4096 *Journal of the American Chemical Society / 101:15 / July 18, 1979*

Ion–Solvent Interaction. Effects of Added Polar Compounds on the Conductances of Lithium, Sodium, and Tri-*n*-butylammonium Picrates in Tetrahydrofuran at 25 °C

W. R. Gilkerson* and M. D. Jackson

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received January 4, 1979*

Abstract: The conductances of lithium picrate have been measured at 25 °C as a function of salt concentration in tetrahydrofuran (THF) with and without small amounts (up to 0.01 M) of added hexamethylphosphoric triamide (HMPA), dimethyl sulfoxide (Me_2SO), and dimethylformamide (DMF). The conductances of sodium picrate and of tri-*n*-butylammonium picrate have been measured as a function of salt concentration in pure THF and in the presence of added HMPA. Values of ion pair dissociation constants, K_D, for each of the salt–ligand systems have been derived from these data using estimated values of the limiting equivalent conductances, Λ^0. The values of K_D increase linearly (except for NaPi–HMPA) with increasing addend concentration. These increases are interpreted as being due to cation–ligand complex formation. The equilibrium constants, $K_1{}^+$, for cation–ligand complex formation have been calculated and are found to be 17 000 M^{-1} for HMPA with Li^+, 140 M^{-1} for Me_2SO with Li^+, 50 M^{-1} for DMF with Li^+, 430 M^{-1} for HMPA with Na^+, and 880 M^{-1} for HMPA with Bu_3NH^+. In conjunction with other results in the literature, it is shown that the exchanges of one ligand for another on these cations are independent of the surrounding solvent to a good first approximation. A strong correlation is found between the standard free energies of exchange of one ligand for another on a cation and the standard free energy of transfer of that cation from one ligand as solvent to the other ligand as solvent.

An important goal in electrolyte solution chemistry is the determination of those factors which to a large extent govern the thermodynamics of transfer of an electrolyte from one solvent to another. The formation of complexes of alkali metal cations with polar molecules in solution can serve as a model for one portion of the overall process of transfer of the alkali metal from one polar solvent to another.[1-5] The present study is an extension of earlier work in THF solvent[3] and in 2-butanone solvent.[5]

We report here the results of a study of the effects of added hexamethylphosphoric triamide (HMPA), dimethyl sulfoxide (Me_2SO), and dimethylformamide (DMF) on the electrical conductivities of dilute solutions ($\sim 10^{-4}$ M) of lithium picrate (LiPi) in THF, of added HMPA on the conductances of solutions of sodium picrate (NaPi) in THF, and of added HMPA on the conductances of tri-*n*-butylammonium picrate (Bu_3NHPi) in THF, all at 25 °C. These salts are extensively associated to form ion pairs in this solvent due to its relatively low dielectric constant, $D = 7.39$ at 25 °C.[6] The ion pairs are in equilibrium with small concentrations of the free ions

$$M^+,X^- \rightleftarrows M^+ + X^- \quad K_D = K_A{}^{-1} \tag{1}$$

where K_A is the ion pair association constant. The increases in conductances of these salt solutions that are observed in THF upon the addition of the ligands above are interpreted[3,5] as being due to an increase in total ion concentration as a result of mass action involving the formation of the cation–ligand complex, M^+,L.

$$M^+ + L \rightleftarrows M^+,L \quad K_1{}^+ = [M^+,L]/[M^+][L] \tag{2}$$

There is, of course, a change in ion mobility upon formation of the complex, but it will be seen that here the mass-action effect is the predominant one.

Experimental Section

THF (Fisher Scientific Co., certified) was first refluxed for 0.5 h over copper(I) chloride to reduce peroxides and then distilled under nitrogen on a 2 × 30 cm column packed with glass helices. The distillate (bp 65.6 °C) was collected in a flask containing sodium ribbon and benzophenone and then was refluxed until the deep blue color characteristic of the sodium ketyl appeared. The THF was then distilled under nitrogen on a 4 × 40 cm column packed with glass helices; a middle fraction (bp 65.8–66.0 °C) was taken and immediately used in the conductance experiments. The specific conductance of the solvent ranged from 1 to 3×10^{-10} Ω^{-1} cm^{-1}.

Lithium picrate, sodium picrate, tri-*n*-butylammonium picrate, HMPA, and Me_2SO were prepared and purified as already reported.[5] DMF (J. T. Baker Chemical Co., GC-spectrophotometric grade) was stored over Type 4A molecular sieve overnight and distilled on a 2 × 15 cm Vigreux column (bp 53 °C, 17 mmHg).

Solution preparation has already been described,[5] as have been the conductance bridge, cells, and oil-filled thermostat. Conductance measurements were carried out at 1 kHz at a temperature of 25.00 ± 0.005 °C.

