Spectrophotometric Acidity Scale of Strong Neutral Brønsted Acids in Acetonitrile

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A continuous self-consistent quantitative UV–vis spectrophotometric pK_a scale of strong acids in acetonitrile has been created. The 36 compounds studied include phenols, phenylmalononitriles, sulfonimides, sulfonic acids, and sulfonimides modified with Yagupolskii's superacceptor substituents. The scale spans about 13 pK_a units and consists of 74 independent equilibrium constant measurements, each describing the relative acidity of two acids. The method of measurements eliminates the need for the direct determination of the acidity of the medium. The most acidic compounds studied have pK_a values around 4 in acetonitrile and can be regarded as true superacids. The scale is anchored to the pK_a value 11.0 for picric acid. The status of 2,4,6-$(SO_2CF_3)_3C_6H_2OH$ as the most acidic phenol presently known ($pK_a = 4.9$) is confirmed. It is shown that the replacement of an =O fragment with =N–SO_2CF_3 in a –SO_2– group in aromatic sulfonimides results in an acidity increase of more than 10^5 times. The most acidic compound in the scale is 4-ClC_6H_4SO(= NSO_2CF_3)NH$SO_2C_6H_4$-4-NO_2 ($pK_a = 3.75$). The present results together with those from the other authors furnish a unified scale of acidity in acetonitrile ranging from 4 to 27 pK_a units and set solid ground for pK_a measurements of strong acids in acetonitrile.

Introduction

Strong acids and their derivatives are receiving increasing attention from both practical (reagents in organic synthesis,[1,2] catalysts in industry[3]) and theoretical[4,5] points of view. Therefore, substantial theoretical and experimental effort has been devoted to development of strongly acidic media and molecules with high intrinsic acidity.[1] Several families of interesting acids have been created: cyanocarbon acids,[6,7] Kuhn's acidic hydrocarbons,[8] acids with Yagupolskii's substituents,[9] superacidic metal hydrides,[10] etc.

Quantitative measurements of acidity are a vital part of studies involving superacids. Contrary to the success in creating superacids, significant experimental difficulties have been met here, and up to date, little consistent acidity data is available for strong acids. In some cases, the situation is almost ridiculous. For the pK_a of perchloric acid in aqueous solution, for example, the values found in the literature range from -1.6 to -14.[4] The uncertainty exceeds 12 orders of magnitude!

The acidity of an acid can be measured in different ways. Gas-phase measurements yield intrinsic acidities, free of any medium effects. A truly absolute scale of acidity in the gas phase has been established, ranging for almost 90 orders of magnitude.[4,11] With very strong acids, the gas-phase measurements have often failed, however, because the latter are usually not volatile enough and tend to undergo fragmentation in the course of the experiments.[4]

Significant effort has been devoted to acidity studies in aqueous solutions of strong acids (sulfuric acid, perchloric acid, etc.). These measurements are complicated,[12] however, because of the leveling of acidities.

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The number of acidity measurements of strong neutral Brønsted acids performed in nonaqueous solvents is smaller than that performed in aqueous medium.[6,13–17] This is true even for dimethyl sulfoxide (DMSO) solution, where due to efforts of Bordwell and others more than 2000 pK_a values for different classes of Brønsted acids have been determined.[16,17,18] DMSO is a rather basic leveling solvent and thus is not very suitable for studies of strong acids (however, see ref 15). Several acidity orders of strong acids have also been reported,[4,19] but quantitative acidity data for strong acids continue to be scarce. The main problems arising in most nonaqueous solvents are the various association processes between charged (and also neutral) species in these solvents (see below) and difficulties in reliable and reproducible determination of medium acidity in these media. Hence, the pK_as determined in different laboratories often differ more than the experimental errors stated.

In view of this situation, a pressing need exists for a self-consistent scale of acidity of strong acids in solution. We report here a spectrophotometric pK_a scale of strong acids in acetonitrile (AN).

