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SOLVATION OF ALKYLLITHIUM COMPOUNDS. HEATS OF INTERACTION OF LEWIS BASES WITH n-BUTYLLITHIUM

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SUMMARY

Heats of interaction of tetrahydrofuran, tetrahydrothiophene, triethylamine, and triethylphosphine with solutions of n-butyllithium in hexane have been determined by high dilution solution calorimetry. The relative heats of interaction of these bases are in the order tetrahydrofuran > triethylphosphine ≈ triethylamine > tetrahydrothiophene. These results are interpreted in terms of an acid–base interaction which is dominated by electrostatic effects. The alkyllithium aggregate is characterized as a relatively hard Lewis acid species.

INTRODUCTION

Lewis bases are effective catalysts for many reactions of organolithium compounds[1-9]. Some insight into the molecular basis for these catalytic effects has been provided by extensive NMR and colligative property measurements which have shown that simple alkyllithiums exist predominantly as hexamers in hydrocarbon solution and as tetramers in basic solvents[10-15]. However, the nature of the base–alkyllithium aggregate interactions responsible for these structural changes is not clear.

The purpose of the study reported herein was to characterize the specific nature of base–alkyllithium interactions by examining the energetics of complexation of bases with alkyllithiums as a function of the structure of the base.

EXPERIMENTAL

Apparatus and procedures

All enthalpy measurements were performed using a high dilution solution calorimeter of the type developed by Arnett *et al.*[16], which had been adapted for use in an argon atmosphere glove box. The argon atmosphere was purified by continuous circulation through towers of molecular sieves and manganous oxide as described by Brown *et al.*[17,18]. Liquid samples were introduced into the calorimeter using Hamilton syringes (500 μl, gas-tight with Chaney adapter) and stainless steel stops to deliver known volumes accurately and reproducibly.

All preparations and transfers involving alkyllithium reagents were performed

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in the argon atmosphere glove box. All glassware was baked at 120° for at least 4 h before being transferred to the antichamber of the glove box.

Solutions of alkyllithium reagents were analyzed using the double titration procedure of Gilman and Cartledge[19].

Materials

All bases used for calorimetric measurements were distilled either on a high vacuum line or inside the argon atmosphere glove box and were used immediately. NMR and IR spectra as well as GLC analyses were used to check for impurities.

Anhydrous diethyl ether (Fisher) was distilled from lithium aluminum hydride under argon, transferred to the glove box, and stored briefly over sodium wire. 1,2-Dibromoethane (Eastman) was distilled from phosphorous pentoxide and used immediately. Hexane (Fisher Certified) was purified according to the procedure recommended by Perrin *et al.*[20], distilled from calcium hydride directly onto molecular sieves under an argon atmosphere, and stored in the glove box. Triethylamine (Eastman) was refluxed and distilled from lithium aluminum hydride under argon followed by a final distillation from n-butyllithium. Tetrahydrofuran (Fisher Certified) was distilled from lithium aluminum hydride. Triethylphosphine was synthesized using the procedure of Raiford and Freyermuth[21] and purified by fractional distillation from calcium hydride (b.p. 128–130°; lit.[21] 128.5–130°). Commercial triethylphosphine (Strem) was obtained in a sealed ampoule and was opened and used in the glove box without further purification. Tetrahydrothiophene (Eastman) was fractionally distilled from lithium aluminum hydride (b.p. 119.5–120°; lit.[22] 120.9°).

Commercial solutions of n-butyllithium in hexane (Foote Mineral Co.) were either stored under refrigeration or in the glove box. Solutions of n-butyllithium in hexane for control runs were prepared from di-n-butylmercury and lithium dispersion[23] using the procedure of Lewis and Brown[11].

Potassium chloride (Fisher Certified) was dried in an oven at 120° for several hours and stored in a desiccator. 2-Amino-2-(hydroxymethyl)-1,3-propanediol (THAM, Fisher Certified Primary Standard) was mechanically ground and stored in a desiccator.

RESULTS AND DISCUSSION

The accuracy and precision of our calorimetric methods were determined by comparison of our data with well-accepted values for the heats of solution of standard substances. Our measured value for the heat of solution of THAM in 0.1 *N* hydrochloric acid is -7.10 ± 0.08 kcal/mole (lit.[24] -7.109 ± 0.001 kcal/mole). Our measured value for the heat of solution of potassium chloride in water is 4.13 ± 0.06 kcal/mole (lit.[25] 4.115 ± 0.01 kcal/mole). Systematic errors were avoided by frequent checks of our calorimeters with these standards.

