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The Determination of Hydrogen Basicities in Acetonitrile

p-Nitrobenzyl Triphenylphosphonium Perchlorate as Reference Acid

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p-Nitrobenzyl triphenylphosphonium perchlorate is a valuable reference acid for the determination of hydrogen basicities in acetonitrile, due to the intense colour of the conjugate base, the ylide.

This reference acid, with a pK_a of 21.2 in acetonitrile, is well suited for the determination of pK_a values in the range 15 to 21 which includes the protonated form of the usual aliphatic amines.

For several bases tested, including aliphatic amines and small iorganic anions of varying concentrations and basicities, the ylide absorbance was of identical form with constant half-band width, suggesting the ylide to heteroconjugate or homoconjugate with acids present to only a negligible extent.

For acids, making very strong homoconjugates with their corresponding anions and, with largely unknown homoconjugation constants, K_f, only the sum of the pK_a and the pK_f values can be determined by this method. For hydrazoic acid, nitrous acid, hydroisocyanic acid and acetic acid, the sums of pK_a and pK_f are found to be 19.15, 19.25, 20.0, and 22.0, respectively.

p-Nitrobenzyl triphenylphosphonium perchlorate is too strong an acid to be suitable for the determination of $pK_a + pK_f$ for the very basic cyanide ion.

As pointed out by Parker,[1] the chemistry of anions in dipolar aprotic solvents differs greatly from their chemistry in water and other protic solvents. The greater solvation of the anions in protic solvents increases the dissociation of the conjugate acids and causes a decrease in the hydrogen basicity of the anions in protic solvents relative to the aprotic solvents. This decrease is highly dependent upon the size and polarizability of the anions, and there is consequently no correlation between the hydrogen basicity of anions in protic and aprotic solvents.[2] Furthermore, due to the different solvation of the acid, the hydrogen ion, and the anion in different aprotic solvents, one cannot safely calculate the hydrogen basicity of an anion or a base in one solvent from experiments in another solvent, even an isodielectric one.[3]

Some knowledge of the hydrogen basicity of an ion in a solvent is generally required in order to understand the ion's behaviour in the solvent. The fluoride ion, a weak base in water, is a very strong base in dimethyl sulfoxide,[4] and at elevated temperatures formation of the dimethylsulfinyl carbanion occurs and this may complicate the use of the fluoride ion in this solvent.[5] In acetonitrile, on the other hand, where bases generally are less basic than in dimethylformamide and dimethyl sulfoxide,[3] tetraethylammonium fluoride has been found to be a valuable reagent for proton abstraction.[6] For a general review on elimination reactions promoted by the halide ions, see Ref. 7. Likewise, the cyanide ion in dimethyl sulfoxide and dimethylformamide, apart from being a powerful nucleophile toward aliphatic carbon in these solvents,[8] is able to catalyze the dimerization of aromatic Schiff bases.[9] The choice of solvent and reagent may thus alter the ratio of elimination to substitution in either the desired or undesired direction.[10,11] The hydrogen basicity of an eliminating reagent may also affect the steric course in bimolecular elimination reactions.[12] Finally, accurate $\mathrm{p}K_\mathrm{a}$ values of the conjugate acids of anions and other bases in aprotic solvents are necessary for an experimental test of the Edwards equation [13] in solvents other than the usual protic ones. The need for determination of hydrogen basicities of anions and other bases in non-aqueous solvents is thus apparent.

From the fundamental works of Kolthoff [14] and Coetzee [15] several methods are now available for the determination of hydrogen basicities in non-aqueous solvents.[3] The glass electrode has been found to be a valuable tool since it responds reversibly to changes in hydrogen ion activity over a very wide range both in acetonitrile [15] and dimethyl sulfoxide.[16,17] Titrations of acids in non-aqueous solutions may be carried out with standard solutions of a tetraalkylammonium hydroxide. Since these solutions always contain protic contaminants and as water is formed during the neutralization, the reliability of this method has been questioned.[18] The indicator method, with coloured indicators, has been used successfully.[19]

We wish to report some studies on the determination of the hydrogen basicity of some bases by a method of the indicator type using *p*-nitrobenzyl triphenylphosphonium perchlorate as the reference acid. The acid-base equilibrium between various onium salts and their corresponding ylides is well documented.[20] Several onium salts, where one or several of the groups attached to the central atom contain both highly electronegative substituents and labile hydrogen on the carbon atom alpha to the central atom, are moderately strong acids. From studies on, especially, acyl onium salts, the acidity is known to depend upon the attached groups, the central atom, and the solvent.[21–26]

