basis set is biased toward pyramidalization of radical centers;[12] with a larger basis set, ^1A_g might be found to be a true minimum. Even with STO-3G, the pyramidalized structure, $^1A_1(1)$, is only a few millihartrees lower than the planar one in energy. The coefficients in the TCSCF wave functions for the two structures are also nearly identical. In beginning these calculations, we had expected the ^1A_g state to be the transition state for interconversion of **3** with its mirror image. This clearly is not true, and the ^1A_g geometry is a relative minimum for motion along the normal coordinate leading to **3**.

Both $^1A_1(2)$ and $^1A_1(3)$ lie well below the planar singlet diradical in energy. The MCSCF coefficients in the wave functions for $^1A_1(2)$ and $^1A_1(3)$ show the importance of transannular bonding in both structures, despite the long transannular bond lengths. This bond in $^1A_1(3)$ is especially interesting, since it is apparently formed between the back lobes of hybrids that point away from each other.[13] The lowest energy path along the surface connecting $^1A_1(2)$ and $^1A_1(3)$ is so flat with the STO-3G basis set and an MCSCF wave function that, if a larger basis set or a more highly correlated wave function were used, only one minimum might be found, with an optimal geometry intermediate between those of $^1A_1(2)$ and $^1A_1(3)$. Analytical gradient, geometry optimization with a SVP basis set, and an MCSCF wave function would be highly desirable but prohibitively expensive.

The relative energies of $^3B_{2u}$ and $^1A_1$ are also problematical. As discussed elsewhere,[14] the "doublet instability problem" makes the RHF geometry for $^3B_{2u}$ deviate considerably from the optimal π CI geometry. The deviation between the TCSCF geometry for $^1A_1$ and the optimal π CI geometry is smaller. Therefore, if the CI calculations in Table I were carried out at the optimal CI geometries, instead of at geometries obtained by RHF/TCSCF calculations, the triplet would be selectively stabilized. Once again, a meaningful prediction of which state lies lowest would require geometry optimizations with large basis sets and highly correlated wave functions.

In the absence of such calculations, it does seem safe to conclude, however, that the combination of electron delocalization in **2** and strain in **3** makes the triplet at least competitive in energy with the closed-shell singlet. Even if $^3B_{2u}$ lies above $^1A_1$ in energy at their equilibrium geometries, it should thus be possible experimentally to populate the triplet thermally.

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Registry No. **2**, 80410-15-7; **3**, 80410-16-8.

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(12) Feller, D.; Tanaka, K.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.*, submitted for publication.

(13) For another example, see Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.*, **1972**, *94*, 773. It should be noted that the bridgehead carbons in the optimized structures for bicyclobutane and $^1A_1(2)$ are also inverted, but much less so than in that for $^1A_1(3)$. The angle between the C–H bond at each of these carbons and the projection of the bond onto the C–C–C plane is respectively 4, 15, and 40°. In each case the C–H bond lies on the same side of the C–C–C plane as the fourth carbon.

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The State of Lithium Tetraphenylborate, Lithium Picrate, and Sodium Picrate Dissolved in 1,2-Dichloroethane Containing One of Several Phase-Transfer Catalysts

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Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received August 14, 1981*

Abstract: 1,2-Dichloroethane solvent containing 1 mM of either dibenzo-18-crown-6 (DBC) or triphenylphosphine oxide (TPPO) dissolves 1 equiv of lithium tetraphenylborate ($LiBPh_4$) to form 1:1 ligand–salt complexes. Conductance studies at 25 °C show the ion association constant K_A to be 1660 M^{-1} for $DBC\,Li^+ + BPh_4^-$ and 7400 M^{-1} for $TPPO\,Li^+ + BPh_4^-$. Lithium bromide, lithium picrate, and sodium picrate do not dissolve to the extent of 1 mM in solvent containing 1 equiv of crown ether. Lithium picrate does dissolve to the extent of 1 mM in solvent containing 1 equiv of either TPPO, hexamethylphosphoramide (HMPA), glyme-4, or glyme-5. Sodium picrate requires at least a tenfold excess of either TPPO, HMPA, or glyme-5 to form 1 mM solutions. Conductance and spectrophotometric studies show that the 1:1 ligand–metal picrate complexes dissociate to a very small extent and do react with additional ligand to form 2:1 and 3:1 ligand–cation complexes, decreasing the extent of ion association. Substitution of sodium for lithium in these ligand–metal picrate complexes has little or no effect on either the conductance or the UV–visible spectra of the solutions. These ligands promote charge separation in solution (as measured by conductance) in the following order: glyme-4 < glyme-5 < TPPO < HMPA < DBC.

There has been a great deal of interest in the use of neutral ligands to promote the solubility of salts in organic solvents such as methylene chloride, chloroform, and benzene in order to obtain larger concentrations of reactive ions in a nonaqueous phase.[2] Such ligands form one class of what are termed *phase transfer catalysts*.[3-5] There have been only a few reports of physicochemical studies of such systems in these relatively poor solvents; Frensdorf has reported[6] a study of the extraction of alkali metal picrates from water in methylene chloride with use of crown ethers (an extension of Pedersen's earlier work[7]) and Nae and Jagur-

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(1) Address correspondence to this author.

(2) (a) Liotta, C. L.; Harris, H. P. *J. Am. Chem. Soc.* **1974**, *96*, 2250–2252. (b) Stott, P. E.; Bradshaw, J. S.; Parish, W. W. *Ibid.* **1980**, *102*, 4810–4815.

