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METHYL GROUP EXCHANGE IN METHYLLITHIUM–LITHIUM BROMIDE SOLUTIONS IN DIETHYL ETHER

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Summary

The 220 MHz ^{1}H NMR spectrum of an ether solution of CH_3Li and LiBr in 10/1 ratio has been examined as a function of temperature. At low temperature distinct resonances, assignable to $Li_4(CH_3)_4$ and $Li_4(CH_3)_3Br$, are seen. Methyl group exchange between the two tetramers is observed in the NMR spectra in the temperature interval −32 to 0°. The exchange is shown to be much slower than the dissociation of $Li_4(CH_3)_4$ tetramer, measured in other work. It is proposed that the rate-determining step is dissociation of $Li_4(CH_3)_3Br$ to form $Li_2(CH_3)_2$ and $Li_2(CH_3)Br$. The rate constant for dissociation, k_2, obeys the equation $\ln k_2 = 36.0 - 8303/T$.

Introduction

It has been well established that alkyllithium compounds are associated, even in basic solvents such as ether or THF [1, 2]. It has further been demonstrated that mixed associated species of the form $Li_nR_yX_{n-y}$ are formed in mixtures of alkyllithium compounds with lithium halides in ether [3–6]. Recent studies employing ^{7}Li and ^{1}H NMR spectra have provided information on the species present in mixed solutions of $LiCH_3$ and LiBr or LiI [6, 7]. In $LiCH_3$–LiBr mixtures in ether [6], $Li_4(CH_3)_4$, $Li_4(CH_3)_3Br$, $Li_4(CH_3)_2Br_2$ and $(LiBr)_n$ were identified. Samples with a high $LiCH_3$/LiX ratio (e.g., about 10) were found to contain predominantly $Li_4(CH_3)_4$ and $Li_4(CH_3)_3X$.

In $LiCH_3$/LiI solutions containing high CH_3/I ratios it is possible to discern in the ^{7}Li NMR spectra at low temperatures separate absorptions for the two chemically distinct lithiums of the $Li_4(CH_3)_3I$ tetramer. As the temperature is raised, the two resonances collapse due to an exchange process. This occurs, however, in a temperature interval in which both of these resonances undergo exchange

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collapse with the ^{7}Li resonance due to the $Li_4(CH_3)_4$ tetramer. While exchange of the two chemically non-equivalent lithiums in the mixed tetramer might occur via an intramolecular process, the exchange of lithiums between the two kinds of tetramer is intermolecular in nature. Exchange might be supposed to occur via dissociation of each tetramer to form dimers, followed by a coupling of dimers from different tetramers. The question arises as to which tetramer dissociation is rate-determining.

We have examined the 220 MHz proton NMR spectra of a $LiCH_3$—LiBr mixture in ether at various temperatures, to ascertain the rate and energetics of the exchange of methyl groups between the $Li_4(CH_3)_4$ and $Li_4(CH_3)_3Br$ tetramers.

Results and discussion

Ether solutions containing a 10/1 $LiCH_3$—LiBr ratio exhibit two symmetrical lines in the 220 MHz ^{1}H NMR spectrum at —50° C [6]. The higher field absorption occurs at the same chemical shift as for pure methyllithium in ether. The less intense absorption at lower field is assigned to the methyl groups of the $Li_4(CH_3)_3Br$ tetramer. In view of the extensive ^{7}Li and ^{1}H NMR spectral data for $LiCH_3$—LiBr mixtures [6], there can be little doubt of the assignment.

As the temperature is raised above —50° C, the methyl groups undergo exchange between the magnetically distinct sites. Figure 1 shows the 220 MHz ^{1}H NMR spectra at various temperatures for a 10/1 $LiCH_3$—LiBr mixture, reported previously [6].

