$$P_d = \rho_{\text{other}}{}^d + \sum_j \rho_j{}^d$$

we get

$$\mathrm{d}\langle I_{zd}\rangle/\mathrm{d}t = 0 = P_d(\langle I_{zd}\rangle - I_{0d}) -$$
$$\sigma_i{}^d I_{0i} + \sum_j{}'' \sigma_j{}^d(\langle I_{zj}\rangle - I_{0j}) \quad (A3)$$

or where the double prime sum means $j \neq i, d$

$$t^d = \frac{\langle I_{zd}\rangle - I_{0d}}{I_{0d}} =$$

$$\frac{\sigma_i{}^d I_{0i}}{P_d I_{0d}} - \frac{1}{P_d}\sum_j{}'' \sigma_j{}^d \frac{I_{0j}}{I_{0d}} \frac{\langle I_{zj}\rangle - I_{0j}}{I_{0j}} \quad (A4)$$

with

$$I_{0j}/I_{0d} = S_j(S_j + 1)\gamma_j/S_d(S_d + 1)\gamma_d$$

and

$$\rho_j{}^d/\sigma_j{}^d = 2S_j(S_j + 1)/S_d(S_d + 1)$$

and $f_i{}^i = (\langle I_{zj}\rangle - I_{0j})/I_{0j}$, the enhancement of j when i is saturated, we get

$$f_i{}^d = \gamma_i\rho_i{}^d/2\gamma_d P_d - (1/2P_d)\sum_k{}'' \gamma_k\rho_k{}^d f_i{}^k/\gamma_d \quad (A5)$$

The second term on the right-hand side of eq A5 is thus the indirect polarization of d through the other spins j when i is saturated.

The Thermodynamics of the Association of Tri-n-butylammonium Cation with a Series of Alcohols and Ethers in o-Dichlorobenzene[1]

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Abstract: The conductances of dilute solutions of tri-n-butylammonium picrate in o-dichlorobenzene with added methanol, n-propyl alcohol, isopropyl alcohol, t-butyl alcohol, tetrahydrofuran, diethyl ether, and triphenylphosphine oxide have been measured at 0, 25, 35, and 45°. Cation–ligand association constants, K_L, for each ligand have been calculated from these data at each temperature. Values of enthalpy and entropy changes for cation–ligand association have been obtained from these results. The affinities of the alcohols for the cation as measured by values of K_L at 25° differ only by 50% but are in the order MeOH > i-PrOH ~ n-PrOH > t-BuOH. The exothermicity ($\Delta H°$) for the association reactions are in the reverse order, that for t-BuOH being almost 2 kcal more negative than that for MeOH. A second molecule of alcohol adds to the cation–alcohol complexes as the alcohol concentrations increase. The ethers and triphenylphosphine oxide do not add a second molecule to the cation–ligand complex.

E quilibrium constants, K_L, for the formation of cation–ligand complexes, eq 1, in medium and low

$$\text{BH}^+ + \text{L} \rightleftharpoons \text{B-H}^+\cdots\text{L} \quad K_L = [\text{BH}^+\text{L}]/[\text{BH}^+][\text{L}] \quad (1)$$

dielectric solvents, have been determined at 25° in a number of laboratories.[2,3] Information concerning the factors which govern the extent of reactions such as eq 1 is important in developing our understanding of specific ion–solvent interaction and all the phenomena in which this latter is involved.

We have now begun a program to determine the enthalpy and entropy changes that accompany reactions of this type. This, our first report under this program, is concerned with the measurements of values of K_L, eq 1, at 45, 35, 25, and 0° for the cation tri-n-butylammonium (Bu₃NH⁺) as BH⁺, with methanol, n-propyl alcohol, isopropyl alcohol, t-butyl alcohol, tetrahydrofuran, diethyl ether, and triphenylphosphine oxide as L. We believe the thermodynamic data ob-

tained from these measurements are among the first of their kind to be reported. The only comparable measurements of which we are aware are those of Kebarle and Searles[4] on the thermodynamics of the gas-phase association of NH₄⁺ with NH₃.

