References and Notes

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(4) For the mechanism of enol ether formation, see A. Kankaanpera, P. Salomaa, P. Juhala, R. Aaltonen, and M. Mattsen, *J. Am. Chem. Soc.*, **95,** 3618 (1973).

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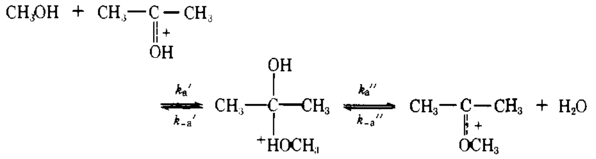
(6) Although step a is composite, with intermediate formation of the conjugated acid of hemiketal, it is not necessary for this purpose to distinguish the two



elementary steps a′ and a″. The rate constants k_a and k_{-a} can be expressed in the following form:

$$k_a = k_a'k_a''/(k_{-a}' + k_a'')$$

$$k_{-a} = k_{-a}'k_{-a}''/(k_{-a}' + k_a'')$$

Since the equilibrium hemiketal concentration is very low (<1%),[10] it is not necessary to take into account hemiketal formation.

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(10) (a) The molar fraction of acetal (x_{eq}) is calculated from the equilibrium constant

$$K = \frac{[\text{ketal}]_{eq}[H_2O]}{[\text{ketone}]_{eq}[CH_3OH]^2} = \frac{x_{eq}[H_2O]}{(1 - x_{eq})[CH_3OH]^2}$$

(b) $K = 4 \times 10^{-4}\ M^{-1}$ (J. M. Bell, D. J. Kubler, P. Sartwell, and R. G. Zepp, *J. Org. Chem.*, **30,** 4284 (1965)).

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(13) The apparent acidity constant in methanol containing small amounts of water is defined by the following equation

$$K_a = [SH^+][B]/[BH^+]$$

where $[SH^+] = [CH_3OH_2^+] + [H_3O^+]$. On the other hand, in pure methanol:

$$(K_a)_m = [CH_3OH_2^+][B]/[BH^+]$$

Equation 7 is directly deduced from these two equations, taking into account the $[CH_3OH_2^+]$ expression:[t2b]

$$[CH_3OH_2^+] = [SH^+]([H_2O]/([H_2O] + 0.23))$$

(14) Equation 9 assumes that proton elimination (rate constant, k_{Et}) is the rate-determining step of enol ether formation. This has been demonstrated for the following reaction:[4]

$$RCH_2CH(OC_2H_5)OC_2H_5 \rightarrow RCH{=}CH(OC_2H_5) + C_2H_5OH$$

For acetone, the sum of the rate constants of ketone–ketal interconversion ($k_H + k_F$) for $[HBr] = 10^{-3}$ M is about 0.05 $M^{-t}\ s^{-t}$ (Table I), that is, a factor of 5×10^3 higher than k_{exp} for the same acidity (Table II). Thus, $k_{Et}/k_{-a}[H_2O]$ is lower that 10^{-3}; k_{Et} [II] is negligible compared to the other rates of formation and destruction of ion II.

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(16) Given eq 10, eq 15 is deduced from the following equation

$$-d[Br_2]/dt = k_A[H^+]a(1 - x_t) + k_B[H^+]ax_t$$

where ax_t and $a(1 - x_t)$ are the ketal and the ketone concentrations, respectively.

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(18) Unpublished results from this laboratory on a comparison of enol ketonization and hydrolysis of the corresponding ethyl or methyl ethers for cycloalkanones and for aryl-substituted acetophenones show that k_{-En}/k_{-Et} is not greater than ten in water.

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Mechanism of Lithium Aluminum Hydride Reduction of Ketones. Kinetics of Reduction of Mesityl Phenyl Ketone[1]

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Abstract: Pseudo-first-order kinetic studies on the reaction of $LiAlH_4$, $NaAlH_4$, and $LiAlD_4$ with mesityl phenyl ketone have been carried out in tetrahydrofuran at 25 °C. The reactions were carried out in excess hydride and found to be first order in hydride and first order in ketone. $LiAlH_4$ is about ten times more reactive than $NaAlH_4$ which indicates the importance of the cation in the mechanism of the reaction. A deuterium kinetic isotope study involving the reaction of $LiAlH_4$ and $LiAlD_4$ with mesityl phenyl ketone gave a value of k_H/k_D of 1.27 which implicates the transfer of the hydride from aluminum to the carbonyl carbon in the rate-determining step of the reaction. Entropies of activation for reduction of mesityl phenyl ketone by $LiAlH_4$ and $NaAlH_4$ indicate that the transition state is considerably more ordered for reduction by $LiAlH_4$ (−26.2 vs. −5.4 eu) and that the transition state is of considerably lower energy (10.5 vs. 18.1 kcal). These data further suggest that the lithium cation is associated with the carbonyl oxygen during reduction.

Introduction

After studying the stereochemistry of metal hydride reduction of a number of cyclic and bicyclic ketones under varying conditions of cation and anion size, concentration, stoichiometry, solvent, and temperature,[3] it is clear that more information is needed about the transition state of the reaction to explain the stereochemical results. Since the nature of the reagent and the mechanism of the reaction are both essential to the establishment of the nature of the transition state, it is clear that some understanding of the composition of $LiAlH_4$ in ether solvent and the mechanism of $LiAlH_4$ reduction of a model ketone is important to an understanding of the stereochemistry of the reaction.

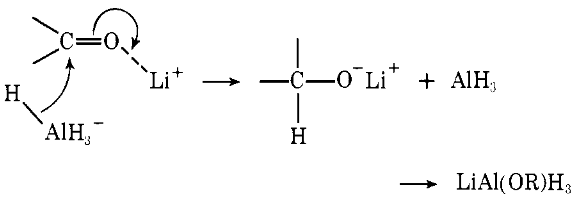
The composition of $LiAlH_4$ and other complex metal hydrides in ether solvents[4] have recently been studied by conductance measurements of the type first reported by Hogen-Esch and Smid.[5] The results of these studies are consistent with the representation of $LiAlH_4$ in THF as free ions and solvent separated ion pairs in dilute solution (10^{-2}–10^{-6} M) and triple ions in more concentrated solution ($>10^{-1}$ M).

Some kinetic studies on the reaction of complex metal hydrides with ketones have already been reported.[6] Most of these studies involve the reaction of $NaBH_4$ in isopropyl alcohol; however, some recent competitive rate studies have been conducted involving aluminohydrides.[6a,j,k] The reduction of ketones by metal borohydrides is first order in each reactant,[6h,i] involves nucleophilic attack of the borohydride ion at the carbonyl carbon atom,[6d-f] and is dependent on the nature of the metal cation present.[7a-d] However, it is uncertain whether the carbonyl oxygen is associated with the boron atom (four-centered transition state), with the metal cation (six-centered transition state), or neither, and where the transition state lies along the reaction coordinate. Recently, several reports have appeared concerning the latter point.[6b,c,8a-c] The position of the transition state along the reaction coordinate is of significant importance in determining the stereochemical control of reduction reactions since a late transition state would support product development control and an early transition state would support torsional strain or other electronic effects.