The accuracy of our calorimetric data for the heats of interaction of bases with alkyllithium compounds could not be compared with predetermined standards since data of this type are not available. However, convincing evidence for the reliability of our data was obtained by demonstrating that the results are independent of the source of n-butyllithium; by showing that n-butyllithium is not decomposing in the presence of bases during the calorimetric runs and is stable in the calorimeter for periods up to 24 h*; and by showing that different experimentalists using different batches of bases over a period of several months can obtain reproducible results. Different sources of bases and different purification procedures were used to determine that the enthalpy measurements were not dependent on these variables. The data in Fig. 1 show a comparison of the enthalpies of interaction as function of the ratio of added base to lithium atoms (*R*) for tetrahydrofuran with commercial and freshly prepared n-butyllithium. The absence of side reactions consuming the alkyllithium reagent in the calorimeter or giving spurious heats of interaction was determined by double titration of several of the base–alkyllithium solutions immediately after the calorimetric runs. The results shown in Table 1 show that no decomposition is occurring during the calorimetric runs, within the experimental error limits of the double titration procedure. The weight of this evidence indicates that the enthalpies of interaction of bases with n-butyllithium in hexane reported herein are indeed an inherent property of the system and are not dependent on trace impurities, experimental procedures, or decomposition reactions.

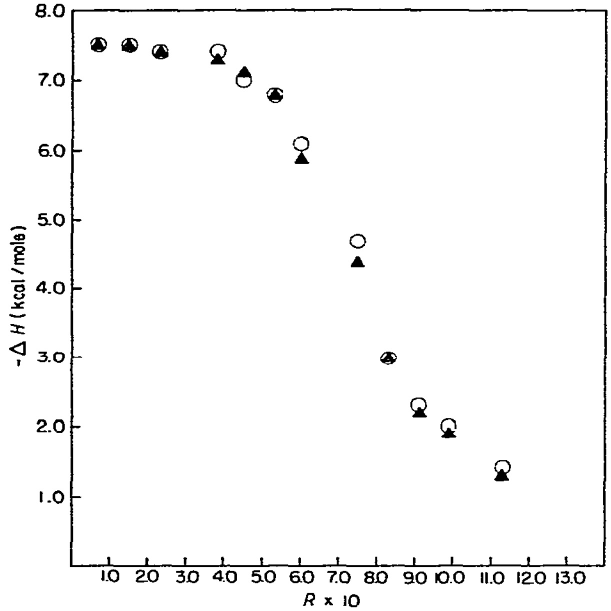

Fig. 1. Enthalpies of interaction of tetrahydrofuran with 0.08 *M* solutions of commercial (▲) and freshly prepared (○) n-butyllithium in hexane. *R* = (base)/(Li), where (Li) is the concentration of lithium atoms in the solution.

The calorimetric data obtained for the interaction of several well-chosen bases with 0.08 *M* and 0.4 *M* solutions of n-butyllithium in hexane as a function of *R* are shown in Fig. 2 and Fig. 3, respectively. All of these measurements are referred to

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* Identical enthalpies (±0.03 kcal/mole) were obtained for the interaction of triethylamine with freshly prepared solutions of n-butyllithium and for solutions which were allowed to remain in the calorimeter for 24 h.

dilute solutions of base in hexane at 25±1° as the standard state to correct for the heats of solution of the bases.

It is appropriate to consider these calorimetric data in relation to the following possible equilibria, since both NMR and colligative property data indicate that hexamers are converted to tetramers in the presence of base at *R* values less than 1.0[11,12]. It is not known, however, at what specific *R* values the hexamer-tetramer

TABLE 1

DOUBLE TITRATION ANALYSES[a] OF BASE/n-BUTYLLITHIUM SOLUTIONS IN HEXANE AFTER CALORIMETRIC RUNS

Base	*Time required for calorimetric run (min)*	*Calculated molarity*[b]	*Observed molarity*[a,c]
Tetrahydro-	70	0.083	0.082±0.01
furan	70	0.83	0.82 ±0.01
Triethyl-phosphine	180	0.42	0.42 ±0.01
Tetrahydro-thiophene	180	0.080	0.079±0.01

[a] Using the procedure of Gilman and Cartledge (ref. 19). [b] Based on the amount of n-butyllithium initially pipetted into the calorimeter before the run. [c] Titration results on solutions resulting from calorimetric runs.

