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SOLVENT EFFECTS ON THE AGGREGATION OF LITHIUM BIS(TRIMETHYLSILYL)AMIDE

BERT Y. KIMURA AND THEODORE L. BROWN
Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61820 (U.S.A.)

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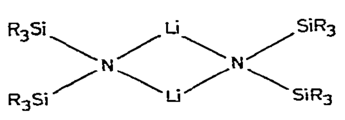
SUMMARY

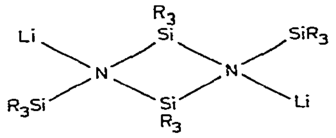
Concentration and temperature dependent ^1H and ^7Li NMR spectra have been evaluated for lithium bis(trimethylsilyl)amide, $LiN[Si(CH_3)_3]_2$, in ethers and hydrocarbon solvents. The results are interpreted in terms of a monomer–dimer equilibrium in THF and a dimer–tetramer equilibrium in hydrocarbon solvents. Thermodynamic parameters, $\Delta H^0 = -4.0$ kcal/mole, $\Delta S^0 = -17$ cal·deg^{-1}·mole^{-1}, obtained for the equilibrium, dimer $\rightleftarrows$ 2 monomer, in THF solutions indicate that the monomer is preferentially solvated in solution. These conclusions are substantiated by isopiestic molecular weight determinations.

The structural and physical properties of alkyl- and aryllithium compounds have been well established through extensive research in recent years. Characteristically, the structural units observed in solution are hexamer, tetramer or dimer, depending on both the nature of the organic group and of the solvent[1,2]. In hydrocarbon solution hexameric association occurs when the alkyl group is primary, whereas tert-butyllithium, on the other hand, is tetrameric. For intermediate degrees of steric requirements of the alkyl groups, the free energy difference between hexamer and tetramer may be small so that an equilibrium between the two forms is observed.

The available evidence suggests that organic groups which allow delocalization of the negative charge on the lithium-bearing carbon have a lower tendency toward higher aggregate formation than the simple alkyl groups. For example, benzyllithium is dimeric in benzene[3] and monomeric in THF[2], whereas n-butyllithium is hexameric in benzene[1] and tetrameric in diethyl ether[2].

To more fully evaluate the effect of solvent on aggregation of organolithium compounds we have investigated the structural properties of lithium bis(trimethylsilyl)amide. Unlike most organolithium derivatives involving Li–N, Li–P, Li–Si or Li–As linkage, lithium bis(trimethylsilyl)amide is readily prepared free of lithium halide, easily purified by sublimation, and soluble in hydrocarbon solvents[4]. Recent X-ray structural data[5] show lithium bis(trimethylsilyl)amide to exist as a cyclic trimer in the solid state. The vibrational spectrum in solution, however, is different from that of the solid. Molecular weight determinations in several solvents indicated dimeric units. Wannagat[6,7] has proposed a structure involving N–Li–N bridges in the dimer. It is claimed that infrared and Raman spectroscopy support (I) rather than (II).


(I)


(II)

Isotopic substitution of ^{6}Li for ^{7}Li enabled identification of vibrations of relatively weak Li–N bonds.

Wannagat reports that the ^{7}Li NMR spectrum of lithium bis(trimethylsilyl)-amide at 30° in aromatic hydrocarbon solution shows only one resonance[7]. Our investigations of the low temperature ^{7}Li and ^{1}H NMR spectra in various solvents show that equilibrium exists between two species of differing degrees of association. The extent of association of each depends on the nature of the solvent.

EXPERIMENTAL

All reagent transfers and preparations, whenever possible, were performed in an argon atmosphere glove box to avoid reaction of the organolithium reagent with oxygen and moisture. Traces of oxygen, water and organic solvents present were removed effectively by continuous circulation of the atmosphere through a purification train[8,9]. Addition of a column 30 cm in length and 8 cm in diameter charged with a mixture of phosphorus pentoxide (Mallinckrodt Aquasorb and J. T. Baker Granusic) and vermiculite aided in reducing the water vapor level to 1 ppm or lower.

