# Acid−Base Equilibria in Nonpolar Media. Absolute pK_a Scale of Bases in Tetrahydrofuran

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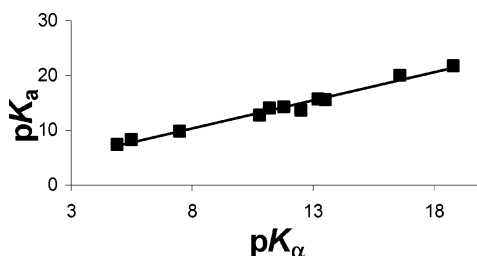
The acidity constants (pK_a) of 11 bases (amines, anilines, pyridines, pyrrolidines, and iminophosphoranes) have been determined in tetrahydrofuran by potentiometry, complemented by conductometric measurements. The pK_a values of the studied bases cover a wide absolute pH range of acidity in tetrahydrofuran, from 7.4 to 21.7. From the pK_a values obtained, a scale of absolute acidity in tetrahydrofuran has been established, which has allowed calculation of the absolute pK_a values of 77 bases from literature relative pK_a data.

Introduction

Tetrahydrofuran (THF) is a saturated cyclic ether belonging to the class of aprotic dipolar protophilic solvents.[1] It is a widely used solvent in synthetic organic chemistry, chemical analysis, and technology and also in industry, as it dissolves organometallic compounds, ionic species, and many polymetric materials.[2−9]

From an analytical point of view, mixtures of THF with water are used as mobile phases in liquid chromatography.[10]

There are some data on ion−ion and ion−solvent interactions in THF. Several of them have been obtained by means of conductometry[11] and ultrasonic relaxation methods,[12,13] whereas other data were based on potentiometry combined with conductometry.[14−16] It is well-known that in solvents of low permittivity, especially if the solvent is also aprotic, such as THF ($\epsilon = 7.39$),[17] all chemical reactions involving ionogens or ionophores, including proton-transfer reactions, are greatly complicated by ion association leading to ion pairs and even larger aggregates.

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In any case, studies on basicity in THF are scarce. However, a relative acidity scale of cationic acids (basic compounds), anchored to the acidity constant of triethylamine in THF, has been recently published.[18−21] To build this scale, relative dissociation constants were determined experimentally from NMR and UV−vis spectrophotometric measurements, and triethylamine was used as the reference compound[18] in order to obtain the pK_a value for the conjugate acids of the studied bases.

In this work, the acidity constants in THF of some bases included in the mentioned scale are determined by potentiometry, complemented by conductometric measurements, to establish the relationship between the acidity constant value relative to the triethylamine and the absolute acidity constant. This correlation should provide an equation capable of transforming a large amount of relative basicity data that have been accumulated to absolute values.[19−21]

Theory. The acidity constant of a base (B) is expressed as the dissociation constant of its conjugate acid (HB$^+$)

$$HB^+ + S \rightleftharpoons HS^+ + B$$

$$K_a = \frac{a_{HS^+}a_B}{a_{HB^+}} = \frac{[HS^+][B]}{[HB^+]} \qquad (1)$$

Nevertheless, in THF, incomplete dissociation of salts should be taken into account[22]

$$HB^+A^- \rightleftharpoons HB^+ + A^-$$

$$K_{salt} = \frac{[HB^+][A^-]\gamma_\pm^2}{[HB^+A^-]} \qquad (2)$$

where $\gamma_\pm$ is the mean ionic activity coefficient.

At relatively high electrolyte concentrations, ternary ion formation must also be considered.[14] The overall formation constant of these ions, $K_{f(tern)}$, is defined according to

$$HB^+A^- + A^- \rightleftharpoons HBA_2^- \qquad HB^+A^- + HB^+ \rightleftharpoons (HB)_2A^+$$

by

$$K_{f(tern)} = \frac{[HBA_2^-] + [(HB)_2A^+]}{[HB^+A^-]([A^-] + [HB^+])} \qquad (3)$$

In this work, a method for the potentiometric determination of acid dissociation constants that minimizes the effect of the ternary ion formation is applied to several selected bases[14] shown in Scheme 1. This method involves previous conductometric determination of the dissociation constant of the salt formed.