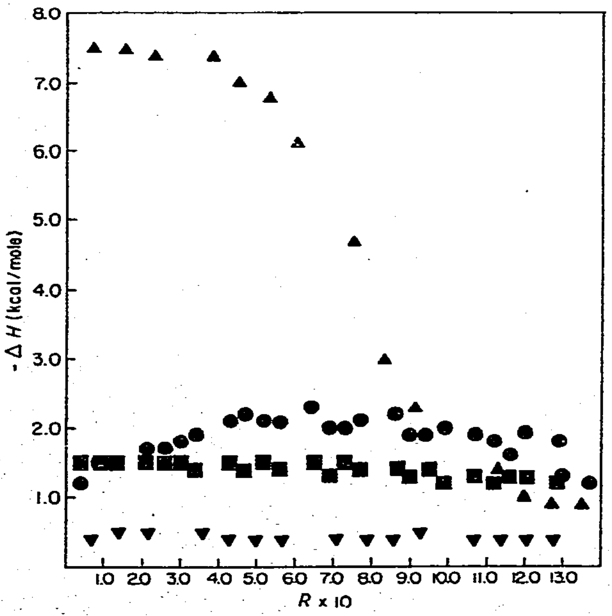

Fig. 2. Enthalpies of interaction of bases with 0.08 *M* solutions of n-butyllithium in hexane: ▲, tetrahydrofuran; ●, triethylamine; ■, triethylphosphine; ▼, tetrahydrothiophene.

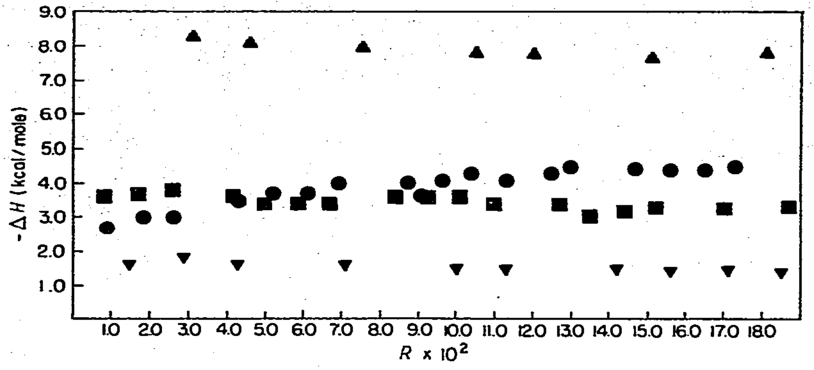

Fig. 3. Enthalpies of interaction of bases with 0.4 *M* solutions of n-butyllithium in hexane: ▲, tetrahydrofuran; ●, triethylamine; ■, triethylphosphine; ▼, tetrahydrothiophene.

$$(\mathrm{RLi})_6 + \mathrm{B} \rightleftharpoons (\mathrm{RLi})_6 \cdot \mathrm{B} \qquad (1)$$

$$(\mathrm{RLi})_6 \cdot \mathrm{B} + \mathrm{B} \rightleftharpoons (\mathrm{RLi})_6 \cdot 2\,\mathrm{B} \qquad (2)$$

$$2(\mathrm{RLi})_6 + 3\,\mathrm{B} \rightleftharpoons 3(\mathrm{RLi})_4 \cdot \mathrm{B} \qquad (3)$$

$$2(\mathrm{RLi})_6 \cdot \mathrm{B} + 2\,\mathrm{B} \rightleftharpoons 3(\mathrm{RLi})_4 \cdot \mathrm{B} \qquad (4)$$

$$(\mathrm{RLi})_6 \cdot 2\,\mathrm{B} + \mathrm{B} \rightleftharpoons 3/2(\mathrm{RLi})_4 \cdot 2\,\mathrm{B} \qquad (5)$$

$$(\mathrm{RLi})_4 \cdot \mathrm{B} + \mathrm{B} \rightleftharpoons (\mathrm{RLi})_4 \cdot 2\,\mathrm{B}, \text{ etc.} \qquad (6)$$

conversion occurs. Plots of enthalpies of interaction *vs.* *R* could reveal such interconversions as breaks in these curves if specific stoichiometries and enthalpies are associated with each type of coordination. Examination of the data in Fig. 2 indicates that a definite break is observed only for tetrahydrofuran. The most effective (exothermic) interaction for tetrahydrofuran occurs at *R* values less than 0.5*. If the initial exothermic interaction corresponds to two bases coordinating with the two empty faces of the hexamer[26] [eqns. (1) and (2)], the decrease in enthalpy beyond $R = 0.5$ could be interpreted as a composite effect of an exothermic base interaction coupled with an endothermic conversion of hexamers to tetramers [eqn. (5)]. Another explanation for this concentration dependence is that coordination with tetrahydrofuran leads directly to the disolvated tetramers [eqns. (3) and (6)], assuming that the energies of the hexamer and tetramer are not greatly different[11].