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Grodzinski have investigated the protonation of crown ethers by organic acids in 1,2-dichloroethane.[8]

The present study was undertaken to see how variations in the nature of the ligand and the anion might affect the solubility and the extent of dissociation of several lithium and sodium salts in a poor solvent. This is a report of studies of the electrical conductivity of millimolar solutions of lithium tetraphenylborate ($LiBPh_4$) solubilized by equimolar amounts of dibenzo-18-crown-6 (DBC) and triphenylphosphine oxide (TPPO) and of the conductivity and UV–visible absorbance spectra of lithium picrate (LiPi) and sodium picrate (NaPi) solubilized by excess TPPO, hexamethylphosphoramide (HMPA), 1,2-bis(2-methoxyethoxy)ethane (glyme-4), and 1,2-bis[2-(2-methoxyethoxy)ethyl] ether (glyme-5) in 1,2-dichloroethane (DCE) as solvent.

Experimental Section

1,2-Dichloroethane (Fisher Scientific Co., Certified) was passed through a 30 × 2 cm column packed with alumina (Alcoa, Grade F-20), distilled, stored over activated molecular sieve[9] (Davison Type 4A) for 2 days, and then distilled under dry nitrogen on a 35 × 2 cm column packed with glass helices, bp 83.5 °C. Solvent prepared in this way has been found to contain 20–30 ppm of water by Karl Fisher titration.[10] Dibenzo-18-crown-6 (2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene, Aldrich Chemical Co., 98%) was recrystallized twice from benzene and once from acetone. The last step produced a fibrous precipitate which when dried in vacuo could be transferred in a nitrogen-filled drybox with ease. Triphenylphosphine oxide (K and K Laboratories) and hexamethylphosphoramide (Matheson Coleman and Bell) were purified as before.[11] Bis[2-(2-methoxyethoxy)ethyl] ether and 1,2-bis(2-methoxyethoxy)ethane (both from Eastman Kodak Co.) were distilled on a 2 × 15 cm Vigreux column at 2 torr, the former boiling at 118–119 °C and the latter at 79–80 °C. The salts lithium tetraphenylborate, lithium picrate, and sodium picrate were prepared and purified as already reported.[11]

Solutions were prepared by weight in a nitrogen-filled drybox. Conductance measurements were carried out at 1 kHz using the cell, bridge, and oil thermostat (at 25.00 ± 0.001 °C) already described.[11] The experimental uncertainties in the salt and ligand concentrations and in the molar conductancies are ±0.1%. Spectra were recorded from 330 to 500 nm on a Cary 14 spectrophotometer, equipped with a thermostated cell compartment maintained at 25.0 ± 0.1 °C. The experimental uncertainties in molar absorptivities are ±1%. Physical properties of the solvent follow: density 1.246 g mL^{-1}, dielectric constant 10.35, and viscosity 0.7834 cP.[12]

Results

Some qualitative observations were made of the solubilization of several alkali metal salts in 1,2-dichloroethane at 25 °C; the solubility of $LiBPh_4$ equals or exceeds 1 mM in DCE containing 1 equiv of either TPPO or DBC. Lithium bromide, LiPi, and NaPi are not solubilized to the extent of 1 mM even by excess DBC. Lithium picrate does dissolve to the extent of forming 1 mM solutions in DCE containing 1 equiv of either TPPO, HMPA, glyme-5, or glyme-4. Sodium picrate does not dissolve to that extent in DCE containing 1 equiv of either TPPO, HMPA, or glyme-5 but does form 1 mM solutions in 0.015 M TPPO, 0.020 M HMPA, and 0.010 M glyme-5 all in DCE.

Several different kinds of conductance experiments were carried out. In the first kind, equimolar solutions of the following salt–ligand pairs were prepared in DCE: $LiBPh_4$ + DBC, $LiBPh_4$ + TPPO, and LiPi + TPPO. Weighed portions of these solutions were in each case added to a known amount of solvent in the conductance cell, the cell was thermostated, and the conductance measured, yielding values of the molar conductance Λ (in Ω^{-1} cm^2 mol^{-1}) as a function of the concentration of the 1:1 salt–ligand complex. The values of Λ for $DBC{\cdot}LiBPh_4$ and for $TPPO{\cdot}LiBPh_4$ are shown plotted vs. salt concentration in Figure 1. Also shown in Figure 1 are the molar conductancies of tetra-*n*-butylammonium picrate in this solvent.[12] Both of the ligand–salt complexes appear to behave like the quaternary ammonium salt with the phosphine oxide complex showing the lower mobility. These Λ–*C* curves are typical of those observed when association of the ions to form ion pairs is the dominant feature of a salt solution.

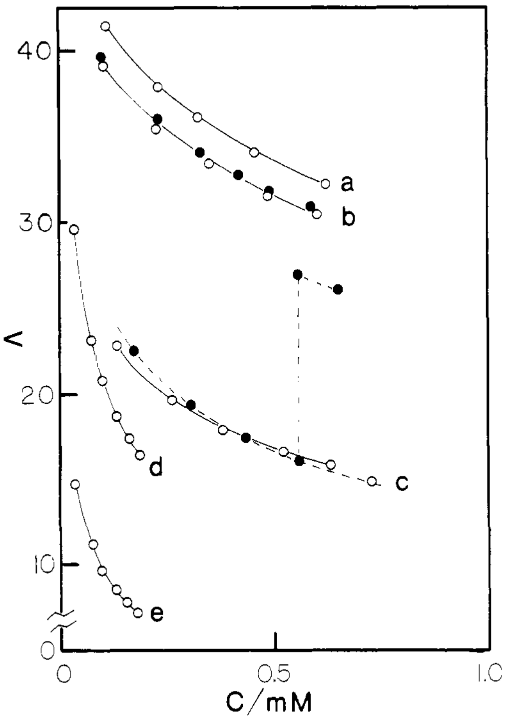

Figure 1. Molar conductancies, Λ, in Ω^{-1} cm^2 mol^{-1}, in DCE at 25 °C as a function of salt concentration *C* in mM: (a) Bu_4NBPh_4 (ref 12); (b) $DBC{\cdot}LiBPh_4$, open circles at $r = 1.001$, closed circles at $r = 1.008$; (c) $TPPO{\cdot}LiBPh_4$, open circles at $r = 1.013$, closed circles at $r = 1.001$; (d) LiPi in 18.7 mM HMPA; (e) LiPi in 39.7 mM glyme-5.

