MIXED ALKYLLITHIUM/LITHIUM ALKOXIDE
AGGREGATES WITH LESS STERICALLY
CROWDED ALKYL GROUPS

THESIS

Presented to the Graduate Council of the
University of North Texas in Partial
Fulfillment of the Requirements

For the Degree of

MASTER OF SCIENCE

By

Terry L. Thornton, B. S.
Denton, Texas
December 1997
Thornton, Terry L., Mixed alkyllithium /lithium alkoxide aggregates with less sterically crowded alkyl groups. Master of Science (Chemistry), December 1997, 61 pp., 3 Tables, 22 Figures, 27 references, 25 titles.

Mixed alkyllithium /lithium alkoxide aggregates in the form (RLi)_n(ROLi)_m were formed by addition of corresponding alcohol compounds at different Li/O ratios. Variable temperature ^13C and ^6Li NMR spectroscopy were used to verify the formation of the mixed aggregates and to study their behavior in hydrocarbon solution. Spectra for the lithium n-propoxide / n-propyllithium and iso-butyllithium / lithium iso-butoxide systems each indicated at least one mixed aggregate.
MIXED ALKYL LITHIUM/LITHIUM ALKOXIDE
AGGREGATES WITH LESS STERICALLY
CROWDED ALKYL GROUPS

THESIS

Presented to the Graduate Council of the
University of North Texas in Partial
Fulfillment of the Requirements

For the Degree of

MASTER OF SCIENCE

By

Terry L. Thornton, B. S.
Denton, Texas
December 1997
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>iv</td>
</tr>
<tr>
<td><strong>CHAPTER</strong></td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. EXPERIMENTAL</td>
<td>5</td>
</tr>
<tr>
<td>Alkyllithium Compounds</td>
<td></td>
</tr>
<tr>
<td>Mixed Alkyllithium / Lithium Alkoxide Compounds</td>
<td></td>
</tr>
<tr>
<td>NMR Spectra</td>
<td></td>
</tr>
<tr>
<td>III. RESULTS AND DISCUSSION</td>
<td>19</td>
</tr>
<tr>
<td>n-Propyllithium</td>
<td></td>
</tr>
<tr>
<td>Lithium n-Propoxide / n-Propyllithium</td>
<td></td>
</tr>
<tr>
<td>Conclusion of Lithium n-Propoxide / n-Propyllithium</td>
<td></td>
</tr>
<tr>
<td>Mixed Aggregates</td>
<td></td>
</tr>
<tr>
<td>iso-Butyllithium</td>
<td></td>
</tr>
<tr>
<td>Lithium iso-Butoxide / iso-Butyllithium</td>
<td></td>
</tr>
<tr>
<td>Conclusion of Lithium iso-Butoxide / iso-Butyllithium</td>
<td></td>
</tr>
<tr>
<td>Mixed Aggregates</td>
<td></td>
</tr>
<tr>
<td><strong>BIBLIOGRAPHY</strong></td>
<td>60</td>
</tr>
</tbody>
</table>
LIST OF TABLES AND FIGURES

TABLES

1. Amounts of iso-butyl alcohol and iso-butyllithium compound used in 5mm NMR tubes........................................13

2. Amounts of n-propyllithium and n-propyl alcohol compound used in 5mm NMR tubes........................................15

3. Panel temperature and actual measured temperatures for NMR samples (°C)....................................................17

FIGURES

1. $^{13}$C NMR spectrum of bis n-propyl mercury at room temperature.................................................................9

2. $^{13}$C NMR spectrum of n-propyllithium at room temperature.................................................................20

3. $^{13}$C NMR spectrum of n-propyllithium, temperature = -63°C.................................................................21

3a. $^{13}$C NMR Spectrum of n-propyllithium, expanded alpha carbon region, temperature = -63°C..............21

4. $^{13}$C{$^1$H,$^6$Li} NMR Spectrum of n-propyllithium, $^1$H and $^6$Li decoupled, temperature = -63°C.......23

4a. $^{13}$C{$^1$H,$^6$Li} NMR Spectrum of n-propyllithium, $^1$H and $^6$Li decoupled, expanded alpha carbon region, temperature = -63°C..................................................23
5. $^6\text{Li}$ NMR Spectrum of $n$-propyllithium, 
temperature = $-95^\circ\text{C}$.................................24

5a. $^6\text{Li}$ NMR Spectrum of $n$-propyllithium, 
temperature = $-68^\circ\text{C}$.................................24

6. $^{13}\text{C}$ NMR spectrum of $n$-propyllithium and $n$-propyl 
alcohol, 0.2:1 RO/Li ratio, room temperature..............27

7. $^{13}\text{C}$ NMR spectrum of $n$-propyllithium and $n$-propyl 
alcohol, 0.2:1 RO/Li ratio, alpha carbon peaks, 
temperature = $-91^\circ\text{C}$. Inset shows expanded alpha 
carbon region.......................................................28

8. $^{13}\text{C}[^1\text{H},^6\text{Li}]$ NMR spectrum of $n$-propyllithium and 
$n$-propyl alcohol, $^1\text{H}$ and $^6\text{Li}$ decoupled, 0.2:1 
RO/Li ratio, alpha carbon range, temperature 
= $-91^\circ\text{C}$. Inset shows alpha carbon region..............29

9. $^6\text{Li}$ NMR spectrum of $n$-propyllithium and $n$-propyl 
alcohol, 0.2:1 RO/Li ratio, temperature = $-86^\circ\text{C}$........31

10. $^{13}\text{C}$ NMR spectrum of $n$-propyllithium and $n$-propyl 
alcohol, 1:1 RO/Li ratio, temperature = $-51^\circ\text{C}$............34

11. $^{13}\text{C}$ NMR spectrum of $n$-propyllithium and $n$-propyl 
alcohol, 1:1 RO/Li ratio, temperature = $-74^\circ\text{C}$............36

12. $^6\text{Li}$ NMR spectrum of iso-butyllithium 
temperature = $-33^\circ\text{C}$.................................................39

13. $^{13}\text{C}$ NMR spectrum of iso-butyllithium and iso-butyl 
alcohol, 0.09:1 RO/Li ratio, temperature = $-51^\circ\text{C}$. 
Inset shows alpha carbon region...............................41
14. $^{13}$C($^{1}$H,$^{6}$Li) NMR spectrum of iso-butyllithium and iso-butyl alcohol, 0.09:1 RO/Li ratio, temperature = -51°C. Inset shows the two collapsed alpha carbon peaks.

15. $^{6}$Li NMR spectra of iso-butyllithium and iso-butyl alcohol, 0.09:1 RO/Li ratio, temperature = -39°C.

16. $^{13}$C NMR spectrum of iso-butyllithium and iso-butyl alcohol 0.2:1 RO/Li ratio, temperature = -56°C. Inset shows the two overlapping alpha carbons.

17. $^{6}$Li NMR spectrum of iso-butyllithium and iso-butyl alcohol 0.2:1 RO/Li ratio, temperature = -39°C.

