THERMAL DECOMPOSITION OF ALKYL LITHIUM

COMPOUNDS IN THE PURE STATE

APPROVED:

[Signatures]

William H. Grae
Major Professor

[Signatures]

Minor Professor

[Signatures]

Director of the Department of Chemistry

[Signatures]

Dean of the Graduate School
THERMAL DECOMPOSITION OF ALKYL LITHIUM COMPOUNDS IN THE PURE STATE

THESIS

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

For the Degree of

MASTER OF SCIENCE

By

Jacob Wen-pin Lin, B. S.
Denton, Texas
January, 1965
TABLE OF CONTENTS

LIST OF TABLES .......................................................... iv
LIST OF ILLUSTRATIONS ............................................... v

Chapter

I. INTRODUCTION ....................................................... 1

II. EXPERIMENTAL PROCEDURE ................................. 12

Materials
Preparation of Alkylolithium Compounds
Purification and Thermal Decomposition
Analysis of Gaseous Decomposition Run

III. RESULTS ............................................................. 20

IV. DISCUSSION ......................................................... 56

BIBLIOGRAPHY ........................................................... 70
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Alkyllithium Compounds</td>
<td>15</td>
</tr>
<tr>
<td>II. Rate Constants of Alkyllithium</td>
<td>21</td>
</tr>
<tr>
<td>III. Indication of Plots</td>
<td>22</td>
</tr>
<tr>
<td>IV. Thermodynamic Constants</td>
<td>54</td>
</tr>
<tr>
<td>V. Product Distributions from the Thermal Decomposition of Lithium Alkyls</td>
<td>54</td>
</tr>
<tr>
<td>VI. Product Distributions of Elimination Reactions Involving sec-Butyl Systems</td>
<td>57</td>
</tr>
<tr>
<td>Figure</td>
<td>Illustration Description</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1.</td>
<td>The Tetrameric Structure of Ethyllithium</td>
</tr>
<tr>
<td>2.</td>
<td>The Proposed Model for the C-Li Framework in t-Butyllithium Tetramer</td>
</tr>
<tr>
<td>3.</td>
<td>The Proposed Structure for the Complex of n-Butyllithium with Ether</td>
</tr>
<tr>
<td>4.</td>
<td>Purification and Decomposition Apparatus</td>
</tr>
<tr>
<td>5.</td>
<td>Thermal Decomposition of Ethyllithium at 98°C, $k = 3.18 \times 10^{-5} \text{sec}^{-1}$</td>
</tr>
<tr>
<td>6.</td>
<td>Thermal Decomposition of Ethyllithium at 98.9°C, $k = 3.13 \times 10^{-5} \text{sec}^{-1}$</td>
</tr>
<tr>
<td>7.</td>
<td>Thermal Decomposition of Ethyllithium at 98.9°C, $k = 3.96 \times 10^{-5} \text{sec}^{-1}$</td>
</tr>
<tr>
<td>8.</td>
<td>Thermal Decomposition of Ethyllithium at 107.5°C, $k = 7.52 \times 10^{-5} \text{sec}^{-1}$</td>
</tr>
<tr>
<td>9.</td>
<td>Thermal Decomposition of Ethyllithium at 107.5°C, $k = 7.90 \times 10^{-5} \text{sec}^{-1}$</td>
</tr>
<tr>
<td>10.</td>
<td>Thermal Decomposition of Ethyllithium at 117.9°C, $k = 1.745 \times 10^{-4} \text{sec}^{-1}$</td>
</tr>
<tr>
<td>11.</td>
<td>Thermal Decomposition of Ethyllithium at 117.9°C, $k = 1.850 \times 10^{-4} \text{sec}^{-1}$</td>
</tr>
<tr>
<td>12.</td>
<td>Thermal Decomposition of Ethyllithium at 130.20°C, $k = 5.502 \times 10^{-4} \text{sec}^{-1}$</td>
</tr>
<tr>
<td>13.</td>
<td>Thermal Decomposition of Ethyllithium at 130.2°C, $k = 6.17 \times 10^{-4} \text{sec}^{-1}$</td>
</tr>
<tr>
<td>Figure</td>
<td>Thermal Decomposition of n-Butyllithium at</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>14</td>
<td>98.9°C, ( k = 3.36 \times 10^{-5} ) sec(^{-1} )</td>
</tr>
<tr>
<td>15</td>
<td>98.9°C, ( k = 3.29 \times 10^{-5} ) sec(^{-1} )</td>
</tr>
<tr>
<td>16</td>
<td>117.8°C, ( k = 1.82 \times 10^{-4} ) sec(^{-1} )</td>
</tr>
<tr>
<td>17</td>
<td>117.8°C, ( k = 1.860 \times 10^{-4} ) sec(^{-1} )</td>
</tr>
<tr>
<td>18</td>
<td>129.9°C, ( k = 4.94 \times 10^{-4} ) sec(^{-1} )</td>
</tr>
<tr>
<td>19</td>
<td>129.9°C, ( k = 5.74 \times 10^{-4} ) sec(^{-1} )</td>
</tr>
<tr>
<td>20</td>
<td>82°C, ( k = 2.45 \times 10^{-5} ) sec(^{-1} )</td>
</tr>
<tr>
<td>21</td>
<td>88.6°C, ( k = 5.20 \times 10^{-5} ) sec(^{-1} )</td>
</tr>
<tr>
<td>22</td>
<td>88.6°C, ( k = 4.28 \times 10^{-5} ) sec(^{-1} )</td>
</tr>
<tr>
<td>23</td>
<td>88.6°C, ( k = 4.97 \times 10^{-5} ) sec(^{-1} )</td>
</tr>
<tr>
<td>24</td>
<td>98.25°C, ( k = 1.105 \times 10^{-4} ) sec(^{-1} )</td>
</tr>
<tr>
<td>25</td>
<td>98.25°C, ( k = 1.287 \times 10^{-4} ) sec(^{-1} )</td>
</tr>
<tr>
<td>26</td>
<td>98.25°C, ( k = 9.17 \times 10^{-5} ) sec(^{-1} )</td>
</tr>
<tr>
<td>27</td>
<td>106.3°C, ( k = 2.07 \times 10^{-4} ) sec(^{-1} )</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>28.</td>
<td>Thermal Decomposition of iso-Propyllithium at 106.3°C, $k = 2.12 \times 10^{-4}\text{sec}^{-1}$.</td>
</tr>
<tr>
<td>29.</td>
<td>Thermal Decomposition of sec-Butyllithium at 78.4°C, $k = 2.83 \times 10^{-5}\text{sec}^{-1}$.</td>
</tr>
<tr>
<td>30.</td>
<td>Thermal Decomposition of sec-Butyllithium at 87°C, $k = 6.10 \times 10^{-5}\text{sec}^{-1}$.</td>
</tr>
<tr>
<td>31.</td>
<td>Thermal Decomposition of sec-Butyllithium at 87°C, $k = 5.47 \times 10^{-5}\text{sec}^{-1}$.</td>
</tr>
<tr>
<td>32.</td>
<td>Thermal Decomposition of sec-Butyllithium at 104°C, $k = 2.980 \times 10^{-4}\text{sec}^{-1}$.</td>
</tr>
<tr>
<td>33.</td>
<td>Thermal Decomposition of sec-Butyllithium at 104°C, $k = 2.57 \times 10^{-4}\text{sec}^{-1}$.</td>
</tr>
<tr>
<td>34.</td>
<td>Arrhenius Plot for the Thermal Decomposition of Alkyllithium.</td>
</tr>
<tr>
<td>35.</td>
<td>The Proposed Tetrameric Structure of sec-Butyllithium.</td>
</tr>
<tr>
<td>36.</td>
<td>Possible Combinations of Ethyl Group in the Tetramer of sec-Butyllithium.</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

