Cross-Association of *t*-Butyllithium. Kinetics of *t*-Butyllithium Dissociation[1]

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Abstract: Intermolecular exchange leading to equilibration of mixtures of *t*-butyllithium (I) and trimethylsilylmethyllithium (II) have been studied using ^{7}Li nuclear magnetic resonance. The exchange is rate controlled by dissociation of *t*-butyllithium tetramers. The first-order rate constant in cyclopentane at 20° is 1×10^{-5} sec^{-1}; the enthalpy of activation is 24 ± 6 kcal/mol. The dissociation is about 20 times more rapid in toluene at 20°. Addition of small quantities of triethylamine to the cyclopentane solutions causes the exchange to become much more rapid; equilibration is achieved in less than 15 min. Mass spectra of samples recovered from cyclopentane solutions made up by mixing I synthesized from ^{6}Li with I synthesized from ^{7}Li exhibit a slow approach to equilibration of the lithium isotopes among the tetramers, commensurate with the nmr results. Mass spectra of samples recovered from mixtures of I with lithium *t*-butoxide, LiO-*t*-C_4H_9, in benzene solution demonstrate the existence of mixed organolithium species in the vapor phase. Similar results were obtained for samples derived from mixtures of I with ethyllithium and with II.

The nmr spectra of mixtures of *t*-butyllithium (I) and trimethylsilylmethyllithium, $(CH_3)_3SiCH_2Li$ (II), in cyclopentane and toluene were reported in an earlier paper from these laboratories.[3] We report here a more detailed investigation of certain kinetic aspects of that system, including a determination of the kinetics of the dissociation of *t*-butyllithium. In addition, we report mass spectral evidence for cross-association of *t*-butyllithium with other organolithium compounds in the vapor phase.

The principal conclusion of the earlier work, based on observation of the ^{7}Li spectra, was that the mixtures of I and II do not reach a rapid equilibrium distribution of alkyl groups on the prevailing organolithium oligomers. It appeared that the rate-determining process involves a dissociation of the *t*-butyllithium tetramer. It was also believed that both I and II are tetrameric under the experimental conditions. It has since been learned[4] that II is predominately hexameric in cyclopentane under the experimental conditions and tetrameric in benzene. This does not affect any conclusions previously reached, nor does it particularly complicate the considerations presented in this paper. Although II may be a hexamer, the steric requirements of the $(CH_3)_3SiCH_2$ group are only marginally permissive of hexamer formation as opposed to the less crowded tetramer. An organolithium species containing even one *t*-butyl group along with the trimethylsilylmethyl groups would very likely exist as a tetramer. Certainly, no more than one *t*-butyl group could exist on a hexamer. It is therefore safe to assume that all species present in solution in toluene are tetramers, and that all species in cyclopentane are tetramers except for II_6 and possibly $(II)_5(I)$. Since our major concern is with the species richest in *t*-butyllithium, no problems are encountered in applying the local environment model to the interpretation of the ^{7}Li spectra.

Kinetics of *t*-Butyllithium Dissociation. It is clear from the temperature dependence of the spectra, as well as from mass spectral evidence discussed below, that dissociation of the *t*-butyllithium species is the rate-determining process in equilibration of mixtures of I and II. We view this dissociation as involving the formation of dimers from the *t*-butyllithium tetramer

$$R_4Li_4 \longrightarrow 2R_2Li_2 \qquad (1)$$

There may be a rapid subsequent dissociation of dimers to monomer, as implied in mechanistic schemes which have been proposed for reaction of organolithium compounds.[5-9] In the present work we are concerned with the nature of the rate-determining step in the dissociation, without being certain of its precise character. It does seem reasonable, however, to postulate a dissociation of tetramers to dimers as the primary process, leaving open the question of what steps may rapidly follow.

The kinetics of the equilibration of mixtures of I and II were measured by observation of the time dependences of the ^{7}Li nmr spectra. A sample set of spectra for a 1:1 mixture of I and II as a function of time is shown in Figure 1. The upfield resonance is due to *t*-butyllithium tetramers. The relative area due to this resonance decreases as reaction proceeds and mixed organolithium species are formed. Observation of the rate of disappearance of I_4 with time is made by integration of the total area under all the ^{7}Li absorptions and integration of the area under the absorption due to I_4. The fraction of I_4 present at time t was converted into fraction of reaction remaining, F, by

$$F = \frac{f_t - f_\infty}{f_i - f_\infty}$$

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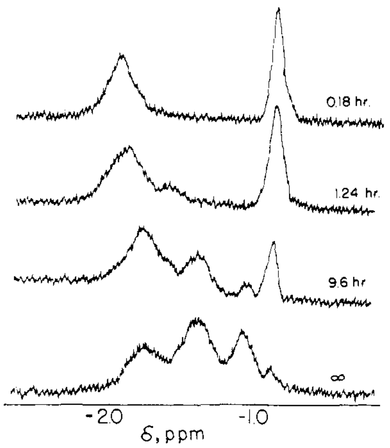

Figure 1. Time dependence of the ^{7}Li spectrum of a 1:1 mixture of *t*-butyllithium and trimethylsilylmethyllithium in cyclopentane at 20°.

where f_i is the initial fractional area under the I_4 absorption, as calculated from the known relative concentration of I and II; f_∞ represents the calculated fractional area under this absorption at equilibrium, assuming that intramolecular exchanges are rapid in the species $(II)(I)_3$; f_t represents the observed fractional area of I_4 at time t. First-order plots of F *vs.* t yielded straight lines of slope k, the apparent first-order rate constant. Because overlap of absorptions is a serious problem as equilibrium is approached, the plots for various mixtures of I and II in cyclohexane and toluene were carried through for only the first half-life or so of the reaction. Figure 2 shows a few representative rate plots based on the area measurements. Table I lists the first-order rate constants obtained for a number of different mixtures of I and II in cyclopentane and toluene.