AN has many properties that make it suitable for our work. It has low basicity and very low ability to solvate anions.[20] The low basicity gives AN an advantage over the other very popular solvent for acid–base studies—DMSO—which is considerably more basic (stronger acceptor of hydrogen bond). AN has a high dielectric constant ($D = 36.0$[20]) and hence favors the dissociation of ion pairs into free ions. The autoprotolysis constant of AN is very low; p$K_{auto} = 33$.[21,22] All these properties put together make it a good differentiating solvent for strong acids. Additional advantages of AN are its transparency down to 190 nm and relative ease of purification.

Starting from the classical works of Kolthoff and Coetzee, a considerable amount of acidity data for various compounds in acetonitrile has been accumulated. Analysis of the literature shows that a rather continuous and self-consistent acidity scale in the pK_a range of 14–27 exists in acetonitrile.[18,20,23–25] Measurements in the lower pK_a range have been made too,[6,13,14] but here, the things are far from satisfactory both in terms of the amount of data available and its self-consistency. The present work

was undertaken to improve the situation by building a unified self-consistent scale of acidity in AN in the range of 4–16 pK_a units, which would be a logical extension of the pK_a scale for the relatively weak acids into the domain of strong and very strong neutral Brønsted acids.

Acidity of an acid HA in solvent S refers to the equilibrium

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

and is expressed as the equilibrium constant K_a or its negative logarithm pK_a.

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

where the a values are the activities of the corresponding species. The acid–base equilibria in weakly solvating solvents such as acetonitrile are more complex than those in water. In addition to the equilibrium 1, there are other equilibria present in the system.[20] In AN, the poorly solvated anions eagerly form hydrogen-bonded complexes with hydrogen-bond donors present in the solution. When the donor is the conjugate acid of the anion, the homoconjugation process takes place.
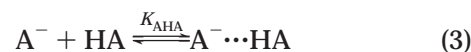
$$A^- + HA \xrightarrow{K_{AHA}} A^- \cdots HA \qquad (3)$$

K_{AHA} (the homoconjugation constant) is the constant of formation of the homoconjugate complex $A^- \cdots HA$.

$$K_{AHA} = \frac{a(A^- \cdots HA)}{a(A^-)\, a(HA)} \qquad (4)$$

If the donor is some other acid HX, then the heteroconjugation process is present.

$$A^- + HX \xrightarrow{K_{AHX}} A^- \cdots HX \qquad (5)$$
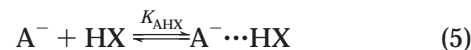
These side reactions have to be suppressed or taken into account if the accurate acidity data are to be obtained.

Because of the problems with measuring the acidity of the medium, $a(H^+)$, in nonaqueous solutions, we use a method that eliminates the need for its determination. Our method of acidity measurement gives relative acidities of the acids HA$_1$ and HA$_2$ according to the following equilibrium:

$$HA_2 + A_1^- \rightleftharpoons A_2^- + HA_1 \qquad (6)$$
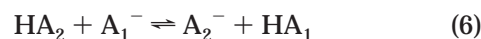
The pK of this equilibrium is the relative acidity (ΔpK_a) of the acids HA$_1$ and HA$_2$.

$$\Delta pK_a = pK_a(HA_2) - pK_a(HA_1) = \log \frac{a(A_1^-)a(HA_2)}{a(A_2^-)a(HA_1)} \qquad (7)$$

The method consists of UV–vis spectrophotometric titration of a solution, where both of the acids are present, with a transparent acid or base.

Experimental Section

Method of pK_a Determination. Relative acidities were measured using a UV–vis spectrophotometric titration technique that was similar to one applied previously to acidity

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measurements in heptane.[26] An acetonitrile solution containing two acids, HA_1 and HA_2 (or the salts of the acids in some cases, see below), was prepared. The acidity of the solution was varied by adding small amounts of acidic or basic titrant. A spectrum was recorded after each addition of titrant. This way, 10–30 spectra with different acidity of the solution were obtained, including those where both acids were in fully anionic or neutral form. Both of the acids were also titrated separately to obtain the spectra of the neutral and the ionized forms of both acids. To test the reversibility of the protonation/deprotonation process, after the addition of one titrant was finished, several portions of the other one were added. From each titration experiment, the ΔpK_a was determined as the mean of 5–20 values.

The calculation methods for ΔpK_a were essentially the same as those described previously.[26] Two additional features were included, however.

