoselectivity of Reductions of Hindered Ketones with Complex Metal Hydrides in THF[a]

	$LiAlH_4$	$NaAlH_4$	$LiBH_4$
3,3,5-Trimethylcyclohexanone	80	59	53
Camphor	91	88	69

[a] The numbers listed are the percentages of the less stable alcohol found in the products.

the solvent-separated ion pair, a comparison was made of the stereochemical results obtained from the reduction of two hindered ketones with the parent hydrides in THF.[12] The results are tabulated in Table II. With the ketones studied, the yield of the less stable alcohol found in the product is significantly smaller for $NaAlH_4$ compared with that of $LiAlH_4$. A comparison of the data for $LiBH_4$ shows that the percentage of the less stable alcohol found in the product is also smaller for $LiBH_4$ with the ketones studied. A similar conclusion is reached when the results of $LiBH_4$ are compared with those of $NaAlH_4$. Apparently the enhanced selectivity of the solvent-separated $LiAlH_4$ ion pairs can be attributed to the ability of the lithium ion to complex the carbonyl oxygen with the displacement of solvent. The decreased selectivity of $LiBH_4$ can be attributed to the decreased availability of the lithium ion to complex the ketones, because triple ions are present with the ions in intimate contact. Intermediate results are obtained for $NaAlH_4$, because substantial amounts of contact ion pairs are present, and because the sodium ion is a poorer complexing cation than lithium ion.

Obviously, the ketone plays an important role in the selectivity and cannot be entirely discounted. The evaluation of other complex metal hydrides in reactions with various ketones is presently under study. Our results, however, suggest strongly that initial complexation by the cation with displacement of solvent occurs in these reductions and may provide an explanation for the enhanced selectivity of the solvent-separated ion pair.[13]

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Composition of Grignard Compounds. X. NMR, Ir, and Molecular Association Studies of Some Methylmagnesium Alkoxides in Diethyl Ether, Tetrahydrofuran, and Benzene

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Abstract: A combination of NMR, ir and molecular association studies has been applied to the study of methylmagnesium alkoxides [where OR = $OC(C_6H_5)_2CH_3$, *t*-OBu, *i*-OPr, and *n*-OPr in diethyl ether, tetrahydrofuran, and benzene. It was found that the steric bulk of the alkoxy group and the coordinating ability of the solvent determine the thermodynamically preferred solution composition. In tetrahydrofuran, solvated dimers are preferred. In diethyl ether, linear oligomers and cubane tetramers are preferred provided the alkoxy group is not bulkier than the *tert*-butoxy group. In benzene, cubane tetramers are observed for alkoxy groups of intermediate bulk such as *tert*-butoxy and isopropoxy, but the less bulky *n*-propoxy group permits the formation of an oligomer containing seven to nine monomer units. For the reagents with alkoxy groups less bulky than *tert*-butoxy, the equilibria involving various structures are established very rapidly. However, the dimer-linear oligomer ⇌ cubane tetramer equilibrium is established very slowly for methylmagnesium *tert*-butoxide compounds. The cubane form is very inert and does not exchange or otherwise interact with dimethylmagnesium in diethyl ether. The dimer-linear oligomer form is quite labile and readily exchanges with dimethylmagnesium forming mixed-bridged compounds. However, in diethyl ether, the mixed bridge is not sufficiently strong to prevent slow conversion of methylmagnesium *tert*-butoxide to the cubane form thus releasing dimethylmagnesium.

The solution composition and solid state structure of organomagnesium alkoxides appear to be more complex and diverse than those of organomagnesium halides.[1] The alkoxy group forms very strong bridge bonds where the oxygen can be either tri- or tetravalent. Coates and coworkers[2a] investigated several alkylmagnesium alkoxide systems by a combination of elemental analysis, molecular association, and NMR studies. They found that bulky alkoxy groups favored the formation of solvated dimers, while compounds with less bulky alkoxy groups often formed unsolvated molecules containing four or even seven monomer units. Structures were proposed, in some cases, which accounted for the