After materials had been brought into the box from outside, the inside port door was generally kept closed at least 10 h, during circulation of the box atmosphere, before performing any operations.

Materials

Unless otherwise indicated, all hydrocarbon solvents were dried by passage through a four-foot column of activated silica gel (grade 40, 6–12 mesh, Davison Chemical Company, Baltimore, Md.) and stored over sodium wire in a glove box. Xylene (natural histological grade, Fisher Scientific Co., Pittsburgh, Pa.) was heated over molten sodium for two days, distilled at atmospheric pressure and stored over sodium wire. Methylcyclohexane was purified by distillation from a solution of crude tert-butyllithium. Crude diethyl ether was dried over lithium aluminum hydride, distilled and stored over sodium wire. Tetrahydrofuran (THF) was redistilled from sodium and stored over freshly prepared sodium wire. Bromobenzene (Fisher Scientific Co.) was refluxed under argon over phosphorous pentoxide, distilled and stored over molecular sieves (Linde 4A, Union Carbide Corp., N.Y.). All reagents were flushed thoroughly with argon before being transferred into the glove box.

Natural abundance lithium containing 1 % sodium was supplied by Lithium Corporation of America, Inc., N.Y. as a dispersion in mineral oil. The metal was freed from oil by repeated washings with a hydrocarbon. 1,1,1,3,3,3-Hexamethyldisilazane (Eastman Organic Chemicals, Rochester, N.Y.) was used without further purification.

Phenyllithium. Bromobenzene (7.9 ml, 11.9 g, 0.076 mole) dissolved in 15 ml ether was added dropwise to a mixture of 2.6 g (0.37 mole) of lithium powder in 35 ml ether. The reaction was executed at 0° outside the glove box while continuously maintaining a positive argon pressure. After 2 h, ether was removed under vacuum and the flask returned to the glove box. The solid was shaken with 50 ml of a 70/30 benzene/ether solution, and filtered through a medium sintered glass frit.

Lithium bis(trimethylsilyl)amide, [$LiN(SiR_3)_2$]. A slight modification of Wannagat and Niederprüm's method[4] was employed. The preparation was performed entirely within the glove box. Hexamethyldisilazane (3.0 ml, 0.014 mole) was dissolved in 30 ml ether. While the amine solution was stirred magnetically, 12 ml of 1.24 *M* (0.015 mole) of phenyllithium solution in 70/30 benzene/ether were added dropwise over a 15 min period. After 2–3 h the reaction mixture is deep orange. Solvent was then removed under vacuum and the resulting tan solid sublimed at 55° and 0.005 mm. The white sublimate is extremely soluble in amine and ether solvents, soluble in aromatic hydrocarbons and slightly soluble in cyclohexane and cyclopentane.

Nuclear magnetic resonance spectra

Solutions of $LiN(SiR_3)_2$ were transferred via syringes into NMR tube assemblies consisting of a NMR tube sealed to a standard stopcock. When desired, a reference capillary was inserted. The sample tubes were sealed off on a vacuum line after degassing. All samples, after being prepared at room temperature, were sealed off and stored at dry-ice temperature without delay to avoid decomposition.

For concentration-dependence studies, a stock solution was prepared by dissolving a weighed amount of freshly sublimed lithium bis(trimethylsilyl)amide in a volumetric flask. Calculated portions were then transferred to the sample tubes using a gas-tight syringe and diluted with solvent, yielding the desired concentrations on a monomer basis.

Concentrations of THF solutions were checked by integrating the absorptions due to the β protons of THF and the methyl resonance of lithium bis(trimethylsilyl)amide on the Varian A-60A spectrometer. The results compared favorably.

Solutions of lithium bis(trimethylsilyl)amide in a THF/toluene solvent system were prepared by mixing desired portions of 0.5 *M* (in monomer) toluene and THF stock solutions.

Physical measurements. ^{7}Li NMR studies were performed with a Varian Associates HA-100 spectrometer at 38.863 MHz operating in the HR mode. Varian A-60A or A-56/60 spectrometers were utilized for proton spectra. Low temperatures were made accessible by use of a V-6040 variable temperature controller with each instrument. Temperatures were measured with a copper–constantan thermocouple inserted in an NMR tube and lowered into the probe. Temperature readings are estimated at ±2°.

