BASE EFFECTS ON THE THERMAL DECOMPOSITION
OF sec-BUTYLLITHIUM SOLUTIONS

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OF sec-BUTYLLITHIUM SOLUTIONS

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CHAPTER I

INTRODUCTION

Colligative Properties

Alkyllithium compounds, first extensively studied by Schlenk and Holtz (17) in 1917, exist in both solid and liquid states at room temperature. Methyl, ethyl, and isopropyllithium are solids and the higher homologs are liquids at room temperature except where symmetrical alkyl branching occurs as in the cases of tert-butyl and neo-pentyllithium which are solids. With the exceptions of methyl and phenyllithium, the solids can often be sublimed and the liquids distilled providing both processes are carried out in high vacuum and at high temperatures (6). Alkyllithium compounds, except methyllithium, are soluble in non-polar solvents such as benzene, cyclohexane, and n-hexane and in polar solvents such as ethyl ether and dioxane (6). These properties are quite different from corresponding organo-sodium, -potassium, -rubidium, and -cesium compounds which are insoluble in non-polar solvents and decompose upon attempted purification.

In 1951 Wittig (22) first reported that alkyllithium compounds were associated species and since then many compounds have been studied. The association numbers for a few
<table>
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<td>Poly iso-propenyl-lithium</td>
<td>Dioxane</td>
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*(b) boiling
alkyllithium compounds are shown in Table I. The association number is a function of both the solvent polarity and branching of the organic moiety. In polar solvents association numbers of one and two are found and in non-polar solvents association numbers of four and six are found. In non-polar solvents the symmetry of the organic moiety directly affects the association number, as exemplified by \( n \)-butyllithium (\( n \)-BuLi), which is a hexamer, and \( t \)-tert-butyllithium (\( t \)-BuLi), which is a tetramer. Only in the case of large or macro-molecules are monomeric species found, and only in polar solvents (13).

Structure of Alkyl Lithium Compounds

The structure of alkyl lithium compounds has been a point of conjecture for many years. Rundle has proposed an electron-deficient or delocalized bonding theory to account for the crystal structures of the tetramethyl platinum tetramer, the trimethyl aluminum dimer, and the dimethyl beryllium polymer, which are similar types of compounds. The theory predicts that delocalized bonding occurs when "an atom (usually metallic) with more low energy orbitals than valence electrons [is] combined with atoms or groups containing no unshared electron pairs . . . . It appears that under these circumstances delocalization of bonding occurs so as to use all of the low energy bonding orbitals of the metallic atom" (16, p. 46). Brown and his coworkers (1, 2) applied this bonding
principle to predict the geometry of the ethyllithium (EtLi) tetramer and hexamer observed in the mass spectrum of ethyllithium vapor. The proposed structures are shown in Figure 1.

Fig. 1—Brown's proposed ethyllithium tetramer and hexamer.

Weiner, Vogel, and West (20) in 1962 proposed the same type of structure for the tetramer of tert-butyllithium. In the proposed structure four center electron deficient bonds involving unspecified orbitals of three lithium atoms and the sp³ orbital of one alpha carbon atom are proposed. In the tetramer four equivalent delocalized bonds would be found.
Eastham, on the other hand, has proposed for the n-
butyllithium tetramer "... that a symmetrical tetramer
is formed by quadrupole association of two dimers, i.e.,
two (BuLi)_2 units ..., face-to-face, with the Li-Li axis
of one orthogonal to that of the other" (7, p. 3519). Thus
two choices, delocalized bonding or ionic association, can
be used to explain the structure of alkyllithium compounds.

Dietrich (8) in 1963 published his findings concerning
the crystal structure in ethyllithium. He found that the
crystalline substance was tetrameric, appeared to be two
associated dimers, and that all carbon-lithium distances
were not equivalent (11, p. 5). In essence his data con-
formed the cyclic structures proposed, but showed that the
tetrahedron of lithium atoms was distorted.

Weiss (21) in 1964 published his findings concerning
crystalline methyllithium. By interpreting x-ray powder
patterns he deduced that solid methyllithium was tetrameric
and that all the carbon-lithium distances were equivalent,
2.27A. He noted that the lithium skeleton formed a perfect
tetrahedron and equidistant over each face of the tetrahedron
was a methyl group. The rather short Li-Li distances observed
for methyllithium tetramers would seem to indicate that a
delocalized description of the bonding is to be preferred.
Eastham (7) has proposed that in the presence of ether the n-butyllithium tetramer* breaks down to ether solvated dimers as shown below:

Brown and coworkers (3) have shown that the addition of triethylamine to ethyllithium does not disrupt the hexamer structure if the base hexamer ratio is less than 3.5; as the ratio is increased, however, the hexamers break down to complexed dimers. Brown, Ladd, and Newman (4) have shown that lithium ethoxide does not break up the hexamer of ethyllithium. At high lithium ethoxide to hexamer ratios they have proposed that clusters of the base are coordinated to the hexamer framework.

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*The discrepancy between the association numbers reported for n-butyllithium in cyclohexane (i = 4 or 6) by two groups of workers has not been explained at this writing (cf. Table I).
Pyrolysis of Alkyl Lithium Compounds

Schorlin (18) in 1910 thermally decomposed ethyl lithium and obtained ethane, ethylene, and lithium hydride. In 1933 Thompson and Stevens (19) thermally decomposed ligroin solutions of ethyllithium and obtained the same gaseous products and a solid which upon hydrolysis yielded an amount of hydrogen corresponding to the solid, being 50 per cent lithium hydride.

Ziegler and Gellert (23) obtained generally the same results when they thermally decomposed ethyllithium and n-butyllithium. Analysis of the hydrocarbon products obtained when n-butyllithium was thermally decomposed in an autoclave showed 92 per cent 1-butene and up to 8 per cent n-butane. A solid resinous product was also found. These results were interpreted in terms of the following reactions:

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Li} \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{LiH} \]  \[1\]

\[ \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{C}_4\text{H}_9\text{Li} \rightarrow \text{CH}_3\text{CHCH}_2\text{CH}_2 + \text{C}_4\text{H}_{10} \]  \[2\]

\[ \text{CH}_2\text{CHCH}_2\text{Li} \rightarrow \text{CH}_2=\text{CHCH}_2\text{Li} \rightarrow \text{polymer} \]  \[3\]

Initially only 1-butane was formed \[1\]. As the reaction proceeded, some of the 1-butane reacted with the n-butyllithium \[2\] to produce the observed butane. The resin would come from the butadiene \[3\], which is known to polymerize in the
presence of alkyllithium compounds. Whenever the decomposition was carried out so as to remove the gases as they were formed, pure 1-butene was the only gaseous product. Boiling solutions of n-butyllithium in n-octane yielded 95 per cent 1-butene and 5 per cent n-butane. Weiner, Vogel, and West (20) obtained 94 per cent isobutylene and 6 per cent isobutane by refluxing solutions of tert-butyllithium in n-heptane.

