Association of Alkyllithium Compounds in Hydrocarbon Media. Alkyllithium–Base Interactions[1]

Harlan L. Lewis and Theodore L. Brown

Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801. *Received January 15, 1970*

Abstract: The aggregations of several alkyllithium compounds in cyclohexane and benzene have been investigated by cryoscopic measurements. The compounds exist in the two solvents as hexameric aggregates unless steric interactions due to branching at either α- or β-carbon favor formation of tetrameric aggregates. Equilibria between these two species are in some instances markedly affected by changes in concentration or solvent. There is no evidence in any of the systems studied for a degree of association less than four. The effects of added tetrahydrofuran (THF), diethyl ether (DEE), cineole, quinuclidine (Q), or triethylamine (TEA) on hydrocarbon solutions of alkyllithium compounds have been studied by observation of ^{1}H and ^{7}Li nmr spectra, and measurements of freezing point lowerings of cyclohexane and benzene solutions. The results are consistent with other evidence that tetrameric alkyllithium species are present in excess base. It appears that conversion of the *n*-alkyllithium compounds from hexamer to solvated tetramer occurs at low base concentrations. The relative extent of interaction with *n*-alkyllithium compounds is in the order THF $\simeq$ Q > DEE > TEA > cineole. Differences in the steric requirements of the bases result in variable numbers of solvating bases per tetramer. The results show that complex formation is more extensive at about −75° than at 0°, but that the general character of the interactions is probably not changed. There is no evidence in the results for a solvated dimer species for any of the monodentate bases, nor for any of the alkyllithium compounds studied.

In the past few years there have been numerous colligative property measurements of the extent of aggregation of alkyllithium compounds in hydrocarbon solvents.[2–12] Some of the results are open to question,[2,3] but most are in rough agreement. The published results of colligative property studies exhibit relatively large uncertainties in the results. The extant data are not adequate to determine whether the extent of association varies with concentration, or is solvent dependent in hydrocarbon solvents.

In this paper we report measurements of the extent of aggregation of a number of alkyllithium compounds in hydrocarbon solutions, over the widest feasible concentration ranges. The organolithium materials selected were ethyl-, *n*-butyl-, isopropyl-, *t*-butyl-, and trimethylsilylmethyllithium. This set provides a variety of structural configurations in the alkyl group.

The technique of freezing point depression, previously employed in this laboratory, was chosen for colligative property measurements. Cyclohexane and benzene were chosen as solvents because of their convenient freezing points and relatively large molal freezing point lowering constants.

The effect of organic bases upon the association and reactivity of organolithium compounds is a matter of great interest. An early study[7] of the degree of association of methyllithium and *n*-butyllithium in ether yielded estimates of about 3 and 5, respectively, for the degrees of association. Eastham and coworkers have contended, on the basis of various data,[13] that *n*-butyllithium in hexane forms a monosolvated dimer on addition of diethyl ether. A similar result has been deduced for interaction of *n*-butyllithium in benzene with THF, and isobutyllithium in pentane with ether. Brown and coworkers[6] inferred from freezing point lowering results that ethyllithium is converted to dimers by triethylamine in cyclohexane.

On the other hand, Waack and West have deduced[14,15] from kinetic and colligative property measurements that methyllithium and *n*-butyllithium are tetrameric in ether, and that *n*-butyllithium is tetrameric in THF. Deviations from nonideal behavior at high concentrations (>1 *M*) in these solvents were interpreted in terms of solvate formation,[15] *e.g.*, the data for methyllithium in ether were interpreted in terms of an octa-solvated tetramer. Since these results depend upon data for very high concentrations of methyllithium, however, it may be doubted that the stoichiometry of the acid–base adduct formed can be deduced with much confidence.

The ^{7}Li spectra of mixtures of methyllithium and ethyllithium in ether[16] provide evidence that both species are tetrameric in this solvent at −50°. More recently, the ^{7}Li spectra of ^{13}C enriched methyllithium[17] confirm the tetrameric character of this substance in THF and triethylamine at −50°.

The weight of the more recent evidence therefore points to the subsistence of alkyllithium compounds as

---

[1] This research was supported by a grant from the National Science Foundation, NSF GP 6396X.

[2] K. B. Piotrovski and M. P. Ronina, *Dokl. Akad. Nauk SSSR*, **115**, 737 (1957).

[3] J. W. Connolly and G. Urry, *Inorg. Chem.*, **2**, 645 (1963).

[4] F. Hein and H. Schramm, *Z. Phys. Chem.*, *A*, **151**, 234 (1930).

[5] T. L. Brown and M. T. Rogers, *J. Amer. Chem. Soc.*, **79**, 1859 (1957).

[6] T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *ibid.*, **86**, 2135 (1964).

[7] G. W. Wittig, F. J. Meyer, and G. Lange, *Ann.*, **571**, 169 (1950).

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

[9] S. Bywater and D. J. Worsfold, *J. Organometal. Chem.*, **10**, 1 (1967).

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

[11] G. E. Hartwell and T. L. Brown, *ibid.*, **3**, 1656 (1964).

[12] R. H. Baney and R. J. Krager, *ibid.*, **3**, 1657 (1964).

[13] (a) J. F. Eastham and G. W. Gibson, *J. Amer. Chem. Soc.*, **85**, 2171 (1963); (b) Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *ibid.*, **85**, 3517 (1963); (c) C. G. Screttas and J. F. Eastham, *ibid.*, **88**, 5668 (1966).

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

[15] P. West and R. Waack, *J. Amer. Chem. Soc.*, **89**, 4395 (1967).

[16] L. M. Seitz and T. L. Brown, *ibid.*, **88**, 2174 (1966).