^{7}Li chemical shifts were measured relative to an aqueous lithium bromide standard (7 g LiBr in 10 ml solution) inserted as a capillary. Each spectrum was recorded several times and calibrated by the sideband technique each time.

^{1}H chemical shifts were generally determined relative to the solvent peaks and converted to the τ scale. The chemical shifts for lithium bis(trimethylsilyl)amide in a THF/toluene system were, however, measured relative to the H_2O protons in an aqueous LiBr external standard.

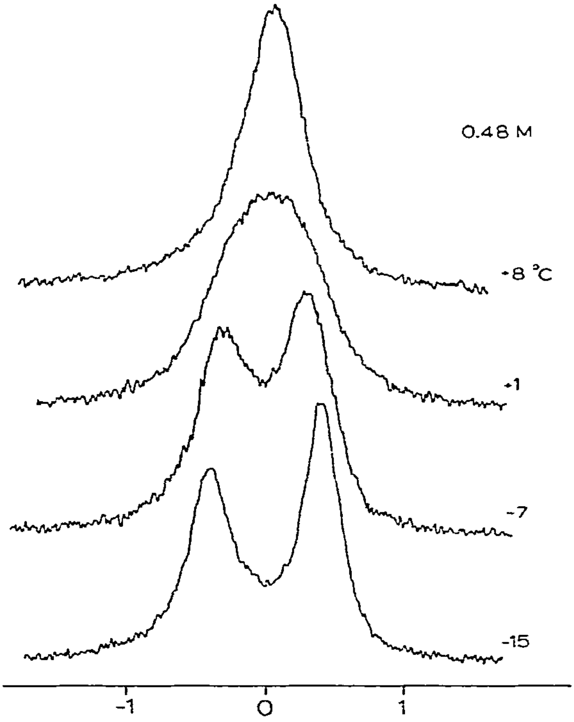
Absorption intensities were measured with a planimeter assuming symmetric line shapes where necessary to resolve partially overlapping bands.

Isothermal distillation for molecular weight determinations were performed in an apparatus modified from a design by Clark[10]. For the side arms, 14/20 joints were attached to vacuum stopcocks, to facilitate transfer of solid samples. The graduated side arms were constructed from Kimax pipets, 2 ml, with 1/100 ml graduations. Filling factors, necessitated because graduated markings did not commence at the tip, were determined by adding known volumes of methanol. The apparatus was tested for accuracy and precision of molecular weight measurement using known quantities of azobenzene or durene with biphenyl as a reference. Volumes were measured daily until the calculated molecular weight became constant. Significant temperature fluctuations were avoided by keeping the apparatus in the glove box.

The apparatus and procedures involved in freezing point measurements are described elsewhere[1,11]. Calibration curves were constructed from freezing point data for a series of biphenyl solutions in benzene.

RESULTS AND DISCUSSION

At room temperature, the ^{1}H NMR spectrum of a THF solution of LiN[Si(CH$_3$)$_3$]$_2$ consists of a sharp singlet at 10.09 τ and observable coupling constants of 117 Hz and 6.1 Hz for $J(^{13}C-^1H)$ and $J(^{29}Si-C-^1H)$ respectively*. A single relatively



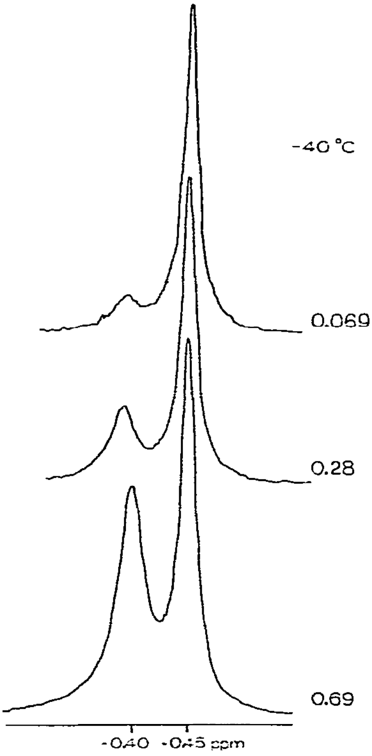


Fig. 1. Temperature dependence of ^{7}Li spectra of lithium bis(trimethylsilyl)amide in THF. Chemical shifts are in ppm relative to external aqueous LiBr.

