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Preliminary communication

SOLVATION OF ALKYLLITHIUM COMPOUNDS. STERIC EFFECTS ON HEATS OF INTERACTION OF BASES WITH TRIMETHYLSILYLMETHYLLITHIUM VERSUS n-BUTYLLITHIUM

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We have recently developed a direct calorimetric method for determining the enthalpies of interaction of bases with alkyllithiums [1]. We report herein measurements of the enthalpies of interaction of tetrahydrofuran (THF), 2-methyltetrahydrofuran (2-MeTHF), and 2,5-dimethyltetrahydrofuran (2,5-Me_2THF) with trimethylsilylmethyllithium (Me_3SiCH_2Li) and n-butyllithium (n-BuLi). These results stand in direct contrast to predictions based on simple steric arguments [2, 3] and further serve to characterize the base—alkyllithium coordination process.

The enthalpies of the initial interaction for this series of bases with Me_3SiCH_2Li and n-BuLi are shown in Table 1. It is obvious that the observed dependence of the magnitudes of the enthalpies on alkyllithium structure ($Me_3SiCH_2Li \gg$ n-BuLi) cannot be explained in terms of the steric requirements of the alkyl groups of the alkyllithiums. Furthermore, the decreases in enthalpy resulting from methyl substitution in the base are larger for n-BuLi (2.8 kcal/mole) than for Me_3SiCH_2Li (ca. 0.6 kcal/mole) which indicates that interactions with n-BuLi are more sensitive to the steric requirements of the base.

As discussed in our previous paper [1], the observed enthalpies [ΔH_{obs}, eqn. 1] may represent a composite of two processes [eqn. 2]:

$$2/3(RLi)_6 + B \xrightleftharpoons{\Delta H_{obs}} (RLi)_4B \qquad (1)$$

$$\Delta H_{obs} = \Delta H_1 + \Delta H_2 \qquad (2)$$

$$2/3(RLi)_6 \xrightleftharpoons{\Delta H_1} (RLi)_4 \qquad (3)$$

$$(RLi)_4 + B \xrightleftharpoons{\Delta H_2} (RLi)_4B \qquad (4)$$

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TABLE 1

STERIC EFFECTS ON ENTHALPIES OF INTERACTION [a]

Base [a]	−ΔH (kcal/mole) [b, c]		
	n-BuLi (hexane)	Me_3SiCH_2Li (cyclohexane)	Me_3SiCH_2Li (benzene)
THF	7.4	10.3	9.4
2-MeTHF	6.3	10.4	9.6
2,5-Me_2THF [d]	4.6	9.7	8.7

[a] See Ref. 1 for experimental details. All bases distilled from (1) $LiAlH_4$ and (2) benzophenone ketyl. [b] All enthalpies obtained at 25° by addition of 50 μl (~0.5 mmole) of base into 195 ml of 0.04*M* RLi (base/Li atom ratio ca. 0.06). [c] All enthalpies corrected for heats of solution of bases in pure solvent at 25 ± 1°C. [d] 53/47 mixture *cis/trans* isomers.

(a) endothermic conversion of hexamers to tetramers [ΔH_1, eqn. 3]; and
(b) exothermic coordination of a base molecule to the tetramers [ΔH_2, eqn. 4]. Colligative property measurements have shown that n-BuLi is hexameric in hydrocarbon solvents [2, 4]; Me_3SiCH_2Li is hexameric in cyclohexane, but tetrameric in benzene (below 0.06 molal) [2]. At higher concentrations in benzene, the degree of aggregation of Me_3SiCH_2Li increases toward the hexamer [2, 5]. Both alkyllithiums are presumably tetrameric in basic solvents [2, 6]. These colligative property results suggest that the hexamer—tetramer interconversion [eqn. 3] is more endothermic for n-BuLi than for Me_3SiCH_2Li [2], thus providing an explanation for the more exothermic heats observed for Me_3SiCH_2Li. The larger enthalpies of interaction for Me_3SiCH_2Li and the smaller sensitivity of the heats of interaction with Me_3SiCH_2Li to increasing spatial requirements of the bases may be a result of Me_3SiCH_2Li tetramers being less hindered than n-BuLi tetramers. This could be a consequence of the longer carbon—silicon bonds (ca. 1.87 Å) [7] relative to carbon—carbon bonds (ca. 1.54 Å) [7] or of a distorted structure for the Me_3SiCH_2Li tetramer [8]*.