[17] L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *ibid.*, **90**, 3244 (1968).

tetramers in ethers and amines. Given this conclusion, however, it is still not clear just how many bases are associated with each tetramer, or the extent to which the bases are bound to the tetrameric moiety. Bartlett, Goebel, and Weber have obtained vapor pressure data[18] which, assuming tetrameric species in solution, can be interpreted in terms of the average number of bases strongly bound to the tetramer. They conclude, for example, that *n*-butyllithium in *n*-heptane at $-25°$ is solvated by dimethyl ether to the extent of 3.6 bases per tetramer when base and alkyllithium are present in 1:1 ratio.

We have examined the proton and ^{7}Li magnetic resonance spectra of solutions of alkyllithium compounds in hydrocarbon solvents, with added bases. Freezing point lowering studies have also been carried out on these systems.

Experimental Section

All operations save for the sublimation purifications were carried out in an inert-atmosphere box.

Materials. Ethyllithium was obtained as a 1 *M* solution in benzene from Alfa Inorganics, Inc. The solvent was removed and the resulting yellow-brown solid recrystallized from cyclohexane, yielding a white powder. Just prior to an experimental study, it was sublimed at 10^{-3} Torr and 80°.

n-Butyllithium was prepared by allowing distilled di-*n*-butylmercury to react in solution with lithium metal powder suspended in the solvent. Lithium metal was obtained as a dispersion in mineral oil from Lithium Corporation of America. The paste was washed on a frit with several portions of dried, degassed *n*-heptane, followed by *n*-pentane. In the preparation of *n*-butyllithium, the di-*n*-butylmercury in solution was added dropwise over a period of about 1 hr to a suspension of lithium metal in a 1.5-fold excess, while the temperature was maintained at 10–15° below the reflux temperature. The system was stirred during addition and then for a further 8 hr. Then the system was cooled and lithium amalgam removed by filtration. The *n*-butyllithium solution was used immediately.

Trimethylsilylmethyllithium was prepared by reacting a solution of trimethylchloromethylsilane (Peninsular ChemResearch) with lithium metal powder suspended in the solvent. The halide in solution was added dropwise at room temperature over a 1-hr period to a suspension of lithium powder in about 1.5-fold excess, with stirring. The system was heated with stirring to 55–60° for 5 hr. Lithium chloride and excess lithium metal were filtered on a frit and the solvent stripped off *in vacuo*. The white solid was sublimed at 10^{-3} to 10^{-4} Torr and 80° just prior to use and then transferred to a solvent.

Isopropyllithium was obtained as a 2 *M* solution in *n*-heptane from Alfa Inorganics, Inc., and was kept under refrigeration until used. Solvent was stripped off by vacuum pumping, leaving either a light-yellow solid or a dark, yellow-orange, viscous oil. In either case the material was sublimed at 30–35° at 10^{-3} to 10^{-4} Torr, and then resublimed. The second sublimate, glassy in appearance, was transferred immediately to the solvent of the study, and aliquots were drawn for each experimental run. No attempt was made to store either the solid or solutions, for they slowly decompose at room temperature.

t-Butyllithium was obtained as a 2 *M* solution in pentane from Alfa Inorganics, Inc.; the solvent was stripped off by vacuum pumping, leaving a white powder. Just prior to an experiment, the solid was sublimed at 10^{-3} to 10^{-4} Torr and 45°, and the sublimate transferred to the proper solvent.

In the case of the hydrocarbon solutions of the alkyllithiums, all except *n*-butyllithium were clear and colorless. The *n*-butyllithium solutions were a pale yellow, probably because of a trace impurity in the di-*n*-butylmercury which was not removed by distillation.

Cyclohexane was obtained as a bulk grade material, generously supplied by Gulf Oil Corp. We found this material to be particularly free of impurities which are not removable by distillation or fractional crystallization, *e.g.*, methylcyclopentane, but which are troublesome in the colligative property work. It was passed over silica gel and distilled from ethyllithium in an inert atmosphere, and stored in ground-glass stoppered storage bottles in the box.

Benzene was obtained from J. T. Baker Co. as Baker Analyzed solvent. It was distilled from ethyllithium before use.

Cyclopentane (reagent grade, Matheson Scientific) was distilled from ethyllithium. Anhydrous analytical grade diethyl ether (DEE) was distilled from ethyllithium. Analytical grade tetrahydrofuran and cineole (eucalyptol, White Label, Eastman Organic Chemicals) were distilled first from lithium aluminum hydride and then from ethyllithium. The THF fraction boiling at 64.5–65° and the cineole fraction boiling at 175–176° were retained.

Triethylamine (TEA) (Fisher Scientific Co., "Certified" Reagent Grade) and N,N,N′,N′-tetramethylethylenediamine (TMEDA) (Eastman Organic Chemicals, "White Label) were distilled from lithium aluminum hydride, and the TEA was further treated by distillation from ethyllithium. Quinuclidine was generously furnished by Mallinckrodt Chemical Works as a colorless solid. It was sublimed at less than 10^{-3} Torr at room temperature onto a cold finger cooled by an ethanol–Dry Ice mixture, and the sublimate was stored in an amber glass screw-cap bottle.

Monomer concentrations for alkyllithium compounds in solutions prepared for colligative property measurements were obtained by hydrolyzing three aliquots of each solution and titrating to a phenolphthalein end point with 0.100 *M* HCl. Some attempts were made to estimate impurity levels in the solutions. Following a modification of a method of Gilman by Glaze and Adams,[19] 1,2-dibromoethane was added to an aliquot of the hydrocarbon solution, followed by hydrolysis and acid titration. For the most reactive compounds, isopropyllithium and *t*-butyllithium, titers corresponding to an impurity level of about 0.2% were obtained. Some estimate of impurity levels was also available from both proton and ^{7}Li nmr spectra, in which there was no evidence of spurious absorptions ascribable to impurities.