No kinetic studies have been reported for reduction of a ketone by lithium aluminum hydride, although studies using lithium tri-*tert*-butoxyaluminohydride [$LiAl(t\text{-}OBu)_3H$] have been reported.[6j,k] The degree to which mechanistic information concerning borohydride reduction of ketones can be applied to aluminohydride reduction is not known. The second, third, and fourth stages of reduction with aluminohydride ion is reported[9a,b] to be slower than the first stage, while the opposite is true for borohydride reduction.[6h,10] It has been shown[9b] that in some cases the second, third, and fourth stages of reduction by aluminohydrides are complicated by the disproportionation of the intermediate alkoxyaluminohydride intermediates [$LiAl(OR)_nH_{4-n}$]. Under conditions of disproportionation, $LiAlH_4$ is the reducing species at all stages of reduction. On the other hand, it is known that many alkoxyaluminohydrides are stable to disproportionation.[11] Thus, in reductions of ketones involving $LiAlH_4$, the AlH_4^- ion may or may not be the only major reducing species, while for borohydride reduction the alkoxy intermediates are known to be important reducing species. In any case, these differences involving the latter stages of reduction indicate nothing about the differences or similarities of the initial step, attack of ketone by $M^+AlH_4^-$ or $M^+BH_4^-$.

Rates of reduction of a series of cyclohexanones using a large excess of $LiAl(t\text{-}OBu)_3H$ showed the reaction to be first order in ketone and first order in $LiAl(t\text{-}OBu)_3H$.[6k] The similarity in the rate of equatorial attack on the cyclohexanones was interpreted to rule out product development control as a factor in the stereochemical control of the reaction. The difference in the total rate of reduction of the cyclohexanones was later interpreted[6a] to show that complexing of the ketone by $LiAl(t\text{-}OBu)_3H$ is not rate determining since the rate of complexation of the cyclohexanones by $LiAl(t\text{-}OBu)_3H$ should be about the same.

A possible mechanism for the reduction of ketones by $LiAlH_4$ has been recently suggested.[12] Based on the work of Brown and Lansbury demonstrating the importance of the lithium ion in borohydride reductions, it was suggested that prior or concurrent association of the carbonyl oxygen by Li^+ as the hydride is transferred from the aluminum to the carbon may be a mechanistic pathway for aluminohydride reduction. Recently we have supported this mechanism based on the large amount of apparent equatorial attack on 2-methylcyclohexanone by $Mg(AlH_4)_2$ and $ClMgAlH_4$.[13] The observations were explained by complexation of the carbonyl oxygen by $MgCl^+$ or $MgAlH_4^+$, resulting in a change in the conformation of the ketone in the transition state.



(1)

The purpose of this work was to determine the kinetic behavior of $LiAlH_4$ in reaction with a ketone. Mesityl phenyl ketone was selected as the model ketone since the rate of reaction of this ketone with $LiAlH_4$ is slow enough to be studied by conventional methods. The importance of the cation was investigated by comparing the rates of reaction of $LiAlH_4$ and $NaAlH_4$. In order to try to determine if transfer of the hydride from aluminum to carbon is the rate-determining step, a deuterium kinetic isotope study was conducted by comparing the rates of reaction of the ketone with $LiAlH_4$ and $LiAlD_4$.

Experimental Section

Materials. $LiAlH_4$ and $NaAlH_4$ were obtained from the Ventron Corp. Aluminum chloride (Fisher Scientific) was sublimed under nitrogen at 200–210 °C. Fisher Reagent Grade benzene and tetrahydrofuran (THF) were distilled under nitrogen from $NaAlH_4$. Fisher Reagent Grade diethyl ether was distilled from $LiAlH_4$. Mesityl phenyl ketone was obtained by the reaction of benzoyl chloride with mesitylene. The product was distilled using a spinning band column (bp 113 °C at 0.30 mm; lit. 180–182 °C at 8.5 mm).[14] GLC analysis of the distilled ketone showed it to be at least 99% pure. The NMR spectrum in CCl_4 using Me_4Si as the reference showed the following signals: δ 7.6 (m, 5 H), 6.85 (s, 2 H), 2.29 (s, 3 H), and 2.02 (s, 6 H). Mass spectral analysis showed major peaks at 224 (M^+, 91), 223 (100), 147 (58), 119 (15), 105 (17), and 77 (27), where the relative intensities are given in parentheses. Uv and visible spectra in THF showed absorbance maxima at 348 mμ (ϵ 93) and 246 mμ (ϵ 15 700). Benzophenone and 2-methylbenzophenone were commercial samples purified by distillation. A commercial (Ames Laboratories) sample of *N,N,N′N″,N‴,N‴*-hexamethyltriethylenetetramine was purified by vacuum distillation (bp 67–70 °C at 0.05 mm). Commercial samples of LiBr and $LiClO_4$ were further dried under vacuum with slight warming.

Apparatus and Procedure. A Cary Model 14 recording spectrophotometer was used for recording visible and uv spectra over a number of wave lengths. A Zeiss PMQ II single-beam spectrophotometer was used for measuring absorbances at a single wavelength. The cells used in this study were 10-mm quartz cells equipped with a two-way Teflon stopcock.

An F and M Model 700 flame-ionization gas chromatograph equipped with a 4-ft glass column (10% Carbowax 20M on Diatoport S) was used for GLC analysis. Column temperature was 195–200 °C.

Calibrated syringes equipped with stainless steel needles were used for transfer of all reagents. All transfers were carried out under nitrogen in a glovebox described elsewhere.[15]

For kinetic studies with excess hydride, accurate volumes of standard hydride solutions were added to a known volume of THF in quartz cells via syringe. The solutions were equilibrated at 25.0 °C in the cell compartment of the Zeiss PMQ II for 15 min, a measured volume of a standard ketone solution injected, the cell shaken, and the disappearance of the $\pi \rightarrow \pi^*$ band followed at 246 mμ.

Preparations. Solutions of $LiAlH_4$, $LiAlD_4$, and $NaAlH_4$ were prepared by distilling THF from $NaAlH_4$ onto the hydride. The mixture was stirred overnight and filtered in the glovebox using a fritted glass funnel and celite filter aid.