Fig. 2. Concentration dependence of the ^{7}Li spectrum of lithium bis(trimethylsilyl)amide in THF.

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* For comparison $J(^{13}C-H)=98$ Hz for methyllithium, 120 Hz for tert-butyllithium, 100 Hz for n-butyllithium, 117 Hz for (trimethylsilyl)methyllithium and $J(^{29}Si-C-H)=6.1$ Hz for (trimethylsilyl)methyllithium.

broad resonance with a line width of 6 Hz is observed at δ −0.11 ppm (relative to aqueous LiBr) in the ^{7}Li spectrum. Two distinct resonances are observed in both ^{1}H and ^{7}Li spectra at low temperatures. Representative ^{7}Li spectra are shown in Fig. 1. Coalescence occurs at 0° in both instances, peak-to-peak separation being 0.21 ppm (^{1}H) and 0.82 ppm (^{7}Li) in the limit of slow intermolecular exchange. The ^{1}H spectra proved more useful for quantitative studies involving integration of absorption intensities because the narrower lines permitted more complete separation of absorptions. Although larger deviations from average values were obtained on integration of ^{7}Li spectra, as a result of greater overlap, comparisons of the intensities of ^{7}Li and ^{1}H spectra at corresponding temperatures yielded consistent results. The spectra are concentration-dependent, as exemplified in Fig. 2, thus ruling out restricted rotation of the $Si(CH_3)_3$ groups or inversion about the nitrogen atom as the cause of the multiplicity.

TABLE 1

EQUILIBRIUM CONSTANTS FOR LITHIUM BIS(TRIMETHYLSILYL)AMIDE IN THF

T (°C)	Concn[a] (M)	Intensity[b]		Concentration		K^c_{eq}	K_{eq}
		Monomer	Dimer	Monomer	Dimer		
^{1}H Data							
−60	0.69	0.700	0.300	0.48	0.10	2.3	2.7
−61	0.48	0.791	0.209	0.38	0.050	2.9	
−61	0.28	0.858	0.142	0.24	0.020	2.9	
−59	0.14	0.914	0.086	0.13	0.006	2.8	
−41	0.69	0.551	0.449	0.38	0.15	0.9	1.1
−41	0.48	0.641	0.359	0.31	0.086	1.1	
−40	0.28	0.731	0.269	0.20	0.038	1.1	
−38	0.14	0.841	0.159	0.12	0.11	1.3	
−39	0.069	0.901	0.099	0.062	0.0034	1.1	
−31	0.48	0.594	0.406	0.28	0.098	0.8	0.9
−30	0.28	0.717	0.283	0.20	0.040	0.9	
−31	0.14	0.804	0.196	0.11	0.014	1.0	
−22	0.69	0.511	0.489	0.34	0.18	0.6	0.8
−22	0.48	0.546	0.454	0.26	0.11	0.6	
−23	0.88	0.699	0.301	0.19	0.042	0.9	
−21	0.14	0.828	0.172	0.12	0.012	1.1	
−23	0.069	0.879	0.121	0.061	0.0042	0.9	
^{7}Li Data							
−62	0.69	0.770	0.230	0.53	0.079	3.5	2.8
−62	0.48	0.743	0.257	0.36	0.062	2.1	
−60	0.28	0.870	0.130	0.25	0.019	3.3	
−59	0.14	0.900	0.100	0.13	0.007	2.3	
−40	0.69	0.529	0.471	0.36	0.16	0.8	0.9
−40	0.48	0.601	0.399	0.29	0.096	0.9	
−42	0.28	0.757	0.243	0.21	0.034	1.3	
−39	0.069	0.864	0.136	0.060	0.0047	0.8	

[a] Concentration in monomer. [b] The intensity data relate only to the relative areas of the two absorptions in each spectrum, and are not comparable from one spectrum to another. [c] Moles/liter.