18. $^{6}$Li NMR spectra of iso-butyllithium and iso-butyl alcohol, 0.2:1 RO/Li ratio, temperature = -57°C.

19. $^{6}$Li NMR spectrum of iso-butyllithium and iso-butyl alcohol 0.2:1 RO/Li ratio, temperature = -80°C.

20. $^{13}$C NMR spectrum of iso-butyllithium and iso-butyl alcohol 1:1 RO/Li ratio, temperature = -56°C.

21. $^{6}$Li NMR spectrum of iso-butyllithium and iso-butyl alcohol, 1:1 RO/Li ratio. Temperatures from bottom to top: -5°C; -28°C; -39°C.

22. $^{6}$Li NMR spectrum of iso-butyllithium and iso-butyl alcohol, 1.5:1 RO/Li ratio. Temperatures from bottom to top: -5°C; -28°C; -39°C.
CHAPTER 1

INTRODUCTION

It is now well known that alkyllithium compounds exist as aggregates, \((RLi)_n\), where \(n\) is dependent on temperature, concentration, solvent and alkyl group. The aggregation states typically are \(n = 2,3,4,6,8\) or 9 \((1,2,3,4)\).

The trend of aggregation states for alkyllithium compounds as a function of particular alkyl group is as follows: straight chain alkyl groups form larger aggregate states; more highly branched alkyl groups form smaller aggregate states. If multiple aggregation states are present, higher concentrations of RLi will favor the larger aggregate state. There is also an effect on the aggregate state depending on the solvent. If a compound is in a hydrocarbon solvent and it shows two or more aggregate states in equilibrium, then the larger aggregate state will normally form at the lower temperature. In coordinating solvents, the reverse of this is true.

Solid state structures are known for the monomer, dimer, tetramer and hexamer \((5,6,7)\). It may be that the solution structures of mixed aggregates are the same as or very similar to the solid state structures. Since the
solution structures are not always known, the solid structures provide a possible indication of the solution structures for different aggregate states.

More recent work by Thomas' group has shown that mixed alkyllithium / lithium alkoxides, \((RLi)\_n(ROLi)\_m\), also exist as aggregates in solution (8). For \(R = t\text{-butyl}\), NMR studies indicate the mixed aggregate is a tetramer or a hexamer, depending on the relative number of \(R\) and \(OR\) groups. With one \(OR\) group, the aggregate is tetrameric. With four or more \(OR\) groups the aggregate is hexameric.

t-Butyllithium exists only as a tetramer in hydrocarbon solution. With the substitution of \(t\text{-butoxide}\) groups for a sufficient number of \(t\text{-butyl}\) groups, the structure becomes hexameric. This is apparently due to the reduced steric requirements of the butoxide group relative to the butyl group.

It was not known how the aggregate state of the mixed aggregates would change with the different \(R\) and \(OR\) groups, or with the size of the \(R\) and \(OR\) groups. Since the \(t\text{-butyl}\) and \(t\text{-butoxide}\) groups are so very bulky, it was felt that less sterically hindered \(R\) and \(OR\) groups might lead to mixed aggregate states larger than hexamer. Two less sterically hindered compounds were chosen for this study: \(n\text{-propyllithium / lithium } n\text{-propoxide}\) and \(iso\text{-butyllithium / iso-butoxide}\).
The n-propyllithium compound at room temperature is in only one aggregate state, a hexamer, in hydrocarbon solution (9). Fraenkel reported in 1980 that as the temperature is lowered, the compound in hydrocarbon solution is in five different aggregate states: hexamer, octamer and three nonamers (10). There is little information about the structures for aggregate states of n = 8, 9.

Initial experimental studies were carried out by Ellington on the n-propyllithium / lithium n-propoxide system (11). He found that this system appeared to form mixed aggregates. This system therefore was investigated as a function of R / OR ratios and temperature.

Since n-propyllithium compound is a complex system, the iso-butyllithium / lithium iso-butoxide system was also included in this study. The iso-butyllithium is a hexamer at all temperatures in hydrocarbon solutions (12). Therefore, it would seem likely that with the introduction of iso-butoxide group into the aggregate it may form higher aggregate states.
Chapter Notes


CHAPTER 2

EXPERIMENTAL

Synthesis of Compounds

Alkyl lithium Compounds

The synthesis of all alkyl lithium compounds in this study was done in two steps. First the dialkylmercury compounds were synthesized using a Grinard reaction starting with the alkyl halide. Second, using the purified dialkylmercury compound, the alkyl lithium compound was synthesized from $^6\text{Li}$ enriched metal (1). The general process is as follows:

$$RX + Mg \rightarrow RMgX \quad [1]$$

$$2RMgX + HgX_2 \rightarrow R_2Hg + 2MgX_2 \quad [2]$$

$$R_2Hg + 2Li \rightarrow 2RLi + Hg \quad [3]$$

Due to the high toxicity, all mercury compounds were handled in a fume hood with normal laboratory precautions. Glassware coming in contact with mercury compounds was washed in concentrated nitric acid, then cleaned and dried in the oven at 250°C for two hours.

The products in equation 3 are very air-sensitive. To
prevent oxygen contamination during this step, all work involving equation 3 was performed using a vacuum line (5x10⁻⁵ mm Hg or less) or an argon atmosphere glove-box. For this study all solvents were dried over LiAlH₄ and degassed on the vacuum line prior to use.

*n-Propyllithium* was synthesized using the following process. A round bottom flask was set-up under an argon flow with a mechanical stirrer, a 250 mL dropping funnel and a condenser. To the flask was added 1400 mL of diethyl ether that had been freshly distilled over LiAlH₄, and 26.74g (1.1 mols) of Mg turnings that had been ground using a mortar and pestle. To the dropping funnel was added 100 mL of diethyl ether, and 100.0 mL (1.1 mols) of 1-bromopropane. Approximately 20 mL of the solution in the dropping funnel was next added to the flask. The reaction would start briefly and then stopped. To restart the reaction, about 2 mL of dibromoethane was added to the flask and the stirring rod was used to gently scrape the Mg. Once the reaction started, stirring was applied and the drop rate from the funnel was matched to the reflux rate. The addition took approximately 1/2 hr to complete. Once the addition of solution was complete, heat was applied and the reaction was refluxed and stirred for 2 1/2 hrs. The reaction was then allowed to cool and settle overnight with an argon flow.
The solution was next transferred to a round bottom flask using a double ended needle with an argon flow. The transfer took approximately 1/2 hr to complete. This reaction flask was then equipped with a mechanical stirrer, a Soxhlet extractor with condenser and an argon flow. Assuming a 60% yield on the above reaction, 112.33 g (0.31 mols) of HgBr$_2$ was placed in the cellulose extraction thimble of the Soxhlet extractor. The complete apparatus was covered in aluminum foil to block light from the reaction. The solution was then gently allowed to reflux for 43 hrs. During this time the solution went from a dark solution to a dull milky white slurry.

