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SOLVATION OF ALKYL LITHIUM COMPOUNDS. STERIC EFFECTS ON HEATS OF INTERACTION OF BASES WITH HEXAMERIC VERSUS TETRAMERIC ALKYL LITHIUMS

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SUMMARY

Heats of interaction of Lewis bases with hexameric and tetrameric alkyl lithiums in hydrocarbon solution at 25° have been determined by high dilution solution calorimetry at low base to lithium atom ratios. The Lewis bases utilized include tetrahydrothiophene, tetrahydrofuran, triethylphosphine, triethylamine, and diethyl ether. The organolithiums investigated were *n*-butyllithium, ethyllithium, isopropyllithium, trimethylsilylmethyl lithium, and *t*-butyllithium. The basicity order based on initial enthalpies of interaction is independent of the alkyl lithium compound. Larger enthalpies of interaction were observed for the tetrameric versus hexameric alkyl lithiums with the exception of tetrameric *t*-butyllithium which does not interact significantly with these bases. The sensitivities of the enthalpies to the steric requirements of the base were probed by comparison of the enthalpies for tetrahydrofuran, 2-methyltetrahydrofuran, and 2,5-dimethyltetrahydrofuran. Base coordination to hexameric *n*-butyllithium is more sensitive to the steric requirements of the tetrahydrofuran bases than is coordination to tetrameric trimethylsilylmethyl lithium or isopropyllithium. These results are interpreted in terms of coordination of tetrahydrofuran bases to the intact hexameric aggregate for *n*-butyllithium; however, it is concluded that the corresponding interaction with hexameric trimethylsilylmethyl lithium leads directly to base-solvated tetramers.

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## INTRODUCTION

Organolithium compounds occupy a prominent position in organometallic chemistry due to their unique combination of structure, solubility, and reactivity.<sup>1,2</sup> A vast array of new procedures utilizing alkyllithiums have been added recently to the armament of synthetic chemists.<sup>3</sup> The success of many of these alkyllithium transformations is contingent on the ability of Lewis bases to serve as catalysts. Basic molecules often dramatically affect the rates, stereochemistry and course of alkyllithium reactions. However, the fundamental nature of the base-alkyllithium interactions responsible for these effects is not understood.

In this paper we report measurements of the enthalpies of interaction of a variety of Lewis bases with several alkyllithium compounds in hydrocarbon solutions. The organolithiums investigated were *n*-butyllithium, ethyllithium, isopropyllithium, trimethylsilylmethylithium, and *t*-butyllithium. The Lewis bases utilized were tetrahydrothiophene, triethylamine, triethylphosphine, diethyl ether, tetrahydrofuran, 2-methyltetrahydrofuran, and 2,5-dimethyltetrahydrofuran. This series provides a range of structural variations with which both the steric and electronic nature of alkyllithium-base interactions can be examined.

The structures of alkyllithium reagents in solution are of fundamental importance to any consideration of the nature of Lewis base-alkyllithium interactions. Alkyllithium compounds are known to exist as polymeric aggregates in hydrocarbon solvents and in solutions of Lewis bases.<sup>4,5</sup> The degree of aggregation is primarily dependent on steric interactions between the alkyl groups. Colligative property studies have shown that in hydrocarbon solution simple, straight-chain alkyllithium compounds (e.g., ethyllithium and *n*-butyllithium) exist predominantly as hexameric aggregates; branched-chain alkyllithiums (e.g., *t*-butyllithium) tend to exist as tetrameric aggregates in solution.<sup>4</sup> For intermediate degrees of steric interactions between the alkyl groups (e.g., trimethylsilylmethylithium and isopropyllithium), a solvent- and concentration-dependent tetramer-hexamer equilibrium has been observed.<sup>4</sup> Vapor-phase osmometric

measurements indicate that simple alkyllithiums are tetrameric in basic solvents such as diethyl ether and tetrahydrofuran.<sup>5</sup> Thus, alkyllithium compounds persist as electron-deficient aggregates even in the presence of Lewis bases, unlike the corresponding trialkylboron and trialkylaluminum analogs.<sup>1</sup>

