The Pyrolysis of *sec*-Butyllithium. Kinetics and Mechanism

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Abstract: The rate of pyrolysis of *sec*-butyllithium in octane solution has been measured by a manometric method. In contrast to similar reactions of other isomeric butyllithiums, the reaction is apparently one-half order in alkyllithium and first order in lithium alkoxide. Equations 1 and 2 are proposed to account for the observed kinetics: $^1/_2(\mathrm{RLi})_4 + \mathrm{B} \rightleftarrows (\mathrm{RLi})_2\mathrm{B}$ (fast), followed by $(\mathrm{RLi})_2\mathrm{B} \rightarrow \mathrm{LiH} +$ olefin (slow), where B is lithium *sec*-butoxide, lithium ethoxide, or lithium phenoxide. Similar mechanisms involving the complexation of hexameric or dimeric alkyllithium are considered; however, molecular weight measurements of *sec*-butyllithium in freezing cyclohexane support eq 1 of the proposed mechanism.

The pyrolytic elimination of lithium hydride from lithium alkyls has been the subject of several investigations including a preliminary mechanism study by Ziegler and Gellert in 1950.[1] More recently, Finnegan and Kutta examined the kinetics of the pyrolysis of *n*-butyllithium,[2,3] isobutyllithium,[3] and *t*-butyllithium[3] in decane. The rate of olefin formation was found to be first order in alkyllithium and proportional to the concentration of lithium alkoxides.[2,3] The pyrolysis of *sec*-butyllithium was also investigated and found to be anomalous, however, and no kinetic order was obtained.[3]

The pyrolysis of unsolvated alkyllithiums was investigated by Glaze, Lin, and Felton.[4] In the absence of solvent (and the apparent absence of alkoxides),[5] the pyrolysis of *sec*-butyllithium is no longer anomalous; rate data obtained for *sec*-butyl-, ethyl-, *n*-butyl-, and isopropyllithium follow the same first-order pattern.[4b]

A further indication of the unusual behavior of *sec*-butyllithium resulted from a study of the distribution of the isomeric butenes obtained from the pyrolysis. Whereas the alkoxide-catalyzed pyrolysis of solvated *sec*-butyllithium yields a typical distribution of the expected olefins (1:2 = 1.05; *cis*-2:*trans*-2 = 0.81), unsolvated pyrolysis unexpectedly favors the formation of *cis*-2-butene (1:2 = 0.51; *cis*-2:*trans*-2 = 3.4).[4] The preponderance of *cis*-olefin is rationalized by observing that pyrolysis of the unsolvated alkyllithium may involve a rather bulky tetramer in which steric effects favoring *cis* orientations of the butyl moiety are operative. The apparent loss of stereoselectivity upon solvation, combined with the anomalous kinetics observed by Finnegan and Kutta, suggested a reinvestigation of the pyrolysis of solvated *sec*-butyllithium, the results of which are reported here.

Results and Discussion

Kinetics. The pyrolysis of *sec*-butyllithium in octane may be conveniently followed by a manometric method since the isomeric olefins are gases at room temperature. Figure 1 is a drawing of the decomposition vessel which was employed in this study. After preparation, the solutions were decomposed in such a vessel at 94.10° (± 0.05°). Pressure readings were taken as often as possible at the beginning of the reaction, and at 0.5-cm intervals thereafter. Values of P_∞ were measured directly and also calculated from the initial concentration of *sec*-butyllithium; the agreement between experimental and calculated values was excellent for all runs reported.

Preliminary treatment of the kinetic data established that the reaction was not first order, verifying the results of Finnegan and Kutta.[2,3] Further treatment showed that an exellent linear fit was obtained if a plot of $(P_\infty - P)^{1/2}$ *vs.* time was made. Figure 2 shows a typical plot. A total of 18 runs were made at various alkoxide and *sec*-butyllithium concentrations, and, with the exception of two unexplained deviations, the corresponding one-half-order plots were linear through several half-lives. Table I summarizes the slopes of these plots, designated k_{obsd}, which were

