Organometallic Exchange Reactions. II. Lithium-7 and Proton Nuclear Magnetic Resonance Spectra of Alkyllithium and Lithium Tetraalkylmetalate Solutions in Ether[1]

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Abstract: The ^1H and ^7Li nmr spectra of ether solutions of the following mixtures were examined in the temperature range +30 to −60°: $LiCH_3$–$LiB(CH_3)_4$, $LiCH_3$–$LiAl(CH_3)_4$, $LiAl(CH_3)_4$–$LiB(CH_3)_4$, $Al(CH_3)_3$–$LiAl(CH_3)_4$, $Al(CH_3)_3$–$LiB(CH_3)_4$, LiC_2H_5–$LiAl(C_2H_5)_4$, LiC_2H_5–$LiGa(C_2H_5)_4$, $LiAl(C_2H_5)_4$–$LiGa(C_2H_5)_4$. In addition the ^7Li and ^1H spectra of the pure components in ether were also obtained. Alkyl group exchange is slow on the nmr time scale in all mixed systems except for $Al(CH_3)_3$–$LiAl(CH_3)_4$. The rate-determining process in this system appears to be formation of solvent-separated ion pairs from contact ion pairs: $Li^+,Al(CH_3)_4^- \rightarrow Li^+ \| Al(CH_3)_4^-$. The Arrhenius activation energy is estimated to be 9.1 ± 1 kcal/mole. ^7Li exchange obeys the same kinetics in the $LiCH_3$–$LiAl(CH_3)_4$ and $LiCH_3$–$LiB(CH_3)_4$ systems. The rate-determining step appears to be dissociation of the methyllithium tetramer: $(LiCH_3)_4 \rightarrow 2(LiCH_3)_2$. The Arrhenius activation energy is estimated, as an average value for the two systems studied, to be 11.2 ± 1 kcal/mole. ^7Li exchange in the $LiMR_4$–$LiM'R_4$ systems is rapid at the lowest temperature studied, about −57°. The mechanism probably involves bimolecular interaction of the two lithium-bearing species, with facile exchange of Li^+.

The exchange of lithium and alkyl groups between bonding sites in metal alkyl compounds is of interest in connection with bonding and structural considerations. Recent studies using nmr techniques have demonstrated that valuable information can be obtained from quantitative kinetic studies of exchange reactions.[3] ^7Li and ^1H spectra of ether solutions of methyllithium and ethyllithium were interpreted in terms of tetramer formation. The inversion of configuration of the metal-bearing carbon has been studied in two alkyl metal systems.[4,5] The exchange of alkyl groups in aluminum alkyls has been studied in basic solvents,[6] but no detailed kinetic data were obtained.

In recent years the structures of alkali metal tetraalkylaluminates have been studied both in solution and the solid state. The crystal structure of lithium tetraethylaluminate indicates a largely ionic structure.[7] The infrared spectra of several tetraalkylaluminates indicate a strong interaction between ether and the aluminates.[8] The conductances of sodium tetraethylaluminate in ether and toluene also point toward specific ion–solvent interaction.[9]

Exchanges of ^7Li and of methyl groups in ether solutions containing mixtures of alkyllithium and lithium tetraalkylmetalate compounds can be considered as prototypes of characteristic reactions of these compounds. In this paper we report extensive nmr data which yield information on these exchanges.

Experimental Section

Materials and Procedures. All operations were performed in a glove box under an argon atmosphere. The most rigorous exclusion of both oxygen and water is essential in obtaining reproducible kinetic data. Concentrations of methyl- and ethyllithium solutions were determined by decomposing aliquot samples with water and immediately titrating to a phenolphthalein end point with standard 0.1 *N* hydrochloric acid. The concentrations of aluminum alkyl and lithium tetraalkylaluminate solutions were determined by decomposing aliquot samples with dilute nitric acid and mixing with an excess of standard 0.1 *N* EDTA. Excess EDTA was then titrated with a standard 0.1 *N* zinc chloride solution using dithizone as indicator.

Aluminum alkyls were obtained from the Ethyl Corp. and Texas Alkyls, Inc., and were used without further purification. Mallinckrodt analytical reagent grade anhydrous ether was distilled from lithium aluminum hydride and stored over sodium wire. Ethyllithium was obtained from Lithium Corporation of America, dimethylmercury from Eastman Organic Chemicals, and boron trifluoride from the Matheson Co., Inc.

Ethyllithium was purified by recrystallization from benzene, and then dissolved in cold ether to give a clear, colorless solution.

Preparations of the following substances were made in accordance with previously published procedures: lithium tetramethylborate, lithium tetraethylaluminate, lithium tetramethylaluminate, methyllithium, and triethylgallium. Lithium tetraethylgallate was prepared by adding ethyllithium in benzene to a solution of triethylgallium in benzene. The white gelatinous precipitate, which closely resembles the analogous aluminum compound, was further purified by recrystallization from benzene.

Lithium tetramethylborate was purified by recrystallization from benzene. The purified compound consisted of white needle-like crystals; it slowly sublimes under vacuum at 140°.

The association of lithium tetramethylborate in cineole was determined by a freezing point depression measurement using the apparatus previously described.[10] Cineole was dried by refluxing over a mixture of calcium hydride and lithium aluminum hydride for 3 hr, followed by distillation. It was then stored in an inert atmosphere.

Measurements of nmr spectra were made in the manner previously reported.[3] Samples were degassed, sealed under vacuum in standard size nmr tubes, and stored in Dry Ice. Special precautions were taken to keep the mixtures of alkyllithium with tetraalkylborates or tetraalkylaluminates cold; precipitates quickly formed in these mixtures at room temperature.