The reaction mixture was allowed to settle for 2 hrs. Next, excess n-propylMgBr was quenched by adding dropwise a saturated NH$_4$Cl solution until this reaction was slow. Next distilled H$_2$O was added until no reaction occurred. This took approximately 600 mL of saturated NH$_4$Cl solution and 200 mL of distilled H$_2$O.

The water and ether mixture was next separated using a 2 liter separatory funnel. The ether solution was washed three times using 100 mL of distilled H$_2$O, then stored over MgSO$_4$ for 18 hrs in the refrigerator. The mixture was next filtered and the ether stripped off using a Rotovap. Next the solution was then vacuum distilled at 41°C - 44°C @ 1 mm. This is consistent with the literature value b.p. of 82-84
°C @ 19 mm (2). A total of 50.48 g (0.176 mol) was collected. This corresponds to a 32% yield from the 1-bromopropane. The $^{13}$C NMR spectrum seen in Figure 1 shows three peaks each flanked by a pair of peaks, which are the $^{199}$Hg satellites. The chemical shifts and the $^{199}$Hg - $^{13}$C coupling constants are 19.9 ppm (103 Hz), 22.3 ppm (24 Hz) and 47.1 ppm (662 Hz). These are consistent with reported literature values of 20.1 ppm (104 Hz), 22.7 ppm (24 Hz) and 47.3 ppm (665 Hz) for bis n-propyl mercury (3).

The bis n-propyl mercury was again distilled and 24.9 g (0.0887 mol) was collected between 41° - 44° C @ 1 mm Hg. The $^{13}$C NMR spectrum as shown with the peaks in Figure 1.

Into a 125 mL Erlenmeyer flask, fitted with a ground glass joint, was added 9.0 grams (0.0314 mol) of bis n-propyl mercury. Using the vacuum line, approximately 50 mL of cyclopentane was cryopumped into the flask. The solution was next degassed using five freeze-pump-thaw cycles and placed in the dry box.

In the dry box, 0.75 g (0.062 mol) of 6Li metal was cut into approximately 1 mm$^2$ pieces (1). The pieces were placed in a reaction vessel and the bis n-propyl mercury in cyclopentane solution was pipetted into the reaction vessel. The reaction vessel was transferred to the vacuum line, degassed seven times using the freeze-pump-thaw method, and flame sealed.
FIGURE 1: $^{13}$C NMR spectrum of bis $n$-propyl mercury at room temperature.
It was next placed on a shaker table for approximately three weeks. Inside the dry box the reaction vessel was opened and an aliquot transferred to an NMR tube. The $^{13}$C NMR spectrum showed two large peaks at 16.9 ppm, 23.0 ppm and numerous smaller peaks.

The peak at 26.5 ppm is the solvent peak. The broad peak at 23.0 ppm is presumed to be overlapping resonances for the beta and gamma carbons. This is consistent with literature values for n-propyl lithium of 16.2, 21.9, and 22.1 ppm (4). No peaks corresponding to bis n-propyl mercury compound were detected (3). After the solution was filtered through a fine frit it retained a light brown color. The light brown color was probably from contamination with apiezon grease that was used to grease joints. A $^{13}$C NMR spectrum run on the grease dissolved in CCl$_4$ displayed a spectrum that corresponded to the numerous smaller peaks noted above. An attempt was made to distill the compound over an inverted Y tube on the vacuum line at 10$^{-6}$ torr and room temp (4,5). No compound was collected. Heat was not added because of the possibility of decomposition of the n-propyl lithium. This compound was stored in a glass vessel using a teflon cap and kept in the drybox for future use.

After an extended period of time the compound had separated into two layers. The top layer was a fine light
brown colored solid material while the bottom layer is a
dark brown viscous liquid. The $^{13}$C NMR spectrum of the
bottom layer was consistent with the original spectrum and
showed no signs of alkoxides or oxygen contamination.

Iso-Butyllithium was synthesized starting with bis iso-
butyl mercury. The bis iso-butyl mercury had been prepared
by previous members of the group (6). The compound was
distilled and 25.1 g (0.80 mol) was collected between 46° -
48° C @ 1 mm Hg. The $^{13}$C NMR spectrum showed peaks at 28.5
ppm {81 Hz}, 29.5 ppm {30 Hz} and 56.9 ppm {676 Hz} which is
consistent with the literature values of 28.5 ppm {82 Hz},
29.6 ppm {29 Hz} and 56.7 ppm {679 Hz}(3).

Next, 25.1 g (0.080 mol) of bis(iso-butyl)mercury was
weighed and pipetted into a 125 mL Erlenmeyer flask and
placed on the vacuum line. To this was cryopumped in
approximately 50 mL of cyclopentane that had been stored
over LiAlH$_4$. The solution was degassed seven times, and
placed in a drybox.

In a drybox, 2.88 grams (0.48 mol) of $^6$Li was cut into
1 mm$^2$ pieces and placed into the reaction vessel (1). Next
the bis(iso-butyl)mercury solution was pipetted into the
reaction vessel. The vessel was degassed eight times and
flame sealed. It was then placed on a shaker table at room
temperature for 22 days.

The reaction vessel was removed and the insoluble
material was allowed to settle in the refrigerator for about 24 hrs. Inside the dry box the reaction vessel was opened and an aliquot was transferred to an NMR tube. The $^{13}$C NMR spectrum displayed peaks of 27.1 ppm and 29.0 ppm which are consistent with the literature values of 27.4 ppm, and 29.3 ppm (4). The peak at 29.0 ppm is a broad peak that is both carbon 2 and 3 overlapping. No peaks were seen that correspond to his iso-butyl mercury compound (3). The solution was filtered twice using fine frits and was a slightly tinted brown color.

In the drybox the solution was next pipetted into a 125 mL erlenmeyer flask equipped with a stopcock. The flask was then placed on the vacuum line, and the cyclopentane was cryopumped off leaving solid, off-white crystals. The crystals were slowly sublimed on a static vacuum line at approximately $5 \times 10^5$ torr and 80° C. After sublimation the clean iso-butyllithium was transferred and stored in the drybox for further use.

**Mixed Alkyl Lithium / Lithium Alkoxide Compounds**

Solutions of mixed alkyl lithium / lithium alkoxide compounds were made in the drybox by adding alcohol to the corresponding alkyl lithium compound.
Lithium iso-butoxide / iso-butyllithium was prepared by adding a solution of iso-butyl alcohol to a solution of iso-butyllithium. The total amount of iso-butyllithium and iso-butyl alcohol used in making NMR tubes was dependent on the size of the NMR tube, the concentration used, and the ratio prepared. Table 1 shows the amounts of iso-butyllithium and iso-butyl alcohol that were used according to the desired ratio.