Results and Discussion

Conductance data for series of solutions of perchlorate salts in THF were fitted to the Fuoss−Kraus equation (see Supporting Information, eq 1).[23−26] By way of example, the Fuoss−Kraus equation for perchlorate of pyrrolidine has been plotted in Figure 1. It shows a straight line which deviates downward with the increase of the concentration because of the triple ion formation. Data were interpreted by means of the ternary ion Fuoss−Kraus theory;[14,27] the dissociation constant of the pyrrolidine salt, pK_{salt}, and the limiting molar conductivity, Λ_o, were evaluated in the range of concentration from 4×10^{-6} to 1.5×10^{-4} M, where the plot fits a straight line since there is no significant ternary ion formation, while the ternary ion formation constant, $K_{f(tern)}$, was evaluated at a concentration higher than 1.5×10^{-4} M when the plot deviates downward.

It is also shown that the concentration of salt, from which ternary ion formation is important, depends on the kind of substance. Figure 2 shows that the plots of 2-Cl−C$_6$H$_4$P$_1$(pyrr) and DBU deviate clearly downward when the concentration of salt is higher than 2.5×10^{-5} and 4×10^{-5} M, respectively. Meanwhile, for pyrrolidine, the deviation is from a much higher value (1.5×10^{-4} M).

The slopes of the plots are also very different since they are $1/K\Lambda_o^2$. Pyrrolidine has a low Λ_o, and it shows a high slope. DBU has a K value similar to the one of pyrrolidine, but a much higher Λ_o, and thus it shows a much lower slope. 2-Cl−C$_6$H$_4$P$_1$(pyrr) has an intermediate Λ_o value, but a much higher constant, and the combination gives a slope lower than that of DBU.

Table 1 summarizes the values of Λ_o, K_{salt}, and $K_{f(tern)}$ for the perchlorate salts studied. Λ_o is the limiting molar conductivity; K_{salt} is the dissociation constant, and $K_{f(tern)}$ is the ternary ion formation constant of the perchlorate salts. The pK_{salt} values of the salts range from 5 to 7, and it is observed that perchlorate salts with a small cation are less dissociated than iminophosphorane salts. At the same time, salts with a small cation have lower Λ_o than iminophosphorane salts. In any case, Λ_o values are very high, and this fact is attributable to the low viscosity of THF.[14,17,22,28] The ternary ion formation constants were about 1000. Ternary ion constants were found to be in the same order of magnitude than those determined for benzoic acids in a previous work.[15]

Also, Table 1 shows the acidity constants of the protonated bases studied in THF (p$K_{a(THF)}$). Potentiometric assays were carried out at a concentration of 5×10^{-4} M. At this concentration, ternary ion formation is very small and it has not been taken into consideration in the pK_a calculation.

By way of example, Table 2 shows the data obtained from one series of potentiometric measurements in solutions of pyrrolidine and its perchlorate salts. Table 2 also shows the mean of the acidity constants computed at any point of the titration before the equivalence point (where HB$^+$ coexists with B, eq 1) and the acidity constant in THF (p$K_{a(THF)}$) determined from the intercept of eq 4.[14,22]