Table I. Rate Constants for the Pyrolysis of *sec*-Butyllithium Solutions[a]

sec-BuLi, moles/l.	*sec*-BuOLi, moles/l.	k_{obsd},[b] cm$^{1/2}$/hr
0.330	0.124	2.74
0.350	0.081	2.19
0.235	0.076	1.89
0.381	0.064	1.00
0.356	0.063	1.76
0.313	0.061	1.68
0.381	0.044	1.14
0.391	0.042	0.63
0.351	0.037	0.68
0.201	0.036	0.66
0.208	0.033	0.60
0.374	0.029	0.75
	$\mathrm{LiOC_6H_5}$	
0.338	0.074	3.10
0.320	0.068	2.67
	LiOEt	
0.242	0.081	3.25
0.502	0.097	2.83

[a] *n*-Octane solvent; 94.10 ± 0.05°. [b] k_{obsd} refers to least-square slope of $(P_\infty - P)^{1/2}$ *vs.* time plot; maximum deviation: ±0.02 (cm of Hg)$^{1/2}$/hr. Because of the instability of *sec*-butyllithium solutions at laboratory temperatures, only single kinetic runs could be made from each batch of reagent.

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(1) K. Ziegler and H. G. Gellert, *Ann. Chem.*, **567**, 179 (1950).

(2) R. A. Finnegan and H. W. Kutta, *J. Org. Chem.*, **30**, 4139 (1965).

(3) H. W. Kutta, M.S. Thesis, The Ohio State University, Columbus, Ohio, 1964.

(4) (a) W. H. Glaze, J. Lin, and E. G. Felton, *J. Org. Chem.*, **30**, 1258 (1965); (b) *ibid.*, **31**, 2643 (1966).

(5) The decompositions were run in a closed system immediately after high-vacuum distillation of the alkyllithium compound.[4]

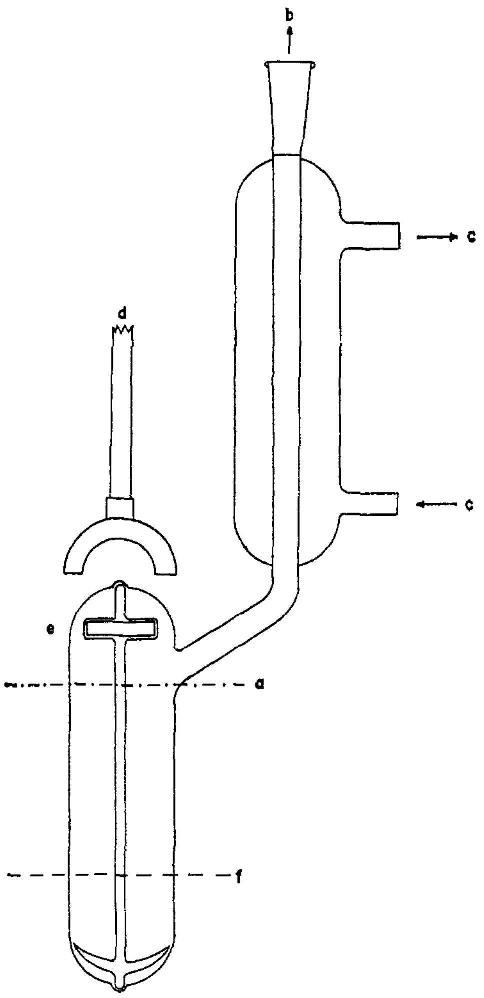

Figure 1. Pyrolysis apparatus: a, level of thermostated bath; b, to vacuum line and manometer; c, condenser water, thermostated; d, horseshoe magnet stirrer motor; e, glass-enclosed bar magnet; f, level of alkyllithium solution.