Bryce-Smith (5) decomposed n-butyllithium in isopropylbenzene at 135°C and obtained butane, 1-butene, and lithium hydride. The absence of coupling products was interpreted to mean that the reaction did not proceed through a free radical pathway.

In 1965 Lin (11) showed that when pure ethyl, isopropyl, and n-butyllithium were thermally decomposed in such a fashion as to insure the removal of the product gases, the olefins were the main products, 99-100 per cent, and only trace quantities of the saturated hydrocarbons were found. sec-Butyllithium was decomposed in the same manner and found to yield about 33 per cent 1-butene, 50 per cent cis-2-butene, and 17 per cent trans-2-butene. The product distribution was found to be only slightly dependent upon the decomposition temperature in the region 78-104°C. All the decompositions were found to be first order in product gases, and Arrhenius plots of the temperature dependence yielded the activation
parameters. Lin proposed that the decomposition proceeds via a cis-elimination pathway from the sterically hindered polymeric alkyl lithium species. The favored cis-orientation of the proposed sec-butyllithium tetramer was used to explain the unprecedented high per cent cis-olefin observed. Glaze, Lin, and Felton (9) have shown that the apparent stereo-specificity of the decomposition of sec-butyllithium is lost when solutions in n-octane are decomposed.

Kutta (10) studied the thermal decomposition of solutions of n-butyl, isobutyl, tert-butyl, and sec-butyllithium. He found that olefins and lithium hydride were the primary reaction products. It was determined that all the decompositions except sec-butyllithium were first order, and Arrhenius plots were made to determine the reported activation parameters. The kinetic isotope effect for the decomposition of \( \alpha,\alpha \)-dideuteron-butyllithium \( (k_H/k_D = 2.96) \) was interpreted in favor of a cis-elimination mechanism. Kutta (10) also showed that the rate of decomposition of n-butyllithium solutions was unaffected by excess lithium hydride and variations in the stirring speed. In addition it was shown that the rate constant for the decomposition of n-butyllithium solutions was increased when lithium n-butoxide was added, and that the increase was a linear function of the amount of base present in solution. The rate data for sec-butyllithium were found to follow neither first nor second order rate laws, and no order was determined.
The pyrolysis of sec-butyllithium in solution was studied in an attempt to understand the loss of stereospecificity and the atypical kinetics that have been reported. Additionally, the effect of added lithium alkoxides was studied to determine their effects on the highly reactive sec-butyllithium substrate.
CHAPTER BIBLIOGRAPHY


CHAPTER II

EXPERIMENTAL

Preparation of Lithium Sand

Reagents

Mineral oil, light viscosity
Lithium metal (99.7 per cent lithium containing 2 per cent sodium (2))
Sodium oleate, reagent grade
n-Pentane, 99 mole per cent minimum purity

Procedure

About 100 milliliters of mineral oil was poured into a dry 250 milliliter Erlenmeyer flask with a ground glass stopper neck. To this was added 7.7 grams of finely divided one-half inch lithium rod and a small amount of sodium oleate, a dispersing agent.

The loosely stoppered flask was placed on a hot plate regulating at maximum setting. As heating proceeded the stopper was frequently loosened to prevent it from blowing out. Heating was continued until silver balls of molten lithium metal were observed. The tightly stoppered flask was removed from the hot plate and vigorously shaken in front of a compressed air jet. After the contents were cool enough so that agglutination of the metal particles could not occur, shaking was stopped and the contents allowed to cool to room temperature.

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About 200 milliliters of \( n \)-pentane was added to the cooled flask and the contents transferred to a Buchner funnel and rapidly filtered. The flask was rinsed with \( n \)-pentane to assure a quantitative transfer. The finely divided sand was sucked dry and quickly transferred to a reaction vessel which had previously been flushed with argon gas.

**Preparation of sec-Butyllithium**

**Reagents**

- Lithium sand, containing 2 per cent sodium
- sec-Butyl chloride, Eastman reagent grade
- \( n \)-Pentane, 99 mole per cent minimum purity
- Argon gas, 99.997 per cent purity

**Procedure**

The preparation was carried out under an argon gas atmosphere in a three-necked, 500 milliliter, round-bottomed flask equipped with a Hirschberg stirrer and Teflon stirring gland, Friedrichs reflux condenser, and a 250 milliliter addition funnel.

Lithium sand, 7.7 grams (1.1 moles), and 100 milliliters of \( n \)-pentane were placed in the flask. Sec-butyl chloride, 53.1 milliliters (0.5 mole), and 100 milliliters of \( n \)-pentane were mixed and placed in the addition funnel. Stirring was started and the flask contents were brought to a slow reflux by raising a warm heating mantle around the flask. After
reflux had begun, 10 per cent of the sec-butyl chloride solution was added to the reaction flask. When a definite color change to purple or blue was noted, slow dropwise addition of the sec-butyl chloride solution was started and the external heat source removed.

Addition was completed in a 3-4 hours and the flask contents brought to reflux with a heating mantle. Reflux was maintained for two hours. The flask was then cooled to room temperature, securely stoppered, and taken into a dry box. The contents were filtered through a medium frit Buchner funnel into a 250 milliliter Erlenmeyer flask equipped with a ground glass stopper neck. Successive washings of the blue residue with n-pentane were needed to assure good yields of sec-butyllithium. The clear n-pentane solution was concentrated by removing the solvent under vacuum. After the solution was concentrated as much as possible, the flask was stoppered and the clear to yellow solution was stored for later use.