Table I. Apparent First-Order Rate Constants for Exchange of *t*-Butyllithium with Trimethylsilylmethyllithium[a]

$[(CH_3)_3CLi]_4$	$[(CH_3)_3SiCH_2Li]_6$	Temp, °C	k (sec^{-1}) × 10^6
	Cyclopentane		
0.025	0.117	20	10
0.0850	0.110	20	11
0.0625	0.0417	20	6
0.125	0.0835	20	7
0.125	0.0167	20	13
0.175	0.0167	20	16
0.125	0.0835	29	32
0.125	0.0835	39	96
	Toluene		
0.025[b]	0.175	20	310
0.175	0.050	20	160
0.125	0.025	20	160

[a] Alkyllithium concentrations are molarity based on tetramer or hexamer, as appropriate. [b] Only a few data points could be obtained for this mixture and the scatter in the data was large.

Although experimental uncertainties in the data are rather larger than desirable, certain important conclusions can be drawn from the data. The first is that the equilibration is indeed first order in *t*-butyllithium and zero order in trimethylsilylmethyllithium. Secondly, the exchange reaction proceeds about twenty times faster in toluene than in cyclopentane.[10]

The variation in rate constant with temperature in cyclopentane leads to a calculated $\Delta H^{\pm}$ of 24 ± 6 kcal/mol and a $\Delta S^{\pm}$ of approximately 0. The low value of $\Delta S^{\pm}$ is rather surprising; it accounts in large measure for the slowness of the exchange process. The enthalpy of activation for dissociation of the *t*-butyllithium tetramer in cyclopentane solution is considerably greater than the only other related value which has been measured, the presumed dissociation of methyllithium tetramer in ether,[11] for which $\Delta H^{\pm}$ is on the order of 11 kcal/mol. There is no doubt considerable solvent participation in the dissociation process for methyllithium in a solvent such as ether.

On the basis of evidence that *t*-butyllithium interacts only very weakly with triethylamine,[4] a quite basic solvent, it would appear that the difference in exchange rates between toluene and cyclopentane must be due principally to solvent interaction with the transition state or intermediate.

The rate of dissociation of *t*-butyllithium tetramers in hydrocarbon solvents is more rapid than the rate at which *t*-butyllithium is observed to react with substrates, *e.g.*, the reaction with fluorene[8] or 1,1-diphenylethylene.[8,9] Hsieh,[12] on the other hand, has reported reaction rates which appear to be comparable to the expected dissociation rate, after correction for the temperature difference. The concentration of substrates in his work is so high, however, that the solvent medium is probably more characteristic of the olefin than a saturated hydrocarbon solvent. It is noteworthy that Hsieh observes a much lower relative reactivity of *t*-butyllithium toward styrene than toward isoprene or butadiene. The demonstration of a direct interaction of the olefinic group in butenyllithium with the lithium centers[13] provides an indication that the olefins and dienes may be more effective than toluene in interacting with whatever species represents the transition state in the dissociation of *t*-butyllithium.

Intramolecular Exchange Rates. It is of interest to learn as much as possible about the rates of intramolecular exchanges in the various mixed organolithium species produced by mixing of I and II. It has already been established that in cyclopentane the nmr spectra of the species richest in *t*-butyl groups are consistent with a slow intermolecular exchange, but rapid intramolecular exchange.[3] In order to examine this more closely, mixtures in various ratios of I and II were examined over a range of temperature. Figure 3 shows spectra of a mixture of I and II in the ratio 5:1, in both cyclopentane and toluene. The calculated relative intensities of the absorptions expected for rapid intramolecular exchange are shown beside the 30° data. The agreement with experimental results is quite satisfactory. In these spectra the species labeled A is $(I)_4$, B is $(II)(I)_3$, and C is $(II)_2(I)_2$. Upon lowering the temperature, the spectrum undergoes a transformation to that characteristic of a slow intramolecular exchange system, in which the local environment determines the ^{7}Li chemical shift. Absorption D represents a local

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(10) A much larger ratio of rates in the two solvents was estimated earlier[3] on the basis of more indirect evidence.

(11) L. M. Seitz and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 2174 (1966).

