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## THE ENTHALPIES OF PROTONATION OF PROPENYLLITHIUMS, PHENYLLITHIUM, AND ETHYLLITHIUM

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### Summary

The enthalpies of protonation of allyllithium (I), *trans*-1-propenyllithium (II), 2-propenyllithium (III), phenyllithium (IV), and ethyllithium (V) in diethyl ether have been determined calorimetrically. The aggregations of I, II, III, and V have been determined by vapor pressure measurements. The significance of the data is discussed.

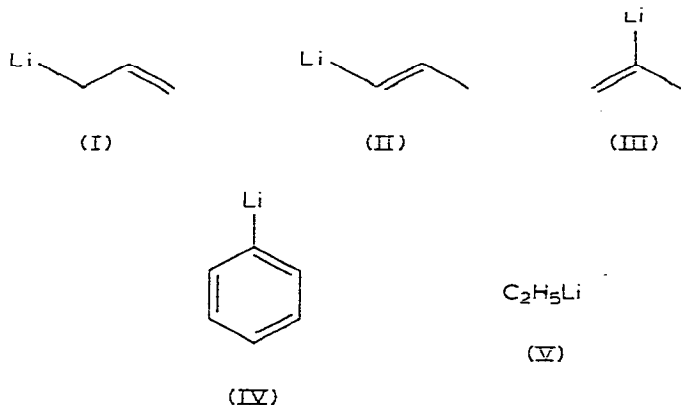
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### Introduction

Although a great deal is known about the structures and reactivities of organolithium compounds [1, 2], substantially less information is available about the energies of these species. The enthalpy data which have been published are the heats of combustion of *n*-butyllithium and ethyllithium [3], the heat of reaction of *n*-butyllithium in petroleum ether with water vapor [4], and Holm's recent report of the heats of reaction of twelve organolithiums in solution or suspension in ether or petroleum ether with hydrogen bromide gas [5]. The heats of formation of *n*-butyllithium provided by these different approaches are  $32.0 \pm 1.7$ ,  $31.4 \pm 0.7$ , and  $26.1 \pm 0.2$  kcal/mole [3–5]. Despite potential complication due to differences between suspensions and solutions, the use of commercial and synthetic organolithiums of undetermined purities, and the assumptions that differences in aggregations, solvations, and vaporations would cancel, the carbon–lithium bond energies derived by Holm are in the order expected for carbanion stabilities of localized systems [5]. That trend in enthalpies resembles the order of free energies of a series of organolithiums and organoiodides determined by Applequist and O'Brien and used by them to provide a quantitative comparison of relative carbanion stabilities [6, 7]. The similar trends observed by Holm and Applequist are interesting and lead to the hope that comparisons of energies of organolithiums might be straightforward. The present work is an effort to assess that prospect.

Some of the uncertainties associated with determinations of absolute

enthalpies can be circumvented by measurements involving conversions of isomers to common products [8]. Such a comparison has been used previously to measure the intramolecular coordinative stabilization for dimeric *ortho*-lithioanisole in di-*n*-butyl ether as  $8.2 \pm 1.0$  kcal/mole relative to the *para* isomer [9]. We now report extension of this approach to determinations of the relative enthalpies of allyllithium (I), *trans*-1-propenyllithium (II), and 2-propenyllithium (III). The heats of hydrolysis of phenyllithium (IV) and ethyllithium (V) have been obtained for comparison. The aggregations of I, II, III, and V in diethyl ether have also been determined.



## Results

Organolithiums I, II, III, and IV were prepared by transmetalation of the corresponding disubstituted tin compound prepared with *n*-butyllithium in diethyl ether/pentane in an inert atmosphere, by procedures similar to those of Seyferth et al. [10] \*. The organolithiums were obtained in yields of 60–80% as free-flowing, white powders uncontaminated by significant amounts of lithium bromide, *n*-butyllithium, or organotin compounds \*\*. Ethyllithium (V), obtained commercially, was purified by sublimation. Compounds I–V were dissolved in diethyl ether for analysis and further use. The enthalpic investigation of *cis*-1-propenyllithium prepared from tetra-*cis*-1-propenyltin was precluded by its insolubility in diethyl ether in the absence of lithium bromide \*\*\*.

The purities of the organolithiums were established by Gilman titrations of total and weak base of weighed samples of I–V in diethyl ether [14]. This provided total base values of 88–91% for I and 90–96% for II–V and weak base impurities of 5–8% for I, 0.5–4% for II and IV, and 1–2% for III and V. Quantitative analysis of the propene in solution produced on reaction of the ether solutions of I, II and III with ethanol indicated  $95 \pm 5\%$  of the theoretical amount at  $-50^\circ\text{C}$  and  $80 \pm 5\%$  at ambient temperature. Similar analysis of V

\* Transmetalations and lithium–halide exchanges at vinylic centers have been shown to proceed with retention of stereochemistry [11].

\*\* If the transmetalation is carried out in pentane or hexane, in the case of cyclopropyllithium, the resulting organolithium precipitate is found to contain up to 20% *n*-butyllithium [12].

\*\*\* Coprecipitation and association of organolithiums with lithium bromide is well known [13].