Lithium alkyls were first prepared by Schlenk (11), who noted that although a few of the lower alkyls, such as methyl, ethyl and iso-propyllithium are solid at room temperature, the higher homologs are liquids. Lithium alkyls are considerably more covalent than the other alkali alkyls and some of the lower lithium alkyls may also be distilled at low pressures, and are often soluble in organic solvents. These properties are quite different from the other simple alkyls and aryls of the other alkali metals--sodium, potassium, rubidium, and cesium which are solid compounds, insoluble in organic solvents and cannot be melted or vaporized without decomposition. Rogers and Young (10) estimated a value of 40 for the molar polarization of n-butyllithium in benzene. This indicates that the carbon-lithium bond must have considerable covalent character, since ion pairs would result in very much higher values of molar polarization (e.g., $p_\infty = 1309$ for LiClO$_4$, a largely polar compound in dioxane solution (7). From the
electronegativity difference, 1.5 units between carbon and lithium, one would predict about 45 per cent ionic character for the carbon-lithium bond and a bond moment of about 1.5 D (Malonis rule) (8, p. 68).

All of the organic derivatives of the alkali metals in which there is carbon-metal bonding are very reactive toward oxidizing agents. All react spontaneously, and usually rapidly, with oxygen upon exposure to the air, and the lower alkyls, both solid and liquid, inflame spontaneously. With water, the reaction is extremely vigorous and often ignition occurs due to the heat of the reaction. Such reactive compounds require special techniques for their preparation, purification, and handling.

The structures of alkyllithium compounds have long been subjects of interest and speculation. The crystal structure of trimethylaluminum and dimethylberyllium, determined by X-ray diffraction (12, 9), have been important in revealing some of the principles governing the bonding in this class of substances. Rundle and co-workers have shown that the configurations assumed by these so-called electron-deficient compounds are largely determined by the tendency of the metal atom to utilize all of its orbitals
in bonding. The resulting structures may be described in terms of three-center bonds involving the overlap of two metal orbitals with simple hybrid orbitals on carbon, producing a four-membered ring similar to the following:

\[
\begin{array}{c}
\text{X} \\
\text{M} \\
\text{X} \\
\text{M}
\end{array}
\]

The metal-metal distances are short enough so that appreciable fractional bond order is indicated by application of Pauling's rule (8), and it seems likely that overlap of the metal orbitals is also of importance in some of these compounds. The lithium alkyls are important members of this class of substances and information concerning their properties should help in the development of the theory of electron-deficient bonding.

Alkyllithium compounds are known to be associated in solution from measurement of their molecular weights by the freezing point and boiling point methods in various solvents (1, 4, 5). Recent studies of the mass spectrum and infrared spectrum of ethyllithium vapor have indicated that this compound is polymeric even in the gaseous state (15). Dietrich (3) studied the crystal structure of ethyllithium by X-ray diffraction. A tetrameric structure in which four ethyllithium molecules are combined
with each other was found. The bond length as well as angles are shown in Figure 1, page 5. The association of alkyl lithium compounds is thought to take place by utilizing multi-center molecular orbitals, similar to those formed in polymeric dimethylberyllium and dimeric aluminum trialkyls (12). Polymerization in such electron-deficient systems is sterically inhibited by alkyl substitution at the alpha carbon atom which must assume a coordination number greater than four. In addition, this inhibition of polymerization has been discussed in terms of decreased electronegative character of the branched alkyl group (16). West and co-workers (16) suggested a tetrahedral structure for the molecules of t-butyllithium from Raman and infrared spectral evidence. The proposed model for the carbon-lithium framework in the t-butyllithium tetramer is shown in Figure 2, page 6.

Brown and Robers (1), who studied spectra of methyl-lithium and ethyllithium as nujol mulls and of ethyllithium in benzene solution, have shown ethyllithium to be associated into hexamers in benzene solution according to freezing point depression measurements. More recently, Eastham (4) and co-workers reported that n-butyllithium (BuLi) exists
Fig. 1--The tetrameric structure of ethyllithium

<table>
<thead>
<tr>
<th>Atom</th>
<th>Distances and angles</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_{10})-C(_6)</td>
<td>3.629 Å</td>
<td>0.005 Å</td>
</tr>
<tr>
<td>Li(_3)-Li(_5)</td>
<td>2.424 Å</td>
<td>0.009 Å</td>
</tr>
<tr>
<td>C(_{10})-Li(_5)</td>
<td>2.252 Å</td>
<td>0.006 Å</td>
</tr>
<tr>
<td>C(<em>9)-C(</em>{10})-Li(_3)</td>
<td>91.0°</td>
<td>0.2</td>
</tr>
<tr>
<td>C(_6)-Li(<em>3)-C(</em>{10})</td>
<td>109.6°</td>
<td>0.2</td>
</tr>
<tr>
<td>Li(_5)-C(_6)-Li(_3)</td>
<td>66.1°</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Fig. 2--The proposed model for the C-Li framework in t-butyllithium tetramer.

