Protonation Constants for Triarylphosphines in Aqueous Acetonitrile Solutions

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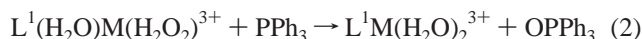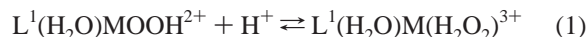*Ames Laboratory, Iowa State University, Ames, Iowa 50011*

Two independent methods were used to determine protonation constants K_H for triarylphosphines in mixed acetonitrile/water media. One method is based on ^{31}P chemical shifts, and the other on the kinetics of debromination of a vicinal dibromide. The protonation constants obtained by the two methods agree well with each other, but they are several orders of magnitude smaller than the values previously reported in the literature for purely aqueous solutions. Moreover, K_H decreases with increasing water content. For PPh_3 at 1.0 M ionic strength ($CF_3SO_3H + CF_3SO_3Li$), the values of K_H are 24.0 ± 0.8 M^{-1} ($CH_3CN/H_2O = 90:10$, v/v), 7.9 ± 0.7 (85:15), 4.2 ± 0.3 (80:20), 2.2 ± 0.1 (70:30), and 1.5 ± 0.3 (50:50). The binding of the proton is weaker at lower electrolyte concentrations, such that at $\mu = 0.40$ M in 90:10 CH_3CN/H_2O K_H for PPh_3 is only 3.9 ± 0.3 M^{-1}.

Introduction

Triarylphosphines and their ring-substituted derivatives are frequent substrates in studies of oxygen atom transfer. Such reactions generate triarylphosphine oxides, $OPAr_3$, which do not readily exchange oxygen with standard solvents.[1] The transfer of isotopically labeled oxygen from a donor to PAr_3 therefore provides unequivocal demonstration of the mechanism. A number of kinetic studies of O atom transfer also have been carried out. The data obtained in that effort provide a useful reactivity scale that allows one to gauge the donor ability of potential new oxygen atom donors.

The majority of the work with triarylphosphines has been carried out in nonaqueous solvents, in part because of the requirements determined by a particular reaction, and in part because of the low solubility of PAr_3 in water. Nonetheless, aqueous and semiaqueous solvents have been used in several instances and will continue to be used in a world looking to replace organic solvents with water where possible. In the case of triarylphosphines, aqueous work is possible by employing water-soluble (sulfonated) phosphines[9−17] or by use of low concentrations of phosphines in mixed aqueous/organic solvents.

Our recent work on O atom transfer from hydroperoxo metal complexes to PAr_3 in mixed H_2O/CH_3CN solvents[18−20] was carried out in the presence of mineral acids that exhibited a strong catalytic effect, thought to arise from the much greater reactivity of the protonated hydroperoxide, eqs 1 and 2 ($L^1 = [14]aneN_4$, $M = Cr^{III}$, Rh^{III}). In all the cases studied, the acid dependence persisted even in strongly acidic solutions (pH < 2).

$$L^1(H_2O)MOOH^{2+} + H^+ \rightleftarrows L^1(H_2O)M(H_2O_2)^{3+} \quad (1)$$

$$L^1(H_2O)M(H_2O_2)^{3+} + PPh_3 \rightarrow L^1M(H_2O)_2^{3+} + OPPh_3 \quad (2)$$

These results seem to contradict the current understanding of acid−base equilibria of phosphines. The pK_a of triphenylphosphonium ion in water, originally reported by Streuli[21] and routinely quoted in the literature,[22−24] is 2.73. This value, which was obtained[21] by extrapolation and manipulation of the data obtained in nonaqueous and semiaqueous solutions, requires that large proportions of the phosphine be present as unreactive phosphonium ions in strongly acidic solutions utilized in our work with hydroperoxides. In fact, the fraction of PPh_3 in that work would be even smaller than predicted by eq 3 because the protonation of the phosphine should be even more extensive in mixed H_2O/CH_3CN solvents than in pure water. Similar