TABLE 1  
ENTHALPIES AND ASSOCIATIONS OF I-V IN DIETHYL ETHER

Compound	$\Delta H_{rxn}^a$	Aggregation	$\Delta H^\circ(RLi)_{(Ether)}$
Allyllithium (I)	$-50.9 \pm 1.3$	Variable	$4.3 \pm 1.3$
<i>trans</i> -1-Propenyllithium (II)	$-52.0 \pm 0.5$	Tetrameric	$5.4 \pm 0.5$
2-Propenyllithium (III)	$-66.7 \pm 2.5$	Dimeric-tetrameric	$20.1 \pm 2.8$
Phenyllithium (IV)	$-59.0 \pm 0.8$	Dimeric <sup>b</sup>	$19.2 \pm 0.8$
Ethyllithium (V)	$-64.6 \pm 1.3$	Tetrameric	$-7.1 \pm 1.3$

<sup>a</sup> kcal/mole; errors are one standard deviation. These values differ from the experimental values in Table 2 by the experimentally determined heats of solution and vaporization of the hydrocarbon products.

<sup>b</sup> Ref. 16.

showed  $80 \pm 5\%$  ethane produced at  $-50^\circ\text{C}$ . Quantitative analysis of the bromides produced on reaction of II-V with 1,2-dibromoethane confirmed the purity and structural integrity of these compounds. Allyllithium (I) was shown by PMR spectroscopy to be uncontaminated by the reagents used in its preparation.

Calorimetric determinations of the heats of protonation of these organolithiums were made for reactions of weighed and analyzed samples of 0.06 M to 0.57 M I-V in diethyl ether with 150 ml of absolute ethanol. Least squares analysis of plots of the amount of organolithium vs. the heat evolved for 9-15 samples in each case provides the heat of reactions listed in the second column of Table 1 [15]. The intercept of these plots is  $6.3 \pm 0.1$  kcal/mole, which is equal to the independently determined heat of solution of ether in ethanol under these conditions except for the case of III. For that material, decomposition of the samples during the enthalpy measurement appears to be the source of a relatively large error in the heat of reaction.

The heats of reaction I-V, were calculated on the basis of the molarity of the strong base as monomeric species. Comparison of different samples of the same compounds which contained different amounts of neutral and weak base impurities suggest these impurities do not significantly affect the observed heat evolved in these cases.

The states of aggregation of allyllithium (I), *trans*-1-propenyllithium (II), 2-propenyllithium (III), and ethyllithium (V) were determined by vapor phase osmometry\*. It has been established previously by this method that phenyllithium (IV) is dimeric at 0.05-0.5 M in ether and that allyllithium has an average aggregation greater than ten at 1.5 M in ether [16, 17, 18]. Ethyllithium has been reported to be tetrameric on the basis of  $^7\text{Li}$  NMR data [19]. The data in Fig. 1 show that II and V are essentially tetrameric in ether over the concentration ranges indicated. The decrease in apparent aggregation at higher concentrations is evident in earlier vapor pressure determinations of organometallic associations [17, 18, 19, 20]. This behavior has been attributed by West and Waack to a decrease in the vapor pressure of the solution occurring as an increased percent of the solvent molecules become involved insoluble-solv-

\* The details are available [15].

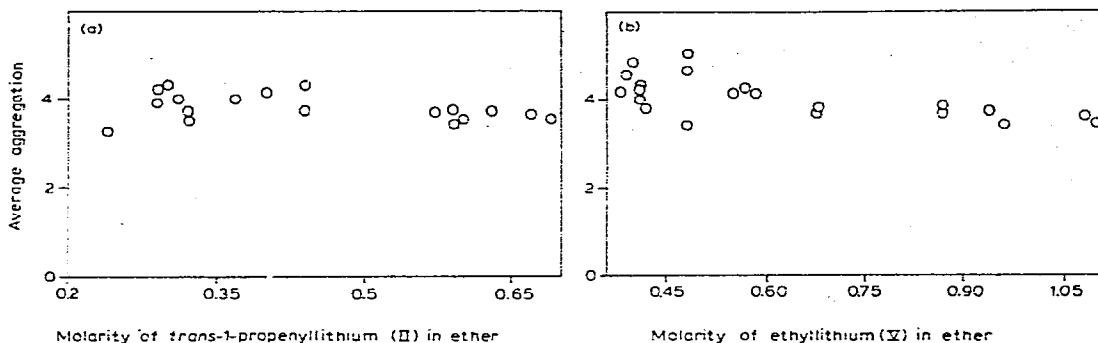


Fig. 1. Average aggregation of *trans*-1-propenyllithium (II) and ethyllithium (V) in diethyl ether.

ent interactions at higher concentrations [16]. The tetrameric association of II is consistent with the assignment of vinyl lithium as a tetramer [18].

On the other hand, the aggregation of allyllithium (I) shows a variation from two to over twelve as the concentration is increased from 0.1 to 1.6 *M* as shown in Fig. 2a. Although the lack of a plateau in the plot seems inconsistent with a specific aggregation, the apparent linear variation in aggregation number also is inconsistent with random aggregation unless the lower aggregates are more highly solvated than the higher aggregated species [21]. The data presented in Fig. 2b show that the average aggregation of 2-propenyllithium (III) changes from slightly over two to slightly under four over the concentration range of 0.04 to 0.84 *M*. These data are considered to reveal a concentration-dependent shift from predominantly dimeric III to predominantly tetrameric III with increasing concentration. The data in Fig. 2a are fit by an equilibrium constant for association of  $4 \times 10^4$  [15,21,22] \*. The heat of reaction of III with ethanol was determined from 0.1 to 0.6 *M*, a range over which III changes from 26 to 60% tetramer. The data, however, are not sufficiently precise to allow accurate determination of the differences in heats evolved from the dimeric and tetrameric states of III. The fact the values obtained at the high and low concentrations do not show any systematic variation from the value of  $66.7 \pm 2.5$  kcal/mole (Table 1) suggest such effects will be minor \*\*.