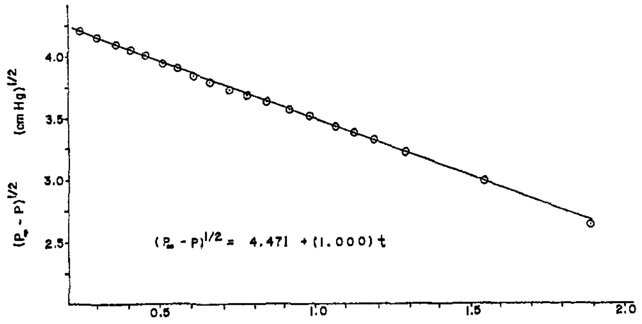

Figure 2. One-half-order kinetic plot of the pyrolysis of *sec*-butyllithium. $[RLi]_0$ = 0.381 *M*; $[sec\text{-}C_4H_9OLi]_0$ = 0.064 *M*; 94.10°.

obtained by least-square regression analysis of the pressure–time data.[6]

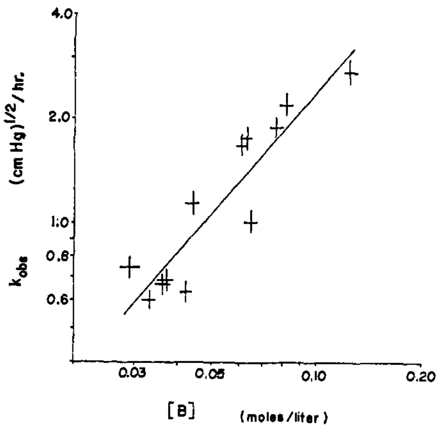

Figure 3. Effect of alkoxide concentration on the observed half-order rate constants for the pyrolysis of *sec*-butyllithium. [B] = concentration of *sec*-C_4H_9OLi. Solid line represents least-squares fit of data: log k_{obsd} = 1.54 + 1.16 (±0.11) log [B].

Figure 3 is a log–log plot of k_{obsd} *vs.* the molar concentration of lithium *sec*-butoxide, as determined by the modified Gilman double-titration procedure.[7] Regression analysis of these data indicates a slope of 1.1 ± 0.1, although it is obvious from the plot that the data are scattered. A limited number of runs were made using lithium ethoxide and phenoxide, as shown in Table I. The kinetic order also appears to be one-half in alkyllithium, but the order with respect to base was not determined. Further work on the effect of various alkoxides is in progress.

The present data indicate that the pyrolysis is one-half order in alkyllithium and first order in alkoxide. It must be admitted that a choice of mechanism is a precarious venture in a system of such complexity; however, our intuition regarding the nature of alkyllithium alkoxide solutions suggests several possible pathways of which the following seems most reasonable.

$$\tfrac{1}{2}(RLi)_n + B \underset{\text{fast}}{\overset{K}{\rightleftarrows}} (RLi)_{n/2}B \qquad (1)$$

$$(RLi)_{n/2}\,B \xrightarrow{k} \text{products} \qquad (2)$$

The proposed mechanism fits the observed kinetics, and, moreover, the existence of a reactive complex has been suggested by earlier workers in this field.[2,8,9] It is important to note that the kinetic data alone are not sufficient to distinguish between various values of *n*, although even integral values (two, four, six, etc.) are suggested by previous studies. Thus, the degree of association of *n*-butyllithium in hydrocarbon solvents has been reported as four[8b] and six,[10] while *t*-butyllithium is apparently tetrameric in benzene.[11] Ethyllithium[12] and methyllithium[13] are tetrameric in

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[6] After examining this manuscript, Dr. R. A. Finnegan has related by private correspondence that he has reanalyzed H. W. Kutta's data, and that one-half order plots fit the data reasonably well; in fact, for a few runs, quite well. Unfortunately, the disparity between temperatures and concentrations prevents a direct comparison of that work and the present data.

[7] H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964). The Gilman procedure, utilizing 1,2-dibromoethane, was modified slightly by eliminating the use of ether in the reaction medium. The substitution of pentane does not significantly effect the rapidity of the coupling reaction and avoids any possible metalation of the ether by *sec*-butyllithium. Finnegan and Kutta have discussed the precision of this method, and, while data at high alkoxide concentrations is subject to doubt, the method is probably accurate to within 5%.[2]

[8] (a) J. F. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, **85**, 2171 (1963); (b) J. F. Eastham, G. W. Gibson, and Z. K. Cheema, *ibid.*, **85**, 3517 (1963).

[9] S. Bywater and D. J. Worsfold, *Can. J. Chem.*, **40**, 1564 (1962).

[10] D. Margerison and J. P. Newport, *Trans Faraday Soc.*, **59**, 2058 (1963).