X-ray crystallographic studies have provided models for the structures of these aggregates in solution. Methyl-<sup>6,7</sup> and ethyllithium<sup>8</sup> exist as tetrameric units in the crystalline state with the lithium atoms occupying the corners of a tetrahedron and the alkyl groups located on the faces of the tetrahedron. A benzene adduct of cyclohexyllithium possesses a hexameric structure in the crystalline state with the lithium atoms situated at the apices of an octahedron and alkyl groups located above six of the eight faces of the octahedron.<sup>9</sup>

Support for the occurrence of these electron-deficient structures in basic solvents at low temperatures has been provided recently by extensive <sup>7</sup>Li, <sup>13</sup>C, and <sup>1</sup>H magnetic resonance studies of alkyllithium compounds.<sup>10</sup>

The calorimetric data reported herein will consider the specific nature of alkyllithium-base interactions in terms of the structures which have been proposed for these species in solution.

## EXPERIMENTAL

### Apparatus and procedures.

Pmr spectra were determined using a Varian A-60 spectrometer. All chemical shifts ( $\delta$ ) are reported in parts per million (ppm) downfield from TMS. Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrometer. Glpc analyses were conducted with a Varian Aerograph Model 90-F gas chromatograph. Hydrocarbon solvents and substituted tetrahydrofurans were analyzed using a 20-ft., 10% di-n-decyl phthalate on chromosorb W-AW DMCS column. Other Lewis bases were analyzed using a 20-ft., 20% carbowax 20M on chromosorb W-AW DMCS column. The calorimeter equipment and procedures are basically as described previously.<sup>11,12</sup>

All preparations, transfers, and calorimetric measurements of alkyllithium reagents except sublimations were performed in an argon atmosphere glove box. All bases used for calorimetric measurements were distilled either on a high vacuum line or inside the argon atmosphere glove box and were used within a few h; most were used immediately after distillation. Pmr and ir spectra as well as glpc analyses were used to check for impurities.

Monomer concentrations and impurity levels for alkyllithium compounds in solution were determined using the double titration procedure of Gilman and Cartledge<sup>13</sup> with 1,2-dibromoethane. The hydrocarbon solutions of the alkyllithium compounds were all clear and colorless, except for *n*-butyllithium in hexane which was pale yellow. All the solutions were stable for long periods of time in the glove box with the exception of isopropyllithium which slowly decomposed at room temperature.

#### Materials.

Ethyllithium was obtained as a 1.2M solution in benzene from the Foote Mineral Company. The benzene was removed by vacuum pumping and the remaining yellow-brown solid was recrystallized from cyclohexane. The resulting white powder was sublimed at 80-85°C and less than 10<sup>-3</sup> Torr. The product, mp 95°C (Lit. [14] m.p. 95°C) was then transferred to the desired solvent and stored in the glove box.

*n*-Butyllithium was obtained as a 1.6M solution in hexane from the Foote Mineral Company and used without purification.

Trimethylsilylmethylithium was prepared from trimethylchloromethylsilane (Penisular Chem Research) with a lithium metal dispersion according to the procedure of Lewis and Brown.<sup>4</sup> After the trimethylsilylmethylithium was prepared and the solvent removed by vacuum pumping, the white solid was sublimed at 100-150°C and less than 10<sup>-3</sup> Torr. The product, mp 112-113°C (Lit. [15] m.p. 112°C) was transferred to the desired solvent and stored in the glove box. Pmr analysis of these solutions agreed with published results<sup>15</sup> and showed no evidence of impurities.

*t*-Butyllithium was obtained as a 1.2M solution in pentane from the Foote Mineral Company and the solvent was removed by vacuum pumping leaving a yellow-white solid. The solid was sublimed three times at 60° and 10<sup>-3</sup> Torr. The colorless product was transferred to the desired solvent and stored in the dry box.

Isopropyllithium was prepared from isopropyl chloride (Aldrich 99%), which had been fractionally distilled from calcium hydride, and a lithium metal dispersion. After the solvent was removed by vacuum pumping, the material was sublimed at 35-40°C and less than 10<sup>-3</sup> Torr. The glassy-appearing product, mp 53°C (Lit. [14] m.p. 52°C), was transferred to the desired solvent and stored in the dry box. The pmr spectrum showed only a doublet (δ 5.95 ppm, 6H) and a multiplet (δ 8.15 ppm, 1H) upfield from benzene as reference signal.