\* The assumption is that the dimer and tetramer are tetra-solvated [15] such that the equilibrium expression is:

$$K = \frac{[\text{Tetramer}][\text{Et}_2\text{O}]^4}{[\text{Dimer}]^2}$$

where  $[\text{Tetramer}] = X(\text{RLi})_4 \cdot (\text{Et}_2\text{O})_4 \cdot \frac{M(\text{RLi})}{4}$  and  $[\text{Dimer}] = X(\text{RLi})_2 \cdot (\text{Et}_2\text{O})_4 \cdot \frac{M(\text{RLi})}{2}$ .

$[\text{Et}_2\text{O}] = M(\text{Et}_2\text{O}^\circ) - M(\text{Et}_2\text{O} \text{ complexed})$ ; *X* refers to mole fractions, *M* refers to molarity.

\*\* The enthalpy of association can be calculated to be  $2 \pm 1$  kcal/mole based on the assumptions that lithium is tetracoordinated with solvent or 2-propenyl groups in the dimer and tetramer [1,20] and that the entropy of association is 113 e.u./tetramer as estimated by the theoretical changes in the translational partition function for association [15,23].

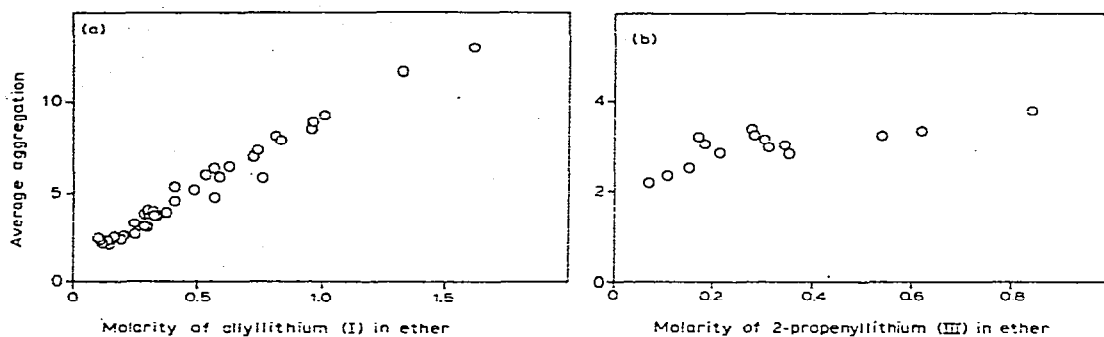


Fig. 2. Average aggregation of allyllithium (I) and 2-propenyllithium (III) in diethyl ether.

## Discussion

The reaction studied and the expression for its enthalpy is given by equations 1 and 2:



$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= \Delta H_{\text{f}}^{\circ}(\text{RH})_{(\text{EtOH})} + \Delta H_{\text{f}}^{\circ}(\text{LiOEt})_{(\text{EtOH})} + \Delta H^{\circ}(\text{Ether})_{(\text{EtOH})} \\ &\quad - \Delta H_{\text{f}}^{\circ}(\text{EtOH}) + \frac{1}{n}\Delta H_{\text{f}}^{\circ}(\text{RLi})_{n(\text{Ether})} \end{aligned} \quad (2)$$

For comparison of I–III The first four terms on the right-hand side of expression 2 cancel. Thus the differences in the heats of reaction provide a reliable measure of the differences in the heats of formation of these isomeric organolithiums in diethyl ether solution. Although further dissection of the relative heats of formation of I–II might be possible if heats of solution of the corresponding solid or liquids were available, the undetermined nature of the intermolecular forces in those states suggests that even with those values a more penetrating analysis could not be made at present.

If we focus on the diethyl ether solutions, the difference in enthalpies of II and III of  $14.7 \pm 3.0$  kcal/mole in favor of III could be interpreted reasonably in terms of the greater stability of an  $sp^2$  secondary carbon lithium bond [5,6,7]. On the other hand, interpretation of the enthalpy of I relative to those of II and III in diethyl ether appears unwarranted because of the clear differences in structure shown by differences in aggregation (Table 1). In fact, earlier work suggests the carbon portion of II is a planar delocalized anion [17,18,24]. Clearly, meaningful enthalpic comparison of isomers should be limited to cases in which the associations are similar. Since heats of formation and solvation data for propene<sub>(g)</sub>, ethene<sub>(g)</sub>, benzene<sub>(l)</sub> [25] \*, ethanol<sub>(l)</sub> and lithium ethoxide in ethanol are available in the literature or were determined in this work [26], the values of  $(1/n)\Delta H_{\text{f}}(\text{RLi})_{n(\text{Ether})} - \Delta H^{\circ} \text{Ether}_{(\text{EtOH})}$  can be calculated. Those

\* The experimental enthalpies associated with formation of these compounds in the states indicated were determined by injection of these products into ethanol in control experiments.

values, which represent the heats of formation, self-association, and specific interaction with diethyl ether of each organolithium, are listed as  $\Delta H_f^\circ(\text{RLi})_{\text{Ether}}$  in Table 1. Comparison of the value of  $-7.1 \pm 1.3$  kcal/mole obtained in this work with the  $\Delta H_{\text{form}}^\circ$  of  $-14.0 \pm 1.3$  kcal/mole for solid ethyllithium reported by Lebedev et al. [3] suggest that solvation and association effects can be significant. A similar conclusion has been reached by Quirk et al. who have shown that large heats can result from the interactions of organolithiums with a variety of bases [27].