[11] M. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, **1**, 654 (1962).

[12] H. Dietrich, *Acta Cryst.*, **16**, 681 (1963).

[13] E. Weiss and E. A. C. Lucken, *J. Organometal. Chem.*, **2**, 197 (1964).

Table II. Interaction of *sec*-Butyllithium with Lithium Alkoxide in Cyclohexane

Concn,[a] moles/1000 g of solvent		$M_{\text{obsd}} = \Delta T_f/K_f$[b]	$^{1}/_{2}(\text{RLi})_4 + \text{B} \rightleftarrows (\text{RLi})_2\text{B}$		$^{1}/_{2}(\text{RLi})_6 + \text{B} \rightleftarrows (\text{RLi})_3\text{B}$		$^{3}/_{4}(\text{RLi})_4 + \text{B} \rightleftarrows (\text{RLi})_3\text{B}$		$^{1}/_{2}(\text{RLi})_2 + \text{B} \rightleftarrows (\text{RLi})\text{B}$	
			M_{calcd}[c]	% dev[d]	M_{calcd}[c]	% dev[d]	M_{calcd}[c]	% dev[d]	M_{calcd}[c]	% dev[d]
0.638	0.041	0.195	0.180	7.8	0.127	34.9	0.169	13.3	0.339	73
0.356	0.030	0.104	0.104	0.0	0.076	26.9	0.097	6.7	0.193	86
0.306	0.041	0.094	0.097	3.2	0.072	23.4	0.089	5.3	0.177	88
0.216	0.026	0.067	0.067	0.0	0.049	26.9	0.061	9.0	0.121	81
0.184	0.046	0.060	0.069	15.0	0.055	8.3	0.059	1.7	0.110	84
0.136	0.046	0.044	0.057	29.3[e]	0.047	6.8	0.048	9.1	0.087	93
0.094	0.021	0.032	0.034	6.2	0.034	6.3	0.029	9.4	0.057	78
0.056	0.017	0.024	0.025	4.1	0.020	20.0	0.021	19.5	0.042	75
0.064	0.030	0.031	0.031	0.0	. . .[f]		. . .[f]		0.048	60
0.034	0.017	0.017	0.017	0.0	. . .[f]		. . .[f]		0.027	59
				Av 6.5%		Av 19.2%		Av 9.2%		Av 78%

[a] [RLi] = molality of *sec*-butyllithium; [B] = molality of lithium alkoxide[13] as determined by the Gilman double-titration procedure. Densities of the solutions were assumed to be that of pure cyclohexane. [b] $K_f = 20.0$. [c] M_{calcd} represents molality of all species calculated by assuming that the equilibrium constant is large, *i.e.*, essentially all of the alkoxide is complexed by RLi. [d] % dev refers to percentage deviation of calculated and observed molalities. [e] Chauvenet's criterion (F. Daniels, *et al.*, "Experimental Physical Chemistry," 4th ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p 357) would justify discarding this point for the tetramer–dimer equilibrium alone, thus lowering the average deviation from 6.5 to 4.0%. [f] Excess base.

the crystalline state. Since the initial step in the proposed mechanism should occur at lower temperatures where subsequent decomposition (eq 2) is slow, a value of n may be suggested from the results of molecular weight measurements of *sec*-butyllithium in the presence of alkoxides. We shall return to this subject in the following section.

The nature of the reactive species of alkyllithium solutions in basic solvents has been discussed recently by Waack and West.[14] Their kinetic study of the metallation of triphenylmethane in tetrahydrofuran by *n*-butyllithium suggests *trimeric* association of the alkyllithium compound. This result is compatible with the mechanism proposed above if n is 6. If n is 4, an alternate stoichiometry is required; *e.g.*

$$^{3}/_{4}(\text{RLi})_4 + \text{B} \rightleftarrows (\text{RLi})_3\text{B} \tag{3}$$

or, in case of multiple association

$$^{3}/_{4}(\text{RLi})_4 + 2\text{B} \rightleftarrows (\text{RLi})_3\text{B}_2 \tag{4}$$

Each of these possibilities has been eliminated by the kinetic data. Equation 3, followed by decomposition of the trimer–base complex, should result in a kinetic order of three-fourths with respect to RLi; thus, a plot of $(P_\infty - P)^{1/4}$ *vs.* time should be linear. Although it is difficult to differentiate between one-half and three-quarter order using kinetic data obtained before one-half completion, the order may be distinguished at long times, and in the present case the one-half order is verified.