Experimental Section

Our experimental approach is based on the following: a salt, typically tri-n-butylammonium picrate, in o-dichlorobenzene solvent, exists principally as the ion pair, Bu₃NH⁺, Pi⁻, in equilibrium with a small fraction present as the free ions, able to conduct an electric current

$$\text{Bu}_3\text{NH}^+, \text{Pi}^- \rightleftharpoons \text{Bu}_3\text{NH}^+ + \text{Pi}^- \quad (2)$$
$$K_0 = [\text{Bu}_3\text{NH}^+][\text{Pi}^-]/[\text{Bu}_3\text{NH}^+,\text{Pi}^-]$$

K_0 has been found[3a] to be 2.9×10^{-10} at 25°. Addition of a reagent such as methanol, which forms a 1:1 complex with Bu₃NH⁺,

$$\text{Bu}_3\text{NH}^+ + \text{MeOH} \rightleftharpoons \text{Bu}_3\text{NH}^+\cdots\text{OMe} \quad (3)$$
$$\text{H}$$

results in an increased free ion concentration, due to mass action, thus an increased electrical conductivity. Measurements of the conductances of the salt solution as a function of the ligand concentration furnish the raw data from which values of the cation–ligand association constants may be obtained by suitable treatment.[3a,c]

In the experiments reported here, all solutions were made up by weight. A salt solution, typically $2-3 \times 10^{-4}$ mol/l., was placed in the conductance cell and thermally equilibrated in the bath. The

(1) This work has been supported in part by Grant No. GP-6949 from the National Science Foundation.
(2) (a) J. F. Coetzee and G. R. Padmanabhan, *J. Amer. Chem. Soc.*, **87**, 5005 (1965); (b) J. F. Coetzee, G. R. Padmanabhan, and G. P. Cunningham, *Talanta*, **11**, 93 (1964).
(3) (a) E. K. Ralph, III, and W. R. Gilkerson, *J. Amer. Chem. Soc.*, **86**, 4783 (1964); (b) W. R. Gilkerson and J. B. Ezell, *ibid.*, **89**, 808 (1967); (c) J. B. Ezell and W. R. Gilkerson, *J. Phys. Chem.*, **72**, 144 (1968); (d) A. L. Mixon and W. R. Gilkerson, *J. Amer. Chem. Soc.*, **89**, 6410 (1967).
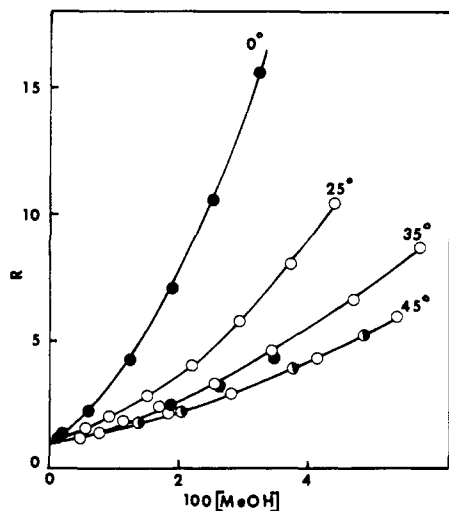(4) S. K. Searles and P. Kebarle, *J. Phys. Chem.*, **72**, 742 (1968).

Figure 1. Conductance ratios R for methanol as ligand with Bu₃-NHPi in o-dichlorobenzene. The salt concentrations used were (in units of μmol/l.): 0°, 92.8; 25°, 158; 35°, 94.1 (open circles), 93.1 (closed circles); 45°, 153 (open circles), 156 (half-filled circles).
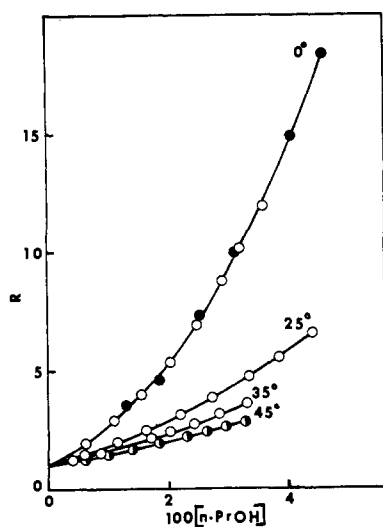