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considerations apply to the reactions with substituted triphenylphosphines for which the pK_a's have been determined[25] by a method almost identical to that in ref 21. In such a scenario, the benefits of protonating the hydroperoxide would be largely canceled by an increase in the concentration of protonated (i.e., unreactive) phosphine. The reported specific rate constants[18−20] would require a major correction (2−4 orders of magnitude) to account for the unfavorable partitioning of the phosphines between the two forms.

$$PPh_3 + H_3O^+ \rightleftarrows HPPh_3^+ + H_2O \qquad K_H \qquad (3)$$
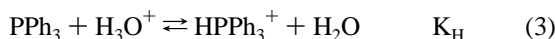
Acidity constants of phosphonium ions are frequently used as anchors in determinations of aqueous pK_a values for other species, such as metal hydrides and hydrogen complexes.[26−29] These determinations are based on proton transfer equilibria between the species of interest and a convenient proton donor, such as phosphonium ions of known pK_a. If the literature values for the phosphine pK_a's are incorrect, then the error will be propagated further, although the relative ordering of the derived pK_a's will be, of course, unaffected by the choice of the standard. This concern, as well as those associated with our own work discussed above, has prompted us to carry out a direct determination of the equilibrium constants K_H for PPh$_3$ and several substituted derivatives in mixed H$_2$O/CH$_3$CN media.

Experimental Section

Solution Preparation. Ice-cold mixtures of PAr$_3$, CH$_3$CN, and H$_2$O were acidified with 2.8 mL of neat CF$_3$SO$_3$H and diluted to 25 mL in a volumetric flask. The total acid concentration in these stock solutions was 1.27 M. The amount of phosphine varied depending on the desired final concentration (5−20 mM) in the NMR solutions. These were prepared by dilution of the stock solutions, often accompanied by partial neutralization of H$^+$ with solid, anhydrous Li$_2$CO$_3$. In a typical experiment, a precisely weighed amount of Li$_2$CO$_3$ was placed into a 5 mL flask. Then 4 mL of the PAr$_3$/CF$_3$SO$_3$H stock solution was slowly injected, and the mixture was allowed to stand until neutralization was completed. At that point, the flask was shaken to expel excess CO$_2$, 0.50 mL of CD$_3$CN was added, and the solution was diluted to 5.0 mL with CH$_3$CN. Samples prepared in this manner had an ionic strength of 1.01 M. A similar procedure was employed for work at different ionic strengths. For several sets of experiments, the neutralization procedure was replaced by simple mixing of acetonitrile solutions of PAr$_3$ with CH$_3$CN, CD$_3$CN, and aqueous solutions of CF$_3$SO$_3$H and CF$_3$SO$_3$Li. In every case, 0.8 mL of the sample was placed in an NMR tube, and a capillary containing pH 7 phosphate buffer (Fisher) was inserted. ^{31}P NMR spectra were recorded at room temperature (20 ± 1 °C inside the NMR probe) with a Varian VXR-400 spectrometer. Most studies were done under air. The effect of air-saturated versus air-free media on chemical shifts in the phosphine/acid system was shown to be negligible in two separate experiments with PPh$_3$ and (*p*-CH$_3$C$_6$H$_4$)$_3$P. Collection times were between 2 and 20 min, depending on the concentration of PAr$_3$. The chemical shift of the external standard was determined against the deuterium lock of the instrument at 1.96 ppm. Kinetic experiments were carried out at 25.0 ± 0.02 °C with a Shimadzu 3101 PC UV−vis spectrophotometer.
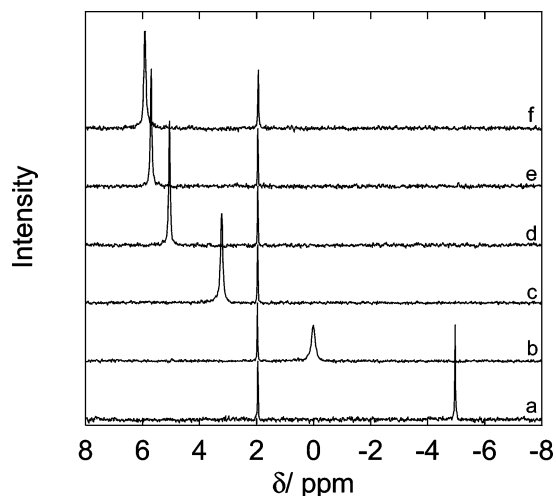
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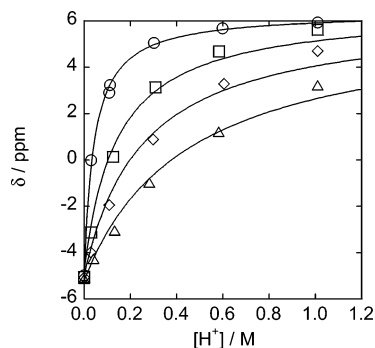
Figure 1. ^{31}P NMR spectra of PPh$_3$ (20−25 mM) in H$_2$O/CH$_3$CN (10:90, v/v) at 1.01 M ionic strength (CF$_3$SO$_3$H + CF$_3$SO$_3$Li). Added [H$^+$] = 0 (a), 0.031 (b), 0.11 (c), 0.30 (d), 0.60 (e), and 1.01 M (f). The resonance at 1.96 ppm is that of an external phosphate buffer standard.