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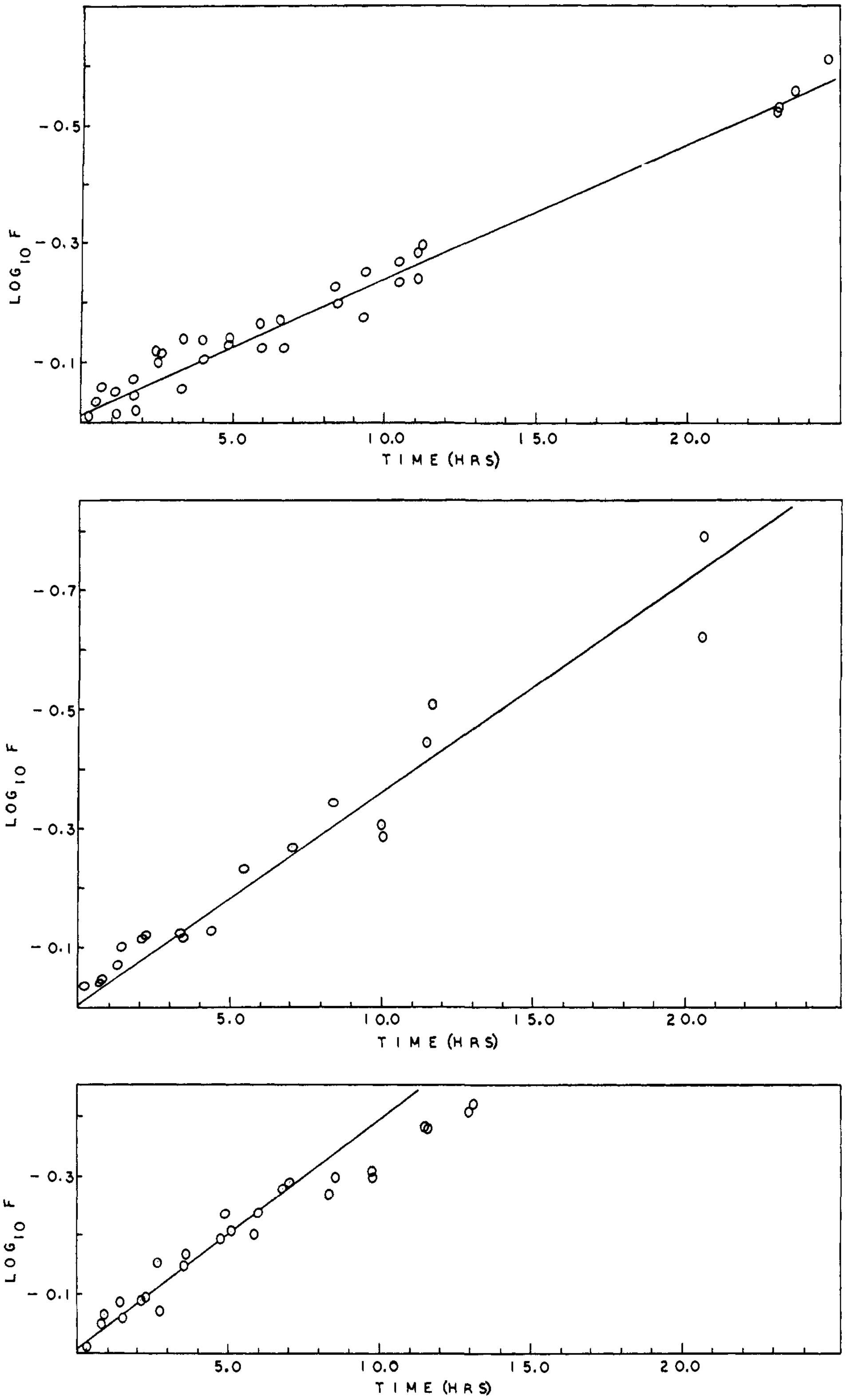

Figure 2. First-order rate plots for intermolecular exchange of *t*-butyllithium in cyclopentane at 20°: A, I = II = 0.25 *M;* B, I = 0.1 *M*, II = 0.7 *M;* C, I = 0.33 *M*, II = 0.66 *M*.

environment of three *t*-butyl groups, E represents a local environment of two *t*-butyl groups and one trimethylsilylmethyl group, etc. The calculated relative intensities for the slow intramolecular exchange condition are shown alongside the low-temperature spectra. Again, agreement with experimental results is excellent.

The intramolecular exchange properties of the $(I)_4$ tetramer are, of course, not evident in these results, since the environment about the ^{7}Li nuclei in this tetramer is the same whether rapid intramolecular exchange occurs or not. The change in the spectrum is due almost entirely, therefore, to the intramolecular exchange properties of the $(II)(I)_3$ species. The most remarkable feature of the results is that the rate of in-

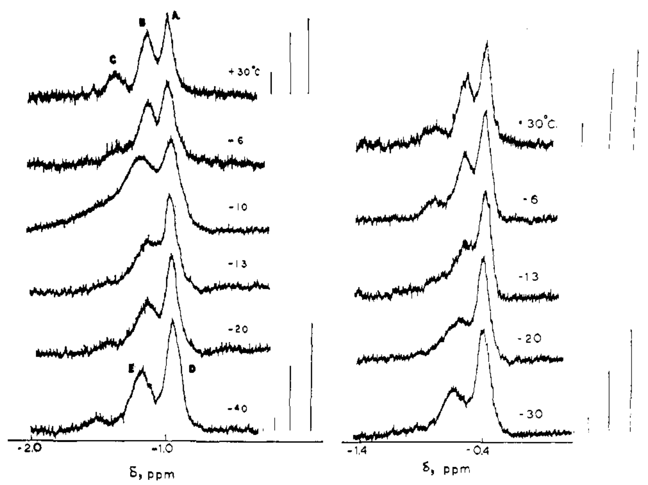

Figure 3. Temperature dependence of the ^7Li spectrum of a 5:1 mixture of *t*-butyllithium and trimethylsilylmethyllithium in cyclopentane (left) and toluene. The labels are identified in the text.