Fig. 3--The proposed structure for the complex of n-butyllithium with ether.
in ether (Et$_2$O) solution as a solvated dimer Et$_2$O : (BuLi)$_2$, and three-center bonding would seem to be applicable. Hence, they propose a structure for the complex of n-butyllithium with ether which is shown in Figure 3, above.

In 1910, Schöorigin (13) reported obtaining ethane, ethylene and lithium hydride from the thermal decomposition of ethyllithium with no evidence of butene formation. Some years later Thompson and Stevens repeated the same decomposition reporting much the same results when the compound was heated in ligroin at 120° C yielding a solid which on hydrolysis gave nearly pure hydrogen corresponding to the content of 50 per cent of lithium hydride. Ziegler (17) and Gellert obtained broadly similar results for the thermal decomposition of ethyl- and n-butyllithium. The analysis of the hydrocarbon product from the latter shows that it consists of about 92 per cent butene-1 and up to 8 per cent butane. The decomposition is therefore a complicated process, and they interpreted the results in the following way:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Li} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}=:\text{CH}_2 + \text{LiH} \\
\text{CH}_3\text{CH}_2\text{CH}=:\text{CH}_2 + \text{C}_4\text{H}_9\text{Li} & \rightarrow \text{CH}_3\text{CHCH}=:\text{CH}_2 + \text{C}_4\text{H}_{10} \\
\text{CH}_3\text{CHCH}=:\text{CH}_2 & \rightarrow \text{CH}_2=\text{CHCH}=:\text{CH}_2 + \text{LiH} \rightarrow \text{polymer}
\end{align*}
\]
Initially only 1-butene is formed (1). This reacts with unreacted butyllithium according to (2) in which butane is formed. The resin formed comes from butadiene which results from (3). Butadiene polymerizes in the presence of lithium alkyls as was established long ago. In the thermal decomposition of ethyllithium, ethane is formed only in very insignificant quantities. Chiefly only ethylene and lithium hydride are formed. Therefore, Ziegler and Gellert concluded that under those conditions where the alkene was taken off as fast as it was formed, the gaseous products from the decomposition of ethyllithium and butyllithium were primarily ethene and butene, respectively. More recently, Bryce-Smith (2) decomposed n-pentyllithium and n-butyllithium at 135° C with evolution of a saturated, an unsaturated hydrocarbon and lithium hydride in each case. Also, he concluded that thermal decomposition of alkali-metal alkyls does not produce alkyl radicals.

Although the properties of alkyllithium compounds have been studied from many aspects, the mechanisms of their many reactions are not generally understood. Interest in the present work has been concentrated on the thermal decomposition of a series of alkyllithium compounds in the
pure state in an attempt to determine the relative stabilities of alkyllithium compounds and to examine the mechanism of the elimination reaction.
CHAPTER BIBLIOGRAPHY


CHAPTER II

EXPERIMENTAL PROCEDURE

Materials

Lithium metal (99.7 per cent lithium, containing 2 per cent sodium) was obtained from the Lithium Corporation of America. Pentane was Phillips's pure grade (99 per cent minimum) without further purification. Ethyl bromide, isopropyl chloride, n-butyl chloride and sec-butyl chloride were obtained from the Eastman Kodak Company.

Preparation of Alkylithium Compounds

The preparation was carried out under an argon atmosphere in a three-necked, one liter reaction flask equipped with a Hirschberg stirrer, Friedrichs reflux condenser, and a dropping funnel. Lithium sand was prepared by rapidly shaking molten lithium metal in mineral oil, with sodium oleate added to disperse the metal as it solidified. The metal was filtered after cooling and transferred to the flask along with approximately 250 ml. dry pentane. The alkyl chloride (ethyl bromide was used to prepare ethyl-lithium), mixed with 150 ml. of pentane, was placed in the
dropping funnel. Approximately 10 per cent of the chloride and a slight amount of heat were added to initiate the reaction, as evidenced by the formation of a purple-colored coating on the metal. The remainder of the halide was added dropwise over a period of four to five hours. After refluxing for two hours longer, the reaction vessel was taken into a dry box and the mixture filtered. The pentane solution of alkylolithium was concentrated by vacuum distillation and used in subsequent experiments as described below.

Purification and Thermal Decomposition

The apparatus shown in Figure 4, page 14, was used for the distillation and decomposition of lithium alkyls.

Approximately 15 ml. of concentrated alkylolithium solution (or impure solid) was transferred to the flask (A) through the side-arm while still in the dry box. After the stopper (B) was put on and the stopcock (C) closed, the apparatus was taken outside of the dry box and attached to a high vacuum line. The side-arm was sealed off (D) while cooling the flask (A) containing the alkylolithium compound with liquid air. After pumping a vacuum on the system until a pressure of less than 50 microns was measured by a McLeod gauge, the flask was then heated with a mineral
A. Flask for storing concentrated alkyllithium solution (or impure solid).

B. Side arm stopper.

C. Stopcock.

D. Place which was sealed before distillation.

E. U-Tube for trapping pure alkyllithium.

F. Place which was sealed off after distillation.

Fig. 4--Purification and decomposition apparatus
oil bath at approximately 90° C. The lithium alkyls distilled and collected in the u-tube, as it was cooled with the liquid air. Lithium alkyls distill easily under these conditions, yielding solids or liquids at room temperature, as indicated in Table I. The distillation flask was then sealed off at the connection tube (F), leaving the u-tube on the vacuum line.