<table>
<thead>
<tr>
<th>Li Conc.</th>
<th>Ratio prepared OR/Li</th>
<th>Amount of iso-butyllithium used</th>
<th>Amount of iso-butyl alcohol used</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 F</td>
<td>0.09 / 1</td>
<td>0.022 grams</td>
<td>2.5 μl</td>
</tr>
<tr>
<td>1.0 F</td>
<td>0.2 / 1</td>
<td>0.044 grams</td>
<td>0.021 grams</td>
</tr>
<tr>
<td>0.5 F</td>
<td>0.4 / 1</td>
<td>0.022 grams</td>
<td>0.021 grams</td>
</tr>
<tr>
<td>0.5 F</td>
<td>1 / 1</td>
<td>0.022 grams</td>
<td>0.026 grams</td>
</tr>
</tbody>
</table>

Table 1: Amounts of iso-butyl alcohol and iso-butyllithium compound used in 5mm NMR tubes (9).

The iso-butyl alcohol was dried over LiAlH₄ for 24 hrs, then degassed eight times on a vacuum line at 10⁻⁴ torr. The iso-butyl alcohol was placed in the drybox and transferred to a storage vessel for further use.

The process for preparing a 5mm NMR tube at a concentration of 0.5 F with iso-butyllithium and iso-butyl alcohol at a ratio of 0.09:1 RO/Li will be described in detail. All NMR tubes were made using the same steps described below.
In the drybox, 0.022 g \((3.49 \times 10^{-4} \text{ mols})\) of iso-butyllithium was placed into a 50 mL beaker. To this was added a few drops of a cyclopentane solvent containing 7.5 % deuterated cyclopentane \((8)\). This was stirred and covered with Al foil. In a 25 mL Erlenmeyer flask was placed 2.5 ul \((2.71 \times 10^{-5} \text{ mols})\) of iso-butyl alcohol. To this was added a few drops of the deuterated cyclopentane solution. This was stirred, and covered with Al foil. Next the iso-butyl alcohol solution was transferred to the iso-butyllithium beaker by dropping the solution down the side of the beaker while constantly swirling the beaker. Upon addition of the iso-butyl alcohol, the solution was transferred by disposable pipette to a 5mm NMR tube. Additional deuterated cyclopentane was added to the 5mm NMR tube to bring the amount of solution to approximately 0.7 mL. The NMR tube was next placed on the vacuum line, degassed five times on a vacuum line and flame sealed.

\textit{n-Propyllithium / lithium n-propoxide} was prepared using the same process as the iso-butyllithium / lithium iso-butoxide. \textit{n-Propyl} alcohol was first dried over CaH\(_2\) for 24 hrs, distilled into a dry 125 mL Erlenmeyer flask, then degassed six times on a vacuum line at 10\(^5\) torr. In the drybox the solution was then transferred into a storage vessel and stored there until used. Amounts of \textit{n-}
propyllithium and n-propyl alcohol used in making sealed NMR tubes are shown in Table 2.

<table>
<thead>
<tr>
<th>Li Conc.</th>
<th>Ratio prepared OR/Li</th>
<th>Amount of n-propyllithium used</th>
<th>Amount of n-propyl alcohol used</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 F</td>
<td>0.2:1</td>
<td>0.0686 grams</td>
<td>1.9 μl</td>
</tr>
</tbody>
</table>

Table 2: Amounts of n-propyllithium and n-propyl alcohol compound used in 5mm NMR tubes.

**NMR Spectra**

Spectra were recorded on a Varian VXR-300 NMR spectrometer at 75 MHz for $^{13}$C and 44 MHz for $^6$Li. Typical conditions for $^{13}$C NMR were 5000 to 17000 Hz spectral width, 32K transform, 128 to 1024 transients, and Waltz proton decoupling. Chemical shifts were set relative to TMS by setting the resonance for protonated cyclopentane to 26.500 ppm, or the resonance for deuterated chloroform to center peak at 77.00 ppm. Typical conditions for $^6$Li NMR were 300 Hz spectral width, 32K transform, and 16 transients.

$^{13}$C NMR spectra with simultaneous $^1$H and $^6$Li nuclei decoupling were recorded using the above instrument equipped with a triple resonance probe from Varian Instruments. The probe is a regular 10 mm tunable probe in which the normal lock channel was changed to irradiate at 44.1 MHz (10).

The temperatures were calculated for the NMR spectrum from a program used by Varian Instruments. The program uses
from a program used by Varian Instruments. The program uses the difference in the chemical shifts of the two proton peaks for methanol. The temperature was measured between room temperature and -90°C at 10 degree intervals with constant N₂ flow rates. The N₂ flow at the instrument was 6.5 LPM, while regulation of the liquid N₂ tank was set at 22 psi. Using the temperatures recorded, Table 3 was prepared comparing the temperature set by the NMR and actual temperatures recorded. When fitted to a straight line, excluding the room temperature data point, the resulting equation is

\[ y = 1.1518 X - 4.8410 \quad r = 0.9919 \]  

(1)

where X is the panel temperature, and Y is the actual temperature.

The temperatures used for the calibration curve were only with the proton decoupler on. When both the proton and lithium decoupler are on there may be a slight increase in the actual temperature, however it is assumed that this increase is small.
<table>
<thead>
<tr>
<th>Panel Temperature</th>
<th>Actual Temperature</th>
<th>Panel Temperature</th>
<th>Actual Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>24</td>
<td>-40</td>
<td>-50.8</td>
</tr>
<tr>
<td>0</td>
<td>-5.2</td>
<td>-50</td>
<td>-62.0</td>
</tr>
<tr>
<td>-15</td>
<td>-22.4</td>
<td>-60</td>
<td>-73.8</td>
</tr>
<tr>
<td>-20</td>
<td>-27.7</td>
<td>-70</td>
<td>-85.9</td>
</tr>
<tr>
<td>-30</td>
<td>-39.0</td>
<td>-80</td>
<td>-97.2</td>
</tr>
</tbody>
</table>

Table 3: Panel temperature and actual measured temperatures for NMR samples (°C).
Chapter Notes

1. Lithium metal was obtained from the U.S. Services and is 95.5\% isotopically enriched $^{6}\text{Li}$.


8. 6.7\% cyclopentane-$d^{10}$ from Wilmad; 99.5\% cyclopentane from Aldrich.

9. iso-Butyl alcohol (0.8018 g/mL) and n-propyl alcohol (0.8035 g/mL) measured using a 10 ul syringe.

CHAPTER 3

RESULTS and DISCUSSION

n-Propyllithium

A 10 mm NMR tube of 2F n-propyllithium was prepared as discussed in Chapter 2. The $^{13}$C NMR spectrum at room temperature shown in Figure 2, shows the three carbon peaks for the n-propyl group at 16.8 ppm, 23.0 ppm, and 23.1 ppm. The 16.8 ppm peak is a broad singlet corresponding to the alpha carbon of n-propyllithium. Peaks at 23.0 ppm and 23.1 ppm are singlets corresponding to the beta and gamma carbons, although the actual peaks are not assigned.