Triarylphosphines (Aldrich, Strem), CF$_3$SO$_3$H (Aldrich), CF$_3$-SO$_3$Li (Aldrich), and CH$_3$CN (Fisher) were used as received. Laboratory-distilled water was further purified by passage through a Millipore MiliQ water purification system.

Results

Two different methods were used to determine the protonation constants K_H. One method relied on ^{31}P NMR chemical shifts, and the other one utilized acid-dependent kinetics of the oxidation of the phosphines with a vicinal dibromide.

NMR Method. All the preliminary work utilized (*p*-CH$_3$-C$_6$H$_4$)$_3$P, the most basic of all the phosphines in this work. This choice made both limits (100% (*p*-CH$_3$-C$_6$H$_4$)$_3$PH$^+$ at high H$^+$, and 100% (*p*-CH$_3$-C$_6$H$_4$)$_3$P in the absence of added acid) experimentally accessible, which provided us with a good opportunity to test the method and check predictions against the experiment in the widest possible range of species distributions and solvent compositions.

In the absence of added acid, a 10 mM solution of (*p*-CH$_3$-C$_6$H$_4$)$_3$P in H$_2$O/CH$_3$CN (10:90 v/v) exhibited a ^{31}P NMR shift at $\delta = -7.60$ ppm. In 1.5 M CF$_3$SO$_3$H, where the phosphine is completely protonated (see below), the chemical shift was at +5.26 ppm. This range of chemical shifts, $(\Delta\delta)_0 = 12.86$ ppm, was affected only minimally (<0.15 ppm) by the change of water content (10−30%), absolute concentration of the phosphine (10−22 mM), and ionic strength (1−1.5 M).

Similar treatment for the parent PPh$_3$ yielded $(\Delta\delta)_0 = 11.3$ ppm in 10:90 H$_2$O/CH$_3$CN, the only solvent composition where complete protonation could be achieved experimentally. It was assumed that $(\Delta\delta)_0$ remained unchanged at other solvent compositions, as was shown to be the case for the *p*-CH$_3$ derivative. At intermediate H$^+$ concentrations, the resonance shifted to some intermediate position between the two limits, as shown in Figure 1. Clearly, in such circumstances, a fraction of the phosphine is present as a phosphonium ion that engages in a rapid H$^+$ exchange with the phosphine.

Figure 2 shows a plot of the chemical shift δ against the concentration of H$^+$ in H$_2$O/CH$_3$CN at four different solvent compositions. Also shown are fits to eq 4, which assumes a direct relationship between the change in chemical shift and the fraction of HPPh$_3^+$ as determined by the position of

Figure 2. Plot of ^{31}P NMR chemical shift vs $[H^+]$ for the protonation of PPh_3 (20 mM) in H_2O/CH_3CN at 1.01 M ionic strength. Vol. % of H_2O in the solvent: 10% (circles), 15% (squares), 20% (diamonds), 30% triangles. Lines are fits to eq 4.