Interpretation of Nmr Data. Information regarding the kinetics of exchange processes can be extracted from nmr data in various ways.[11] In this work use has been made of two methods: measurement of line half-intensity widths in the slow-exchange region, and

(1) This research was sponsored by a grant from the National Science Foundation.
(2) Alfred P. Sloan Research Fellow.
(3) L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 2174 (1966).
(4) M. Witanowski and J. D. Roberts, *ibid.*, **88**, 736 (1966).
(5) G. Fraenkel and D. T. Dix, *ibid.*, **88**, 979 (1966).
(6) (a) T. Mole and J. R. Surtees, *Australian J. Chem.*, **17**, 310 (1964); (b) T. Mole, *ibid.*, **18**, 1183 (1965).
(7) R. L. Gerteis, R. E. Dickerson, and T. L. Brown, *Inorg. Chem.*, **3**, 872 (1964).
(8) K. Mach, *J. Organometal. Chem.* (Amsterdam), **2**, 410 (1964).
(9) M. C. Day, H. M. Barnes, and A. J. Cox, *J. Phys. Chem.*, **68**, 2595 (1964).
(10) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Am. Chem. Soc.*, **82**, 2135 (1964).
(11) C. S. Johnston, Jr., *Advan. Magnetic Resonance*, **1**, 33 (1965).

calculation of the over-all line shape for a two-site exchange as a function of τ.

It is worth pointing out that the systems under investigation are particularly suitable for nmr analysis of rates because the individual components of the two site system can each be examined throughout the entire temperature range of interest. Thus, the line half-intensity widths and the chemical shift difference in the absence of exchange are known.

The most reliable method for evaluation of exchange rate from the nmr spectral data consists in matching the observed spectra with a series of calculated spectra in which the exchange rate is varied. In the present case it is possible to assign values of $1/T_2$, $\delta\omega$, p_A, and p_B at each temperature, and thus to calculate a realistic line shape as a function of exchange rate. The line-shape function is given by suitable modifications of the Bloch phenomenological equations as developed by Gutowsky and Holm,[12] but retaining terms involving the transverse relaxation times.

$$v = \frac{\left\{P\left[1+\tau\left(\frac{p_B}{T_{2A}}+\frac{p_A}{T_{2B}}\right)\right]+Q\left[R+\tau\left(\frac{1}{T_{2B}}-\frac{1}{T_{2A}}\right)\frac{\delta\omega}{2}\right]\right\}\omega_1 M_0}{P^2+R^2+\tau^2\left(\frac{1}{T_{2B}}-\frac{1}{T_{2A}}\right)^2\left(\frac{\delta\omega}{2}\right)^2+2R\tau\left(\frac{1}{T_{2B}}-\frac{1}{T_{2A}}\right)\frac{\delta\omega}{2}} \quad (1)$$

$$P = \tau\left[\frac{1}{T_{2A}T_{2B}}-\Delta\omega^2+\left(\frac{\delta\omega}{2}\right)^2\right]+\frac{p_A}{T_{2A}}+\frac{p_B}{T_{2B}}$$

$$Q = \tau\left[\Delta\omega-\frac{\delta\omega}{2}(p_A-p_B)\right]$$

$$R = \Delta\omega\left[1+\frac{\tau}{T_{2A}}+\frac{\tau}{T_{2B}}\right]+\frac{\delta\omega}{2}(p_A-p_B)$$

$$\tau = \frac{\tau_A\tau_B}{\tau_A+\tau_B} \quad (2)$$

The notations employed in these expressions have their usual denotations: v, the transverse component of the resultant magnetic moment perpendicular to the rotating field H_1, which is proportional to the absorption intensity; ω_1, the applied rotating radiofrequency field; $\Delta\omega$, the difference in frequencies of the applied radiofrequency and the frequency at the center of the two resonance components; $\delta\omega$, the difference of the resonance frequencies corresponding to the states A and B; τ_A, τ_B the mean lifetimes for a stay on A and B sites; p_A, p_B, the fractional populations of A and B sites; T_2, the transverse relaxation times (we assume that these are obtainable from the half-intensity line width for the pure component); M_0, the equilibrium value of the z component of the resultant magnetic moment.

A Fortran program was written to compute a normalized line-shape function over the frequency range of interest, for a given set of input parameters. The requisite values of the variables were obtained from measurements on the pure components over the entire temperature range. The chemical-shift difference between pure components was obtained from measurements of the chemical shifts of each component at room temperature, and of the chemical-shift difference in a mixed solution at a temperature well below the exchange range. These values were usually close. Any change in $\delta\omega$ was assumed to be linear with temperature. p_A and p_B were obtained from integrations of areas on a number of spectra at low temperatures, well below the exchange region.

Calculation of the over-all line shape is most effective as a means of evaluating τ when the relative populations of the two sites are not grossly different. It is sometimes possible to test a mechanism by evaluating the dependences of the individual τ_A and τ_B values on concentration, or on a ratio of two concentrations. For this purpose it is best to examine the individual line widths at a temperature corresponding to slow exchange. Under these conditions, the mean lifetime at site i, τ_i, is related to the line width at half-intensity, $\Delta_{1/2}$, by the expression

$$1/\tau_i = \pi(\Delta_{1/2} - \Delta_{1/2}^0) \quad (3)$$

(12) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

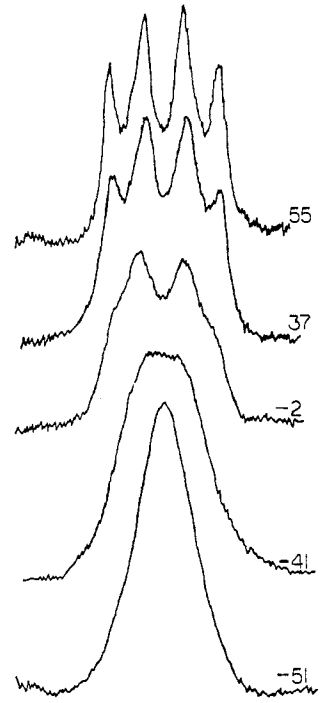


Figure 1. ^{1}H spectrum of $LiB(CH_3)_4$ in ether as a function of temperature.

where $\Delta_{1/2}^0$ is the measured half-intensity width for the ith component in the absence of exchange.