All hydrocarbon solvents were purified by stirring over concd H<sub>2</sub>SO<sub>4</sub>, washing with water, aq 10% Na<sub>2</sub>CO<sub>3</sub>, and water, drying over anhyd MgSO<sub>4</sub>, followed by reflux and distillation from calcium hydride or lithium aluminum hydride under nitrogen. A central fraction was collected and stored in the glove box over Linde 4A molecular sieves or sodium wire. Glpc analysis gave only one peak (<0.1% impurities) for all of the hydrocarbon solvents except hexane, which was a mixture of isomers.

2-Methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran (Aldrich) were purified by first reflux and fractional distillation from lithium aluminum hydride followed by fractional distillation from sodium benzophenone ketyl. Glpc analyses of the collected fraction of 2-methyltetrahydrofuran, bp 79-80°C (Lit. [16] b.p. 77-80°C), showed less than 1% impurities. Glpc analyses of the collected fraction of 2,5-dimethyltetrahydrofuran, bp 91-92°C (Lit. [17] b.p. 91-92°C), gave two peaks which corresponds to a 47/53 mixture of *cis*- and *trans*-isomers. Pmr spectra indicated no impurities for either cyclic ether. All other bases (diethyl ether, tetrahydrofuran, tetrahydrothiophene, triethylamine, and triethylphosphine) were purified as described previously.<sup>11</sup>

## RESULTS AND DISCUSSION

The heats of interaction of alkyllithium compounds and Lewis bases were obtained at  $25 \pm 1^\circ$ , unless otherwise noted, and were corrected for the heats of solution of the bases in pure hydrocarbon as shown in eqn. (1),

$$\Delta H = \Delta H_{\text{obs}} - \Delta H_{\text{sol}} \quad (1)$$

where  $\Delta H_{\text{obs}}$  is the experimentally observed enthalpy;  $\Delta H_{\text{sol}}$  is the heat of solution of the base in pure hydrocarbon solvent; and  $\Delta H$  is the heat of transfer of the base from pure hydrocarbon solvent to a hydrocarbon solution of the alkyllithium.

The initial enthalpies of interaction of small amounts ( $< 1$  mmol) of Lewis bases with dilute solutions (0.04 - 0.08M) of alkyllithium reagents in hydrocarbon solution at  $25^\circ$  are shown in Table 1. For all the initial enthalpies listed in Table 1, the ratio of the concentration of base to the concentration of lithium atoms in solution ( $R$ ) is less than 0.08. The absence of side reactions and decomposition processes contributing to the observed enthalpies was established by analysis of the alkyllithium-base solution after the calorimetric runs using the double titration procedure of Gilman and Cartledge<sup>13</sup> to determine the amount of carbon-bound lithium. Without exception the results of double titration analysis of the calorimeter solutions for all bases indicated that within the error limits of this analytical method no decomposition of any alkyllithium reagents occurs under these conditions.\* Since it is known that tetrahydrofuran is particularly susceptible to cleavage by alkyllithium compounds,<sup>18-20</sup> representative double titration results for this base are shown in Table 2. The reliability of the calorimetric results for these reactive organometallic compounds is further substantiated by our observation that the results obtained were all quite reproducible ( $\pm 0.1$  kcal/mole) and the results obtained do not depend on (1) the source or method of purification of the base or the solvent; (2) the source or method of preparation of the

\* Triethylamine-alkyllithium runs were not analyzed by this procedure because of the possible reactions of this base with ethylene dibromide.