Physical properties of THF at 25 °C have been reported:[6] density, 0.880 g mL^{-1}; viscosity, 0.460 cP; dielectric constant, $D = 7.39$.

Results

The molar conductances Λ (Ω^{-1} cm^2 mol^{-1}) as a function of salt concentration C (mol L^{-1}) of LiPi, NaPi, and Bu_3NHPi in pure THF and in the various solutions of ligands in THF, all at 25 °C, are listed in supplementary Table III of the microfilm edition of this journal. The experimental uncertainty in the salt concentrations is ±0.1% and in the molar conductances ±0.1%. The concentrations of ligands are listed in millimolarity units.

Values of the limiting molar conductances, Λ^0, had been estimated earlier[3] to be 100 molar conductance units. It is clear that all of these salts are highly associated to ion pairs at the concentrations used here. The Shedlovsky conductance equation, which is applicable when association is large,[7] is

$$1/\Lambda S = 1/\Lambda^0 + S\Lambda C y_\pm{}^2/(\Lambda^0)^2 K_D \tag{3}$$

where S is the Shedlovsky function.[7a] $y_\pm$ is the mean ionic activity coefficient, taken to be given by a form of the Debye–Hückel limiting law.[7] The systems studied here are all too highly associated to allow reliable extrapolation of the Shedlovsky equation to infinite dilution to obtain independent values of Λ^0. In order to obtain values of K_D from the slopes of plots of $(1/\Lambda S)$ vs. $S\Lambda C y_\pm{}^2$, we have estimated new values of Λ^0 using more recent conductance data than that used earlier.[3] Using the values of Λ^0 90 for $LiBPh_4$,[8] 86 for $NaBPh_4$,[8] 103 for KPi,[9] and 86 for $KBPh_4$,[10] we estimate that Λ^0 in THF at 25 °C is 107 for LiPi and 103 Ω^{-1} cm^2 mol^{-1} for NaPi. These are the values used to calculate the ion pair dissociation constants for LiPi and NaPi listed in Table I. There

0002-7863/79/1501-4096$01.00/0

Table I. Conductance Parameters and Cation-Ligand Association Constants in THF at 25 °C

ligand concn, mM	Λ° [a]	$10^8 K_D$ [b]	K_1^+ [c]
	LiPi		
none	107	1.00	
0.99 HMPA	100	17.6	17 000
4.47	99.2	79.8	
6.86	99.0	124	
9.65	99.0	178	
2.40 Me_2SO	107	1.37	140
7.34	107	2.43	
9.30	107	2.82	
2.80 DMF	107	1.16	50
5.11	107	1.30	
7.70	107	1.48	
9.92	107	1.63	
	NaPi		
none	106	1.05	
1.39 HMPA	104	1.78	430
4.69	102.6	4.13	
6.58	102.2	6.02	
9.47	101.9	9.27	
	Bu_3NHPi		
none	97.5	4.60	
2.10 HMPA	97.5	13.1	880
4.66	97.5	23.8	
7.09	97.5	34.1	
9.49	97.5	44.2	

[a] Molar conductance units. Estimated as described in text. [b] In M^{-1} units. Estimated uncertainty in the absolute values of K_D is ±10%. [c] In M^{-1} units. Estimated uncertainty is ±10%.

are no data available to make a similar calculation of Λ^0 for Bu_3NHPi, so that we assumed Walden's product, $\Lambda^0\eta$, where η is the solvent viscosity, to be the same in THF as in 2-butanone;[5] Λ^0 is thus estimated to be 106 Ω^{-1} cm^2 mol^{-1}. This value was used to obtain the ion pair dissociation constant listed in Table I for this salt.

When a Lewis base forms a complex with a cation in solution in which the salt is principally in the form of ion pairs, there are two effects contributing to changes in the overall conductance: the ion mobility of the salt changes as a result of the formation of the cation-ligand complex, and the conductance increases as a result of mass action leading to an increase in total ion concentration, eq 2 plus the reverse of eq 1. In a ligand-THF solvent mixture of ligand concentration [L], both the apparent ion pair dissociation constant and the limiting equivalent conductance of a salt are changed. If a 1:1 cation-ligand complex is the only ligand complex formed, it has been shown[11] that the ion pair dissociation constant is given by

$$K_D = K_D^0(1 + K_1^+[L]) \qquad (4)$$

where K_D^0 is the ion pair dissociation constant in the absence of ligand, while the apparent limiting equivalent conductance, Λ_a^0, is given by

$$\Lambda_a^0 = (\Lambda_0^0 + \Lambda_1^0 K_1^+[L])/(1 + K_1^+[L]) \qquad (5)$$

where Λ_0^0 is the limiting equivalent conductance in the absence of ligand and Λ_1^0 is the corresponding value for the salt consisting of cation-ligand complex plus anion. The formation of cation-ligand complexes has been found to change the value of Λ^0 by as much as 15-20%.[5,11]

The conductances of the salts in the presence of ligands were still too small to allow the use of eq 3 to extrapolate the conductance data to infinite dilution to obtain independent values of Λ_a^0 and K_D. Having values of Λ_1^0 in hand for several of the salt-ligand systems in 2-butanone,[5] values of Λ_1^0 in THF were estimated by assuming that Walden's product is a constant.