Table 1. Summary of Protonation Constants for $(X-C_6H_4)_3P$ in H_2O/CH_3CN

X	H_2O/CH_3CN	μ^a	$K_H/M^{-1\,b}$	method
H	10:90	1.0	24.0 (± 0.8)	NMR
	10:90	0.4	3.6 (±1.1)	NMR
	10:90	0.4	3.9 (± 0.3)	kinetics
	15:85	1.0	7.9 (± 0.7)	NMR
	15:85	1.0	11.1 (± 1.4)	kinetics
	20:80	1.0	4.2 (± 0.3)	NMR
	30:70	1.0	2.2 (± 0.1)	NMR
	30:70	1.0	2.9 (± 0.3)	kinetics
	50:50	1.2	1.5 (± 0.3)	NMR
p-CH₃	15:85	1.0	150 (±4)	kinetics
	33:67	1.36	41 (±11)	NMR
o-CH₃	33:67	1.36	8.4 (± 0.8)	NMR
m-CH₃	33:67	1.36	6.8 (± 0.9)	NMR
p-F	15:85	1.0	1.67 (± 0.34)	kinetics
p-Cl	15:85	1.0	0.844 (± 0.054)	kinetics

^{a} Ionic strength ($[CF_3SO_3H] + [CF_3SO_3Li]$). ^{b} Obtained from fits of data sets (5−10 points each) to eq 3, 7, or 8; see text. Numbers in parentheses represent one standard deviation.

protonation equilibrium. In eq 4, δ_0 is the chemical shift in the absence of added acid, K_H is defined in eq 3, and $(\Delta\delta)_0$ is the chemical shift difference between the unprotonated and fully protonated phosphines, as discussed above. The value of $(\Delta\delta)_0$ was fixed at 11.3 ppm in the calculations of K_H. The fit of the data in Figure 2 to eq 4 gave K_H values that varied from 24.0 to 1.5 M^{-1} as the water content of the solvent increased from 10% to 50%, Table 1.

$$\delta = \delta_0 + (\Delta\delta)_0 \frac{K_H[H^+]}{1 + K_H[H^+]} \qquad (4)$$

The fit to eq 4 in Figure 2 was slightly less satisfactory at the high end of acid concentrations at larger concentrations of water. A superb fit could be obtained by allowing $(\Delta\delta)_0$ to float, but in that case the calculated and experimental values of $(\Delta\delta)_0$ differed by an unacceptably large margin (>1 ppm). The deviations at high $[H^+]$ in Figure 2 are believed to be related to the changes in the reaction medium as Li^+ is replaced by H^+. This change may affect the degree of ion pairing, which in turn affects the apparent proton binding constant. We rule out the possibility that the deviations are caused by uncertainties in chemical shifts, because the data obtained by the kinetic method (see below) exhibited identical behavior.

Clearly, the basicity of PPh_3 in water is much lower than reported in the literature. In 50:50 H_2O/CH_3CN (v/v), K_H is only about 1.5 ($pK_a = 0.18$). On the basis of the trend in Table 1,

one expects the K_H to decrease even more as the solvent changes to pure water. However, even if this additional correction is ignored, the K_H for PPh_3 is still more than 300 times lower than the literature value ($pK_a = 2.73$, $K_H = 537$).[21]