$$pK_{a(comp)} = pK_{a(THF)} - sv_s \qquad (4)$$

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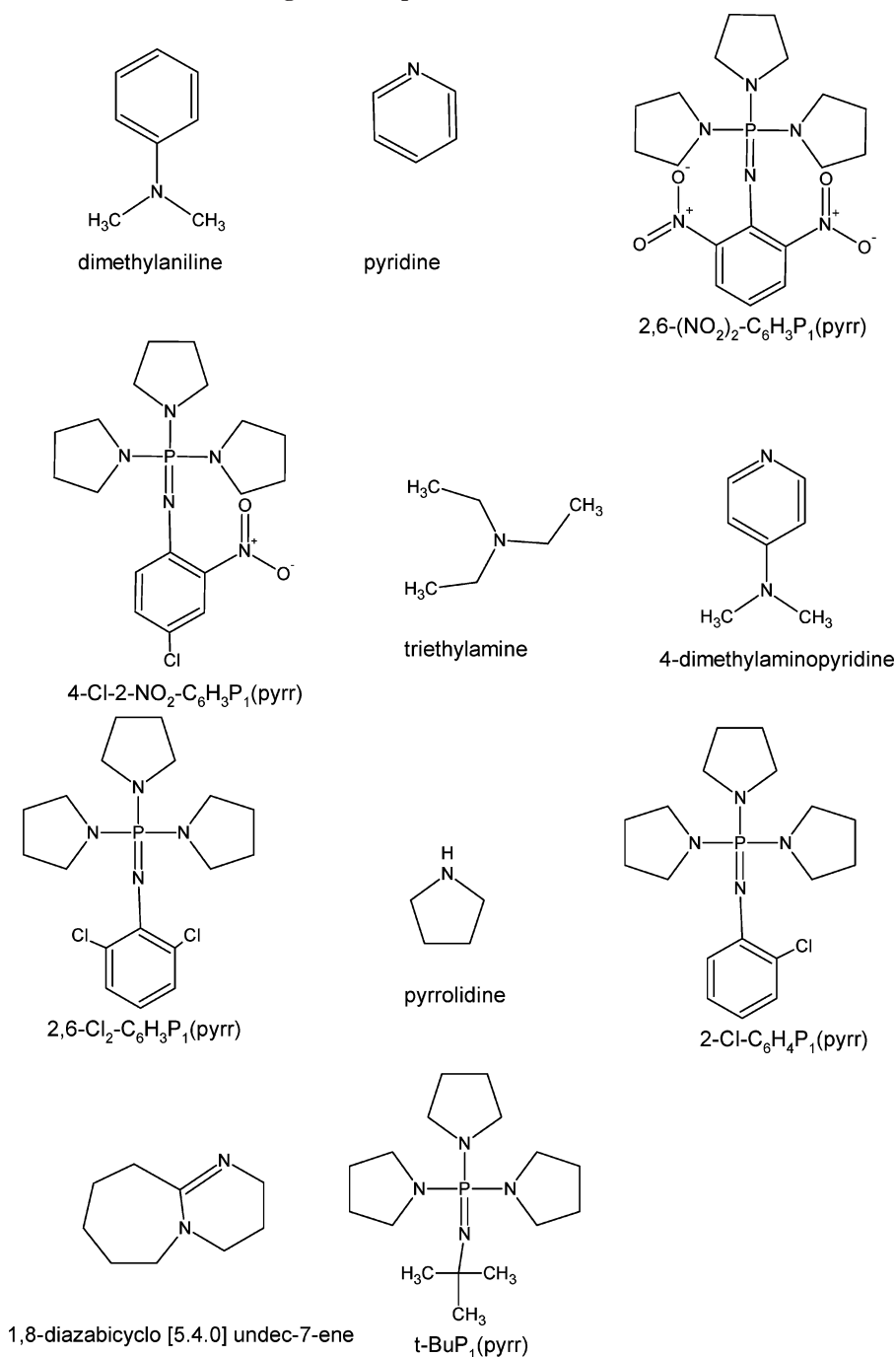(23) Fuoss, R. M.; Kraus, C. A. *J. Am. Chem. Soc.* **1933**, *55*, 476−488.

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SCHEME 1.   Studied Bases Placed in Increasing Order of pK_a

dimethylaniline

pyridine

$2,6\text{-}(NO_2)_2\text{-}C_6H_3P_1(pyrr)$

$4\text{-}Cl\text{-}2\text{-}NO_2\text{-}C_6H_3P_1(pyrr)$

triethylamine

4-dimethylaminopyridine

$2,6\text{-}Cl_2\text{-}C_6H_3P_1(pyrr)$

pyrrolidine

$2\text{-}Cl\text{-}C_6H_4P_1(pyrr)$

1,8-diazabicyclo [5.4.0] undec-7-ene

$t\text{-}BuP_1(pyrr)$

where $pK_{a(comp)}$ values are the pK_a values computed at any point of the titration; v_s is the volume fraction of titrant added, and s is related to the change in $pK_{a(comp)}$ caused by the addition of titrant solution that involves the small additions of water.