Equipment. The inert atmosphere glove box was purchased from Vacuum Atmospheres Corp. of Los Angeles, Calif. Argon is employed as atmosphere; it is continually circulated by a pump and passed through a purification system external to the box, but part of a closed cycle. The purification system has been described elsewhere.[20] Clean glass equipment which had been baked at 140° for more than 3 hr was transferred *via* an evacuable port to the box and allowed to stand for at least 4 hr before any manipulations were begun.

The freezing point lowering apparatus described previously[7] has been modified by constructing the thermistor-containing element as an all-glass structure. In addition, the low-temperature well has been redesigned so that cooling is achieved by a liquid nitrogen boil-off. The cold nitrogen passes in an isolated line through the box wall into the cold chamber and out again. The minimum temperature attainable with this apparatus is about $-110°$. For freezing point depression studies the well temperature was maintained about 5–10° below the freezing point of the solvent, and controlled to within 1°. Molalities were determined graphically from a calibration graph of freezing point depression *vs.* molality for standard solutions of biphenyl, and checked with *p*-chlorobenzonitrile.

Proton magnetic resonance spectra were obtained using a Varian Associates Model A60A spectrometer and a Varian V-6040 temperature controller. A copper–constantan thermocouple was inserted into an nmr tube and placed in the sample probe to monitor temperatures. All temperatures are reproducible to ±2°. The chemical shifts are given in terms of an upfield shift of the center of the proton multiplet for the α-hydrogens with respect to the position of the cyclopentane singlet. When samples containing low base to hexamer ratios, about 0.5, were allowed to stand at room temperature for about 48 hr and then reexamined, no significant change in either molality or nmr spectra was observed. For high ratios (greater than 12), however, evidence of decomposition was observed in nmr spectra after 48 hr at room temperature.

The ^{7}Li nmr spectra were obtained with either a Varian DP60 spectrometer at 23.318 MHz in a field of 14,092 G, or an HA100 spectrometer at 38.863 MHz in a field of 23,490 G. Base-line stabilization was achieved by use of a Varian nmr integrator, Model V3521. Low temperature in the probe of the DP60 was attained by a controlled liquid N_2 boil-off, with circulation of the cold gas

---

[18] P. D. Bartlett, C. V. Goebel, and W. P. Weber, *J. Amer. Chem. Soc.*, **91**, 7425 (1969).

[19] W. H. Glaze and G. M. Adams, *ibid.*, **88**, 4653 (1966), footnote 7.

[20] G. E. Hartwell, Ph.D. Thesis, University of Illinois, 1966.

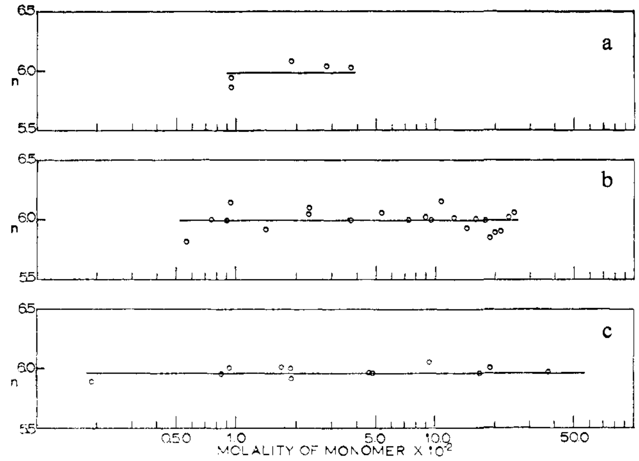

Figure 1. Association data for (a) ethyllithium in cyclohexane, (b) ethyllithium in benzene, and (c) *n*-butyllithium in cyclohexane.

around the probe. In the HA100, temperature control was similar to that used on the A60A. All ^{7}Li chemical shifts are relative to the singlet of a 3 *M* aqueous LiBr solution in a sealed capillary inserted into each sample tube, and are downfield from this reference. A calibrating side band was impressed on each spectrum. The estimated uncertainty in chemical shift measurements is about 0.05 ppm.

The concentration of each stock solution for cryoscopic acid–base studies was determined as described above. The molalities of at least three samples were measured by freezing point lowering, and compared with the molalities calculated from the titration data, corrected for degree of association of the alkyllithium. If the difference was greater than 1% a new stock solution was prepared from fresh sublimate. Samples were then prepared by combining aliquots of acid and base and diluting to a measured volume, usually 5.00 ml. The samples were run within 20 min of preparation; duplicates and redeterminations were used to assure reproducibility.

Samples for nmr studies were prepared by combining aliquots of alkyllithium solution with base solution at room temperature and cooling immediately to −40°. Sealed samples were stored at −75 to −80° and spectra obtained within 24–36 hr.

Results and Discussion

Association in Pure Hydrocarbon Solvents. In the following figures, the results of the association studies are given graphically. The data are generally from two or more separate studies on each system. The individual points were not recorded consecutively according to increasing or decreasing concentration, but rather random concentrations were often selected and previous results periodically rechecked during a series. This procedure avoided error due to decomposition, although over the 6–8 hr required for a study, no detectable decomposition was noted for any system except isopropyllithium. In this last case, studies on a given stock solution were limited to about 3 hr, and freshly sublimed material was used to continue a series.

Not unexpectedly, ethyllithium (Figure 1) is hexameric in both cyclohexane ($n_{av} = 5.98$) and benzene ($n_{av} = 6.01$), as noted previously by other workers. The present data indicate that there is no significant shift in the degree of association, *n*, with change in concentration. It appears that precipitation of ethyllithium due to saturation at the freezing point occurs in cyclohexane at about 0.037 *m* monomer (0.006 *m* hexamer), and in benzene, at about 0.26 *m* monomer (0.04 *m* hexamer).