When one of the attached groups is a *p*-nitrobenzyl group, the corresponding bases or ylides are highly coloured and are stable in non-aqueous solvents not containing carbonyl groups.[27] *p*-Nitrobenzyl onium salts are stable acids which are easily synthesized and purified, and cover a wide range of acidities according to the hetero-atom and substituents present. Most important, the conjugate base, the ylide, is well suited for quantitative determination by means of UV spectroscopy. The relative acidities of carbon-hydrogen acids are far less dependent upon solvents than are oxygen and nitrogen acids.[25]

As the onium cations useful in this method are of rather similar size and structure, the dependence upon the cation of the calculated pK_a values of the anion's conjugate acids is effectively diminished.[28–30] By using tetraphenylarsonium salts as the source of the anions, as in this work, the cations of the acid and the base will be of the same size and of similar structure.

Acetonitrile was chosen as the solvent due to its very large autoprotolysis constant,[31] the length of the relative scale of acidity, and especially its differentiating effect.[32] Furthermore, salts of large ions are known to dissociate very well in acetonitrile.[33,34]

Although acetonitrile is known to form complexes with Pt(II) substrates through the lone pair electrons on nitrogen,[35] and to act as a proton acceptor in hydrogen bond formation with phenol,[36] acetonitrile is an extremely weak base.[37,38] This makes acetonitrile a poor solvating agent for both the undissociated acids [29,39,40] and their anions.[41,42] As a result, homoconjugation between anions and conjugate acids is far more pronounced in acetonitrile than in other more basic isodielectric solvents like dimethyl sulfoxide and dimethylformamide.[3,17,30] As the homoconjugation constants for a large number of bases in acetonitrile are known,[15] the complexities due to homoconjugation which arise when determining hydrogen basicities in acetonitrile can be easily coped with. Acetonitrile is, however, a sufficiently strong base to cause complete dissociation of perchloric acid.[14,43] The perchlorate salt is therefore used as the source of the *p*-nitrobenzyl triphenylphosphonium cation in this work.

In using *p*-nitrobenzyl triphenylphosphonium perchlorate as reference acid, here called PH^+, the procedure is to determine the amount of ylide, P, given by its absorbance at 510 mμ, for different concentrations of reference acid and added base, B. The following two consecutive equilibria will be established:

$$PH^+ + B \overset{K}{\rightleftharpoons} P + BH^+ \tag{1}$$

$$BH^+ + B \overset{K_f}{\rightleftharpoons} B_2H^+ \tag{2}$$

From the concentration of the ylide, calculated by the usual Benesi-Hildebrand method,[44] the equilibrium constants, K, for the reaction between the reference acid and some amines of known hydrogen basicity in acetonitrile could be calculated allowing for the necessary corrections due to homoconjugation.[15] (See experimental part.)

The plot between the logarithms of the calculated equilibrium constants, and the literature [15] pK_a values in acetonitrile of the protonated form of the tested amines, benzylamine, morpholine, triethylamine, and piperidine, was linear with a slope of 1.07 ± 0.03. The proton acceptor power of these amines was thus found to be independent of the type of reference acid used, as required for a general method. The linear plot suggests the following relation for the calculation of unknown pK_a values in acetonitrile from the equilibrium constant K determined by the present method:

$$pK_a = 1.07^{-1} (\log K + 22.7) \tag{3}$$

In the case of the inorganic anions, cyanate, azide, acetate, and cyanide, the homoconjugation constants in acetonitrile, K_f, are very large and mostly unknown. Salts of $H(NO_2)_2^-$, $H(CN)_2^-$ and $H(OAc)_2^-$ are known to be stable in acetonitrile.[45] The presence of large counter-ions, as used in this work, will further increase the homoconjugation.[46]

The calculation of equilibrium constants confirmed the existence of the homoconjugation equilibria. The 1:2 reaction of hydrogen ion with the cyanate and the azide ion, where the homoconjugated ions appear to be previously unknown, was further confirmed by IR measurements at 2140 cm^{-1} and 2005 cm^{-1}, respectively,[47] using IR liquid cells and reference acid in excess.

When the homoconjugation constant, K_f, is large and unknown, the present method does not allow the calculation of the pK_a of the corresponding acid of an anion. The measured equilibrium constants will be the product of the equilibrium constants K and K_f. For studies on elimination reactions in dipolar aprotic solvents where small inorganic anions are the eliminating reagent, the sum of the pK_a and the pK_f values will be of more importance than the pK_a values alone.