1. With some acids, it was necessary to take the homoconjugation process into account. Two cases have to be treated separately.

a. One of the acids (HA) forms the homoconjugation complex, and the other does not. In this case, the analytical concentration C of the acid HA can be expressed as follows:

$$C = [A^-] + [HA] + 2[A^-\cdots HA] \quad (8)$$

We assume that the molar absorption coefficient ϵ of the homoconjugation complex $HA\cdots A^-$ between acid HA and its anion A^- can be expressed as a sum.

$$\epsilon(A^-\cdots HA) = \epsilon(HA) + \epsilon(A^-) \quad (9)$$

From eqs 8 and 9, it follows that, for the homoconjugating acid, the indicator ratio I (see ref 26) as it is found from the spectrum of the mixture is not equal to the conventional $[A^-]/[HA]$, but

$$I = ([A^-] + [A^-\cdots HA])/([HA] + [A^-\cdots HA]) \quad (10)$$

Using eqs 4, 8, and 10 and assuming that the activities in eq 4 can be replaced with concentrations, the relative concentration of the complex $A^-\cdots HA$ can be found.

$$\frac{[A^-\cdots HA]}{C} = \frac{1 + (1/(CK_{AHA}))}{2} - \sqrt{\left(\frac{1 + (1/(CK_{AHA}))}{2}\right)^2 - \alpha(1 - \alpha)} \quad (11)$$

where $\alpha = 1/(1 + (1/I))$. Now $[A^-]/[HA]$ can be calculated.

$$\frac{[A^-]}{[HA]} = \frac{\alpha - ([A^-\cdots HA]/C)}{1 - \alpha - ([A^-\cdots HA]/C)} \quad (12)$$

With known $[A^-]/[HA]$, the calculation of ΔpK_a is straightforward (see ref 26).

b. Both of the acids form homoconjugation complexes. In this case, we assume that they also form heteroconjugation complexes. In this work, we take homoconjugation into account only when dealing with sulfonic acids (see results section). We assume that for all the sulfonic acids the homoconjugation constants are equal and that all the heteroconjugation constants are equal to the homoconjugation constants. In this case, it can be shown that the four species, HA_1, HA_2, A_1^-, and A_2^-, are consumed proportionally to their concentrations for the formation of the homo- and heteroconjugation complexes, and the relative decrease of their concentrations will cancel out so that the formation of the complexes can be ignored when calculating ΔpK_a.

2. Two acids in the present work are cationic acids. When calculating the relative acidity of a neutral and a cationic acid

according to the eq 13, then the assumption that the ratios of

$$HA + B \rightleftharpoons A^- + BH^+ \quad (13)$$

the activity coefficients are equal (see ref 26) is not valid anymore and the ΔpK_a value is:

$$\Delta pK_a = \log\frac{[B][HA]}{[A^-][BH^+]} - 2\log f \quad (14)$$

where the activity coefficients $f = f(A^-) = f(BH^+)$ and $f(B) = f(HA) = 1$ (these approximations are valid, since very dilute solutions are used). The value of $\log f$ was calculated using the Debye–Hückel equation that follows:[20]

$$\log f = -\frac{1.64Z^2\sqrt{J}}{1 + 0.48a\sqrt{J}} \quad (15)$$

where J is the ionic strength of the solution, Z is the charge of the ion, and a is the size parameter of the ion that was taken to be 6 Å. The $\log f$ is not very sensitive to this parameter.