$$M^+ + X^- \rightleftarrows M^+,X^- \qquad K_A = a_{MX}/a_M a_X \tag{1}$$

A number of theoretical equations for the electrical conductance of electrolyte solutions such as those above have been developed, all based on the Debye–Hückel theory of interionic attraction.[13] If it is assumed as usual that the ion pairs do not contribute to the conductance all of these equations for symmetrical electrolytes may be represented by the forms

$$\Lambda = \gamma[\Lambda^0 - f(\Lambda^0,R,C\gamma)] \tag{2}$$

$$K_A = (1 - \gamma)/C\gamma^2 y_\pm^{\,2} \tag{3}$$

$$y_\pm^{\,2} = \exp[-2\kappa q/(1 + \kappa R)] \tag{4}$$

where $\kappa^2 = (16\pi N/1000)\, q(C\gamma)$, the square of the Debye–Hückel characteristic inverse distance, Bjerrum's characteristic distance $q = z^2e^2/2DkT$, and *R* is a distance parameter such that the ions of opposite charge within that distance of one another are considered to be paired, and are free at greater distances. The activity coefficient of the ion pair has been taken to be unity in the dilute solutions encountered here. Fuoss's 1977 conductance equation[14] was used in eq 2 to fit the conductance data for the salt systems $DBC{\cdot}LiBPh_4$ and $TPPO{\cdot}LiBPh_4$ to eq 2 to 4, using a nonlinear least-squares program patterned after one due to Fuoss.[15] We set the value of *R* in eq 2 and 4 equal to Bjerrum's *q*.[16] The

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(15) We are grateful to Professor Fuoss for supplying us with a preprint of his paper: Fuoss, R. M. *J. Phys. Chem.* **1978**, *82*, 2427–2440.

Table I. Conductance Parameters for Salts in DCE at 25 °C

ligand concn,[a] mM	Λ^0 [b]	σ_0 [c]	$10^{-3}K_A$	σ_K [d]	σ [e]
			DBC		
$LiBPh_4$					
1.001[f]	46.2	0.1	1.664	28	0.060
1.008[f]	46.7	0.1	1.651	20	0.043
			TPPO		
$LiBPh_4$					
1.001[f]	37.6	0.2	7.370	160	0.035
1.013[f]	32.0	0.4	4.320	240	0.110
			HMPA		
LiPi					
2.03	63.2	2.0	693	52	0.048
5.02	63.0	2,4	278	24	0.053
9.28	56.9	0.7	115	4	0.033
18.7	54.0	0.2	48.3	0.6	0.027
			Glyme-5		
LiPi					
1.65	66.4	0.5	517	9	0.017
4.78	66.5	0.9	510	15	0.011
10.3	63.8	0.4	452	7	0.006
20.1	60.7	0.4	398	5	0.006
29.3	58.9	0.4	369	5	0.005
39.7	58.4	0.4	353	6	0.007
			Glyme-4		
LiPi					
10.0	53.6	9.1	10900	3900	0.012
18.6	56.6	13	7700	3600	0.007
28.4	58.8	2.2	6220	480	0.004
			HMPA		
NaPi					
19.9	53.9	0.5	42.8	1.2	0.082
31.0	52.6	0.2	21.6	0.2	0.044
40.7	51.8	0.1	13.6	0.1	0.036
50.0	51.84	0.05	10.31	0.04	0.020
			TPPO		
NaPi					
28.0	45.3	0.2	38.6	0.6	0.033
35.8	44.4	0.1	23.6	0.3	0.040
47.9	43.6	0.1	13.6	0.2	0.042
			Glyme-5		
NaPi					
10.5	59.9	0.8	779	24	0.009
20.3	56.2	0.6	522	13	0.011
29.6	55.6	0.3	441	6	0.006
47.5	54.6	0.6	317	8	0.014
56.6	53.5	0.5	266	6	0.013

[a] Except for the results for $LiBPh_4$ where the ratios of ligand concentration to salt concentration, *r*, are listed. [b] Units are Ω^{-1} cm^2 mol^{-1}. [c] Standard deviations in the calculated value of Λ^0. At least six data pairs were measured and used for each solvent-ligand mixture. The salt concentrations ranged from 0.2 to 0.02 mM in these experiments. [d] Standard deviation in the calculated value of K_A. [e] Standard deviation in the fit of Λ(calcd) to Λ(obsd). [f] Ratio of ligand concentration to salt concentration.

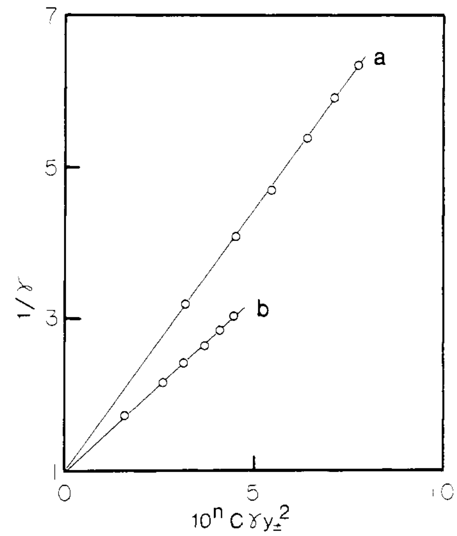

Figure 2. The conductance of LiPi in excess HMPA assuming a simple ion association equilibrium and using Onsager's limiting law for the conductance function to calculate γ, the fraction of salt dissociated as described in the text: (a) 2.03 mM HMPA with $n = 6$, (b) 18.7 mM HMPA with $n = 5$.

