SOLVATION OF INDENYLLITHIUM AND INDENYLPOTASSIUM STUDIED BY ^{13}C NMR SPECTROSCOPY

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Polarization of the π-electron systems of indenyllithium (In$^-$Li$^+$) and indenylpotassium (In$^-$K$^+$), which is generally indicative of the degree and tightness of contact ion pairing, was investigated by ^{13}C NMR spectroscopy. The effect of changing solvent is about two thirds as great for In$^-$K$^+$ as for In$^-$Li$^+$. The indenyl anion is more strongly polarized with Li$^+$/dimethyl sulfoxide than with Li$^+$/ammonia, whereas the reverse is observed for In$^-$K$^+$. Complexation of In$^-$K$^+$ in tetrahydrofuran (THF) by cryptand(2,2,2) results in a π-electron distribution identical with that of In$^-$Li$^+$ in hexamethylphosphoramide, indicative of solvent- or agent-separated ion pairs or free ions. Small but significant cation–anion interactions are observed for In$^-$K$^+$ in hexamethylphosphoramide and for In$^-$N$^+$Me$_4$ in THF.

INTRODUCTION

An understanding of the mechanisms of solvation of organometallic compounds has become increasingly important in recent years. Solvation affects ion pairing,[1,2] which in turn affects chemical reactivity[2,3] to a significant degree. An experimental solvent scale is important for preparative work and a knowledge of charge-density distribution and ion pair structure is essential for an understanding of the regioselectivity of many carbanionic reactions.

In a previous ^{13}C NMR study of the solvation of indenyllithium (In$^-$Li$^+$) by a principal components data analysis, a solvation scale was established for ether solvents and other relatively inert and polar solvents.[4] The scale ranges from solvents such as diethyl ether (Et$_2$O), in which In$^-$Li$^+$ exists predominantly as contact ion pairs (c.i.p.s), to hexamethylphosphoramide (HMPA), in which solvent-separated ion pairs (s.s.i.p.s) or 'free' ions predominate. This solvation scale was derived primarily for the prediction of solvent effects on lithium salts of delocalized carbanions.

This study had the following aims: (a) to construct a solvation scale for indenylpotassium (In$^-$K$^+$) and to compare it with that for In$^-$Li$^+$; (b) to include an important solvent, ammonia, in both scales; and (c) to assess the effectiveness of various strategies for separating the centers of positive and negative charge by employing a complexing agent [cryptand(2,2,2)] for In$^-$K$^+$ or a bulky counter ion [tetramethylammonium (Me$_4$N$^+$)]. By this approach we sought to gain a better understanding of the specific interactions involved in solvation.

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RESULTS AND DISCUSSION

The indenyl anion (1) constitutes an ideal model system for solvation and ion pairing studies of delocalized carbanions because of its rigidity, thermal stability and sensitive ^{13}C chemical shift dependence on changes in charge density and ion pairing. Consequently, its alkali metal salts have been extensively investigated by UV–visible[5] and NMR[4,6] spectrometry and by x-ray diffraction.[7] NMR[6b–d] and x-ray[7a] studies have shown that the cation in the contact ion pair of $In^- Li^+$ has a preferred position(s) above the five-membered ring, resulting in the polarization of the π-electron system toward this ring. When the solvation of the cation is increased, changes occur in the interionic distances, which in turn cause a decreased π-electron polarization and a redistribution of charge from the five-membered ring to C_4–C_7 in the six-membered ring. Consequently, the ^{13}C resonances of the five-membered ring (most noticeably those of C_2 and $C_{3a,7a}$) move downfield, whereas those of $C_{4,7}$ and $C_{5,6}$ are shifted upfield (Table 1).

We employ the difference in the two most affected chemical shifts ($\delta C_{3a,7a} - \delta C_{5,6} = \Delta\delta$) as a measure of the polarization of the indenyl anion. We have determined that $\Delta\delta$ correlates well ($r = 0 \cdot 99$) with the difference between the average ^{13}C chemical shift (δ_{av}) for C_4–C_7 and δ_{av} for the five-membered ring carbons for both $In^- Li^+$ and $In^- K^+$. The $\Delta\delta$ value reflects the 'tightness' of the overall ion pairing, which is dependent on two factors, the proportion of c.i.p.s and the degree of cation–anion interaction within the c.i.p.s.
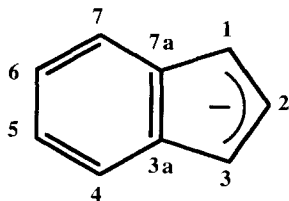
A change in the average distance between the anion and the cation can result from both a change in the ion pairing equilibrium and, to a lesser extent, from a change in the effective radius of the solvated cation in a c.i.p., i.e. to variable external solvation of the c.i.p. Furthermore, different c.i.p.s may exist that have different degrees of external solvation and different interaction sites in the anion.[8] Any estimation of c.i.p./s.s.i.p. ratios from NMR chemical shifts alone will therefore be only approximate. [le Noble[9] has pointed out that s.s.i.p.s may not be important energy minima for heavier cations.]