Table II. Complex Formation Constants for Li^+ and Na^+ in Several Solvents at 25 °C [a]

ligand	K_1^+ in solvent			
	PC	AN [d]	MEK [f]	THF
H_2O	5.4 (1.2) [b]	4 (2.6) [e]		60 [g]
	8.(1.8) [c]	16 (2.5) [c]		
DMF		16 (2.5)		50 [h]
DMA	24.5 (3.7) [i]	65 (5.3)		(37) [j]
Me_2SO	(5.5) [i]	49 (6.0)	12	140 [h]
TPPO			250 (18)	3500 (250) [k]
HMPA		2100 (29)	1500 (37)	17,000 (430) [h]

[a] Values of K_1^+ un M^{-1}. Values in parentheses are for Na^+; the others are for Li^+. [b] Reference 1. Converted from molality to molarity scale. [c] Reference 16. [d] Reference 17, unless otherwise noted. [e] Reference 18. [f] Reference 5. [g] Reference 19. [h] This work. [i] Reference 2b. [j] Reference 20. [k] Reference 3a.

The following iterative procedure was carried out to estimate Λ_a^0 and thus obtain values of K_D for the salts at each ligand concentration: an initial estimate of K_D was made by assuming that Λ_a^0 was the same value as Λ_0^0. These values of K_D were used to construct a graph of R (= K_D/K_D^0) vs. [L], eq 4. The slopes of these plots yielded a first estimate of K_1^+ for each ligand. These values of K_1^+ were then used in eq 5 to estimate values of Λ_a^0 at each ligand concentration. These values of Λ_a^0 were then used at the beginning of a new cycle of calculations to obtain better values of K_D from the conductance data using eq 3. The process was continued at each ligand concentration until the last value of K_D calculated agreed with the previous value within 1%. The values of Λ_a^0, K_D, and K_1^+ so obtained are listed in Table I.

The final plot of R vs. [L] for NaPi with added HMPA was the only one of the systems studied here to show curvature, curving up as [L] increased. This is indicative that a 1:2 cation-ligand complex may be forming in addition to the 1:1 complex:

$$ML^+ + L \rightleftarrows ML_2^+ \quad K_2^+ = [ML_2^+]/[ML^+][L] \qquad (6)$$

$$R = K_D/K_D^0 = 1 + K_1^+[L] + K_1^+K_2^+[L]^2$$

with the result that a plot of $(R - 1)/[L]$ vs. [L] should give K_1^+ as the intercept as [L] goes to zero. The value of K_1^+ shown in Table II for HMPA with Na^+ was obtained in this manner. We have not attempted to extract values of K_2^+ from the slopes of such plots, preferring to focus on what we believe to be the more reliable values of K_1^+.

Discussion

The extent of ion-pair dissociation as measured by the magnitude of K_D is 5% larger for sodium picrate than for lithium picrate (Table II) and has been found to be greater by a factor of 9 for potassium picrate.[9] These variations are to be contrasted with the more ordered increases in K_D found for the alkali metal dinitrophenolates[3a] where K_D is four times greater for sodium than for lithium, 16 times greater for potassium than sodium, and twice as great for rubidium as for the potassium salt. Smid and co-workers[6] had found that for the tetraphenylborate salts K_D was 7% greater for the sodium salt than for the lithium salt but the value for potassium was 60% smaller than K_D for the sodium salt. The balance between cation-anion interaction and ion-solvent interaction is a complex function of the cation radius and the nature of the anion.