The concentration-dependence (Table 1) suggests that the NMR observations are best interpreted in terms of an equilibrium between two organolithium species, one twice as highly associated as the other:

$$[\mathrm{LiN(SiR_3)_2}]_n\cdot(\mathrm{THF})_x + y\,\mathrm{THF} \rightleftarrows 2\,[\mathrm{LiN(SiR_3)_2}]_{n/2}\cdot(\mathrm{THF})_{(x+y)/2} \tag{1}$$

$$K_{\mathrm{eq}} = \frac{\{[\mathrm{LiN(SiR_3)_2}]_{n/2}\}^2}{\{[\mathrm{LiN(SiR_3)_2}]_n\}}$$

A model involving a single aggregation, but differing degrees of solvation is an alternative to the above:

$$[\mathrm{LiN(SiR_3)_2}]_n\cdot(\mathrm{THF})_x + y\,\mathrm{THF} \rightleftarrows [\mathrm{LiN(SiR_3)_2}]_n\cdot(\mathrm{THF})_{x+y} \tag{2}$$

$$K_{\mathrm{eq}} = \frac{\{[\mathrm{LiN(SiR_3)_2}]_n\cdot(\mathrm{THF})_{x+y}\}}{\{[\mathrm{LiN(SiR_3)_2}]_n\cdot(\mathrm{THF})_x\}}$$

The equilibrium constant results, however, also eliminate this possibility.

In a basic solvent, both species in eqn. (1) are undoubtedly solvated, although probably not to the same extent. Two possibilities are reasonable for n, 4 or 2, *i.e.*, a tetramer–dimer or a dimer–monomer equilibrium. Lithium bis(trimethylsilyl)amide was initially reported as dimeric in benzene[4]. THF, a more strongly interacting solvent, should promote dissociation of an organolithium aggregate, so a dimer–monomer equilibrium is a likely possibility in this solvent.

Unlike alkyl- and aryllithium compounds, lithium bis(trimethylsilyl)amide is stable to decomposition in solution. ^{1}H NMR spectra for THF solutions left at room temperature for several weeks remain apparently unchanged. Because of this stability the determination of apparent molecular weight utilizing the isopiestic method is feasible. The results of colligative property measurements (Table 2) support the conclusions based on NMR data. The isopiestic data for THF are not quantitatively very reliable, because the solvent does not have sufficiently high vapor pressure for best results with this technique, but they suggest that lithium bis(trimethylsilyl)amide is considerably less than two-fold associated under the experimental conditions. The data for ether also clearly show that the solute is less than two-fold associated.

TABLE 2

ASSOCIATION OF LITHIUM BIS(TRIMETHYLSILYL)AMIDE IN VARIOUS SOLVENTS

Method[a]	Solvent	Concn.[b] (M)	Apparent mol.wt.	n[c]
Freezing point lowering	Benzene	0.257	358	2.14
Isopiestic	Ether	0.0939	268	1.60
Isopiestic	Ether	0.171	268	1.60
Isopiestic	Ether	0.235	296	1.77
Isopiestic	THF	0.105	172	1.03
Isopiestic	THF	0.100	173	1.03
Isopiestic	THF	0.112	192	1.15

[a] All isopiestic determinations performed at 23°. [b] Concentration in monomer. [c] Degree of association.

Thermodynamic parameters for the observed equili rium in THF were obtained by a plot of log K_{eq} *vs.* $1/T$ for data in the temperature range −22 to −82° (Fig. 3): $\Delta H^0 = -4.0$ kcal/mole, $\Delta S^0 = -17$ cal·deg^{-1}·mole^{-1}. It is noteworthy that the dissociation process in THF is *exothermic*. The negative values of ΔH and ΔS reflect the role of the solvent in preferentially solvating lithium in the more dissociated species. The extent of solvation could not be determined specifically. It is expected that there should be a facile exchange between uncoordinated and coordinated THF molecules at a rate greater than the rate of dissociation and recombination of $[LiN(SiR_3)_2]_2$.

