Acid−Base Equilibria in Nonpolar Media. 1. A Spectrophotometric Method for Acidity Measurements in Heptane

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A UV−vis spectrophotometric method for measurements of relative acidities in heptane has been developed. The phosphazene base t-BuP_4 is used as the deprotonating agent. Its protonated form is a good counterion for the anions of the acids because it is bulky, has delocalized charge, and therefore does not have specific interactions with the anions. A self-consistent scale of relative acidities in heptane spanning for 3 pK_a units has been constructed.

Introduction

Acidity measurements of organic compounds have a long history dating back to the end of the 19th century, when the first pK_as were measured.[1] Since then a vast body of data on acidities in various solvents has been collected.[2−5] The measurements have mostly been limited to polar solvents however, water being by far the most exploited medium, followed by alcohols and dipolar aprotic solvents.

Acidity data in solvents of low polarity are also very valuable for many reasons. (1) The acidity of a compound in a given medium is influenced by both electronic effects of the substituents and the solvent effects of the medium. In polar solvents the solvent effects are strong and analysis of the acidity data in terms of electronic effects is difficult. In nonpolar solvents the medium has less influence on the acidities and the acidities are better differentiated. (2) Systems of extremely high acidity can be studied in nonpolar solvents. (3) Acidities of very weak acids can be measured in nonpolar solvents. (4) Many processes in organic synthesis and in the chemical industry involving acids and bases are carried out in nonpolar media, and acidity data in nonpolar media are needed to be able to understand and to quantitatively describe these processes.

The first ion-pair acidity scales in low-polarity media were set up by Conant et al.[6] in diethyl ether (dielectric constant $D = 4.20$) and McEwen[7] in benzene ($D = 2.27$). Since then several others have been created: in cyclohexylamine[8] ($D = 4.73$), in 1,2-dimethoxyethane[9] ($D = 7.20$), and in tetrahydrofuran[10] ($D = 7.58$). All these scales were built using metalation with alkali metals for deprotonation of the acids under study. This approach has been criticized by Konovalov et al.,[11] who state that because the ions in nonpolar media exist as ion-pairs (or larger associates), the alkali metal cations in nonpolar solvents will have strong specific interactions with the anions of the acids studied. The extent of the interaction is dependent on the anion as well as the cation, and therefore these scales lack the significance necessary for carrying out accurate analysis of substituent effects. These authors propose use of the lithium [2.1.1]cryptate as the counterion. The interactions between this ion and the anions are limited to electrostatic and van der Waals forces. The specific interactions are eliminated because the metal cation is coordinatively saturated and the cryptate ion is large (radius 5 Å).[11] Using this technique the Russian authors have built acidity scales in tetrahydrofuran[12] ($D = 7.58$), *N*-methylmorpholine[13] ($D = 4.3$), and benzene[14] ($D = 2.27$).

The least polar solvent in which a scale of acidity has been set up is benzene.[14] It would be of considerable interest to perform acidity measurements also in media with $D < 2$. This is because the $D = 2$ medium is halfway between polar solvents and the gas phase.

When measuring acidities in polar solvents, equilibrium (1) is studied usually:

$$HA + S \rightleftarrows A^- + SH^+ \qquad (1)$$

where S refers to the solvent. This equilibrium is also used to define the term “acidity of a compound”, which is usually expressed as pK_a, where K_a is the equilibrium

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constant:

$$K_a = \frac{a(\mathrm{SH}^+)a(\mathrm{A}^-)}{a(\mathrm{HA})} \qquad (2)$$

where *a* is the activity of the corresponding species. In nonpolar (and particularly in nonbasic) solvents the equilibrium (1) is shifted strongly to the left. In these solvents it is almost impossible to study the equilibrium directly. It is common to study the following equilibrium instead:

$$\mathrm{HA}_2 + \mathrm{A}_1^- \rightleftarrows \mathrm{A}_2^- + \mathrm{HA}_1 \qquad (3)$$

The p*K* of this equilibrium is the relative acidity (ΔpK_a) of the acids HA_1 and HA_2:

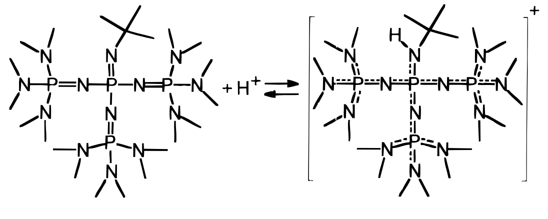
$$\Delta pK_a = pK_a(\mathrm{HA}_2) - pK_a(\mathrm{HA}_1) = \log\frac{a(\mathrm{A}_1^-)a(\mathrm{HA}_2)}{a(\mathrm{A}_2^-)a(\mathrm{HA}_1)} \qquad (4)$$

Analyzing real systems according to eq 1 and eq 3 is certainly a simplification. In reality various association processes between ions (ion pairing), between ions and neutrals, and between neutrals occur as well. The less polar the solvent, the more complicated the picture.

Alkanes are solvents with very weak solvating power toward polar and especially ionic species. To prevent extensive aggregation and eventually precipitation of ionic compounds in such solvents, the ions should have the following properties: (1) The charge of the ion should be as delocalized as possible (the ion should have no well-defined ionic centers, such as $-O^-$ or $-NH_3^+$). (2) The ion should be as large as possible.

The neutral acids themselves should also be as nonpolar as possible and should not have polar centers, such as $-OH$. This restricts both the number of acids that can be studied in heptane and the choice of the method of deprotonation of the acids and the counterion. To the best of our knowledge, no systematic acidity measurements have been performed in alkanes to date.

An ideal deprotonating agent would be a very strong base, which is soluble in heptane and able to deprotonate acids in nonpolar medium, and the protonated form of this base would meet all the criteria setup for ions above. There are bases—phosphazenes[15,16]—which meet all these requirements. We use phosphazene *t*-BuP$_4$ [the systematic name of *t*-BuP$_4$ is 3-(*tert*-Butylimino)-1,1,1,5,5,5-hexakis(dimethylamino)-3-{[tris(dimethylamino)phosphoranylidene]amino}-1λ^5,3λ^5,5λ^5-1,4-triphosphazadiene] for our work. It is a very strong base [pK_a(DMSO) = 30.2[16]] which upon protonation gives a bulky cation (its radius has been estimated to about 7 Å[17]) with strongly delocalized charge:



t-Bu-P$_4$ (5)

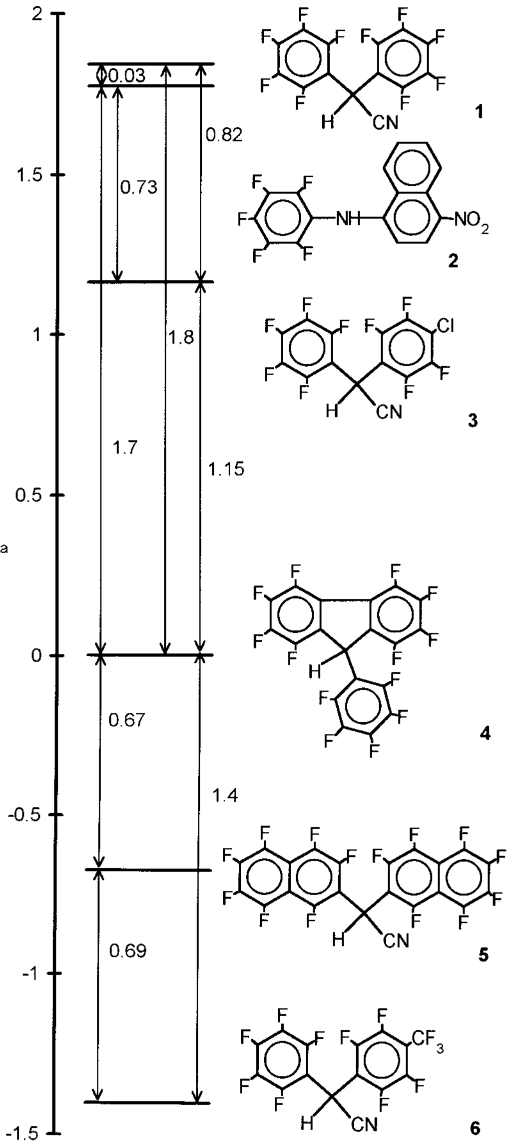


Figure 1. Interlocking ladder of relative acidities in heptane. The ladder is anchored to arbitrarily chosen reference compound **4**.