$LiAlH_4$ was recrystallized from a THF–benzene solvent mixture by addition of benzene, followed by partial removal of the solvent under vacuum. The white solid was collected and dried under vacuum before dissolving in freshly distilled THF. Analysis of the resulting solution showed an Al:H:Cl ratio of 1.00:3.96:0.010. A solution of $LiAlH_4$ without any purification showed an Al:H:Cl ratio of 1.00:

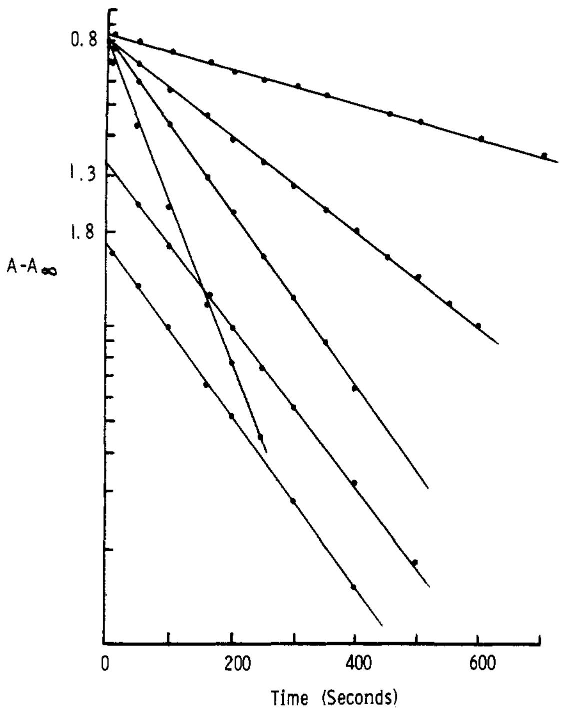


Figure 1. Reaction of mesityl phenyl ketone with excess $LiAlH_4$. Concentrations are given in Table I: (a) run 3, (b) run 7, (c) run 14, (d) run 20, (e) run 13, (f) run 17.

3.91:0.028. $NaAlH_4$ was purified in the same manner as $LiAlH_4$. A solution in THF showed a Li:Al:H:Cl ratio of 0.003:1.00:4.00:0.00. $LiAlD_4$ was used without further purification (Al:H:Cl ratio = 1.00:3.90:trace).

Solutions of mesityl phenyl ketone were prepared by dissolving a known amount of the ketone in the solvent in a volumetric flask equipped with a two-way stopcock. This solution was further diluted using a calibrated syringe and similar volumetric flasks. Reproducibility was better than ±1.0%. Solutions of benzophenone and 2-methylbenzophenone were prepared similarly.

Solutions of *N,N',N',N'',N''',N'''*-hexamethyltriethylenetetramine, LiBr, and $LiClO_4$ were prepared similarly to the mesityl phenyl ketone solutions.

Product Analysis. Mesityl phenyl ketone (0.017 M) was allowed to react with $LiAlH_4$ (0.059 M) in THF for 4 h. The reaction mixture was quenched with water and the THF removed under vacuum. The resulting mixture was extracted three times with diethyl ether. The ether washings were dried over $MgSO_4$ and then the ether removed under vacuum. The NMR of the product in CCl_4 with Me_4Si as the reference showed the following absorptions: δ 7.18 (s, 5 H), 6.75 (s, 2 H), 6.16 (s, 1 H), 2.84 (s, 1 H concentration dependent), 2.22 (s, 3 H), and 2.12 (s, 6 H), which is in good agreement with the spectrum reported for mesitylphenylcarbinol.[16] Mass spectral analysis showed major peaks at 226 (M^+, 52), 208 (67), 193 (100), 149 (49), 147 (53), 121 (66), 105 (65), 79 (21), and 77 (36) where the relative intensities are given in parentheses.

In a similar reaction mesityl phenyl ketone (0.095 M) was allowed to react with $LiAlD_4$ (0.16 M) in THF. The reaction mixture was worked up as in the case of $LiAlH_4$. The NMR spectrum of the product in CCl_4 with Me_4Si as reference showed the following absorptions: 7.18 (s, 5 H), 6.75 (s, 2 H), 3.32 (concentration dependent, s, 1 H), 2.22 (s, 3 H), and 2.12 (s, 6 H), which is in good agreement with the spectrum expected for mesitylphenylcarbinol with deuterium incorporation at the carbinol carbon atom. Mass spectral analysis showed peaks at 227 (M^+, 42), 209 (67), 194 (100), 150 (44), 147 (44), 122 (38), 105 (69), 80 (17), and 77 (20), where the relative intensities are given in parentheses.

The product of several reaction mixtures of mesityl phenyl ketone with $LiAlH_4$ showed only a single GLC peak with the same retention time (30.5 min). A sample of the product was collected from the gas chromatograph and identified by NMR and spectral analysis as that of mesitylphenylcarbinol. Response ratios for mesityl phenyl ketone and the carbinol product were determined and the ketone used as the internal standard since GLC analysis had previously shown in each case that ketone was absent from the product mixture. Yields were essentially quantitative.

Table I. Reaction of $LiAlH_4$ with Mesityl Phenyl Ketone in THF at 25.0 °C

Exp.	Concn of $LiAlH_4$, M × 10^3	Concn of ketone, M × 10^5	k_{obsd} × 10^3, s^{-1}	k_2, l. mol^{-1} s^{-1}
1	1.02	5.27	0.538	0.528
2	1.02	5.27	0.534	0.524
3	2.04	5.25	1.24	0.607
4	2.04	5.25	1.13	0.552
5	4.05	5.21	2.22	0.549
6	4.05	5.21	2.49	0.616
7	6.02	5.17	3.50	0.582
8	6.19	5.31	3.50	0.566
9	8.19	5.27	4.28	0.522
10	8.19	5.27	4.88	0.596
11	8.19	5.27	5.25	0.641
12	9.93	1.02	5.98	0.602
13	10.2	2.10	5.98	0.589
14	10.1	5.22	6.24	0.618
15	10.1	8.32	6.36	0.629
16	10.1	10.4	6.24	0.618
17	10.1	12.4	6.18	0.613
18	12.1	5.18	7.30	0.603
19	16.0	5.24	9.63	0.602
20	20.0	5.15	11.7	0.587
21	4.68	5.21	2.77	0.591
22	7.74	5.19	5.10	0.659
23	15.1	1.02	9.25	0.612
24	15.1	5.06	9.50	0.628
25	14.9	12.0	9.25	0.620
26	30.2	5.04	16.9	0.560
27	45.1	5.04	25.6	0.568

