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Solution Structures of *tert*-Butyllithium/Lithium *tert*-Butoxide Mixed Aggregates. Observation of a Nonrandom Fluxional Exchange Process in Hexameric Organolithium Compounds

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Alkyllithium compounds react with alcohols or molecular oxygen to form lithium alkoxides.[1] For less than stoichiometric amounts of the oxygen compounds, mixed alkyllithium/lithium alkoxide species have been observed.[2–4] However, the structures are not always known. Several X-ray crystal structures have recently appeared,[5] but it is unclear that these are necessarily representative of the solution structures, particularly in hydrocarbon solvents. The nature of these complexes in solution is of particular interest in light of the large effect alkoxides have on the reactivity of organolithium compounds.[6] Such alkyllithium/lithium alkoxide mixed systems may also serve as models for understanding the so-called "superbases" formed from RLi and MOR, M = Na, K, Cs,[7] although a recent study provides evidence that superbases in THF do *not* consist of a mixed aggregate.[8]

We now report on the mixed hexameric complexes $(RO)_{6-n}R_nLi_6$, $n = 1,2$ for R = *tert*-butyl in hydrocarbon solvent, in addition to the $(RO)R_3Li_4$ complex we observed earlier.[3] We have determined the solution structures and have found evidence for a nonrandom fluxional exchange mechanism in the hexamers. There are many studies of the various exchange processes in organolithium compounds,[3,9] including hexameric aggregates,[10] but almost nothing is known about the fluxional exchange in hexamers due to the inability to slow the exchange even at low temperatures. The use of mixed aggregates in the current study provided an opportunity to explore the exchange processes even under rapid fluxional exchange conditions.

The ^{13}C proton-decoupled spectrum of a 0.7:1 mixture of *tert*-butyl alcohol and *tert*-butyllithium-^{6}*Li* at −15 °C in cyclopentane shows five multiplets in the α-carbon region, 8–12 ppm. Introduction of ^{6}Li decoupling converts the multiplets to five singlets at 9.52, 9.67, 9.83, 11.38, and 11.40 ppm,[11] confirming the assignment of the multiplets as carbons bonded to lithium. The resonances at 11.38 and 9.67 are the previously observed fluxional R_4Li_4 and $(RO)R_3Li_4$, respectively. The other three resonances each have couplings of approximately 2.5 Hz, compared to 3.8 and 4.1 Hz for the fluxional tetramers, indicating that they are fluxional hexamers.[12] The multiplicity of the resonances and the relative intensities are also consistent with this interpretation. Each of these multiplets consists of at least 10 lines with the relative intensities expected for a ^{13}C nucleus coupled to six ^{6}Li nuclei ($I = 1$). We interpret these results as the 13-line multiplets expected for a fluxional hexameric aggregate, but with the outermost peaks indistinguishable from the noise. In any case, the results exclude a fluxional or a static tetramer which would exhibit a nine- or a seven-line multiplet, respectively. The existence of butoxide-rich mixed aggregates as hexamers is consistent with the hexameric nature of lithium *tert*-butoxide.[13] Apparently, replacement of some of the *tert*-butyl groups by *tert*-butoxide groups lowers the steric interactions sufficiently to allow hexamers to form.

The ^{6}Li spectrum at −15 °C contains six resonances (see Figure 1). The resonance at 0.0 ppm is that of *tert*-butyllithium, R_4Li_4. The resonances at −0.12 and −0.78 ppm are the two nonequivalent sets of ^{6}Li nuclei in the nonfluxional $(RO)R_3Li_4$ mixed tetramer. The three new resonances at −0.81, −0.82, and −0.86 ppm are presumably the three butoxide-containing hexamers. A one-to-one correspondence between these three ^{6}Li resonances and the three hexamer peaks in the ^{13}C spectrum was confirmed using ^{13}C,^{6}Li heteronuclear correlated 2D NMR.[14] This strongly suggests that these are three different aggregates. No changes are observed in the ^{6}Li spectrum upon lowering the temperature to −80 °C.

A ^{6}Li,^{1}H heteronuclear 2D NOE experiment (HOESY),[15] Figure 1, was used to identify the *tert*-butyl and *tert*-butoxy groups within the same aggregate. ^{1}H resonances correlating to the same ^{6}Li resonance are assumed to be from the same aggregate. Correlations arising from intermolecular interactions were considered unlikely since (a) there was no correlation to the solvent resonance even at $t_{mix} = 5$ s and (b) the correlations were still present, although attenuated for the alkoxide correlations, at $t_{mix} = 2$ s. Unexpectedly, two of the ^{6}Li hexamer resonances showed correlations to two different butoxide resonances. Integration of the corresponding butyl and butoxide ^{1}H peaks led to the