Table II. Conductances of LiPi in TPPO-DCE Solutions at 25 °C

salt concn, mM	ligand concn, mM	Λ, Ω^{-1} cm^2 mol^{-1}
0.4321	0.4374	0.1963
0.6467	0.6547	0.1860
0.7731	0.7826	0.1814
0.8454	0.8558	0.1795
0.8454	1.689	0.3361
0.8454	2.543	0.5661
0.8454	3.466	0.8464
0.8454	4.414	1.150
0.8454	5.402	1.474
0.8454	6.122	1.712
0.3478	1.539	0.7504
0.5267	1.539	0.4999
0.6409	1.539	0.4061
0.7724	1.539	0.3321

conductance parameters Λ^0 and K_A derived in this manner are listed in Table I, together with the precise ratios *r* of ligand-to-salt concentrations used to prepare the solutions. Addition of excess DBC ligand to a 0.483 mM solution of $DBC{\cdot}LiBPh_4$ resulted in a small *decrease* in conductance: at $r = 1.054$, $\Lambda = 32.02$; at $r = 1.147$, $\Lambda = 31.87$; at $r = 1.239$, $\Lambda = 31.75$. In contrast, addition of excess TPPO ligand to $TPPO{\cdot}LiBPh_4$ solutions resulted in pronounced increases in conductance as shown in Figure 1.

In a second kind of conductance experiment, a series of ligand-DCE mixtures of fixed composition were used as solvents to prepare LiPi or NaPi salt-solvent stock solutions. Weighed portions of these salt stock solutions were then added to known quantities of solvent of the same ligand-DCE composition in the conductance cell, and the conductances of the thermostated solutions were measured. The results of two runs, LiPi in 18.7 mM HMPA in DCE and LiPi in 39.7 mM glyme-5 in DCE, are shown in Figure 1. The sets of Λ, C data for each ligand-DCE solvent mixture were fitted to eq 2-4 using the same approach as outlined above. Values of Λ^0 and K_A for LiPi with HMPA, glyme-4, and glyme-5 and for NaPi with HMPA, TPPO, and glyme-5 are listed in Table I at each ligand concentration. The salt concentrations in these conductance runs were kept below 0.3 mM. These data were also fitted to eq 2-4 using Onsager's limiting law in eq 2; i.e., $\Lambda = \gamma[\Lambda^0 - S(C\gamma)^{1/2}]$, where $S = \alpha\Lambda^0 + \beta$, the limiting slope. The computer program used was otherwise the same as that used above. The values of K_A so obtained were 1-10% lower and the values of Λ^0 were 1-2% lower than those listed in Table I. For an illustration of how well these salts follow a simple ion association equilibrium in these ligand-containing solvents, eq 3 can be rearranged to $1/\gamma = 1 - K_A C\gamma y_{\pm}^2$, which is of the same form as the Fuoss conductance equation.[17] The data for LiPi at two concentrations of HMPA in DCE are plotted in Figure 2. In each case the final values of Λ^0 and K_A from the computer least-squares fitting using Onsager's limiting law were used to

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(16) The least-square adjustment of the conductance data is not sensitive to the value of *R* chosen in medium- and low-dielectric solvents; σ shows a shallow minimum near $R = q$. See, for example: (a) Justice, J. C. *J. Chim. Phys. Phys.-Chim. Biol.* **1968**, *65*, 353-367. (b) Justice, M. C.; Justice, J. C., *J Solution Chem.* **1977**, *6*, 819-826.

(17) (a) Fuoss, R. M.; Kraus, C. A. *J. Am. Chem. Soc.* **1933**, *55*, 476-488. (b) Fuoss, R. M.; Shedlovsky, T. *Ibid.* **1949**, *71*, 1496-1497.

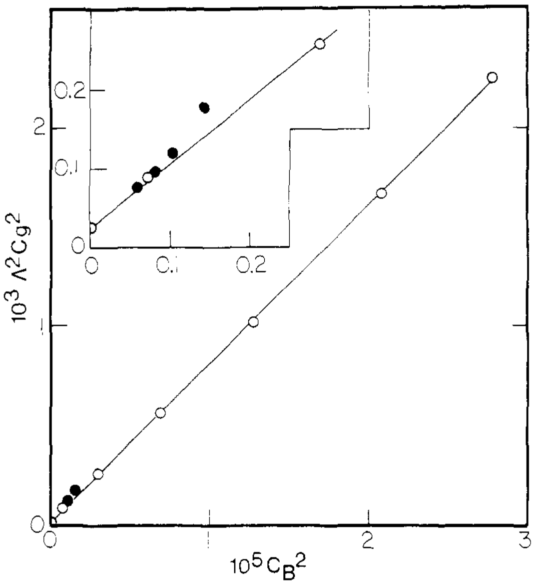

Figure 3. The conductance function (eq 6) for LiPi plotted vs. the square of the excess TPPO concentration, C_B. The scale of the axes in the insert has been expanded to show the data at low concentrations. The straight lines in the main graph and the insert have the same slope.

calculate values of $\Lambda^0 - S(C\gamma)^{1/2}$; these latter were then used to calculate γ by rearranging eq 2 to yield $\gamma = \Lambda/[\Lambda^0 - S(C\gamma)^{1/2}]$.