Figure 2. Conductance ratios R for n-propyl alcohol as ligand with Bu₃NHPi in o-dichlorobenzene. The salt concentrations used were (in units of μmol/l.); 0°, 95.5 (open circles), 93.2 (closed circles); 25°, 94.4; 35°, 75.7; 45°, 97.5.

titrant was made up by dissolving a weighed amount of ligand in a known weight of the salt solution. The ligand–salt titrant was then added in weighed increments to the salt solution in the conductance cell. It will be noted that the final concentrations of ligands are maintained some ten times greater or more than the salt concentration.

The purification of solvent, o-dichlorobenzene, has been described before.[3a] The preparation and purification of salt, tri-n-butylammonium picrate, has been described previously.[3a] Triphenylphosphine oxide was purified as reported before.[5] Tetrahydrofuran was purified as before.[6] Methanol was treated as before.[3a] In the course of this work we tried the method of purification of methanol reported by Hartley and Raikes[7] and used by a number of workers in conductance studies in methanol as solvent. This method of purification involves refluxing the methanol over a mercury–aluminum amalgam, and then distilling the methanol from the amalgam. We noted that one or more very small drops of mercury appeared at the top of the column in the still head.

(5) W. R. Gilkerson and J. B. Ezell, *J. Amer. Chem. Soc.*, 87, 3812 (1965).
(6) J. B. Ezell and W. R. Gilkerson, *ibid.*, 88, 3486 (1966).
(7) H. Hartley and H. R. Raikes, *J. Chem. Soc.*, 525 (1925).

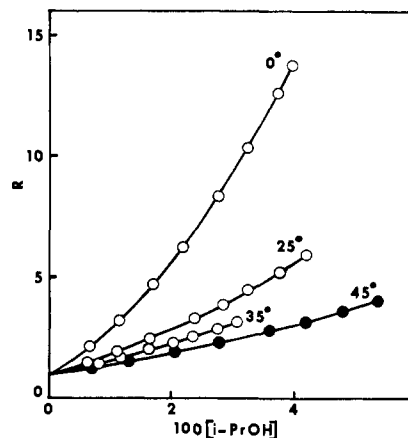Figure 3. Conductance ratios R for isopropyl alcohol as ligand with Bu₃NHPi in o-dichlorobenzene. The salt concentrations used were (in units of μmol/l.): 0.7°, 94.4; 25°, 94.2; 35°, 97.0; 45°, 95.8.
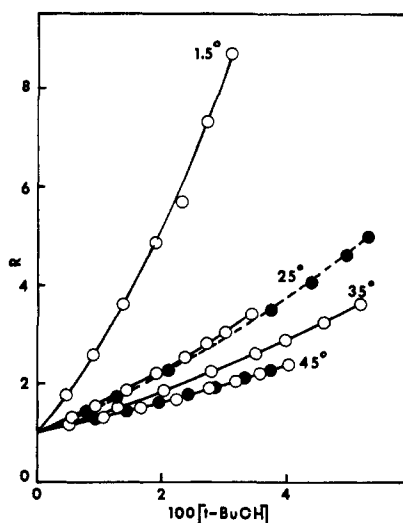

Figure 4. Conductance ratios R for t-butyl alcohol as ligand with Bu₃NHPi in o-dichlorobenzene. The salt concentrations used were (in units of μmol/l.): 1.5°, 97.8; 25°, 87.2 (open circles), 99.6 (closed circles); 35°, 84.6; 45°, 83.6 (open circles), 97.7 (closed circles).