### TABLE I

**ALKYL lithium COMPOUNDS**

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>State at Room Temperature</th>
<th>Color</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl-lithium</td>
<td>CH₃CH₂Li</td>
<td>Solid</td>
<td>white</td>
<td>80° C</td>
</tr>
<tr>
<td>n-Butyl-lithium</td>
<td>CH₃(CH₂)₃Li</td>
<td>viscous liquid</td>
<td>colorless</td>
<td></td>
</tr>
<tr>
<td>iso-Propyl-lithium</td>
<td>CH₃CHLi</td>
<td>solid</td>
<td>white</td>
<td>67° C</td>
</tr>
<tr>
<td>sec-Butyl-lithium</td>
<td>CH₃CH₂CHLi</td>
<td>viscous liquid</td>
<td>colorless</td>
<td>-10° C</td>
</tr>
</tbody>
</table>

The decomposition was carried out at several temperatures. A thermo-regulated oil bath at the desired temperature (±0.05° C) was raised around the u-tube, and the
decomposition followed manometrically. It was sometimes necessary to pump on the sample at room temperature before a kinetic run was made in order to remove any decomposition products frozen out in the u-tube during the distillation.

The vacuum line was equipped with a capillary manometer (ca. 2 mm. I.D.). Sample sizes varied, but were approximately two grams. Some runs were made in which helium or argon gas was added before the decomposition was begun and no noticeable differences in rate were observed. Pressure readings were taken every ten or twenty minutes and plotted by the method of Guggenheim (1), where the final reading is unknown. If times $t_1$, $t_2$, $t_3$, etc., and $t_1+A$, $t_2+A$, $t_3+A$, etc., are selected where $A$ is a constant increment, then the following equations are true:

\begin{align*}
(P_\infty - P_1) &= (P_\infty - P_\ast)e^{-kt_1} \quad (1) \\
(P_\infty - P_1') &= (P_\infty - P_\ast)e^{-k(t_1+A)} \quad (2)
\end{align*}

where $P_1$ and $P_1'$ are pressures at $t_1$ and $t_1+A$, respectively and the usual first-order equation is written in exponential form. Subtracting (2) from (1) gives

\begin{align*}
(P_1' - P_1) &= (P_\infty - P_\ast)e^{-kt_1}(1-e^{-kA}) \\
k t_1 + \ln(P_1' - P_1) &= \ln((P_\infty - P_\ast)(1-e^{-kA})) = \text{constant}.
\end{align*}
Similar equations would be true for $t_2$ and $t_2^+$. The time interval between $p$ and $p'$ was approximately one and one half times the half life of the reaction. The reaction appears to be the first-order and the rate constants ($k$) were determined graphically by the equation

$$k = -2.303 \times \text{slope}$$

**Analysis of Gaseous Decomposition Run**

The gaseous products were collected in a trap at $-70^\circ$ C and subsequently transferred to a second vacuum line in series with a gas sample valve and a gas chromatograph. Analysis of the sec-butyllithium and ethyllithium decomposition products was made on a twenty-foot by one-fourth inch column with 20 per cent didecylphthalate substrate on Chromasorb -P treated with hexamethyl disilazine. Peaks were identified by comparison of retention times with standards supplied by the Matheson Company and standardization was accomplished by preparing a mixture from C.P. grade olefins. An SE-30 column was used for analyzing the n-butyllithium and iso-propyllithium decomposition gaseous products. Infrared spectra from 2-16 microns of ethyllithium, n-butyllithium and iso-propyllithium decomposition products are identical to the reference spectra.
of ethene, propylene and 1-butene, respectively. In the case of sec-butyllithium decomposition products, a synthetic mixture prepared from the pure olefins in appropriate amounts gave essentially the same infrared spectra and chromatogram. The spectra were taken on a Perkin-Elmer 237 infrared spectrophotometer in a 10 cm. path-length cell.
CHAPTER BIBLIOGRAPHY


CHAPTER III

RESULTS

Kinetic Investigation

The decomposition of four lithium alkyls were studied, and the rates determined. All were found to give first order kinetics over the entire course of the reaction.

The rate constants were determined by following the increase in pressure on a vacuum line due to the formation of volatile reaction products.

First-order rate constants were determined for ethyl, n-butyl, iso-propyl, and sec-butyllithium. The stability of the two primary lithium alkyls proved to be nearly the same, while the secondary lithium alkyls are much more reactive than primarys. Each lithium alkyl was studied at several temperatures. The experimental results are shown in following figures in which the logarithm of $(p'-p)$ is plotted against the time by the method of Guggenhein (1). The first-order rate constants $(k)$ were determined graphically by the equation $k = -2.303 \times \text{slope}$, where the slope is that of the plot of $\log (p'-p)$ versus time for a
given compound and temperature. The first-order rate constants determined in this manner are shown in Table II. Some runs were plotted by log \((P_\infty - p)\) versus time, and first-order kinetics were also observed.

**TABLE II**

RATE CONSTANTS OF ALKYL LITHIUM

<table>
<thead>
<tr>
<th>Alkyl Lithium</th>
<th>Temperature</th>
<th>(k \times 10^5 \text{ sec}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl Lithium</td>
<td>98.0</td>
<td>3.16 ± 0.60</td>
</tr>
<tr>
<td></td>
<td>98.9</td>
<td>3.54 ± 0.21</td>
</tr>
<tr>
<td>Ethyl Lithium</td>
<td>107.5</td>
<td>7.71 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>117.5</td>
<td>17.97 ± 0.52</td>
</tr>
<tr>
<td></td>
<td>130.2</td>
<td>56.36 ± 3.34</td>
</tr>
<tr>
<td>n-Butyl Lithium</td>
<td>98.9</td>
<td>3.33 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>117.8</td>
<td>18.63 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>129.9</td>
<td>53.40 ± 4.00</td>
</tr>
<tr>
<td>iso-Propyl Lithium</td>
<td>82.0</td>
<td>2.47 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>88.65</td>
<td>4.82 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>98.25</td>
<td>11.03 ± 1.84</td>
</tr>
<tr>
<td></td>
<td>106.3</td>
<td>20.85 ± 0.15</td>
</tr>
<tr>
<td>sec-Butyl Lithium</td>
<td>78.4</td>
<td>2.83 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>87.0</td>
<td>5.78 ± 0.31</td>
</tr>
<tr>
<td></td>
<td>104.0</td>
<td>27.75 ± 2.05</td>
</tr>
</tbody>
</table>

*Temperature = degrees at Centigrade.