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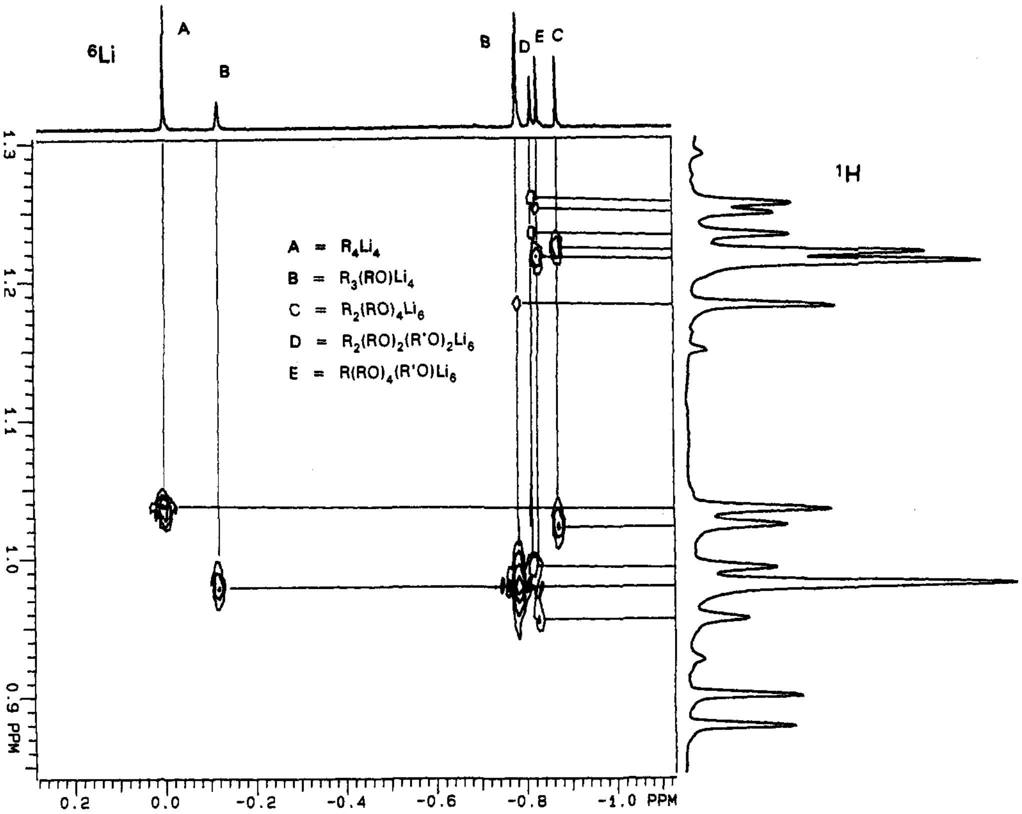
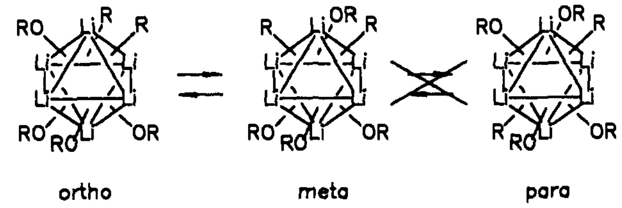


Figure 1. 44-MHz ^{6}Li,^{1}H 2D heteronuclear NOE (HOESY) spectrum of 0.7:1 *t*-BuOH/*t*-Bu^{6}Li in cyclopentane (3.0 M in Li) at −20 °C. t_{mix} = 4.0 s.

Scheme I



assignment of the following five organolithium species: R_4Li_4, $(RO)R_3Li_4$, $(RO)_4R_2Li_6$, $(RO)_2(R'O)_2R_2Li_6$, and $(RO)_4(R'O)RLi_6$. R'O denotes *tert*-butoxide groups which are within the same aggregate but magnetically distinct from the RO *tert*-butoxide groups. The possibility of either nonequivalent protons on the same methyl group or nonequivalent methyl groups within the same *tert*-butoxide group was eliminated on the basis of one-bond and two-bond ^{13}C,^{1}H heteronuclear correlated 2D NMR experiments, respectively.

Both the magnitude of the ^{13}C–^{6}Li coupling and the multiplicity of the ^{13}C resonance for each of the hexameric aggregates *requires* that the *tert*-butyl groups are rapidly fluxional over six ^{6}Li nuclei. However, the nonequivalence observed for the alkoxide groups in two of the hexamers suggests that the alkoxide groups are not randomly exchanged relative to the other *tert*-butyl and *tert*-butoxide groups. A fluxional mechanism which incorporates both of these seemingly contradictive requirements is one in which groups on opposite faces of the hexamer must remain opposite one another.

Assuming a distorted octahedral structure similar to those found for unsolvated hexameric organolithium compounds,[16] hexamers with the empirical formula $(RO)_4R_2Li_6$ can exist as three different isomers, Scheme I. If the groups are required to remain opposite one another, the ortho and meta isomers will be interconverted and have two magnetically nonequivalent sets of *tert*-butoxide groups in the ratio of 2:2. These would not interconvert with the para isomer, which has four equivalent butoxide groups. By similar arguments, a $(RO)_5RLi_6$ aggregate would have two magnetically nonequivalent butoxide resonances in the ratio of 4:1.

If this nonrandom fluxionality is the correct interpretation of the data, we might expect a much slower, random fluxional exchange process which produces magnetic equivalence of the butoxide groups and of the butyl groups for the 4:2 isomers and magnetic equivalence of the *tert*-butoxide groups for the 5:1 hexamer. Although broadening and eventual disappearance of the ^{13}C *tert*-butoxide resonances of the (2:2):2 complex above −5 °C suggests such a process, it was not definitive. However, a ^{13}C 2D exchange NMR spectrum,[17] clearly shows a slow exchange between the *tert*-butyl resonance for $(RO)_2(R'O)_2R_2$ (the ortho and meta isomers of the 4:2 hexamer) and the *tert*-butyl resonance for $(RO)_4R_2Li_6$ (the para isomer of the 4:2 hexamer). It also shows exchange between the two types of butoxides in the 5:1 hexamer and the expected exchange among the butoxide methyls of the (2:2):2 hexamer, and the 4:2 hexamer. Efforts to test the generality of this nonrandom fluxional exchange by extending the study to other types of mixed organolithium hexamers are currently underway.

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