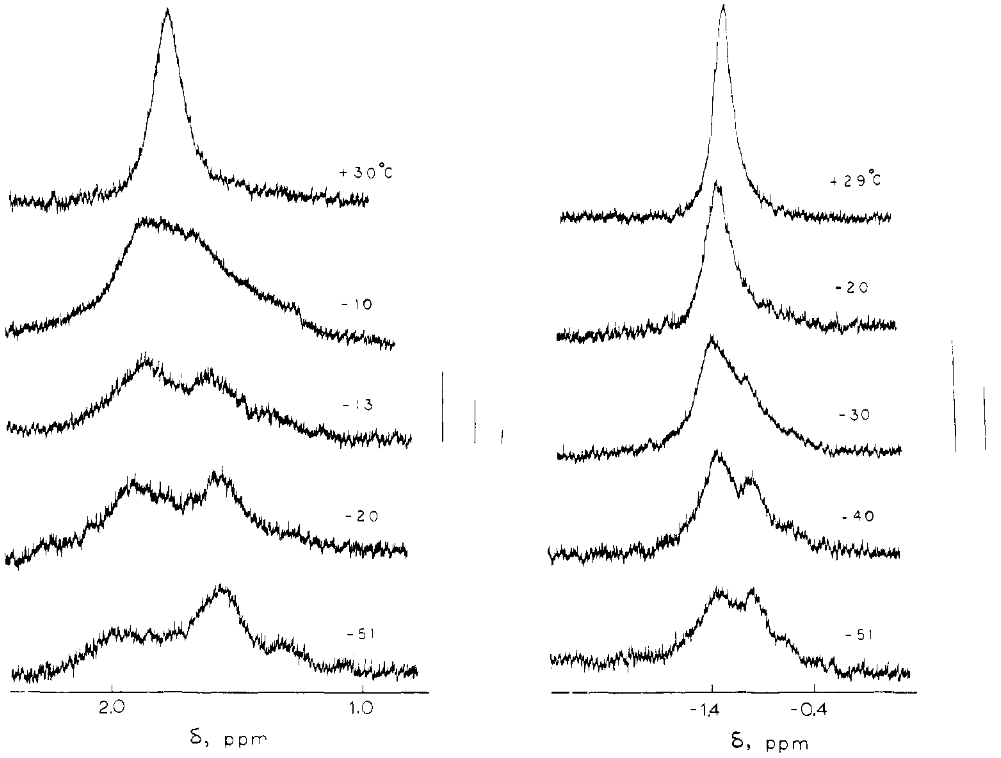

Figure 4. Temperature dependence of the ^7Li spectrum of a 1:7 mixture of *t*-butyllithium and trimethylsilylmethyllithium in cyclopentane (left) and toluene.

tramolecular exchange of this species is, within the experimental limits, identically the same in cyclopentane and toluene. The implications of this result are that the solvent is not involved significantly in the transition state for the intramolecular exchange in this species.

Evidence regarding intramolecular exchanges in species rich in II is difficult to obtain, because the ^7Li spectra are broad and ill defined at low temperatures. Nevertheless, some important conclusions can be established from the data. Figure 4 shows spectra of mixtures of I and II in the ratio 1:7 in both cyclopentane and toluene. From the appearance of the spectra at room temperature it is evident that intermolecular exchange between the predominant species is rapid. At −13° in cyclopentane and −30° in toluene the intermolecular processes involving the prevalent species (probably $(II)_6$ or $(II)_4$, $(II)_3(I)$, etc.) are slowed. With a further lowering of temperature the spectra appear to approach a slow intramolecular exchange limit, but broadening of the resonances precludes detailed analysis of the relative intensities. These results establish that intermolecular exchanges involving species rich in II are much more rapid than for species rich in I. Furthermore, the intermolecular exchanges are more rapid in toluene than in cyclopentane, although the difference is not so great as was estimated from the earlier studies.[3] Mixtures of ethyllithium and *t*-butyllithium yield nmr results very similar to those seen in Figures 3 and 4.

Mass Spectral Results. Table II lists the masses and assigned formulas for ions produced from mixed *t*-butyllithium–*t*-butoxyllithium samples. The results clearly demonstrate the existence of mixed *t*-butyl–*t*-butoxyllithium species in the vapor phase. It is difficult to infer the composition of the vapor from the ion intensity distribution, since the possibility exists that in the fragmentation process leading to the $Li_4R_n(OR)_{3-n}^+$ ions one of the groups, R or OR, is preferentially lost. If, however, it is assumed that there are no appreciable differences in the volatilities of the various $Li_4R_n(OR)_{4-n}$ tetramers or in ionization cross sections, the conclusion must be that the alkoxide groups are lost preferentially.