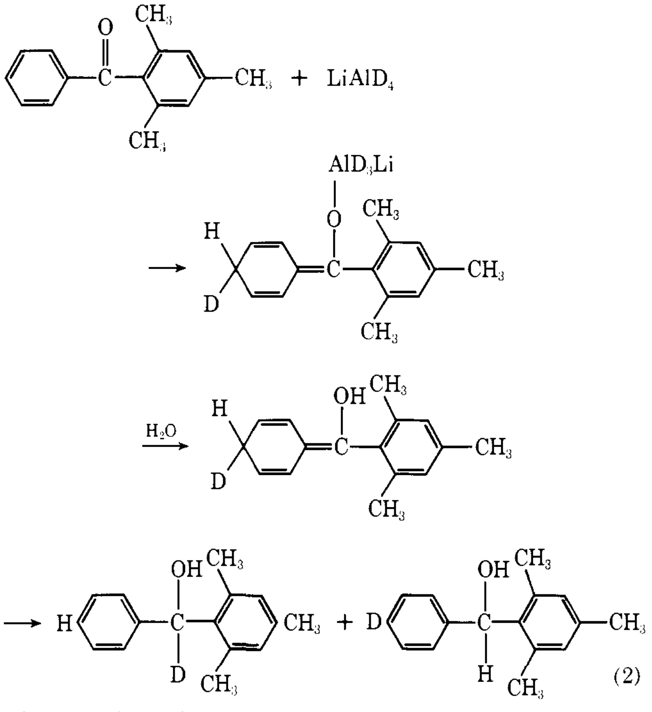
Results and Discussion

Kinetics of Reduction of MPK by Lithium Aluminum Hydride. Mesityl phenyl ketone (MPK) reacts with excess lithium aluminum hydride in tetrahydrofuran (THF) to produce on hydrolysis mesitylphenylcarbinol, in essentially quantitative yield. The reaction was followed spectrophotometrically by observing the disappearance of the $\pi \rightarrow \pi^*$ transition of MPK at 246 mμ (ϵ 15 700). Neither $LiAlH_4$ in THF nor the product (ϵ_{246} 325) solution absorbs significantly in this region compared with MPK. In order to observe the transfer of only one of the hydrogens from $LiAlH_4$ to the ketone, the reaction was studied using $LiAlH_4$ in a 20 to 400 molar excess. Using excess $LiAlH_4$ should avoid any significant reaction by any slower reacting alkoxy intermediate.

The ultraviolet region from 200 to 300 mμ was scanned after initiating reaction. The maximum absorption band (carbonyl $\pi \rightarrow \pi^*$) remained at 246 mμ with no changes detected except for disappearance of the band with time. In a separate reaction the 300- to 450-mμ region was scanned. The maximum absorption band due to the $n \rightarrow \pi^*$ transition of the carbonyl group remained at 348 mμ with no changes detected except for the disappearance of the band with time. Thus, no band attributable to a complex between the carbonyl oxygen and lithium is observable in the ultraviolet or visible regions. This does not mean that a complex is not formed between the ketone and lithium since the concentration of the complex may be simply too small to detect or the complex band may be hidden under the free carbonyl band.

When MPK was added to excess $LiAlH_4$, the absorbance at 246 mμ disappeared in a first-order manner (Figure 1, Table I), indicating that the reaction is first order in ketone. A plot of k_{obsd} vs. $LiAlH_4$ concentration for 15 kinetic experiments produced a straight line passing through the origin (Figure 2), indicating that the reaction is first order in $LiAlH_4$. If the reaction is indeed first order in ketone, k_{obsd} should not change when the ketone concentration is varied at a constant $LiAlH_4$ concentration. This was found to be the case for a 12-fold change in ketone concentration (see runs 12–17, Table I).

Conjugate addition of Grignard reagents to sterically hindered benzophenones is well known;[17] therefore, it was of concern that disappearance of the carbonyl group could be a result of 1,4 and 1,6 addition as well as 1,2 addition. This possibility was checked by allowing MPK to react with $LiAlD_4$. If 1,4 or 1,6 addition was occurring, then deuterium should be incorporated into the phenyl ring and hydrogen incorporated at the carbinol carbon since either the hydrogen or deuterium in A can migrate to form the products (eq 2). NMR analysis of the product of MPK and $LiAlD_4$ showed two absorptions for aromatic protons in 5:2 ratio, and no absorption was observed for a hydrogen attached to the carbinol carbon atom. Thus, it appears that reduction of MPK by $LiAlH_4$ takes place entirely in a 1,2 fashion.



(2)

Further characterization of the product of the reaction of MPK with $LiAlH_4$ was established by running the reaction on a large scale and isolating the product, followed by NMR and mass spectral analysis. The product was shown to be pure mesitylphenylcarbinol.

The second-order rate constant (k_2) for a particular kinetic run was calculated by dividing k_{obsd} by the concentration of $LiAlH_4$. The average value for runs 1-20 (Table I) is 0.587 l. mol^{-1} s^{-1}. The values obtained ranged from 0.522 to 0.641 l. mol^{-1} s^{-1}. Very careful attention was given to runs 9, 10, and 11 which were carried out under identical conditions, yet k_{obsd} varied from 4.28 to 5.25. The results indicate that the system is very sensitive. The reaction rate could not be related to any variable, such as, difference in uv cells, length of time reagent is in the cell before reactions, etc. The low values for k_2 in runs 1 and 2 are attributed to hydrolysis of $LiAlH_4$ for such low concentrations. Our experience has been that manipulation of $LiAlH_4$ solutions at concentrations $<10^{-3}$ M require high vacuum techniques[5] which would have been extremely difficult to use in this study. Thus, the variation in k_2 ($\pm$10%) is due to experimental limitations. In spite of the observed variation, it is clear that the data is good enough to demonstrate first-order behavior of the ketone and $LiAlH_4$.

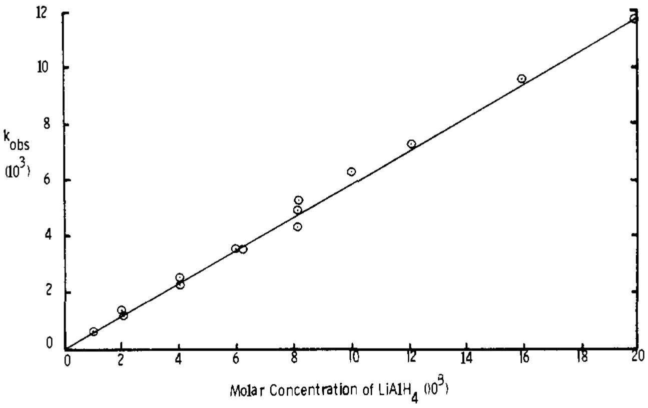


Figure 2. Reaction of 5.2×10^{-5} M mesityl phenyl ketone with varying concentrations of $LiAlH_4$. Data taken from runs 1-11, 14, 18-20 of Table I.