It is also important to note that the protonated basicity center of this phosphazenium ion is sterically strongly hindered and has, therefore, a low ability to specifically interact (e.g., hydrogen bonding) with the anions of the acids, which are very bulky too and devoid of well-defined charged centers. An additional advantage of *t*-BuP$_4$ is that its cation is transparent practically across the entire UV spectral range.

In this paper we report a method for determining relative acidities in heptane ($D = 1.92$) utilizing *t*-BuP$_4$ as the deprotonating agent. The acids studied in this work form extensively delocalized anions and are presented in Figure 1. As a result of our measurements we have set up a continuous, self-consistent acidity scale in heptane.

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Experimental Section

Method of pK_a Determination. The relative acidities were measured using a UV–vis spectrophotometric titration technique: a solution containing two acids, HA_1 and HA_2, was titrated with a solution of *t*-BuP_4 in heptane. A spectrum was recorded after each addition of the titrant. The number of titration points per experiment ranged from 10 to 30. Both of the acids were also titrated separately to obtain the spectra of the neutral and the ionized forms of both acids. All titrations came to a point where further addition of the titrant did not change the spectrum. This was considered the equivalence point of the titration. From the spectra the relative acidity of the two acids could be calculated. The calculation methods are presented below.

The calculations assume constant analytical concentrations of the acids. The spectra were corrected for the dilution due to titrant addition.

We assume that the ratio of the activity coefficients of the anion and the neutral $f(A^-)/f(HA)$ in heptane is constant for all acids, so that the ratios of activities in eq 4 can be replaced by the ratios of concentrations. These ratios (indicator ratios) were measured from the absorbance spectra of the compounds. The prerequisite for this is that the two compounds must have different spectra in the UV–vis region and the spectrum of the acid must be different from that of the anion. These criteria are met by all the acids under study.

When two partially ionized acids HA_1 and HA_2 are in the same solution, their UV–vis spectra usually overlap and the following equation holds for absorbance A^λ at wavelength λ:

$$A^\lambda = [HA_1]\epsilon^\lambda_{HA_1} + [A_1^-]\epsilon^\lambda_{A_1^-} + [HA_2]\epsilon^\lambda_{HA_2} + [A_2^-]\epsilon^\lambda_{A_2^-} \quad (6)$$

The ϵ values are molar absorption coefficients of the respective species; the optical path length is equal in all cases and can be included in A. If we use the concentrations of the acids as normalized to 1, we may write $[HA_1] = 1 - [A_1^-]$ and $[HA_2] = 1 - [A_2^-]$ and the equation can be rewritten:

$$A^\lambda = \epsilon^\lambda_{HA_1} + \epsilon^\lambda_{HA_2} + [A_1^-](\epsilon^\lambda_{A_1^-} - \epsilon^\lambda_{HA_1}) + [A_2^-](\epsilon^\lambda_{A_2^-} - \epsilon^\lambda_{HA_2}) \quad (7)$$

And finally:

$$\frac{A^\lambda - \epsilon^\lambda_{HA_1} - \epsilon^\lambda_{HA_2}}{(\epsilon^\lambda_{A_2^-} - \epsilon^\lambda_{HA_2})} = [A_1^-]\frac{(\epsilon^\lambda_{A_1^-} - \epsilon^\lambda_{HA_1})}{(\epsilon^\lambda_{A_2^-} - \epsilon^\lambda_{HA_2})} + [A_2^-] \quad (8)$$

This expression represents a linear equation with slope $[A_1^-]$ and intercept $[A_2^-]$. All the ϵ values are constants at a fixed wavelength, and they can be determined from spectra containing only one acid in entirely ionized or neutral form. If we take a spectrum of a solution containing both acids in partially ionized form and vary the λ, the terms containing absorbance and the extinction coefficients are variables and the $[A_1^-]$ and $[A_2^-]$ are constants, which can be determined from regression analysis and the relative acidity can be calculated as follows:

$$\Delta pK_a = \log\frac{[A_1^-](1 - [A_2^-])}{[A_2^-](1 - [A_1^-])} \quad (9)$$

This general calculation method is universal, but it has the drawback that the concentration of the acids HA_1 and HA_2 in the solutions (or at least the ratio of the concentration in the mixture and in the solution from which the ϵ values were found) must be known precisely. Even small errors in concentrations tend to introduce large errors in ΔpK_a values. The errors are the larger the bigger the ΔpK_a.