Table 1. Initial Enthalpies of Interaction of  
Bases with Alkylolithiums

Alkylolithium	-ΔH(kcal/mole) <sup>a,b</sup>							
	THF	2-CH <sub>3</sub> -THF	2,5-(CH <sub>3</sub> ) <sub>2</sub> -THF	Et3P	Et3N	(CH <sub>2</sub> ) <sub>4</sub> S	Et <sub>2</sub> O	
C <sub>2</sub> H <sub>5</sub> Li <sup>e</sup>	7.4 <sup>c</sup> (0.08)	--	--	1.4 <sup>d</sup> (0.04)	1.1 <sup>d</sup> (0.05)	--	--	
n-C <sub>4</sub> H <sub>9</sub> Li <sup>f</sup>	7.5 <sup>c</sup> (0.08) 7.6 <sup>d</sup> (0.07)	6.3 <sup>c</sup> (0.06)	4.6 <sup>c</sup> (0.05)	1.5 <sup>d</sup> (0.04)	1.2 <sup>d</sup> (0.04)	0.4 <sup>d</sup> (0.07)	1.8 <sup>d</sup> (0.06)	
(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> Li <sup>e</sup>	10.3 <sup>c</sup> (0.08)	10.4 <sup>c</sup> (0.06)	9.7 <sup>c</sup> (0.05)	4.6 <sup>c</sup> (0.05)	3.5 <sup>c</sup> (0.05)	1.6 <sup>c</sup> (0.08)	6.3 <sup>c</sup> (0.06)	
(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> Li <sup>g</sup>	9.4 <sup>c</sup> (0.08)	9.6 <sup>c</sup> (0.08)	8.7 <sup>c</sup> (0.05)	3.3 <sup>c</sup> (0.05)	2.1 <sup>c</sup> (0.05)	0.9 <sup>c</sup> (0.08)	5.3 <sup>c</sup> (0.06)	
(CH <sub>3</sub> ) <sub>2</sub> CHLi <sup>g</sup>	8.5 <sup>c</sup> (0.08)	--	6.1 <sup>c</sup> (0.05)	--	--	--	--	
(CH <sub>3</sub> ) <sub>3</sub> CLi <sup>e</sup>	0.1 <sup>d</sup>	--	--	0.2 <sup>d</sup>	0.0 <sup>d</sup>	--	--	

<sup>a</sup>All enthalpies obtained at 25° by addition of 0.050 ml or less into 195 ml of 0.04M or 0.08M alkylolithium (base/Li atom ratio ≤ 0.08).

<sup>b</sup>The numbers in parenthesis represent the [Base]/[Li atom] ratio for each measurement.

<sup>c</sup>0.04M.

<sup>d</sup>0.08M.

<sup>e</sup>Cyclohexane solvent.

<sup>f</sup>Hexane solvent.

<sup>g</sup>Benzene solvent.

Table 2. Double Titration Analyses of Tetrahydrofuran -  
Alkyl lithium Solutions after Calorimetric Runs

RLi	Solvent	Time Required for Calorimetric Run (min.)	Calculated Molarity before Run <sup>a</sup>	Observed Molarity <sup>b</sup> after Run
$(\text{CH}_3)_3\text{SiCH}_2\text{Li}$	Benzene	40	0.040	$0.042 \pm 0.001$
$(\text{CH}_3)_3\text{SiCH}_2\text{Li}$	Cyclohexane	40	0.400	$0.41 \pm 0.01$
$(\text{CH}_3)_2\text{CHLi}$	Benzene	40	0.040	$0.039 \pm 0.001$
$(\text{CH}_3)_3\text{CLi}$	Cyclohexane	30	0.040	$0.040 \pm 0.001$
$\text{CH}_3\text{CH}_2\text{Li}$		100	0.040	$0.039 \pm 0.001$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$	Hexane	70	0.083	$0.082 \pm 0.001$

<sup>a</sup>Based on the amount of alkyl lithium initially pipetted into the calorimeter before the run.