Preparation of Lithium Alkoxides

Reagents
Lithium dispersion, 30 per cent in wax, Lithium Corporation of America
Ethyl alcohol, absolute, redistilled
sec-Butyl alcohol, reagent grade
Phenol, reagent grade
Benzene, thiophene free, redistilled
n-Pentane, 99 mole per cent minimum purity
Procedure

The benzene and n-pentane were distilled from lithium aluminum hydride to assure dryness. The ethyl alcohol was distilled from magnesium metal to assure dryness.

Thirteen grams of the lithium dispersion were taken into the dry box, dispersed in about 400 milliliters of n-pentane, and filtered. The cleaned, micron-size lithium particles and 125 milliliters of n-pentane were placed in a three-necked, 500 milliliter, round-bottomed flask equipped with a Hirschberg stirrer and Teflon stirring gland in the center neck and two ground glass stoppers in the side necks. The stoppered flask was brought out of the dry box and fitted with a 250 milliliter addition funnel and a Friedrichs condenser. The flask was initially flushed with argon gas and an argon gas blanket was maintained during the entire reaction. Cold water was circulated through the condenser from an ice-water reservoir with a circulating pump.

A mixture of 0.6 mole of alcohol in 100 milliliters of solvent (ethyl alcohol and benzene, sec-butyl alcohol and n-pentane, or phenol and benzene) was placed in the addition funnel. Stirring was started and about 10 per cent of the contents of the addition funnel were added. The system warmed, gas was evolved, and when a slow reflux was reached, addition was initiated to maintain the reflux rate. Total addition time was from four to eight hours. When benzene was
used as a solvent the system was heated gently with a heating mantle during the entire reaction. After addition was completed the system was heated at vigorous reflux for an additional two to six hours. The system was then cooled to room temperature, securely stoppered, and taken into the dry box.

The flask contents were transferred to a 250 milliliter Erlenmeyer flask and the solvent removed by vacuum distillation. The resulting solid was transferred to a 100 milliliter, single-neck, round-bottomed flask. The flask was stoppered with a stopcock adapter and brought out of the dry box. The flask with adapter was fitted onto a vacuum line to which another flask submerged in a Dewar of liquid nitrogen was attached. The flask containing the alkoxide was heated at 100°C for four to six hours to drive off any remaining solvent or alcohol. The flask was taken back into the dry box and the adapter replaced with a glass stopper. The alkoxide was stored for later use.

Lithium ethoxide and phenoxide were white crystalline solids, while lithium sec-butoxide was a light grey crystalline solid.

**Purification of sec-Butyllithium**

**Reagents**

- sec-Butyllithium, crude
- n-Octane, 99 mole per cent minimum purity, redistilled
Procedure

The apparatus shown in Figure 3, page 20, was used to distill the crude sec-butyllithium on a vacuum line as shown in Figure 5, page 21.

In the dry box, 5-7 milliliters of the crude sec-butyllithium was pipetted into the 50 milliliter bulb of the distillation apparatus. A few glass beads were added to prevent severe bumping during the subsequent distillation. The sidearm was stoppered with a glass stopper and the U-tube was stoppered with a vacuum stopcock adapter. The apparatus was brought out of the dry box and fitted onto the vacuum line. The bulb was frozen in liquid nitrogen, the system evacuated, and the side-arm torched off at point a.

The bulb contents were allowed to warm slowly to room temperature under vacuum. After reaching room temperature the entire system was evacuated until a minimum pressure of 50 microns was noted on the McLeod gauge. While the system was evacuating the arm between the bulb and the U-tube was wrapped with heating tape.

When the minimal pressure was reached, a Dewar of liquid nitrogen was raised around the U-tube and an oil bath at 100-105°C was raised around the bulb. The heating tape was turned on and set to heat at about 90°C. Distillation began immediately. The bulb was thumped occasionally to prevent severe bumping. Two or three times during the distillation
Fig. 3—Distillation vessel

Fig. 4—Decomposition vessel
the Dewar of liquid nitrogen was lowered and the pure sec-butyllithium which had frozen in the arm of the U-tube was allowed to warm slightly and flow into the bottom of the U-tube. The bulb was distilled to dryness and then the oil bath removed. The Dewar was lowered and the pure sec-butyllithium warmed to room temperature. While the sec-butyllithium was warming the heating tape was removed and the system evacuated for about thirty minutes to remove any condensed decomposition gases arising from a partial decomposition of the crude sec-butyllithium during distillation.

The distillation apparatus was removed from the vacuum line and taken into the dry box. The vacuum stopcock adapter was removed and about five milliliters of n-octane was pipetted into the U-tube. The solution was pipetted into a flask containing a known amount of n-octane. The resulting solution was immediately analyzed and used.

Preparation of Pure and Base-added sec-Butyllithium Solutions

Reagents

sec-Butyllithium, pure
Lithium phenoxide
Lithium ethoxide
Lithium sec-butoxide
n-Octane, 99 mole per cent minimum purity, redistilled
n-Pentane, 99 mole per cent minimum purity, redistilled
1,2-Dibromoethane, reagent grade
Procedure

The \textit{n}-octane and \textit{n}-pentane stored in the dry box were distilled from lithium aluminum hydride to ensure dryness.

The solutions of \textit{sec}-butyllithium were analyzed by the method of Gilman and Cartledge (1) using 1,2-dibromoethane. \textit{n}-Pentane was used as the solvent for the analysis instead of ether since \textit{sec}-butyllithium cleaves ether at a very rapid rate. Analysis of dilute solutions using both methods gave excellent agreement.

About five grams of the desired alkoxide was placed in a 125 milliliter Erlenmeyer flask which contained about 30 milliliters of a pure \textit{sec}-butyllithium solution, usually 0.8 N in \textit{sec}-butyllithium. The flask was securely stoppered and brought out of the dry box. The flask was placed in a mechanical shaker and shaken for the required number of days dependent upon the alkoxide being used (five days for lithium \textit{sec}-butoxide and phenoxide and one day for lithium ethoxide). The resulting solution was yellow to red in color. The flask was taken back into the dry box and the solution filtered and analyzed.