Several decomposition runs were carried at each temperature for each compound in most cases. The plots which were used for evaluating rate constants are indicated in Table III and shown graphically on the following pages.
TABLE III

INDICATION OF PLOTS

<table>
<thead>
<tr>
<th>Alkyllithium</th>
<th>Temperature*</th>
<th>Figure Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>98.0</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>98.9</td>
<td>6, 7</td>
</tr>
<tr>
<td>Ethyllithium</td>
<td>107.5</td>
<td>8, 9</td>
</tr>
<tr>
<td></td>
<td>117.9</td>
<td>10, 11</td>
</tr>
<tr>
<td></td>
<td>130.2</td>
<td>12, 13</td>
</tr>
<tr>
<td></td>
<td>98.9</td>
<td>14, 15</td>
</tr>
<tr>
<td>n-Butyllithium</td>
<td>117.8</td>
<td>16, 17</td>
</tr>
<tr>
<td></td>
<td>129.9</td>
<td>18, 19</td>
</tr>
<tr>
<td>iso-Propyllithium</td>
<td>82.0</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>88.65</td>
<td>21, 22, 23</td>
</tr>
<tr>
<td></td>
<td>98.25</td>
<td>24, 25, 26</td>
</tr>
<tr>
<td></td>
<td>106.3</td>
<td>27, 28</td>
</tr>
<tr>
<td>sec-Butyllithium</td>
<td>78.4</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>87.0</td>
<td>30, 31</td>
</tr>
<tr>
<td></td>
<td>104.0</td>
<td>32, 33</td>
</tr>
</tbody>
</table>

*Temperature = degrees at Centigrade.

A plot of the logarithm of the average value of rate constants at each temperature vs. 1/T showed a straight line, indicating that the decomposition reactions obey Arrhenius' equation

\[ k = Ae^{-Ea/RT} \]

within the temperature range for these four alkyllithiums.
Fig. 5--Thermal decomposition of ethyllithium at 98°C, 
\[ k = 3.13 \times 10^{-5}\text{sec}^{-1}. \]
Fig. 6--Thermal decomposition of ethyllithium at 98.9°C, 
k = 3.13 x 10^{-5} \text{sec}^{-1}.
Fig. 7--Thermal decomposition of ethyllithium at 98.9°C, 
k = 3.96 x 10^{-5} \text{sec}^{-1}.
Fig. 8.—Thermal decomposition of ethyllithium at 107.5°C, 
$k = 7.52 \times 10^{-5}\text{sec}^{-1}$. 
Fig. 9--Thermal decomposition of ethyllithium at 107.5°C, $k = 7.90 \times 10^{-5}$ sec$^{-1}$.
Fig. 10—Thermal decomposition of ethyllithium at 117.9°C, 

\[ k = 1.745 \times 10^{-4} \text{sec}^{-1} \]
Fig. 11--Thermal decomposition of ethyllithium at 117.9°C, 
$k = 1.850 \times 10^{-4} \text{sec}^{-1}$. 
Fig. 12--Thermal decomposition of ethyllithium at 130.20°C, 
k = 5.502 x 10^{-4} \text{sec}^{-1}.
Fig. 13--Thermal decomposition of ethyllithium at 130.2°C, $k = 6.17 \times 10^{-4}\text{sec}^{-1}$. 
Fig. 14—Thermal decomposition of n-butyllithium at 98.9°C, $k = 3.36 \times 10^{-5}\text{sec}^{-1}$. 
Fig. 15--Thermal decomposition of n-butyllithium at 98.8°C, $k = 3.29 \times 10^{-3}$ sec$^{-1}$. 
Fig. 16 -- Thermal decomposition of n-butyllithium at 117.8°C, \( k = 1.82 \times 10^{-4}\text{sec}^{-1} \).
Fig. 17—Thermal decomposition of n-butyllithium at 117.8° C, \( k = 1.860 \times 10^{-4} \text{sec}^{-1} \).
Fig. 18--Thermal decomposition of n-butyllithium at 129.9° C, $k = 4.94 \times 10^{-4}$ sec$^{-1}$. 
Fig. 19--Thermal decomposition of n-butyllithium at 129.9°, $k = 5.74 \times 10^{-4}\text{sec}^{-1}$.
Fig. 20--Thermal decomposition of iso-propyllithium at 82°C, $k = 2.47 \times 10^{-5} \text{sec}^{-1}$. 
Fig. 21--Thermal decomposition of iso-propyllithium at 88.65°C, $k = 5.20 \times 10^{-5}\text{sec}^{-1}$. 
Fig. 22--Thermal decomposition of iso-propyllithium at 88.65°C, $k = 4.28 \times 10^{-5}\text{sec}^{-1}$. 

$log \left( \frac{p' - p}{p} \right)$

Time, (sec $\times 10^{-2}$)
Fig. 23—Thermal decomposition of *iso*-propyllithium at 88.65°C, $k = 4.97 \times 10^{-5} \text{sec}^{-1}$. 
Fig. 24--Thermal decomposition of iso-propyllithium at 98.25° C, \( k = 1.105 \times 10^{-4} \text{sec}^{-1} \).
Fig. 25—Thermal decomposition of iso-propyllithium at 98.25°, $k = 1.287 \times 10^{-4} \text{sec}^{-1}$. 
Fig. 26—Thermal decomposition of **iso-propyllithium**
at 98.25°C, $k = 9.17 \times 10^{-5}\text{sec}^{-1}$. 
Fig. 27--Thermal decomposition of iso-propyllithium at 106.3°C; \( k = 2.07 \times 10^{-4} \text{sec}^{-1} \).
Fig. 28--Thermal decomposition of iso-propyllithium at 106.3°C, $k = 2.12 \times 10^{-4}\text{sec}^{-1}$. 
Fig. 29—Thermal decomposition of sec-butyllithium at 78.4°C, \( k = 2.83 \times 10^{-5} \text{sec}^{-1} \).
Fig. 30—Thermal decomposition of sec-butyllithium at 87°C, $k = 6.10 \times 10^{-5}\text{sec}^{-1}$. 