A combination of the kinds of conductance experiments described above was carried out on the system TPPO plus LiPi in DCE. The *concentration, molar conductance* data for 1:1 TPPO·LiPi are listed in Table II. Inspection of these date indicates that the molar conductance approaches a shallow minimum as the salt concentration increases; this is characteristic of the effects of triple ion formation induced as the salt concentration increases.[18] The effects on Λ of adding excess TPPO to the most concentrated salt solution (0.8454 mM) in the 1:1 TPPO·LiPi series are also listed in Table II; the molar conductance is seen to increase markedly as TPPO is added. In contrast, the molar conductance is seen to decrease upon adding salt to a solution in which the TPPO concentration is fixed, Table II. these changes in conductance are not a simple function of the ligand-to-salt ratio; it will be shown below that the conductance data may be rationalized if it is assumed that at least 1 mol of TPPO per mol of salt is bound up in the formation of a 1:1 ligand–salt complex, which is only slightly dissociated into current carriers, with excess ligand serving to induce further dissociation of the complex.

Triple-ion formation may involve the formation of one or two new ionic species

$$C^+,A^- \rightleftharpoons C^+ + A^- \qquad K_D = K_A^{-1}$$

$$C^+ + C^+,A^- \rightleftharpoons C_2A^+ \qquad K_+$$

$$C^+,A^- + A^- \rightleftharpoons CA_2^- \qquad K_-$$

Two limiting cases have been considered in the literature; the symmetrical case, formation of both kinds of ion triple[19] leading to the conductance function

$$\Lambda C^{1/2} g = \Lambda^0_1 K_D^{1/2} + (\Lambda^0_3 K_3^{1/2}) C (1 - \Lambda/\Lambda^0_1) \qquad (5)$$

where g is a correction for ion atmosphere effects,[19] Λ^0_1 is the molar conductance of $C^+ + A^-$, Λ^0_3 is that for $C_2A^+ + CA_2^-$, and $K_3 = K_D K_+ K_-$ (for the solutions in the absence of excess ligand, g does not differ from unity by more than 1%, while the factor $1 - \Lambda/\Lambda^0_1$ is within 2% of 1), and the unsymmetrical case,[20] where

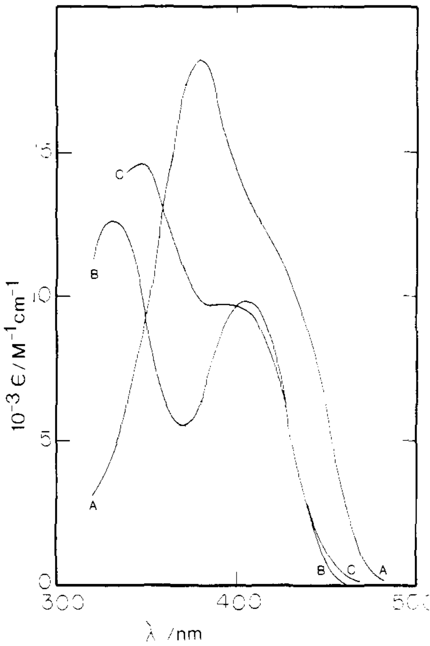

Figure 4. Spectra of picrate salts at 25 °C, molar absorptivity in M^{-1} cm^{-1} vs. wavelength in nm: (A) 0.0485 mM Bu_4NPi in DCE, (B) 0.124 mM TPPO·LiPi in DCE, (C) 0.670 mM LiPi in 15.3 mM $LiBPh_4$ in 2-butanone.

only one of the two possible triple ions is formed preferentially (with formation constant K_i) yielding the conductance function

$$\Lambda^2 C g^2 = \Lambda^0{}_1{}^2 K_D + F \Lambda^0{}_1{}^2 K_D K_i C (1 - \Lambda/\Lambda^0) \qquad (6)$$

where $F = (2\Lambda^0_2/\Lambda^0_1) - 1 + (1 - \Lambda^0_2/\Lambda^0_1)^2/[1 + 1/K_iC]$. Plots of $\Lambda C^{1/2}$ vs. C and of $\Lambda^2 C$ vs. C for TPPO·LiPi are both linear so that no clear choice between the two extremes noted above can be made based on these data.

Consider now the effect of excess TPPO on the conductance of TPPO·LiPi; it is found, Figure 3 that $\Lambda^2 C g^2$ is a linear function of the square of the concentration of TPPO in excess of the salt, $C_B = C_B{}^0 - C$, where $C_B{}^0$ is the formal ligand concentration and C is the salt concentration. Λ^0_1 has been taken to be 51 Ω^{-1} cm^2 mol^{-1} in calculating the values of g (see the Discussion section below). Note that both sets of results, those obtained at a fixed salt concentration and those obtained at a fixed ligand concentration, appear to fall on the same almost straight line and that the intercept as $C_B \rightarrow 0$ almost coincides with the intercept as $C \rightarrow 0$ of a plot of $\Lambda^2 C$ vs. C in the absence of excess ligand.

Examination of the results of the conductivity studies of LiPi and NaPi solubilized in DCE by added HMPA, TPPO, and glyme-5 yielded the observation that in a plot of $\Lambda^0 K_D{}^{1/2}$ (or $\Lambda C^{1/2} g$ in the case of TPPO·LiPi) vs. C_B the data points for a given ligand with LiPi were almost coincident on the same straight line with those for NaPi.