Detailed lineshape analyses were carried out over the temperature range of 0° to —32° C. The lineshape analysis was difficult, because three of the four parameters needed to fit the lineshape [P_A (population of site A), T_{2A}, T_{2B}, and δ (peak separation)] were unknown. Only T_2 for the pure methyllithium tetramer could be estimated, from spectra of a pure methyllithium solution. Since the tetramer containing three methyl groups and one bromide cannot be isolated as a pure species, it was impossible to accurately evaluate its T_2 value or the value of δ in the intermediate exchange region. The most troublesome problem proved to be the estimation of relative populations. The value of P_A, obtained by integration of spectra in the slow exchange region, slowly decreases as the temperature is raised. This occurs because the equilibrium constants for equilibria between the different tetramers change with temperature. In systems with high CH_3Li/LiBr ratio, the predominant species are $Li_4(CH_3)_4$ and $Li_4(CH_3)_3Br$, but these species are in equilibrium with $Li_4(CH_3)_2Br_2$ and $(LiBr)_n$ present in low concentrations. This is shown in eqns. 1 and 2.

$$2Li_4(CH_3)_3Br \rightleftharpoons Li_4(CH_3)_2Br_2 + Li_4(CH_3)_4 \quad (1)$$
$$4Li_4(CH_3)_3Br \rightleftharpoons Li_4Br_4 + 3Li_4(CH_3)_4 \quad (2)$$

The equilibrium constants for eqns. 1 and 2 change as temperature is varied.

A value for P_A, obtained from a slow exchange spectrum, was used to obtain a best fit value for T_2 of the mixed tetramer. Then, while holding T_{2A} and T_{2B} constant, P_A and δ were varied at each temperature until the best fit was obtained. The calculated lineshapes are shown in Fig. 1.

In order to calculate values of a rate constant from τ values obtained in the lineshape fitting it is necessary to devise a mechanism consistent with the NMR