Table II. Reaction of $NaAlH_4$ with Mesityl Phenyl Ketone in THF at 25.0 °C

Exp.	Concn of $NaAlH_4$, M × 10^3	Concn of ketone, M × 10^5	k_{obsd} × 10^3, s^{-1}	k_2 × 10, l. mol^{-1} s^{-1}
28	5.34	5.25	0.284	0.532
29	18.7	12.4	1.06	0.567
30	18.9	5.21	1.06	0.561
31	18.9	5.21	0.905	0.479
32	40.4	5.24	1.98	0.490

Reproducibility of runs 1–20 in Table I were checked against a second solution of $LiAlH_4$ (runs 21-27). Runs 1-20 were carried out using $LiAlH_4$ purified by fractional recrystallization, whereas runs 21-27 were carried out with uncrystallized $LiAlH_4$ from a different lot number. The two solutions gave average values for k_2 of 0.587 and 0.605 l. mol^{-1} s^{-1}, which are well within experimental error. This indicates, at least under pseudo-first-order conditions, that the purity of $LiAlH_4$ is not crucial (see Experimental Section for analysis of the different samples).

The rate of reaction of MPK and $LiAlH_4$ at low ratio (1:1) also exhibits simple second-order kinetics. A plot of 1/A (uncorrected) against time gave a straight line for 75% of the reaction. The value of k_2 was found to be 0.50 l. mol^{-1} s^{-1} in close agreement with the results obtained using excess $LiAlH_4$. These results indicate that the rate of reaction of MPK with the intermediate lithium alkoxyaluminohydrides is slow compared with that of $LiAlH_4$.

In conclusion then, the reaction of MPK with $LiAlH_4$ is second order; first order in ketone and first order in $LiAlH_4$. The kinetic results are reproducible and not sensitive to the purity of $LiAlH_4$.

Kinetics of Reduction of MPK by Sodium Aluminum Hydride. Several kinetic runs were carried out using $NaAlH_4$ under the same reaction conditions used for $LiAlH_4$. Just as in the case of $LiAlH_4$, solutions of $NaAlH_4$ in THF did not absorb significantly at 246 mμ, and thus the disappearance of the carbonyl group was followed as a measure of the rate of reaction. The band at 246 mμ disappeared in a first-order fashion (Figure 3), establishing the reaction to be first order in ketone. The values of k_{obsd} and k_2 are given in Table II. The average value of k_2 is 0.0526 mol^{-1} s^{-1} over an eightfold change in the concentration of $NaAlH_4$. As with $LiAlH_4$, the results are not as reproducible as one would like although extreme precautions were taken to insure reproducibility. Even identical experiments (runs 30 and 31) showed a 16% variation

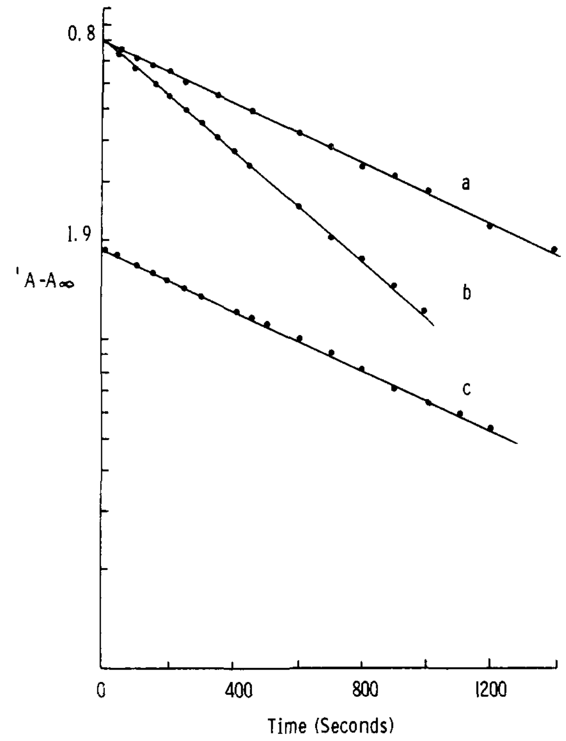
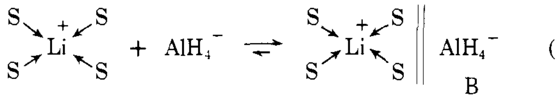


Figure 3. Reaction of mesityl phenyl ketone with excess $NaAlH_4$. Concentrations are given in Table II: (a) run 30, (b) run 32, (c) run 29.

in k_2. However, the experimental error is not much greater than that observed with $LiAlH_4$, and because of the extreme sensitivity of dilute solutions of complex metal hydrides, these results are probably about as reproducible as one can obtain under the most carefully controlled conditions. In any event, it appears clear that the reaction is first order in ketone and first order in $NaAlH_4$ and that mesityl phenyl ketone reacts about eleven times slower with $NaAlH_4$ compared with $LiAlH_4$.

Discussion of Mechanism. All indications are that reaction of $MAlH_4$ with ketones is not independent of the cation; if it were, equal rates of reaction of $LiAlH_4$ and $NaAlH_4$ would be expected. However, it is not entirely clear how the cation participates. The cation could possibly affect the reactivity of the ketone or the aluminohydride ion, or both.

Recent conductance studies[4] carried out in this laboratory show that $LiAlH_4$ in THF exists predominantly as solvent separated ion pairs B under the conditions of these kinetic studies (1×10^{-3} to 4×10^{-2} M, 25 °C), whereas $NaAlH_4$ appears to be a mixture of solvent separated C and contact ion pairs D (eq 3, 4). Under the reaction conditions a small fraction of each hydride is present as free ions and triple ions.



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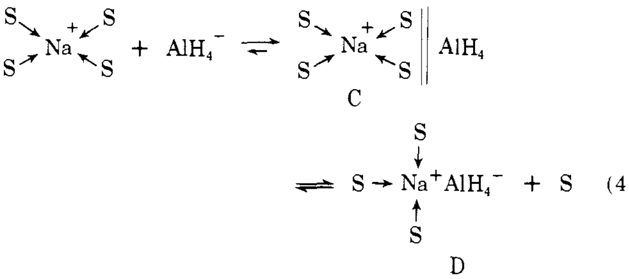
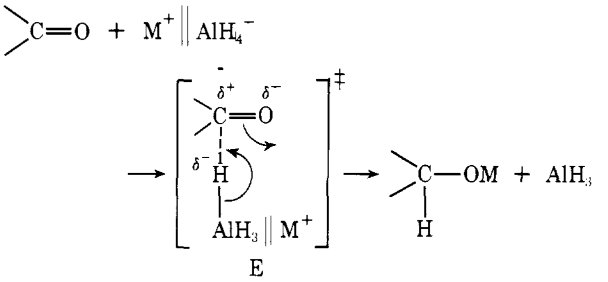


(4)

of each hydride is present as free ions and triple ions.