Multiple association is apparently a factor when high base concentrations are present, but in the present case, the data were obtained at rather low alkoxide concentrations. The apparent first order with respect to alkoxide would appear to rule out multiple association as an important factor in the systems under consideration.

Molecular Association Studies. The proposed mechanism for the pyrolysis of *sec*-butyllithium (eq 1 and 2) suggests a prior, rapid dissociation of the alkyllithium oligomer by alkoxide. Brown, Ladd, and Newman[15] have concluded that such is *not* the case when the ethyllithium hexamer is complexed by lithium ethoxide. An investigation of the effect of base on the structure of *sec*-butyllithium was apparently in order.

Freshly distilled *sec*-butyllithium was dissolved in cyclohexane and the molecular weights of the resulting solutions measured by depression of the freezing point. Alkoxide concentration was measured by the modified Gilman double titration.[7,16] The results of the cryoscopic measurements are shown in Table II in which the observed molalities are compared with values calculated for various equilibria. It is significant to note that hexameric or dimeric association of *sec*-butyllithium in the presence of negligible quantities of base will *not* explain the present data, regardless of the value of the equilibrium constant of reaction 1 (with $n = 6$ or 2). Moreover, the best fit appears to be obtained if we assume that *sec*-butyllithium is *tetrameric* in cyclohexane ($n = 4$), and that moderate concentrations of base serve to dissociate the tetramer into a complexed dimer, $(\text{RLi})_2\text{B}$. This conclusion is apparently justified although there remains some doubt concerning the precision of the concentration data in Table II at high alkoxide/alkyl ratios.

Although the kinetic data and the molecular weight measurements were obtained at different temperatures, their apparent agreement represents strong evidence in favor of the proposed mechanism (eq 1 and 2, $n = 4$). It should be noted, however, that no conclusions regarding the mechanisms of other organolithium reactions can necessarily be drawn from these data. The nature of the transition states for other reactions, such as polymerizations and bimolecular reactions of other types, will certainly be affected by the steric and electrical properties of other substrates. Furthermore, the degree of association of a high molecular weight lithium alkyl may be entirely different than that of a smaller alkyl.[17] The present work should serve to emphasize that the presence of alkoxides in alkyllithium solutions can have a marked effect on the kinetics and

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(14) R. Waack and P. West, *J. Organometal. Chem.*, **5**, 188 (1966).

(15) T. L. Brown, J. A. Ladd, and G. N. Newman, *ibid.*, **3**, 1 (1965).

(16) The Gilman double-titration measures total base and RLi molarities, but will not distinguish between lithium alkoxide and other bases which may be present in the solution, such as lithium oxide. It has been assumed in this work that the value of the "other base," obtained from the titration, is a measure of alkoxide concentration, an assumption which is not vital to the basic conclusions of this work.

(17) M. Morton and L. J. Fetters, *J. Polymer Sci.*, **A2**, 3311 (1964).

mechanisms of any reactions, and, furthermore, that branched alkyllithiums may behave in an entirely different manner than the simple alkyllithiums which have been studied more thoroughly. Apparently, the branching of the alkyl chain introduces considerable steric crowding into the tetramer and hexamer structures usually assumed by alkyllithium compounds. The resulting strain is evidenced by lower thermal stability, higher reactivity, and greater susceptibility to dissociation by bases.

Finally, we point out that the use of the term "base" to represent the catalytic species in this work is perhaps ill advised. In fact, an alkoxide may be looked upon as *both a Lewis base and acid*, and the possibility of assistance of the cation in the removal of the hydride ion appears to be real. Further studies in this area are currently in progress.