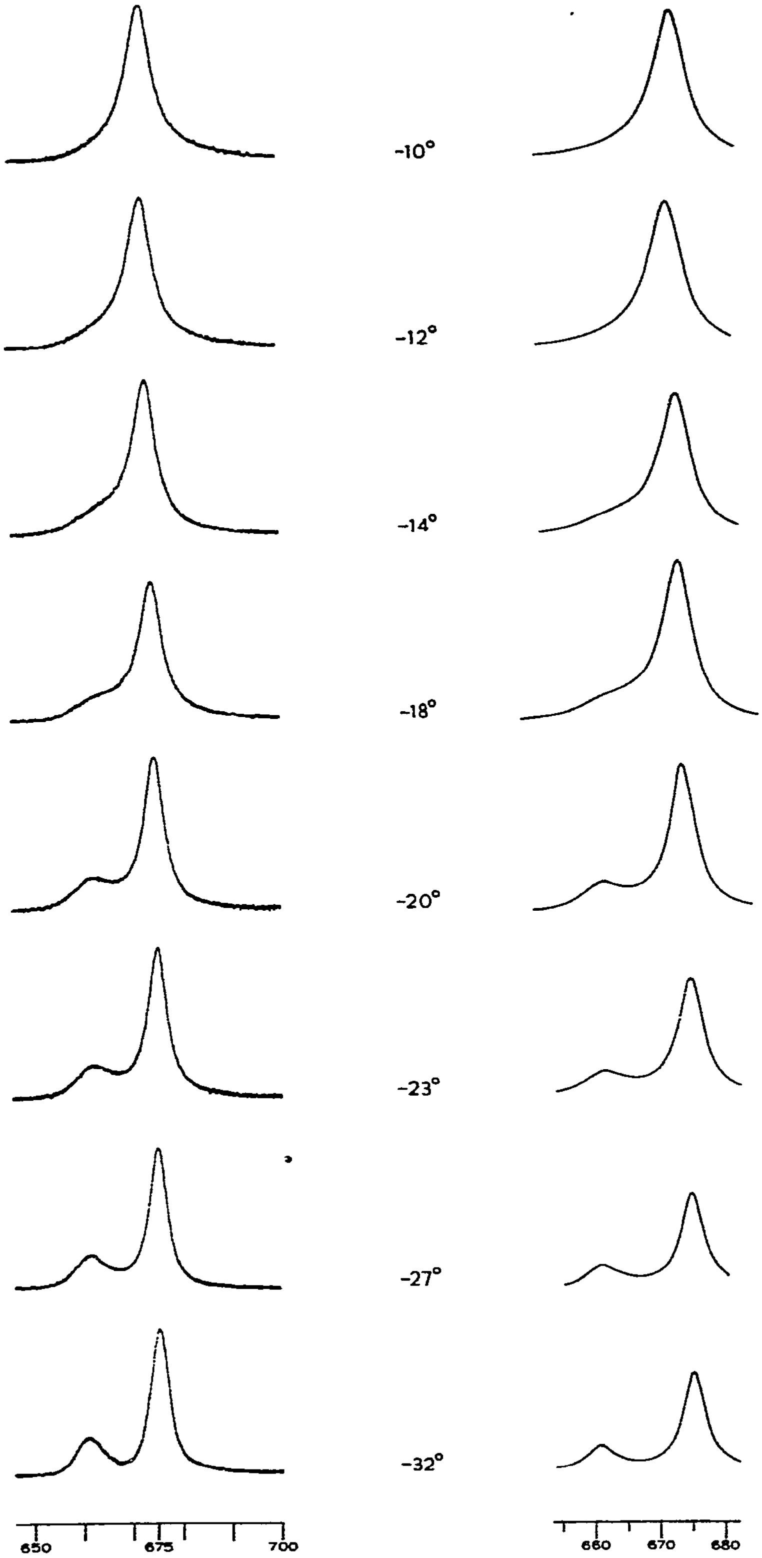

Fig. 1. 220 MHz ^{1}H NMR spectra of a 10/1 $LiCH_3$—LiBr mixture in ether. Observed spectra on the left, calculated spectra on the right.

data and to determine the relationship between k and τ. Initially it was presumed that dissociation of methyllithium tetramer would be the rate-determining step [6]. The kinetics of exchange would then be similar to those seen in the $LiCH_3$—$LiAl(CH_3)_4$ system [8, 9]. The present data should then yield values for k, and the activation energy similar to those obtained from ^{7}Li exchange data in $LiCH_3$—$LiAl(CH_3)_4$ solutions. Using the previously developed equations [9], a weighted average time between the exchanges of $Li_4(CH_3)_4$ and $Li_4(CH_3)_3Br$ obtained from the line shape analysis is thus:

$$\frac{1}{\tau} = k_1 \left[1 + \frac{[Li_4(CH_3)_4]}{[Li_4(CH_3)_3Br]} \right] \tag{3}$$

A graph of ln $1/\tau$ vs. $1/T$ for the $Li_4(CH_3)_4$—$Li_4(CH_3)_3Br$ system has a slope corresponding to an activation energy of 16.3 kcal mole^{-1}. The uncertainty in the activation energy is ± 2.6 kcal mole^{-1} at the 99% confidence level.

The activation energy of 16.5 kcal mole^{-1} is considerably greater than the value of 12.4 kcal mole^{-1} obtained for the CH_3Li—$LiAl(CH_3)_4$ system. A comparison of rate constants at various temperatures is shown in Table 1. The greater activation energy and smaller rate constants for exchange in the $Li_4(CH_3)_4$—$Li_4(CH_3)_3Br$ system mean that dissociation of the methyllithium tetramer is fast compared to methyl group exchange. A different rate-determining step must therefore be involved.

Several alternative mechanisms might be considered. Ionization of $Li_4(CH_3)_4$, eqn. 4, could be involved in the exchange.

$$Li_4(CH_3)_4 \rightarrow Li_4(CH_3)_3^+ + CH_3^- \tag{4}$$

Witanowski and Roberts [9] have reported on the rate of inversion at the metal-bearing carbon of neohexyllithium in ether. Inversion could occur via an ionic pathway analogous to eqn. 4. The reported inversion rates are, however, smaller than the exchange processes we observe, so exchange via ionization of the tetramers seems rather doubtful.

Association into larger aggregates such as hexamers, eqn. 5, could be involved in the rate-determining step.

$$Li_2(CH_3)_2 + Li_4(CH_3)_3Br \rightarrow Li_6(CH_3)_5Br \tag{5}$$

No evidence can presently be given to discount this mechanism, but it seems unlikely. Both tetramer and dimer are solvated. Displacement of solvent would thus be required in order to form a relatively unstable species. It seems more reasonable that the rate-determining step involves dissociation of the mixed tetramer into dimers.