A solution of the desired concentrations in base and \textit{sec}-butyllithium was prepared by mixing appropriate quantities of analyzed solutions of pure \textit{sec}-butyllithium in \textit{n}-octane and based-added \textit{sec}-butyllithium in \textit{n}-octane with the necessary quantity of \textit{n}-octane. The resulting solution was reanalyzed to insure concentrations of \textit{sec}-butyllithium and base.
Thermal Decomposition of sec-Butyllithium Solutions

Reagents
Analyzed solution of sec-butyllithium and lithium alkoxide

Procedure
Twenty milliliters of the analyzed sec-butyllithium solution was pipetted into the decomposition vessel shown in Figure 4, page 20. The vessel was stoppered with a vacuum stopcock adapter, brought out of the dry box, and fitted onto the vacuum line. The lower part of the vessel which contains the solution was submerged in a Dewar of liquid nitrogen. After the solution was completely frozen the vessel was evacuated and the entire system flushed three or four times with argon gas introduced into the system through the gas port tube, Figure 5, page 21. After the last flushing a residual pressure of 25 centimeters of argon gas was retained and the system cut off from the vacuum pump. The Dewar of liquid nitrogen was removed and the solution warmed to room temperature. While the solution was warming a stirring motor fitted with a horseshoe magnet was positioned above the bar magnet of the decomposition vessel and the condenser of the decomposition vessel was connected to a circulating water reservoir regulating at 31.00 ± 0.5°C.

After the solution was completely warmed to room temperature, stirring was started and the manometer pressure
was recorded, using a cathetometer accurate to ±0.1 millimeter. The barometric pressure was recorded. A regulating water-ethylene glycol bath (about a 1:1 mixture) previously set at 94.10° ± 0.05°C was raised around the entire lower end of the decomposition vessel. Simultaneously a timer, reading seconds to ±1 sec., was started. Manometer pressures and barometer pressures were recorded at various time intervals. During the initial moments of the decomposition data were recorded as often as possible. After the gas evolution had leveled off data were recorded every 0.25 or 0.50 centimeter of pressure until the reaction appeared to stop.

After the reaction appeared to stop the vacuum stopcock adapter connecting the decomposition vessel to the vacuum line was closed and the hot water-ethylene glycol bath was lowered. The gases were subsequently analyzed on a gas chromatograph.

A plot of the total corrected pressure versus time was made and in all cases found to conform to the general shape of the curve shown in Figure 6, page 26.

The rapid initial rise was found to be primarily due to the solvent coming to equilibrium at the condenser temperature, and in all runs the slope and height of the initial rise were approximately the same.
Fig. 6—A typical pressure versus time plot for decomposition gases.

The data points falling in the straight line region of the graph shown in Figure 6 were utilized in a least-squares curve fit to determine the equation of the straight line. The intercept value \((t = 0)\) was taken as the pressure change due to the n-octane solvent vapor and subtracted from the above data points to obtain the pressure increase due to the olefin gases.
The pressure due to the olefin gases, \( P(\text{olefin}) \), was utilized in the following equation

\[
+ \left[ P_\infty - P(\text{olefin}) \right]^{\frac{3}{2}} = kt + C
\]

where \( t \) is the time in hours and \( C \) is an integration constant.

The pressure at infinite time, \( P_\infty \), was calculated in the following manner

\[
P_\infty = \frac{(V_l)(RL_i)RT}{V_g}
\]

where \( V_l \) is the volume of the liquid phase, \( RL_i \) is the gross initial alkyl lithium concentration, \( T \) is the absolute temperature of the gases, \( R \) is the international gas constant, and \( V_g \) is the volume occupied by the gases. Agreement between the calculated pressure at infinite time and the observed pressure at infinite time was excellent, as seen in Table II.

**TABLE II**

**DIFFERENCES IN \( P_\infty \) OBSERVED AND CALCULATED**

<table>
<thead>
<tr>
<th>RL_i (moles/liter)</th>
<th>( P_\infty ) Observed (cm./Hg)</th>
<th>( P_\infty ) Calculated (cm./Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.381*</td>
<td>18.24</td>
<td>18.80</td>
</tr>
<tr>
<td>0.381*</td>
<td>20.99</td>
<td>20.96</td>
</tr>
<tr>
<td>0.239</td>
<td>11.81</td>
<td>11.80</td>
</tr>
<tr>
<td>0.502</td>
<td>25.25</td>
<td>24.78</td>
</tr>
<tr>
<td>0.208</td>
<td>9.48</td>
<td>10.27</td>
</tr>
</tbody>
</table>

*Two different decomposition vessels were used and the \( P_\infty \) difference is a reflection of the difference in their respective volumes.*
A graph of $+\frac{1}{2}[P_\infty - P(\text{olefin})]^{\frac{3}{2}}$ versus time was constructed and, with the exception of a few points near time equal zero, was found to be linear. Least-square analysis of the data was used to evaluate $k$ and $C$ in equation 4.

Analysis of Gaseous Products

Reagents

Product gases from the thermal decomposition

Procedure

The gases were identified on a Wilkins Aerograph gas chromatograph using a 20 feet by $\frac{1}{8}$ inch column packed with 20 per cent didecylphthalate substrate on Chromosorb-P treated with hexamethyldisilazane. A filament current of 200 milliamps was used. Column temperature was maintained at $40^\circ C$ and the detector oven was maintained at $200^\circ C$. Helium carrier gas flowed at a rate of 49.1 milliliters per minute. The recorded peaks were identified by comparison of retention times with known standards (3). Relative volume per cents were determined by the method of peak height times the width at half peak height.

Gas samples were obtained by two methods. In one method a $1/8$ inch diameter copper tube was connected directly from the gas port tube of the vacuum line to a one milliliter gas sample loop on the chromatograph and the gases were sampled
directly from the vacuum line. In a second method the gases were condensed in a trap with liquid nitrogen and transferred to a vacuum line in series with the chromatograph and then sampled with the gas loop. Both methods yielded the same results. Figure 7, page 30, shows a typical chromatogram. The unidentified peak has been shown to be n-pentane, the solvent used in the preparation of both the sec-butyllithium and the lithium sec-butoxide.

