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Basicity of Some Phosphines in THF

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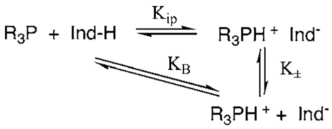
ABSTRACT



The reaction of several phosphines with an acidic indicator gives both ion pairs and free ions. The value obtained for the pK_a of tribenzylphosphine is shown to be reasonable by MO computations. An important limitation is demonstrated for the Fuoss equation of dissociation of ion pairs.

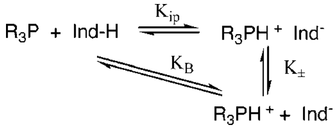
pK_a data are available in polar solvents for many protonated bases such as amines[1] and phosphines,[2−6] but these bases are frequently used in nonpolar solvents where ion pairs are involved. Ion pair basicity values have been reported recently for amines in THF[7−9] and for some phosphines.[10] The Morris group,[10] in particular, measured relative phosphine basicities by proton-transfer equilibria with NMR and estimated ion pairing effects using the Fuoss equation.[11] In this paper we report some results for the basicity of three phosphines, triethylphosphine (Et_3P), tricyclohexylphosphine (Cy_3P), and tribenzylphosphine (Bn_3P), using an indicator method.

1,3-Bis-(tetrafluoropyridyl)indene (BTPI) is sufficiently acidic to give measurable amounts of indicator anion with trialkylphosphines. In Figure S1 (Supporting Information), the spectrum of a solution of Et_3P with BTPI in THF is similar to that of the lithium salt, a solvent-separated ion pair (SSIP). In particular, λ_{max} is the same within a few nanometers. We assume that the phosphine forms the ion pair according to eq 1 and that the extinction coefficient of the ion pair is the same as that of the lithium salt.

$$R_3P + H\text{-}Ind \overset{K_{ip}}{\rightleftharpoons} R_3PH^+Ind^- \qquad (1)$$

The ion-pair equilibrium constant $K_{ip} = [R_3PH^+Ind^-]/[R_3P][H{-}Ind]$. This equation implies that the observed concentration of the indicator anion should be proportional to the product of $[R_3P]$ and [BTPI]. Figure 1 shows that such a proportionality does not hold. The observed curvature suggests that a significant fraction of the ion pairs have dissociated to the individual ions, Scheme 1. Accordingly, the total indicator anion concentration as measured by spectroscopy is given by eq 2 in which $\{A^-\} = [Ind^-] + [R_3PH^+Ind^-]$.

Scheme 1



$$\{A^-\} = (K_B[R_3P][H{-}Ind])^{1/2} + K_{ip}[R_3P][H{-}Ind] \qquad (2)$$

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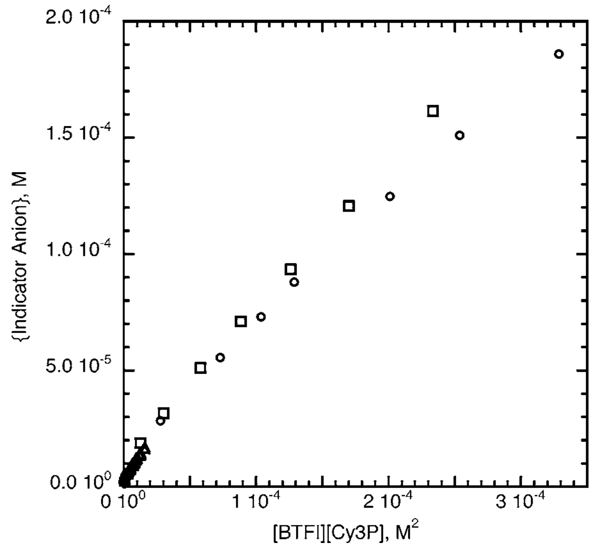

Figure 1. Plot of the observed indicator anion concentration vs the product of the phosphine and indicator, showing curvature. Four runs are shown for tricyclohexylphosphine as circles, squares, triangles, and diamonds.

A plot of {A^-} vs ($[R_3P][H{-}Ind]$)$^{1/2}$ gives a curve that can analyzed by least squares to give K_B and K_{ip} from which $K_\pm = K_B/K_{ip}$. This analysis is shown for Cy_3P in Figure 2. The other two phosphines were analyzed similarly to give the results detailed in Table S1 and Figures S2 and S3 (Supporting Information) and summarized in Table 1.

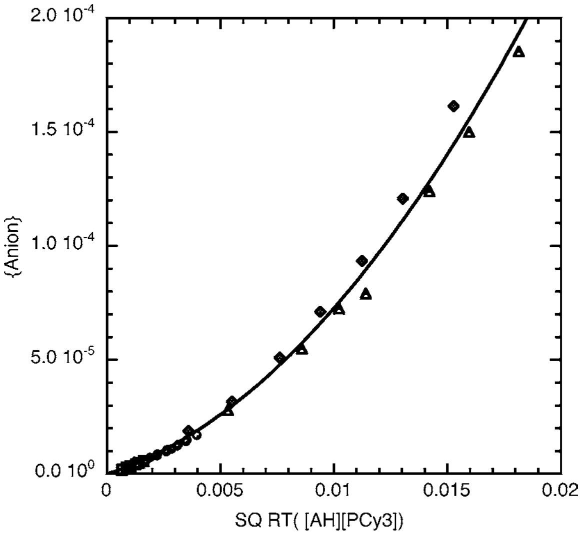

Figure 2. Plot of the observed indicator anion concentration vs the square root of the product of the phosphine and indicator. Four runs are shown for tricyclohexylphosphine as in Figure 1. The curve through the points and the origin is $y = (0.00312 \pm 0.000334)x + (0.4155 \pm 0.0251)x^2$, $R^2 = 0.992$.