The values of K_1^+ for the ligands HMPA, triphenylphosphine oxide (TPPO),[3a] and Me_2SO decrease in that order in complexation with lithium cation in THF. We have found this same order of ligand complex forming strength with lithium cation in 2-butanone solvent[5] and with tri-n-butylammonium

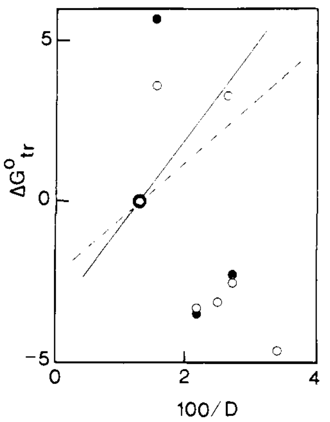


Figure 1. Free energy of transfer (kcal mol^{-1}) of Li^+ (closed circles) and Na^+ (open circles) from water to other solvents at 25 °C vs. the reciprocal of the solvent dielectric constant D. The slopes of the straight lines were calculated using the Born equation and ionic crystal radii for Li^+ (solid line) and Na^+ (dashed line).

cation in *o*-dichlorobenzene solvent.[12] The value of $K_1{}^+$ for HMPA is greater than for TPPO in complexation with both sodium cation and tri-*n*-butylammonium ion in both THF (this work) and in 2-butanone solvent.[5]

Figure 1 shows the shotgun pattern frequently obtained[2a] when one plots the free energy of transfer at 25 °C, $\Delta G°_{tr}$

$$M^+ \text{ (in } H_2O) \rightarrow M^+ \text{ (in solvent L)} \quad (7)$$

vs. the reciprocal of the dielectric constant, $1/D$. Included here are values for lithium cation (filled circles) and sodium cation (open circles) being transferred to the solvents DMF, DMA, Me_2SO, and PC.[13] It is clear that these results do not follow the Born equation[15] for the free energy of transfer of 1 mol of ions of charge ze and radius R from a fluid of dielectric constant D_1 to a fluid of dielectric constant D_2:

$$\Delta G°_{Born} = (Nz^2e^2/2R)(1/D_2 - 1/D_1) \quad (8)$$

A coordination model has been applied[1,2] to the transfer of cation M^+ from solvent A to solvent B.

$$M^+,A_n + nB \rightarrow M^+,B_n + nA \quad (9)$$

In this model, the bulk solvent beyond the first coordination shell is presumed to have no influence on $\Delta G°_{tr}$, the entire free-energy change being attributed to the difference in the free energy of interaction of the central cation with the n solvent molecules surrounding the cation in the first coordination sphere. Clune, Waghorne, and Cox, using a coordination number of 4, have shown that $\Delta G°$ for the exchange of complexing ligands is the same within experimental error as $\Delta G°_{tr}$ from solvent A to solvent B for the systems Li^+ (PC to DMA solvent), Na^+ (PC to DMA solvent), and Na^+ (PC to Me_2SO solvent).[2b] Grunwald et al.[1] have used this model to compare the $\Delta G°_{tr}$ of Li^+ and Na^+ from H_2O to PC with the values of $\Delta G°_{ex}$ for the reaction

$$M^+,PC + H_2O \rightarrow M^+,H_2O + PC \quad (10)$$

in which one molecule of H_2O displaces one specifically solvating molecule of PC from the cations Li^+ and Na^+ in PC solvent. Their results indicated that between two and three molecules of solvent are exchanged in the transfer process.

We wish to establish the reaction

$$M^+,L_1 + L_2 \rightarrow M^+,L_2 + L_1 \quad (11)$$

wherein one molecule of L_2 displaces one molecule of L_1 from the cation M^+ as a model for one part of the overall process of transfer of the ion M^+ from the solvent L_1 to the solvent L_2. To be useful for this purpose, the equilibrium constants K_{ex} for reaction 11 should be independent of the solvent; that is, the values of K_{ex} should depend primarily on the relative affinity of M^+ for the two ligands with changes in specific interactions between the four species in eq 11 and the solvent being of minor importance.[5] To examine this factor, values of cation–ligand formation constants for both Li^+ and Na^+ with a number of ligands at 25 °C in the solvents propylene carbonate (PC), acetonitrile (AN), 2-butanone (MEK), and THF have been gathered from several sources and appear in Table II.

The values of $K_1{}^+$ in Table II, together with the present and earlier[12] values for Bu_3NH^+ with THF, TPPO, and HMPA, have been used to calculate values of K_{ex} for a number of ligands with the cations Bu_3NH^+, Na^+, and Li^+ in several solvents at 25 °C. A listing of these values follows.

Bu_3NH^+. For the displacement of THF by TPPO, K_{ex} is 2950 in *o*-dichlorobenzene (DCB) and 2800 in THF; TPPO by HMPA, K_{ex} is 3.9 in MEK, 6.1 in DCB, and 3.8 in THF.