Our results suggest additional information will be needed before quantitative understanding of the enthalpies of organolithiums can be claimed. The present work shows that structural differences can obscure the significance of enthalpic comparisons even for structural isomers. More information about the effects of association, solvation, and comparisons of enthalpies and free energies clearly are needed.

## Experimental

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Associates A-60A and are reported relative to tetramethylsilane as internal standard. Infrared spectra were recorded on a Beckman IR 12 spectrometer. Elemental analyses were performed by J. Nemeth and associates. All boiling points are from distillations and are uncorrected.

All compounds were synthesized under argon using oven-dried glassware. All transfers were carried out in a dry box. Analyses of organolithiums for weak and total base were carried out by the method of Gilman [14]; weighed samples of the organolithium were diluted with a known amount of ether and this solution was titrated against 0.100 N HCl after quenching with 1,2-dibromomethane and/or ethanol and water, respectively.

Diethyl ether (Mallinckrodt) and THF (Aldrich) were distilled from sodium benzophenone ketyl under argon or nitrogen. Pentane (Burdick and Jackson, distilled in glass) was distilled from butyllithium prior to use. n-Butyllithium (Ventron, 2.4 N in hexane) was shown to contain 2% weak base, by the Gilman titration, and  $7 \times 10^{-3}$  mol/l of LiCl as determined by hydrolysis of a portion of n-butyllithium and analysis for chloride.

Gas chromatography was performed with a Varian 1800 gas chromatograph with a flame ionization detector, using helium as carrier gas with a back pressure of 10 psi over a  $\frac{1}{4}$ "  $\times$  8' column of XF-1150 on AWD-MCS Chromosorb P. Ether solutions of organolithium compounds were quenched with 1,2-dibromomethane and then water, and a portion of the ether layer analyzed for alkyl bromide products. Resolution of all four propenyl bromide isomers and n-butyl bromide was possible with appearance in the order: 2-bromopropene *cis*-1-bromopropene, *trans*-1-bromopropene, allyl bromide and n-butyl bromide. The response factors for *cis*- and *trans*-1-bromopropene were determined to be within 5% of each other and in a ratio of  $0.6 \pm 0.1$  to n-butyl bromide. The column was programmed to increase in temperature at  $8^\circ/\text{min}$  from 70 to  $140^\circ\text{C}$  to allow detection of bromobenzene. The relative response of bromobenzene to *trans*-1-bromopropene, toluene and n-butyl bromide were found to be  $2.08 \pm 0.02$ ,  $0.42 \pm 0.02$  and  $1.2 \pm 0.1$ , respectively. Quantitative analyses of

alkyl bromides were performed with benzene or toluene as internal standard.

For analyses of the reactions of ether solutions of organolithium compounds with ethanol, a known amount of *n*-butylbenzene was added as an internal standard. The column temperature was held at 80°C until the ether peak was complete, and then increased at 8°/min to 130°C. The response factors of benzene, pentane, propane and *n*-butylbenzene have been reported to be  $1.00 \pm 0.02$ ,  $1.04 \pm 0.02$ ,  $1.00 \pm 0.02$  and  $0.98 \pm 0.02$ , respectively; a value of  $1.02 \pm 0.02$  has been used for propene based on its similarity to these compounds. The relative peak areas were determined using the height-times-width-at-half-height method, or planimetry.

Tetra-*trans*-1-propenyln [29], tetra-*cis*-propenyln [30], and tetra-2-propenyln [10] were prepared by literature procedures. NMR and IR spectra and elemental analyses were in agreement with the assigned structures.

#### *Di-n-butyl-di-trans-1-propenyln*

A 15.1 g (0.125 mol) portion of *trans*-1-bromopropene (Chem samples, 95% *trans*) was added with stirring to 1.75 g (0.25 mol) of sliced lithium wire (2% sodium) in 200 ml of ether at 0°C over a 1 h period. The solution was allowed to warm to ambient temperature and then heated to reflux temperature for 1 h. A 10.0 g (0.033 mol) portion of di-*n*-butyltin dichloride (ROC/RIC) in 30 ml of ether was added over a 2 h period, while the solution was maintained at reflux temperature. After an additional 2 h reflux period, the solution was stirred overnight at ambient temperature, quenched with saturated aqueous ammonium chloride, the ether extract dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent removed in vacuo. Distillation yielded 9.1 g (86%) of di-*n*-butyl-di-*trans*-1-propenyln, b.p. 92–95°C/1 mmHg; NMR (CDCl<sub>3</sub>)  $\delta$  0.7–1.7(m, 18), 1.85(d, 6), 5.93(m, 4) ppm; IR (neat) 2965, 2940, 2920, 2880, 2860 (all C–H), 1608, 1468, 1447, 1382, 983, 662 cm<sup>-1</sup>.

Anal. Found: C, 53.43; H, 8.96%. C<sub>14</sub>H<sub>28</sub>Sn calcd.: C, 53.37; H, 8.96.