Measurement of $1/\tau_i$ for a single sample at a series of temperatures in the temperature region below coalescence can also be employed to determine the activation energy for exchange. Although the temperature range is limited, the method has the advantage, in certain of the systems reported on here, that $\Delta_{1/2}^0$ can be accurately evaluated.

Results and Discussions

The ^{7}Li resonance absorptions of all compounds investigated in ether solution appear as single, symmetrical lines throughout the temperature range of interest, +30 to −60°. The ^{7}Li chemical shifts at 30° measured in ppm relative to aqueous lithium bromide in an external capillary reference, are as follows: CH_3Li, −1.32; $LiAl(CH_3)_4$, +1.30; $LiB(CH_3)_4$, +1.63; C_2H_5Li, −0.58; $LiAl(C_2H_5)_4$, +1.47; $LiGa(C_2H_5)_4$, +1.73. Resonances which appear downfield from the standard are assigned a negative chemical shift.

The ^{1}H spectrum of $LiGa(C_2H_5)_4$ is similar to those of LiC_2H_5 and $LiAl(C_2H_5)_4$, previously reported.[7] It consists of a triplet centered at τ 8.9 and a quartet centered at τ 10.2. The single J_{AX} coupling constant is 8.0 cps. The ^{1}H spectrum of $LiB(CH_3)_4$ consists of a quartet centered at τ 10.5 which is partially collapsed at room temperature. At 56°, the highest temperature studied, the spectrum more nearly approximates a quartet of lines of equal intensity, with a 3.4-cps separation, arising from B–CH_3 coupling (I for ^{11}B is $^3/_2$). This value is close to the 4.0 cps observed[13] for B–CH_2–CH_3 coupling in $B(C_2H_5)_4^-$. With a decrease in temperature the quartet progressively collapses, and consists of a broadened symmetrical absorption at −52°. A few proton resonance spectra of representative temperatures are shown in Figure 1. It is interesting to note that no evidence of B–CH coupling was observed

(13) A. G. Massey, E. W. Randall, and D. Shaw, *Spectrochim. Acta*, 20, 379 (1964).

in the ^{11}B spectrum of $LiB(CH_3)_4$.[14] We examined the ^{11}B spectrum at temperatures up to +55°, but were unable to resolve the multiplet structure. The absorption band shape no doubt results from a slight inherent broadness of the ^{11}B absorption, coupled with the rather sharp central peaking of the 13-line multiplet resulting from boron–proton coupling.

The ^1H spectrum of $LiAl(CH_3)_4$ consists of a single, symmetrical absorption at all temperatures, with a τ value of 11.1. The line width steadily *decreases* with decreasing temperature, in the range +50 to −50°. The half-intensity widths at these two temperatures are 3.8 and 1.7 cps, respectively. ^{27}Al possesses a nuclear spin of $^5/_2$, with a nuclear magnetic moment which is somewhat smaller than the moment of the ^{11}B nucleus. It is to be expected, therefore, that ^{27}Al–CH coupling might be operative in those cases where the relaxation time of ^{27}Al is sufficiently long. Such a scalar coupling might not be evidenced by a distinct multiplet structure in the proton spectrum, but rather by a broadening of the proton resonance. A shortening of the relaxation time of ^{27}Al would result in a collapse of the unresolved proton resonance multiplet, with a consequent apparent sharpening of the line. The proton resonance data for $LiB(CH_3)_4$ and $LiAl(CH_3)_4$ thus show the same type of temperature dependence.

The lithium tetraalkylmetalates are polar compounds and probably subsist as ion pairs in a solvating medium such as ether. It is less clear that this would be the case for $LiBR_4$ compounds, but even these should show some tendency to ionize in a polar, strongly solvating medium. Recent work with alkali metal salts of various kinds, but particularly with fluorenyl salts, reveals a distinct equilibrium between contact and solvent-separated ion pairs.[15] In a very strongly solvating medium such as THF, fluorenyllithium is largely in the form of solvent-separated ion pairs, whereas the reverse is true for the sodium salt. In less strongly solvating and less polar media (*e.g.*, dioxane), on the other hand, both substances are largely in the form of contact ion pairs. Although quantitative data are not available, it is quite likely that the tetraalkylmetalates which are of interest in the present study are largely in the form of contact ion pairs in ether, and that an equilibrium exists between the contact and solvent-separated ion pairs. In agreement with this, the freezing point lowerings of cineole solutions of $LiB(CH_3)_4$ yield association numbers n = 1.07, 0.99, 0.97, and 0.89 for solutions of molalities 0.0518, 0.0146, 0.0143, and 0.0271, respectively.

The tetrahedral symmetry of the environment about the metal atom in the tetraalkylmetalate anion is strongly perturbed by the formation of a contact ion pair, whereas only a slight effect should be evidenced in the solvent-separated ion pairs. So long as the equilibrium between the two forms of ion pairs is rapid, the effective field gradient experienced by the central atom on the anion should be small, and quadrupolar relaxation of the nuclear spin on the central atom should be slow. This is the condition which characterizes the $Al(CH_3)_4^-$ and $B(CH_3)_4^-$ ions at higher temperatures in ether. With a lowering of temperature, the equilibrium between contact and solvent-separated ion pairs is slowed; quadrupolar relaxation of the ^{11}B and ^{27}Al nuclear spins becomes important, and the scalar coupling with methyl protons is obliterated.