The effect of the addition of a small percentage of water with the titrant was taken into consideration through the slope of eq 4, where s is related to the change in pK_a, pK_{salt}, and reference potential, $E_a^o + E_j$, caused by the presence of the water in the medium due to the specific solvation of the anion by the water added.[14-16] When s is markedly negative, approximately lower than -20, the effect of water solution is important and affects significantly the computed acidity constant. The slope, s, for

pyrrolidine is -6.44, and thus the effect of water addition can be neglected; it was lower than 0.02% in the neutralization point of the titration. Therefore, the mean of pK_a computed at any point of the titration, before the equivalence point, agrees with the $pK_{a(THF)}$ determined from eq 4, and it is taken as the pK_a in tetrahydrofuran ($pK_{a(THF)}$).

The pK_a values given in Table 1 for the studied bases range from 7.39 (*N,N*-dimethylaniline) to 21.67 (*t*-BuP_1(pyrr)), and hence, this study covers a wide range of pK_a values. The weak bases studied are aromatic compounds whose nitrogen-associated lone electron pair can be easily delocalized. The pK_a values of these aromatic compounds depend on the effects of the
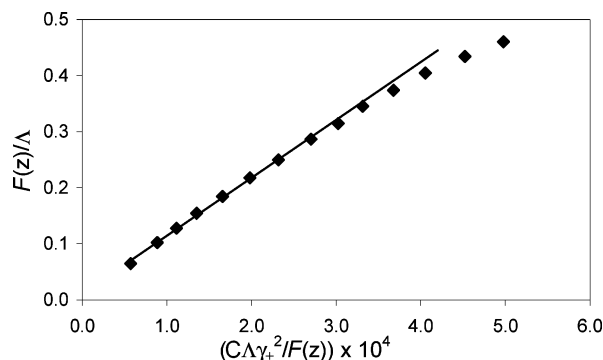
FIGURE 1. Conductance Fuoss−Kraus plot in the concentration range 4×10^{-6}−3×10^{-4} M for the perchlorate salt of pyrrolidine.
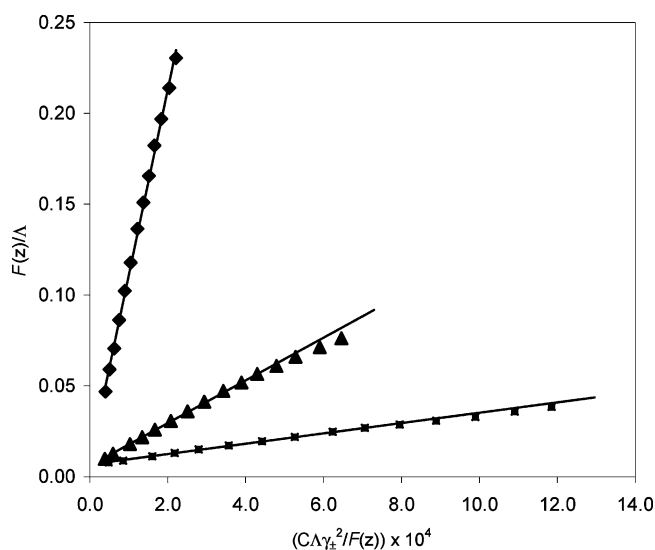

FIGURE 2. Conductance Fuoss−Kraus plots for perchlorate salts of (♦) pyrrolidine, (▲) DBU, and (■) 2-Cl−$C_6H_4P_1$(pyrr) in the concentration range 5×10^{-7}−6×10^{-5} M.

substituents in the ring (inductive, electrostatics, and resonance effects).[29−31]

In a previous work, a relative acidity scale of basic compounds, which includes all bases studied in this work, was published.[19−21] The pK_α was used to denote the acidity constant in THF, instead of pK_a, because it was considered an estimate of the pK_a of the bases in THF. In that work, a relative ion pair acidity constant, ΔpK_{ip}, was determined using the UV−vis and/or ^{13}C NMR methods to measure the concentration ratio between the studied protonated base and a reference one. Those experimental results were corrected for ion pairing effects, which were theoretically calculated by means of the Fuoss equation,[32] from the estimated molecule volume,[19] and a relative ion acidity constant was obtained (ΔpK_α). To obtain pK_α values from ΔpK_α,

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pK_α of triethylamine was used as a reference to anchor the scale by minimizing the sum of squares of differences between directly measured ΔpK_α values, and the assigned pK value, while keeping the pK_α value of triethylamine constant and equal to 12.5.[19−21]

The pK_α of triethylamine was also a relative dissociation constant determined by the Morris group using NMR measurements and anchored in the aqueous pK_a of tricyclohexylphosphonium tetraphenylborate, $[HPCy_3]BPh_4$.[18] Morris et al. used the hypothesis that the pK_a value of tricyclohexylphosphonium tetraphenylborate in THF was the same as that in water. Obviously, there were some doubts on the suitability of this relative value as an anchoring point, but before this present work, there was no absolute data in THF available in the literature that could be used to anchor the scale better than triethylamine.