Na^+. For the displacement of DMA by HMPA, K_{ex} is 5.5 in AN and 12 in THF; TPPO by HMPA, K_{ex} is 2.1 in MEK and 1.7 in THF; DMA by Me_2SO, K_{ex} is 1.5 in PC and 1.1 in AN; H_2O by DMA, K_{ex} is 3.1 in PC,[1] 2.1 in PC,[16] 2.0 in AN,[18] and 2.1 in AN.[16]

Li^+. For the displacement of Me_2SO by HMPA, K_{ex} is 43 in AN, 125 in MEK, and 121 in THF; TPPO by HMPA, K_{ex} is 6.0 in AN and 4.9 in THF; H_2O by DMF, K_{ex} is 4.0 in AN,[18] 1.0 in AN,[16] and 0.83 in THF; H_2O by DMA, K_{ex} is 4.5 in PC,[1] 3.1 in PC,[16] 16.0 in AN,[18] and 4.1 in AN;[16] H_2O by Me_2SO, K_{ex} is 12.0 in AN,[18] 3.1 in AN,[16] 2.3 in THF, and 0.4 in Me_2SO.[12]

To contrast the relative effects of solvent on $K_1{}^+$ and on K_{ex}, note that, for Bu_3NH^+ with HMPA as ligand, $K_1{}^+$ is 220 M^{-1} in MEK[5] and 2.2×10^6 in DCB,[12] and falls to 880 M^{-1} in THF solvent, while, for the displacement of TPPO by HMPA on Bu_3NH^+, K_{ex} is almost the same in THF as in MEK and only 56% larger in DCB than in MEK. The values of K_{ex} listed above for a given pair of ligands display remarkably small changes from solvent to solvent considering the changes in the separate values of $K_1{}^+$. The agreement between results obtained in different laboratories for the same solvent is in most cases satisfactory except for that involving Li^+ with H_2O as ligand in AN reported by Chantooni and Kolthoff;[18] values of K_{ex} calculated using their value of $K_1{}^+$ are clearly out of line with the other values of K_{ex} in AN, PC, and THF solvent. We shall use the value of $K_1{}^+$ for H_2O with Li^+ in AN reported by Benoit[16] in the discussion that follows.

Several general features emerge from an inspection of the values of K_{ex} listed above; for a given set M^+, L_1, and L_2, the values of K_{ex} in THF are very close to the values found in PC and MEK solvents, the values in DCB are slightly higher in the two instances available, while the values in AN tend to be lower by as much as ½ to ⅓. Variation of ligand activity is evident in the displacement of H_2O by Me_2SO in Me_2SO solvent.[21]

If we exclude this last result, the displacement of H_2O by Me_2SO from Li^+ in Me_2SO solvent, the changes in K_{ex} with solvent are small enough in the solvents utilized here for us to conclude that reaction 11 is, to a good first approximation, independent of solvent.

We now wish to compare the free energy of transfer, $\Delta G°_{tr}$, for the transfer of Li^+ (and Na^+) from H_2O to a series of polar aprotic solvents, with the free energy of displacement of H_2O by the solvent as ligand from the cation, $\Delta G°_{ex}$ ($= -RT \ln K_{ex}$). The solvents PC and AN can be added to the list of ligands displacing H_2O from Li^+ and Na^+ using a procedure to calculate K_{ex} and thus $\Delta G°_{ex}$ similar to that outlined for Me_2SO.[21] On Li^+, for the displacement of H_2O by PC, K_{ex} is 0.016[1] and 0.011;[16] for the displacement of H_2O by AN, K_{ex} is 0.0033.[16] On Na^+, for the displacement of H_2O by PC, K_{ex} is 0.071[1] and 0.047;[16] for the displacement of H_2O by AN, K_{ex}

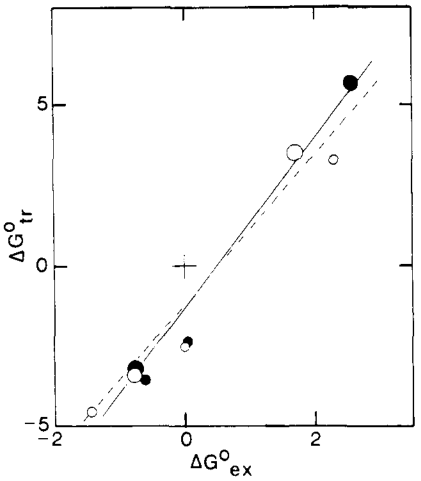


Figure 2. Free energy of transfer from water to other solvents for $\mathrm{Li^+}$ (filled circles) and $\mathrm{Na^+}$ (open circles) vs. free energy of exchange of a water molecule for a molecule of the other solvent at 25 °C in solution. Units are kcal $\mathrm{mol^{-1}}$ for both free energy changes. Solid line, least-squares fit for $\mathrm{Li^+}$; dashed line, least-squares fit for $\mathrm{Na^+}$.