It is perhaps worth emphasizing that the proton resonance data for $LiB(CH_3)_4$ and, with less certainty, for $LiAl(CH_3)_4$, rule out a rapid exchange process of the form

$$LiM(CH_3)_4 = LiCH_3 + M(CH_3)_3$$

Such an exchange would result in an absence of scalar coupling between M and the protons, contrary to what is observed.

A number of mixed solution systems were examined for evidence of fast- or slow-exchange processes, as revealed in the ^1H and ^7Li spectra. In some instances our results are limited to observation at a few temperatures only; in others, detailed temperature dependence studies were carried out. The following mixed systems were examined and will be referred to in the ensuing discussion: $LiCH_3$–$LiB(CH_3)_4$, $LiCH_3$–$LiAl(CH_3)_4$, $LiAl(CH_3)_4$–$LiB(CH_3)_4$, $Al(CH_3)_3$–$LiAl(CH_3)_4$, $Al(CH_3)_3$–$LiB(CH_3)_4$, LiC_2H_5–$LiAl(C_2H_5)_4$, LiC_2H_5–$LiGa(C_2H_5)_4$, $LiAl(C_2H_5)_4$–$LiGa(C_2H_5)_4$.

In all systems containing more than one type of lithium-bearing species (*e.g.*, $LiCH_3$–$LiB(CH_3)_4$), ^7Li exchange is rapid at room temperature. In all systems containing alkyl groups in more than one chemically distinguishable site, alkyl group exchange is slow at room temperature, with one exception, the $Al(CH_3)_3$–$LiAl(CH_3)_4$ system. The proton resonance spectra of a representative solution of $Al(CH_3)_3$ and $LiAl(CH_3)_4$ at various temperatures are shown in Figure 2.

The mechanism of this exchange can be understood in terms of the equilibrium between the contact and solvent-separated ion-pair forms of $LiAl(CH_3)_4$.

$$\underset{A}{Li^+,Al^*(CH_3)_4^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{C^*}{Li^+||Al^*(CH_3)_4^-} \qquad (4)$$

Solvent-separated ion pairs are very much more reactive in general than the contact ion pairs.[15] Exchange with $Al(CH_3)_3$ thus may be assumed to proceed *via* the solvent-separated ion-pair species.

$$\underset{C^*}{Li^+||Al^*(CH_3)_4^-} + \underset{B}{Al(CH_3)_3} \xrightarrow{k_2} \underset{C}{Li^+||Al(CH_3)_4^-} + \underset{B^*}{Al^*(CH_3)_3} \qquad (5)$$

(The symbols under the chemical formulas, and the asterisks, are a shorthand notation useful in discussing the rate expressions which apply to this system.) The expressions for reciprocal mean lifetimes for type A and B methyl groups can be obtained by deriving the usual kinetic expressions

$$\frac{d(C^*)}{dt} = k_1(A) - k_{-1}(C^*) - k_2(C^*)(B) = 0$$

$$(C^*) = \frac{k_1(A)}{k_{-1} + k_2(B)}$$

$$\frac{d(B^*)}{dt} = k_2(C^*)(B) = \frac{k_2k_1(A)(B)}{k_{-1} + k_2(B)}$$

$$\frac{1}{\tau_A} = \frac{3}{4}\frac{1}{(A)}\frac{d(B^*)}{dt} = \frac{3}{4}\frac{k_2k_1(B)}{k_{-1} + k_2(B)} \qquad (6)$$

(14) R. J. Thompson and J. C. Davis, Jr., *Inorg. Chem.*, **4**, 1464 (1965).
(15) J. Smid and T. E. Hagen-Esch, *J. Am. Chem. Soc.*, **88**, 307, 318 (1966).

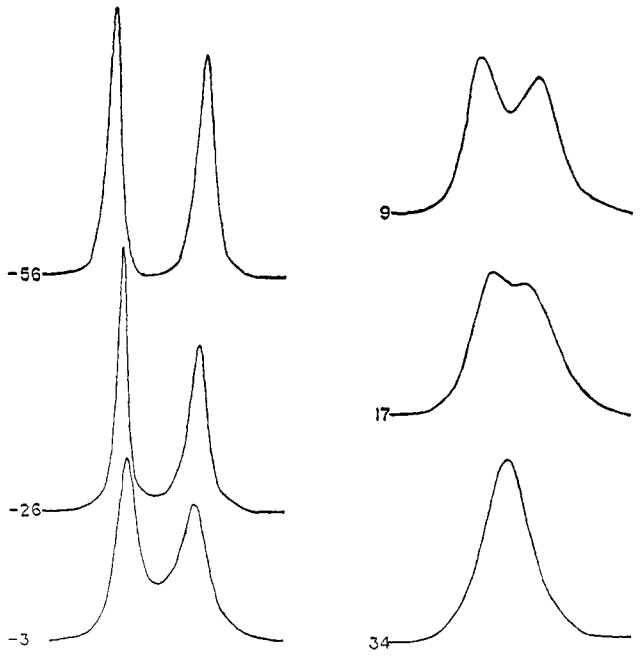


Figure 2. The ^1H resonance spectrum of an $Al(CH_3)_3$–$LiAl(CH_3)_4$ solution in ether, at various temperatures.

(The factor $^3/_4$ arises because one of the four methyl groups, in being transferred to $Al(CH_3)_3$, retains the character of $Al(CH_3)_4^-$-type methyl group.)

$$\frac{1}{\tau_B} = \frac{1}{(B)}\frac{d(B^*)}{dt} = \frac{k_2k_1(A)}{k_{-1} + k_2(B)} \quad (7)$$

for $k_2(B) \gg k_{-1}$

$$\frac{1}{\tau_A} = \frac{3}{4}k_1 \qquad \frac{1}{\tau_B} = k_1\frac{(A)}{(B)} \quad (8)$$

for $k_{-1} \gg k_2(B)$

$$\frac{1}{\tau_A} = \frac{3}{4}k_2K_i(B)\frac{1}{\tau_B} = k_2K_i(A)\ K_i = k_1/k_{-1}$$

The two different assumptions about the relative magnitudes of k_{-1} and $k_2(B)$ lead to quite different expectations for the concentration dependences of the exchange rate. The ^1H spectra of a series of solutions containing varying concentrations of $LiAl(CH_3)_4$ and $Al(CH_3)_3$ were examined at a temperature in the slow-exchange region, $-31°$. The reciprocal mean exchange times for the two types of protons sites were determined from measurements of the half-intensity widths (see Experimental Section); the results are listed in Table I.

