Evidence for C–H as a Proton Donor Stabilizing Cation–Oxide Ligand Complexes[1a]

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Abstract: Conductances of a series of piperidinium picrates in chlorobenzene solvent at 25° have been studied in the presence of the addends tetrahydrofuran and triphenylphosphine. Cation–ligand association constants, K_L, have been derived from these data. The following order in K_L is found with nonoxygen-containing ligands: piperidinium > 1-methylpiperidinium > 1-ethylpiperidinium. With tetrahydrofuran and triphenylphosphine oxide as ligands, the order of the latter two cations is reversed: 1-ethylpiperidinium > 1-methylpiperidinium. These results are interpreted in terms of interaction, leading to a lowering in the potential energy, between a hydrogen atom on the ethyl group on the cation and one or more lone pairs of electrons on the oxygen atom in the ligand.

We had noted[2] that in chlorobenzene (PhCl) solvent at 25°, the cation–ligand association constants, K_L (eq 1), for Ph_3PO as ligand with piperidinium

$$AH^+ + L \rightleftarrows AH^+,L \quad K_L = [AH^+,L]/[AH^+][L] \qquad (1)$$

($PipH^+$), 1-methylpiperidinium ($MePipH^+$), and 1-ethylpiperidinium ($EtPipH^+$) cations decreased in the order $PipH^+ > EtPipH^+ > MePipH^+$. This order was in contrast to the effects of cation structure on the K_L's with the free piperidines themselves and with 2,6-dimethylpyridine (Lut) as ligands. In these latter cases, the order was $PipH^+ > MePipH^+ > EtPipH^+$. This last ordering is that which one would expect on the basis of steric effects alone. We thought that the reversal of $MePipH^+$ and $EtPipH^+$ in the series with Ph_3PO might be due to specific interaction between a C–H proton on the end of the ethyl substituent on the cation and one of the lone pairs of electrons on the phosphoryl oxygen. This paper is a report of further work undertaken to test this hypothesis. The same three cations are studied with tetrahydrofuran (THF) and triphenylphosphine (Ph_3P) as ligands.

Experimental Section

The picrate salts PipHPi, MePipHPi, and EtPipHPi were prepared and purified as before.[2] Chlorobenzene solvent was purified as before.[3] THF was purified as reported elsewhere.[4] Ph_3P (K & K Laboratories, Inc.) was recrystallized from ethanol. Conductance measurements were carried out using the bridge, bath, and cells previously described.[3] All measurements were carried out at 25°.

Results

Cation–ligand association constants were determined using a titration method (method II).[4,5] Solutions of each of the three salts were titrated with weighed increments of ligand dissolved in a separate portion of the same salt solution in PhCl. Values of the ratio, $R = (L/L_0)^2$, were calculated from the specific conductance, L_0, prior to addition of ligand, and L, the specific conductance at a given concentration of either THF or Ph_3P. These ratios, for THF, appear in Figure 1, plotted *vs.* the molar concentration of ligand, [THF], in the resulting solution. The slopes of these straight lines are taken to be values of K_L and are listed in Table I. Distinct curvature up was seen in a similar plot for Ph_3P as ligand. We have plotted in Figure 2 the quantities $(R - 1)/[L]$ *vs.* [L] for these systems in an effort to extrapolate to $[L] \rightarrow 0$, where the intercept should be[3-5] K_L. This extrapolation was uncertain due to curvature down in these plots (Figure 2). The intercepts, taken to be K_L, are listed in Table I. These values for Ph_3P as ligand are probably uncertain by some 10%. Those values with THF as ligand are uncertain by no more than 5%. Also listed in Table I are K_L values for Lut and Ph_3PO previously determined.[2]

Table I. Cation–Ligand Association Constants in PhCl at 25°

	$10^{-3}K_L$			
Cation	Lut[a]	Ph_3P[b]	Ph_3PO[a]	THF[b]
$PipH^+$	3.9	17	650	0.304
$MePipH^+$	0.75	14	150	0.043
$EtPipH^+$	0.44	8.5	280	0.061

[a] Reference 2. [b] This work.