Kinetic Method. To confirm this result, we sought another, independent method for the determination of K_H. Ideally, such a method would utilize kinetics of a reaction of PPh_3 with a substrate that does not engage in acid−base equilibria. The reaction itself should also be acid-independent, so that the PPh_3/PPh_3H^+ equilibrium is the only possible source of any acid effect on the PPh_3/substrate reaction. Literature search revealed vicinal dibromides, $R_2C_2H_2Br_2$, as potential substrates. We expected that the dibromide in eq 5 should be quite reactive owing to the presence of two electron-withdrawing nitro groups, which increase the rate of nucleophilic attack by PPh_3 at one of the bromine atoms.[30] This expectation was confirmed experimentally; the measured second-order rate constant k_5, eq 5, in neat CH_3CN in the absence of added H^+ was 1.3 M^{-1} s^{-1}. The reasonably large rate constant for the reaction with PPh_3 is essential so that the reaction remains measurably fast even at high acid concentrations, where most of the phosphine is protonated and the apparent rate decreases accordingly. Another advantage of reaction 5, which we adopted as the basis for our kinetic method, is the large accompanying absorbance change at 360 nm ($\Delta\epsilon = 1.28 \times 10^4$ M^{-1} cm^{-1}).
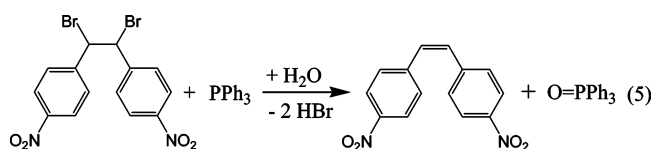
The study of reaction 5 utilized pseudo-first-order conditions with the phosphine (5−16 mM) present in large excess over $R_2C_2H_2Br_2$ (R = 4-NO_2-C_6H_4). Under these conditions, kinetic traces were exponential, and the observed pseudo-first-order rate constants increased linearly with the concentration of phosphine at constant $[H^+]$, establishing a mixed second-order rate law of eq 6, where $[PPh_3]_T$ represents the total phosphine concentration, i.e., $[PPh_3]_T = ([PPh_3] + [PPh_3H^+])$.

$$-d[R_2C_2H_2Br_2]/dt = k_{obs}[PPh_3]_T[R_2C_2H_2Br_2] \qquad (6)$$

As expected, the reaction was slower at higher acid concentrations. Figure 3 shows the results for solutions containing 15% and 30% water in acetonitrile and the respective fits to eq 7. The parameter k_0 is the rate constant in the absence of added
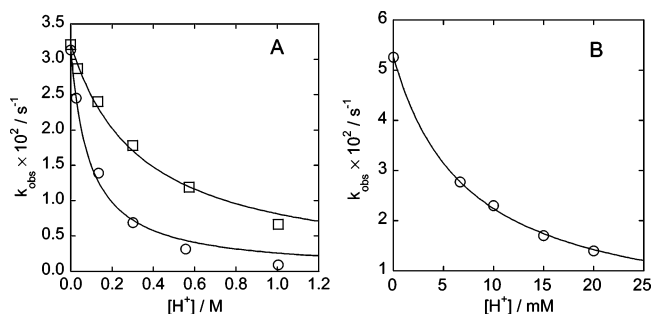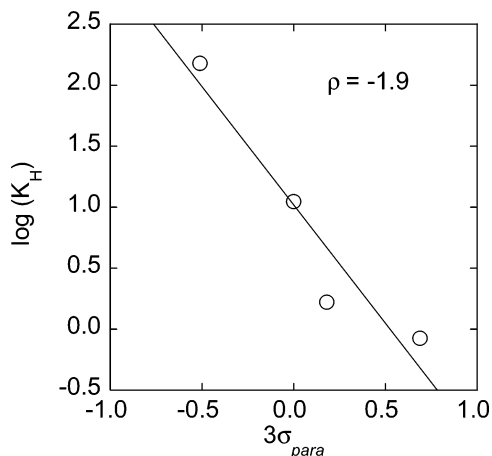

Figure 3. Plots of the rate constants for the protonation of PAr_3 as a function of $[H^+]$ in H_2O/CH_3CN at 1.01 M ionic strength. Panel A: Ar = Ph; water content = 15% (circles) and 30% (squares). Panel B: Ar = (p-CH_3-C_6H_4), water content 15%. Lines are fits to eq 7 (panel A) or eq 8 (panel B).