The spectra of most of the compounds studied contain features which allow simpler methods of calculation to be used. There are isosbestic points in the spectra, and often one of the acids absorbs at a longer wavelength than the other and its indicator ratio can be determined from the spectrum of the mixture in the presence of that other acid. A couple of simple methods will be outlined below.

If for both acids HA_1 and HA_2 a wavelength can be found at which the absorbance of the other acid (that is HA_2 and HA_1, respectively) does not change in the course of titration, then the indicator ratios $[A^-]/[HA]$ of both acids in the same solution can be directly determined from the spectra of the mixture without using spectra of solutions of pure compounds. A very simple relationship holds for the indicator ratio:

$$\frac{[A^-]}{[HA]} = \frac{A^\lambda - A_n{}^\lambda}{A_i{}^\lambda - A^\lambda} \quad (10)$$

where $A_n{}^\lambda$ and $A_i{}^\lambda$ are the absorbances of solution containing both acids in neutral and ionized forms, respectively. The wavelength λ is one at which the absorbance of the other acid does not change during the titration. When the indicator ratios are known, the ΔpK_a can be calculated using eq 4. This is a very simple and accurate method since the spectra from only one titration are involved and the values of the concentrations of the acids in the solution are unimportant.

For carbon acids such as those studied in this work, it is very common that the anions absorb at long wavelengths where the neutrals are transparent. If a range of wavelengths can be found at which both anions absorb and both neutrals are transparent, then an elegant calculation method can be applied. Absorbance A^λ of the mixture at any wavelength λ in that wavelength region can be expressed as a linear combination of the absorbances of the anions $A_1{}^\lambda$ and $A_2{}^\lambda$:

$$A^\lambda = b_1A_1{}^\lambda + b_2A_2{}^\lambda \quad (11)$$

where b_1 and b_2 are constants for a given mixture within that wavelength range and are determined using a least-squares method. For each spectrum of the titration, b_1 and b_2 can be found and ΔpK_a can be calculated as follows:

$$\Delta pK_a = \log\frac{b_1(b_2{}^i - b_2)}{b_2(b_1{}^i - b_1)} \quad (12)$$

where $b_1{}^i$ and $b_2{}^i$ are the coefficients of the mixture in which both acids are fully ionized. Again, the concentrations of the acids in solutions are unimportant with this method.

For each measurement the most appropriate calculation method was chosen. The simpler methods were preferred over the general one because of their higher accuracy. In difficult cases several methods were used.

Solvent. The solvent suitable for our work must be very dry and be low in any acidic and basic impurities and those that absorb UV radiation. Heptane (Reakhim, "pure") (1.75 L) was stirred three times, 4 h each time, with 15 mL of concentrated sulfuric acid. The last portion of sulfuric acid was only slightly yellowish after stirring. Then the solvent was stirred twice with 20 mL of of 0.5 N solution of potassium permanganate (Reakhim, analytical grade) in 5 N sulfuric acid for 4 h each time. The solvent was washed with 200 mL of water and then with 200 mL of a 10% solution of sodium hydroxide and then stirred with solid potassium hydroxide for 4 h. Finally it was distilled through a 1.2 m column packed with Teflon chips from P_2O_5 (Reakhim, analytical grade) with magnetic stirring (to avoid possible decomposition processes at the bottom of the distillation flask). The first and last 10% portions of the solvent were discarded. A stream of dry argon was passed through the solvent during the distillation. The solvent was stored over anhydrous magnesium perchlorate in airtight bottles. The absorbance values of the middle fraction (1 cm cell, vs H_2O) at 207, 210, 220, 230, and 260 nm are 1.0, 0.85, 0.16, 0.07, and 0.03, respectively.