is 0.021[16] and 0.020.[18] Values[13] of $\Delta G^\circ_{\rm tr}$ for the transfer of $\mathrm{Li^+}$ from $\mathrm{H_2O}$ to DMA, $\mathrm{Me_2SO}$, DMF, and PC are plotted vs. values of $\Delta G^\circ_{\rm ex}$ in Figure 2. The sizes of the circles for each cation–solvent system indicate the range in experimental values of $\Delta G^\circ_{\rm ex}$. The least-squares line drawn through the points for $\mathrm{Li^+}$ has a slope of 2.66 and a correlation coefficient of 0.97; that drawn through the points for $\mathrm{Na^+}$ has a slope of 2.34 and a correlation coefficient of 0.95.

The correlations found between $\Delta G^\circ_{\rm tr}$ and $\Delta G^\circ_{\rm ex}$ for $\mathrm{Li^+}$ and for $\mathrm{Na^+}$ are high, indicating that $\Delta G^\circ_{\rm ex}$ is a good measure of the relative magnitudes of the energy changes that occur when an alkali metal ion is transferred from one solvent to another. These correlations are very similar to that found by Grunwald and co-workers[1] for the transfer of ions from water to PC. Applying the coordination model of ionic solvation[2] (eq 9) to these systems, we would expect the slopes of the $\Delta G^\circ_{\rm tr}$ vs. $\Delta G^\circ_{\rm ex}$ lines to correspond to the number of solvent molecules bound to the ions in the first coordination sphere, eq 9, provided that the energetics for the formation of the second and subsequent bonds between $\mathrm{M^+}$ and A (or B) are not too different from the energetics for the formation of the first bond. The slopes obtained here thus indicate that between two and three molecules of solvent are exchanged in the transfer of $\mathrm{Li^+}$ and $\mathrm{Na^+}$ from one solvent to another. Similar values were obtained by Grunwald et al.[1] Clune, Waghorne, and Cox, using a coordination number of 4, have shown that ΔG° for the exchange of complexing ligands, eq 11, is the same within experimental error as $\Delta G^\circ_{\rm tr}$ from solvent A to solvent B for the systems $\mathrm{Li^+}$ (PC to DMA solvent), $\mathrm{Na^+}$ (PC to DMA solvent), and $\mathrm{Na^+}$ (PC to $\mathrm{Me_2SO}$ solvent).[2b] We take the fact that the slopes we find here in the $\Delta G^\circ_{\rm tr}$ vs. $\Delta G^\circ_{\rm ex}$ plots yield *n* values less than 4 to mean that the values of $K_{\rm ex}$, eq 8, deviate to some extent from the simple statistical relationship to the overall equilibrium constant for reaction 9 that one would expect if only electrostatic interactions were involved between ligands and cation.

Popov has found the ^{23}Na NMR chemical shift, $\Delta\sigma$, of sodium tetraphenylborate in solution to vary with solvent in a manner suggesting that the shifts depend on ion–solvent interaction.[22] Comparisons with the ^{23}Na chemical shift show that both $\Delta G^\circ_{\rm tr}$ and $\Delta G^\circ_{\rm ex}$ increase as $\Delta\sigma$ increases but there is a large amount of scatter (correlation coefficeint of 0.86 for $\Delta G^\circ_{\rm ex}$ with $\Delta\sigma$). It is possible that factors other than the energetics of ion–solvent interaction are involved in the chemical shift results. Gutmann has shown that his donor numbers, DN, are related to a number of measures of ion–solvent interactions.[23] We find a strong but nonlinear correlation between $\Delta G^\circ_{\rm tr}$ and DN, Figure 3, a type of behavior previously noted[23] between free-energy changes and donor numbers.

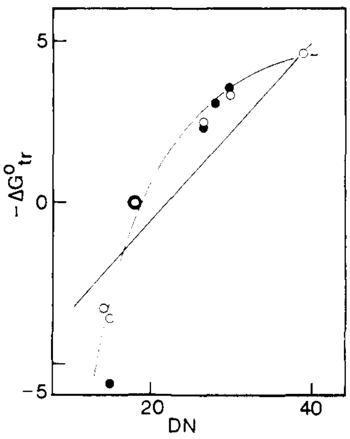


Figure 3. Free energy of transfer of $\mathrm{Na^+}$ from water at 25 °C to other solvents vs. the Gutmann donor number, DN, for the solvents. The least-squares straight line has a correlation coefficient of 0.94. The curve does not indicate a fundamental relation, but is a freehand drawing.