#### *Allyllithium (I)*

A modification of the method of Seyferth and Weiner was used [10]. A 7.4 ml portion of 2.4 *M* *n*-butyllithium in hexane (10.6 mmol) was added with stirring to a solution of 2.5 g (8.8 mmol) of tetraallyln (Ventron) in 30 ml of ether and 20 ml of pentane. The solution was stirred for 15 min at ambient temperature, after which the solvent was removed in vacuo. A 20 ml portion of pentane was added to the resulting oil, which yielded an off-white solid after scratching. The resulting heterogeneous mixture was stirred for 1 h, the precipitate collected by filter, washed with pentane and placed under reduced pressure for several hours to yield 0.49 g (96%) I. Hydrolysis and elemental analysis of a portion of this solid showed it to contain 0.027% tin. The NMR spectrum in THF-*d*<sub>6</sub> is consistent with published spectra [10]. Amplification of the signal showed no detectable signals from *n*-butyllithium under conditions such that 0.5% would be detectable. Gilman titration of an ethereal solution revealed 92% of the theoretical amount of base, of which 5% was weak base. Analysis of the reaction of an ether solution of I with ethanol at –50°C revealed 95 ± 5% of the theoretical amount of propene, based on comparison with a known amount of *n*-butylbenzene.

### *trans-1-Propenyllithium (II)*

A modification of the procedure of Seyferth and Vaughan was used [10]. A 10.6 ml portion of 2.4 M n-butyllithium in hexane (25.4 mmol) was added with stirring to a solution containing 3.62 g (12.8 mmol) of tetra-*trans*-1-propenyltin in 10 ml of pentane and 50 ml of ether. This solution was stirred for 3 h, after which the solvent was removed in vacuo. The isolation procedure was identical to that described above and yielded 0.98 g (80%) of II. Gas chromatographic analysis of an ether solution of II which had been quenched with 1,2-dibromoethane and then with water revealed a 4 : 96 ratio of *cis/trans*-1-bromopropene. Analysis of the reaction of an ether solution of I with ethanol at  $-50^{\circ}\text{C}$  revealed  $95 \pm 5\%$  of the theoretical amount of propene, based on comparison with a known amount of n-butylbenzene. Gilman titration revealed 93% of the theoretical amount of total base of which 2% was weak base.

### *2-Propenyllithium (III)*

A modification of the procedure of Seyferth and Vaughan was used [10]. A 8.2 ml portion of 2.4 M n-butyllithium in hexane (19.7 mmol) was added with stirring to a solution of 2.77 g (9.8 mmol) of tetra-2-propenyltin in 40 ml of pentane. This solution was stirred for 1 h, after which time a few ml of ether were added, the solvent was removed in vacuo, and the product was isolated as described above to yield 0.57 g (60%) of III. Gas chromatographic analysis of an ether solution of III which had been quenched with 1,2-dibromomethane and then with water revealed 2-bromopropene and  $<1\%$  n-butyl bromide. The same analysis with benzene as internal standard revealed  $75 \pm 10\%$  of the theoretical amount of 2-bromopropene. Analysis of the reaction of ether solutions of V with ethanol revealed  $95 \pm 5\%$  of the theoretical amount of propene if the reaction was carried out at  $-50^{\circ}\text{C}$ , and  $80 \pm 5\%$  if the reaction was carried out at ambient temperature under calorimetric conditions.

### *Phenyllithium (IV)*

A 7.9 ml portion of 2.4 M n-butyllithium in hexane (19 mmol) was added to a solution containing 4.9 g (12.7 mmol) of di-n-butyldiphenyltin (ROC/RIC) in 10 ml of ether and 30 ml of pentane. After the solution had been stirred for 30 min, the product was isolated as above to yield 0.96 g (60%) of IV. Gas chromatographic analysis of an ether solution of IV after it had been quenched with 1,2-dibromomethane and then water revealed a 1.5% impurity of n-butyllithium and  $100 \pm 5\%$  bromobenzene using toluene as an internal standard. Gilman titration revealed 96% of the theoretical amount of base, of which 1% is weak base.

### *Ethyllithium (V)*

Gilman titration of ether solutions of V revealed it to contain 1–2% weak base and 90–95% of the theoretical amount of total base. Analysis of a solution of V after its reaction with 1,2-dibromomethane revealed only ethyl bromide. Analysis of a solution of V after its reaction with 100 ml of ethanol at  $-50^{\circ}\text{C}$  revealed  $80 \pm 5\%$  of the expected amount of ethane.

### *Calorimetric procedure*

The calorimeter and general procedure used have been previously described



[30]. The length of resistance wire used for calibration was inadvertently altered after the calorimetry had been completed. Data collected from ether solutions of V after this change were 3% higher than those collected before, and the observed enthalpy of neutralization of 1.0 ml of 1.49 N NaOH with 150 ml of 0.01 M HCl was 3% above the calculated value [26]. It is, therefore, presumed that data collected prior to this change is both consistent and accurate.

#### *Typical calorimetric run*

A 333.6 mg sample of *trans*-1-propenyllithium in 20.0 ml of diethyl ether was prepared. Gilman titrations of 2 ml aliquots performed in duplicate, established the solution to be  $0.323 \pm 0.001$  M (93% of theoretical) in total base, and  $0.013 \pm 0.001$  M in weak base (2.6% of total) or 0.31 M in propenyllithium. Reaction vials for the calorimeter were charged with known amounts of this organolithium solution, and ether was added so that the total volume of each was 2 ml. All measurements were made with volumetric or Mohr pipets, which were shown by calibration with water to be accurate to within 1%. Typical quantities of organolithium solution used were 2.0, 1.5, 1.0, and 0.5 ml. Samples were analyzed calorimetrically in order of decreasing concentration, the total time elapsed for the analysis of four samples was 3 h. Data from reaction of samples I, II, III, IV and V in ether are reported in Table 2.