Discussion

K_L values for Ph_3P are in the same order we previously found for the amines: $PipH^+ > MePipH^+ > EtPipH^+$. We have already discussed the significance of the magnitudes of these decreases in terms of the necessity for the N-substituted cations, normally in an equatorial conformation, to undergo the unfavorable equatorial → axial transformation in order to form the most stable cation–ligand complex. THF as ligand shows the same reversal already noted in the case of Ph_3PO: $EtPipH^+ > MePipH^+$. The oxygen atoms in these latter ligands have available more than one lone pair of electrons, while the nitrogen in the amines and the phosphorus in the phosphine have only one lone pair of electrons available for interaction with the cations. We believe the enhancement in K_L, cited above for $EtPipH^+$ with THF and Ph_3PO, is strong evidence for specific interaction between a hydrogen

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(1) (a) This work has been supported in part by a grant from the National Science Foundation, GP-3955; (b) author to whom inquiries should be addressed.

(2) A. L. Mixon and W. R. Gilkerson, *J. Am. Chem. Soc.*, **89**, 6410 (1967).

(3) E. R. Ralph, III, and W. R. Gilkerson, *ibid.*, **86**, 4783 (1964).

(4) J. B. Ezell and W. R. Gilkerson, *ibid.*, **88**, 3486 (1966).

(5) J. B. Ezell and W. R. Gilkerson, *J. Phys. Chem.*, in press.

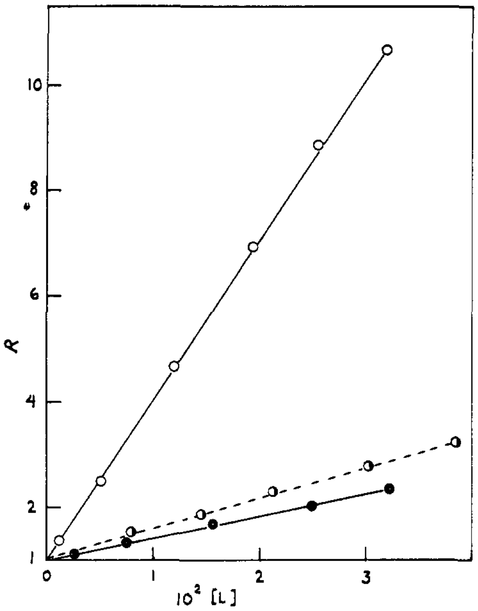


Figure 1. THF as a ligand in PhCl: ○, 2.61 × 10^{-4} *M* PipHPi; ●, 3.42 × 10^{-4} *M* MePipHPi; ◑, 3.40 × 10^{-4} *M* EtPipHPi.

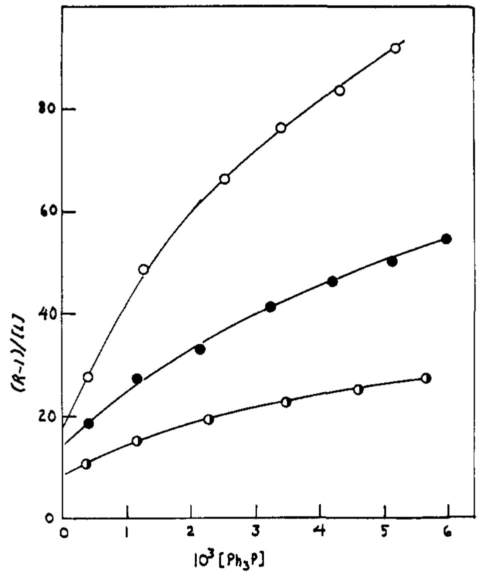
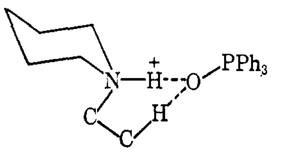


Figure 2. Ph_3P as ligand in PhCl: ○, 2.77 × 10^{-4} *M* PipHPi; ●, 3.39 × 10^{-4} *M* MePipHPi; ◑, 2.92 × 10^{-4} *M* EtPipHPi.