<sup>b</sup>Double titration results for solutions resulting from calorimetric runs.



alkyllithium;<sup>11</sup> and (3) the sodium content of the lithium metal used to prepare the alkyllithiums.\* Furthermore, the calorimetric equipment was regularly calibrated with internationally accepted standards for solution calorimetry.<sup>11</sup>

#### Basicity Order and Steric Effects.

The initial enthalpies measured for the addition of small amounts of Lewis bases to alkyllithiums ( $R \leq 0.08$ ) as shown on Table 1 provide a quantitative measure of the relative strength of these interactions. The basicity order which emerges from relative initial enthalpies of interaction is the same for every alkyllithium reagent examined, i.e., tetrahydrofuran (THF) > 2-methyltetrahydrofuran ( $2\text{-CH}_3\text{THF}$ ) > 2,5-dimethyltetrahydrofuran ( $2,5\text{-(CH}_3)_2\text{THF}$ ) > diethyl ether > triethylphosphine > triethylamine > tetrahydrothiophene.\*\* This result was not expected since the alkyllithium compounds examined include species, some of which are present as hexameric aggregates in hydrocarbon solution, and some of which exist predominately as tetrameric aggregates in hydrocarbon solution (see Table 3). Because of the unique structural characteristics of alkyllithium hexamers and tetramers,<sup>14</sup> it was anticipated that each type of aggregate would interact in a different, characteristic manner with bases. The observed results, i.e., no dependence of the enthalpimetric basicity order on structure or degree of aggregation of the alkyllithiums, imply that the basicity order represents a fundamental property of alkyllithium - base interactions.<sup>11</sup>

It is significant to note that for all Lewis bases the enthalpies

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\*The initial enthalpies of interaction of tetrahydrofuran with trimethylsilylmethylithium prepared from lithium wire containing 1% or 0.005% sodium are -9.4 kcal/mole and -9.3 kcal/mole, respectively.

\*\*The only exception is t-butyllithium. A basicity order cannot be deduced for this highly hindered alkyllithium because it does not interact significantly with any of these Lewis bases.

Table 3. Degrees of Aggregation of Alkylolithium Compounds in Solution<sup>a</sup>

Alkylolithium	Solvent	Degree of Aggregation
Ethylolithium	Cyclohexane	6
<u>n</u> -Butylolithium	Benzene	6
Trimethylsilylmethylolithium	Cyclohexane	6
Trimethylsilylmethylolithium	Benzene	4 <sup>b</sup>
Isopropylolithium	Benzene	4 <sup>c</sup>
<u>t</u> -Butylolithium	Cyclohexane	4

<sup>a</sup>See ref. 4.

<sup>b</sup>Association toward hexameric species occurs above 0.06 m in monomer.

<sup>c</sup>Association toward hexameric species occurs above 0.03 m in monomer.

of interaction decrease in the order  $(\text{CH}_3)_3\text{SiCH}_2\text{Li}$  (hexamer) >  $(\text{CH}_3)_3\text{SiCH}_2\text{Li}$  (tetramer) > i-PrLi (tetramer) > n-C<sub>4</sub>H<sub>9</sub>Li (hexamer) ≈ EtLi (hexamer) >> t-C<sub>4</sub>H<sub>9</sub>Li (tetramer).<sup>\*</sup> These enthalpies of interaction do not decrease monotonically with increasing branching in the alkyl group as expected. Although the highly hindered t-butylolithium does not interact significantly with these bases<sup>4</sup>, the branched alkylolithiums, trimethylsilylmethylolithium and isopropylolithium, have larger enthalpies of interaction than relatively unhindered ethylolithium and n-butylolithium.

<sup>\*</sup>This same general order [excluding tetrameric  $(\text{CH}_3)_3\text{SiCH}_2\text{Li}$  and i-PrLi] has been reported by Lewis and Brown for the extent of interaction of triethylamine with these alkylolithiums at low R values as deduced from colligative property measurements (see ref. 4).