#### *Calorimetric determination of the stability of ethyllithium (V) in ether*

A series of three aliquots, each containing 1.1 mmol of V in 2 ml of ether was allowed to react with 156 ml of ethanol. The three samples yielded heats of reaction of -60.8, -59.7 and -57.8 cal, with 1 h separating the first two reactions and 1.75 h separating the first and third. When this experiment was repeated using 0.8 mmol of V in 2 ml of ether, heats of -45.3, -44.5, -43.4, and -42.9 cal were observed, after 0.75, 1.5, 2.3, and 3.2 h of standing at ambient temperature prior to reaction. These data correlate roughly to a 2% decomposition rate per hour.

#### *Enthalpy of solution and/or vaporization of hydrocarbons and ether*

Injection at ambient temperature of 20 ml samples of ethane, propene and benzene into 150 ml of ethanol under normal experimental calorimetry conditions, yielded absolute enthalpies of solution and vaporization of -0.1, -2.1 and 0.3 kcal/mole respectively. Addition of 2 ml aliquots of pure ether to 150 ml of ethanol yields enthalpies of solution of 6.4, 6.25 and 6.3 cal/2 ml of diethyl ether. The Y intercepts of the plots of heat evolved vs. millimoles of organolithium were I,  $5.2 \pm 0.4$  cal; II,  $6.1 \pm 0.4$  cal; III,  $8.3 \pm 1.5$  cal; IV,  $6.6 \pm 0.4$  cal; V,  $6.2 \pm 0.3$  cal.

#### *Differential vapor pressure measurements*

All differential pressure measurements were made with a Granville-Philips Capacitance Manometer Series 212, Model 03, designed to measure pressure differences of 0.01 to 100 Torr to within 3%. The sample and reference sides of the manometer were attached to the sample and reference manifold through metal to glass seals. The pump and mercury manometer were separated from the remainder of the system by liquid nitrogen and dry ice traps respectively.

TABLE 2

ENTHALPIES OF REACTION OF ALLYLITHIUM (I), *trans*-1-PROPENYLITHIUM (II), 2-PROPENYLITHIUM (III), PHENYLITHIUM (IV), AND ETHYLITHIUM (V) WITH ETHANOL (cal)

RLi (mmol)	RLi/2 ml of ether (cal)		$\Delta H_{rxn}(RLi)^a$ (cal/mmol) (Intercept)
I <sup>b</sup>	0.86 (38.8)	0.75 (34.5)	-53.0 ± 1.2 (6.2 ± 0.4)
	0.64 (28.5)	0.65 (27.7)	
	0.57 (23.9)	0.56 (23.6)	
	0.48 (19.6)	0.43 (15.9)	
	0.38 (13.3)	0.32 (11.3)	
	0.19 ( 3.9)	0.16 ( 2.5)	
II <sup>c</sup>	0.99 (47.0)	0.82 (38.3)	-54.1 ± 0.4 (6.1 ± 0.4)
	0.63 (28.4)	0.62 (27.7)	
	0.61 (26.9)	0.47 (20.3)	
	0.41 (16.4)	0.37 (13.7)	
	0.32 (10.8)	0.16 ( 2.2)	
III <sup>d</sup>	1.15 (72.4)	0.86 (52.6)	-68.8 ± 2.4 (8.3 ± 1.5)
	0.77 (42.7)	0.58 (27.5)	
	0.56 (28.5)	0.38 (16.2)	
	0.29 (15.4)	0.26 (10.3)	
IV <sup>e</sup>	0.80 (40.1)	0.72 (36.8)	-58.7 ± 0.7 (6.6 ± 0.4)
	0.70 (33.5)	0.65 (31.3)	
	0.60 (28.9)	0.54 (25.6)	
	0.53 (23.5)	0.49 (22.2)	
	0.40 (17.4)	0.36 (14.6)	
	0.35 (13.8)	0.33 (12.6)	
	0.20 ( 5.5)	0.18 ( 3.8)	
V <sup>f</sup>	0.85 (49.3)	0.74 (41.9)	-64.7 ± 1.2 (6.2 ± 0.3)
	0.63 (32.3)	0.63 (32.9)	
	0.54 (30.0)	0.48 (25.5)	
	0.46 (24.0)	0.40 (20.7)	
	0.37 (16.9)	0.34 (15.8)	
	0.27 (12.2)	0.23 ( 8.6)	
	0.21 ( 7.0)	0.14 ( 2.3)	
	0.12 ( 1.1)		

<sup>a</sup> Error limits are one standard deviation. <sup>b</sup> Samples originated from three solutions, containing 5–7% weak base and 8–14% neutral impurity. <sup>c</sup> Samples originated from three solutions, containing 4% neutral impurity, 2% weak base; 7% of the propenylithium had the *cis* configuration. <sup>d</sup> Samples originated from three solutions, containing 1% weak base and 3–5% neutral impurity. <sup>e</sup> Samples originated from four solutions, containing 1–4% weak base and 4–12% neutral impurity. <sup>f</sup> Samples originated from five solutions, containing 1–2% weak base and 4–8% neutral impurity.