Solvent effects

The tightness of the ion pairing decreases on going from ether solvents to dipolar aprotic solvents, as expected. However, several interesting points emerge from the data in Table 1. Although the polarization of $In^- K^+$ in HMPA is less than for this species in ether solvents, the $\Delta\delta$ value is smaller (i.e. greater polarization of the anion) than the nearly identical $\Delta\delta$ values observed for $In^- Li^+$ in HMPA and $In^- K^+$ in THF–cryptand(2,2,2). The ion pairing equilibria in the latter systems are probably completely shifted towards solvent-separated ion pairs (or free ions) with negligible anion–cation interaction. Hence the use of HMPA is not sufficient to cause complete solvent separation of $In^- K^+$. Evidence for contact ion pairing has previously been observed for cyclooctatetraenedipotassium in HMPA[10] and for 1-phenylallylpotassium in HMPA–THF.[11] The present results provide evidence for a small but significant degree of contact ion pairing of the potassium salt of a delocalized monoanion in neat HMPA.

The corresponding $\Delta\delta$ values indicate that $In^- Li^+$ is more polarized in DMSO than in NH_3, whereas the reverse is observed for $In^- K^+$. This illustrates the important point that solvent scales for carbanions can display counter ion dependence. This reversal may reflect the greater polarizabilities of DMSO and K^+ relative to ammonia and Li^+, respectively (principle of hard and soft acids and bases),[12] although evidence presented below suggests that hydrogen bonding between In^- and NH_3 may play a role.

Evidence for the interaction of solvents with carbanions has been obtained from pulsed high-pressure mass spectrometric studies of anion-solvent clusters.[13] Previous studies by IR,[14] UV–visible[2,15] and ESR[16] spectroscopy have led to the conclusion that carbanions and other anions are solvated by or hydrogen bonded with NH_3 and primary amines. However, the exact nature of these interactions is unknown, although in several studies structural models involving cation-assisted hydrogen bonding have been proposed.[2,14] Recently, an x-ray diffraction study of a complex of fluorenyllithium with two diaminoethylenes indicated that the fluorenyl anion was stabilized by hydrogen bonding with amine hydrogens directed towards the C_9 position.[17]

With this background, it is of considerable interest that $\Delta\delta$ decreases (increased polarization) on decreasing the temperature of the $In^- Li^+$–NH_3 and $In^- K^+$–NH_3 systems. This behavior is exactly the opposite of that observed for these compounds in THF. The latter result has been satisfactorily explained on the basis of a shift toward s.s.i.p.s at lower temperatures owing to a negative entropy change on going from c.i.p.s. to s.s.i.p.s.[1,2]

We propose that a similar shift occurs in NH_3 but that increased polarization of In^- results owing to hydrogen bonding between NH_3 and the sites of highest negative charge density in In^- (primarily C_1 and C_3). This idea was tested by investigating $In^- Li^+$ and $In^- K^+$ in ND_3. The observation (see Table 1) that $\Delta\delta$ is ca $0 \cdot 2$ ppm greater for ND_3 than for NH_3 at $- 65\,°C$ is fully consistent with this proposal.

Table 1. ^{13}C NMR chemical shifts of indenyllithium and indenylpotassium in various solvents[a]

Solvent[b]	Counter ion	Concentration (M)	Temperature (°C)	$C_{1,3}$	C_2	$C_{3a,7a}$	$C_{4,7}$	$C_{5,6}$	$\Delta\delta(C_{3a,7a} - C_{5,6})$
Et$_2$O[c]	Li	0·27	25	92·13	115·42	128·14	120·66	116·13	12·01
THF		0·5	25	91·70	115·58	129·64	119·62	114·00	15·64
THF		0·5	−58	91·94	116·21	130·27	118·99	112·73	17·54
DMSO[c]		0·28	25	94·12	118·93	130·81	118·79	111·71	19·10
NH$_3$		0·77	25	93·42	118·49	131·18	118·57	111·45	19·73
NH$_3$		0·77	−65	93·41	118·58	130·52	118·48	111·52	18·99
NH$_3$ − d_3		0·58	−65	93·41	118·58	130·65	118·52	111·46	19·20
HMPA[c]		0·20	25	93·24	117·98	131·33	118·15	110·19	21·14
Et$_2$O	K	0·1	25	93·71	117·61	128·27	119·18	114·58	13·69
THF		0·30	25	93·50	117·75	129·19	118·97	113·28	15·91
THF		0·30	−58	93·41	117·70	129·35	118·94	112·92	16·43
NH$_3$		0·69	25	93·55	118·33	130·37	118·93	112·26	18·11
NH$_3$		0·69	−65	93·44	118·33	129·86	118·77	112·04	17·81
NH$_3$ − d_3		0·66	−65	93·44	118·37	130·01	118·79	112·02	17·99
DMSO		0·4	25	94·10	118·86	130·80	118·79	111·75	19·05
HMPA		0·2	25	93·28	117·91	130·76	118·30	110·86	19·90
THF−cryptand(2,2,2)		0·15	25	93·16	117·93	131·52	118·22	110·37	21·15
THF	Me$_4$N$^+$	0·5	25	93·8	118·6	130·6	118·7	111·9	18·7