In contrast to the results generally found for alkyllithium species,[14,15] ions in which all four groups remain attached are seen in the spectra. Although the parent molecular ions were not observed, ions in which all four

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Table II. Mass Spectra of Mixed *t*-Butyllithium–*t*-Butoxyllithium, Prepared from Normal Abundance Lithium[a]

Ion formula[b]	Mass number[c]	Relative intensity,[d] 70 eV A[e]	B[f]
$\text{Li}_6(\text{O-}t\text{-Bu})_6 - 15$	465	0.3	
$\text{Li}_6(\text{O-}t\text{-Bu})_5$	407	0.4	
$\text{Li}_4(\text{O-}t\text{-Bu})_4 - 15$	305	0.5	
$\text{Li}_4(t\text{-Bu})(\text{O-}t\text{-Bu})_3 - 15$	289	0.9	0.2
$\text{Li}_4(t\text{-Bu})_2(\text{O-}t\text{-Bu})_2 - 15$	273	1.6	0.6
$\text{Li}_4(t\text{-Bu})_3(\text{O-}t\text{-Bu}) - 15$	257	0.3	0.2
$\text{Li}_4(\text{O-}t\text{-Bu})_3$	247	0.2	0.2
$\text{Li}_4(t\text{-Bu})(\text{O-}t\text{-Bu})_2$	231	1.9	1.2
$\text{Li}_4(t\text{-Bu})_2(\text{O-}t\text{-Bu})$	215	45	29
$\text{Li}_4(t\text{-Bu})_3$	199	37	43
$\text{Li}_3(\text{O-}t\text{-Bu})_2$	167	0.7	
$\text{Li}_3(t\text{-Bu})(\text{O-}t\text{-Bu})$	151	3.7	1.7
$\text{Li}_2(\text{O-}t\text{-Bu})_2 - 15$	145	4.9	1.6
$\text{Li}_3(t\text{-Bu})_2$	135	4.1	4.5
$\text{Li}_2(t\text{-Bu})(\text{O-}t\text{-Bu}) - 15$	129	2.1	1.0
$\text{Li}_2(\text{O-}t\text{-Bu})$	87	100	73
$\text{O-}t\text{-Bu}$	73	0.7	
$\text{Li}_2(t\text{-Bu})$	71	84	100
$\text{Li}(\text{O-}t\text{-Bu}) - 15$	65	5.7	3.5
$t\text{-Bu}$	57	71	55
Li	7	43	39

[a] Samples introduced at room temperature into the TOF spectrometer. Sample recovered from benzene. [b] The symbol *t*-Bu refers to $t\text{-C}_4\text{H}_9$, O-*t*-Bu to $\text{O-}t\text{-C}_4\text{H}_9$. −15 following the ion composition refers to loss of one CH_3 group from that ion. [c] The mass number listed is that characteristic of the all ^{7}Li ion. Adjacent mass peaks corresponding to varying content of ^{6}Li were observed. [d] Based on 100 for the most intense ion peak. [e] 62% *t*-butyl, 38% O-*t*-butyl. [f] 88% *t*-butyl, 12% O-*t*-butyl.

Table III. Mass Spectra of Mixed *t*-Butyllithium–Trimethylsilylmethyllithium, Prepared from Normal Abundance Lithium[a]

Ion formula[b]	Mass number[c]	Relative intensity,[d] 70 eV A[e]	B[f]
$\text{Li}_4(\text{SI})_3$	289	0.2	2.0
$\text{Li}_4(\text{SI})_2(t\text{-Bu})$	259	3.9	13
$\text{Li}_4(\text{SI})(t\text{-Bu})_2$	229	18	19
$\text{Li}_4(t\text{-Bu})_3$	199	35	12
$\text{Li}_3(\text{SI})_2$	195		1.5
$\text{Li}_3(\text{SI})(t\text{-Bu})$	165	2.1	3.5
$\text{Li}_3(t\text{-Bu})_2$	135	3.9	1.7
$\text{Li}_2(\text{SI})$	101	67	100
SI	87	12	8
$\text{Li}_2(t\text{-Bu})$	71	100	46
$t\text{-Bu}$	57	49	35
Li	7	48	40

[a] Samples recovered from cyclopentane solution. [b] The symbol *t*-Bu refers to $t\text{-C}_4\text{H}_9$, SI refers to $-\text{CH}_2\text{Si}(\text{CH}_3)_3$. [c] The mass number listed is that for the all ^{7}Li ion. Adjacent mass peaks corresponding to varying content of ^{6}Li were seen as expected. [d] Based on 100 for the most intense ion. [e] 80% *t*-butyl, 20% $-\text{CH}_2\text{Si}(\text{CH}_3)_3$. [f] 40% *t*-butyl, 60% $-\text{CH}_2\text{Si}(\text{CH}_3)_3$.

groups remain attached to the tetramer, with loss of a methyl group, are observed, *e.g.*, $[\text{Li}_4(t\text{-Bu})_n(t\text{-OBu})_{4-n} - \text{CH}_3]^+$. Mass spectra of *t*-butyllithium alone also fail to reveal the parent molecular ion; $\text{Li}_4(t\text{-butyl})_3^+$ is the highest molecular weight species derived from the tetramer.