Figure 3 shows the correlation between the absolute acidity constants (pK_a) and the pK_α values relative to the triethylamine, given in refs 19−21, for the bases studied in this work. Compounds cover a wide range of pK_a values in the tetrahydrofuran scale and show a linear fit which provides the relationship of eq 5 (SD = 0.608, r^2 = 0.9814 for 11 points)

$$pK_{a(THF)} = 1.02(\pm 0.04)pK_{\alpha(THF)} + 2.14(\pm 0.54) \quad (5)$$

The slope of eq 5, close to 1, shows that the estimated theoretically ion pair dissociation constants agree with the constants determined by means of conductometric measurements and shows that the Fuoss equation[32] is a suitable equation to estimate these values. On the other hand, the intercept, which is related to the anchoring point of the scale, is far from the expected value (intercept equal to 0). In fact, the pK_α value of triethylamine used as the anchoring point is lower than the absolute pK_a determined in this work.

Thus, eq 5 provides an expression capable of transforming the large amount of literature relative basicity data to absolute values. Table 3 shows pK_α of bases[19−21] and their absolute pK_a according to eq 5. Some bases had similar structure to the compounds studied in this work, while others were very different.

Conclusions

The analysis of the conductance data of the perchlorate salts of the 11 bases studied has allowed determination of the dissociation constants of these salts in THF by means of the Fuoss−Kraus method. Dissociation constants are in the range 10^{-5}−10^{-7}, similar to those obtained for other compounds in previous studies.[14−16] The triple ions formation constants of the perchlorate salts have been also determined at high concentrations. The values are about 1000, which are similar to those of other salts.[15]

The absolute acid dissociation constant (pK_a) of the bases studied has been determined by potentiometric titration of the base by perchloric acid. A low working concentration (5×10^{-4} M) has been selected to avoid triple ion formation. Thus, the pK_a has been computed from the titration data taking into account the partial dissociation of the perchlorate salt formed.

Finally, the determined absolute pK_a values in THF have been used as 11 new points to anchor the relative pK_α values

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TABLE 1. Dissociation Constants of the Studied Bases and their Perchlorate Salts in THF

	$\Lambda_o{}^a$	$pK_{salt}{}^a$	$\log K_f{}^{a,b}$	$pK_a{}^c$
dimethylaniline	79	6.71 ± 0.14	3.44 ± 0.43	7.39 ± 0.10
pyridine	73	6.21 ± 0.17	3.55 ± 0.19	8.25 ± 0.19
$2,6\text{-}(NO_2)_2\text{-}C_6H_3P_1(pyrr)$	107	5.31 ± 0.07	2.37 ± 0.42	9.79 ± 0.07
$4\text{-}Cl\text{-}2\text{-}NO_2\text{-}C_6H_3P_1(pyrr)$	101	5.98 ± 0.07	2.95 ± 0.80	12.75 ± 0.08
triethylamine	120	7.03 ± 0.18	3.98 ± 0.16	13.66 ± 0.05
4-dimethylaminopyridine	144	6.35 ± 0.06	2.68 ± 0.40	14.07 ± 0.11
$2,6\text{-}Cl_2\text{-}C_6H_3P_1(pyrr)$	106	5.30 ± 0.08	3.57 ± 0.74	14.21 ± 0.05
pyrrolidine	88	6.88 ± 0.19	3.81 ± 0.20	15.56 ± 0.05
$2\text{-}Cl\text{-}C_6H_4P_1(pyrr)$	151	5.84 ± 0.03	3.62 ± 0.36	15.62 ± 0.11
DBU	224	6.81 ± 0.07	3.56 ± 0.59	19.97 ± 0.10
$t\text{-}BuP_1(pyrr)$	173	6.18 ± 0.04	3.33 ± 0.14	21.67 ± 0.11

[a] Conductometric results for THF medium $\pm SD$ ($n \geq 3$). [b] Formation constants of ternary ions. [c] Potentiometric results for THF medium $\pm SD$ ($n \geq 3$).