In an attempt to obtain information regarding the relative sensitivity of alkyllithium-base interactions to steric effects, we have determined the enthalpies of interaction of several of these alkyllithiums with tetrahydrofuran (THF), 2-methyltetrahydrofuran (2-CH<sub>3</sub>THF), and 2,5-dimethyltetrahydrofuran [2,5-(CH<sub>3</sub>)<sub>2</sub>THF] (see Table 1).<sup>\*</sup> For each of these bases the magnitude of the enthalpies are in the order (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Li (hexamer) > (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Li (tetramer) > *i*-PrLi (tetramer) > *n*-BuLi (hexamer). The relative extent of interaction of these bases with each alkyllithium compound, i.e., THF > 2-CH<sub>3</sub>THF > 2,5-(CH<sub>3</sub>)<sub>2</sub>THF, is consistent with the expected steric requirements of the bases. The actual enthalpies of coordination for 2,5-dimethyltetrahydrofuran are smaller than the heats of interaction with tetrahydrofuran by the following amounts: 2.8 kcal/mole for *n*-butyllithium, 2.4 kcal/mole for isopropyllithium, 0.6 kcal/mole for hexameric trimethylsilylmethylithium, and 0.7 kcal/mole for tetrameric trimethylsilylmethylithium. If it is assumed that for a given alkyllithium compound the same coordination process is involved for both tetrahydrofuran and its methyl derivatives, then the magnitude of the decrease in enthalpy resulting from methyl substitution can be taken as a measure of the relative sensitivity of the coordination process to the spatial requirements of the base for each alkyllithium. Thus, if tetrahydrofuran coordinates with *n*-butyllithium to form the solvated hexamer, then it is assumed that 2,5-dimethyltetrahydrofuran also coordinates to produce the corresponding base-solvated hexamer. If this analysis is valid for this series of alkyllithiums, then the calorimetric data indicate that the *n*-butyllithium-base coordination process is most sensitive to the steric requirements of the base while the trimethylsilylmethylithium-base coordination process is least sensitive.

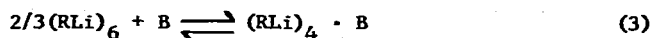
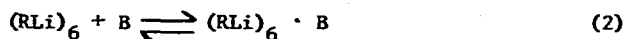
#### Hexamer versus Tetramer Coordination.

Consideration of the nature of alkyllithium compounds in solution is of fundamental importance for any meaningful discussion of the calorimetric

<sup>\*</sup> See reference 12 for a preliminary report of part of this study.

results. As mentioned in the Introduction, alkyllithium compounds are present in solution as electron deficient, polymeric aggregates. The degrees of aggregation of the alkyllithium compounds studied herein are listed in Table 3. It is noteworthy that Lewis and Brown<sup>4</sup> could conclude only that hexamer-to-tetramer interconversion is complete at  $\underline{R} < 1$  based on extensive colligative property measurements and analysis of <sup>1</sup>H and <sup>7</sup>Li NMR spectra. With regard to a detailed analyses of our calorimetric data, it is of critical significance to know whether interaction of bases with hexameric alkyllithiums leads to base-coordinated hexamers or tetramers at these low  $\underline{R}$  values.

Unfortunately, calorimetry cannot by itself define the nature of the process being investigated; however, any proposed model for the coordination process must be consistent with the calorimetric data. As we<sup>11,12</sup> and others<sup>4</sup> have discussed previously, the addition of Lewis bases to hexameric alkyllithium compounds at low  $\underline{R}$  values in hydrocarbon solvents could involve either coordination to intact hexamers [eqn. 2] or conversion to base-solvated tetramers [eqn. 3].\* If one postulates that



the interaction of bases with hexameric *n*-butyllithium in hydrocarbon solution at low  $\underline{R}$  values leads to solvated tetramers [eqn. 3], it is difficult to understand why this process would be more sensitive to the steric requirements of the base than the interaction of bases with tetrameric isopropyllithium or trimethylsilylmethylithium. An *n*-butyllithium tetramer would be expected to be less hindered with respect to base coordination than an isopropyllithium tetramer or a trimethylsilylmethylithium tetramer. However, an *n*-butyllithium hexamer may be more hindered with respect to interaction with bases than an isopropyllithium

\* It is generally assumed that the interaction of bases with the tetrameric alkyllithiums we have studied involves coordination to the intact tetramer (see reference 4).

or trimethylsilylmethylithium tetramer. The relative steric crowding in hexamers versus tetramers can be deduced from the data listed in Table 3 which show that when the steric requirements of the alkyl groups increase due to branching at either the  $\alpha$ - or  $\beta$ - carbon, tetrameric versus hexameric aggregation is favored. The aggregation data imply that the steric environment of an alkyl group in a tetramer is less congested than in the corresponding hexamer. On this basis it is tentatively proposed that the interaction of tetrahydrofuran bases with *n*-butyllithium at low  $R$  values in hydrocarbon solvent involves the formation of base-solvated hexamers [eqn. 2].