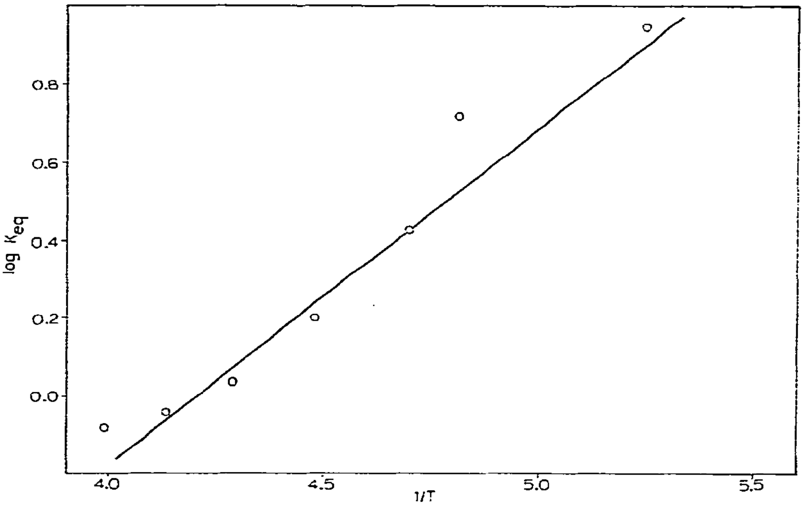

Fig. 3. Plot of log K_{eq} *vs.* $1/T$ (°K) based on a dimer–monomer equilibrium for lithium bis(trimethylsilyl)amide in THF.

In a polar solvating medium such as THF, alkali metal salts exist as solvent-separated ion pairs in equilibrium with contact ion pairs[12–14]. It is conceivable that lithium bis(trimethylsilyl)amide may behave similarly:

$$LiN(SiR_3)_2 \rightleftharpoons Li^+ + N(SiR_3)_2^- \quad (3)$$

or,

$$[LiN(SiR_3)_2]_2 \rightleftharpoons Li^+ + Li[N(SiR_3)_2]_2^- \quad (4)$$

Equilibrium (3) is improbable on the basis of colligative property measurements. In THF, the observed degree of association is greater than 1.0, whereas under the conditions of (3), it should be less than 1.0.

The ^7Li chemical shift data are helpful in ruling out both equilibria (3) and (4). Lithium tetraalkylmetallates, $LiMR_4$ (M = Al, B or Ga), are polar compounds which subsist as ion pairs in strongly solvating media[12,14]. Their ^7Li chemical shifts at 30° in ether solution range from +1.3 to +1.7 ppm relative to aqueous lithium bromide. On this basis, the above equilibria are improbable, since the ^7Li chemical shift of the higher field resonance observed for lithium bis(trimethylsilyl)amide in THF is only +0.45 ppm at −45°.

Attempts to evaluate a monomer–dimer equilibrium in diethyl ether proved unsuccessful. At 0°, precipitation of a crystalline white solid, presumably an etherate complex, occurs, even for a 0.1 *M* ether solution. Wannagat and Niederprum[4] have isolated and characterized a 1/1 ether complex of lithium bis(trimethylsilyl)amide.

In cyclohexane, cyclopentane, methylcyclohexane, toluene, xylene and mesitylene, two distinct ^{1}H resonances are observed upon cooling the respective solutions. Only one extremely broad ^{7}Li resonance is discernible in toluene solutions at lower temperatures. Consequently, only ^{1}H NMR spectra were observed for hydrocarbon solutions. As in THF solutions, the spectra exhibit concentration dependence; the downfield resonance corresponds to the more highly associated species. Examination of the calculated equilibrium constants in methylcyclohexane (Table 3) suggests that the equilibrium is of the same general type as in THF, *i.e.*,

$$[\mathrm{LiN(SiR_3)_2}]_n \rightleftarrows 2\,[\mathrm{LiN(SiR_3)_2}]_{n/2} \qquad (5)$$