TABLE 2. Dissociation Constant of Pyrrolidine Based on Measurements on Mixtures of the Base and its Perchlorate Salt;[a] $pK_{a(THF)}$ Obtained as Average of $pK_{a(comp)}$ and Calculated with eq 4

V (mL)	E (mV)	$pH_{(comp)}$	v_s	C_b (M)	C_{salt} (M)	$pK_{a(comp)}$
0.10	-751.72	18.40	5.00×10^3	4.85×10^3	5.26×10^4	15.63
0.20	-740.35	18.24	1.00×10^2	4.30×10^3	1.05×10^3	15.67
0.30	-728.50	18.07	1.50×10^2	3.76×10^3	1.56×10^3	15.65
0.40	-718.40	17.93	2.00×10^2	3.22×10^3	2.07×10^3	15.65
0.50	-708.87	17.80	2.40×10^2	2.69×10^3	2.58×10^3	15.64
0.60	-699.63	17.67	2.90×10^2	2.16×10^3	3.08×10^3	15.63
0.70	-675.85	17.52	3.40×10^2	1.64×10^3	3.58×10^3	15.64
0.80	-655.63	17.33	3.80×10^2	1.12×10^3	4.07×10^3	15.64
0.90	-564.72	17.02	4.30×10^2	6.13×10^4	4.56×10^3	15.62
					mean	15.64 ± 0.01
eq 4	$s = -6.44$				$pK_{a(THF)}$	15.64 ± 0.01

[a] $E_a^{\circ}{}_{(THF)} + E_{j(THF)} = 332.9$ mV; $V_{initial} = 20$ mL; $V_{eq} = 1.02$; $C_{titrant} = 0.1058$ M; $pK_{salt(THF)} = 6.88$.
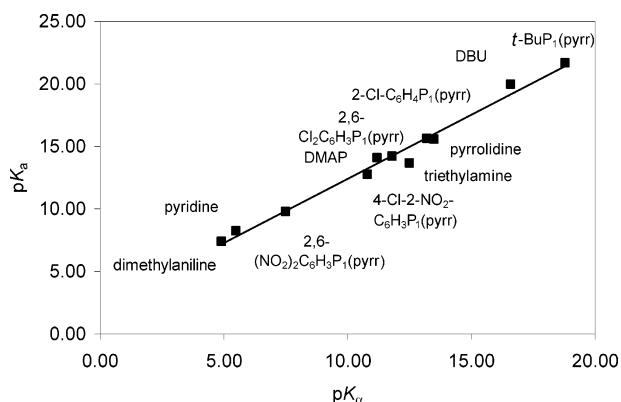
FIGURE 3. Correlation between pK_a values from Table 1 and pK_α relative to the triethylamine for the studied bases.

previously obtained for a host of bases and, thus, to obtain the absolute pK_a values of these bases. These new anchoring points provide a better option than the pK_a values determined in mediums different from THF which were used in previous works. By using them, 77 new absolute pK_a values of bases have been calculated from their relative pK_a data reported in the literature.

Experimental Section

Apparatus. A conductometer and a cell with a constant of 1.037 cm^{-1} were used for conductivity measurements. For potentiometric measurements, a pH meter (accuracy ± 0.1 mV) equipped with a glass electrode and a saturated silver nitrate solution in THF/Ag reference electrode was used. A 0.1 M tetrabutylammonium perchlorate solution in THF was used as a double salt bridge.[14] All

the potentiometric assembly was automatically controlled with the computer program VALORA, specially designed for titrations in nonaqueous media.[23]

Reagents. Tetrahydrofuran with a water content $\leq 0.03\%$ and a conductivity of 0.011 $\mu\Omega^{-1}$ cm^{-1} was used as solvent everywhere. Picric acid was vacuum dried. Tetra-n-butylammonium hydroxide solution, 0.1 M Bu$_4$NOH, in propan-2-ol and perchloric acid were used as titrant solutions. Tetrabutylammonium perchlorate and silver nitrate were used to prepare the salt bridge solutions.