The near-UV spectrum due to the picrate moiety of 0.124 mM TPPO·LiPi in DCE, Figure 4, shows a larger blue shift of the short-wavelength peak (λ_{max} 332 nm) than that observed in the case of LiPi in the presence of excess $LiBPh_4$ in 2-butanone (λ_{max} 345 nm) when compared with that for Bu_4NPi in either 2-butanone[13] or in DCE (λ_{max} 380 nm in both). LiPi plus $LiBPh_4$ in 2-butanone is almost completely in the ion pair form[13] while Bu_4NPi has been found[21] to be ~80% dissociated into the free ions at the concentration employed here. Almost no changes were observed in the ϵ vs. λ curves of 1:1 TPPO LiPi upon increasing the concentration tenfold from 0.124 mM to 1.13 mM, Figure 5, curve a. Upon addition of excess TPPO to this last solution, both absorption maxima are seen to undergo moderate red shifts as well as moderate increases in molar absorptivity at the maxima, curves a–d and f. Sodium picrate (1.02 mM) in 15.5 mM TPPO exhibits almost the same spectrum, curve e, as a similar lithium picrate solution, curve d. It was not possible to compare the spectra of the two 1:1 salt–ligand complexes since the sodium salt requires

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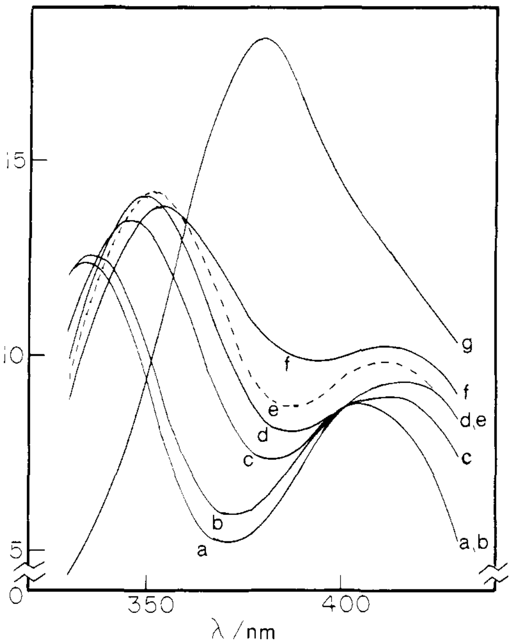

Figure 5. Spectra of LiPi and NaPi in TPPO–DCE solutions, molar absorptivity in M^{-1} cm^{-1} vs. wavelength in nm: 1.13 mM LiPi in (a) 1.15 mM TPPO, (b) 2.14 mM TPPO, (c) 7.60 mM TPPO, (d) 15.5 mM TPPO, (e) 1.02 mM NaPi in 15.5 mM TPPO, (f) 0.845 mM LiPi in 36.0 mM TPPO, and (g) 0.0485 mM Bu_4NPi (83% dissociated) in pure DCE.

an excess of TPPO to dissolve in DCE. The UV–visible spectra of the system glyme-5·LiPi are very similar to those with TPPO as ligand: 1.21 mM LiPi in 1.51 mM glyme-5 had λ_{max} 342 nm (ϵ 1.39 × 10^4 M^{-1} cm^{-1}), λ_{max} 403 nm (ϵ 0.92 × 10^4 M^{-1} cm^{-1}), shifting slightly upon increasing the ligand concentration to 17.6 mM, λ_{max} 347 nm (ϵ 1.43 × 10^4 M^{-1} cm^{-1}), λ_{max} 410 nm (ϵ 0.95 × 10^4 M^{-1} cm^{-1}). In summary, the spectra of LiPi and NaPi in the presence of TPPO and of LiPi in the presence of glyme-5, all in DCE solvent, resemble the spectrum of the lithium picrate ion pair observed in 2-butanone and showed only slight indications of the changes due to the growth of a peak due to "free" picrate ion (represented by the Bu_4NPi spectrum) upon the addition of even a 40-fold excess of ligand in one case (0.845 mM LiPi plus 36.0 mM TPPO).[22]

Discussion

The conductance parameters listed in Table I for DBC·$LiBPh_4$ are taken to be those characteristic of DBC·Li^+ + BPh_4^- in DCE and those listed for TPPO·$LiBPh_4$ at r = 1.001 are for TPPO·Li^+ + BPh_4^- in DCE. The value of Λ^0 = 37.6 at r = 1.001 for this latter salt is very close to the value 40.5 expected assuming Walden's product, $\Lambda^0\eta_0$, is constant and using results obtained in 2-butanone.[11] The values of Λ^0 listed in Table I for DBC·Li^+ + BPh_4^- are very close to an estimate of 47 Ω^{-1} cm^2 mol^{-1} based on the data on DBC·Na^+ + BPh_4^- in acetonitrile,[24] the observation that small changes in Λ^0 occur upon replacing sodium with potassium in crown ether complexes[24,25] leading to the assumption that no change occurs in Λ^0 upon replacing sodium with lithium, and finally, constancy of Walden's product.

It is reasonable that ion association is more extensive for TPPO·Li^+ than for DBC·Li^+ with BPh_4^-; charge separation in the ion pair should be smaller for the monodentate phosphine oxide than for the crown ether complex. The complex DBC·Li^+, free or paired with BPh_4^-, does not appear to react with excess DBC to bind more than one molecule of crown ether per lithium cation nor to undergo dissociation to free ligand plus cation since addition of excess crown ether had only a slight effect on the conductivity of a salt solution. The large increase in conductance that resulted upon the addition of excess TPPO to a solution of TPPO·$LiBPh_4$ is due to binding of more than one ligand to the Li^+ ion, decreasing the extent of ion association. This effect could be responsible in part for the decrease in Λ^0 and K_A at r = 1.013 for this salt (Table I).