Product Distribution Versus Time

Reagents

sec-Butyllithium, pure
Analyzed solution of sec-butyllithium and lithium alkoxide

Procedure

A pure sec-butyllithium sample was treated as before (3, p. 13) and the relative product distribution versus time was determined. The pure sec-butyllithium was pyrolyzed at 104°C. The rate constant for the pyrolysis is $27.52 \pm 2.05 \text{ sec}^{-1}$ (4, p. 21) therefore pyrolysis proceeded with a half-life of 2518 seconds. The sample was decomposed for 4.8 half-lives. At intervals of about 800 seconds a chromatograph injection of the product gases was made, with the first injection made 416 seconds after decomposition was started. It was found that the relative product distribution remained constant with
RUN 26

0.373 M sec-Butyllithium
0.391 M Lithium sec-Butoxide

I  air
II  53% 1-Butene
III 26% trans-2-Butene
IV 21% cis-2-Butene

Fig. 7—Gas chromatogram of pyrolysis gases
Fig. 8—Product distribution versus time
time at the values of 36.1 per cent 1-butene, 19.0 per cent trans-2-butenes, and 44.8 per cent cis-2-butenes. A total of sixteen samples was analyzed.

Two analyzed solutions of sec-butyllithium and lithium sec-butoxide were treated as if for thermal decomposition. The kinetics of the decomposition was not determined, but rather the product distribution versus time was determined. The same method of gas analysis was used as discussed in the analysis of gaseous products section in this chapter. The results of one of these determinations is shown graphically in Figure 8, page 31. In both cases the relative per cent of 1-butene initially drops, the relative per cent of trans-2-butenes initially increases, and the relative per cent of cis-2-butenes remains constant. The final relative values in both cases correspond to the product distribution observed when lithium sec-butoxide was used to catalyze the thermal decompositions from which kinetic data were obtained.
CHAPTER BIBLIOGRAPHY


CHAPTER III

RESULTS AND DISCUSSION

It has been reported by Brown and his co-workers (2) that the ethyllithium hexamer does not disassociate upon reaction with lithium ethoxide, but rather a complex results in which an alkoxide moiety is complexed onto one or both of the open faces of the octahedral hexamer. The same results were noted with triethylamine (1) except at high base to alkyllithium ratios, where the hexamer disassociates to form complexed dimers. On the other hand, it has been shown that the tert-butyllithium tetramer, which does not have open faces, must disassociate before complexation with triethylamine can occur (4).

Kutta (6) has shown that the pyrolysis of n-butyllithium solutions is catalyzed by lithium n-butoxide, and that the reaction is first order in alkyllithium for all of the isomeric butyllithiums except sec-butyllithium. In this work, the pyrolysis of the sec-butyllithium tetramer* in n-octane was found to be catalyzed by various lithium alkoxides. The distribution of olefin products, 1-butene, trans-2-butene, and cis-2-butene, does not appear to result from a stereospecific

*Preliminary studies indicate that sec-butyllithium exists as a tetramer in hydrocarbon solution at room temperature.

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elimination as has been reported for the unsolvated pyrolysis of the same compound (5).

The observed elimination to produce the olefins and lithium hydride could proceed by one of the following mechanisms. (RLi refers to sec-butyllithium, B refers to lithium alkoxide or other bases.)

Mechanism 1.

\[
\begin{align*}
(RLi)_4 + B & \xrightarrow{K} (RLi)_4 B \\
(RLi)_4 B & \xrightarrow{k_{\text{slow}}} \text{olefin} + \text{LiH} + (RLi)_3 B \\
\frac{d \left[ \text{olefin} \right]}{dt} & = k \left[ (RLi)_4 B \right] \\
& = kK \left[ (RLi)_4 \right] \left[ B \right] \\
& = k' \left[ (RLi)_4 \right]
\end{align*}
\]

Mechanism 2.

\[
\begin{align*}
\frac{1}{2}(RLi)_4 + B & \xrightarrow{K} (RLi)_2 B \\
(RLi)_2 B & \xrightarrow{k_{\text{slow}}} \text{olefin} + \text{LiH} + RLi B \\
\frac{d \left[ \text{olefin} \right]}{dt} & = k \left[ (RLi)_2 B \right] \\
& = kK \left[ (RLi)_4 \right]^{\frac{1}{2}} \left[ B \right] \\
& = k' \left[ (RLi)_4 \right]^{\frac{1}{2}}
\end{align*}
\]

Mechanism 3.

\[
\begin{align*}
\frac{1}{2}(RLi) + B & \xrightarrow{K} (RLi) B \\
(RLi) B & \xrightarrow{k_{\text{slow}}} \text{olefin} + \text{LiH} + B \\
\frac{d \left[ \text{olefin} \right]}{dt} & = k \left[ (RLi) B \right] \\
& = kK \left[ (RLi)_4 \right]^{\frac{1}{2}} \left[ B \right] \\
& = k' \left[ (RLi)_4 \right]^{\frac{1}{2}}
\end{align*}
\]
Mechanism 1 results in the following pressure relationship (see Appendix B):

\[ +\log(P_\infty - P) = k_{\text{obs}} + C \]

where \( P \) is the pressure at infinite time, \( P \) is the pressure due to the olefin gases at any time \( t \), \( k_{\text{obs}} \) is the observed rate constant, and \( C \) is an integration constant. A plot of the above function was not linear, indicating that the data do not fit this mechanism.

Mechanism 3 results in the following pressure relationship (see Appendix B):

\[ + (P_\infty - P)^{3/4} = k_{\text{obs}} + C. \]

A plot of this function was not linear, indicating that the data do not fit this mechanism.

Mechanism 2 results in the following pressure relationship (see Appendix B):

\[ + (P_\infty - P)^{1/2} = k_{\text{obs}} + C. \]

As shown in Appendix A, the observed data fit this relationship, suggesting that mechanism 2 is operative in this pyrolysis.