Attempts were made to determine the equilibrium constant for the reaction between *p*-nitrobenzyl triphenylphosphonium perchlorate and the very basic cyanide ion, but in this case the reference acid was found to be too strong. For all combinations of concentrations of the reference acid and tetraphenylarsonium cyanide, the amount of ylide was found to be identical to the concentration of *p*-nitrobenzyl triphenylphosphonium perchlorate. A minimum value of 23 for $pK_a + pK_f$ of hydrocyanic acid is thus suggested. The experiments with the cyanide confirmed the extinction coefficient of the ylide at 510 mμ as calculated for the less basic bases from the Benesi-Hildebrand plot. No attempt was made to obtain the desired ylide pure as previous attempts to purify this compound have failed.[27]

Even the acetate ion was close to being a too strong base in acetonitrile to allow an accurate determination of $pK_a + pK_f$ of acetic acid. The calculated value, 22.0 ± 0.2, is in good agreement with a previously obtained value, 22.3.[3]

Table 1. Equilibrium constants, K, for $PH^+ + B \rightleftharpoons P + BH^+$ and KK_f for $PH^+ + 2B \rightleftharpoons P + B_2H^+$ at an ionic strength of 0.01 M.

Base (B)	K	KK_f	pK_a(AN)	$pK_a + pK_f$(AN)
Morpholine	1.2×10^{-5} [a]		16.61 [b]	17.61 [b]
Benzylamine	1.8×10^{-5} [a]		16.76 [b]	17.94 [b]
Triethylamine	1.3×10^{-3} [a]		18.46 [b]	18.46 [b]
Piperidine	4.0×10^{-3} [c]		18.92 [b]	20.33 [b]
N_3^-		6.3×10^{-3} [d]		19.15 ± 0.1 [e]
NO_2^-		7.6×10^{-3} [d]		19.25 ± 0.1 [e]
OCN^-		4.7×10^{-2} [d]		20.0 ± 0.1 [e]
CH_3COO^-		7.0 [d]		22.0 ± 0.2 [e]
CN^-		> 100 [d]		> 23 [e]
Reference acid			21.2 [f]	

[a] Calculated by eqn. (9). [b] Ref. 15. [c] Calculated by eqn. (7). [d] Calculated by eqn. (11). [e] From eqn. (3). [f] Calculated from pK_a values of the conjugate acids of amines.[15]

The experimentally determined equilibrium constants and the calculated $pK_a + pK_f$ values are listed in Table 1.

For the amines used in these experiments a correction due to homoconjugation was found to be necessary for only the most basic one, piperidine. When applied to amines, the method described in this work for the determination of hydrogen basicities in acetonitrile thus appears to be best suited when the equilibrium constant K is small.

For all the bases tested, the ylide absorbance at 510 mμ was found to be of identical form with a half-band width of approximately 35 mμ. In the case of the cyanate ion, a slight increase of the absorbance was experienced after some time. This effect was due neither to an aging of the solution of ionic cyanate, nor to a possible Wittig reaction between the ylide and the cyanate ion or the hydrogendicyanate ion, as solutions of the reference acid and tetraphenylarsonium cyanate did not yield any trace of triphenylphosphine oxide even after prolonged periods. The increase may be due to some instability of the $H(NCO)_2^-$ ion yielding basic contaminants.

Kolthoff and co-workers [48] have stressed that caution must be observed in the use of acid-base indicators for the spectrophotometric determination of pK_a values in acetonitrile and other aprotic solvents due to homoconjugation and heteroconjugation between species present. Usually, uncharged oxygen acids like substituted phenols have been used as reference acids. These acids are known to homoconjugate strongly with their conjugate bases, the negatively charged phenolate anions, where the homoconjugates have absorbance spectra different from those of both the phenols and the phenolate anions.

The origin of these difficulties is primarily due to the poor ability of dipolar aprotic solvents to solvate negatively charged ions. Positively charged ions are known to be far better solvated by dipolar aprotic solvents than are anions.[49] Homoconjugation between a reference acid and its conjugate base should therefore be far less pronounced when a positively charged acid is applied, as in this work. The large size of the reference acid and its conjugate base, as in the case of *p*-nitrobenzyl triphenylphosphonium perchlorate, will further reduce the difficulties due to homoconjugation. The identical form of the ylide absorbance, regardless the size, the basicity, and the concentration of the added base, as observed in this work, suggests that the ylide is homoconjugating with acids present only to a negligible extent.

The reference acid used in this work, *p*-nitrobenzyl triphenylphosphonium perchlorate, with a calculated pK_a in acetonitrile of 21.2, appears to be well suited for the determination of pK_a values ranging from 15 to 21. In other, more basic dipolar aprotic solvents where the homoconjugation between small anions and their conjugate acids is far less pronounced,[48] this method may allow the direct determination of the pK_a values of inorganic acids in these solvents. Further applications of this method are being investigated in this laboratory.