TABLE 3

EQUILIBRIUM CONSTANTS FOR LITHIUM BIS(TRIMETHYLSILYL)AMIDE IN METHYLCYCLOHEXANE

T (°C)	Concn. (M)	Intensity		Concentration		K_{eq}	$\overline{K_{eq}}$
		Monomer	Dimer	Monomer	Dimer		
−45	0.32	0.578	0.422	0.185	0.0675	0.51	0.36
−44	0.15	0.627	0.373	0.0941	0.0280	0.32	
−44	0.11	0.690	0.310	0.0759	0.0171	0.34	
−45	0.064	0.748	0.252	0.0479	0.00806	0.28	
−14	0.32	0.535	0.465	0.171	0.744	0.39	0.36
−15	0.15	0.647	0.353	0.0971	0.0265	0.36	
−14	0.11	0.661	0.339	0.0727	0.0186	0.35	
−14	0.064	0.773	0.227	0.0495	0.00726	0.34	

Large fluctuations in the calculated equilibrium constants result from solubility limitations, which necessitated working with low concentrations in a small range (0.1–0.3 *M* in monomer). Nevertheless, it does appear from the dependence of K_{eq} on temperature that ΔH^0 is approximately zero or slightly positive. In the presence of a strongly interacting solvent such as THF, the monomer is preferentially solvated, as discussed earlier, and ΔH is negative. On the other hand, in methylcyclohexane or mesitylene, solvent participation is absent or occurs to a much lesser degree. If the equilibrium involved dissociation of dimer to monomer, ΔH^0 should be large and positive, contrary to what is observed. A tetramer–dimer equilibrium must thus be considered as an alternative possibility. It is consistent with a tetramer–dimer equilibrium that coalescence in the NMR spectra of the saturated hydrocarbon solutions occurs at +30°, only slightly higher than for THF. If the same equilibrium were involved in both THF and hydrocarbon solutions, the coalesence temperature for the latter should be much higher than for THF. As expected, coalesence in mesitylene occurs at a lower temperature (−30°) than in cycloalkanes. The fact that coalescence of the two absorptions in mesitylene occurs at a much lower temperature than coalescence in THF also strongly suggests that different equilibria are involved.

Solvent effects

Comparison of ^1H spectra for toluene, xylene and mesitylene solutions of the same concentration at a given temperature corresponding to slow intermolecular exchange reveals an interesting and somewhat surprising effect (Fig. 4): The relative concentration of the species we presume to be tetramer (represented by the lower field resonance) increases in the order toluene < xylene < mesitylene. This order is just the reverse of solvent basicity, and, therefore, also of the expected order of shift toward dimer in accord with the hypothesis that the shift is due mainly to solvent interaction. The diminished solvent effect in xylene, and even further in mesitylene, is attributed to steric hindrance which impedes packing of solvent molecules about a solute particle. Thus, on this basis, the lithium bis(trimethylsilyl)amide tetramer is more strongly solvated in toluene than in mesitylene.

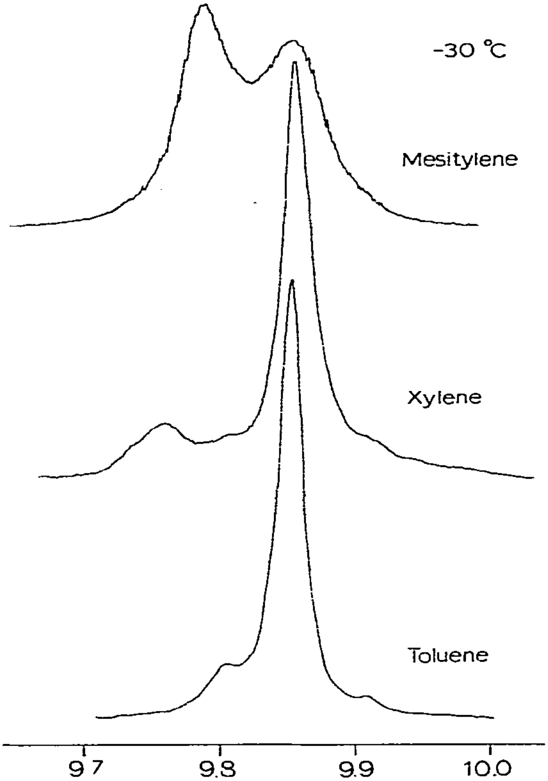

Fig. 4. Solvent dependence of the ^1H spectrum of lithium bis(trimethylsilyl)amide in aromatic solvents. Chemical shifts are given as τ values.