Variable temperature $^{13}$C NMR studies of this compound show that as the temperature is lowered the peak at 16.8 ppm broadens and shifts slightly upfield. At -22°C a new peak at 19.3 ppm appears; at -62°C a third peak at 18.1 ppm also grows in but is much smaller. These peaks are the alpha carbons from the three aggregate states that form at these temperatures, as earlier reported by Fraenkel (1).

At -63°C the $^{13}$C − $^6$Li coupling, shown in Figures 3 and 3a, is measured at 3.1 Hz for the peak at 16.3 ppm. The coupling of 3.1 Hz is consistent with that observed by Fraenkel and is now understood to be an indicator of a hexamer (1,2).
FIGURE 2: $^{13}$C NMR Spectrum of $n$-propyllithium at room temperature.
FIGURE 3: $^1$H NMR spectrum of $n$-propyllithium, temperature = $-63^\circ$C.

FIGURE 3a: $^1$C NMR spectrum of $n$-propyllithium, expanded alpha carbon region, temperature = $-63^\circ$C.
Coupling for the peaks at 18.1 and 19.3 ppm were not observed. To show that the peaks at 16.3 ppm, 18.1 ppm, and 19.3 ppm are carbon atoms bonded to lithium atoms, a $^{13}$C NMR spectrum, shown in Figures 4 and 4a, was run in which both $^1$H and $^6$Li nuclei were decoupled. When $^6$Li is decoupled, all three of the peaks collapsed into lines with a smaller line width, thus showing that the carbons are coupled to $^6$Li nuclei.

$^6$Li NMR spectra of this compound were taken between room temperature and $-97^\circ$C. At room temperature the $^6$Li NMR spectrum displays one large peak representing the hexamer, and multiple smaller peaks. For this study the hexamer peak was referenced at 0.0 ppm.

Figure 5a shows that as the temperature is reduced the singlet splits into additional peaks. At $-68^\circ$C there are two large peaks, one broad and one narrow, at 0.00 ppm and $-0.15$ ppm. At this temperature there are also two small broad peaks at $-0.69$ ppm and $-0.84$ ppm. At $-95^\circ$C, the spectrum in Figure 5 shows three large peaks at 0.00 ppm, $-0.08$ ppm and $-0.16$ ppm.
FIGURE 4: $^1$H,$^6$Li NMR Spectrum of $n$-propyllithium, $^1$H and $^6$Li decoupled, temperature = -63°C.

FIGURE 4a: $^1$C NMR Spectrum of $n$-propyllithium, $^1$H and $^6$Li decoupled, expanded alpha carbon region, 2F, temperature = -63°C.
FIGURE 5: $^6$Li NMR Spectrum of $n$-propyllithium, temperature = -95°C.

FIGURE 5a: $^6$Li NMR Spectrum of $n$-propyllithium, temperature = -68°C.
In this work, the $^{13}$C NMR spectrum of n-propyllithium is not consistent with the reports from Fraenkel's group. They reported five alpha carbon singlets. A hexamer (16.3 ppm), octamer (18.1 ppm), and three nonamers (19.3 ppm, 19.6 ppm, 20.0 ppm). This work shows only three alpha carbon singlets. A hexamer (16.3 ppm), octamer (18.1 ppm), and a nonamer (19.3 ppm). The two downfield nonamers at 19.6 ppm and 20.0 ppm were not detected.

The $^6$Li NMR spectrum in this study was also not consistent with the work from Fraenkel's group. Between -60°C and -96°C, they reported a total of five lithium peaks: three larger peaks and two small peaks and assigned as a hexamer, octamer and three nonamers. This work displays three large peaks representing the hexamer, octamer and one nonamer. The two smaller peaks of the second and third nonamer were not seen. The two small peaks in this work at -68°C are much farther upfield than the peaks Fraenkel had observed.

Lithium n-Propoxide / n-Propyllithium

NMR tubes of 2F n-propyllithium and n-propyl alcohol in two different ratios (0.2:1 and 1:1 RO/Li) were prepared as discussed in chapter two. $^{13}$C and $^6$Li NMR spectra were recorded for these solutions between room temperature and -98°C.
Lithium n-Propoxide / n-Propyllithium Mixed Aggregate

(RO/Li= 0.2:1).

For the 0.2:1 RO/Li ratio sample at room temperature, shown in Figure 6, the $^{13}$C NMR spectrum exhibits singlets at 10.5, 16.9, 23.1, 29.6 and 65.6 ppm, and three broad peaks at 14.8, 30.8 and 67.8 ppm. It is important to note that the peak at 23.1 ppm is two unresolved peaks corresponding to carbons two and three.

When the temperature is lowered the alpha carbons begin to separate. At -91°C, the $^{13}$C NMR spectrum, shown in Figure 7 displays six peaks in the alpha carbon region at 16.3, 17.0, 17.2, 18.1, 18.4 and 19.3 ppm for the n-propyllithium compound. Three of the alpha peaks are the aggregates of the hexamer (16.3 ppm), octamer (18.1 ppm) and nonamer (19.3 ppm). The broad peak at 18.4 ppm is assumed to be an alpha carbon from a lithium n-propoxide / n-propyllithium mixed aggregate. The two sharp singlets at 17.0 ppm and 17.2 ppm are from propane which is produced by the addition of n-propyl alcohol to n-propyllithium.

To determine which carbon peaks are bonded to $^6$Li atoms, a $^{13}$C {$^1$H, $^6$Li} NMR spectrum was also taken at -91°C. In this spectrum, shown in Figure 8, the peaks at 16.3 ppm, 18.1 ppm, 18.4 ppm and 19.3 ppm all collapse into sharp singlets. Also a sharp peak is observed at 17.1 ppm between the two propane peaks at 17.0 ppm and 17.2 ppm (3).
FIGURE 6: $^1$H NMR spectrum $n$-propyllithium and $n$-propyl alcohol, 0.2:1 RO/Li ratio, room temperature.
FIGURE 7: $^{13}$C NMR spectrum of $n$-propyllithium and $n$-propyl alcohol, 0.2:1 RO/Li ratio, alpha carbon peaks, temperature = -91°C. Inset shows expanded alpha carbon region.
FIGURE 8: $^{13}$C($^1$H,$^6$Li) NMR spectrum of n-propyllithium and n-propyl alcohol, $^1$H and $^6$Li decoupled, 0.2:1 RO/Li ratio, alpha carbon peaks, temperature = -91°C. Inset shows expanded alpha carbon region.
The peak at 18.4 ppm is small compared to the peak at 17.1 ppm. The sharpening of the peaks with the $^6$Li decoupler shows that these peaks are alkyl groups coupled to Li in a different environment.

The peaks at 16.3 ppm, 18.1 ppm and 19.3 ppm have previously been shown to be alpha carbons of aggregates. The peaks at 17.1 ppm and 18.4 ppm are new alkyl groups bonded to lithium. Therefore this is strong evidence for mixed aggregates of the type $(RLi)_a(ROLi)_m$, as opposed to merely a mixture of RLi and ROLi in solution.