atom, on the terminal carbon of the ethyl substituent, with the one or more lone pairs of electrons on oxygen which are not involved in direct interaction with the protonated nitrogen on the cation, structure **1**. We shall call this interaction between H (bonded to C) and an oxygen lone pair a hydrogen bond. We do so knowing full well that many readers will take exception to our use of the term in this case. Allerhand and Schleyer[6] related a referee's objection on this point in their survey of C–H groups as proton donors in H bonding. It has been stated[6,7] that "methyl groups in any molecule do not hydrogen bond." We believe the particular feature in the complexes with N-ethylpiperidinium cation which favors H bonding with the C–H proton is the presence of the positive charge due to the proton on the ring nitrogen. One can envisage a polarization of the N–C and C–C bond electrons in the ethyl group due to the positive charge, finally resulting in a more polar terminal C–H bond with the center of positive charge at the hydrogen end of the bond. The fact that K_L's for $EtPipH^+$ are enhanced but those for $MePipH^+$ are not is consistent with the spatial requirements (bond lengths and angles) which render six-membered rings more stable than five- or seven-membered rings.[8]



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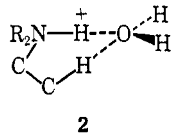
Effects similar to those observed here may be noted in the base strengths of amines in water. We list the pK_a's for a series of these in Table II.[9] The set on the left in Table II illustrates the effect of substitution, for H, of Me, Et, Pr (propyl), and Bu (butyl) groups on the basicity of dimethylamine. Replacement of H by Me produces a decrease in basicity of 1 pK_a unit. Replacing Me by Et results in an *increase* of 0.25 p*K* unit. Replacing Et by Pr or Bu produces essentially no change. The set on the right illustrates the effect of successive substitution of Et for Me groups on Me_3N. The increases, ΔpK_a, upon replacement of each Me group by an Et group are almost constant, 0.25 to 0.32 p*K* unit. We interpret these effects as due to the terminal C–H on the ethyl group in the protonated amine acting as a proton donor to form a hydrogen bond with a water molecule. The latter is one of the primary solvating water molecules in cation **2**. The resulting increase in stability of the cation due to the H bond accounts for the increased basicity. In fact, the increase in cation stability, presumed due to H bonding, upon replacement of Me by Et in the case of our piperidinium–oxide ligand complexes, log (K_L(Et)/K_L(Me)) ≃ 0.15 to 0.28, is about the same as the values of ΔpK_a observed in the water-solvated ammonium cations.

Table II. Basicities of Amines in Water at 20°

Amine	pK_a	Amine	pK_a
Me_2NH	10.92	Me_3N	9.91
Me_2NMe	9.91	Me_2NEt	10.16
Me_2NEt	10.16	$MeNEt_2$	10.46
Me_2NPr	10.16	NEt_3	10.78
Me_2NBu	10.19		



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A report[10] of a microwave investigation of barriers to internal rotation of *n*-propyl fluoride showed that the

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[6] A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1715 (1963).

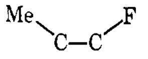
[7] See also W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).

[8] See, for example, G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, Chapter 5.

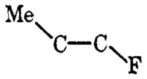
[9] All of these are from the compilation of D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths & Co., Ltd., London, 1965.

[10] E. Hirota, *J. Chem. Phys.*, **37**, 283 (1962).

terminal Me group together with the fluorine atom favored the *gauche* configuration (**3a**) over the *trans* (**3b**)



3a



3b

with $\Delta H_{g \rightarrow t} = 0.47$ kcal/mole. The implication here is that real interaction, lowering the net free energy, must be taking place between one or more hydrogens on the Me group and the fluorine atom, when in the *gauche* form, in order to overcome those energy differences which result in many molecules with structures similar to **3** preferring the *trans* configuration in the gas phase.[11] We suggest that the interaction leading to **3a** being preferred is a hydrogen bond, albeit a weak one, such as we have postulated, between a hydrogen atom on the Me group and one or more lone pairs on the fluorine atom.