Table III lists the mass numbers and assigned formulations of ions produced from mixed *t*-butyllithium–trimethylsilylmethyllithium samples. The results are analogous to those just discussed. The existence of mixed organolithium species in the vapor is clearly shown. It is evident that tetrameric species rich in *t*-butyl groups predominate in the spectra, but it is not possible to say whether this is the result of preferential loss of the trimethylsilylmethyl group upon electron impact or of differential volatility in the various tetramers. The latter should be a factor of some importance, since *t*-butyllithium is more volatile than trimethylsilylmethyllithium. Mixtures of *t*-butyllithium and ethyllithium produced entirely analogous mass spectral results.

Mixtures of $(t\text{-C}_4\text{H}_9{}^6\text{Li})_4$ and $(t\text{-C}_4\text{H}_9{}^7\text{Li})_4$ were allowed to equilibrate in cyclopentane or benzene solution for varying periods of time before solvent was removed. The samples were sealed off under vacuum and stored under liquid nitrogen or Dry Ice before examination of their mass spectra. The mass spectra were recorded in the 195–199 mass range to observe the relative intensities of the peaks corresponding to the ions, $(t\text{-C}_4\text{H}_9)_3{}^6\text{Li}_n{}^7\text{Li}_{4-n}{}^+$. Since the exchange of lithium atoms between tetramers must occur through some form of dissociative process, the observation of a slow exchange in this experiment, with a characteristic rate commensurate with that observed in the nmr exchange experiment described above, would confirm the hypothesis that the exchange does in fact involve a dissociation of the tetramer rather than, for example, dissociation of a carbanion from the tetamer, or any other model which would not involve breaking up the Li_4 core. Figure 5 shows a few spectra for representative samples of a given starting mixture (50.3% of 96% $t\text{-C}_4\text{H}_9{}^6\text{Li}$, 49.7% of 99.9% $t\text{-C}_4\text{H}_9{}^7\text{Li}$) taken at various times. The spectra observed confirm the model proposed. The samples taken from solutions after the shortest possible times for equilibration, which should have exhibited no mass peaks at 196, 197, and 198 after correction for ^{13}C, ^{2}H, and incomplete isotopic purity of the starting lithium metals, did in fact invariably exhibit intensity which varied from sample to sample. Further, various samples showed differing relative intensities among the three lines, although the samples always contained close to 50% abundance of each isotopically rich starting material. For example, the relative intensities expected for the peaks at $t = 0$ for the sample shown in Figure 5, assuming no exchange, but accounting for isotopic abundances, are 195, 37; 196, 13; 197, 2.6; 198, 2.5; and 199, 46. The intermediate mass peaks are more intense than calculated, even for the sample taken at 0.3 hr. The species of intermediate mass probably arise from fragmentation of $\text{Li}_4(t\text{-C}_4\text{H}_9)_3(\text{O-}t\text{-C}_4\text{H}_9)$, present as an impurity. This species gives rise to a set of lines at 211–215 mass number, corresponding to $\text{Li}_4(t\text{-C}_4\text{H}_9)_2(\text{O-}t\text{-C}_4\text{H}_9)^+$ ions with the five possible distributions of ^{6}Li and ^{7}Li. It is important to note that *this multiplet invariably showed relative intensities characteristic of complete equilibration of the lithium isotopes.* It is evident from the nmr results that the presence of even one alkyl group other than *t*-butyl on a tetramer leads to rapid intermolecular exchange behavior. Similar behavior should result when the unique group is an alkoxide. All of the species of the form $\text{Li}_4\text{R}_3\text{OR}$ should therefore attain an equilibrium distribution of lithium isotopes essentially instantaneously on the time scale of the mass spectral experiment. The $^6\text{Li}:{}^7\text{Li}$ ratio in the 211–215 multiplet in the spectra of samples equilibrated for a short time need not equal the overall relative abun-