Table I. Concentration Dependences of the Reciprocal Mean Exchange Times for CH_3 Group Exchange in the $Al(CH_3)_3$–$LiAl(CH_3)_4$ System in Ether at $-31°$

A $[LiAl(CH_3)_4]$	B $[Al(CH_3)_3]$	$1/\tau_A$	$1/\tau_B$
0.379	0.673	2.7	0.80
0.337	0.401	2.6	1.5
0.253	0.215	2.7	3.1
0.169	0.0730	1.9	5.4
0.126	0.027	1.8	7.3

It appears from these data that the exchange rate for $LiAl(CH_3)_4$ is essentially independent of the concentration of either component, in agreement with the expectations based on eq 8; the test of expression 8 for the $Al(CH_3)_3$ exchange rate is shown in Figure 3. With the exception of one data point (which might very well be at variance because the spectrum for that sample is rather far removed from the slow-exchange approximation), the relationship is reasonably well obeyed and extrapolates to near the origin, as it should. As a further test of rate expressions 8, it can be noted that the slope of the line in Figure 3 should correspond to k_1; from the observed slope a value of 2.2 is obtained for k_1. k_1 is also given by $^4/_3(1/\tau_A)$; from the average of the values of $1/\tau_A$ listed in Table I, k_1 is 3.1. Considering the uncertainties and difficulties in reliably reducing the nmr data, this is quite satisfactory agreement and provides strong indication that methyl exchange in the $Al(CH_3)_3$–$LiAl(CH_3)_4$ system is rate determined by formation of solvent-separated ion pairs from contact ion pairs. The data are not in agreement with the hypothesis that the rate-determining step is eq 5, or that $k_{-1} \gg k_2(B)$. Our analysis does not identify the role of free ions, as compared with solvent-separated ion pairs. In the absence of strong solvation of the anion, the reactivities of solvent-separated ion pairs and free anions should be about the same. The present data are not adequate for a test of this point, inasmuch as accurate conductivity and other requisite information are lacking.

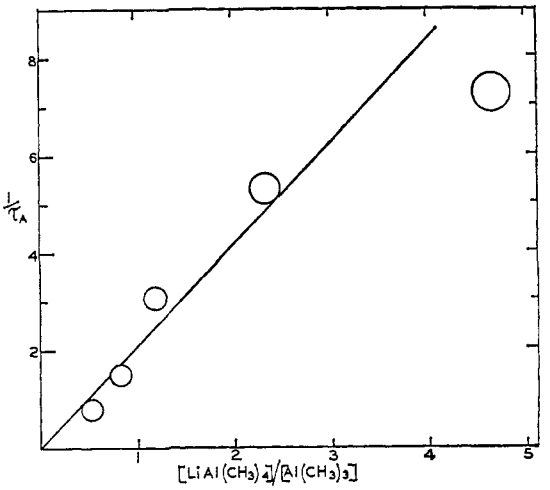


Figure 3. Dependence of reciprocal mean exchange time for $Al(CH_3)_3$ methyl groups on the ratio $[Al(CH_3)_3]/[LiAl(CH_3)_4]$, at $-31°$ in ether.

On the basis of the comparative exchange behavior of the $Al(CH_3)_3$–$LiAl(CH_3)_4$ and $Al(CH_3)_3$–$LiB(CH_3)_4$ systems, it appears that the process

$$Li^+||B(CH_3)_4^- + Al(CH_3)_3 \longrightarrow Li^+||Al(CH_3)_4^- + B(CH_3)_3 \quad (9)$$

does not proceed readily. The equilibrium must in any case lie far to the left; there is no evidence in the nmr spectra of $LiAl(CH_3)_4$ formation after many days. $B(CH_3)_3$ is weakly solvated by ether as compared with $Al(CH_3)_3$.[16] It is therefore understandable that the activation energy for reaction 9 should be large; the transition state for methyl exchange no doubt involves solvent in an important degree. The slow exchange of $Al(CH_3)_3$ with $LiB(CH_3)_4$ is in all probability not due

(16) F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958).

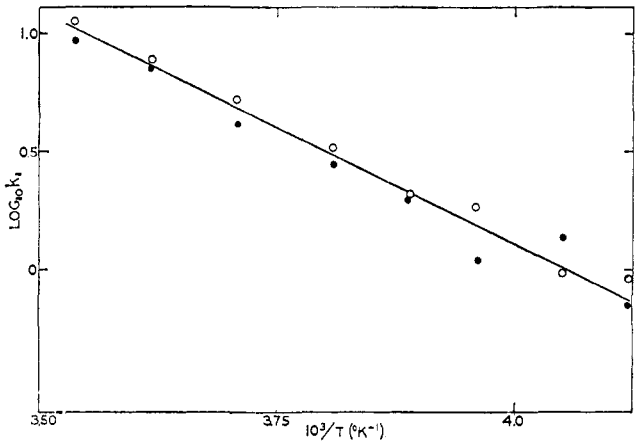


Figure 4. Arrhenius plot of log k_1 *vs.* $1/T$ for methyl group exchange in the $Al(CH_3)_3$–$LiAl(CH_3)_4$ system in ether: ○, $^4/_3(1/\tau_A)$; ●, $(B)/(A)\tau_B$. The line is described by the equation $\log k_1 = -1975(1/T) + 8.0$.