The graph shows the plot of $\log (p' - p)$ against time, with time in minutes.
Fig. 31—Thermal decomposition of sec-butyllithium at 87°C, $k = 5.47 \times 10^{-5}\text{ sec}^{-1}$.
Fig. 32--Thermal decomposition of sec-butyllithium at 104°C, $k = 2.980 \times 10^{-4}\sec^{-1}$. 
Fig. 33--Thermal decomposition of *sec*-butyllithium at 104°C, \( k = 2.57 \times 10^{-4} \text{sec}^{-1} \).
The equations for the lines, determined by the method of least squares, are:

- Ethyllithium: $\ln k = 25.47 - 1.33 \times 10^4 / T$
- n-Butyllithium: $\ln k = 25.47 - 1.33 \times 10^4 / T$
- iso-Propyllithium: $\ln k = 22.61 - 1.17 \times 10^4 / T$
- sec-Butyllithium: $\ln k = 23.37 - 1.19 \times 10^4 / T$

These four lines are plotted in Figure 34. It is quite interesting that, within experimental error, ethyllithium and n-butyllithium lay on the same line while iso-propyllithium and sec-butyllithium are parallel to each other.

From the equations one obtains the Arrhenius' activation energy, $E_a$, and evaluates pre-exponential factor $A$. The entropy of activation and enthalpy of activation are also calculated by the Eyring equation (1),

$$k = \left(\frac{kT}{h}\right)e^{\frac{A_s}{R}}e^{-\frac{\Delta H^\ddagger}{RT}}$$

where $k$ is Boltzmann's constant and $h$ is Planck's constant.

These thermodynamic constants are indicated in Table IV, page 54.

The gaseous decomposition products have been analyzed through both infrared absorption spectroscopy and gas-liquid chromatography. The product distributions are shown in Table V, page 54.
Fig. 34--Arrhenius plot for the thermal decomposition of alkyllithium.
### TABLE IV

**THERMODYNAMIC CONSTANTS**

<table>
<thead>
<tr>
<th>Alkyl-lithium</th>
<th>$A \times 10^{-10}$</th>
<th>$E_a$ KCal/Mole</th>
<th>$\Delta S^\dagger$ Cal/deg</th>
<th>$\Delta H^\dagger$ KCal/Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl-lithium</td>
<td>$16^{t}10$</td>
<td>$26.4^{t}0.45$</td>
<td>$-10.4^{t}1.2$</td>
<td>$25.6^{t}0.45$</td>
</tr>
<tr>
<td>n-Butyl-lithium</td>
<td>$16^{t}10$</td>
<td>$26.4^{t}0.45$</td>
<td>$-10.4^{t}1.2$</td>
<td>$25.6^{t}0.45$</td>
</tr>
<tr>
<td>iso-Propyl-lithium</td>
<td>$0.7^{t}0.3$</td>
<td>$23.4^{t}0.34$</td>
<td>$-16.0^{t}0.92$</td>
<td>$22.7^{t}0.34$</td>
</tr>
<tr>
<td>sec-Butyl-lithium</td>
<td>$1.9^{t}1.1$</td>
<td>$23.6^{t}0.69$</td>
<td>$-14.4^{t}1.8$</td>
<td>$22.9^{t}0.34$</td>
</tr>
</tbody>
</table>

### TABLE V

**PRODUCT DISTRIBUTION FROM THE THERMAL DECOMPOSITION OF LITHIUM ALKYLS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Product</th>
<th>Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl-lithium</td>
<td>Ethylene 99%</td>
<td>98° -- 130°C</td>
</tr>
<tr>
<td></td>
<td>Ethane 1%</td>
<td></td>
</tr>
<tr>
<td>n-Butyl-lithium</td>
<td>Butene 98%</td>
<td>99° -- 129°C</td>
</tr>
<tr>
<td></td>
<td>Butane 1.8%</td>
<td></td>
</tr>
<tr>
<td>iso-Propyl-lithium</td>
<td>Propylene 99%</td>
<td>82° -- 98°C</td>
</tr>
<tr>
<td>sec-Butyl-lithium</td>
<td>cis-2 butene 54</td>
<td>104.0°C</td>
</tr>
<tr>
<td></td>
<td>trans-2 butene 17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1-butene 29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>53.2</td>
<td>87.0°C</td>
</tr>
<tr>
<td></td>
<td>15.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>51</td>
<td>78.4°C</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER BIBLIOGRAPHY

CHAPTER IV

DISCUSSION

The findings of the present study indicate that the decomposition of lithium alkyls at 80°-130°C yields the corresponding olefins and lithium hydride by a first-order reaction.* The evidence suggests that the process under investigation is represented by equation (I) of the Ziegler mechanism (14).

(1) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{Li} \rightarrow \text{CH}_3\text{CH}_2\text{CH} = \text{LiH} \)

(2) \( \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 + \text{CH}_3\text{CH}_2\text{CH}_2\text{Li} \rightarrow \text{CH}_3\text{C} = \text{LiCH} = \text{CH}_2 + \text{C}_4\text{H}_{10} \)

(3) \( \text{CH}_3\text{C} = \text{LiCH} = \text{CH}_2 \rightarrow \text{CH}_2 = \text{C} = \text{CH} = \text{CH}_2 + \text{LiH} \)

\[ \rightarrow \text{polymer} \]

The absence of appreciable amounts of saturated hydrocarbon and the purity of the lithium hydride are indications that subsequent reactions have been avoided. The precise classification of the elimination mechanism is not possible at this time. However, as shall be discussed later, it appears

*This is the correct stoichiometry provided that \( \beta \)-hydrogen is available. Other experiments indicate that the decomposition of methyllithium and neo-pentyllithium proceed via entirely different mechanisms.
very likely that a cis- elimination mechanism involving a four-center transition state is involved.