Summarized in Table III are the results of the pyrolysis data obtained in this work. The rate constants, \( k_{\text{obs}} \), were obtained as slopes from plots of \((P_\infty - P)^{1/2}\) versus time (see Table III, page 37). The results summarized are those in which the dimer to base ratio is greater than one. At lower dimer to base ratios, complexation by more than one base species may occur and mechanism 2 may not be the only mode of decomposition.
### TABLE III*

**PYROLYSIS** OF sec-BUTYL LITHIUM SOLUTIONS

<table>
<thead>
<tr>
<th>Run No.</th>
<th>(sec-BuLi) (moles/liter)</th>
<th>s-BuOLi (moles/liter)</th>
<th>k&lt;sub&gt;obs&lt;/sub&gt; (cmHg)&lt;sup&gt;5/8&lt;/sup&gt;/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>0.330</td>
<td>0.124</td>
<td>2.743</td>
</tr>
<tr>
<td>41</td>
<td>0.350</td>
<td>0.081</td>
<td>2.193</td>
</tr>
<tr>
<td>38</td>
<td>0.235</td>
<td>0.076</td>
<td>1.894</td>
</tr>
<tr>
<td>7</td>
<td>0.381</td>
<td>0.064</td>
<td>1.000</td>
</tr>
<tr>
<td>40</td>
<td>0.356</td>
<td>0.063</td>
<td>1.757</td>
</tr>
<tr>
<td>30</td>
<td>0.313</td>
<td>0.061</td>
<td>1.684</td>
</tr>
<tr>
<td>12</td>
<td>0.381</td>
<td>0.044</td>
<td>1.141</td>
</tr>
<tr>
<td>32</td>
<td>0.391</td>
<td>0.042</td>
<td>0.635</td>
</tr>
<tr>
<td>36</td>
<td>0.351</td>
<td>0.037</td>
<td>0.683</td>
</tr>
<tr>
<td>37</td>
<td>0.201</td>
<td>0.036</td>
<td>0.663</td>
</tr>
<tr>
<td>35</td>
<td>0.208</td>
<td>0.033</td>
<td>0.602</td>
</tr>
<tr>
<td>34</td>
<td>0.374</td>
<td>0.029</td>
<td>0.747</td>
</tr>
</tbody>
</table>

LiOØ

<table>
<thead>
<tr>
<th>Run No.</th>
<th>(sec-BuLi) (moles/liter)</th>
<th>s-BuOLi (moles/liter)</th>
<th>k&lt;sub&gt;obs&lt;/sub&gt; (cmHg)&lt;sup&gt;5/8&lt;/sup&gt;/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>0.338</td>
<td>0.074</td>
<td>3.102</td>
</tr>
<tr>
<td>15</td>
<td>0.320</td>
<td>0.068</td>
<td>2.672</td>
</tr>
<tr>
<td></td>
<td>LiOEt</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.242</td>
<td>0.081</td>
<td>3.250</td>
</tr>
<tr>
<td>21</td>
<td>0.502</td>
<td>0.097</td>
<td>2.833</td>
</tr>
</tbody>
</table>

*See Appendix A for individual runs

**Pyrolysis temperature is 94.10 ± 0.05°C

To determine the kinetic order of the base catalyst the following relationships were used:

\[
\frac{k_{\text{obs}}}{k B} = B^n
\]

\[
\log (k_{\text{obs}}) = \log K + n \log B
\]

\[
\log (k_{\text{obs}}) = n \log B
\]

\[
\log (k_{\text{obs}})/\log B = n
\]
A plot of log $(k_{\text{obs}})$ versus log $B$ was made (see Figure 9, page 39) using the data for lithium sec-butoxide summarized in Table III, page 37. The data were subjected to least-squares analysis and found to have a slope of $1.16 \pm 0.11$. The slope determined is the kinetic order, $n$ of the base catalyst. Deviations in $k_{\text{obs}}$ are probably due to the presence of a higher base concentration than determined by analysis. The higher base concentration arises from a reaction of sec-butyllithium with trace impurities of water and oxygen trapped in the decomposition vessel while the decomposition solution was being prepared in the dry box or handled on the vacuum line (see Chapter II, p. 24). The reactions would produce lithium sec-butoxide and lithium oxide. These species would increase the base concentration and make $k_{\text{obs}}$ appear too large for the analyzed base concentrations.

The data summarized in Table III, page 37, indicate that the catalytic effect of the bases used is in the order

- Lithium ethoxide (LiOEt)
- Lithium phenoxide (LiOØ)
- Lithium sec-butoxide (s-BuOLi)

However, it is felt there are not sufficient data to determine an exact relationship between the catalysts, since only a few runs were made with LiOEt and LiOØ. Furthermore, it is possible that the s-BuOLi is present as an impurity in all runs.
Fig. 9--Graph of log (k_{obs}) versus log (B)

\[ \log(k_{obs}) = 1.539(\pm 0.139) + 1.157(\pm 0.108) \log(B) \]

- actual points
- least squares calculated points
More data must be obtained before a complete discussion of the base effect is possible.

The product distribution observed in the pyrolysis remained constant as the concentration of lithium sec-butoxide was changed, as shown in Table IV. It was also found that the product distributions observed when the other two alkoxides were used as catalysts remained constant.

**TABLE IV**

AVERAGE PRODUCT DISTRIBUTION VERSUS THE ALKOIDE MOIETY*

<table>
<thead>
<tr>
<th>Alkoxide</th>
<th>% 1-Butene</th>
<th>% trans-2 Butene</th>
<th>% cis-2 Butene</th>
<th>% 2-Butene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium ethoxide</td>
<td>72.6 ±1.9</td>
<td>15.5 ±1.3</td>
<td>11.9 ±0.4</td>
<td>2.65</td>
</tr>
<tr>
<td>Lithium phenoxide</td>
<td>63.4 ±3.6</td>
<td>18.2 ±1.1</td>
<td>17.8 ±2.0</td>
<td>1.76</td>
</tr>
<tr>
<td>Lithium sec-butoxide</td>
<td>51.4 ±4.4</td>
<td>27.3 ±3.1</td>
<td>21.3 ±1.2</td>
<td>1.06</td>
</tr>
</tbody>
</table>

*See Appendix A for values of individual runs

By comparing the observed product distribution to the product distribution obtained from other sec-butyl systems, Table V, it can easily be seen that a cis-elimination pathway is suggested.