Conclusions

It is shown that the ligand exchange equilibrium constants, eq 11, are dependent principally on the nature of the cation and the two ligands involved and only to a small extent on the nature of the surrounding solvent. Using this result, it has been shown that there is a strong linear correlation between the free energy of ligand exchange and the free energy of transfer of an alkali metal ion from one ligand as solvent to another. A further study of a wider range of ligand exchange equilibria may furnish some greater insight into the relationship between molecular structure and solvating ability.

Acknowledgment. We wish to thank the referees for a number of helpful suggestions, and in particular for calling to our attention a very importance reference.

Supplementary Material Available: Table III, molar conductances of lithium picrate, sodium picrate, and tri-*n*-butylammonium picrate in pure tetrahydrofuran and in various solutions of ligands in tetrahydrofuran, all at 25 °C (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) D. R. Cogley, J. N. Butler, and E. Grunwald, *J. Phys. Chem.*, **75**, 1477 (1971).
(2) (a) B. G. Cox, A. J. Parker, and W. E. Waghorne, *J. Phys. Chem.*, **78**, 1731 (1974); (b) G. Clune, W. E. Waghorne, and B. G. Cox, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1294 (1976).
(3) (a) H. B. Flora and W. R. Gilkerson, *J. Phys. Chem.*, **77**, 1421 (1973); (b) *ibid.*, **80**, 679 (1976).
(4) A. Hourdakis and A. I. Popov, *J. Solution Chem.*, **6**, 299 (1977).
(5) M. D. Jackson and W. R. Gilkerson, *J. Am. Chem. Soc.*, **101**, 328 (1979).
(6) D. N. Battacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).
(7) (a) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938); (b) R. M. Fuoss and T. Shedlovsky, *J. Am. Chem. Soc.*, **71**, 1496 (1949).
(8) D. Nichols, C. Sutphen, and M. Szwarc, *J. Phys. Chem.*, **72**, 1021 (1968).
(9) M. Bourgoin, K. H. Wong, J. Y. Hui, and J. Smid, *J. Am. Chem. Soc.*, **97**, 3462 (1975).
(10) S. Boileau, P. Hemery, and J.-C. Justice, *J. Solution Chem.*, **4**, 873 (1975).
(11) (a) J. Macau, L. Lamberts, and P. Huyskens, *Bull. Soc. Chim. Fr.*, **7**, 2387 (1971); (b) E. R. Ralph and W. R. Gilkerson, *J. Am. Chem. Soc.*, **86**, 4783 (1964); (c) J. B. Ezell and W. R. Gilkerson, *J. Phys. Chem.*, **72**, 144 (1968).
(12) (a) H. W. Aitken and W. R. Gilkerson, *J. Am. Chem. Soc.*, **95**, 855 (1973); (b) J. B. Ezell and W. R. Gilkerson, *ibid.*, **88**, 3486 (1966).
(13) Free energies of transfer of individual ions have been obtained using one or more extrathermodynamic assumptions. See ref 14.
(14) (a) B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, *Aust. J. Chem.*, **27**, 477 (1974); (b) G. R. Hedwig, D. A. Owensby, and A. J. Parker, *J. Am.*

Chem. Soc., **97**, 3888 (1975).

(15) C. M. Criss and M. Salomon in "Physical Chemistry of Organic Solvent Systems", A. K. Covington and T. Dickinson, Eds., Plenum Press, New York, 1973, p 260.

(16) R. L. Benoit and S. Y. Lam, *J. Am. Chem. Soc.*, **96**, 7385 (1974).

(17) T. Nakamura, *Bull. Chem. Soc. Jpn.*, **48**, 1447 (1975).

(18) M. K. Chantooni, Jr., and I. M. Kolthoff, *J. Am. Chem. Soc.*, **89**, 1582 (1967). The value of K_1^+ for Li^+ is uncertain by ±1 unit.

(19) H. B. Flora, II, Ph.D. Thesis, University of South Carolina, 1971.

(20) M. L. Junker, unpublished work, this laboratory.

(21) Benoit has reported (ref 16) a value of $K_1^+ = 0.2$ for Li^+ with H_2O in Me_2SO solvent. This value, when multiplied by the concentration of Me_2SO in Me_2SO solvent, $[Me_2SO] = 14$ M, yields a value of $K_{ex} = 2.8$ for the displacement of Me_2SO by H_2O; the reciprocal of this yields the value listed in the text. This latter value is an order of magnitude less than those for the same reaction in PC and in AN. The vapor pressures of H_2O above 1 M solutions of H_2O in these three solvents (also reported in ref 16) indicate that H_2O interacts much more strongly with Me_2SO solvent than with either AN or PC.

(22) R. H. Erlich and A. I. Popov, *J. Am. Chem. Soc.*, **93**, 5620 (1971).