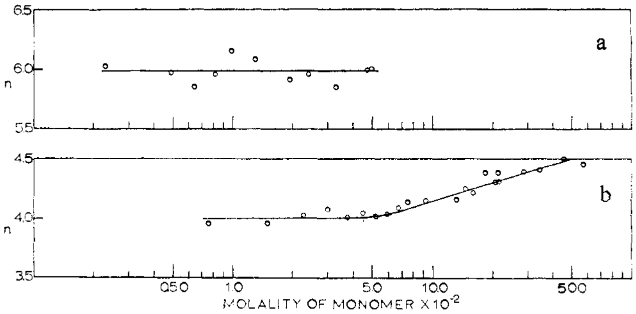

Figure 2. Association data for trimethylsilylmethyllithium in (a) cyclohexane and (b) benzene.

n-Butyllithium has been reported as hexameric in benzene and hexane by Margerison and Newport[8] on the basis of isopiestic measurements. However, *n* values of 6.25 and 6.17, respectively, were obtained in the two solvents. The deviation from 6.0 was attributed to a systematic error. In this work (Figure 1) the average *n* value is 5.97; probably the only significant species in hydrocarbon solvents such as cyclohexane is the hexamer. It should be noted, however, that because of steric interactions of the *n*-butyl groups, and in light of the results for trimethylsilylmethyllithium (see below), a tetramer might be present in significant proportions at low concentrations, *e.g.*, 10^{-3} *m*, particularly in benzene.

Trimethylsilylmethyllithium is clearly hexameric (Figure 2) in cyclohexane ($n_{av} = 5.98$). In benzene, it is essentially tetrameric to about 0.06 *m* in monomer; at higher concentrations a shift toward hexameric species is observed. It thus appears that where the steric requirement of the alkyl group is low, a hexameric aggregate is preferred for alkyllithium compounds. As the steric requirement increases a tetrameric aggregate is relatively more stable. Such behavior is noted also for isopropyllithium (see below). That the tetramer–hexamer proportion can be shifted significantly upon concentration change suggests that the free energies of the two forms are not greatly different. The results of Baney and Krager,[12] in which only a tetrameric species was observed for this alkyllithium, can be rationalized by recalling that their data were obtained by ebullioscopic measurements. At 80 and 60° for the solvents benzene and 2-methylpentane, respectively, it is not unreasonable that the tetramer would predominate. Hartwell and Brown[11] observed a trend in the *n* values which is compatible with the present data, although the concentration at which the *n* values begin to deviate above 4.0 is somewhat higher than in the present work.

From the colligative property data it appears that the steric effect of the isopropyl group is such that in both solvents at relatively low concentration, the tetramer is the favored structure (Figure 3). Above a molality (based on monomer) of about 0.03 in cyclohexane and 0.1 in benzene, aggregation to what is probably a hexameric structure occurs.

The alkyl group in *t*-butyllithium is apparently too bulky to permit aggregation above a tetramer (Figure 4, $n_{av} = 4.02$). Previous observations[10] in benzene and hexane at their boiling points confirm this. The results of the present work are summarized as follows.

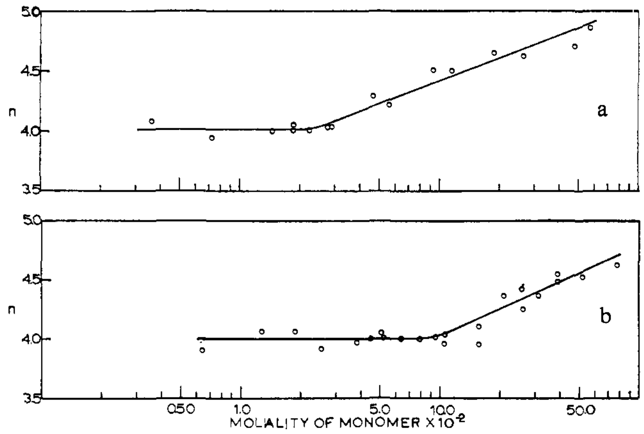

Figure 3. Association data for isopropyllithium in (a) cyclohexane and (b) benzene.

Within the concentration range studied, the predominant species for ethyl- and *n*-butyllithium in hydrocarbon solution is the hexamer. On the other hand, with more highly branched alkyl systems the nature of the hydrocarbon solvent as well as the working temperature become important in determining the hexamer–tetramer equilibrium. When steric factors are not prohibitive, the hexameric form appears to be the preferred configuration in saturated or aromatic hydrocarbon solvents. These results represent the first colligative property evidence for a hexamer–tetramer equilibrium involving a single organolithium substance in a given solvent. *In no instance is there evidence for a degree of aggregation lower than fourfold.*

Alkyllithium–Base Interactions. The behavior of the ^{7}Li chemical shift upon addition of base provides a useful probe for evaluating the effect of added base. Figure 5 shows, for example, the effect of added THF on the ^{7}Li chemical shift for *n*-butyllithium in cyclopentane, at 0 and −75°. The chemical shift change, in parts per million from the aqueous LiBr standard in a sealed capillary, is graphed *vs.* R, the ratio of added base to lithium atoms. At −75° a sharp break in the graph is seen at $R = 1$. The value for the chemical shift of ^{7}Li at R = 14 is −0.94, so it is evident that, insofar as this observable is capable of showing, complex formation is complete at $R = 1$.