[a] The chemical shifts in the organic solvents were measured relative to cyclohexane as an internal standard by using $\delta = 27·70$ on the TMS scale. The chemical shifts in ammonia were measured relative to trimethylamine as an internal standard by using $\delta = 47·98$ at 25 °C and $\delta = 48·02$ at −58 °C on the TMS scale.
[b] Et$_2$O = diethyl ether; THF = tetrahydrofuran; NH$_3$ = ammonia; DMSO = dimethyl sulfoxide; HMPA = hexamethylphosphoramide; (2,2,2) = cryptand(2,2,2).
[c] Ref. 4a.

Counter ion effects

A plot of the change in the value of $\Delta\delta$ for In$^-$Li$^+$ versus that for In$^-$K$^+$ gives a straight line ($r = 0·97$), with a slope that indicates that the potassium salt is affected about two thirds as strongly as the lithium salt by changes in the ion pairing. This result expands on earlier observations that cation−anion interactions in c.i.p.s decrease as the radius of the cation increases.[1,2]

The tetramethylammonium (Me$_4$N$^+$) salt of In$^-$ was investigated in order to assess the extent to which a bulky counter ion will diminish cation−anion interactions. Delocalization in the indenyl anion in THF increases in the order Li$^+$ < K$^+$ < Me$_4$N$^+$ as the size of the cation increases and the anion−cation interaction diminishes, but a detectable polarization of In$^-$ is still present in In$^-$N$^+$Me$_4$. This result parallels that of an earlier study of the Me$_4$N$^+$ salt of the fluorenyl anion by UV−visible spectroscopy.[18]

In$^-$K$^+$ in THF shows a significantly smaller decrease in polarization than In$^-$Li$^+$ on lowering the temperature. This is consistent with a primarily c.i.p. structure for In$^-$K$^+$ and a c.i.p./s.s.i.p. mixture for In$^-$Li$^+$. In the latter case, the equilibrium is known to favor c.i.p.s at 25 °C, but s.s.i.p.s at −58 °C in ether solvents.[6f] These data contradict the recent statement that the calculated π charges for In$^-$ imply that In$^-$Li$^+$ in THF exists as s.s.i.p.s.[7b]

CONCLUSIONS

This study has led to some important conclusions regarding solvation of salts of the indenyl anion that have broad implications.

Solvation scales can be counter-ion dependent. This is illustrated by the observation that In$^-$Li$^+$ is more polarized by DMSO than by NH$_3$, whereas the reverse holds for In$^-$K$^+$.

Hydrogen bonding of ammonia to the indenyl anion can be inferred from the greater polarization observed for the anion in NH$_3$ relative to ND$_3$. This is also consistent with a decrease in $\Delta\delta$ found for In$^-$Li$^+$ and In$^-$K$^+$ on lowering the temperature.

The effect of changing solvent on π polarization is about two thirds as great for In$^-$K$^+$ as for In$^-$Li$^+$.

Cryptand(2,2,2) causes complete anion−cation separation of In$^-$K$^+$ in THF but small anion−cation interactions are still observed for In$^-$K$^+$ in HMPA and for In$^-$N$^+$Me$_4$ in THF.

EXPERIMENTAL

The alkali metal salts of In$^-$ in NH$_3$ were generated from indene and lithium or potassium amide according to a previously described procedure.[19] The NMR tubes were sealed under vacuum after the addition of indene. Solutions of In$^-$Li$^+$ in organic solvents were obtained

from indene and n-butyllithium as previously described,[4a] whereas solutions of In⁻K⁺ in organic solvents were prepared slightly differently from an earlier method.[2b] Typically, 2 mmol or less of indene in 5 ml of dry Et_2O or THF was purged with purified nitrogen and kept at 0 °C. After the addition of an excess of freshly cut potassium, the solution was stirred for 1·5–2 h, at which time the yield was found to be quantitative. For the DMSO samples, In⁻K⁺ was first prepared in Et_2O. After evaporation of the ether with nitrogen, deoxygenated DMSO was added to the dry salt. Only small amounts (less than 0·1 equiv. with respect to In⁻) of Et_2O remained in the samples as determined from the NMR signal intensities. For the cryptand(2,2,2) solutions, 1·1–1·2 equiv. of the cryptand was added to freshy prepared In⁻K⁺ in THF. In⁻N⁺Me₄ was prepared by adding a slight excess of Me₄NCl to a THF solution of In⁻Li⁺. The solution was sonicated until the ⁷Li NMR chemical shift reached the same shift value as that of a solution of LiCl in THF of the same concentration. The solutions were transferred to NMR tubes with a syringe. ¹³C NMR spectra were obtained on a Varian XL-200, a GE GN300 or a Bruker WM-250 spectrometer at ¹³C frequencies of 50·31, 75·47 or 62·89 MHz, respectively.

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