An examination of the distribution of products from the pyrolysis of sec-butyllithium in Table V (see page 54) makes it evident that this reaction does not resemble any of the previously studied elimination reactions of 2-butyl systems. The distribution of butene isomers in the decomposition of several 2-butyl systems is shown in Table VI.

TABLE VI
PRODUCT DISTRIBUTIONS OF ELIMINATION REACTIONS INVOLVING SEC-BUTYL SYSTEMS

<table>
<thead>
<tr>
<th>Substituent</th>
<th>1-butene %</th>
<th>cis-2 butene %</th>
<th>trans-2 butene %</th>
<th>Probable Mechanism</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OCOCH3</td>
<td>57</td>
<td>15</td>
<td>28</td>
<td>cis</td>
<td>(9)</td>
</tr>
<tr>
<td>-OCSSCH3</td>
<td>42</td>
<td>18</td>
<td>40</td>
<td>cis</td>
<td>(6)</td>
</tr>
<tr>
<td>-(CH3)2N*+O-</td>
<td>67</td>
<td>12</td>
<td>21</td>
<td>cis</td>
<td>(4)</td>
</tr>
<tr>
<td>-NH2, HNO2</td>
<td>25</td>
<td>19</td>
<td>56</td>
<td>trans</td>
<td>(11)</td>
</tr>
<tr>
<td>-Br, C2H5O-</td>
<td>20</td>
<td>21</td>
<td>59</td>
<td>trans</td>
<td>(13)</td>
</tr>
<tr>
<td>-OTS</td>
<td>10</td>
<td>43</td>
<td>47</td>
<td>E-l</td>
<td>(1)</td>
</tr>
</tbody>
</table>

The first three reactions have been shown to proceed unimolecularly through cyclic transition states in which a β-hydrogen is eliminated while in a cis-position with respect to the other leaving group (4). The fourth and
fifth reactions are supposedly by typical E-2 mechanism. The removal of a $\beta$-proton by the base, the formation of the double bond, and the displacement of the leaving group occur simultaneously through a trans-planar transition state. The sixth reaction probably takes place via the E-1 mechanism which consists of a preliminary formation of a 2-butyl carbonium ion which may then eliminate a $\beta$-proton to give an olefin. The elimination reactions which have been studied in 2-butyl systems show that the majority of the 2-butene is the trans-isomer no matter which mechanism occurs. The preference of the trans- over the cis-isomer is consistent with reduction of steric hindrance in the transition state.* The 1-butene / 2-butene ratio is not always predictable from statistical considerations, although internal olefins are more stable than terminal isomers as a general rule.

Comparison of these data with the results obtained in the decomposition of sec-butyllithium suggests that in the elimination of lithium hydride, the preference for the trans-conformation in the transition state has diminished.

---

*The planarity of the carbonium ion in the E-1 mechanism eliminates the preference for the trans-configuration resulting in a nearly 1:1 ratio of cis and trans isomers.
In order to explain this result, it is important to recall that alkyllithium compounds inevitably exist as associated species in the pure state and in solution. As mentioned previously, the crystal structure of ethyllithium has been determined from X-ray diffraction data by Dietrich (7). The results of his study indicate that the primary building block is the dimer, which may then combine to produce tetramers, or perhaps hexamers. In hydrocarbon solutions, ethyllithium is hexameric as is n-butyllithium (2); t-butyllithium, on the other hand, is tetrameric in benzene (12).

From these results, it is certainly reasonable to assume that sec-butyllithium is polymeric under the conditions employed in this study. Dietrich's tetramer structure has been used to illustrate the effect of this association on the products to be expected from the pyrolysis of sec-butyllithium (7). Figure 35 represents various conformations and projections of such a structure. As the figures indicate, the tetramer is built up of two dimers which are strongly associated to each other. The four lithium atoms are in a nearly regular tetrahedral arrangement surrounded by the sec-butyl groups, with each lithium bonded to three-carbon atoms. The bonding in the dimer is the same
Fig. 35--The proposed tetrameric structure of sec-butyllithium.
electron-deficient type of bonding which has been observed in the alkyl-aluminum and -beryllium compounds. The association of dimers into tetramers or hexamers may be accomplished primarily by electrostatic bonding (8).

Concerning the mechanism by which lithium hydride is eliminated, it appears that a free-radical mechanism cannot be reconciled with the experimental observations. If the decomposition proceeds through the formation of an intermediate butyl radical, the following reactions might be expected:

1. \[ \text{CH}_3\text{CH}_2\text{CHLi} \rightarrow \text{Li}^+ + \text{CH}_3\text{CH}_2\text{CH}^- \]

2. \[ \text{CH}_3\text{CH}_2\text{CH}^+ + \text{CH}_3\text{CH}_2\text{CH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH(CH}_3\text{)}\text{CH(CH}_3\text{)}\text{CH}_2\text{CH}_3 \]

3. \[ \text{C}_2\text{H}_5\text{CH}^+ + \text{C}_2\text{H}_5\text{CH}^- \rightarrow \text{C}_2\text{H}_5\text{CH}_2 + \text{C}_4\text{H}_8 \]

4. \[ \text{Li}^+ + \text{C}_4\text{H}_9^- \rightarrow \text{LiH} + \text{C}_4\text{H}_8 \]

Lithium metal and 3,4-dimethyl hexane, as well as n-butane, were not found in significant quantities, indicating that the free radical mechanism is incorrect. Furthermore, D. Bryce-Smith (3) reported that no evidence was found for the formation of n-butyl radicals when n-butyllithium was pyrolyzed in isopropyl benzene. The nonformation of 2,3-dimethyl-2,3-diphenylbutane was taken as an indication of a non-radical reaction.
Next, the decomposition is considered to have been accomplished by \textit{trans}-elimination. The typical second-order E-2 type reaction may be pictured as follows:

\[
\begin{array}{c}
\text{H}
\end{array} \quad 2 \quad \begin{array}{c}
R
\end{array}
\begin{array}{c}
\text{B}
\end{array}
\begin{array}{c}
\text{R}
\end{array}
\begin{array}{c}
\text{C}
\end{array} \quad \begin{array}{c}
\text{1}
\end{array}
\begin{array}{c}
\text{R}
\end{array}
\begin{array}{c}
\text{Y}
\end{array}
\rightarrow \begin{array}{c}
\text{C} = \text{C}
\end{array}
+ \begin{array}{c}
\text{BH} + \text{Y}
\end{array}
\]