The complexities indicated by the $(R - 1)/[\mathrm{L}]$ *vs.* [L] plots in the cases of the cations with Ph_3P as ligand are not unlike those noted[2] in the case of Ph_3PO with $PipH^+$. Further study of these systems is warranted. Additional complexes of the type $PipH^+(PPh_3)_2$ and $PipH^+Pi^-(PPh_3)$ might be forming in these systems. In any case, uncertainties involved in the extrapolation (Figure 2) to obtain K_L values for Ph_3P are not great enough to affect the relative order of cation–ligand affinity, just its magnitude. It is curious, however, that the large differences found with other ligands between the $PipH^+$, $MePipH^+$, and $EtPipH^+$ cation–ligand association are so small in the case of Ph_3P with these same cations. Other ligands similar to Ph_3P need to be studied in an effort to understand this contrasting behavior.

Our arguments for the existence of a weak hydrogen bond between a terminal hydrogen atom on the N-ethyl group in N-ethylpiperidinium cation and the oxygen atom in Ph_3PO ligand (or THF) would, of course, be strengthened by a demonstration of appropriate shifts in the pmr spectra or in the infrared spectra of these systems. The concentrations of the cation–ligand complex species in our solutions are typically of the order of 10^{-6} *M*, less than ${}^{1}/_{100}$ of the total salt concentration. We are unaware of either proton magnetic resonance techniques or infrared spectroscopic techniques which are sufficiently sensitive to detect species at such low concentrations. Increasing the concentrations of salt and ligand would serve no useful purpose in this connection. At concentrations higher than the 10^{-4} *M* range, salt solutions in low dielectric solvents such as PhCl become extremely complex, consisting of charged and uncharged clusters of ions of increasing molecular weight. Interpretation of the spectra (pmr or infrared) of such systems would be extremely difficult, if not impossible. We, at any rate, would be very skeptical of any such interpretation.

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[11] See, for instance, (a) S. Mizushima, *Pure Appl. Chem.*, 7, 1 (1963); (b) E. B. Wilson, Jr., *Advan. Chem. Phys.*, 2, 367 (1959).

Translational Diffusion of Common Monocyclic Hydrocarbons in Carbon Tetrachloride

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Abstract: Measurements have been made of the translational diffusion coefficients of cyclopentane, cyclohexane, and cycloheptane in carbon tetrachloride. The results have been examined in terms of the theories proposed by Kirkwood and Tchen, respectively. Although both theories take into account the hydrodynamic interaction between the solute and solvent, the experimental results do not agree closely with the theoretical values.

One of the best known theoretical studies of the diffusion of polymer chains is that of Kirkwood.[1] The formula (eq 2) for the frictional coefficient derived from this theory is somewhat in error, as has been pointed out by many authors including Zwanzig[2] and Erpenbeck and Kirkwood.[3] For weak hydrodynamic interactions, however, this error may be negligible and, hence, it may be hoped that the formula retains a practical usefulness.

Indeed, the applicability of the Kirkwood formula to short-chain (5 to 28 carbon atoms) *n*-alkanes has already been demonstrated by Dewan and Van Holde,[4] who obtained good agreement between the calculated and observed values of the frictional coefficient. Further applications of this equation to multi-subunit macromolecules, and a generalization to different size subunits have been presented.[5,6] However, uncertainties as to the range of validity of the theory require that data for more substances of known molecular structure be made available.

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[1] J. G. Kirkwood, *J. Polymer Sci.*, 12, 1 (1954).

[2] R. Zwanzig, *J. Chem. Phys.*, 45, 1858 (1966).

[3] J. J. Erpenbeck and J. G. Kirkwood, *ibid.*, 38, 1023 (1963).

[4] R. K. Dewan and K. E. Van Holde, *ibid.*, 39, 1820 (1963).

[5] V. Bloomfield, W. O. Dalton, and K. E. Van Holde, *Biopolymers*, 5, 135 (1967).

[6] V. Bloomfield, K. E. Van Holde, and W. O. Dalton, *ibid.*, 5, 149 (1967).