We do not know whether the mercury reached the top of the column by entrainment or what. The distilling column used is 35 × 3 cm, packed with glass helices. At any rate, we returned to the former method of purification.[3a] Diethyl ether, n-propyl alcohol, isopropyl alcohol, and t-butyl alcohol, all reagent grade chemicals, were each refluxed for 4–6 hr over calcium hydride, and then distilled therefrom, using a 30 × 1 cm Vigreux column, retaining the middle fraction. These ligands were then passed through a 30 × 1 cm column packed two-thirds full with fired alumina (Alcoa, F-20) and the remaining third with molecular sieve (Linde, Type 4A), and were then used the same day. The 25° oil bath and the conductance bridge have already been described.[3a] The 45 and 35° baths were filled with transformer oil and maintained within 0.05° of the value stated in Table I. The 0° bath consisted of a plastic bucket of stirred transformer oil sitting in an ice–water slush. The conductance cell (Kraus type, bright platinum electrodes), equipped with a Teflon-enclosed magnetic stirring bar, was placed in the oil bath. The entire affair was placed over a large magnetic stirrer drive. Temperature regulation of this bath left something to be desired. The temperature of the oil bath containing the conductance cell remained constant within 0.5° during a run.

Results

Values of $R = (g/g_0)^2$, where g is the conductance of the salt solution at a ligand concentration [L], and g_0 is
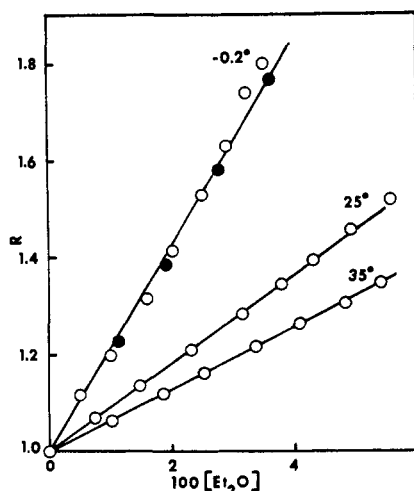
Figure 5. Conductance ratios R for diethyl ether as ligand with Bu$_3$NHPi in o-dichlorobenzene. The salt concentrations used were (in units of μmol/l.): $-0.2°$, 93.9 (open circles), 94.2 (closed circles); 25°, 95.4; 35°, 91.3.
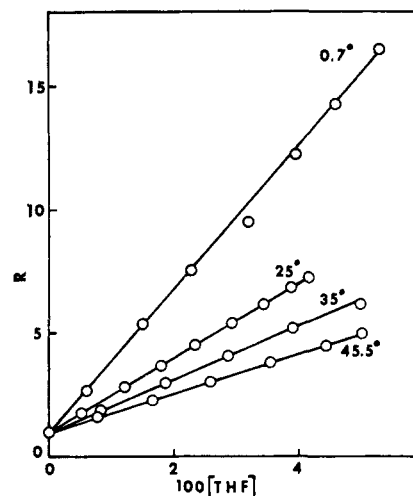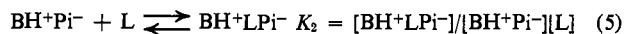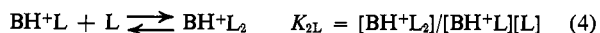

Figure 6. Conductance ratios R for tetrahydrofuran as ligand with Bu$_3$NHPi in o-dichlorobenzene. Salt concentrations used were (in units of μmol/l.): 0.7°, 93.2; 25°, 93.0; 35°, 91.6; 45.5°, 91.0.

that in the absence of ligand, are plotted at the various temperatures vs. [L] in the cases of each of the alcohols, Figures 1 through 4, and for diethyl ether, Figure 5, tetrahydrofuran, Figure 6, and triphenylphosphine oxide, Figure 7.