The base attacks the hydrogen atom on C$_1$, simultaneously displacing the electron pair to form the C$_1$-C$_2$ double bond, and displacing the leaving group. In the present case, if there is some sort of reagent which serves as a catalyst, it may either be electrophilic or nucleophilic. Such a catalyst might remove the hydrogen atom as a hydride ion, or remove the lithium atom as a positive ion.* However, since sec-butyllithium has been assumed to be associated as tetramers, a carbon atom from an adjacent part of the tetramer might serve as a kind of intramolecular self-catalyst which associates with the leaving lithium atom in a \textit{trans}-elimination mechanism. Such a process looks quite difficult to carry out smoothly when one examines a

*The kinetics of this type of elimination would appear to be second-order, first order in catalyst and first order in alkyllithium. Since the decompositions were carried out in the absence of solvent, the order with respect to alkyllithium and any catalyst which may have been present was not determined.
model of the tetramer, however. Now the results of the kinetic study indicate that the decomposition in the pure state obeys first-order law with respect to product formation and exhibits negative entropies of activation. This suggests that several degrees of freedom are lost in the transition state; thus, motion is more restricted in the transition state than in the reactants, and it is suspected that a ring forms during the activation process.

These considerations suggest that the decomposition might be a cis-elimination with a four-center type transition state as pictured below:

\[
\begin{align*}
| & | \\
\text{C} & \text{C} \\
| & | \\
\text{H} & \text{Li}
\end{align*}
\rightarrow
\begin{align*}
| & | & | & | \\
\text{C} & \ldots & \text{C} & | \\
| & | & | & | \\
\text{H} & \ldots & \text{Li} \\
\text{transition state}
\end{align*}
\rightarrow
\begin{align*}
| & | \\
\text{C} & \text{C} & + \text{LiH}
\end{align*}
\]

Molecular models of the tetramer suggest that cis-elimination of lithium hydride will proceed smoothly. If free rotation around the all carbon-carbon bonds is permitted, a random distribution of cis, trans conformations will result. However, molecular models of the tetramer of sec-butyllithium suggest that certain conformations of the sec-butyl groups are not favorable for the formation of the four-center
transition state. As pointed out earlier, most cis-eliminations involving such a transition state result in a preponderance of trans-2-butene over the cis-isomer, due to the interaction of the methyl groups in the cis-conformation. The stability of the trans-2-butene still is to be considered in the present case, but other steric factors are evident in the tetramer, as seen from Figure 36 on the following page. For example, it is evident that when ethyl groups (I) and (II) are positioned as in Figure 36(C) a rather serious interaction exists. This interaction may be alleviated by rotation of either one or both ethyl groups, resulting in conformations (D) and (E), which would, upon decomposition, yield 100 per cent and 50 per cent cis-2-butene, respectively. It is possible, of course, that complete rotation of one or both of the ethyl groups will take place so that the ethyl and methyl groups of a sec-butyl group will exchange positions (see Figure 36 (A) and (B). However, as these figures illustrate, another severe interaction exists if the ethyl groups are oriented as in (A), that being with the lithium atoms of the adjacent dimer. This may be diminished, as indicated in (B), by rotating the ethyl group. The result
Fig. 36--Possible combinations of ethyl group in the tetramer of sec-butyllithium.
again is a conformation which would result in cis-2-butene upon decomposition.

It is important to note that the models which were constructed for the considerations outlined above were made to scale from styrofoam balls, using the data of Dietrich (7) and the accepted covalent radii of carbon, hydrogen, and lithium (10). Nevertheless, the models are only approximately accurate, and the conclusions drawn are tentative. It is further suspected that the same mechanism applies to the decomposition reaction of ethyl-, iso-propyl-, and n-butyllithium, because the first-order rates and negative entropies of activation are also obtained for these three alkyllithiums.

It is also important to observe that the relative stabilities of these four lithium alkyls are in the order:

$$\text{CH}_3\text{CH}_2\text{Li} \approx \text{CH}_3\text{CH}_2\text{CH}_2\text{Li} > \text{CH}_3\text{CH}_2\text{Li} > \text{CH}_3\text{CH}_2\text{CH}_2\text{Li}$$

An examination of the Arrhenius plot shows that within experimental error, ethyllithium and n-butyllithium lay on the same line. On the other hand, iso-propyllithium and sec-butyllithium are parallel to each other. Therefore, it appears that the decomposition of alkyllithium compounds do not differ greatly in rate and energy of activation when
the alkyl groups are primary. On the other hand, secondary alkyllithium compounds show significantly lower activation energies and higher reaction rates over those with primary alkyl groups. A comparison of iso-propyl to sec-butyllithium indicates that although the energies of activation are the same within the experimental error, yet the effect of A (the pre-exponential Arrhenius factor) results in a considerably lower rate constant for iso-propyllithium. The steric strain existing in the sec-butyllithium polymer is expected to be greater than iso-propyllithium, and considerably greater than for both n-butyl and ethyllithium. It is suspected that the relative stability of these four lithium alkyls is primarily due to this steric effect. Electronic effects do not appear to have a significant effect toward stabilizing the four-membered ring. The higher reactivity of sec-butyllithium might be illustrated simply by steric strain both in the polymer and activated complex. sec-Butyllithium is more crowded in both situations than iso-propyllithium. This might be the reason why they both have the same activation energy. The difference in pre-exponential factor results in the observed difference in rates of decomposition.
CHAPTER BIBLIOGRAPHY


BIBLIOGRAPHY

Books


Articles


Fomin, W. and N. Sochanski, "Uber die Wasser abspaltung aus Pinakolin-alkohol und Tertiabutyl-athylen," Berichte Der Deutschen Chemischen Gesellschaft, XLVI (1913), 244.