Support for the assumption that the interaction of bases with hexameric alkyllithiums leads directly to solvated tetramers can be deduced from thermometric titration data we have obtained for hexameric vs. tetrameric Me_3SiCH_2Li (Fig. 1)**. The solid line was obtained by plotting the heat evolved for the interaction of 2-MeTHF with hexameric Me_3SiCH_2Li (0.04*M*, cyclohexane) vs. tetrameric Me_3SiCH_2Li (0.04*M*, benzene) for successive additions of base. The linear relationship indicates that the same process is involved for both systems***, i.e., there is no evidence for direct coordination to Me_3SiCH_2Li hexamers. A similar plot for hexameric n-BuLi (0.04*M*, hexane) vs. tetrameric Me_3SiCH_2Li (0.04*M*, benzene) is shown by the broken line in Fig. 1. This plot is not linear, but consists of two linear segments which intersect at $R \approx 0.30$. The linearity of both segments of this plot suggests that the coordination processes for each alkyllithium are the same***. The smaller slope for the initial segment of the n-BuLi

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*It should be noted that data for tetrameric Me_3SiCH_2Li in ref. 8 were obtained using 0.81*M* solutions for which significant association toward hexameric species has been reported (refs. 2 and 5).

**Similar plots are obtained for each of the bases reported herein.

***The linearity of this type of plot could be consistent with different processes occurring in each system if the corresponding enthalpies are proportional, i.e., if enthalpies of coordination to hexamers and subsequent conversion to tetramers at *R* less than 1.0 (see Ref. 2) are proportional to enthalpies of coordination to tetramers.

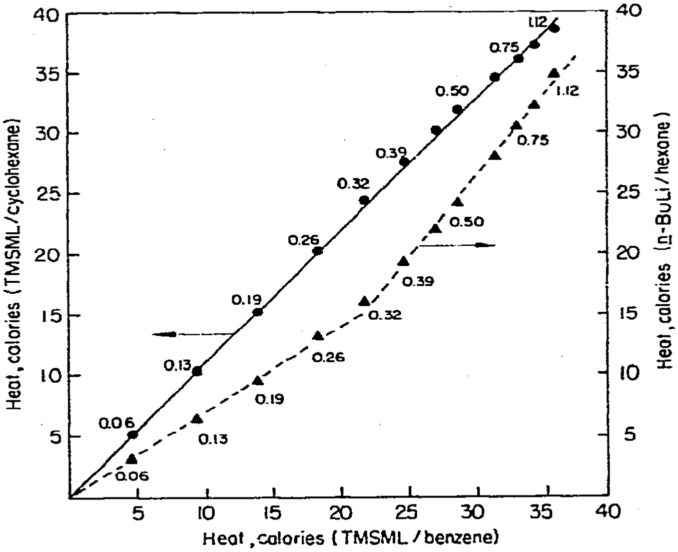

Fig. 1. Comparative enthalpimetric titration plots for the interaction of 2-methyltetrahydrofuran with 0.04*M* solutions of trimethylsilylmethyllithium (TMSML) in cyclohexane (●) and 0.04*M* solutions of n-butyllithium in hexane (▲) vs. 0.04*M* solutions of trimethylsilylmethyllithium in benzene. Numbers by points indicate the *R* value at which the points were obtained. *R*= [base] /[Li], where [Li] is the concentration of lithium atoms in the solution.

plot compared to the Me_3SiCH_2Li plot is a manifestation of the more exothermic heats observed for Me_3SiCH_2Li (see Table 1). The change in slope for the n-BuLi plot indicates that the interaction of bases with n-BuLi is more exothermic relative to Me_3SiCH_2Li beyond $R \approx 0.3$, which is not consistent with expectations based on initial coordination of base to hexameric n-BuLi followed by more endothermic coordinations involving conversion to tetramers. However, this behavior is consistent with direct conversion to solvated tetramers and different extents of coordination of n-BuLi vs. Me_3SiCH_2Li. Colligative property measurements show that the effective number of coordinated bases are related to the spatial requirements of the alkyl group of the alkyllithium [i.e., C(1) > C(2) > C(3)] [2, 9]. Thus, beyond $R \approx 0.3$, tetrameric Me_3SiCH_2Li does not interact strongly with further base molecules, while tetrameric n-BuLi continues to interact strongly with several base molecules.

In summary, these preliminary results suggest that base coordination to both hexameric n-BuLi and Me_3SiCH_2Li may lead directly to solvated tetramers.

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