The substances tested are shown in Scheme 1. The phenyl-substituted iminophosphoranes 2-Cl-C$_6$H$_4$P$_1$(pyrr), 2,6-(NO$_2$)$_2$-C$_6$H$_3$P$_1$(pyrr), 2,6-Cl$_2$-C$_6$H$_3$P$_1$(pyrr), and 4-Cl-2-NO$_2$-C$_6$H$_3$P$_1$(pyrr) (where pyrr denotes 1-pyrrolidinyl (N(CH$_2$CH$_2$)$_2$) radical and P$_1$-(pyrr) the structure R'N=P(pyrr)$_3$) were synthesized according to literature.[19,34] All other substances were commercial products with a purity higher than 98%.

Procedure. For conductometric measurements, solutions of $10^{-5}-10^{-3}$ M of perchlorate salts were prepared by dissolving the base in THF and neutralizing it with 0.1 M HClO$_4$ (the HClO$_4$ solution was prepared by diluting aqueous 70% HClO$_4$ (w/w) in THF). Increasing amounts of salt were added to 50 mL of THF in the conductivity cell, and the conductivity was measured after each addition. The values obtained were the mean of at least three different determinations at different concentrations.

For potentiometric measurements, 20 mL of a 5×10^{-3} M solution of the base was titrated with a 0.1 M perchloric acid solution (prepared in the same way as that for conductometry). The potential was measured at various titration points. The stabilization criterion for the electromotive force was ± 0.2 mV, controlled by the VALORA program.[33] The values obtained were the mean of at least three different determinations. The glass electrode was stored in water when not in use and soaked for 20 min in THF before potentiometric measurements. The potentiometric system was

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TABLE 3. pK_α Values Relative to the Triethylamine, Given in refs 19−21 and Absolute pK_a Values Calculated with eq 5[a,b]