The $^6$Li NMR spectrum is much simpler. At room temperature there are seven peaks. As the temperature is reduced these peaks shift upfield and become more narrow. The peak at 0.00 ppm is the hexamer aggregate which was referenced using $n$-propyllithium. At -86°C, as seen in Figure 9, it is clear that there are seven separate peaks. The three larger peaks at 0.00 ppm, -0.08 ppm and -0.16 ppm are at the same location and separation as the three large peaks (hexamer, octamer and nonamer) observed for $n$-propyllithium.
FIGURE 9: $^6$Li spectrum of n-propyllithium and n-propyl alcohol, 0.2:1 RO/Li ratio, temperature = -86°C.
In this study the $^6$Li NMR spectra shows two small peaks at -0.35 ppm and -0.44 ppm upfield of the three larger peaks at 0.00 ppm, -0.08 ppm and -0.16 ppm. The peak at -0.35 ppm is the same location as the second nonamer peaks reported by Fraenkel’s group, but this may be a coincidence, since the third nonamer peak reported by Fraenkel’s group is not seen in this study.

Two more larger peaks are observed upfield at -0.52 ppm and -2.02 ppm. Since these peaks are observed when the alkoxide group was added to the alkyl solution, it is assumed that these peaks are from either lithium n-propoxide / n-propyllithium mixed aggregate or a lithium n-propoxide aggregate. Therefore this is again strong evidence for aggregates of RLi and ROLi compounds as opposed to merely a mixture of RLi and ROLi in solution.

**Lithium n-Propoxide / n-Propyllithium ($RO/Li = 1:1$).**

In the 1:1 RO/Li ratio at room temperature the $^{13}$C NMR spectrum shows narrow peaks at 10.5 ppm, 14.7 ppm, 29.6 ppm and 31.1 ppm; and broad peaks at 17.1 ppm, 30.5 ppm, 24 ppm, 30 ppm and 66 ppm. All of these peaks were detected as small peaks in the lower RO/Li ratio sample and were not detected in the n-propyllithium compound spectrum.
As the temperature is lowered to -51°C the $^{13}$C NMR spectrum in Figure 10 shows narrow peaks at 10.5 ppm, 14.7 ppm, 17.0 ppm, 23.7 ppm, 23.9 ppm, 29.5 ppm and 66.4 ppm; and broad peaks at 17.1 ppm, 27.5 ppm, 28.3 ppm, 31.2 ppm and 66.5 ppm.

At this temperature in the $^{13}$C NMR spectrum for the sample with the lower RO/Li ratio, there were at least five aggregate states observed, hexamer (16.3 ppm), octamer (18.1 ppm), nonamer (19.3 ppm) and mixed aggregates at 18.4 ppm and 17.1 ppm. In this sample with an RO/Li ratio of 1:1, the $^{13}$C NMR spectrum has only one broad peak in the alpha range at 17.1 ppm.

In attempting to produce a 1:1 RO/Li ratio it may be that the actual ratio was not exactly 1:1. It is likely that the actual ratio was <1:1 RO/Li. This would account for the alpha carbon peak that was detected at 17.0 ppm.

The $^6$Li NMR spectrum of this sample was taken in a series of temperatures between room temperature and -98°C. At room temperature the spectrum is a group of overlapping peaks. As the temperature is lowered the peaks begin to separate and become more resolved. At -51°C, the peaks have become a broad peak at -0.52 ppm and numerous smaller unresolved peaks upfield.
FIGURE 10: $^{13}$C NMR spectrum of $n$-propyllithium and $n$-propyl alcohol, 1:1 RO/Li ratio, temperature = -51°C.
As the temperature is lowered to -74°C, Figure 11 displays two singlets at -0.52 ppm and -2.02 ppm and a broad peak at -1.70 ppm. At this ratio the hexamer (0.00 ppm), octamer (-0.08 ppm) and nonamer (-0.16 ppm) are not observed.

Conclusion of Lithium n-Propoxide / n-Propyllithium Mixed Aggregates.

When n-propanol is added to n-propyllithium in the ratio of less RO than Li both the $^{13}$C and $^6$Li NMR spectra show new peaks not present in the n-propyllithium compound. This shows that there is strong evidence for the formation of aggregates of RLi and ROLi compounds as opposed to merely a mixture of RLi and ROLi in solution. As the ratio is moved to 1:1 RO/Li the hexamer, octamer and nonamer peaks are no longer observed in either the $^{13}$C or $^6$Li NMR spectra. This would suggest that all of the n-propyllithium has reacted with the alcohol and are no longer present.

When alkoxides are added to the alkyllithium compound in small ratios aggregates may be either be a mixed alkyllithium /lithium alkoxide aggregates in the form (RLi)$_n$(ROLi)$_m$, or a complete lithium alkoxide aggregates.
FIGURE 11: $^6$Li NMR spectrum of $n$-propyllithium and $n$-propylalcohol, 1:1 RO/Li ratio, temperature = $-74^\circ$C.
**iso-Butyllithium**

Studies by Thomas' group in 1983 found that the iso-butyllithium exists only as a hexamer in hydrocarbon solvent (4). Due to the simpler spectra with only one aggregate, it was felt that this compound would provide an easier means of obtaining structural information for larger mixed aggregates.

The iso-butyllithium was prepared as discussed in Chapter two. The solution was prepared in a 5mm NMR tube, at a concentration of approximately 2F. The $^{13}$C NMR spectrum for iso-butyllithium at room temperature shows the three carbon peaks for the iso-butyl group at 28.0 ppm, 29.9 ppm and 30.0 ppm. These peaks are consistent with the reported values of 28.1 ppm, 29.9 ppm and 30.1 ppm (5). The 28.0 ppm peak is a broad singlet and corresponds to the alpha carbon. The peaks at 29.9 ppm and 30.0 ppm are singlets that correspond to carbon two and three, although the actual peaks are not assigned.

Temperature studies on iso-butyllithium showed that in lowering the temperature from room temperature to approximately -70°C there was little change in peak location for the $^{13}$C NMR peaks. Below approximately -70°C, the peaks are no longer detected. This is probably due to the compound precipitating from solution at this temperature.

The $^{13}$C and $^6$Li NMR spectra for iso-butyllithium were
recorded at -33°C. The $^{13}$C NMR spectrum clearly shows a multiplet at 27.9 ppm. The coupling was measured at 3.1 Hz. This coupling corresponds to a hexamer aggregate state.

The $^6$Li spectrum, shown in Figure 12, shows one large singlet with $^{13}$C satellites and two very small singlets at -0.14 and -0.37 ppm. The large peak corresponds to the hexamer and was referenced to 0.00 ppm for this study. The two other peaks are of small size relative to the large singlet.

*Lithium iso-Butoxide / iso-Butyllithium*

The mixed compound was prepared as in chapter two using a 0.5 F or 1.0 F Li concentration. Four different ratios of iso-butyllithium to iso-butyl alcohol were studied. NMR temperature studies were done on each of these solutions. Lithium iso-butoxide / iso-butyllithium (RO/Li = 0.09:1).