(23) V. Gutmann, *Electrochim. Acta*, **21**, 661 (1976); *Angew. Chem., Int. Ed. Engl.*, **9**, 843 (1970).

(Cross-conjugated dienyl)tricarbonyliron Cations. 2. 4-Methyl Derivatives

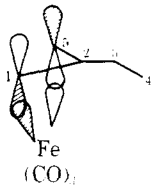
Benedict R. Bonazza, C. Peter Lillya,* Elaine S. Magyar, and Gary Scholes

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003. *Received August 3, 1978*

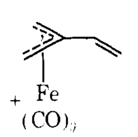
Abstract: Tricarbonyl(cross-conjugated dienyl)iron cations have been generated from precursor alcohols in strong acid solutions and studied by NMR spectroscopy in the temperature range 0 to −50 °C. The 4-*anti*-methyl cation (**11**) coordinates reversibly, but slowly, with fluorosulfonate ion to give the adduct **12**. Broadening of ^1H and ^{13}C NMR signals in the region −40 to −9 °C demonstrates rotation about the C_2–C_3 bond of **11**. The observations exclude **12** as an intermediate in the rotation process. Relief of steric strain associated with the 4-*anti*-methyl enhances the driving force for FSO_3 coordination and lowers the barrier for C_2–C_3 rotation. The 4-*syn*-methyl cation (**15**) does not give a fluorosulfonate adduct and fails to exhibit NMR signal broadening caused by C_2–C_3 rotation at temperatures below 0 °C. Neither cation coordinates with carbon monoxide. Lack of evidence of coordinative unsaturation and the substantial barrier to C_2–C_3 rotation rule out the η^3-allyl type structure predicted by the simplest (one interaction) frontier orbital model.

Introduction

A simple frontier orbital model which treats bonding in terms of dominant frontier orbital interactions enjoys considerable success when used to predict structures of metal π complexes of ligands which offer several nonequivalent coordination sites.[1] The title cations were conceived to make a severe test of a simple (one interaction) frontier orbital model. If spatial overlap for donation of electrons from an occupied frontier orbital of the $Fe(CO)_3$ fragment to the LUMO of the dienyl cation is maximized (**1**), the η^3 or "allyl" structure, **2**, will result. However, this structure can be achieved only at the expense of several other potentially important frontier orbital interactions and by sacrifice of a filled metal valence shell. The $Fe(CO)_3$ fragment possesses a degenerate pair of low-lying frontier orbitals occupied by a single electron pair.[2] Only one of these orbitals (see **1**) finds a suitable partner on the dienyl ligand in this structure. Alternatively, two coordinatively saturated structures, **3** and **4**, can be written for which η^4-diene-[3] and η^4-trimethylenemethane-[4,5] $Fe(CO)_3$ complexes offer structural precedent. The characteristics which should distinguish a cation of structure **2** from one of structures **3** or **4** are coordinative unsaturation and facile (almost free) rotation about the C_2–C_3 bond.

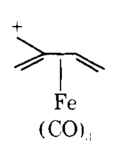


1



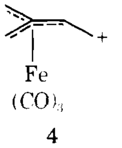
2

"allyl" structure



3

"diene" structure

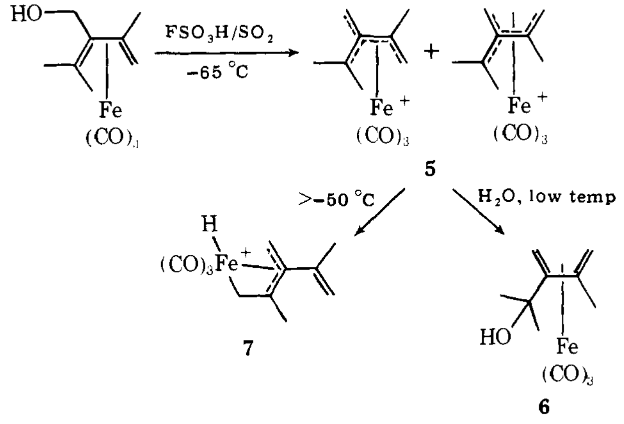


4

"trimethylenemethane" structure

Trimethyl-substituted (cross-conjugated dienyl)tricarbonyliron cations, **5**, have been generated in strong acid media, and formation of isomerized quench products (e.g., **6**) has demonstrated that C_2–C_3 rotation occurs (Scheme I).[2a] The possibility that rotation could occur during quenching owing to reversible formation of **8** led to a search for less ambiguous

Scheme I. Chemistry of the Tricarbonyl(1,1,3-trimethyl-cross-conjugated dienyl)iron Cation in Liquid Sulfur Dioxide



0002-7863/79/1501-4100$01.00/0