EXPERIMENTAL

Acetonitrile was purified with P_2O_5 and CaH_2 as earlier.[47] *Benzylamine, morpholine, pyridine,* and *triethylamine* were purified according to Coetzee and Padmanabhan.[15]

Tetraphenylarsonium cyanide, *cyanate*, *azide*, and *acetate* were prepared according to the procedure described previously,[47] and were dried to constant weight prior to use.

Tetraphenylarsonium perchlorate was prepared as described by Springer *et al.*[50]

Tetraphenylarsonium nitrite was made by adding a concentrated solution of potassium nitrite to an aqueous solution of tetraphenylarsonium chloride. Tetraphenylarsonium nitrite precipitated immediately. A near quantitative yield was obtained after leaving the reaction mixture in the refrigerator overnight. The solid was washed repeatedly with benzene and ether, dried in vacuum, dissolved in acetonitrile, filtered, and precipitated with ether. The product was finally recrystallized from acetone and dried to constant weight prior to use.

p-*Nitrobenzyl triphenylphosphonium perchlorate* was made from the corresponding bromide by adding an equivalent amount of lithium perchlorate in a water/ethanol mixture. A quantitative amount of the perchlorate precipitated immediately. The salt was washed several times with cold water, then with cold acetone and finally recrystallized twice from acetonitrile. The salt was dried to constant weight prior to use. M.p. 196 – 197°C.

Stock solutions of the tetraphenylarsonium salts and *p*-nitrobenzyl triphenylphosphonium perchlorate were prepared by weighing the salts immediately after drying, adding acetonitrile and diluting to desired volume. Stock solutions of the amines were made with care to avoid contamination by atmospheric moisture.

Equilibrium mixture of acids and bases were prepared by pipetting from the stock solutions and diluting in volumetric flasks. In the runs where the reference acid was in excess, the concentration of this acid was 1×10^{-2} M. In other cases where the total ionic strength due to the reference acid and the ionic bases was less then 1×10^{-2} M, the necessary amount of tetraphenylarsonium perchlorate was added. The concentrations of both acid and bases were in the 5×10^{-5} M to 1×10^{-2} M range.

The measurements were performed at the absorption maximum of the *p*-nitrobenzyl triphenylphosphonium ylide at 510 mμ. This was the only species in the reaction mixtures absorbing at this wavelength. The method of Benesi and Hildebrand[44] was used to determine the extinction coefficient of the ylide. The calculated extinction coefficient for the ylide from all measured bases and inorganic anions was identical. The UV measurements were performed with a Beckman DB-GT Spectrophotometer using 1 cm quartz cells and cell compartments thermostated at 25 ± 0.3°C.

CALCULATIONS

For the reaction between a base, B, and *p*-nitrobenzyl triphenylphosphonium perchlorate, PH^+, in acetonitrile, the following two consecutive equilibria will be established:

$$PH^+ + B \overset{K}{\rightleftharpoons} P + BH^+ \tag{1}$$

$$BH^+ + B \overset{K_f}{\rightleftharpoons} B_2H^+ \tag{2}$$

K is the equilibrium constant and K_f is the homoconjugation constant as defined by Coetzee and Padmanabhan.[15] P is the ylide. By applying the following relations:

$$[PH^+]_0 = [PH^+] + [P] \tag{4}$$

$$[B]_0 = 2[B_2H^+] + [BH^+] + [B] \tag{5}$$

$$[P] = [BH^+] + [B_2H^+] \tag{6}$$

the following expression for the equilibrium constant K is obtained:

$$K = \frac{[B]_0 - [B]}{[PH^+]_0 - [P]} \; \frac{[P]}{(2K_f[B] + 1)[B]} \tag{7}$$

where [B] is obtained by solving the equation:

$$K_f[B]^2 + (1 + 2K_f[P] - K_f[B]_0)B - ([B]_0 - [P]) = 0 \tag{8}$$

For small values of K_f, the homoconjugation equilibrium (2) can be neglected, and the combined expressions (7) and (8), by putting $K_f = 0$, reduce to:

$$K = \frac{[P]^2}{([PH^+]_0 - [P])[(B]_0 - [P])} \tag{9}$$

Eqn. (9) was used for all amines except for piperidine, where eqns. (7) and (8) were used.

In the case of the inorganic anions, the 1:2 reaction gives the following equilibrium:

$$PH^+ + 2B \overset{KK_f}{\rightleftharpoons} P + B_2H^+ \tag{10}$$

where KK_f is given by:

$$KK_f = \frac{[P]^2}{([PH^+]_0 - [P])([B]_0 - 2[P]^2)} \tag{11}$$

The equilibrium constants listed in Table 1 are the average values from 4 to 8 measurements with varying concentrations of both the reference acid and the base.

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