Because the reaction rate of MPK with $MAlH_4$ depends upon the nature of the cation, M^+, it seems reasonable to assume that the transition state involves the presence of the cation and not just the free aluminohydride ion.[12,13] The fact that the stereoselectivity of $MAlH_4$ reductions are also dependent[3,13] on the cation (M^+) is further support for the presence of the cation in the transition state. Two possible mechanistic pathways for the reduction of MPK by $MAlH_4$ should be considered: (1) the cation does not complex the carbonyl oxygen and (2) the cation does complex the carbonyl oxygen. Since $NaAlH_4$ consists of both contact and solvent separated ion pairs in THF to about the same degree, reaction through both types of ion pairs needs to be considered. $LiAlH_4$ will be considered to react through the solvent separated ion pair since this is by far the most abundant species present in THF solution at ambient temperature.

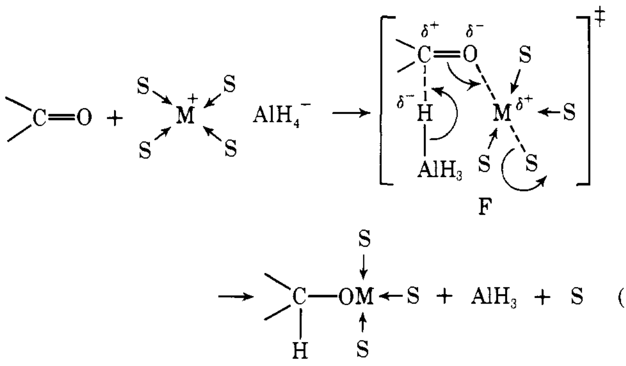
The first mechanism suggested involves nucleophilic attack by the $M^+AlH_4^-$ ion pair on the carbonyl carbon without the cation complexing the carbonyl oxygen (eq 5). If one compares the solvent separated ion pair of $NaAlH_4$ (C) with the contact ion pair (D), it might be expected that C is the better nucleophile because the negative charge of the aluminohydride ion is less neutralized by the completely solvated Na^+ ion compared with the partially solvated ion. Since C should react faster than D and since C and D are present in about equal amount, it appears likely that C would be the major reactive species. If the reactive species is the solvent separated ion pair of $LiAlH_4$ (B) and $NaAlH_4$ (C), then $NaAlH_4$ and $LiAlH_4$ would be expected to have similar reaction rates according to transition state E since the expected difference between completely solvated lithium and sodium ions should be small. However, $LiAlH_4$ is about eleven times more reactive toward MPK than $NaAlH_4$, a difference that is not easily explained on the basis of transition state E.



(5)

Perhaps the difference in the reaction rates of $LiAlH_4$ and $NaAlH_4$ (as described through transition state E) could be better explained by $LiAlH_4$ reacting through the solvent separated ion pair B while $NaAlH_4$ reacts as the contact ion pair D or a mixture of D and the solvent separated ion pair C. The solvent separated ion pair B should be more reactive than D because, as mentioned earlier, the partially solvated sodium ion in D neutralizes the charge of the aluminohydride ion more than the completely solvated lithium ion in B. However, using the same reasoning, it was pointed out that probably C and not D is the most reactive species for $NaAlH_4$; therefore, to explain any rate differences in terms of B and D does not seem reasonable. Also such an explanation would not be consistent with the fact that NR_4AlH_4 is less reactive[3] than $NaAlH_4$ toward camphor. Although NR_4AlH_4 is a contact ion pair in solution, its center to center distance is greater than that of $NaAlH_4$ contact ion pair.[5] Thus, NR_4^+ should neutralize the charge of the aluminohydride ion less than Na^+ and should be more reactive. This is not the case. Clearly, transition state E would appear more reasonable if the reaction rates of $LiAlH_4$ and $NaAlH_4$ toward MPK were more similar.

A second possible mechanism involves attack by the $M^+AlH_4^-$ ion pair on the carbonyl group where the cation is bound to the carbonyl oxygen during reduction (F). This process may simply involve the displacement of one molecule



(6)

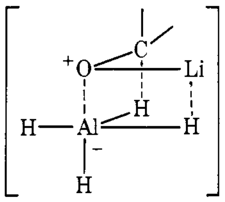
of THF solvent attached to M^+ by one molecule of ketone. In this case $LiAlH_4$ would be expected to react faster than $NaAlH_4$ since Li^+ would associate more strongly than Na^+ with the carbonyl oxygen and hence more strongly polarize the C=O bond.

It has been shown[4] that ketones associate with lithium ions in THF solutions of lithium salts. It is further known[7a,b] that $LiBH_4$ is more reactive than $NaBH_4$ toward ketones and that this difference in reactivity has been explained on the basis of the difference in the electrophilic nature of the lithium and sodium ions.[7b-d] Further evidence for complex formation between lithium ions and ketones is demonstrated by the substantial equilibrium constant (1.3 l. mol^{-1}) for complex formation between $LiClO_4$ and benzophenone in diethyl ether as determined by uv studies. Infrared studies of acetone in THF and diethyl ether show that increasing the $LiClO_4$ concentration broadens and shifts the carbonyl absorption from 1725 to 1720 cm^{-1}.[18] NMR studies of cyclohexanone (1.0 M) in diethyl ether show that addition of $LiClO_4$ (0.4 M) shifts the α protons of cyclohexanone 8 Hz and the β and γ protons 2 Hz downfield from the ether triplet.[19] Participation by the cation in the transition state is also indicated, not only by the difference in the reaction rates of $MAlH_4$ with ketones ($LiAlH_4 > NaAlH_4 > NR_4AlH_4$), but also by the dependence of the stereoselectivity of reduction of alicyclic ketones by $MAlH_4$ compounds.[3,13]

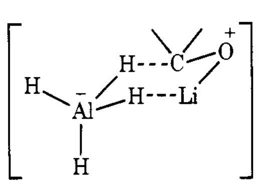
If the ketone is associating with the lithium cation during reduction by $LiAlH_4$ in THF, then causing the ketone to compete against a solvating agent stronger than THF should reduce the rate of reaction. This is found to be the case. The rate of reduction of MPK by excess $LiAlH_4$ in the presence of *N,N,N′,N′′,N′′′,N′′′*-hexamethyltriethylenetetramine (complexes lithium cation)[20] is reduced to about one-half ($k_2 = 0.29$ l. $mol^{-1}\ s^{-1}$) when amine:Li = 2:1. The kinetics of these experiments were complicated by the fact that the $LiAlH_4$–amine mixtures absorb in the region of 246 mμ and disappearance of the $\pi \rightarrow \pi^*$ band was still first order. All of the above studies providing evidence of association of ketones with lithium salts in ether solvents support transition state F, which represents the reduction of ketone by $LiAlH_4$ as proceeding via a prior or synchronous association of the ketone with Li^+ with respect to transfer of the hydride ion.