Chemicals. The following compounds were synthesized according to a procedure from the literature:[27] **9** (mp 173–174. ^{13}C NMR 145.73, 138.71, 130.50, 128.42, 21.53.), **11** (mp 158–159. ^{13}C NMR 142.02, 134.30, 129.97, 128.27.), **12** (mp 162.5–163.3. Anal. Calcd for $C_{13}H_{12}ClNO_4S_2$: C, 45.15; H, 3.50; N, 4.05. Found: C, 45.41; H, 3.53; N, 4.43. ^{13}C NMR: 145.79, 140.55, 140.44, 138.64, 130.52, 130.14, 130.02, 128.40, 21.53.), **14** (mp 208.8–210.4. ^{13}C NMR: 141.48, 140.17, 130.03, 129.95.), **16** (mp 202.4–203.8. Anal. Calcd for $C_{13}H_{12}N_2O_6S_2$: C, 43.81; H, 3.39; N, 7.86. Found: C, 43.58; H, 3.47; N, 8.01. ^{13}C NMR 151.33, 148.33, 142.31, 140.61, 128.43, 127.72, 126.22, 123.28, 20.71.), **17** (mp 151.3–151.8. Anal. Calcd for $C_{13}H_{11}ClN_2O_6S_2$: C, 39.95; H, 2.84; N, 7.17. Found: C, 40.01; H, 2.77; N, 7.47. ^{13}C NMR 148.65, 145.16, 143.20, 139.41, 133.65, 132.60, 131.39, 130.33, 128.24, 125.32, 21.49.) **18**[28] (mp 222.7–223.4. ^{13}C NMR 151.09, 149.73, 142.59, 139.54, 129.81, 129.53, 124.77.), **20**[29] (mp 239–242 dec. ^{13}C NMR 150.96, 150.68, 129.41, 124.70.). The starting materials were sulfonyl chlorides from Aldrich. The compounds were purified by recrystallization from mixtures of ethyl alcohol and concentrated hydrochloric acid.

The sulfonic acids **19**, **23**–**25** were synthesized[30] from the corresponding sulfonyl chlorides (from Aldrich). The sulfonic acid **21** was obtained from REAKHIM. Sulfonic acids are inconvenient to handle and were used as salts. The acid **19** was converted to tetramethylammonium salt according to ref 31. **19a** (mp 255.0–255.9 dec. Anal. Calcd for $C_{11}H_{19}NO_3S$: C, 53.85; H, 7.81; N, 5.71. Found: C, 54.18; H, 7.64; N, 5.57. ^{13}C NMR 144.03, 141.63, 129.85, 126.93, 56.20, 21.30.). The salt was purified by recrystallization from aqueous acetone. The acids, **21** and **23**–**25**, were converted into the corresponding triethylammonium salts according to ref 31. **21a** (mp 149.6–150.3. Anal. Calcd for $C_{16}H_{23}NO_3S$: C, 62.11; H, 7.49; N, 4.53. Found: C, 62.08; H, 7.72; N, 4.41. ^{13}C NMR 142.27, 135.52, 132.27, 130.30, 129.27, 127.74, 127.53, 127.11, 126.52, 125.32, 47.96, 9.12.), **23a** (mp 93.0–95.3. Anal. Calcd for $C_{12}H_{20}ClNO_3S$: C, 49.06; H, 6.86; N, 4.77. Found: C, 49.46; H, 6.93; N, 4.71. ^{13}C NMR: 145.45, 137.07, 129.41, 128.65, 48.2 (obscured by solvent), 9.25.), **24a** (mp 78.2–78.9. Anal. Calcd for $C_{12}H_{20}N_2O_5S$: C, 47.36; H, 6.62; N, 9.20. Found: C, 47.61; H, 6.89; N, 9.03. ^{13}C NMR 149.37, 148.70, 132.99, 131.01, 125.66, 121.89, 48.2 (obscured by solvent), 9.32.), and **25a** (mp 120.9–122.5. Anal. Calcd for $C_{12}H_{20}N_2O_5S$: C, 47.36; H, 6.62; N, 9.20. Found: C, 47.10; H, 6.90; N, 9.46. ^{13}C NMR

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152.65, 150.07, 128.33, 124.59, 48.2 (obscured by solvent), 9.30.). The salts were purified by recrystallization from acetone.

The following compounds were of commercial origin. Some of them were purified prior to use: **1** (REAKHIM, sublimed in vacuo, mp 113.2−113.7), **4** (Aldrich, 99+%), **13** (REAKHIM, recrystallized from EtOH, mp 121.2−122.7), TfOH (Aldrich, 99+%), tetramethylammonium hydroxide (Aldrich, 25% solution in MeOH), Et_3N (REAKHIM, distilled under atmospheric pressure, stored under argon in refrigerator, small amounts for measurements distilled second time as needed), $HClO_4$ (REAKHIM, "special purity"), acetic acid (REAKHIM, "chemically pure").