The scatter of the data about the line shown is possibly outside the experimental uncertainty. Some nonlinearity in the curve might very well be seen if the equilibria are essentially complete, and if there is at some point corresponding to one or two base molecules per hexamer ($R < 0.3$) a shift from hexameric to tetrameric association. It is significant also that the ^{7}Li shift at $R = 1$, when corrected for change in bulk susceptibility of the medium, is essentially the same as for the alkyllithium compound in neat base. Since the compounds are tetrameric in the neat bases, the constancy of chemical shift suggests that the conversion from hexamer to tetramer is complete at $R = 1$. It is, of course, possible that the hexamer and tetramer of a given alkyllithium compound exhibit essentially the same chemical shift; the constancy of chemical shift is therefore not compelling evidence for tetramer formation at low base concentration, although it certainly suggests this. Attempts to identify separate ^{7}Li resonances due either to variously solvated species, or to hexamers and tetramers, in these solutions have not been successful, although spectra have been examined at temperatures as low as −100°. One expects, however, that transfer of base from one species to another, and intermolecular exchanges between hexamer and tetramer, should be very rapid.

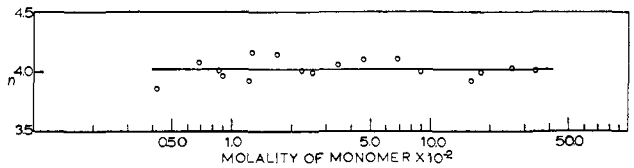

Figure 4. Association data for *t*-butyllithium in cyclohexane.

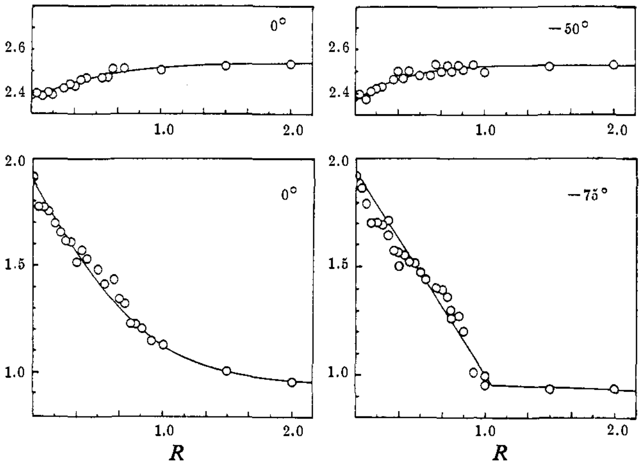

Figure 5. ^{1}H and ^{7}Li nmr chemical shifts (ppm) *vs.* base–lithium ratio for addition of THF to *n*-butyllithium in cyclopentane.

The variation of ^{7}Li chemical shift as a function of added base at 0° follows generally the same pattern as at −75°. The major differences seen are the magnitudes of overall change in chemical shift, and the sharpness of the break in the vicinity of $R = 1$. These results suggest that the equilibria at higher temperature are less complete, but otherwise the same as those at −75°. The chemical shifts of the α protons exhibit small, positive chemical shifts on base addition, closely corresponding to the results for the ^{7}Li chemical shifts.

Results similar to those shown in Figure 5 were obtained with the other bases studied. The results of a number of nmr studies, with various alkyllithium compounds and various bases, are summarized in Table I.

Colligative property studies of the effect of added bases on hydrocarbon solutions of the alkyllithium compounds are carried out by adding successive quantities of base to a series of solutions containing the same concentration of the alkyllithium compound, and noting the effect on the freezing point. Analysis of the data is extremely difficult because of the multitude of equilibria which might be operative. The hexamer species are most troublesome in this regard, since the hexamer apparently reverts to a tetrameric form at some point in the addition of base. It seems quite clear from the accumulated evidence that alkyllithium compounds are largely tetrameric in solutions of even strongly basic substances such as diethyl ether (DEE), tetrahydrofuran (THF), or triethylamine (TEA). On the basis of the nmr results it appears that the shift from hexamer to tetramer occurs in the

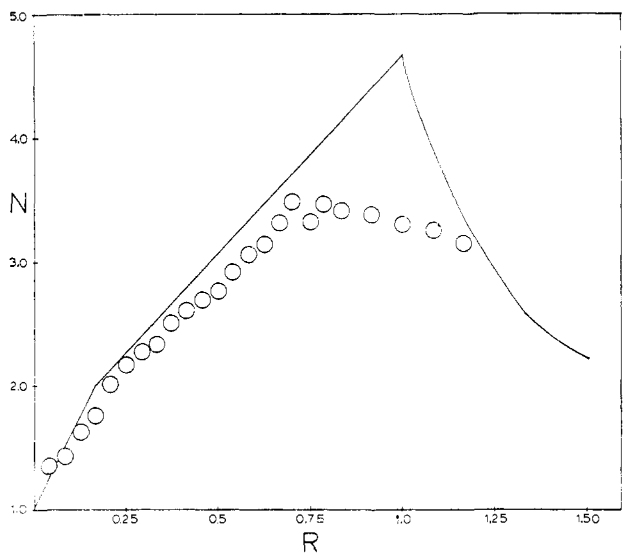

Figure 6. Limiting behavior of N *vs.* R assuming 1:1 hexamer-base complex and subsequent conversion to tetrasolvated tetramer at $R = 1$. Data points represent results for 0.050 *m* *n*-butyllithium with added THF in cyclohexane.

region of base concentration corresponding to less than one base per lithium atom.