An interesting question arises with regard to the nature of the coordination process for hexameric trimethylsilylmethylithium since it shows much less sensitivity to the steric requirements of the tetrahydrofuran bases compared to hexameric *n*-butyllithium. We previously proposed that the interaction of bases with hexameric trimethylsilylmethylithium leads directly to solvated tetramers.<sup>12</sup> This hypothesis provides a simple rationale for the observation that both hexameric and tetrameric trimethylsilylmethylithium display the same sensitivity to increasing steric requirements of the substituted tetrahydrofurans as shown in Table 1; both systems would be producing the base-solvated tetramer. Further support for this proposal can be obtained from a comparison of the initial enthalpies of interaction of hexameric versus tetrameric trimethylsilylmethylithium for all of the bases reported herein as shown in Figure 1. In addition, we have previously shown that an excellent linear relationship is also obtained from a comparative enthalpimetric titration plot for the interaction of 2-methyltetrahydrofuran with hexameric versus tetrameric trimethylsilylmethylithium over a range of  $R$  values from 0.06 to 1.12. Although it is possible that these excellent linear relationships are fortuitous, these results certainly support the suggestion that the same processes (formation of base-solvated tetramers) are involved for both hexameric and tetrameric trimethylsilylmethylithium regardless of the nature of the base.

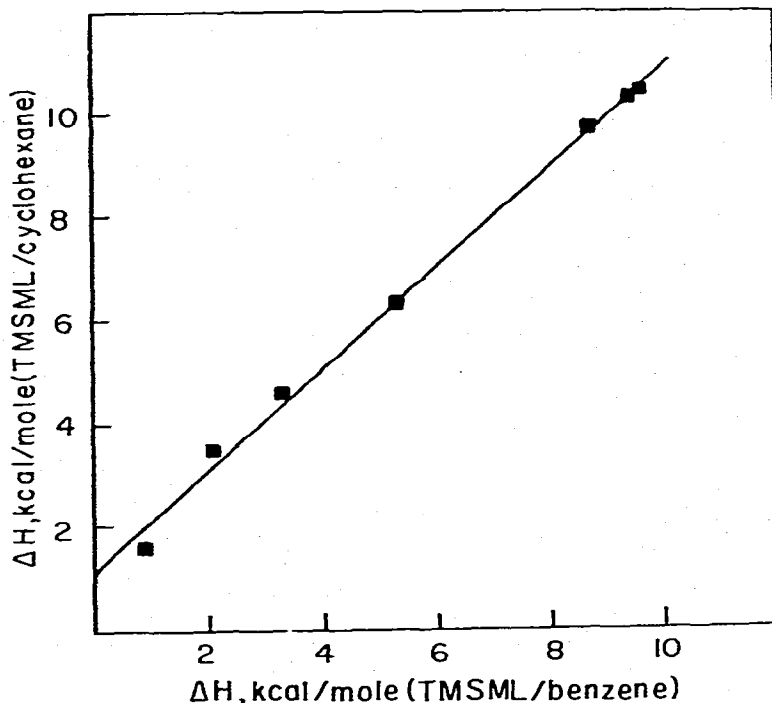


Fig.1. Comparison of the initial enthalpies of interaction of bases with 0.04 M solutions of trimethylsilylmethyl lithium in cyclohexane vs. 0.04 M solutions of trimethylsilylmethyl lithium in benzene.

In summary, the calorimetric data reported herein provide unique insight into the detailed nature of alkyllithium-base interactions. An enthalpimetric basicity order has been obtained which is independent of the alkyllithium compound. The sensitivity of the observed enthalpies of base coordination to systematic variations in the steric requirements of the base suggests that the initial interaction of bases with hexameric n-butyllithium produces base-coordinated hexamers at low R values; however, it is proposed that the interaction of bases with hexameric trimethylsilylmethyl lithium leads directly to base-coordinated tetramers.

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