The cis-elimination mechanism assumes a cyclic transition state in which the \( \_ \_ \_ \) -hydrogen is eliminated while in the \( \_ \_ \_ \_ \_ \_ \) position with respect to the other leaving group.
TABLE V

ELIMINATION REACTION PRODUCT DISTRIBUTION FOR sec-BUTYL SYSTEMS (3)

<table>
<thead>
<tr>
<th>Substituent</th>
<th>1-Butene</th>
<th>% trans-2 Butene</th>
<th>% cis-2 Butene</th>
<th>Probable Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>-(CH\textsubscript{3})\textsubscript{2}N -O\textsuperscript{-}</td>
<td>67</td>
<td>21</td>
<td>12</td>
<td>cis</td>
</tr>
<tr>
<td>-OCOCH\textsubscript{3}</td>
<td>57</td>
<td>28</td>
<td>15</td>
<td>cis</td>
</tr>
<tr>
<td>-OCSSCH\textsubscript{3}</td>
<td>42</td>
<td>40</td>
<td>18</td>
<td>cis</td>
</tr>
<tr>
<td>-NH\textsubscript{2}, HNO\textsubscript{2}</td>
<td>25</td>
<td>56</td>
<td>19</td>
<td>trans</td>
</tr>
<tr>
<td>-Br, C\textsubscript{2}H\textsubscript{5}O</td>
<td>20</td>
<td>59</td>
<td>21</td>
<td>trans</td>
</tr>
<tr>
<td>-OTs</td>
<td>10</td>
<td>47</td>
<td>43</td>
<td>E\textsubscript{1}</td>
</tr>
</tbody>
</table>

The observed pyrolysis products, olefin and lithium hydride, could be produced from somewhat ionic or polar transition states as represented in Figure 10, and Figure 11, page 42.

![Fig. 10—Possible transition state leading to 1-butene](image-url)
Addition of alkoxide to either of the transition states shown in Figures 10 and 11 would serve to stabilize the ionic nature of the transition state, and result in an increase of olefin character. The overall result would be to stabilize the polar transition state in the non-polar solvent.

Due to its intimate association in the transition state, the alkoxide would be expected to influence both the rate of pyrolysis, as has already been shown, and the observed product distribution. As the basicity of the alkoxides increases the transition state shown in Figure 11 would become more stable and an increase in the amount of 2-olefin or a decrease in the 1-olefin/2-olefin ratio would be expected. The relative basicities of the alkoxide used in this study should be in the following order of decreasing strengths:

\[ \text{s-BuOLi} > \text{LiOEt} > \text{LiO}\]
As seen in Table IV, page 40, when lithium sec-butoxide is used as the catalyst more 2-olefin is produced; however, the relative amounts of 2-olefin are lower for lithium ethoxide than for the phenoxide case. This is in reverse order to that expected. The relative steric volumes of the alkoxides should follow the trend:

\[ s\text{-BuOLi} > LiOEt, \quad s\text{-BuOLi} > LiO\phi \]

and it would be expected that as the steric volume increases the relative amounts of 1-butene should increase. As seen in Table IV, page 40, this is contrary to the observed trend.

It is also possible that the orientation of the complexed dimer accounts for the observed product distribution. However, our knowledge of the geometry of the complex is insufficient to produce accurate models to evaluate this possibility.

Additionally, the elimination may proceed through an assisted pathway in which the lithium ion of the alkoxide ion pair becomes associated with the leaving hydride ion. Further experiments are suggested in which other metal alkoxides (such as sodium) and neutral bases are used as pyrolysis catalysts.

The suggested mechanism, mechanism 2, does not take into account possible decomposition of the uncomplexed tetramer. However, this process would be expected to have a higher activation energy than that proposed by mechanism 2. The
preparation of base free solutions of sec-butyllithium is very difficult and has not been accomplished at the time of this writing.
CHAPTER BIBLIOGRAPHY


RUN 12

0.381 M sec-BUTYLLITHIUM
0.044 M LITHIUM sec-BUTOXIDE

\[
\left[ P_0 - P(\text{olefin}) \right]^{1/2} = 4.836 - 1.141 t
\]

Product distribution:

<table>
<thead>
<tr>
<th>% 1-Butene</th>
<th>50.7%</th>
</tr>
</thead>
<tbody>
<tr>
<td>% trans-2-Butene</td>
<td>28.2%</td>
</tr>
<tr>
<td>% cis-2-Butene</td>
<td>21.1%</td>
</tr>
</tbody>
</table>
RUN 15
0.320 M sec-BUTYLLITHIUM
0.068 M LITHIUM PHENOXIDE

\[
[P_0 - P(olefin)]^v = 4.216 - 2.672 t
\]

Product distribution:

- % 1-Butene: 59.7%
- % trans-2-Butene: 19.3%
- % cis-2-Butene: 19.9%
RUN 17

0.338 M sec-BUTYLLITHIUM
0.074 M LITHIUM PHENOXIDE

\[ [P_0 - P(\text{olefin})]^\% = 4.370 - 3.102 t \]

Product distribution:

\%

- 1-Butene: 67.0%
- trans-2-Butene: 17.1%
- cis-2-Butene: 15.8%
RUN 18

0.239 M sec-BUTYLLITHIUM
0.283 M LITHIUM ETHOXIDE

Product distribution:

<table>
<thead>
<tr>
<th>Butene Type</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butene</td>
<td>71.3%</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>16.8%</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>11.9%</td>
</tr>
</tbody>
</table>
RUN 19

0.235 M sec-BUTYLLITHIUM
0.173 M LITHIUM ETHOXIDE

Product distribution:

<table>
<thead>
<tr>
<th></th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butene</td>
<td>75.5%</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>13.6%</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>11.3%</td>
</tr>
</tbody>
</table>
RUN 20

0.242 M sec-BUTYLLITHIUM
0.081 M LITHIUM ETHOXIDE

\[ [P_0 - P(\text{olefin})]^2 \text{ (cm. Hg)}^2 = 3.953 - 3.250 t \]

Product distribution:

- % 1-Butene = 71.1%
- % trans-2-Butene = 16.2%
- % cis-2-Butene = 12.6%
RUN 21
0.502 M sec-BUTYLLITHIUM
0.097 M LITHIUM ETHOXIDE

Product distribution:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butene</td>
<td>60.7%</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>21.2%</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>18.1%</td>
</tr>
</tbody>
</table>
RUN 22
0.695 M sec-BUTYL LITHIUM
0.152 M LITHIUM sec-BUTOXIDE

\[
[P_\infty - P_{\text{olefin}}]^{\frac{1}{2}} = 6.502 - 8.372 t
\]

Product distribution:

<table>
<thead>
<tr>
<th>Product</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butene</td>
<td>48.3%</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>29.3%</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>22.4%</td>
</tr>
</tbody>
</table>
RUN 30