Acids. The acids were prepared at the Institute of Organic Chemistry in Novosibirsk, and their preparation has been previously described: **1**, **3**, **6**;[18] **2**;[19] **4**;[20] **5**.[21]

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Phosphazene *t*-BuP$_4$. This compound was prepared according to the procedures described in the literature.[15,16,22,23]

Experimental Setup. The solutions were prepared in 10 mL vials. Care was taken to prevent air getting into contact with the solutions. All operations were performed using standard syringe techniques. All the glassware used was dried at 150 °C and cooled in a desiccator over P_2O_5.

The titration was carried out directly in the spectrophotometer cell. The cell contained a small Teflon-coated stirring bar for mixing the solution. The amount of titrant added was measured by weighing the cell.

The concentrations of the acids were chosen as low as possible to prevent precipitation and association of ions during titration. The average values were in the range 1 to 5×10^{-5} M. The concentrations of the titrant were around 1×10^{-3} M. The solutions of the acids and the solution of the titrant were made fresh daily.

Spectrophotometry. A Perkin-Elmer Lambda 2S UV−vis spectrophotometer equipped with cell holders thermostated to 25 °C was used for all the measurements. The spectrophotometer was controlled from a PC, and the spectra were stored in digital form. Fused silica cells with an optical path length of 1 cm were used. The reference cell contained pure heptane.

Results and Discussion

The results of the measurements are presented in Figure 1. The compounds as well as their salts with *t*-BuP$_4$ are sufficiently soluble in heptane. In some cases, however, precipitation occurred during the titration as the concentration of the salt increased. This was recognized by opalescence of the solution and shift of the base line of the spectrum away from zero. This problem was remedied by reducing the concentration of the acid.

Beer's law was found to hold for the acids and their anions at the low concentrations (1 to 5×10^{-5} mol/L) used. Sharp isosbestic points were observed with all compounds. At higher concentrations the spectra sometimes changed in an odd way. This was often caused by precipitation, but in some cases the solution remained clear and the shape of the spectrum changed. This can probably be attributed to some aggregation process, but further investigations are needed to give a conclusive answer.

Each arrow on Figure 1 represents one measurement of relative acidity. To make the results more reliable and to be able to estimate the consistency of the results, we carried out multiple overlapping measurements. The entire range from **1** to **6** involves two independent pathways of measurements, and the relative acidity of any two acids can be obtained by combining at least two independent sets of measurements. The uncertainties of the results are best estimated from Figure 1 by observing how good the agreement is between different pathways of measurements. The most uncertain measurements are those of the pairs **1**−**4**, **2**−**4**, and **4**−**6**. These pairs of acids have large ΔpK_as, and this is the reason for the low precision of these results. We estimate the uncertainties of these three measurements as large as 0.2 pK_a unit and the uncertainties of the rest of the measurements 0.05−0.1 pK_a unit. Taking into account that the large ΔpK_a values cannot be measured with high precision, the agreement between different pathways is good and the scale can be considered self-consistent.

The method used lets us obtain only relative acidities. Compound **4** has been taken as an arbitrary reference compound, and the acidities of all others are expressed relative to that of **4**. We assign the following ΔpK_a values (all relative to **4**) to the acids investigated: **1** 1.8; **2** 1.8; **3** 1.1_5; **4** 0; **5** -0.6_7; **6** −1.4. No attempt is made in this paper to convert the relative acidities to absolute numbers.