The first ratio studied was 0.09:1 ratio of iso-butyl alcohol and iso-butyllithium. Temperature studies were done between room temperature and -51°C.

At -51°C the $^{13}$C NMR spectrum shown in Figure 13 displays numerous peaks. There are two singlets at 14.6 ppm, and 20.5 ppm. Downfield there are three singlets at 30.0, 30.4, and 30.7 ppm. At 34.5 ppm and 72.8 ppm there are smaller peaks.
FIGURE 12: $^6$Li spectrum of iso-butyllithium, temp = -33°C.
The large peak at 26.5 ppm is protonated cyclopentane. At this temperature, as seen in the inset in Figure 13, there are two alpha carbons, a multiplet at 27.9 ppm with a coupling of 3.1 Hz and a second broad peak upfield at approximately 27.4 ppm.

The multiplet at 27.9 ppm is the alpha carbon for the iso-butyllithium compound, again with a coupling measured at 3.1 Hz. The second alpha carbon at 27.4 ppm is a broad singlet that is relatively small compared to the peak at 27.9 ppm. The coupling could not be measured for the peak at 27.4 ppm.

To determine if the peaks at 27.4 ppm and 27.9 ppm are carbons bonded to lithium atoms, a $^1$C{^1}H,$^6$Li} NMR spectrum was run as shown in Figure 14. The narrowing of the peaks with the $^6$Li decoupler shows that these peaks are alkyl groups coupled to Li in different environments. This shows that with the addition of iso-butyl alcohol to form lithium iso-butoxide, there is one new mixed aggregate created. Therefore this is strong evidence for mixed aggregates of RLi and ROLi compounds as opposed to merely a mixture of RLi and ROLi in solution.
FIGURE 13: $^1$H NMR spectrum of iso-butyllithium and iso-butyll alcohol 0.09:1 RO/Li ratio, temperature = -51°C. Inset shows the two overlapping alpha carbons.
FIGURE 14: $^1$C($^1$H,$^6$Li) NMR spectrum of iso-butyllithium and iso-butyl alcohol 0.09:1 RO/Li ratio, temperature = -51°C. Inset shows the two collapsed alpha carbon peaks.
$^6$Li NMR spectra between -5°C and -39°C display three singlet peaks at 0.00 ppm, -0.37 ppm, -0.98 ppm and numerous smaller lithium peaks between -1.3 ppm and -1.9 ppm. The large peak set at 0.00 ppm is the hexamer peak of the iso-butyllithium. As the temperature lowers, the peaks at -0.37 ppm and -0.98 ppm become smaller relative to the hexamer peak at 0.00 ppm. At -39°C, as shown in Figure 15, there are small singlets at 0.00 ppm, -0.37 ppm, -0.98 ppm. The large peak at 0.00 ppm is the hexamer peak of the iso-butyllithium. The peak at -0.37 ppm was present in the iso-butyllithium compound, but was very small. With the addition of the iso-butyl alcohol to the iso-butyllithium compound, this peak became larger in intensity. Because the peak grew in intensity with the addition of iso-butyl alcohol it is either lithium iso-butoxide or a mixed aggregate.

There is also present in the $^6$Li NMR spectrum numerous other small peaks which are observed between -1.20 ppm and -1.90 ppm. These are lithium atoms in an environment different from the (RLi)$_6$ hexamer. This provides more evidence for mixed aggregates.
FIGURE 15: $^6$Li NMR spectra of iso-butyllithium and iso-butyl alcohol, 0.09:1 RO/Li ratio, temperature = -39°C.
iso-Butyl alcohol / iso-butyllithium (RO/Li = 0.2:1 and 0.4:1)

The 0.4: 1 RO/Li ratio was completed early in the research and the solution was made at 1F in Li. Samples with a RO/Li ratio of 0.2:1 were all run at 0.5F. This change was due to excess compound falling out of the solution at lower temperatures, for the higher concentration samples.

Again temperature studies were done at temperatures between room temperature and -85.9°C. The differences found between the ratios of 0.09:1, 0.2:1 and 0.4:1 RO/Li ratio were minimal. These three ratios all have the same characteristic features of a iso-butyllithium hexamer aggregate at the 27.9 ppm and a mixed iso-butyllithium / lithium iso-butoxide mixed aggregate at 27.4 ppm in the $^{13}$C NMR spectra.

Integration of the $^1$H and $^6$Li NMR spectra shows that as the oxygen is increased the aggregates shift from hexamer to the mixed aggregate. The $^{13}$C NMR spectra show that when the RO/Li ratio is increased from 0.09:1 to 0.2:1 the iso-butyllithium hexamer peak at 27.9 ppm reduces by 1.5 in size and the iso-butyllithium/lithium iso-butoxide mixed aggregate peak at 27.4 ppm increases by 1.25 in size. The $^6$Li NMR spectra show similar results in that with the same
ratio increase the iso-butyllithium hexamer peak at 0.00 ppm reduces by 1.5 in size and the iso-butyllithium/lithium iso-butoxide mixed aggregate peak at -0.79 ppm increases by 1.8 in size.

As seen in the $^{13}$C NMR spectrum at a ratio of 0.2:1 in Figure 16 at -56°C, the alpha carbon region again contains two peaks overlapping. Coupling was measured on the 27.9 ppm peak for the 0.2:1 RO/Li ratio at 3.2 Hz and is now understood to be an indicator of a hexamer (2). Again the two alpha carbon peaks at 27.4 ppm and 27.9 ppm both collapse into singlets with $^6$Li decoupling.

The integration of the $^{13}$C($^1$H,$^6$Li) NMR spectra of peaks 27.4 ppm and 27.9 ppm peaks shows that as the oxygen ratio is increased from 0.09:1 RO/Li to 0.2:1 RO/Li, the iso-butyllithium hexamer peak at 27.9 ppm reduces by 1.5 in size and the iso-butyllithium/lithium iso-butoxide mixed aggregate peak at 27.4 ppm increases by 1.25 in size. This integration shows that as the oxygen is increased the aggregates shift from hexamer to the mixed aggregate.