Assuming the series of equilibria, eq 1, 4, and 5 in addition to 2, where BH$^+$L$_2$ represents the cation with

$$BH^+ + L \rightleftharpoons BH^+L \qquad K_L = [BH^+L]/[BH^+][L] \qquad (1)$$

$$BH^+L + L \rightleftharpoons BH^+L_2 \qquad K_{2L} = [BH^+L_2]/[BH^+L][L] \qquad (4)$$

$$BH^+Pi^- + L \rightleftharpoons BH^+LPi^- \quad K_2 = [BH^+LPi^-]/[BH^+Pi^-][L] \quad (5)$$

two molecules of ligand attached to it, and BH$^+$LPi$^-$ represents a complex formed between the ion pair and ligand, it has been shown[3] that R is related to the ligand concentration by

$$R = (1 + K_L[L] + K_LK_{2L}[L]^2)/(1 + K_2[L]) \qquad (6)$$

Each of the plots of R vs. [L] for the alcohols, Figures 1 through 4, shows distinct curvature up, while those for ethers and Ph$_3$PO are quite linear. Curvature down as the [L] increases does not appear in any of these systems. This last observation together with the observation that, in all of these systems except that with triphenylphosphine oxide as ligand, the value of R clearly approaches unity as the ligand concentration goes to zero, are good evidence that complexing of the ligands with the ion pair itself, eq 5, is unimportant in these systems. With Ph$_3$PO as ligand, the values of R are already so large at the ligand concentrations used that the limit of R as [L] goes to zero cannot be clearly seen. The linearity of the plots for diethyl ether (Et$_2$O), tetrahydrofuran (THF), and Ph$_3$PO indicates that only eq 1 is important with these as ligands. The slopes of the plots of R vs. [L] for these latter three ligands are taken to be the values of K_L for these and are listed in Table I. The curvature upward for the alcohols implies that equilibria such as eq 4 are important in addition to eq 1.

$$(R - 1)/[L] = K_L + K_LK_{2L}[L] \qquad (7)$$

In these cases, plots of $(R - 1)/[L]$ vs. [L], eq 7, were made. These plots were linear with the following ex-
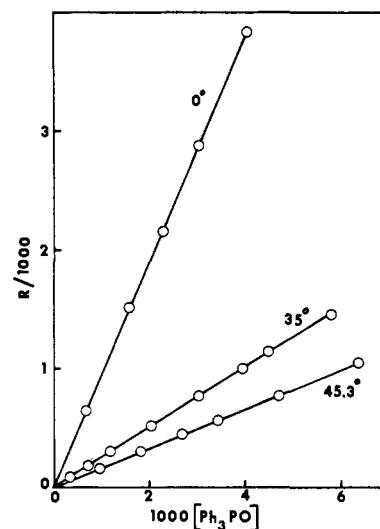

Figure 7. Conductance ratios R for triphenylphosphine oxide as ligand with Bu$_3$NHPi in o-dichlorobenzene. Salt concentrations used were (in units of μmol/l.): 0°, 95.1; 25°, 87.2; 35°, 87.4; 45.3°, 87.2.

ceptions; the two values of $(R - 1)/[L]$ at the lowest methanol concentrations at 45° fell below the straight line formed by all the others, so the two low values were ignored in fitting the data to eq 7. The methanol plots are shown in Figure 8. The plot of eq 7 for n-PrOH at

Table I. Ligand Association Constants with Bu$_3$NH$^+$ in ODCB

Ligand	0°	25°	35°	45.3°
		K_L, l./mol		
MeOH	144 (154)[a]	84	63	45 (48)
n-PrOH	154 (137)	72	56	43
i-PrOH	150	74	54	39
t-BuOH	153	56	37	30
Et$_2$O	22	9.2	6.5	
THF	284	152	110	80
Ph$_3$PO	950,000	366,000[b]	255,000	165,000
		K_{2L}, l./mol		
MeOH	75 (56)	34	21	16 (20)
n-PrOH		16	12	9.0
i-PrOH	26	13	10	7.1
t-BuOH	18	7.6	7.1	4.3