Solubilization of LiPi and NaPi by the ligands TPPO, HMPA, glyme-4, and glyme-5 is taken to be due to specific interaction of the ligands with the cations to yield salt–ligand complexes. The variations in molar conductance with salt concentration in the ligand–DCE solvent mixtures have been shown to fit eq 2–4 (simple ion association) very well, Table I and Figure 2. In all cases except LiPi in glyme-4, the values of both Λ^0 and K_A decrease as the ligand concentration increases. In these experiments where the maximum salt concentrations were kept some 25 times less than the ligand concentration in a given solvent mixture it seems reasonable that the distribution of the number of ligands bound per ion and per ion pair would be approximately constant and would change only as the ligand concentration was changed. As the ligand concentration increases it is expected that the number of ligands bound to the cations would increase, thus accounting for both the decrease in Λ^0 and the decrease in K_A. Assuming Walden's product to be constant, estimates of Λ^0 = 59 for HMPA·Li^+ + Pi^- and Λ^0 = 51 for TPPO·Li^+ + Pi^- are obtained for DCE solvent, based on results in 2-butanone.[11] These estimates are consistent with the values of Λ^0 listed in Table I.

It is proposed that the results for LiPi and NaPi with HMPA and TPPO are due to the interactions of the salt cations M^+, already binding one ligand molecule each, with excess ligand B to bind one or more additional ligand molecules each.

$$\mathrm{BMX} \rightleftharpoons \mathrm{BM^+} + \mathrm{X^-} \qquad K_1 \tag{7}$$

$$\mathrm{BM^+} + \mathrm{B} \rightleftharpoons \mathrm{B_2M^+} \qquad K_2 \tag{8}$$

$$\mathrm{B_2M^+} + \mathrm{B} \rightleftharpoons \mathrm{B_3M^+} \qquad K_3 \tag{9}$$

For such a system it has been shown[26] that the conductance function becomes

$$K_d{\Lambda^0_a}^2 = \Lambda^2 C{y_\pm}^2/F^2(1 - \Lambda/F\Lambda^0_a) \tag{10}$$

where $\Lambda^0_a = (\Lambda^0_1 + \Lambda^0K_2[B] + \Lambda^0K_2K_3[B]^2)/(1 + K_2[B] + K_2K_3[B]^2)$, $K_D = K_1(1 + K_2[B] + K_2K_3[B]^2)$, and F is similar to Fuoss's function,[17] correcting Λ^0 for ion atmosphere effects; i.e., $F\Lambda^0_a = \Lambda^0_a - f(\Lambda^0_a,R,\gamma C)$ in eq 2.

When the degree of ion association is large, as is the case with the TPPO–LiPi system, eq 10 reduces to $K_D{\Lambda^0_a}^2 = \Lambda^2Cg^2$. The small changes in Λ^0_a in Table I for LiPi and NaPi at much larger ligand concentrations are justification for assuming that Λ^0_a is almost constant in this case and equal to 51 Ω^{-1} cm^2 mol^{-1}, that estimated for TPPO·Li^+ + Pi^- in DCE. Values of K_D (= $\Lambda^2Cg^2/{\Lambda^0_a}^2$) were thus calculated for the LiPi–TPPO system in DCE. The equation relating K_D to [B] may be rearranged to

$$(K_D - K_1)/[B] = K_1K_2 + K_1K_2K_3[B] \tag{11}$$

Only in the case of LiPi with TPPO is K_1 large enough to be distinguishable from zero when compared with K_D; a value of K_1 = 0.96 × 10^{-8} is available for this system (see Figure 3). K_1 was taken to be zero in fitting the data for LiPi with HMPA, and for NaPi with both TPPO and HMPA to eq 11, Figure 6. The changes in K_D in the presence of the glymes were not large enough for a meaningful fit to be made to eq 11; a semilog plot of K_D vs. C_B for these ligands is included, Figure 7, for comparison with one another and with the other ligands. The values of K_1K_2 and $K_1K_2K_3$ obtained in a least-squares fit of the data to eq 11 are listed in that order: for LiPi with TPPO, (0.04 ± 0.02) × 10^{-4} and (2.96 ± 0.08) × 10^{-2}; for NaPi with TPPO, (0.80 ± 0.36)

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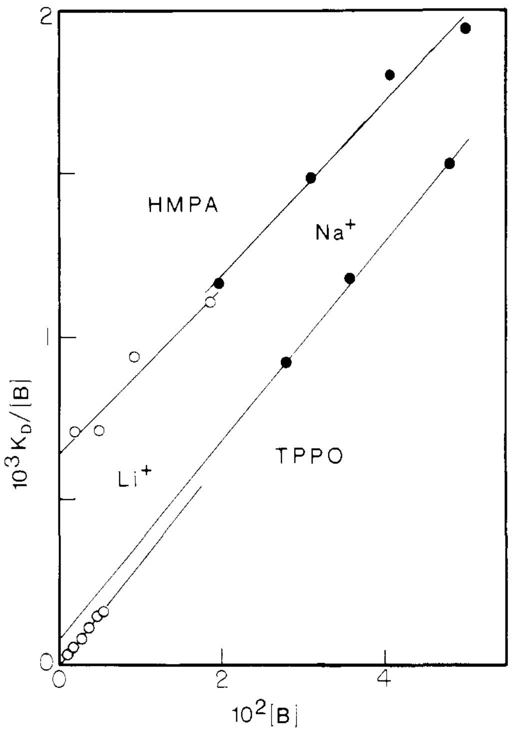

Figure 6. Ion pair dissociation of LiPi and NaPi as a function of the concentration, [B], of excess HMPA and TPPO in DCE at 25 °C. A plot of eq 11 of the text: LiPi, open circles, and NaPi, closed circles.