Experimental Section

Preparation of Solutions for Kinetic and Molecular Weight Studies. *sec*-Butyllithium was prepared by the conventional procedure from purified 2-chlorobutane (Eastman Kodak Co.) in pentane solvent.[4a] After removal of the solids by filtration of the reaction mixture in a drybox, the solvent was removed under vacuum until a thick, syrupy liquid remained. A portion of this liquid was transferred to one bulb of a simple distillation apparatus.[4a] Using particular precautions to avoid contact with air, the distillation apparatus was transferred to a vacuum line where the remainder of solvent was removed by evacuation. Subsequently, the *sec*-butyllithium was distilled into a U tube which was cooled with liquid nitrogen. Distillation of the alkyllithium proceeds with moderate decomposition at *ca.* 100° and a residual vacuum line pressure of *ca.* 50 μ. After distillation was complete, the U tube was warmed to room temperature, and the clear, colorless, viscous condensate was evacuated for several minutes to remove any condensed decomposition products. The entire apparatus was removed to the drybox where solutions of appropriate concentrations were prepared. *n*-Octane (Phillips Petroleum Co., Pure Grade), redistilled from $LiAlH_4$, was used as the solvent.

Lithium ethoxide, phenoxide, and *sec*-butoxide were prepared in benzene or pentane by dropping the appropriate alcohol (or phenol) onto a suspension of lithium sand. After removal of the solids in the drybox, the solutions were evaporated to dryness and the crystalline alkoxides dried by heating on a vacuum line.

Alkoxide-enriched solutions of *sec*-butyllithium were prepared by shaking a concentrated solution of the alkyllithium with the alkoxide until a desired concentration was achieved. Lithium ethoxide was observed to dissolve rapidly while phenoxide and *sec*-butoxide required several days of shaking.

Kinetic Procedure. A known quantity of the analyzed[7] *sec*-butyllithium solution (20.0 ml) was transferred in the drybox to the apparatus shown in Figure 1. The drybox was rigorously cleaned for this step. The apparatus containing the solution was transferred to the vacuum line, and the solution was frozen with liquid nitrogen. After evacuating the system, the vacuum line was twice swept with purified argon; a residual pressure (*ca.* 20 cm) of argon remained after the final flush. The solution was then allowed to warm to room temperature, and thermostated water was connected to the condenser (31.0 ± 0.1°). The lower portion of the vessel was immersed in an ethylene glycol-water thermostat bath (94.10 ± 0.05°), and pressure and time readings were taken as rapidly as possible. A rapid pressure rise was observed in each run as the vapor pressure of the solution reached equilibrium at the condenser temperature. The magnitude of the initial pressure rise was very similar in all runs; therefore, pressure data within this period were not used in the kinetic treatment. Figure 2 is a typical plot of the kinetic data; the function $(P_\infty - P)^{1/2}$ was chosen for plotting after several other functions of the pressure, including $\ln (P_\infty - P)$ proved to be nonlinear in time. Rate constants, k_{obsd}, were taken as the slopes of these plots and are tabulated in Table I.

Freezing Point Depression Measurements. Cyclohexane solutions of *sec*-butyllithium were prepared on the vacuum line by distillation of purified cyclohexane onto previously distilled *sec*-butyllithium. The solution was transferred to a drybox which contained the apparatus for the determination of freezing points. The apparatus, which employs a Sargent thermistor thermometer, is similar to that described by Brown[18] and Selman.[19] Analysis[7] of the solution was made immediately after its freezing point was determined. The remaining solution was diluted and another freezing point determined. Sample freezing points were duplicated and reproduced to ±0.01°.

Product Distribution Analysis. Following each kinetic run, the olefin gases were analyzed by glpc as reported earlier.[4] The results of extensive product distribution studies will be reported later; however, it is significant to note that the possibility of isomerization of the olefins was eliminated. In one run, the product gases were sampled continuously and analyzed. With the exception of the very short period of time at the beginning of the reaction, the composition of the gas mixture was observed to remain constant.

Acknowledgment. The financial assistance of The Robert A. Welch Foundation is gratefully acknowledged. We also wish to thank Gary Peyton for assistance in the molecular weight measurements.

[18] T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Am. Chem. Soc.*, **86**, 2135 (1964).

[19] C. M. Selman, M. S. Thesis, North Texas State University, Denton, Texas, 1966.