The $^6$Li NMR spectra show similar results with the same ratio increase. The iso-butyllithium hexamer peak at 0.00 ppm reduces by 1.5 in size and the iso-butyllithium/lithium iso-butoxide mixed aggregate peak at -0.79 ppm increases by 1.8 in size.
FIGURE 16: $^{13}$C NMR spectrum of iso-butyllithium and iso-butyl alcohol 0.2:1 RO/Li ratio, temperature = -56°C
More detailed information is obtained in the $^6$Li NMR spectra than the $^{13}$C NMR spectra for this temperature range. The $^6$Li NMR spectra between room temperature and $-86^\circ$C as seen in Figures 17, 18 and 19 display numerous peaks in the addition of the peaks at 0.00 ppm and -0.79 ppm. At all temperatures the peak at 0.00 ppm is the hexamer aggregate of the iso-butyllithium compound. At room temperature the $^6$Li NMR spectrum displays two broad peaks at 0.00 ppm and -0.79 ppm. At $-5^\circ$C there are peaks at 0.00 ppm, -0.37 ppm, -0.92 ppm, -1.09 ppm, -1.23 ppm and -1.31 ppm. As the temperature decreases to $-56^\circ$C there are again two peaks at 0.00 ppm and -0.37 ppm, the other peaks have broadened, decreased in intensity and shifted upfield slightly. After $-56^\circ$C the $^6$Li NMR spectra displays peaks at 0.00 ppm, -0.37 ppm, -0.69 ppm and -1.58 ppm. These peaks narrow and increase in intensity as the temperature is lowered.

The peak at -0.37 ppm was present in both the iso-butyllithium compound and the 0.09:1 RO/Li ratio. It was a larger peak in the 0.09:1 RO/Li ratio than the iso-butyllithium compound. Because this peak grew in intensity with the addition of iso-butyl alcohol, it is evidence of an RO/Li containing aggregate. There are also present in the $^6$Li NMR spectrum numerous other small peaks.
FIGURE 17: $^6$Li NMR spectrum of iso-butyllithium and iso-butyl alcohol 1:0.2 RO/Li ratio, temperature $= -39^\circ$C.
FIGURE 18: $^6$Li NMR spectra of iso-butyllithium and iso-butyl alcohol, 1:0.2 RO/Li ratio, temperature = -57°C.
FIGURE 19: $^6$Li NMR spectrum of iso-butyllithium and iso-butyl alcohol 1:0.2 RO/Li ratio, temperature = -80°C.
These are all lithium atoms in an environment different from the \((\text{RLi})_6\) hexamer. This gives more evidence that there are multiple mixed aggregates.

When the RO/Li ratio is increased from 0.2:1 to 0.4:1 there is little change in the $^{13}\text{C}$ and $^6\text{Li}$ NMR spectra. In the $^{13}\text{C}$ NMR spectra for the same temperature range there are two alpha carbons, one at 27.9 ppm which displays a coupling measured at 3.1 Hz and a peak at 27.6 ppm. Coupling could not be measured for the peak at 27.6 ppm. No peaks are displayed at the ratio of 0.4:1 RO/Li that are not displayed in the 0.2:1 RO/Li ratio. The $^6\text{Li}$ spectra also display similar results for the 0.2:1 RO/Li ratio sample and the 0.4:1 RO/Li ratio sample.

Integration of the $^6\text{Li}$ NMR spectra for the increase from 0.2:1 RO/Li to 0.4:1 RO/Li at the same temperature shows that as the oxygen ratio is increased, the size of the iso-butyllithium hexamer peak at 0.00 ppm decreases by 6.5 and the iso-butyllithium/lithium iso-butoxide mixed aggregate peak increases by 2.9 in size. Since there are no new peaks, there were no additional aggregate states formed when the ratio was increased. $^{13}\text{C}$ NMR data was not available for the integration at this ratio.
Lithium iso-butoxide / iso-Butyllithium (RO/Li = 1:1 and 1.5:1)

Next a sample with a RO/Li ratio of 1:1 was studied in the same temperature range. For this ratio both the iso-butyllithium and iso-butyl alcohol compounds were measured using a balance in a drybox environment. An attempt was made to get as close to a 1:1 ratio as possible. Temperature studies were done between room temperature and -56°C.

From the $^{13}$C NMR spectrum seen in Figure 20, the 1:1 ratio at a temperature of -56°C has fewer peaks than the lower ratios. There are four large peaks at 20.1 ppm, 25.0 ppm, 34.9 ppm and 72.4 ppm, and one small peak at 14.6 ppm. It can also be seen that in the alpha carbon region there are two small peaks at 27.5 ppm and 28.3 ppm. These peaks were very small and no coupling was detected. From the $^{13}$C NMR spectrum in Figure 21 it is assumed that at a RO/Li ratio of 1:1 the majority of compound forms an aggregate that is iso-butyllithium alkoxides.

The $^6$Li NMR spectrum shown in Figure 21 shows that there are five separate $^6$Li peaks. At -5°C, peaks are observed at 0.00 ppm, -0.07 ppm, -0.09 ppm and -0.23 ppm. In Figure 21 it can also be seen that as the temperature is lowered, the $^6$Li peaks tend to shift upfield slightly.
FIGURE 20: $^{13}$C NMR spectrum of iso-butyllithium and iso-butyl alcohol 1:1 RO/Li ratio, temperature $= -56^\circ$C. Inset shows two alpha carbon peaks.
FIGURE 21: $^6$Li NMR spectrum of iso-butyllithium and iso-butyl alcohol. 1:1 RO/Li ratio. Temperatures from bottom to top: -5°C; -28°C; -39°C.
The most downfield peak has been placed at 0.00 ppm for convenience. It is assumed that it is not a iso-butyllithium hexamer aggregate.

In this study $^6$Li NMR spectra as seen in Figure 22 were recorded for a sample with a ratio of 1.5:1 RO/Li ratio between -5°C and -39°C. The $^{13}$C NMR spectrum is not available for this ratio. The $^6$Li NMR spectrum displays seven peaks at -39°C. The peaks were not referenced since it is assumed that no iso-butyllithium hexamer peak is present. No other work was performed using the 1.5:1 RO/Li ratio.

Conclusions for iso-Butyllithium/Lithium iso-Butoxide Mixed Aggregates

It had previously been shown that the iso-butyllithium compound exists as a hexamer in hydrocarbon solution. This is consistent with the measured coupling constant of 3.1 Hz for the alpha carbon multiplet in the $^{13}$C NMR spectra. The $^6$Li NMR spectrum also shows this with one large singlet that corresponds to the hexamer aggregate state.

This study suggests there are numerous iso-butyllithium/lithium iso-butoxide mixed compounds. Evidence for this is the numerous $^{13}$C and $^6$Li NMR peaks. Data presented for samples with less iso-butyl alcohol than iso-butyllithium show two things: unreacted iso-butyllithium compound in the hexamer aggregate state and possibly one
mixed aggregate. The aggregate state of the mixed iso-
butyllithium and iso-butyllithium alkoxide that is formed
has not been determined at this time.

Integration results show that as the oxygen is
increased there is a shift from the iso-butyllithium hexamer
to the iso-butyllithium/ lithium iso-butoxide mixed
aggregates.
FIGURE 22: $^6$Li NMR spectrum of iso-butyllithium and iso-butyl alcohol. 1.5:1 RO/Li ratio. Temperatures from bottom to top: -5°C; -28°C; -39°C
Chapter Notes


BIBLIOGRAPHY


Bauer, W.; Winchester, W.R.; P.v.R. Scheyler, Organometallics, 6, 2371.


Brown, T. L. Accounts of Chemical Research, 1968, 1, 23.