Table I. Limiting ^{7}Li nd ^{1}H Chemical Shift Changes for Addition of Base to 0.075 *M* Cyclopentane Solutions of Alkyllithium Compounds

Alkyl group	Base[a]	Temp, °C	^{7}Li chemical shifts[b]	^{1}H chemical shifts[b]
C_2H_5	THF	25	0.75	0.23
		−75	0.85	
n-C_4H_9	THF	0	1.00	0.18
		−75	1.00	
C_2H_5	DEE	0	0.60	0.13
		−75	0.65	
n-C_4H_9	DEE	0	0.65	0.15
		−75	0.75	
C_2H_5	TEA	0	0.25	
		−76	0.35	
n-C_4H_9	TEA	0	0.25	0.15
		−75	0.50	
i-C_3H_7[c]	TEA	28	0.16	
		−95	0.15	
t-C_4H_9[c]	TEA	28	0	
		−75	0	
n-C_4H_9	Quin	0	0.84	0.34
		−75	1.00	
C_2H_5	Quin	0	0.80	0.39
		−75	0.90	
n-C_4H_9	TMEDA	0	0.20	0.31
		−75	0.20	
C_2H_5	Cineole	−25	0.3	
		−75	0.4	

[a] THF = tetrahydrofuran; DEE = diethyl ether; TEA = triethylamine; Quin = quinuclidine; TMEDA = tetramethylethylenediamine. [b] The estimated limiting value for the upfield change in ppm in ^{7}Li or ^{1}H chemical shift upon addition of base, in the region of low base concentration, *i.e.*, when $20 > R > 6$. The proton chemical shifts refer to the estimated centers of the α-methylene multiplets. [c] [RLi] = 0.125 *M*.

Following the convention of earlier work, we define a function N as

$$N = \frac{m_{\mathrm{Li}} + m_{\mathrm{b}}}{m_{\mathrm{obsd}}} \qquad (1)$$

where m_{Li} and m_{b} represent the initial molalities of the alkyllithium oligomer and base, respectively, and m_{obsd} represents the molality as determined from the freezing point lowering. This function does measure departure from a simple solution of noninteracting alkyllithium compound and base, although it does not correspond to an average number of bases associated per lithium atom, or some similar physically simple concept. Such functions can be defined for cases where the total molality of the acid species in the acid–base system is constant,[21] but hexamer–tetramer conversion obscures their quantitative significance in the systems under study here. It is possible, however, to gain an appreciation for the nature and extent of the equilibria present in the alkyllithium–base systems if a few assumptions are granted on the basis of the results obtained from colligative property and nmr studies in neat base, and the nmr chemical shift results presented here. We assume that the addition of base to hexameric alkyllithium compounds leads to formation of solvated tetramers, and that the shift to tetramers occurs at low base/Li ratios, *i.e.*, $R < 1$. Similarly, we assume that interaction of bases with alkyllithium tetramers leads only to solvation of tetramers, as opposed to extensive dissociation of the tetrameric units to solvated dimers or monomers.

If the solvation of an alkyllithium hexamer proceeded smoothly to form tetrasolvated tetramer

$$R_6Li_6 + 6B \longrightarrow {}^3/_2R_4Li_4 \cdot B_4 \qquad (2)$$

and if the reaction went to completion, the N value at $R = 1$ would be 4.67. We assume that this occurs through initial formation of a 1:1 complex with hexamer

$$R_6Li_6 + B \longrightarrow R_6Li_6 \cdot B \qquad (3)$$

Subsequent addition of base is then assumed to lead to a gradual shift from hexamer to tetramer. With these assumptions the N *vs.* R graph should follow the solid line shown in Figure 6. The data for 0.0500 *m* *n*-butyllithium with THF in cyclohexane are depicted on the figure for comparison. In general, at low R, the data follow the solid line quite well. The departure from the results expected for completed equilibria at R values of about 0.75 and higher is presumably due to the diminishing formation constant for successive additions of base. Assuming that all the *n*-butyllithium has been converted to tetramer, the observed value of N for $R = 1.0$ corresponds to an average of 3.6 bases coordinated per *n*-butyllithium tetramer.

It should be noted in passing that the general character of the N *vs.* R graphs in the range of $R = 1$ or less for the stronger bases is inconsistent with the assumption that dimers are formed as the predominant solvated alkyllithium species. In order for N to attain a maximum value in the range $R < 1$, the ratio of solvating base to lithium in the predominant species formed must not be too different from 1. This means that the major species formed if dimers were predominant would be a mono- or disolvated dimer

$$R_6Li_6 + 3B = 3R_2Li_2 \cdot B \qquad (4)$$

$$R_6Li_6 + 6B = 3R_2Li_2 \cdot B_2 \qquad (5)$$

---

[21] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, pp 43, 260.

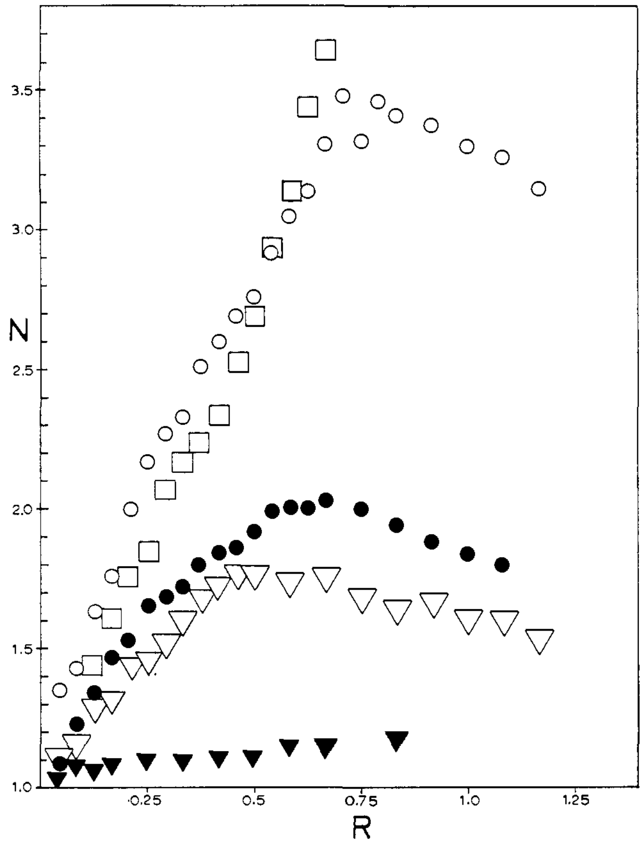

Figure 7. Colligative property data for 0.0500 m solutions of $(n\text{-}C_4H_9Li)_6$ in cyclohexane with added bases: ○, THF; ●, diethyl ether; ▽, triethylamine; □, quinuclidine, 0.0250 m $(n\text{-}C_4H_9Li)_6$; ▼, 0.0250 m $(C_2H_5Li)_6$ + cineole; R = (base)/(Li), where (Li) is the concentration of lithium atoms in the solution.