A flask containing pure ether and a tared flask containing the ether organolithium solution was connected to the sample manifold using Buna rubber O-ring joints. These flasks were suspended in a stirred 24.0°C water bath, which contains two air driven stirrers in order to allow the sample and solvent solutions to be stirred during the equilibration and measurement period. The bath could be lowered to allow the solutions to be degassed by the freeze-thaw method while attached to the sample manifold. The temperature of the bath was controlled by balancing a Precision Temperature Controller, Model 123, from Bayley Instrument Company, against a small cooling coil at the base of the bath. By this method the temperature varied by less than 0.005°C over a

TABLE 3

DETERMINATION OF THE AGGREGATION OF ALLYLITHIUM (I), *trans*-1-PROPENYLITHIUM (II), 2-PROPENYLITHIUM (III), AND ETHYLITHIUM (V)

Organolithium	Molarity (observed aggregation)
I <sup>a</sup>	0.10 (2.5) 0.11 (2.4) 0.12 (2.4)
	0.14 (2.4) 0.14 (2.4) 0.17 (2.5)
	0.19 (2.4) 0.20 (2.6) 0.24 (3.4)
	0.24 (2.6) 0.27 (3.1) 0.28 (3.9)
	0.29 (3.0) 0.29 (4.0) 0.30 (4.0)
	0.32 (3.8) 0.33 (3.8) 0.33 (3.7)
	0.37 (4.0) 0.40 (5.4) 0.40 (4.7)
	0.41 (4.1) 0.47 (5.1) 0.50 (4.7)
	0.53 (6.1) 0.56 (4.7) 0.56 (6.3)
	0.58 (6.0) 0.62 (6.6) 0.72 (7.0)
	0.74 (7.4) 0.75 (6.0) 0.82 (8.2)
	0.83 (8.0) 0.95 (8.6) 0.96 (8.8)
1.00 (9.4) 1.33 (11.6) 1.61 (13.0)	
II <sup>b</sup>	0.24 (3.2) 0.28 (4.2) 0.29 (3.9)
	0.30 (4.3) 0.31 (4.0) 0.32 (3.7)
	0.32 (3.5) 0.37 (4.0) 0.40 (4.1)
	0.44 (4.3) 0.44 (3.7) 0.50 (3.6)
	0.57 (3.7) 0.59 (3.6) 0.59 (3.7)
	0.60 (3.5) 0.62 (3.9) 0.63 (3.7)
III <sup>c</sup>	0.07 (2.2) 0.11 (2.3) 0.15 (2.4)
	0.17 (3.2) 0.18 (3.0) 0.21 (3.0)
	0.27 (2.8) 0.28 (3.2) 0.31 (2.9)
	0.33 (2.9) 0.34 (3.0) 0.35 (2.8)
	0.54 (3.2) 0.62 (3.3) 0.84 (3.8)
V <sup>c</sup>	0.38 (4.1) 0.39 (4.5) 0.40 (4.8)
	0.41 (4.2) 0.41 (5.0) 0.48 (4.6)
	0.48 (3.4) 0.48 (5.0) 0.55 (4.1)
	0.57 (4.2) 0.57 (4.1) 0.68 (3.7)
	0.68 (3.8) 0.87 (3.7) 0.87 (3.8)
	0.94 (3.7) 0.96 (3.4) 1.08 (3.6)
	0.94 (3.7) 0.96 (3.4) 1.08 (3.6)
1.10 (3.4)	

<sup>a</sup> Measurements were made on five different solutions. <sup>b</sup> Measurements were made on four different solutions. <sup>c</sup> Measurements were made on three different solutions.

15 minute period, as measured by a thermistor. The bath water was also circulated through a jacket surrounding the sample manifold, and the reference manifold was wrapped with 1/2" fiberglass insulation, to reduce the effect of temperature changes in the environment.

Since the meter response is an arbitrary scale, the capacitance manometer did not allow direct readout of differential pressure. Therefore a series of solutions of biphenyl, *para*-di-butylbenzene and triphenylmethane were used to correlate the meter response to the expected differential pressure.

The observed molecular weight of a compound in ether is determined from the expression shown in eq. 3, where the value of 74.12 is the molecular weight of ether. The weight of organolithium,  $M(\text{RLi})$ , was based on a titration of

$$\text{Molecular Weight} = 74.12 \frac{M(\text{RLi})}{M(\text{ether})} \left( \frac{P_{\text{ref}}}{\Delta P_{\text{calc}}} - 1 \right) \quad (3)$$

total base from an aliquot of the solution from which the sample solution was obtained, and the molecular weight of the monomeric organolithium. The weight of ether,  $M(\text{ether})$ , was determined by subtracting the weight of the flask, stirring bar and organolithium, from the weight of the flask and its contents immediately after the pressure measurement was made. The reference pressure,  $P_{\text{ref}}$ , was read directly from the mercury manometer and the  $\Delta P_{\text{calc}}$  was determined from the observed meter response and the previously discussed calibration factors. The average degree of aggregation is the observed molecular weight divided by the monomer molecular weight, and the molarity was based on the weight of ether, a density of 0.713 ml/g for ether, and the titrated value for the moles of base present. Calculations were based on total base because alkoxides are known to become incorporated into the aggregates of organolithium compounds in coordinating solvent [17].

In a typical experiment, a 10.0 ml aliquot from a 213.5 mg sample of *trans*-1-propenyllithium (II) dissolved in 20.0 ml of ether was introduced into the sample flask of the vapor pressure apparatus and several ml of pure ether were used to wash the solution from the neck of the flask. A 5 ml portion of the ether solution of II was quenched with water and shown to contain 0.96 mmol of base by quenching of the solution with ethanol and water, and titration of that solution against 0.1005 *M* HCl. On this basis the solution used for vapor pressure measurements was considered to contain 1.92 mmol or 92.2 mg of II. All volumes were determined with volumetric pipets which were shown to be accurate to within 0.5%. Typically stabilization of the instrument and measurement of the upper pressure requires 2–4 h. Experimental data for ether solutions of I, II, III, IV and V are listed in Table 3.