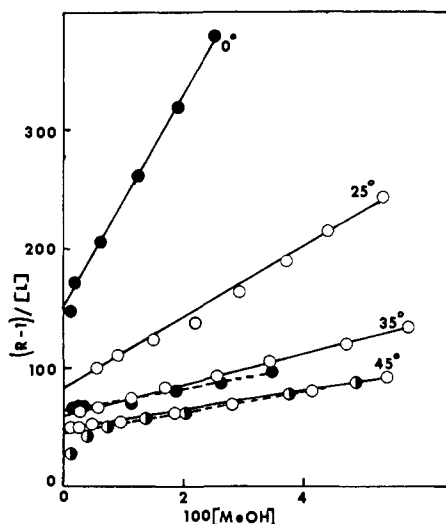[a] Results in parentheses are for repeated runs. [b] Reference 6.

Figure 8. Plots of the extrapolation function, $(R - 1)/[L]$, vs. [L] for methanol as ligand with Bu₃NHPi. Salt concentrations are given under Figure 1.
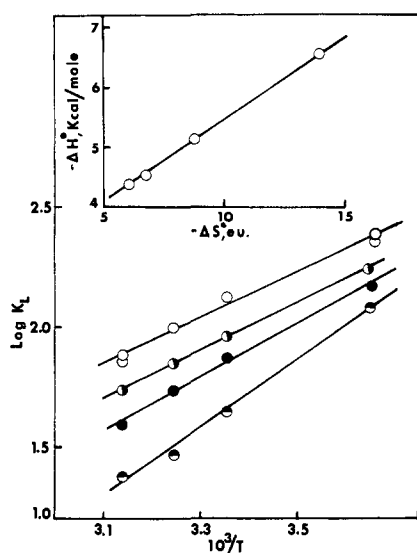

Figure 9. Temperature dependence of the cation–ligand association constants for the alcohols as ligands with tri-n-butylammonium cation in o-dichlorobenzene solvent: open circles, MeOH (log $K_L + 0.2$); right-half-filled circles, n-PrOH (log $K_L + 0.1$); closed circles, i-PrOH (log K_L); upper-half-filled circles, t-BuOH (log $K_L - 0.1$). The enthalpy change for each alcohol is plotted vs. the corresponding entropy change in the insert.

0° showed distinct upward curvature at higher alcohol concentrations. The intercepts as [L] approached zero were taken to be the values of K_L for these runs. No attempt to obtain values of K_{2L} from the slopes of these plots at 0° was made. The slopes of the remainder of the plots of eq 7 were used, together with the values of K_L from the intercepts, to calculate values of K_{2L}. The values of K_L and K_{2L}, on a molarity concentration scale, are tabulated in Table I.

We are certain that the effects of these added ligands on the conductance of tri-n-butylammonium picrate in o-dichlorobenzene are primarily due to interaction of the ligands with the tri-n-butylammonium cation rather than any involvement with the picrate anion. The conductance of a 1.705×10^{-4} M solution of tetra-n-butylammonium picrate, Bu_4N^+, Pi^-, in ODCB at 25° was
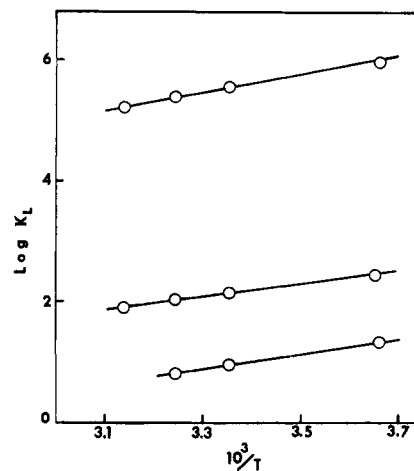

Figure 10. Temperature dependence of the cation–ligand association constants for triphenylphosphine oxide (upper line), tetrahydrofuran (middle line), and diethyl ether (lower line) as ligands with tri-n-butylammonium cation in o-dichlorobenzene solvent.