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Figure 4. Hammett plot for the protonation of PAr$_3$ in H$_2$O/CH$_3$-CN (15:85, v/v).

Figure 5. Plot of δ/ppm vs [H$^+$] for the protonation of PPh$_3$ (19 mM) in H$_2$O/CH$_3$CN (10:90 v/v) at nonconstant ionic strength.

acid, i.e., when all the phosphine is present as PPh$_3$.

$$k_{obs} = k_0/(1 + K_H[H^+]) \qquad (7)$$

In deriving eq 7, we made a reasonable assumption that PPh$_3$ is the only reactive form of the phosphine. It would be difficult to see how the phosphonium ion could engage in a nucleophilic attack without prior deprotonation. As already mentioned, the fits to eq 7 in Figure 3 show the same minor deviations at high [H$^+$] as observed in the NMR experiments. Again, the data could be made to fit a perfect curve, but this would require adding a term with a negative rate constant for the reaction of the protonated form, clearly not an acceptable solution.

The values of K_H obtained by this method, 11.1 ± 1.4 M^{-1} (15% H$_2$O) and 2.94 ± 0.26 M^{-1} (30% H$_2$O), are both within less than 30% of the values obtained in the NMR experiments, Table 1. We consider this a good agreement given that two fundamentally different methods were used.

Substituted Triarylphosphines. Once the agreement between the two methods was established, we adopted the kinetic approach to study several *p*-substituted phosphines, P(*p*-X-C$_6$H$_4$)$_3$ (X = CH$_3$, Cl, F). The much greater sensitivity of the kinetic approach made it possible to determine the K_H even for the weakly basic P(*p*-Cl-C$_6$H$_4$)$_3$, for which the level of phosphonium ions was too low for a precise determination by NMR.

The reaction of the *p*-Cl derivative became inconveniently slow at high acid concentrations. To remedy the problem, initial rates were used in place of the rate constants, and data treatment utilized a modified eq 7, in which the parameters k_{obs} and k_0 were replaced by (vi)$_{obs}$ and (vi)$_0$ (vi = initial rate in M/s).

P(*p*-CH$_3$-C$_6$H$_4$)$_3$ is the most basic of the phosphines studied. Unlike in all the other cases, where acid concentrations were always much higher than [PAr$_3$]$_T$, the experimentally meaningful acid concentrations in the experiments with P(*p*-CH$_3$-C$_6$H$_4$)$_3$ were quite low and comparable to the phosphine concentrations. As a result, eq 8 was used, which takes into account the fact that concentrations of the free and total H$^+$ are not the same. The fit to eq 8 is shown in Figure 3B, which gives $K_H = 150$ M^{-1} in 15% H$_2$O/CH$_3$CN.
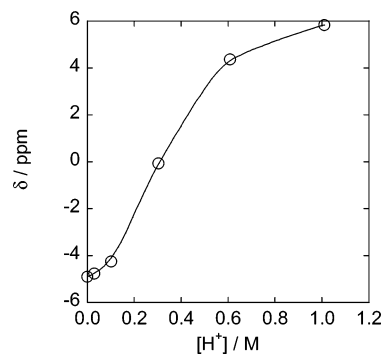
Protonation constants obtained under a constant set of conditions respond to the electron-donating power of the substituents on the phosphine. A plot of log(K_H) against the Hammett sigma value for the reaction in 15% H$_2$O at 1.0 M ionic strength is shown in Figure 4. The slope of the line gives $\rho = -1.9$. Qualitatively, the tolylphosphines at 1.3 M ionic strength, Table 1, also fit this picture, as the *para* isomer has a higher K_H than both the *meta* and *ortho* isomers.

Ionic Strength Effect. Most of the data were collected at a constant electrolyte concentration of 1.0 M (CF$_3$SO$_3$H + CF$_3$-SO$_3$Li). When the ionic strength was not kept constant, so that $\mu = $ [H$^+$], the relationship between the NMR shift and [H$^+$] became more complex than predicted by eq 4. As shown in Figure 5, there is an apparent nonuniform increase in K_H as the acid (i.e., electrolyte) concentration increases.