The synthesis and purification of the following compounds has been described previously: **2**,[32] **3**,[33] **5**,[34] **6**,[35] **7**,[35] **8**,[36] **10**,[33] **15**,[35] **22**,[37] **26−28**,[9] **29**,[39] **30**,[9] **31**,[38] **32**,[9] **33**,[9] **34**,[39] **36**.[9] A sample of **35**[6] was donated by the late Prof. R. W. Taft.

^{13}C NMR. The spectra were run on a Bruker AC-200 instrument. The solvent was CD_3OD, except for **16**. DMSO-d_6 was used with this compound. Tetramethylsilane was used as the internal standard.

Solvent. Acetonitrile suitable for our work must be dry and must not contain impurities that absorb UV radiation. Impurities with a UV spectrum that changes with changing acidity of the medium are especially dangerous. Merck "Lichrosolv" AN was used. It was distilled from P_2O_5 through a 1.2 m long 2 cm id column packed with PTFE chips prior to use to reduce its water content and to further purify it. Alternatively, REAKHIM "pure" AN was distilled through the same column from $KMnO_4$ and then from P_2O_5. Preference was given to the acetonitrile from Merck. The solvent was stored in dark bottles in a desiccator over P_2O_5.

Experimental Setup. The setup was very similar to that described previously.[26] Only the significant differences are given here.

A solution of TfOH in AN was used as the acidic titrant in most cases. In a few experiments, a solution of $HClO_4$ was used. This solution was prepared from a 25% solution of $HClO_4$ in acetic acid. A solution of triethylamine in acetonitrile was used as the basic titrant. The standard syringe techniques could not be used due to the strongly acidic media involved. Instead, the vials, solvent bottle, and spectrophotometer cell (all capped with rubber septa) were interconnected with thin PTFE tubing, through which the solutions were siphoned by means of aspiration with a syringe.

The concentrations of the acids were in the following ranges: **2**, **3**, **5−8**, **15**, **16**, **18**, **20**, **24**, **25**, **29**, **31**, **32**, **34−36**, $(1-7) \times 10^{-5}$ M; **1**, **10**, **13**, $(1-3) \times 10^{-5}$ M; **4**, **9**, **11**, **12**, **14**, **17**, **22**, **26−28**, **30**, **33**, 8×10^{-5} to 5×10^{-4} M; **19**, **23**, $(1-1.5) \times 10^{-3}$ M. The concentrations of the titrants were chosen for each titration experiment according to the concentrations of the acids and ranged from 5×10^{-3} to 5×10^{-2} M. All solutions were made fresh daily.

The water content of the solution in the cell was determined after the measurement using Karl Fisher titration. This approach ensures that the amount of water in the solution during titration is less than or equal to that determined. The water content of the solution was mostly between 1 and 2 mM and never higher than 3.5 mM.

Spectrophotometry. A Perkin-Elmer Lambda 2S UV−vis spectrophotometer equipped with cell holders thermostated

Table 1. pK_a Values of the Acids Derived from the Results of the ΔpK_a Measurements