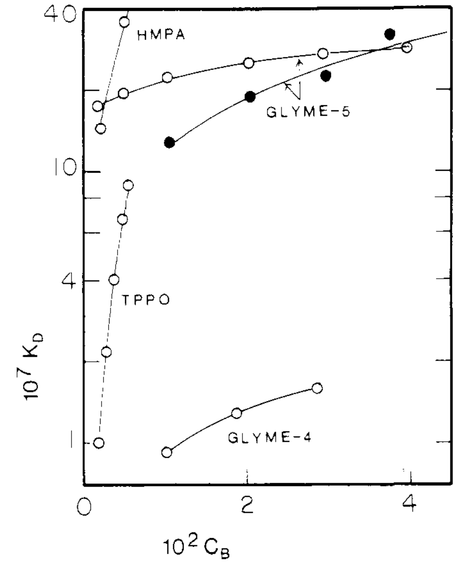

Figure 7. Ion pair dissociation of LiPi and NaPi as a function of the concentration C_B of excess HMPA, TPPO, glyme-5, and glyme-4 in DCE.

$\times 10^{-4}$ and (3.04 ± 0.09) $\times 10^{-2}$; for LiPi with HMPA, (6.45 ± 0.38) $\times 10^{-4}$ and (2.55 ± 0.01) $\times 10^{-2}$; for NaPi with HMPA, (6.70 ± 0.92) $\times 10^{-4}$ and (2.63 ± 0.25) $\times 10^{-2}$. The uncertainties listed are the standard deviations in the intercept and the slope, respectively. Replacement of LiPi with NaPi has little effect on the values of the constants K_1K_2 and K_3 with either TPPO or HMPA as ligand. Data are not available for a direct comparison with the same reactions in other solvents, but equilibrium constants for the reaction HMPA (or TPPO) + MPi $\rightleftharpoons$ HMPA (or TPPO)·M$^+$ + Pi$^-$ decrease by a factor of 10 or more when sodium replaces lithium as M in either 2-butanone[11] or in tetrahydrofuran solvent.[27,28] For LiPi with TPPO, the known value of K_1 (see above) may be used to obtain $K_2 \sim 400$ M^{-1} and $K_3 \sim 7000$ M^{-1}. K_3 is ~400 M^{-1} for NaPi with TPPO and falls to 40 M^{-1} for both LiPi and NaPi with HMPA; this is the reverse of the order of ligand affinity reported[11,27] for binding one ligand molecule per cation. This reversal and the similarity in behavior (seen both in conductance and UV–visible spectra) of the lithium and sodium salt–ligand systems here may be explained in terms of steric effects; once the cation is bound to at least one ligand, the importance of cation size is diminished and replaced by the steric repulsions of the substituent groups on the bound ligand interacting with those on the picrate anion or on any ligand in the process of binding. The small increases in molar absorptivity and the shifts of $\lambda_{\max}$ toward longer wavelength, Figure 5, indicate that the free picrate ion concentration is increased in the presence of excess ligand, just as is shown by the conductance data. The lack of a clear isosbestic point in the spectra is consistent with the formation of more than two species, eq 7–9.

The marked difference between the effects of excess glyme-4 and glyme-5 (figure 7) and the effects of excess HMPA and TPPO on the conductance of both LiPi and NaPi (Figure 6) are of particular interest. These results suggest that lithium and sodium cations tend to bind only one molecule of glyme per cation. The UV–visible spectra of LiPi solubilized by glyme-5 indicate that the picrate anion approaches the cation as closely in the glyme-5 ion pair as it does in the TPPO·Li$^+$, Pi$^-$ ion pair. Polyethers such as the glymes have been shown to wrap around cations, leaving space for coordination with an anion.[29] The fact the K_A is larger for LiPi with the shorter glyme-4 than with glyme-5 indicates that the anion is able to approach the center of positive charge more closely when glyme-4 is the ligand.

The solubilizing actions of HMPA, TPPO, and the glymes toward lithium and sodium picrates are more effective than that of DBC possibly because complexation by DBC produces a greater charge separation in the ion pair (see the conductance results for the tetraphenylborates). The charge separation in the TPPO·Li$^+$, Pi$^-$ ion pair in solution, for example, may more closely resemble (while the charge separation in the DBC·Li$^+$, Pi$^-$ in solution is much greater than) that of Li$^+$, Pi$^-$ in the solid phase. The tetraphenylborate anion may produce such a large charge separation in the crystalline solid that this factor is less important in the case of the solubilization of alkali metal tetraphenylborates by either DBC or TPPO. The ligands studied here can be arranged in order of increasing ability to promote charge separation in solution: short-chain glymes < long-chain glymes < TPPO, HMPA < DBC.

The choice of anion in a salt–ligand system can be seen to have almost as profound an effect as choice of ligand on ease of solubilization and on the resulting charge separation in solution. Applications involving phase-transfer catalysis will most often restrict the variables to choice of ligand and of cation. The glymes have been found[2a] to be as effective as crown ethers in promoting the reaction of aqueous potassium thiocyanate with chloroform solutions of *p*-nitrobenzyl bromide. The results obtained in this study are in agreement with the conclusion[2a] that glymes are the ligands of choice for these systems, based on cost.

Registry No. LiBPh$_4$, 14485-20-2; LiPi, 18390-55-1; NaPi, 3324-58-1; DBC, 14187-32-7; TPPO, 791-28-6; HMPA, 680-31-9; Glyme-5, 1191-87-3; Glyme-4, 143-24-8.

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