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### References

- 1 T.L. Brown, *Pure Appl. Chem.*, 23 (1970) 447; G.D. Stucky, *Advan. Chem. Ser.*, No. 130 (1974) 56; B.J. Wakefield, *The Chemistry of Organolithium Compounds*, Pergamon Press, Oxford, 1974; M. Schlosser, *Struktur und Reaktivität Polarer Organometalle*, Springer-Verlag, Berlin, 1973.
- 2 For recent discussions see M. Walczak and G.D. Stucky, *J. Amer. Chem. Soc.*, 98 (1976) 5531; G. Frankel, W.E. Beckenbaugh and P.P. Yang, *ibid.*, 98 (1976) 6878; R. Kiert and T.L. Brown, *J. Organometal. Chem.*, 77 (1974) 289; S.G. Smith, L.F. Charbonneau, D.P. Novak and T.L. Brown, *J. Amer. Chem. Soc.*, 94 (1972) 7059 and ref. cited therein.
- 3 Y.A. Lebedev, E.A. Miroshinchenko and A.M. Chakin, *Dokl. Akad. Nauk. SSSR.*, 145 (1962) 1288.
- 4 P.A. Fowell and C.T. Mortimer, *J. Chem. Soc.*, (1961) 3792.
- 5 T. Holm, *J. Organometal. Chem.*, 77 (1974) 27.
- 6 D.E. Applequist and D.F. O'Brien, *J. Amer. Chem. Soc.*, 85 (1963) 743.
- 7 D.J. Cram, *Fundamentals of Carbanion Chemistry*, Academic Press, New York, 1965.
- 8 For examples see P. Beak, D.S. Mueller and J. Lee, *J. Amer. Chem. Soc.*, 96 (1974) 3867; R.B. Turner, B.L. Mallon, T. Tichy, W. von E. Doering, W.R. Roth and G. Schröder, *ibid.*, 95 (1973) 8605; D.M. Lemal and C.H. Dunlap, Jr., *ibid.*, 94 (1972) 6563; E.M. Arnett, J.C. Sanda, J.M. Bollinger and M. Barber, *ibid.*, 89 (1967) 5389; W. Adam and J.C. Chang, *Int. J. Chem. Kinet.*, 1 (1969) 487; J.F.M. Oth, *Rec. Trav. Chim. Pays-Bas*, 87 (1968) 1195.
- 9 P. Beak and B. Siegel, *J. Amer. Chem. Soc.*, 96 (1974) 6803.

- 10 D. Seyferth and M.A. Weiner, *J. Org. Chem.*, 26 (1961) 4797; D. Seyferth and L.G. Vaughan, *J. Amer. Chem. Soc.*, 86 (1964) 883.
- 11 D. Seyferth and L.G. Vaughan, *J. Organometal. Chem.*, 1 (1963); A.N. Nesmeyanov, A.E. Borisov and N.V. Novikov, *Izv. Akad. Nauk. SSSR Otd. Khim. Nauk.*, (1959) 1216; D.Y. Curtin and J.W. Crump, *J. Amer. Chem. Soc.*, 80 (1958) 1922; A.S. Drieding and R.J. Pratt, *ibid.*, 76 (1954) 1902.
- 12 D. Seyferth and H.M. Cohen, *Inorg. Chem.*, 2 (1963) 625.
- 13 D.P. Novak and T.L. Brown, *J. Amer. Chem. Soc.*, 94 (1972) 3793; T.V. Talshaeva, A.N. Rodionov and K.A. Kocheshkov, *Dokl. Akad. Nauk. SSSR*, 140 (1961) 847.
- 14 H. Gilman and I.F. Cartledge, *J. Organometal. Chem.*, 2 (1964) 447.
- 15 G.R. Brubaker, Ph.D. Thesis, University of Illinois, 1976, University Microfilms, Ann Arbor, Michigan 48106.
- 16 P. West and R. Waack, *J. Amer. Chem. Soc.*, 89 (1967) 4395.
- 17 P. West, J. Purmont and S. McKinley, *J. Amer. Chem. Soc.*, 90 (1968) 797.
- 18 P. West, R. Waack and J.I. Purmort, *J. Amer. Chem. Soc.*, 92 (1970) 840.
- 19 L.M. Seitz and T.L. Brown, *J. Amer. Chem. Soc.*, 88 (1966) 2174.
- 20 H. Hashimoto, T. Nakamo and H.O. Kada, *J. Org. Chem.*, 30 (1965) 1234.
- 21 E.U. Schrier, *J. Chem. Ed.*, 45 (1968) 176.
- 22 H.L. Lewis and T.L. Brown, *J. Amer. Chem. Soc.*, 92 (1970) 4664.
- 23 K.B. Wiberg, *Physical Organic Chemistry*, Wiley, New York, 1964, p. 221.
- 24 W.T. Ford and T. Thompson, unpublished work, 1976.
- 25 American Petroleum Institute Research Project Report 44, Carnegie Press, Pittsburgh, Pennsylvania, 1953.
- 26 F.D. Rossini, D.D. Wagman, W.H. Evans, S. Levine and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards Circ. 500, U.S. Government Printing Office, Washington, D.C., 1952.
- 27 R.P. Quirk and D.E. Kester, *J. Organometal. Chem.*, 72 (1974) 623; 127 (1977) 111.
- 28 W.A. Deitz, *J. Gas Chromatography*, 15 (1967) 68.
- 29 D. Seyferth and L.G. Vaughan, *J. Organometal. Chem.*, 1 (1963) 138.
- 30 P. Beak, J. Bonham and J.T. Lee, *J. Amer. Chem. Soc.*, 90 (1968) 1569.