measured as a function of added methanol. At [MeOH] = 0, the equivalent conductance of the solution was found to be 11.64 ohm⁻¹ cm² equiv⁻¹. The equivalent conductance increased linearly to a value of 11.97 at 0.0222 M methanol. This small 2.8% increase in the conductance of this solution of Bu_4NPi is to be compared with the 90% increase in conductance we observe (Figure 1) for a 1.60×10^{-4} M solution of Bu_3NHPi when the methanol concentration is made 0.022 M. If the small increase in conductance of the Bu_4NPi salt solution if attributed solely to interaction of methanol with picrate anion, then one may estimate a value of $K_L = 1.03$ for the association of picrate anion with methanol.[8] We feel the anion–ligand interactions in the systems studied here are thus negligible in magnitude when compared to the cation–ligand interactions.

The thermodynamic quantities $\Delta H_L°$ and $\Delta S_L°$ for formation of the 1:1 cation–ligand complex, eq 1, were evaluated using a least-squares fit of the equation

$$\log K_L = \Delta S_L°/2.30R - (\Delta H_L°/2.30R)(1/T) \quad (8)$$

assuming that both $\Delta H_L°$ and $\Delta S_L°$ are constant in the range of temperature studied here. Figure 9 shows plots of K_L vs. $1/T$ for the alcohols while Figure 10 shows similar plots for the remaining three ligands. The straight lines in each case are the least-squares fitted lines. The values of $\Delta H_L°$ and $\Delta S_L°$ for 1:1 cation–ligand complex formation appear in Table II. The probable errors are listed for each value and were calculated using relations given in Margenau and Murphy.[9]

The values of K_{2L} are more uncertain than values of K_L, both from an experimental and from an interpretative point of view. Consequently, straight lines were eyeballed through the points on the plots of log K_{2L} vs. $1/T$. The slopes of the lines yielded values of $\Delta H_{2L}°$. From these values and those for log K_{2L}, values of $\Delta S_{2L}°$ were calculated and these appear also in Table II.

(8) This value of K_L is obtained after making the appropriate corrections for the extensive ion pair dissociation of Bu_4NPi in this system and the ion atmosphere efforts resulting from the dissociation, using eq 9 of ref 3a.

(9) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand and Co., Inc., New York, N. Y., 1943, p 502.

Table II. Thermodynamics of Association with
Bu_3NH^+ in ODCB

Ligand	$-\Delta H_L^\circ$, kcal/mol	$-\Delta S_L^\circ$, cal/(mol deg)	$-\Delta H_{2L}^\circ$, kcal/mol	$-\Delta S_{2L}^\circ$, cal/(mol deg)
MeOH	4.38 ± 0.51	6.1 ± 1.7	5.5	25
n-PrOH	4.54 ± 0.04	6.75 ± 1.4	5.5	24
i-PrOH	5.14 ± 0.16	8.77 ± 0.54	4.6	20
t-BuOH	6.56 ± 0.25	13.9 ± 0.8	5.5	22
Ph_3PO	6.56 ± 0.20	-3.37 ± 0.6		
THF	4.84 ± 0.24	6.40 ± 0.8		
Et_2O	5.71 ± 0.14	14.8 ± 0.5		

Discussion

One outstanding feature of these results is that with the alcohols as ligands, the cation–ligand complexes tend to add a second molecule of ligand while the ethers and phosphine oxide as ligands do not show this behavior with tri-n-butylammonium cation. The enthalpy and entropy changes accompanying the addition of a second molecule of one of the alcohols to the cation–alcohol complex are all remarkably the same, from alcohol to alcohol. These values of ΔH_{2L}° and ΔS_{2L}° are very similar to those found for the formation of the alcohol dimers in carbon tetrachloride.[10] We take these facts as indicative that the second alcohol ligand molecule is hydrogen-bonded to the first in the complex, rather than both alcohol molecules in the complex being symmetrically bound to the cation.