It is noteworthy that for reactions of n-butyllithium with n-butyl bromide or 1-bromooctane it has been observed that the rate of reaction increases with increasing concentration of base up to *R* values of 0.5 for such bases as tetrahydrofuran and diethyl ether[1,27]. These results suggest that calorimetric measurements may provide insight into the role of base coordination in some reactions of alkyllithiums, even though more complex kinetic dependence on base concentration has often been observed[28].

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* For 0.4 *M* solutions of n-butyllithium, the enthalpy of interaction for tetrahydrofuran also decreases dramatically beyond an *R* value of 0.5.

The observed enthalpy values cannot be interpreted simply in terms of the molar heats of formation of specific base–alkyllithium complexes, because of the unknown extent of hexamer–tetramer interconversion. If it is assumed that initial coordination of base occurs with the intact hexamer[11,29] [eqn. (1)], however, then the magnitudes of the enthalpies measured at low values of R can be interpreted in terms of the relative strengths of this interaction for each base. The resultant basicity order at both 0.4 M (see Fig. 3) and 0.08 M (see Fig. 2) is tetrahydrofuran > triethylphosphine ≈ triethylamine > tetrahydrothiophene. Although the absolute magnitudes of the enthalpies are concentration dependent*, the relative basicity order is not dependent on the concentration of n-butyllithium.

This particular series of bases was chosen for initial study to examine the relative importance of steric hindrance *vs.* electronic effects as factors affecting the coordination of bases with alkyllithiums. The inversion of effectiveness of 2nd row *vs.* 1st row analogs in going from Group V to Group VI (*i.e.*, $P \approx N$, but $O \gg S$) indicates that electronic effects can be important. The large difference in heats of interaction (ca. 7 kcal/mole) for such structurally similar bases as tetrahydrofuran and tetrahydrothiophene obviously cannot be ascribed to a steric effect. However, since the geometry of phosphines is quite different from amines[31,32], it is not possible to interpret the effectiveness of triethylphosphine relative to triethylamine as also resulting from an electronic effect.

In order to gain more insight into the nature of the base-coordination process, these calorimetric data (initial enthalpies) have been analyzed using the empirical Drago–Wayland relationship[33,34] to compare with other fundamental acid–base interactions. This four-parameter equation [eqn. (7)] has been used to correlate

$$-\Delta H = E_A \cdot E_B + C_A \cdot C_B \tag{7}$$

the enthalpy of adduct formation in poorly solvating media using two empirically determined parameters to characterize the acid (A) and base (B). The E parameters have been described as the susceptibility of the acid or base to undergo electrostatic interaction while the C parameters have been associated with the susceptibility to form covalent bonds. The C/E ratio has been interpreted[35] in terms of the relative

TABLE 2

DRAGO–WAYLAND PARAMETERS FOR SELECTED BASES[a]

Base	C_B	E_B
Trimethylamine	11.54	0.808
Triethylamine	11.09	0.991
Tetrahydrofuran	4.27	0.978
Tetrahydrothiophene	7.90	0.341
Trimethylphosphine	6.55	0.838

[a] These values were taken from ref. 34.

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* The increase in enthalpy with increasing concentration of n-butyllithium is expected for formation of more polar aggregates since the dielectric constant of solutions of alkyllithiums is known to increase as base is added to the solution[29,30].

"hardness" or "softness" of the interaction in terms of Pearson's HSAB model[36]. Using the enthalpy data at low R values and available values for the bases, listed in Table 2, the organolithium aggregate can be characterized as a relatively hard acid since the calculated ratio of C_A/E_A* is quite small (ca. 0.06) as expected for lithium atom coordination. Furthermore, in terms of the Drago–Wayland equation, the interaction of bases with n-butyllithium is dominated by the electrostatic terms, whose relative magnitudes can be used to predict the inversion which is observed between Group V and Group VI analogs. Thus, even though the observed order is rather unusual, it is consistent with structural parameters derived from a variety of standard acid–base systems.

Calorimetric studies of the interaction of other alkyllithiums with bases are currently being investigated to further characterize the acid–base properties of alkyllithium compounds.