The actual state of the ions in solution is an important issue. It is well-known that ions in nonpolar media exist as ion pairs or higher aggregates. Depending on the ions involved and the solvating properties of the medium, two types of ion pairs can be distinguished: contact ion pairs and solvent-separated ion pairs.[24] It has been shown that as the ions get larger, the spectral properties of contact ion pairs approach those of solvent-separated ion pairs and that the spectral properties of solvent-separated ion pairs and free ions generally do not differ.[24] Konovalov et al.[11] have carried out detailed spectrophotometric and conductometric investigations of the state of lithium [2.1.1]cryptate ion in solvents of low polarity. These investigations are particularly relevant to our case because the phosphazenium ion present in our solutions is similar in size to that of the cryptate ion used by Konovalov et al. These investigators varied the solvent polarity (ranging from DMSO to hexane) as well as the degree of charge delocalization of the anions. It was found that the cryptate ion and the anion exist as ion pairs in all the solvents studied (except DMSO in which the ion pairs dissociate) and that in all the media the spectral characteristics of the ion pair are indistinguishable from those of solvent-separated ion pairs. The authors proposed the term "cryptate-separated ion pair" for this type of ion pair. The results of conductometric investigations showed that if the concentration of the cryptate ion in solution is less than 1×10^{-4} mol/L, then the ion pairs in a solvent with $D < 15$ do not associate significantly into larger aggregates.[11]

Taking into account the structural properties of the compounds involved in the equilibria, the results of Konovalov et al., and the very low concentrations of the acids used in this work, we predict that the ions exist as "loosely bound" ion pairs, analogous to the cryptate-separated ion pairs described by Konovalov et al. This means that although neither of the two ions in the ion pair is solvated in heptane to an appreciable extent, there are no specific interactions between the ions because they are bulky and have delocalized charge.

Some support for this prediction can also be drawn from the fact that Beer's law holds for the salts and that isosbestic points are observed. This means that under our experimental conditions the state of the ion pair in terms of specificity of interactions between the ions does not change with increasing concentration of the salt relative to the neutral acid. On the other hand, as the spectral properties of the distant ion pairs and free ions do not differ, these results do not say anything about the extent to which the ion pairs dissociate into free ions as well as about possible aggregation of the loosely bound ion pairs.

It is not possible to thoroughly discuss substituent effects or correlations of the results with measurements

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in other media because at present our scale contains too few compounds and these are not very common. However, acidities of compounds **1**, **3**, **4**, and **6** have been measured in the gas phase (ΔG_{acid} = 312.4,[25] 311.8,[26] 301.8,[25] and 307.5[25] kcal/mol, respectively) and in DME solution[27] (pK_a = 6.4, 5.4, 5.3, and 3.9, respectively).

The correlation of pK_a(heptane) vs pK_a(DME) is not very good: $r^2 = 0.91$, slope 0.70 (pK_a in heptane is on abscissa) and standard error $s = 0.38$. No obvious outlier was detected. It must be noted that these pK_a values in DME have been obtained using Li^+ as the counterion and the anions exist in DME solution as contact ion pairs with Li^+.[27] Specific interactions between ions cannot be neglected here, but there are too few data to draw far-reaching conclusions.

In the gas phase the correlation is good: $r^2 = 0.993$ and slope 0.92 (ΔG_{acid} values are transformed to pK_a scale prior to the correlation analysis) if the compound **4** is excluded from the correlation analysis. This compound severely deviates from the correlation line. If we take that one of the measurements (that is pK_a in heptane or ΔG_{acid} in the gas phase) is correct, then the other one must be in error by approximately 5 orders of magnitude (!) in order to fit into the correlation. Compound **4** is of a different family from compounds **1**, **3**, and **6**, and this can be partially the reason for the enormous deviation. It can be expected that charge in the deprotonated **4** is more delocalized than that in **1**, **3**, and **6**, which have CN groups attached directly to the acidic center. This CN group will carry significant negative charge in these anions, and they are more strongly solvated in the liquid phase than the deprotonated **4**. The three anions are also expected to interact more strongly with traces of water and with counterions than the deprotonated **4**. Thus one can expect that going from the gas phase to the liquid phase the increase in acidity of **1**, **3**, and **6** is larger than that of **4**. This is really the case: the pK_a of **4** in heptane (and in DME too) relative to the other three compounds is about 5 units higher than that predicted from the gas phase measurements. Nevertheless, neither heptane nor DME has strong ability to solvate anionic centers and this difference in solvation cannot be the only reason for this phenomenon. Further experiments are necessary.

Work is in progress in our laboratory to further extend the acidity scale. Also the actual state of the ions in solution needs to be further studied by other methods.

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