To examine the ionic strength effect under more controlled conditions, a set of experiments was carried out with PPh$_3$ at $\mu = 0.40$ M. The measured protonation constant, $3.6 (\pm 1.1)$ M^{-1} by NMR or $3.9 (\pm 0.3)$ M^{-1} by the kinetic method, was significantly smaller than that measured at $\mu = 1.0$ M, Table 1.

In all of the experiments in Table 1, the ionic strength was maintained with CF$_3$SO$_3$H + CF$_3$SO$_3$Li. Some of our earlier work, however, utilized HClO$_4$ + NaClO$_4$.[18−20] One set of experiments was therefore conducted for PPh$_3$ at the highest perchlorate concentrations ($\mu = 0.83$ M) and the highest CH$_3$-CN content (CH$_3$CN/H$_2$O = 2:1, v/v) used in that work so that the earlier results could be properly corrected for the fraction of PPh$_3$H$^+$ present under those conditions. The K_H, determined by the kinetic method, was 3.3 ± 0.8, comparable to that obtained with CF$_3$SO$_3$H + CF$_3$SO$_3$Li. This value was used to calculate the actual concentrations of unprotonated PPh$_3$ at each acid concentration used in the earlier work and to correct the rate constant for the PPh$_3$/L^{1}CrOOH^{2+}/H$^+$ reaction (L^1 = [14]-aneN$_4$). The new value is $(3.9 \pm 0.6) \times 10^3$ M^{-2} s^{-1}, i.e., approximately 5 times greater than previously reported (8.5×10^2).[19,20] The values of K_H for substituted phosphines in 0.83 M (HClO$_4$ + LiClO$_4$) were estimated by use of the Hammett ρ value (-1.9) obtained in Figure 4. These data were used to correct the rate constants; the new values are $(2.0 \pm 0.3) \times 10^3$ M^{-2} s^{-1} (*p*-F, previously 6.70×10^2 M^{-2} s^{-1}), $(8.4 \pm 1.2) \times 10^2$ (*p*-Cl, previously 5.3×10^2), and $(3.3 \pm 0.5) \times 10^2$ (*p*-CF$_3$, unchanged). The new Hammett ρ value for O-transfer from L^{1}CrOOH^{2+} to the phosphines is -0.7. Except for the noted-

$$k_{obs} = k_0 \times \left[1 - \frac{[PAr_3]_T + [H^+]_T + 1/K_H - \sqrt{([PAr_3]_T + [H^+]_T + 1/K_H)^2 - 4[PAr_3]_T[H^+]_T}}{2[PAr_3]_T} \right] \qquad (8)$$

Table 2. Comparison of Literature pK_a Values for P(p-X-C$_6$H$_4$)$_3$H$^+$ in H$_2$O with Those Determined in This Work in CH$_3$CN/H$_2$O (85:15, v/v)

X	pK_a (literature)[a]	pK_a (this work)[b]
CH$_3$	3.84	2.18 ± 0.01
H	2.73	1.05 ± 0.06
F	1.97	0.22 ± 0.09
Cl	1.03	−0.07 ± 0.03

[a] In water by extrapolation of data from nitromethane (refs 21, 25). [b] Experimental data in CH$_3$CN/H$_2$O (85:15, v/v). Values in H$_2$O are smaller by at least one pK_a unit.

numerical corrections, the conclusions reached in our previous work remain valid; that is, the PAr$_3$/L^{1}CrOOH^{2+} reaction is strictly first order in [H$^+$] and, under all experimentally attainable conditions, much slower than the corresponding PAr$_3$/L^{1}Cr(V) reaction. The rest of our previous work[18] was carried out at low acid and electrolyte concentrations (μ = 0.10 M) and at high H$_2$O content (50%).[18] Under those conditions, the value of K_H is small and, in our best estimate, all the published data remain correct to within 10%.