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REFERENCES

1 E. A. Kovrizhnykh and A. I. Shatenshtein, *Russ. Chem. Rev.*, 38 (1969) 840.
2 J. M. Brown, *Chem. Ind. (London)*, (1972) 454.
3 J. M. Mallan and R. L. Bebb, *Chem. Rev.*, 69 (1969) 693.
4 A. W. Langer, *Trans. N.Y. Acad. Sci.*, 27 (1965) 741.
5 D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, 85 (1963) 743.
6 P. D. Bartlett, C. V. Goebel and W. P. Weber, *J. Amer. Chem. Soc.*, 91 (1969) 7425.
7 J. G. Carpenter, A. G. Evans, C. R. Gore and N. H. Rees, *J. Chem. Soc. B*, (1969) 908.
8 M. Szwarc, "*Carbanions, Living Polymers, and Electron Transfer Processes*," Interscience, New York, 1968.
9 C. Agami, *Bull. Soc. Chim. Fr.*, (1970) 1619.
10 T. L. Brown, *Pure Appl. Chem.*, 23 (1970) 447.
11 H. L. Lewis and T. L. Brown, *J. Amer. Chem. Soc.*, 92 (1970) 4664.
12 P. West and R. Waack, *J. Amer. Chem. Soc.*, 89 (1967) 4393.
13 D. Margerison and J. D. Pont, *Trans. Faraday Soc.*, 67 (1971) 353.
14 L. M. Seitz and T. L. Brown, *J. Amer. Chem. Soc.*, 88 (1966) 2174.
15 L. D. McKeever, R. Waack, M. A. Doran and E. B. Baker, *J. Amer. Chem. Soc.*, 91 (1969) 1057.
16 E. M. Arnett, W. G. Bentrude, J. J. Burke and P. McC. Duggleby, *J. Amer. Chem. Soc.*, 87 (1965) 1541.
17 T. L. Brown, D. W. Dickerhoff, D. A. Bafus and G. L. Morgan, *Rev. Sci. Instrum.*, 33 (1962) 491.
18 D. F. Shriver, "*The Manipulation of Air-Sensitive Compounds*," McGraw-Hill, New York, 1969.

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* The calculated values for C_A and E_A are -0.55 and 9.0, respectively, using the Drago–Wayland parameters for triethylamine, tetrahydrofuran, and tetrahydrothiophene. However, these numbers must be regarded only as estimates because of the limited data available.

19 H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, 2 (1964) 447.
20 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, "*Purification of Laboratory Chemicals*," Pergamon, New York, 1966.
21 L. C. Raiford and H. B. Freyermuth, *J. Org. Chem.*, 8 (1943) 234.
22 W. E. Haines, R. V. Helm, G. W. Bailey and J. S. Ball, *J. Phys. Chem.*, 58 (1954) 270.
23 P. D. Bartlett, S. J. Tauber and W. P. Weber, *J. Amer. Chem. Soc.*, 91 (1969) 6362.
24 J. O. Hill, G. Öjelund and I. Wadsö, *J. Chem. Thermodyn.*, 1 (1969) 111.
25 V. B. Parker, "*Thermal Properties of Aqueous Univalent Electrolytes*", National Standard Reference Data Series, National Bureau of Standards, 2, Washington, D.C., 1965.
26 T. L. Brown, *Advan. Organometal. Chem.*, 3 (1966) 365.
27 J. F. Eastham and G. W. Gibson, *J. Amer. Chem. Soc.*, 85 (1963) 2171.
28 R. Waack, M. A. Doran and P. E. Stevenson, *J. Organometal. Chem.*, 3 (1965) 481.
29 T. L. Brown, R. L. Gerteis, D. A. Bafus and J. A. Ladd, *J. Amer. Chem. Soc.*, 86 (1964) 2135.
30 F. A. Settle, M. Haggerty and J. F. Eastham, *J. Amer. Chem. Soc.*, 86 (1964) 2076.
31 D. R. Lide and D. E. Mann, *J. Chem. Phys.*, 29 (1958) 914.
32 D. R. Lide and D. E. Mann, *J. Chem. Phys.*, 28 (1958) 572.
33 R. S. Drago and B. B. Wayland, *J. Amer. Chem. Soc.*, 87 (1965) 3571.
34 R. S. Drago, G. C. Vogel and T. E. Needham, *J. Amer. Chem. Soc.*, 93 (1971) 6014.
35 G. Klopman, *J. Amer. Chem. Soc.*, 90 (1968) 223.
36 R. G. Pearson, *J. Chem. Ed.*, 45 (1968) 581, 643, and references cited therein.