While polarization of the C=O bond by M^+ gives an understandable explanation of rate differences between $LiAlH_4$ and $NaAlH_4$, the effect of polarization or charge neutralization of the aluminohydride ion by M^+ on the reaction rate is more speculative. It appears reasonable that the further away the cation is from the anion the easier it will be in the rate-determining step for AlH_4^- to release hydride ion to the carbonyl carbon atom. Hence, free ions should react more readily than solvent separated ion pairs which should react more readily than contact ion pairs. Since the degree of ion pair separation is directly related to the ease of hydride transfer and also polarization of the carbonyl group by the cation, it is not possible in these systems to separate the two factors since their effect is in the same direction. However, the ability of the cation to complex and hence polarize the carbonyl group would appear to be the most important single factor in explaining the rate difference between $LiAlH_4$ and $NaAlH_4$.

Structures E and F are not drawn as detailed transition states, but are intended only to reflect possible participation of the cation in the transition state. Transition state F can be represented in more detail by structure G or H which represent



G



H

boat and chair conformations, respectively. Although the boat transition state might seem less probable because the orbital on oxygen is not correctly oriented to overlap the back lobe of Al-H orbital which is involved in bond breaking, there are at least two factors in favor of this transition state. First, interaction between aluminum and oxygen will lower the activation energy of the reaction and provide a pathway in which collapse of the transition state results directly in formation of the product ($LiAl(OCH)H_3$) without formation of an intermediate step. The second point is that such a boat transition state can be validly suggested if one assumes pentavalent aluminum involving pseudo rotation about the aluminum axis. The Li-H-Al interaction shown in G and H is reasonable also on the basis that M-H-M bridge bond systems are well known and would in addition add stability to the transition state. Such an interaction should lower E_a and result in a more negative $\Delta S^{\ddagger}$, which is the case as we shall see later on in this paper. Although kinetic data does not allow for the drawing of such detailed transition states, these suggestions do appear reasonable.

It has been assumed that the reactive species is the ion pair, $M^+AlH_4^-$, because both M^+ and AlH_4^- are present in the transition state. If the ion pair is the attacking species, the attack by M^+ on the carbonyl oxygen may be prior to or synchronous with a rate-determining hydride transfer step. Since complexation of metal ions such as Li^+ with ketones is extremely rapid, it is reasonable that complex formation takes place ahead of the rate-determining hydride transfer step. However, it is also possible that the attacking species is not the ion pair $M^+AlH_4^-$ but free ions. In this case the carbonyl group associates with free M^+ and then is attacked by a free AlH_4^-. Since this pathway produces the same transition state F, these studies do not allow one to distinguish between these possibilities; however, the nature of the transition state of the rate-determining step is the more vital concern, rather than how it is formed.

Activation Parameters. The reaction rates at several temperatures for the reduction of MPK by $LiAlH_4$ and $NaAlH_4$ in THF were obtained and the activation parameters calculated for each case. The results are tabulated in Table III. The enthalpy of activation for $LiAlH_4$ (10.5 kcal) is considerably lower than that for $NaAlH_4$ (18.1 kcal). This may be explained by the difference in polarization of the carbonyl group due to complexation by the cation in the transition state. The lithium ion because of its smaller size should polarize the carbonyl group more than sodium; thus, the hydride ion is more easily transferred from the aluminum atom to the carbon atom in the case of lithium. The much more negative value for the entropy of activation for $LiAlH_4$ (−26.2 eu) than for $NaAlH_4$ (−5.4 eu) requires that the transition state for $LiAlH_4$ reduction be considerably more ordered than that for $NaAlH_4$. Again, this would be consistent with the cation associating with the oxygen

Table III. Activation Parameters for the Reduction of Mesityl Phenyl Ketone by $LiAlH_4$ and $NaAlH_4$ in THF at 25 °C

	Rate constants, k_2 (l. mol^{-1} s^{-1})				Thermodynamic parameters			
	25 °C	35 °C	40 °C	45 °C	E_a, kcal	$\Delta H^{\ddagger}$, kcal	$\Delta G^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
$LiAlH_4$	0.595	1.02		1.82	10.5	9.9	17.7	−26.2
$NaAlH_4$	0.0587	0.176	0.212	0.440	18.1	17.5	19.1	−5.4

Table IV. Reaction of $LiAlD_4$ with Mesityl Phenyl Ketone in THF at 25.0 °C

Exp.	Concn of $LiAlD_4$, M × 10^3	Concn of ketone, M × 10^5	k_{obsd} × 10^3, s^{-1}	k_2, l. mol^{-1} s^{-1}
33	5.07	5.13	2.40	0.473
34	9.86	12.5	4.58	0.460
35	9.95	5.25	4.59	0.466
36	19.7	5.21	8.72	0.443

of the carbonyl group in the transition state. The lithium cation would order to a much greater extent the ketone molecule and both primary and secondary solvent molecules about itself than the sodium cation. Such a large negative value is also consistent with a six-center transition state such as shown in structures G and H. Since Li-H-Al bridge bonds should be considerably more stable than Na-H-Al bridge bonds, the large negative $\Delta S^{\ddagger}$ for the $LiAlH_4$ reaction compared with $NaAlH_4$ can also be attributed to some extent as being due to the restriction brought about in the transition state by this type of interaction.

Kinetics of Reduction of MPK by Lithium Aluminum Deuteride. Four kinetic experiments were carried out using excess $LiAlD_4$ to reduce MPK. The values of k_{obsd} and k_2 are given in Table IV. The disappearance of the $\pi \rightarrow \pi^*$ band was first order in the case of $LiAlD_4$, as was observed for $LiAlH_4$. The value of k_2 is independent of the $LiAlD_4$ concentration and the ratio of ketone to $LiAlD_4$ within experimental error.

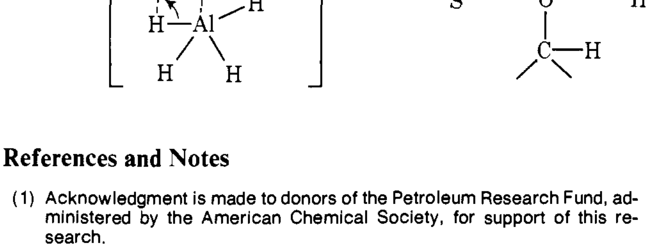
The average value of k_2 for the reaction of MPK with $LiAlD_4$ is 0.461 mol^{-1} s^{-1} and the value of k_H/k_D is 1.27 ± 0.14. Interpretation of k_H/k_D is not straightforward because it represents both primary and secondary deuterium isotope effects.