At 25°, we obtain a value of $K_L = 56 \ M^{-1}$ with t-BuOH as ligand, while for Ph_3PO as ligand, we find $K_L = 370,000 \ M^{-1}$. The values of ΔH_L° for these two ligands are the same within experimental error, Table II. The principal source of the variations in the magnitudes of the cation–ligand association constants studied here is the entropy change, ΔS_L°. Even so, the values of ΔS_L° for the ligands studied here, with the exception of t-BuOH and Et_2O, are relatively small in magnitude. These small entropy changes are to be contrasted with those for adding a second molecule of alcohol to the cation–ligand complex, $\Delta S_{2L}^\circ \simeq -20$ to -25 eu. We have proposed[3b] that the formation of the 1:1 cation–ligand complexes in solution involves displacement of a solvating solvent molecule from the cation by the incoming ligand, eq 9. The entropy

$$BH^+, S + L \rightleftarrows BH^+, L + S \qquad (9)$$
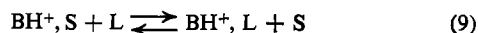
changes due to changes in translational degrees of freedom for such a process should be small. We take the small values of ΔS_L° for most of these ligands as further indication that eq 9 is a valid description for these systems. The loss of some 15 eu in the cases of t-BuOH and Et_2O as ligands would indicate that steric factors are involved with these two.

The linear relation between ΔH_L° and ΔS_L°, Figure 9, can only be qualitatively accounted for. As the po-

tential energy of interaction between cation and alcohol becomes more negative, the ligand is bound more firmly, losing more translational and rotational entropy in the process.[11] The increasing exothermicity with increasing methyl substitution on the carbon attached to the hydroxyl group in the series of alcohols can be attributed to short-range interaction increasing with methyl substitution. The added methyl groups result in a larger polarizability of the alcohol so the cation can induce a larger dipole in the alcohol. London dispersion forces acting between cation and alcohol increase with increasing polarizability and thus with increasing methyl substitution[12] and would also result in increasing negative values of ΔH_L°.

We can compare some of our results with those of Kolthoff and Chantooni,[13] who measured the equilibrium constants for the association of several ligands with solvated proton in acetonitrile solvent at 25°. These workers reported the proton affinities to be in the order t-BuOH $\gg$ MeOH $>$ n-BuOH. At 25° and above, we find the order MeOH $>$ n-PrOH $>$ t-BuOH as ligands toward tri-n-butylammonium cation in o-dichlorobenzene. The t-BuOH is displaced in our series relative to that of Kolthoff and Chantooni. The order of the values of ΔH_L° for our ligands does follow the order observed by Kolthoff and Chantooni, ΔH_L° being more negative for t-BuOH than for MeOH. The steric requirements of the tri-n-butylammonium cation are much greater than those of the proton (solvated by acetonitrile). Indeed, if the values of ΔS_L° for cation–ligand association were the same for MeOH and t-BuOH with Bu_3NH^+ (rather than being so different, Table II) in ODCB solvent, then the difference in free energy changes for the two alcohols as ligands would be equal to the difference in enthalpy changes. One may thus calculate, using the values of ΔH_L° in Table II, that K_L for t-BuOH would be greater than K_L for MeOH by a factor of 38. This is to be compared to a factor of 10 for these two ligands as proton bases in acetonitrile. We see that differences in steric requirements are more than sufficient to account for the differences in our experimental results and those of Kolthoff and Chantooni. We have not discussed the possible effects the two different solvents might have on the ordering of the relative basicities because we believe these would be second-order effects, and difficult to assess.

In conclusion, we had expected to find that the magnitude of K_L was determined principally by values of ΔH_L°. We find, however, that entropy changes dominate the process for the systems examined here. We intend to carry out experiments in which structural entropy (steric) effects will be minimized to determine if other entropy effects are playing any role in these processes.

(10) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, pp 355, 356.

(11) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 321.
(12) (a) E. Grunwald, R. L. Lipnick, and E. K. Ralph, *J. Amer. Chem. Soc.*, 91, 4333 (1969); (b) E. Grunwald and E. K. Ralph, *ibid.*, 89, 4405 (1967).
(13) I. M. Kolthoff and M. K. Chantooni, *ibid.*, 90, 3320 (1968).