^1H NMR spectra in a mixed THF/toluene system at −40°, a temperature corresponding to slow intermolecular exchange, were obtained in order to gain further insight as to the effect of a more basic solvent medium. Lithium concentrations remained constant from sample to sample as the THF/toluene ratio was varied. As base is added initially, the two resonances assigned to tetramer and dimer in pure toluene merge, indicating that all tetramers have been converted to dimers. With large THF/toluene ratios two peaks are present, one (dimer) at lower field insensitive of base concentration and another (monomer) progressively increasing in chemical shift and intensity (Fig. 5). The increase in monomer intensity with increasing amounts of THF parallels the intensity changes observed for the concentration dependence of THF solutions as described previously. It is evident from the spectra that the chemical shift of the resonance due to the monomer species moves upfield relative to the dimer with increasing fraction of polar solvent. Whereas the dimer species (I) involves four-coordination at nitrogen, the monomer possesses a lone pair of electrons on this atom. This lone pair of electrons is subject to delocalization onto the two $Si(CH_3)_3$ groups through p_π–d_π bonding. The extent of this delocalization can be expected to vary with the degree of coordination of the lithium atom bound to nitrogen. Thus, on a time-averaged basis, the upfield shift of the methyl resonances of the monomer should be sensitive to increasing extent of solvation by THF with increasing THF concentration.

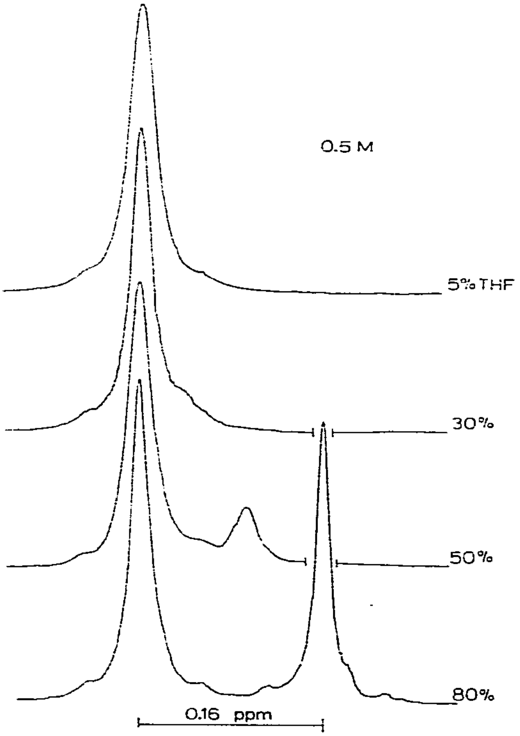

Fig. 5. ^1H spectra of lithium bis(trimethylsilyl)amide in a THF/toluene mixed solvent system.

In comparing the degrees of association of alkyllithium (tetramer), phenyllithium (monomer–dimer) and benzyllithium (monomer) in basic solvents, West and Waack[2] have indicated that formation of strong bridge bonds involving carbon is associated with localization of charge on the bridging atoms Although information is lacking, similar considerations probably also apply to nitrogen and oxygen bridged systems. Lithium tert-butoxide is hexameric in solution and in the vapor phase[15]; the related siloxy compound, $LiOSi(CH_3)_3$, is hexameric or even more highly associated[16]. Lithium bis(trimethylsilyl)amide, on the other hand, appears to be more closely related to benzyllithium, which is much less extensively associated. Furthermore, both behave similarly with regard to solubility and both are comparatively unreactive, even with THF. Delocalization of charge in the amide moiety might be responsible for this behavior. The interaction of the nitrogen p_π orbital with a vacant d_π orbital of silicon would facilitate removal of charge from the bridging nitrogen as previously suggested by the NMR observations of lithium bis(trimethylsilyl)amide in THF/toluene mixed solvent.

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