TABLE 1

VALUES OF k_1 (sec^{-1}) AT VARIOUS TEMPERATURES FOR THE $LiCH_3$—$LiAl(CH_3)_4$ AND $Li_4(CH_3)_4$—$Li_4(CH_3)_3Br$ SYSTEM IN ETHER, ASSUMING RATE-DETERMINING STEP $Li_4(CH_3)_4 \rightarrow 2Li_2(CH_3)_2$

	0° C	—25° C	—50° C
$Li_4(CH_3)_4$—$Li_4(CH_3)_3Br$	27.6	1.35	0.034
CH_3Li—$LiAl(CH_3)_4$	1720.0	173	10.3

The following mechanism, with dissociation of the mixed tetramer as the rate-determining step, can be used to interpret the NMR data.

$$\mathrm{Li_4R_3^{\star}X} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Li_2R_2^{\star}} + \mathrm{Li_2R^{\star}X}\ \text{(slow)} \tag{6}$$

$$\mathrm{Li_4R_4} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{Li_2R_2} \tag{7}$$

$$\mathrm{Li_2R_2^{\star}} + \mathrm{Li_2R_2} \xrightarrow{k_{-1}} \mathrm{Li_4R_2^{\star}R_2} \tag{8}$$

The kinetics analysis of these processes yields for the weighted average time between exchanges (see Appendix):

$$\frac{1}{\tau} = \frac{k_2}{6}\left[4 + 3\,\frac{[\mathrm{Li_4R_3X}]}{[\mathrm{Li_4R_4}]}\right] \tag{9}$$

Eqn. 9 can be used to calculate values of k_2 from the τ values obtained in the lineshape analysis. The values of the $[\mathrm{Li_4(CH_3)_3X}]/[\mathrm{Li_4(CH_3)_4}]$ ratio are calculated from the P_A/P_B ratio obtained from the lineshape analysis. Values of k_2 at various temperatures can be used to obtain a corrected value for the activation energy. A graph of ln $1/\tau$ vs. $1/T$ does not give quite the correct activation energy for this system because k_2 is dependent on the ratio $[\mathrm{Li_4R_3X}]/[\mathrm{Li_4R_4}]$, which is temperature-dependent. Thus $1/\tau$ is not directly related to k_2 but to k_2 times a temperature-dependent ratio.

Figure 2 shows a graph of ln k_2 plotted against $1/T$. The slope of this graph gives an activation energy of 16.5 kcal mole^{-1} and a value of $A = 4.38 \times 10^{15}$ sec^{-1} The uncertainty in the activation energy is ± 2.6 kcal mole^{-1} at the 99% confidence level.

Unfortunately it is not possible to further test the proposed mechanism by carrying out ratio studies similar to those done with the $\mathrm{LiCH_3}$—$\mathrm{LiAl(CH_3)_4}$ system. If the concentration of LiBr becomes too great, other mixed species such as $\mathrm{Li_4(CH_3)_2Br_2}$ form in significant amounts, and further complicate the kinetics.

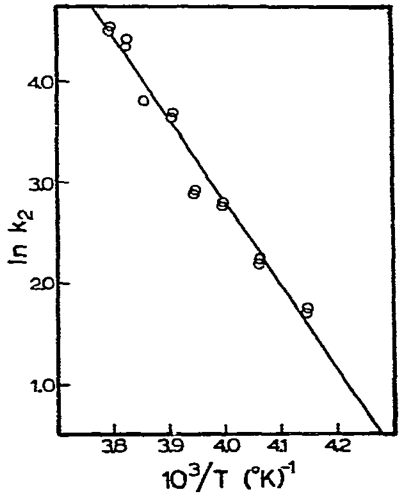

Fig. 2. Ln k_2 vs. $1/T$ for dissociation of $\mathrm{Li_4(CH_3)_3Br}$ in ether. Ln $k_2 = 36.0 - 8303/T$.

In summary, the results for the $Li_4(CH_3)_4$—$Li_4(CH_3)_3Br$ system show conclusively that the rate-determining step for methyl exchange is not the same as that operative in the $Li_4(CH_3)_4$—$LiAl(CH_3)_4$ mixtures. We suggest that the rate-determining step is dissociation of the mixed tetramer $Li_4(CH_3)_3Br$, and that this occurs at a significantly slower rate than dissociation of the methyllithium tetramer.