Table 1. Ionic and Ion Pair Basicities of Phosphines in THF

R_3P	K_{ip}	K_B ($\times10^{-6}$)	$K_\pm$ ($\times10^{-5}$)
Et_3P	0.014 ± 0.002	1.00 ± 0.03	7.1
Cy_3P	0.42 ± 0.03	9.7 ± 1.1	2.3
Bn_3P	0.17 ± 0.01	3.6 ± 0.5	2.1

The triethylphosphine results are based on fewer measurements and might be less accurate than the others. However, K_B is the basicity in terms of free ions relative to the same indicator and therefore is equivalent to the pK_a differences between the protonated phosphines. The pK_a difference found between Et_3P and Cy_3P of 0.99 is essentially the same as that found by Streuli[1] in nitromethane,[12] 1.01. We have not found any other experimental measures of the pK of Bn_3P. Our finding of a basicity between that of Et_3P and Cy_3P (pK_a = 9.26 on Streuli's scale[5]) was surprising given that tribenzylamine is much less basic than triethylamine: pK_a values of the ammonium salts are 3.65[13] and 9.0,[1] respectively, in DMSO. The phenyl group is well-known to be inductively electron-attracting. It is noteworthy that attempts to correlate phosphonium pK_a values with polar substituent parameters have been few and rather limited. An early correlation with Taft's σ^* values was dominated by cyano groups and did not include 2-alkoxyethyl or 2-phenylethyl phosphines.[4] The latter phosphines deviate markedly from the published correlations. Accordingly, we looked to ab initio computations to determine whether proton affinities (PA) of phosphines can be modeled with modest basis sets. Results at the HF/6-31G(d) level are summarized in Table 2; the detailed computations are given in Table S2 (Supporting Information). The calculated PA values agree well with the limited experimental values available.[14] In particular, the phenylphosphines have calculated and experimental

Table 2. Proton Affinities (PA) and pK_a of Phosphines (energies in kcal mol^{-1})

phosphine	PA calcd[a]	PA exptl[b]	p$K_\pm$[c]	solvation[d]
$MePH_2$	205.25	203.5		
Me_2PH	218.63	218.0		
Me_3P	229.62	229.2	8.65	−9.70
Et_3P	235.56	235.3	8.69	−7.67
$n$$Pr_2PMe$	236.54	235.1		
$(CH_2)_5PMe$	234.09	231.7		
$PhPMe_2$	233.54	231.6	6.50	−8.34
Ph_2PMe	237.14	232.3		
Ph_3P	240.31	232.5	2.73	−6.94
Cy_3P	247.71		9.70	−6.08
Bn_3P	242.63		9.26[e]	−6.18
$Me_2PCH_2CH_2CN$	220.46		6.37	−10.41
$MeP(CH_2CH_2CN)_2$	211.13		3.61	
$P(CH_2CH_2CN)_3$	202.13		1.37	−12.53
$P(CH_2CH_2Ph)_3$	238.32		6.60	
$P(CH_2CH_2OR)_3$	232.01[f]		8.03[g]	−8.89[f]

[a] E(RHF, 631Gd) + unscaled ZPE. [b] Reference 15. [c] In nitromethane, ref 5. [d] E(RHF) + unscaled ZPE for formation of a complex between R_3PH^+ and Me_2O. [e] This work in THF extrapolated to Streuli, ref 5. [f] R = Me. [g] R = ^{n}Bu.

values that are comparable to those of the trialkylphosphines. The results in solution, however, are not nearly as satisfactory. A plot of Streuli's pK_a values vs the computed PA values shows a correlation from which the phenylphosphines differ markedly, Figure 3. The use of experimental PA values would have given comparable results; that is, the phenylphosphines are relatively much less basic in solution than in the gas phase. The difference must be due to solvation, but these solvation differences are not modeled well by dielectric continuum models of the PCM type. Results with such a model still show large deviations by the phenylphosphines, Figure S4 (Supporting Information). Our result for tribenzylphosphine, however, still fits in well with the other trialkylphosphines, but we cannot be overly sanguine with this result given the large deviation of its homologue, tris(2-phenylethyl)phosphine. The interplay of polarization and inductive effects for phosphorus is clearly different and more complex than for nitrogen; we note for example that the computed gas-phase proton affinities for the series RPH_2, R_2PH, and R_3P are quite similar for R = isopropyl and benzyl (Table S3, Supporting Information).