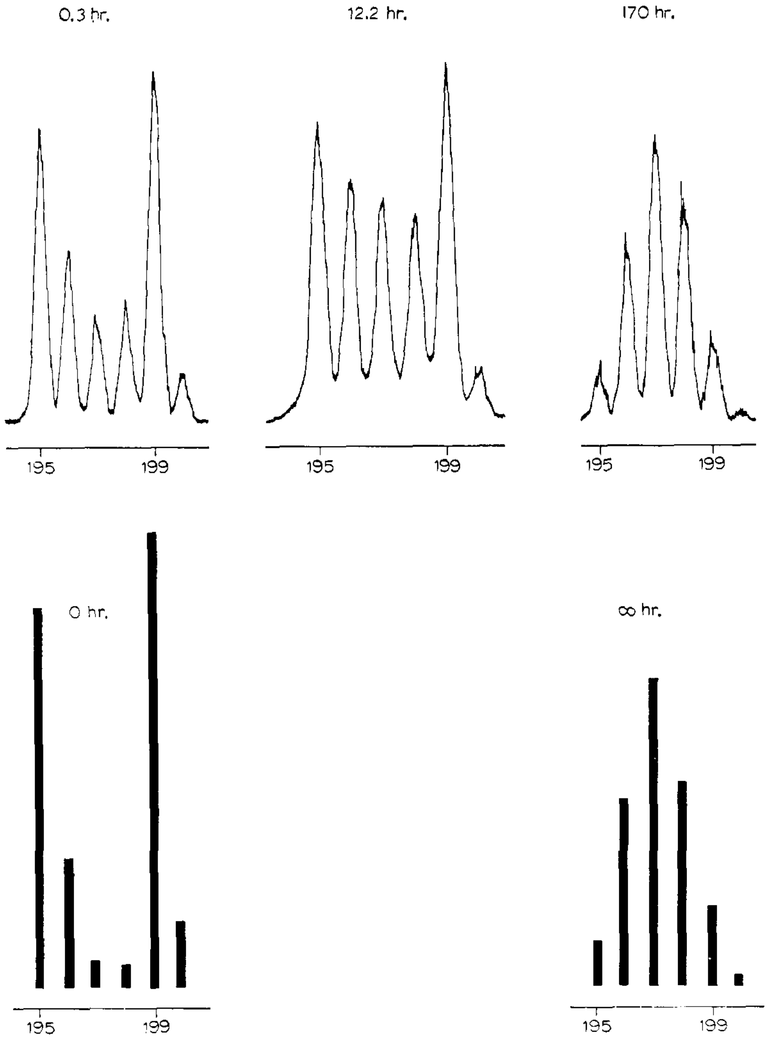

Figure 5. Mass spectra of samples recovered after varying times from a cyclopentane solution initially containing equal quantities of $^6Li_4(t\text{-}C_4H_9)_4$, 96% isotopic purity, and $^7Li_4(t\text{-}C_4H_9)_4$, 99.9% isotopic purity. The bar graphs show calculated relative intensities after accounting for isotopic distributions.

dances of the two isotopes. Rather it is determined by the relative quantities of impurity present in the two samples mixed. This was found to vary from sample to sample. The oxygen-containing impurity is important for the 195–199 multiplet, because $Li_4(t\text{-}C_4H_9)_3(O\text{-}t\text{-}C_4H_9)$ might fragment to give $Li_4(t\text{-}C_4H_9)_3^+$. The appearance of the 196–198 mass peaks in the samples equilibrated for short times is accounted for in this way. One line of evidence which suggests that this is indeed their source is the similarity of relative intensities in the 196–198 set and the 211–215 set. When ^7Li-containing material is the major source of oxygen-containing impurity, so that mass 215 is more intense than 211, the corrected intensity of the 198 peak is greater than that of the 196 peak.

The variation in spectra for samples which have been allowed to equilibrate in solution for varying periods of time provides dramatic evidence of the slow intermolecular exchange of *t*-butyllithium as a function of time (Figure 5). By contrast, samples of ethyllithium prepared from ^6Li and ^7Li and mixed for the minimum possible time in solution (perhaps 2 min) show complete equilibration in the mass spectrum. The mass spectral results thus confirm the general correctness of the nmr spectral interpretations, although detailed quantitative comparisons are precluded by the complications mentioned above, as well as others.

There is apparently some exchange among the tetramers in the gas phase. A sample consisting of approximately equal amounts of the two isotopically enriched forms of *t*-butyllithium was prepared by mixing the two solids in the absence of a solvent. The sample was placed on the mass spectrometer, and its spectrum noted. The valve connecting the sample to the instrument was then closed and the sample allowed to stand under its own vapor pressure for 45 min at 23°. Then the valve was reopened and the mass spectrum immediately taken. The observed relative intensities in the two cases are

Mass number	195	196	197	198	199	200
Original sample	26	11	5	6	46	6
After 45 min	12	13	14	22	32	6

Upon protracted pumping, the relative intensities of the mass peaks approached the original values, indicating that the change in composition occurred in the vapor over the sample, but not to a significant degree in the solid itself. It is not known whether the exchange reaction occurs in the vapor phase or involves a wall reaction.

Discussion

Among the systems so far studied, *t*-butyllithium tetramer is uniquely slow in undergoing intermolecular exchange. Lack of data for a wide variety of alkyl groups, especially those involving a secondary carbon, makes it difficult to assess the relative importances of steric and electronic effects. Nevertheless, it does appear that steric rather than electronic properties of the *t*-butyl group are responsible. The very rapid intermolecular exchanges seen for ethyllithium, for example, may be ascribed to the ready dissociation of a hexamer to form dimer plus tetramer: $R_6Li_6 \rightarrow R_2Li_2 + R_4Li_4$. So long as even a small amount of hexamer may be present in the composition of a given alkyllithium compound in solution, the dissociation of this hexamer, followed by rapid uptake of the dimer by tetramer, provides a mechanism for exchange, since the momentarily formed hexamer may dissociate to yield a new dimer. By contrast, the tetramer of *any* alkyllithium compound may dissociate only very slowly. If there is no significant quantity of hexamer present in *t*-butyllithium solutions, and if the steric requirements of the *t*-butyl group are such that addition of any other alkyllithium dimer is precluded, the *t*-butyllithium tetramer is not capable of participating in the characteristically rapid exchange processes. Substitution of even one *t*-butyl group by an alkyl moiety which is less demanding sterically (*e.g.*, ethyl or trimethylsilylmethyl) results in a dramatic increase in rate of intermolecular exchange. This is much easier to understand in terms of a lowering of the free-energy barrier for addition of a dimer to the $(t\text{-butyl})_3RLi_4$ tetramer than in terms of differences in electronic properties of the alkyl groups.