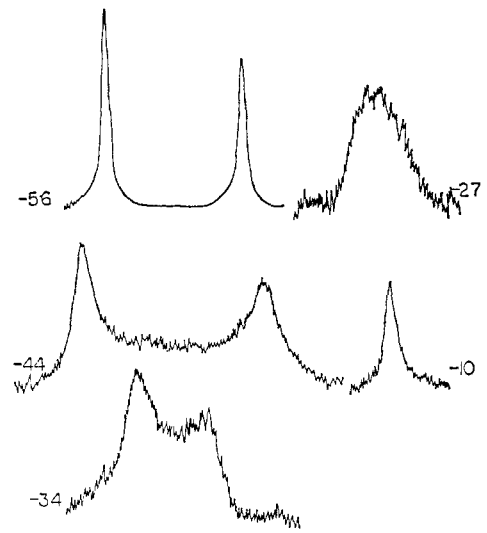


Figure 5. Representative ^7Li spectra for the $LiCH_3$–$LiB(CH_3)_4$ system in ether.

to a slow equilibrium between contact and solvent-separated ion pairs in $LiB(CH_3)_4$, inasmuch as the ^1H spectrum of this compound indicates a rapid exchange at temperatures where the exchange of eq 9 is still slow.

The temperature dependences of the line widths of both absorptions in a sample containing $LiAl(CH_3)_4$ (A), and $Al(CH_3)_3$ (B), present in such relative concentrations as to give equal absorption areas for the two types of methyl groups, were observed in the temperature range -30 to $+10°$. According to eq 8, $^4/_3(1/\tau_A)$ and $(B)/(A)\tau_B$ should both equal k_1. Figure 4 shows a graph of the logs of both these quantities *vs.* $1/T$. The data from both sets of measurements describe a single straight line. From the slope, an Arrhenius activation energy of 9.1 kcal/mole, with an estimated uncertainty of 1 kcal/mole, is obtained. This represents the activation energy for formation of solvent-separated from contact ion pairs in $LiAl(CH_3)_4$.

Mixtures of $LiB(CH_3)_4$ and $LiAl(CH_3)_4$ exhibit rapid ^7Li exchange at the lowest temperature studied, $-57°$; from this it may be deduced that a process of the form

$$Li^+,M(CH_3)_4^- \longrightarrow Li^+ \,|\, M(CH_3)_4^- \qquad (10)$$

(or the production of free ions) is *not* rate determining in the exchange. The rate of (10) for $LiAl(CH_3)_4$ is known from the data for methyl group exchange in the $LiAl(CH_3)_4$–$Al(CH_3)_3$ system, discussed above. Judging from the temperature dependence of the proton spectrum of $LiB(CH_3)_4$ it seems unlikely that process 10 is faster for this compound than for the aluminum analog. ^7Li exchange probably occurs by a simple bimolecular reaction involving contact ion pairs, in which transfer of $^7Li^+$ should be quite facile. These same considerations also probably apply in the $LiAl(C_2H_5)_4$–$LiGa(C_2H_5)_4$ system, in which ^7Li exchange is rapid at $-57°$.

Solutions containing either $LiAl(CH_3)_4$ or $LiB(CH_3)_4$ with methyllithium exhibit rapid ^7Li exchange at room temperature. On lowering the temperature the slow-exchange limit in both instances is reached before $-50°$. Some representative ^7Li spectra for the $LiCH_3$–$LiB(CH_3)_4$ system are shown in Figure 5.

The temperature dependences of the spectra are closely similar for the $LiCH_3$–$LiAl(CH_3)_4$ and $LiCH_3$–$LiB(CH_3)_4$ systems. The calculated rate constants and activation energies for the two systems are identical within experimental error. The following mechanism is consistent with the nmr data.

$$\underset{(T)}{(Li^*CH_3)_4} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(D)}{2(Li^*CH_3)_2} \qquad (11)$$

$$\underset{(D)}{(Li^*CH_3)_2} + \underset{C}{LiM(CH_3)_4} \xrightarrow{k_2} \underset{C^*}{Li^*M(CH_3)_4} + \underset{D}{(LiCH_3)_2}$$

$$\frac{d(D)}{dt} = 2k_1(T) - 2k_{-1}(D)^2 - k_2(D)(C) = 0$$

$$(D) = \frac{2k_1(T)}{2k_{-1}(D) + k_2(C)}$$

$$\frac{d(C^*)}{dt} = k_2(D)(C) = \frac{2k_1k_2(T)(C)}{2k_{-1}(D) + k_2(C)}$$

assuming $k_2(C) \gg 2k_{-1}(D)$

$$\frac{d(C^*)}{dt} = 2k_1(T)$$

$$\frac{1}{\tau_C} = \frac{1}{(C)}\frac{d(C^*)}{dt} = 2k_1\frac{(T)}{(C)}\frac{1}{\tau_T} = \frac{1}{4}\frac{1}{(T)}\frac{d(C^*)}{dt} = \frac{k_1}{2} \qquad (12)$$

$$\frac{1}{\tau} = \frac{1}{\tau_C} + \frac{1}{\tau_T} = \frac{k_1}{2}\left(\frac{4(T) + 1}{(C)}\right)$$

$$\frac{1}{\tau} = \frac{k_1}{2}\left(\frac{4[(LiCH_3)_4]}{[LiM(CH_3)_4]} + 1\right) \qquad (13)$$

$[(LiCH_3)_4]$ represents the concentration of methyllithium computed as tetramer.

This mechanism, in which dissociation of methyllithium tetramer is rate determining, requires that (a) the exchange rate depends only on the dissociation rate constant k_1, and on the ratio (methyllithium)/(complex); (b) the methyllithium line width should be independent of concentrations; (c) the increase in complex line width due to exchange should vary linearly with tetramer/complex ratio.