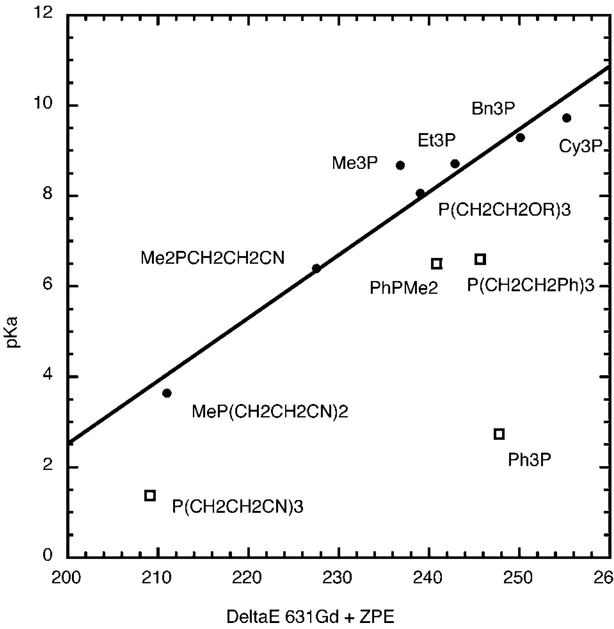

Figure 3. pK_a of protonated phosphines vs computed PA. Equation of line shown is $-25.34 + 0.1393x$, $R^2 = 0.94$.

Our final observation concerns the values of the ion pair dissociation constants, $K_\pm$, which are unexpectedly high. An ab initio structure of $Me_3PH^+C_5H_5^-$ (Figure 4) shows the two ions in close juxtaposition with an interionic distance of about 3 Å, which, according to the Fuoss equation,[11] would lead to a $K_\pm$ of about 10^{-9} in THF. The Fuoss equation is based on globular ions of the tetraalkylammonium type in which specific solvation of the ions is unimportant. In protonated phosphines, however, the proton is sufficiently exposed that such specific solvation can become significant. This point was shown by calculations of the 1:1 complex formed from the phosphonium ions and dimethyl ether (as a model for THF). The results summarized in Table 2 show that these complexes are stable by 6−12 kcal mol^{-1} relative to the uncomplexed components. The complex formed from protonated trimethylphoshine and dimethyl ether is shown in Figure 4. The O−P distance in this structure is 3.32 Å. Note that the solvation complex formed with protonated triethylphosphine is somewhat more stable than that with tribenzyl- or tricyclohexylphosphine. This result readily rationalizes the finding (Table 1) that $K_\pm$ is greater for the smaller Et_3P than for either Bn_3P or Cy_3P.

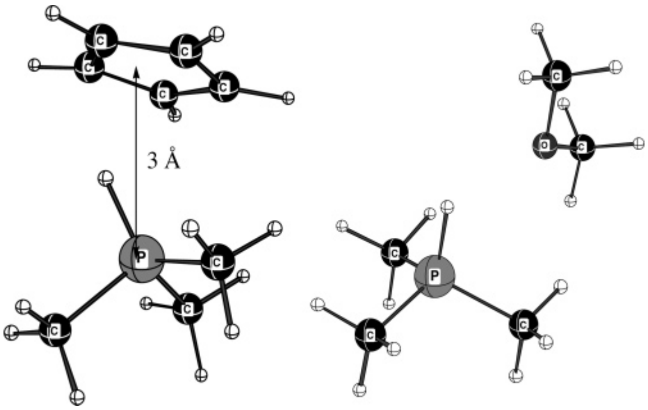

Figure 4. 6-31Gd structure of $Me_3PH^+Cp^-$ (left) and the complex between Me_3PH^+ and dimethyl ether (right).

The Fuoss equation has been used recently to estimate dissociation constants of several types of ion pairs involving protonated substrates.[10,15] It seems clear that the Fuoss equation should not be used for such ion pairs without independent justification. For comparison, in a number of crystal structures of protonated phosphines the PH bond is oriented toward the counteranion and sometimes hydrogen-bonded to it.[16]

Our conclusions are that ion pair basicities of phosphines can be determined in THF by equilibration with a suitable

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(12) pK_a values in Streuli's paper are quoted as aqueous values, but the measurements were made in nitromethane and extrapolated to water.

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(17) The indicator, 1,3-bis-(tetrafluoropyridyl)indene, was available from another study.[18] THF was purified as described previously.[19] The phosphines were commercial materials purified by recrystallization or vacuum distillation. All operations were carried out in a glovebox−spectrometer system.[20] Known increments of the phosphine were weighed out on a microbalance in the glovebox and added to known amounts of THF and indicator. The mixture was allowed to reach equilibrium, and the spectrum was taken. Alternatively, known increments of THF were added to known solutions of phosphine and indicator. The experimental results are tabulated in Table S1 (Supporting Information).

indicator.[17] The equilibria can also involve the separated ions. The corresponding equilibrium constants can be determined by a straightforward handling of the data. The pK_a of tribenzylphosphine determined in this manner is found to be consistent with the other trialkylphosphines measured and computed.[21] The Fuoss equation is shown to be inapplicable to such protonated compounds in a donor solvent.

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Supporting Information Available: Figures and tables of experimental data and computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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