0.313 M sec-BUTYLLITHIUM
0.061 M LITHIUM sec-BUTOXIDE

\[ [P_0 - P(\text{olefin})]^k \text{(cm. Hg)}^k = 4.232 - 1.68t \]

Product distribution:

<table>
<thead>
<tr>
<th>Compound</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butene</td>
<td>48.2%</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>29.2%</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>22.5%</td>
</tr>
</tbody>
</table>
RUN 31

0.330 M sec-BUTYLLITHIUM
0.124 M LITHIUM sec-BUTOXIDE

Product distribution:

% 1-Butene 46.1%
% trans-2-Butene 31.8%
% cis-2-Butene 22.0%
RUN 32
0.391 M sec-BUTYLLITHIUM
0.042 M LITHIUM sec-BUTOXIDE

\[ [P_\infty - P(\text{olefin})]^{\frac{1}{2}} = 4.590 - 0.635 \, t \]

Product distribution:

- % 1-Butene: 48.6%
- % trans-2-Butene: 28.2%
- % cis-2-Butene: 23.3%
RUN 3

0.374 M sec-BUTYLLITHIUM

0.029 M LITHIUM sec-BUTOXIDE

Product distribution:

| % 1-Butene | 49.3% |
| % trans-2-Butene | 28.8% |
| % cis-2-Butene | 21.9% |
RUN 35
0.208 M sec-BUTYL LITHIUM
0.033 M LITHIUM sec-BUTOXIDE

$[\text{P(olefin)}]^\% = 3.328 - 0.602 \ t \ (\text{hr.})$

Product distribution:
- 48.4% 1-Butene
- 30.2% trans-2-Butene
- 21.3% cis-2-Butene
PRODUCT DISTRIBUTION:

1-BUTENE: 47.0%
TRANS-2-BUTENE: 30.2%
CIS-2-BUTENE: 22.8%
RUN 37
0.201 M sec-BUTyllIthIUM
0.036 M LITHIUM sec-BUTOXIDE

\[ [P_\infty - P(\text{olefin})]^2 = 3.296 - 0.663 \, t \]

Product distribution:

| % 1-Butene    | 48.6% |
| % trans-2-Butene | 29.9% |
| % cis-2-Butene  | 21.5% |
RUN 38
0.235 M sec-BUTYL LITHIUM
0.076 M LITHIUM sec-BUTOXIDE

Product distribution:

% 1-Butene 63.7%
% trans-2-Butene 19.7%
% cis-2-Butene 16.5%
RUN 40

0.356 M sec-BUTYLLITHIUM

0.063 M LITHIUM sec-BUTOXIDE

\[
\left[ P_\infty - P(\text{olefin}) \right]^2 = 4.435 - 1.757 t
\]

Product distribution:

<table>
<thead>
<tr>
<th></th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butene</td>
<td>60.8%</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>20.5%</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>18.7%</td>
</tr>
</tbody>
</table>
Product distribution:

% 1-Butene 60.0%
% trans-2-Butene 22.2%
% cis-2-Butene 17.8%
APPENDIX B

RLi = sec-Butyllithium
B = Base

\[ n \{(RLi)_{4}\}_t = n \{(RLi)_{4}\}_o - n \{(RLi)_{4}\}_{\text{decomposed}} = n \{(RLi)_{4}\}_o - 4n(\text{olefin})_t = 4n(\text{olefin})_o - 4n(\text{olefin})_t \]

\( n = \text{number of moles} \quad \circ = \text{initial amount} \quad t = \text{amount at time } t \)

\[ [\text{olefin}] = \frac{n(\text{olefin})}{V_l} \quad [\text{olefin}] = \text{concentration} \quad V_l = \text{volume of liquid phase} \]

\[ P(\text{olefin}) = k X(\text{olefin}) \quad k = \text{Henry's Law constant} \quad X = \text{mole fraction} \]

\[ [\text{olefin}] = \frac{n(\text{olefin})}{V_l} = \frac{P(\text{olefin})}{k''} \]

\[ (1/k'') [dP(\text{olefin})/dt] = d[\text{olefin}]/dt \]

\[ [(RLi)_{4}] = (V_l)[n(\text{RLi})_{4}] \]

\[ (V_l)[(RLi)_{4}]_t = 4(V_l)(1/k'') [P_o - P(\text{olefin})] \]

\[ [(RLi)_{4}]_t = (4/k'') [P_o - P(\text{olefin})] \]

From Mechanism 1, page 35.

\[ d[\text{olefin}]/dt = k' [(RLi)_{4}] \quad k' = kK[B] \]

Substituting from the above relationships

\[ (1/k'') [dP(\text{olefin})/dt] = (k')(4/k'') [P_o - P(\text{olefin})] \]

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\[ \int \frac{dP(\text{olefin})}{[P_\infty - P(\text{olefin})]} = 4k' \int dt \]
\[ \log [P_\infty - P(\text{olefin})] = k_{\text{obs}} t + C \]

For Mechanism 2, page 35.
\[ \frac{d[\text{olefin}]}{dt} = k'[\left((RLi)_4\right)^{1/2}] \quad k' = kK[B] \]
which on substitution yields
\[ \frac{1}{k''}[dP(\text{olefin})/dt] = 2k'(1/k'')^{1/2}[P_\infty - P(\text{olefin})]^{1/2} \]
\[ \int \frac{dP(\text{olefin})}{[P_\infty - P(\text{olefin})]^{1/2}} = 2k'(1/k'')^{1/2} \int dt \]
\[ -2[P - P(\text{olefin})]^{1/2} = 2k'(k'') t + C \]
\[ [P - P(\text{olefin})]^{1/2} = k_{\text{obs}} t + C \]

For Mechanism 3, page 35.
\[ \frac{d[\text{olefin}]}{dt} = k'[\left((RLi)_4\right)^{1/4}] \quad k' = kK[B] \]
reduces as in the above case to
\[ \int \frac{dP(\text{olefin})}{[P_\infty - P(\text{olefin})]^{1/4}} = k'(4/k'')^{1/4} \int dt \]
which yields on integration
\[ [P - P(\text{olefin})]^{1/4} = k_{\text{obs}} t + C \]
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