In the first instance the maximum attainable value for N would be 1.33 at R = 0.5; in the second case, it would be 2.33 at R = 1. Obviously, neither of these possibilities is in accord with the results for the stronger bases studied, *i.e.*, for THF or quinuclidine (*vide infra*). It might be argued that dimers are formed in more concentrated base, but the nmr[16,17] and colligative property[15] evidence supports rather the hypothesis that the alkyllithiums subsist as solvated tetramers in the solvents studied.

The graphs of N *vs.* R for a given alkyllithium compound with a series of bases should reveal a relative order of extent of interaction of the bases with the alkyllithium compound. In Figure 7 are shown the data for interaction of n-butyllithium in cyclohexane with a series of bases. The results with quinuclidine could unfortunately not be extended reliably beyond the range of R = 0.6 because of precipitation, but the indications are that N attains values in excess of 4. The general trend of the data at low R values suggests that quinuclidine and THF possess comparable abilities to interact with n-butyllithium, that triethylamine and diethyl ether are similar, and that the highly hindered base, cineole, interacts very little with alkyllithium. Assuming that the n-butyllithium is in the form of solvated tetramer at R = 1, the average number of bases coordinated to each tetramer can be calculated from the value of N to be 3.6, 2.5, and 2.1 for THF, diethyl ether, and triethylamine, respectively. Data for n-butyllithium with diethyl ether at two different concentrations of the alkyllithium reagent are shown in Figure 8. A lower value for the maximum value of N attained in the more dilute solution, but an otherwise similar N *vs.* R graph, is consistent with the existence of incomplete equilibria. Similar data were obtained for a number of alkyllithium compounds with a variety of bases.

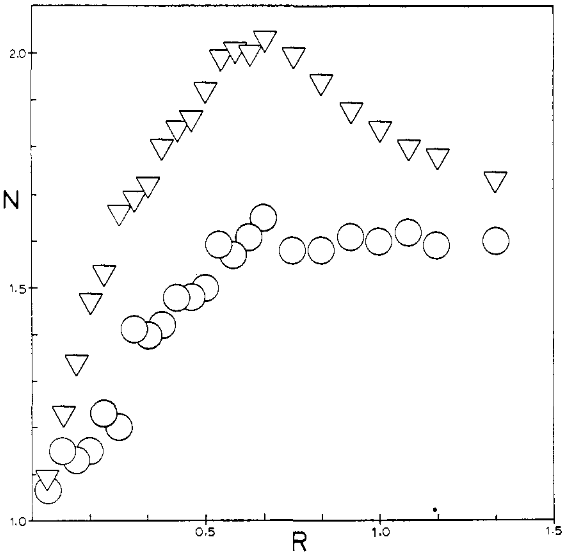

Figure 8. Colligative property data for n-butyllithium in cyclohexane with diethyl ether: ○, 0.0125 m $(n\text{-}C_4H_9Li)_6$; ▽, 0.0500 m $(n\text{-}C_4H_9Li)_6$.

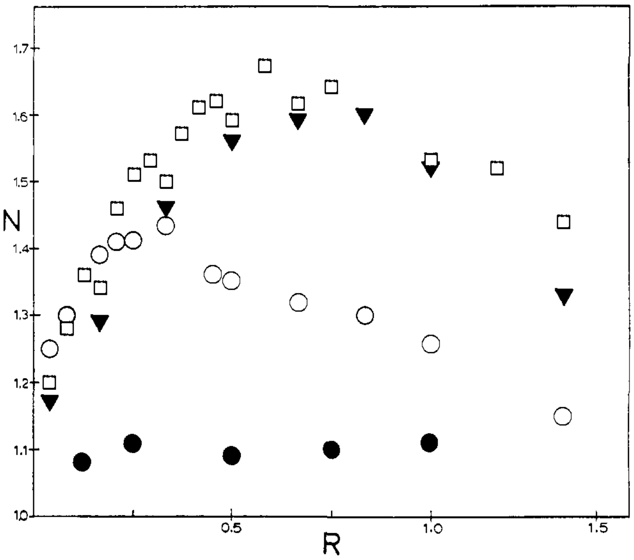

Figure 9. Colligative property data for various alkyllithium compounds in cyclohexane with added triethylamine: ○, 0.0250 m $[(CH_3)_3SiCH_2Li]_6$; ▼, 0.0250 m $(n\text{-}C_4H_9Li)_6$; □, 0.0250 m $(C_2H_5Li)_6$; ●, 0.0250 m $(t\text{-}C_4H_9Li)_4$.