Experimental

Samples were prepared and analyzed in the manner previously described [6]. The ^1H NMR spectra were obtained on a Varian Associates HR-220 NMR spectrometer. All lineshape analyses were carried out with the aid of a computer program [11] which provides an iterative fit to observed spectra, based on a minimum residual difference between observed and calculated intensities of magnetization at many points along the absorption envelope. Since decoupling of the ^7Li and ^1H spin systems was not feasible, the observed ^1H linewidths reflect a contribution from the ^7Li—^1H scalar coupling [1]. This undoubtedly has some effect on the rates derived from the lineshape fits, but the errors due to this are expected to be small. The present case is analogous to that arising in the ^7Li spectra of $LiCH_3$—$LiAl(CH_3)_4$ mixtures [9]. Decoupling of ^1H made only a small change in the estimated values of E_a for ^7Li exchange.

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Appendix

The species $Li_2R_2^*$, derived from $Li_4R_3^*X$ as shown by eqn. 6, undergoes alkyl group exchange in the course of reaction with Li_2R_2 from the Li_4R_4 tetramer, as shown in eqns. 7 and 8. The methyl group in Li_2R^*X does not undergo exchange of magnetization site, because Li_2R^*X reacts with Li_2R_2 to reform the mixed tetramer Li_4R_3X. A steady-state expression for the intermediate $Li_2R_2^*$ yields eqns. 10 and 11.

$$\frac{d[Li_2R_2^*]}{dt} = 0 = k_2\,[Li_4R_3^*X] - k_{-2}\,[Li_2R_2^*]\,[Li_2R^*X] - k_{-1}\,[Li_2R_2]\,[Li_2R_2^*] \tag{10}$$

$$[Li_2R_2^*] = \frac{k_2\,[Li_4R_3^*X]}{k_{-2}\,[Li_2R^*X] + k_{-1}\,[Li_2R_2]} \tag{11}$$

The rate at which the exchanged product $Li_4R_2^*R_2$ is formed is given by:

$$\frac{d[Li_4R_2^*R_2]}{dt} = k_{-1}\,[Li_2R_2]\,[Li_2R_2^*] \tag{12}$$

Substituting for $Li_2R_2^*$ and assuming $k_{-1}\,[Li_2R_2] \gg k_{-2}\,[Li_2RX]$ (since dissociation of $Li_4R_3^*X$ is assumed to be the slow step and the concentration of Li_4R_4 is much greater than $Li_4R_3^*X$), we obtain:

$$\frac{d[Li_4R_2^*R_2]}{dt} = k_2\,[Li_4R_3^*X] \tag{13}$$

We have:

$$\frac{1}{\tau(Li_4R_4)} = \frac{1}{[Li_4R_4]} \times \frac{-d[Li_4R_4]}{dt} \tag{14}$$

$$\frac{1}{\tau(Li_4R_3^*X)} = \frac{1}{[Li_4R_3^*X]} \times \frac{-d[Li_4R_3^*X]}{dt} \tag{15}$$

Eqn. 15 can be rewritten as:

$$\frac{1}{\tau(Li_4R_3^*X)} = \frac{1}{[Li_4R_3^*X]}\,\frac{2}{3}\,\frac{d[Li_4R_2^*R_2]}{dt} \tag{16}$$

The factor of 2/3 arises from the fact that only two of the three alkyl groups of $Li_4R_3^*X$ are exchanged by the process shown in eqn. 8.

Eqn. 14 can be rewritten as:

$$\frac{1}{\tau(Li_4R_4)} = \frac{1}{[Li_4R_4]}\,\frac{1}{2}\,\frac{d[Li_4R_2^*R_2]}{dt} \tag{17}$$

The factor of 1/2 arises because the process shown in eqn. 8 exchanges only two of the four alkyl groups of Li_4R_4. Substitution for $d[Li_4R_2^*R_2]/dt$ in eqn. 16 and 17 yields:

$$\frac{1}{\tau(Li_4R_3^*X)} = \frac{2}{3}k_2 \tag{18}$$

$$\frac{1}{\tau(Li_4R_4)} = \frac{1}{2}k_2\,\frac{[Li_4R_3^*X]}{[Li_4R_4]} \tag{19}$$

The weighted average time between exchanges is thus:

$$\frac{1}{\tau} = \frac{k_2}{6}\left[4 + 3\,\frac{[Li_4R_3^*X]}{[Li_4R_4]}\right] \tag{20}$$

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