Discussion

The basicity of triarylphosphines in aqueous acetonitrile is demonstrably much lower than reported in the literature for aqueous solutions. Our data in semiaqueous media cannot be simply extrapolated to pure water, but the trend of decreasing K_H with increasing water content and with decreasing ionic strength clearly places the aqueous K_H below the lowest measured values in Table 1. Any extrapolation of our data to a low ionic strength would be meaningless not only because the proper function has not been determined but also because our new, small protonation constants in fact require high concentrations of acid, and thus high ionic strength, to achieve some level of protonation. The differences between our results and those published previously are probably best illustrated by the calculated proportions of PPh$_3$H$^+$ under a given set of conditions. The earlier data require 50% protonation at pH 2.73 in pure water. Our data (Figure 5) show no measurable amount of PPh$_3$H$^+$ at pH 2.7 and only about 1% at pH 1.5 in 90% CH$_3$-CN. These values will decrease much more as the water concentration increases. A similar situation applies to substituted phosphines as well. Table 2 summarizes the published aqueous pK_a values and our data at a fixed set of conditions (15% H$_2$O, 1.0 M ionic strength). On the basis of the trend observed for PPh$_3$, we estimate that true aqueous pK_a's have to be at least one pK_a unit smaller than those listed for the mixed solvent in Table 2.

The increase in K_H with increasing electrolyte concentration is undoubtedly related to the strong hydration of the cations. ^{7}Li NMR experiments have shown that Li$^+$ exhibits an overwhelming preference for water over acetonitrile in the inner solvation sphere.[31] Adding large amounts of Li$^+$ (up to 1.3 M)

to solvent mixtures that have only 10−30% (~5−15 M) water, as we have done in this work, will dramatically decrease the actual concentration of free water, even under the assumption that the cation takes up only four solvent molecules, i.e., neglecting the second coordination sphere. Our data show that Na$^+$ exhibits a similar preference for H$_2$O.

Ion pairing is believed to be unimportant in dilute aqueous and highly polar semiaqueous solutions,[29] but some ion pairing is probably involved at the high electrolyte concentrations in Table 1 and may be another source of the observed electrolyte effect. The simple equilibrium relating PPh$_3$ and HPPh$_3$$^+$ in eq 3 should not exhibit significant ionic strength dependence because the number of charged species on both sides of the equation is the same, but ion pairing would facilitate protonation by converting some of the HPPh$_3$$^+$ to {HPPh$_3$$^+$,CF$_3SO_3$$^-$} and thus displacing the equilibrium in eq 3 to the right.

In this work, no attempts were made to correlate our data by use of empirical parameters or to extract the "true" protonation constant by correcting the data for various phenomena such as ion pairing, hydrogen bonding, or solvation of solution species. Any such correction would be highly imprecise under our conditions (mixed solvents and high concentrations of electrolytes) and was not considered appropriate. Instead, we focused on obtaining good quality experimental data that allow one to calculate, or at least estimate, the proportion of unprotonated phosphine under realistic experimental conditions. Such knowledge is especially important in work with transition metal complexes, which often require acidic conditions, use of constant ionic strength, and mixed solvents owing to the low solubility of triarylphosphines in water.

It is difficult to pinpoint the exact reason for the highly inflated pK_a's of triarylphosphines in the literature.[21,25] Possibly, it is the accumulation of several sources of error. In that work,[21,25] the data were obtained in nitromethane and transferred to water by use of parameters determined for simple amines. This treatment may be an oversimplification, especially in the case of triarylphosphines, which are much less basic than amines. The use of less than perfect parameters in a different pH regime to determine the more acidic pK_a's for PAr$_3$ may have led to the observed error. This argument suggests that published data[21,25] for the more basic trialkyl phosphines may be more reliable, although this point remains to be addressed experimentally.

(31) Maciel, G. E.; Hancock, J. K.; Lafferty, L. F.; Mueller, P. A.; Musker, W. K. *Inorg. Chem.* **1966**, *5*, 554−557.