	pK_α	pK_a		pK_α	pK_a
N-EtP$_1$(tmg)	29.7	32.6	4-Me$_2$N−C$_6$H$_4$P$_1$(pyrr)	17.1	19.7
t-BuP$_1$(tmg)	29.1	32.0	DBU	16.6	19.1
4-MeO−C$_6$H$_4$P$_3$(pyrr)	28.9	31.7	4-MeO−C$_6$H$_4$P$_1$(pyrr)	16.6	19.1
HP$_1$(tmg)	28.6	31.4	2-Cl−C$_6$H$_4$P$_2$(dma)	16.3	18.8
PhP$_1$(pyrr)	28.1	30.9	PhP$_1$(pyrr)	15.9	18.4
4-MeO−C$_6$H$_4$P$_3$(dma)	27.7	30.5	PhP$_1$(dma)$_2$Me	15.5	18.0
PhP$_4$(dma)	27.0	29.8	TMG	15.3	17.8
4-Br−C$_6$H$_4$P$_4$ (pyrr)	26.9	29.7	4-Br−C$_6$H$_4$P$_1$(pyrr)	15.3	17.8
t-BuP$_1$(tmg)$_2$(NEt$_2$)	26.8	29.6	PhP$_1$(dma)	15.3	17.8
2-Cl−C$_6$H$_4$P$_4$(pyrr)	26.6	29.4	4-CF$_3$−C$_6$H$_4$P$_1$(pyrr)	14.6	17.1
EtP$_2$(pyrr)	26.6	29.4	1-naphtP$_1$(pyrr)	14.2	16.7
4-MeO−C$_6$H$_4$P$_3$(pyrr)	25.7	28.5	PhTMG	14.0	16.5
EtP$_2$(dma)	25.3	28.1	pyrrolidine	13.5	16.0
PhP$_1$(tmg)	24.3	27.0	4-NO$_2$−C$_6$H$_4$P$_1$(pyrr)	13.3	15.8
PhP$_3$(pyrr)	24.1	26.8	2-Cl−C$_6$H$_4$P$_1$(pyrr)	13.2	15.7
4-MeO−C$_6$H$_4$P$_3$(dma)	23.5	26.2	triethylamine	12.5	14.9
PhP$_3$(dma)	23.5	26.2	2-Cl−C$_6$H$_4$P$_1$(dma)	12.5	14.9
4-CF$_3$−C$_6$H$_4$P$_3$(pyrr)	23.1	25.8	2,5-Cl$_2$−C$_6$H$_3$P$_1$(pyrr)	11.9	14.3
2-Cl−C$_6$H$_4$P$_3$(pyrr)$_6$NEt$_2$	22.0	24.7	2,6-Cl$_2$−C$_6$H$_3$P$_1$(pyrr)	11.8	14.2
4-CF$_3$−C$_6$H$_4$P$_3$(dma)	21.7	24.4	4-Me$_2$N−pyridine	11.2	13.6
EtP$_1$(pyrr)	21.5	24.2	DMAN[e]	11.1	13.5
PhP$_1$(tmg)$_2$(dma)	21.5	24.2	4-Cl−2-NO$_2$−C$_6$H$_3$P$_1$(pyrr)	10.8	13.2
4-MeO−C$_6$H$_4$P$_2$(pyrr)	21.3	24.0	5-Cl−2-NO$_2$−C$_6$H$_3$P$_1$(pyrr)	10.1	12.5
HP$_1$(pyrr)	20.8	23.4	2-NO$_2$−4-CF$_3$−C$_6$H$_3$P$_1$(pyrr)	9.6	12.0
2-Cl−C$_6$H$_4$P$_3$(dma)$_6$NEt$_2$	20.8	23.4	2,4,6-Me$_3$−pyridine	8.1	10.4
H$_2$NP$_1$(pyrr)	20.8	23.4	2,4-(NO$_2$)$_2$−C$_6$H$_3$P$_1$(pyrr)	8.0	10.3
MeP$_1$(dma)	20.7	23.3	2,6-Cl$_2$−4-NO$_2$−C$_6$H$_2$P$_1$(pyrr)	7.8	10.1
PhP$_2$(pyrr)	20.5	23.1	2,6-(NO$_2$)$_2$−C$_6$H$_3$P$_1$(pyrr)	7.5	9.8
2,5-Cl$_2$−C$_6$H$_3$P$_3$(pyrr)$_6$NEt$_2$	20.2	22.8	4-MeO−pyridine	7.3	9.6
t-BuP$_1$(pyrr)	20.2	22.8	2,6-Me$_2$−pyridine	7.2	9.5
4-Br−C$_6$H$_4$P$_2$(pyrr)	20.0	22.6	4-MeO−aniline	6.5	8.8
HP$_1$(dma)	19.7	22.3	2-Me−pyridine	6.3	8.6
PhP$_2$(dma)	19.6	22.2	pyridine	5.5	7.8
TBD[c]	19.4	22.0	aniline	5.2	7.5
t-BuP$_1$(dma)	18.8	21.4	2-Me−aniline	5.1	7.4
PhP$_1$(dma)$_2$(tmg)	18.4	21.0	*N,N*-Me$_2$−aniline	4.9	7.2
MTBD[d]	17.9	20.5	4-Br−aniline	4.0	6.2
2-Cl-C$_6$H$_4$P$_2$(pyrr)	17.5	20.1	2-MeO−pyridine	2.6	4.8
2-Cl−C$_6$H$_4$P$_2$(pyrr)	17.3	19.9			

[a] dma denotes the dimethylamino (N(CH$_3$)$_2$) radical; pyrr denotes the 1-pyrrolidinyl (N(CH$_2$CH$_2$)$_2$) radical, and tmg denotes the *N,N,N′,N′*-tetramethylguanidine radical. [b] P$_1$ denotes the structure R′N=PR$_3$; P$_2$ denotes the structure R′N=P(R$_2$)N=P(R$_3$); P$_3$ denotes R$_3$P=NP(=NR′)R″N=PR$_3$; P$_4$ denotes R$_3$P=N−P(=NR′)(=NR$_3$)N=PR$_3$. [c] TBD denotes 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-a]pyrimidine. [d] MTBD denotes 1,3,4,6,7,8-hexahydro-1-methyl-2*H*-pyrimidol[1,2-a]pyrimidine. [e] DMAN denotes 1,8-bisdimethylaminonaphthalene.

standardized by titration of picric acid with tetrabutylammonium hydroxide, according to the method described in ref 14.

In all experiments, there was a little percentage of water due to the solution of perchloric acid used. In any case, the percentage of water in both potentiometric and conductometric assays was negligible since the added water was lower than 0.02% (v/v).

All data were obtained at 25 ± 0.1 °C.