Two kinds of data were obtained for the $LiCH_3$–$LiM(CH_3)_4$ systems. Samples with nearly unit ratio of $LiCH_3/LiM(CH_3)_4$ were studied over a wide tem-

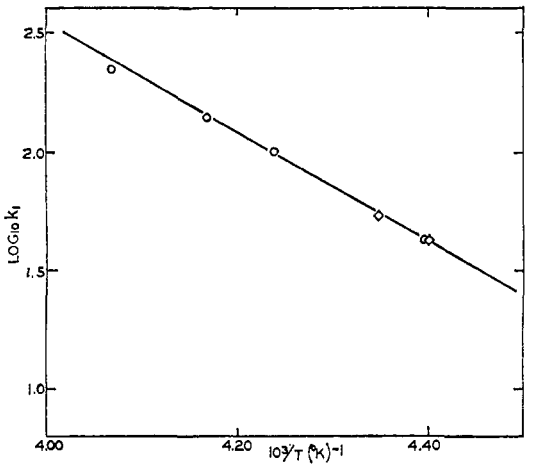


Figure 6. Log k_1 *vs.* $1/T$ for ^{7}Li exchange in ether solutions of $LiCH_3$ and $LiAl(CH_3)_4$: □, $(LiCH_3)_4$ = 0.447 *M*, $LiAl(CH_3)_4$ = 0.464 *M*; ○, $(LiCH_3)_4$ = 0.567 *M*, $LiAl(CH_3)_4$ = 0.506 *M*. The line is described by the equation log $k_1 = -2300(1/T) + 11.75$.

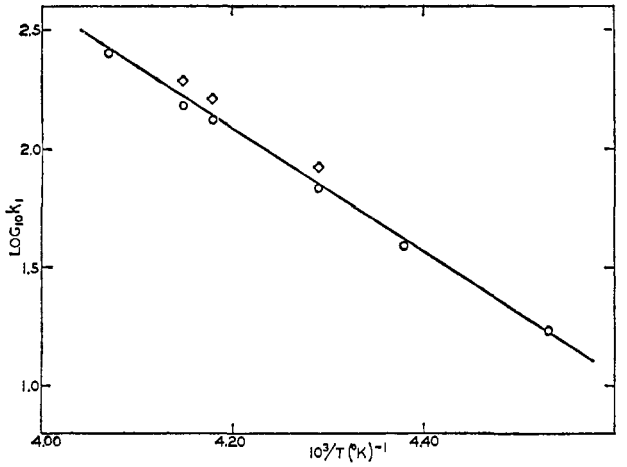


Figure 7. Log k_1 *vs.* $1/T$ for ^{7}Li exchange in ether solutions of $LiCH_3$ and $LiB(CH_3)_4$: □, $(LiCH_3)_4$ = 0.659 *M*, $LiB(CH_3)_4$ = 0.745 *M*; ○, $(LiCH_3)_4$ = 0.812 *M*, $LiB(CH_3)_4$ = 0.622 *M*. Log $k_1 = -2600(1/T) + 13.0$.

perature range, and τ values were determined by comparison of observed and calculated line shapes. Values of k_1 were then calculated from eq 13. Figure 6 shows a graph of log k_1 *vs.* $1/T$ for the $LiCH_3$–$LiAl(CH_3)_4$ system. From the line an Arrhenius activation energy of E_a = 10.5 kcal/mole, and log A = 11.75 is obtained. A similar plot (Figure 7) for the $LiCH_3$–$LiB(CH_3)_4$ system yields E_a = 11.9, log A = 13.0. Within experimental error, the parameters are the same for the two systems.

In a second set of experiments, a number of samples with varying $[(LiCH_3)_4]/[LiM(CH_3)_4]$ ratio were examined at a single temperature in the slow-exchange region. Samples with $(LiCH_3)_4/LiAl(CH_3)_4$ ratios from 0.0634 to 0.739 were studied at −47°, at which temperature the slow-exchange approximation is reasonable. According to eq 12 $1/\tau_T$ should be invariant to the ratio, whereas $1/\tau_C$ should increase linearly with increasing ratio, with slope $2k_1$. The experimental data for $1/\tau_C$ are given in Figure 8. The line which best accommodates the data does not pass through the origin, as it should. The slope of the line is about 104, which is to be compared with $2k_1$ = 76 based on the graph in Figure 6. In view of the experimental difficulties in obtaining accurate and reproducible ^{7}Li line-shape data the agreement is as good as can be expected. Certainly the qualitative features of the data fit the proposed mechanism quite well. It is possible that the nonzero intercept is real, and that a second pathway for exchange is operative, but the good linearity of the data in Figure 6 indicates that an alternative pathway is not important. Failure of the spectra at higher ratios to fit the slow-exchange approximation is the most probable cause of the discrepancy.

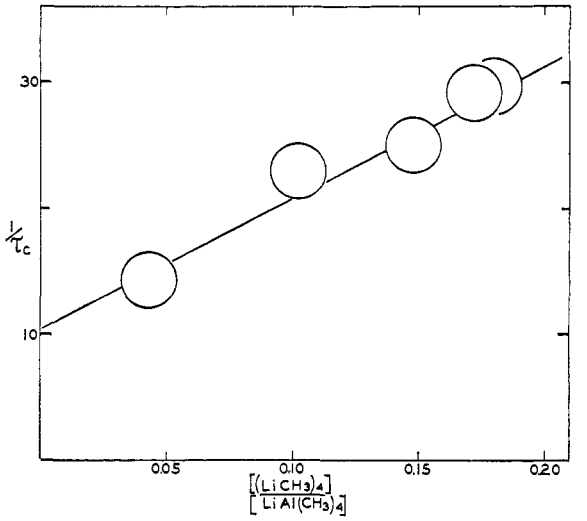


Figure 8. $1/\tau$ for the ^{7}Li resonance of $LiAl(CH_3)_4$ in ether solutions with $LiCH_3$, at −47°, as a function of $[(LiCH_3)_4]/[LiAl(CH_3)_4]$.