The steric effect of the bases on the extent of interaction with n-butyllithium, exemplified in the data shown in Figure 7, has its counterpart in the effect of varying steric properties of the alkyllithium compound. Figure 9 shows the N *vs.* R graphs for a series of alkyllithium compounds with triethylamine. It is quite evident that increased branching in the alkyl group, especially in the α position, impedes complexation. Although the extent to which the interaction is impeded is dependent on the base also, similar

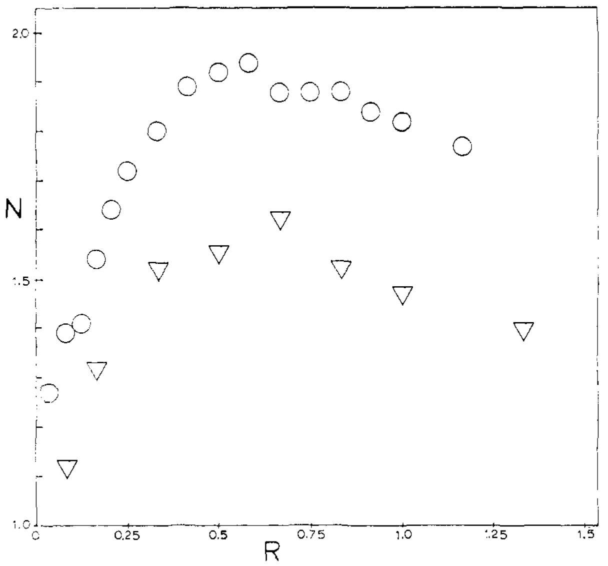

Figure 10. Colligative property data for 0.0250 *m* $(C_2H_5Li)_6$ with added diethyl ether in: ○, cyclohexane; ▽, benzene.

data for a limited number of other systems indicate the same general trend shown in Figure 9. In the case of trimethylsilylmethyllithium, the results suggest that formation of an adduct with the first molecule of base must proceed quite readily, but that steric factors come into play with addition of further base molecules. Assuming conversion to solvated tetramer, the value of N at $R = 1.0$ corresponds to an average of only 1.3 bases per tetramer. Although there are significant differences in concentrations and temperature, the present studies are in very satisfactory general agreement with the results reported by Bartlett and coworkers[18] for alkyllithium–dimethyl ether interactions.

The effect on the alkyllithium–base interaction of changing solvent from a saturated to an aromatic hydrocarbon is shown in Figure 10, in which N *vs.* R is shown for ethyllithium with added diethyl ether in cyclohexane and benzene. The equilibria appear to proceed to a smaller extent in benzene. This may be a reflection of the competition between added base and aromatic solvent for coordination to alkyllithium. Interaction of benzene or other aromatic hydrocarbons with alkyllithium compounds is suggested by the observation that certain of the alkyllithium compounds are hexameric in cyclohexane and tetrameric in benzene. In addition rates of intermolecular exchanges between alkyllithium oligomers appear to be faster in toluene than in cyclopentane.[22]

In summary, the present work provides new colligative property data of greater extent and precision than heretofore available regarding the associations of alkyllithium compounds in hydrocarbon solvents. Colligative property and nmr data indicate that bases interact with alkyllithium compounds in hydrocarbon solution to produce solvated tetrameric species at base concentrations corresponding to one base per lithium, or less. The number of solvating bases per tetramer is related to the steric requirements of the alkyl group in the $(RLi)_4$ species, to the steric requirements of the base, and to inherent donor ability of the base.

Acknowledgments. The authors are indebted to Dr. R. W. Lauver and Dr. D. L. Tibbetts for helpful discussions, and to Mr. Robert Thrift for assistance in obtaining nmr spectra.

(22) M. Y. Darensbourg, B. Y. Kimura, G. E. Hartwell, and T. L. Brown, *J. Amer. Chem. Soc.*, **92**, 1236 (1970).

Kinetics of the Reaction of Trialkyl Phosphites with Benzil

Yoshiro Ogata and Mitsuji Yamashita

Contribution No. 149 from the Department of Applied Chemistry,
Faculty of Engineering, Nagoya University, Chikusa-ku, Nagaya, Japan.
Received November 18, 1969

Abstract: The reaction of trialkyl phosphites with benzil to form a cyclic adduct (**1**) has been studied kinetically in anhydrous dioxane and benzene. The rate is expressed as $v = k[(RO)_3P][PhCOCOPh]$. An Arrhenius plot gives the values of 8.41 kcal mol^{-1} and -47.5 eu for the activation energy and entropy, respectively. The rate constant increases with increasing dielectric constant of the solvent. In a benzene solution the rate constant increases with an increasing amount of added organic acid (*e.g.*, acetic acid) and decreases with an increasing amount of added triethylamine. The plot of k *vs.* [acid] or [base] gives a straight line at low concentrations. The reactivity of trialkyl phosphites is affected by alkyl groups in the order of Me < *sec*-Bu < Et < *i*-Pr. A mechanism involving a nucleophilic attack of the phosphorus atom on the carbonyl carbon is postulated and discussed.

The reaction of trialkyl phosphites with α-diketones such as biacetyl and benzil was first reported by Kukhtin, *et al.*[1] Ramirez, *et al.*,[2,3] have postulated a cyclic structure (**1**) for the 1:1 addition product (2,2,2-trialkoxy-1,3,2-dioxaphosphole) of trialkyl phosphite

---

(1) (a) V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, **121**, 466 (1958); *Chem. Abstr.*, **53**, 1105*a* (1959); (b) V. A. Kukhtin and K. M. Cerakhova, *Zh. Obshch. Khim.*, 30, 1208 (1960); *Chem. Abstr.*, **55**, 358*h* (1961); (c) V. A. Kukhtin, T. N. Voskoboeva, and K. M. Kirillova, *ibid.*, **32**, 2333 (1962); *Chem. Abstr.*, **58**, 9127*g* (1963); (d) K. M. Kirillova and V. A. Kukhtin, *ibid.*, **32**, 2338 (1962); *Chem. Abstr.*, **58**, 9128*c* (1963).

(2) (a) F. Ramirez, R. B. Mitra, and N. B. Desai, *J. Amer. Chem. Soc.*, **82**, 2651 (1960); (b) F. Ramirez and N. B. Desai, *ibid.*, **82**, 2652 (1960); (c) F. Ramirez and N. Ramanathan, *J. Org. Chem.*, **26**, 3046 (1961); (d) F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, **85**,