Small traces of bases have a very marked effect in accelerating the rates of *t*-butyllithium reactions.[16-18] If it is assumed that bases do not effectively interact with the tetrameric form of *t*-butyllithium because of steric hindrance, it is possible to understand their effect in terms of relatively greater stabilization of the dissociated species. It has been observed, however, that the reaction of *t*-butyllithium with ethylene in the presence of bases is first order in alkyllithium,[17] so that base stabilization of the dissociation products cannot account for their catalytic effect.

Triethylamine is reported to interact very weakly with *t*-butyllithium in hydrocarbon solution.[19] Addition of triethylamine to *t*-butyllithium in cyclohexane or cyclopentane produces no change in the ^7Li chemical shift, nor any evidence from freezing point lowerings of an acid–base interaction.[18] The fact that triethylamine in low concentrations does markedly accelerate the exchange of *t*-butyllithium with trimethylsilylmethyllithium,[18] by a factor of at least 50, does demonstrate an interaction between base and tetramer which has important kinetic consequences. Interaction of base with the transition state in both the exchange and reaction with ethylene must be held accountable for the increased rates.

Experimental Section

Preparation of Isotopically Enriched *t*-Butyllithium. Lithium metal (^6Li samples varying from 96.0 to 99.3%, or 99.9% ^7Li), obtained from Union Carbide Corp., Stable Isotopes Division, separated from an ingot in an inert atmosphere glovebox, was placed with a small amount of mineral oil into a 500-ml Morton flask in a drybox. Sodium (0.04 g (2%)) was then added and the metal was converted into a fine sand outside the glovebox, but under an argon atmosphere, by immersing the flask into a hot oil bath (approximately 200°) and agitating the mixture with a high speed Dumore KB-210 stirrer for 10 min. The flask was returned to the box. The lithium sand was washed free of mineral oil using dry *n*-pentane or cyclohexane (ether, THF, or cyclopentane were used on occasion). The metal was retained in a medium-frit sintered-glass funnel and washed again with several portions of a hydrocarbon solvent, generally *n*-pentane.

The Li sand was placed into a 125-ml erlenmeyer flask with 50 ml of *n*-pentane. *t*-Butyllithium was produced by dropwise addition of 4.0 ml of *t*-butyl chloride (purified by distillation and stored over 4A Linde molecular sieves after being synthesized by the reaction of *t*-butyl alcohol with concentrated HCl) dissolved in 25 ml of *n*-pentane at room temperature. Normally the reaction was allowed to continue overnight (12–15 hr) in a tightly closed system to ensure retention of the solvent. A white solid was finally isolated after filtering the mixture through a medium-frit sintered-glass funnel and removal of the solvent under vacuum.

The product was then purified by repeated sublimations (at least twice) at 45–50°. Mass spectral samples were prepared initially as follows. A 1.1 *M* solution (20 ml) of $^6Li\text{-}t\text{-}C_4H_9$ and $^7Li\text{-}t\text{-}C_4H_9$ in cyclopentane or benzene was mixed at 26°. The solvent was then stripped off at reduced pressure from aliquots taken at various time intervals. These samples were then sealed off in sample tubes designed for a direct sample inlet system and stored under liquid N_2 or Dry Ice.

A modified procedure was employed for some samples in an attempt to reduce the level of oxygen-containing species present in the mass spectrum. Thirty-five milligrams each of ^6Li-and ^7Li-rich samples were placed into two side arms of a specially designed sublimation apparatus and then sublimed at 50–60° into the central portion cooled with liquid nitrogen. The sublimate was then dissolved in 2 ml of cyclopentane by distilling the solvent from *t*-butyllithium directly into the central section. The solvent was removed at a selected time interval. The apparatus was then mounted directly onto the mass spectrometer without delay. These samples exhibited less oxygen-containing ions in the mass spectrum than others, but significant intensities were still observed.

A Bendix Corp. time-of-flight mass spectrometer, Model 14-206, was used in the mass spectral studies.

All other materials and solvents were prepared as previously described. The ^7Li spectra were obtained at 23.3 MHz, using a Varian Associates Model DP 60 spectrometer. Chemical shifts are measured relative to an external standard consisting of a sealed capillary containing 3 *M* aqueous LiBr.

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(16) P. D. Bartlett, S. Friedman, and M. Stiles, *J. Amer. Chem. Soc.*, **75**, 1771 (1953).

(17) P. D. Bartlett, C. V. Goekel, and W. P. Weber, *ibid.*, **91**, 7425 (1969).

(18) H. L. Lewis, unpublished observations. A mixture of I and II in a 7:1 ratio in cyclopentane (total Li concentration 0.5 *M*, to which has been added a small quantity of triethylamine such that the base:Li ratio is in the range 1:4–1:1) exhibits ^7Li spectra characteristic of the completely equilibrated mixture within a period of about 15 min at 25°.

(19) F. A. Settle, M. Haggerty, and J. F. Eastham, *J. Amer. Chem. Soc.*, **86**, 2076 (1964).