A similar study in the $LiCH_3$–$LiB(CH_3)_4$ system at approximately −57° yielded the results for $1/\tau_C$ shown in Table II. The slope of the line which passes through the origin and which best fits the data is 22. A marked deviation from linearity is due to the failure of the solutions at higher ratios to fit the requirements of the slow-exchange approximation. By way of comparison, $2k_1$ = 20 based on the k_1 *vs* $1/T$ data shown in Figure 7. In this system it was also possible to obtain fairly accurate values for $1/\tau_T$, which is expected to be insensitive to the $[(LiCH_3)_4]/[LiB(CH_3)_4]$ ratio. As the data in Table II show, $1/\tau_T$ is reasonably independent of the ratio; twice the average value, which should equal k_1, is 6 sec^{-1}, in reasonable agreement with the value 10 sec^{-1} obtained from Figure 7.

Table II. Concentration Dependences of the Reciprocal Mean Exchange Times for ^{7}Li Exchange in the $LiCH_3$–$LiB(CH_3)_4$ System at −54°

$[(MeLi)_4]/[LiBMe_4]$	$1/\tau_{(MeLi)_4}$	$1/\tau_{LiBMe_4}$
0.0634	3.2	...
0.178	3.0	4.5
0.231	2.8	4.9
0.324	3.2	7.2
0.739	2.3	9.5

The ^{7}Li spectra of LiC_2H_5–$LiAl(C_2H_5)_4$ and LiC_2H_5–$LiGa(C_2H_5)_4$ mixtures reveal a faster exchange than in the methyl system. This is in agreement with the proposed mechanism, since it has been shown previously[3]

that exchange is faster in ethyllithium than in methyllithium.

The results obtained on the $LiCH_3$–$LiM(CH_3)_4$ systems provide an accurate and reliable value for the rate and activation energy of the process

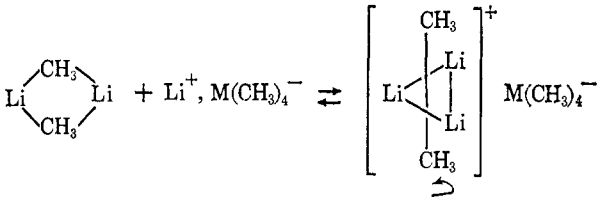
$$(LiCH_3)_4 \longrightarrow 2(LiCH_3)_2$$

It is rather striking that the activation energy for tetramer dissociation should be as high as 11 kcal/mole in ether. Under these same conditions the trimethylaluminum dimer is completely dissociated, and dimethylmagnesium is probably largely in monomeric form.[17] On the basis of what is now known, homolytic dissociation of tetramers is apparently much faster than ionization,[4] which might be envisaged as occurring from either the tetramer or dimer

$$Li_4R_4 \rightleftharpoons Li_4R_3^+ + R^-$$

$$Li_2R_2 \rightleftharpoons Li_2R^+ + R^-$$

^7Li exchange *via* the mechanism proposed involves a rapid exchange between Li_2R_2 and Li^+, $M(CH_3)_4^-$. We suggest that this proceeds through intermediate formation of $Li_3R_2^+$, $M(CH_3)_4^-$. Ions of the form $Li_nR_{n-1}^+$ are abundant in the mass spectrum of organolithium compounds.[18,19] The detailed form of the exchange, excluding consideration of the solvent, is then probably



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Organometallic Exchange Reactions. III. Lithium-7 and Proton Nuclear Magnetic Resonance Spectra of Methyllithium–Dimethylmagnesium and Methyllithium–Dimethylzinc in Ether[1]

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Abstract: Proton and ^7Li nuclear magnetic resonance spectra of ether solutions of methyllithium with dimethylmagnesium and dimethylzinc have been examined over a range of temperatures. The spectra show that complex species of the form $Li_2M(CH_3)_4$ and $Li_3M(CH_3)_5$ (M = Zn or Mg) are formed. No 1:1 complex is observed. Exchange of ^7Li between $LiCH_3$ and complex appears to occur at about the same rate, and with the same activation energy, as methyl-group exchange. The exchange processes are faster in the zinc than in the magnesium system. It appears that in the zinc system the rate-determining process is dissociation of methyllithium tetramer to dimers. Exchange of methyl groups between $Mg(CH_3)_2$ and $Li_2Mg(CH_3)_4$ is quite rapid, despite a comparatively high activation energy, 15 kcal/mole. The analogous exchange is rapid in the zinc system at −107°, the lowest temperature studied.

It is well known that alkyl- and aryllithium compounds react with other organometallic compounds to form mixed organometallic complexes.[3] Wittig and co-workers studied the phenyllithium–diphenylmagnesium and phenyllithium–diphenylzinc systems and isolated solid mixed complexes of 1:1 stoichiometry, *e.g.*, $LiMg(C_6H_5)_3$.[4] Hurd succeeded in isolating a 2:1 complex, $Li_2Zn(CH_3)_4$, by adding methyllithium to dimethylzinc in ether.[5] Aside from this work, no other investigation of the reaction of methyllithium with dimethylmagnesium or dimethylzinc has been reported.

In view of the 1:1 complexes reported by Wittig, *et al.*, for the phenyl compounds and the 2:1 complex reported by Hurd, it was of interest to determine the stoichiometry of the complexes in solution. We report here the results of a ^7Li and ^1H magnetic resonance study of the reaction of methyllithium with dimethylmagnesium and dimethylzinc in ether, which reveal the presence of two complexes in solution under certain conditions. The data relate to the stoichiometry of each complex and provide information on the rates of various exchange processes involved. The results of a similar study of the corresponding phenyl compounds will be reported in another paper.

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