Sodium borohydride reduction of ketones as well as aqueous hydrolysis of $NaBH_4$ gives a k_H/k_D value of about 0.7.[8b,21,22] The inverse isotope effect for hydrolysis was thought to consist[22,23] of two parts: (1) a small, normal, primary kinetic isotope effect arising from the B-H bond breaking in the rate-determining step and (2) an inverse secondary kinetic isotope effect arising from the stiffening of the B-H bonds that do not break in the rate-determining step. The inverse secondary kinetic isotope effect was said to mask the primary effect. The secondary B-H bonds of borane have higher vibrational frequencies than those of the borohydride ion, thus the explanation that the secondary B-H bonds stiffen in the transition state. The alcoholysis of $LiAlH_4$ gave a k_H/k_D = 0.93 and 0.99 at −78 and −25 °C, respectively, and $NaBH_4$ gave a k_H/k_D = 0.53 and 0.63 at the same temperatures. The smaller isotope effect for $LiAlH_4$ compared with $NaBH_4$ was explained on the basis of less bond stiffening for the Al-H bonds than the B-H bonds in the transition state. The difference in vibrational frequencies between $LiAlH_4$ (1724 cm^{-1}) and AlH_3 (1778 cm^{-1}) are less than $NaBH_4$ (2264 cm^{-1}) and BH_3 (2560 cm^{-1}).

It is reasonable that the reduction of ketones by sodium borohydride gives an inverse isotope effect[22] because the secondary isotope effect masks the small primary isotope effect. If the secondary isotope effects for $NaBH_4$ and $LiAlH_4$ are inverse, but smaller for $LiAlH_4$ than $NaBH_4$, then the small value of k_H/k_D reported here for $LiAlH_4$ may be explained by a small primary isotope effect which is not completely masked by secondary effects. The small isotope effect would then be consistent with a rate-determining step involving transfer of the hydride from the aluminum to the carbonyl carbon. The small value of k_H/k_D is consistent with both an early or late transition state. However, the interpretation of the magnitude of the isotope effect is not clear not only because of the secondary isotope effect, but also because of the uncertainty of the Al···H···C angle in the transition state, and other possible factors.[23] In recent years an increasing number of theories and examples have been presented contrary to the concept of product development control, which supposedly requires a late transition state. Although the small k_H/k_D value presented is not proof for an early transition state, the above considerations suggest that this is the case.

Conclusions

The reaction of $LiAlH_4$ with MPK in THF under the conditions of this study is first order in $LiAlH_4$ and first order in MPK. The deuterium kinetic isotopic effect, k_H/k_D = 1.27 ± 0.14, indicates that the rate-controlling step is the transfer of the hydride from the aluminum to the carbonyl carbon in an early transition state. The results reported herein are best explained by reaction of $LiAlH_4$ and $NaAlH_4$ as solvent separated ion pairs and/or free ions. The greater reactivity of $LiAlH_4$ compared with $NaAlH_4$ may be explained by the stronger coordination of lithium compared with sodium with the carbonyl oxygen, thus assisting to a greater degree in the hydride transfer. The entropies of activation indicate that Li^+ is more strongly bound in the transition state to the carbonyl oxygen than Na^+ and suggests the possibility of a cyclic transition state. The following mechanism is consistent with the data reported herein:



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Effects of Reduction on the Olefinic Bond in Two Stilbene Dilithium Complexes

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Abstract: Two complexes containing a dilithiated stilbene fragment have been prepared and isolated from the reactions of 1,2-diphenylethane with N-chelated butyllithium reagents. The molecular and crystal structures of these compounds, stilbene bis(lithium tetramethylethylenediamine) and stilbene bis(lithium pentamethyldiethylenetriamine), have been determined by x-ray diffraction techniques. Each structure contains two amine-solvated lithium atoms located above and below the olefinic bond of a stilbene molecule. The compound containing tetramethylethylenediamine exhibits crystallographic $2/m$ symmetry, and the stilbene group is thus required by symmetry to be planar. The pentamethyldiethylenetriamine complex has crystallographic $\bar{1}$ symmetry; however, the stilbene group is also planar. In both structures, the stilbene molecule is in a trans configuration about the C(7)–C(7)′ bond. The planar configuration is in contrast to results from solution studies of disproportionation of arylethylene anions and the photochemistry of stilbene, where a twisted structure was proposed. The planar dianion allows the maximum amount of electron density around each lithium atom. The stilbene group is disordered in each structure, occupying either of two orientations about the crystallographic inversion center. The C(7)–C(7)′ distance has increased in each structure by ~0.1 Å compared with the distance in *trans*-stilbene. Stilbene bis(lithium tetramethylethylenediamine) crystallizes in the monoclinic space group $C2/m$ with two molecules in a unit cell of dimensions a = 12.613 (7) Å, b = 13.899 (6) Å, c = 8.179 (5) Å, and β = 105.89 (3)°. Stilbene bis(lithium pentamethyldiethylenetriamine) crystallizes in the monoclinic space group $P2_1/c$ with two molecules in a unit cell of dimensions a = 10.387 (5) Å, b = 11.531 (6) Å, c = 15.470 (5) Å, and β = 113.07 (2)°. Full-matrix least-squares refinement of each structure has given final R_w factors of 0.064 for stilbene bis(lithium tetramethylethylenediamine), based on 1260 observations, and 0.064 for stilbene bis(lithium pentamethyldiethylenetriamine), based on 2547 observations.

Introduction

There has been extensive speculation concerning the geometry of the stilbene molecule in its reduced form as the mono- or dianion. Garst and Szwarc have observed that the metal cation, solvent, aggregation, and steric effects are important in determining the equilibrium position in the disproportionation of arylethylene radical anions.[1-2] Studies of monoanions of the sterically strained hydrocarbons tetraphenylethylene[2-4] and α-methylstilbene[5] show that they disproportionate much more readily than the stilbene monoanion, suggesting a relief of steric strain upon disproportionation. A change in structural geometry on formation of the dianion would relieve steric strain, assuming the monoanions were required to be planar, but the dianion could twist by 90° about the ethylenic carbon–carbon bond.[5] Szwarc recently reported the existence of distinct *cis*- and *trans*-stilbene dianions in the electron transfer induced cis–trans isomerization of stilbene.[7] He proposed that cations associated with both phenyl groups in the cis dianion stabilized the cis configuration to rotation of one phenyl group with the other.

As pointed out by Walsh[8] and more recently Pearson,[9] there is a direct correspondence between the excited state and anion geometry, if the extra one or two electrons of the mono- or dianion are in the same molecular orbital as the one which is populated in the excited state. The point group symmetries of the two systems should be the same, and information about the geometry of one species can be obtained from studies of the other. In particular, Garst has observed that photochemical studies of the cis–trans conversion of stilbene are related to the question of the dianion's geometry.[5] Results from several photochemical studies have been interpreted in terms of the lowest energy excited state of stilbene being a twisted triplet configuration.[10,11] Calculations[12,13] have also shown a twisted