No.	Acid	Directly measured ΔpK_a	pK_a
1	2,4-dinitrophenol	0.54	16.66
2	$(4-CF_3C_6F_4)_2CHCN$	1.92	16.14
3	$3-CF_3C_6H_4CH(CN)_2$	1.43	14.72
4	Saccharin	0.15 / 0.84	14.58
5	$4-CH_3C_6F_4CH(CN)_2$	0.71	13.88
6	$C_6F_5CH(CN)_2$	0.87 / 0.89	13.01
7	$4-HC_6F_4CH(CN)_2$	0.03 / 0.04 / 0.79	12.98
8	$2-C_{10}F_7CH(CN)_2$	0.74	12.23
9	Tos_2NH	1.38 / 0.26	11.97
10	$4-NO_2C_6H_4CH(CN)_2$	0.62	11.61
11	$(C_6H_5SO_2)_2NH$	0.28 / 1.21 / 0.98	11.34
12	$4-ClC_6H_4SO_2NHTos$	0.60^a / 0.60	11.10
13	Picric acid	0.36 / 1.43 / 0.10	11.00
14	$(4-ClC_6H_4SO_2)_2NH$	0.79 / 0.91 / 0.82	10.20
15	$4-CF_3C_6F_4CH(CN)_2$	−0.01 / 0.13	10.19
16	$4-NO_2C_6H_4SO_2NHTos$	0.14 / 1.06 / 0.52	10.06
17	$4-Cl-3-NO_2C_6H_3SO_2NHTos$	1.05	9.69
18	$4-NO_2C_6H_4SO_2NHSO_2C_6H_4-4-Cl$	0.53	9.15
19	TosOH	0.56 / 2.3 / 1.73	8.6
20	$(4-NO_2C_6H_4SO_2)_2NH$	1.21 / 0.23 / 1.3 / 0.25	8.31
21	$1-C_{10}H_7SO_3H$	0.50	8.00
22	$C_6H_5CHTf_2$	0.19 / 1.04	7.83
23	$4-ClC_6H_4SO_3H$	0.54 / 1.25	7.3
24	$3-NO_2C_6H_4SO_3H$	0.53 / 0.51	6.76
25	$4-NO_2C_6H_4SO_3H$	0.51 / 1.28	6.71
26	TosNHTf	0.44 / 0.75 / 0.62	6.29
27	$C_6H_5SO_2NHTf$	0.36 / 0.83	6.01
28	$4-ClC_6H_4SO_2NHTf$	0.98 / 0.70	5.46
29	$2-NO_2C_6H_4NH_3^+$	0.77	5.30
30	$4-ClC_6H_4SO(=NTf)NHTos$	0.53^a / 0.35^a	5.27
31	$2,4,6-Tf_3C_6H_2OH$	0.38 / 0.82 / 0.75	4.93
32	$4-NO_2C_6H_4SO_2NHTf$	0.41^a / 0.94 / 1.17^a	4.53
33	$4-ClC_6H_4SO(=NTf)NHSO_2C_6H_4-4-Cl$	0.05 / 1.1 / 0.87	4.48
34	$4-Cl-2-NO_2C_6H_3NH_3^+$	1.10^a / 1.15 / 0.31	4.36
35	2,3,5-tricyanocyclopentadiene	0.74 / 0.20^a	4.16
36	$4-ClC_6H_4SO(=NTf)NHSO_2C_6H_4-4-NO_2$	0.50	3.75

^{a} Perchloric acid was used as the acidic titrant. Tos denotes $4-CH_3C_6H_4SO_2-$; Tf denotes CF_3SO_2-.

to 25 °C was used for all 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 AN.

Results

The results of the measurements are presented in Table 1. Each arrow represents the ΔpK_a from one titration experiment. 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 acidity range covered involves at least 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.

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Table 2. Comparison of the pK_a Values Determined in This Work with Those Reported in the Literature (Values of Obviously Low Quality Have Been Omitted)

acid	pK_a in AN		
	this work	lit.	difference
2,4-dinitrophenol	16.66	16.0[a]	+0.7
		18.4[b]	−1.7
picric acid		11.0[c]	
TosOH	8.6	8.01[d]	+0.6
		8.73[b]	−0.1
2-NO$_2$C$_6$H$_4$NH$_3$$^+$	5.30	4.95[e]	+0.35
4-Cl-2-NO$_2$C$_6$H$_3$NH$_3$$^+$	4.36	4.2[e]	+0.16
2,3,5-tricyanocyclopentadiene	4.16	3.00[f]	+1.16

[a] Reference 40. [b] Reference 41. [c] Reference 42. [d] Reference 13. [e] Reference 43. [f] Reference 6.

To assign absolute pK_a values to the acids of Table 1, the scale has to be anchored to a reference compound with pK_a reliably established. This compound should be a "well-behaved" compound; that is, it should not undergo homo- or heteroconjugation reactions to a marked extent and it should have favorable UV−vis spectral characteristics. For several of the acids belonging to the scale, a pK_a value in AN has been reported in the literature. These acids are presented in Table 2. Analysis of the data in Table 2 shows that picric acid is the compound of choice as it is a well-behaved compound, and its pK_a in acetonitrile has been determined with great care by Kolthoff et al.[42] using three different experimental methods and has been found to be 11.0 ± 0.1. Using **13** as the anchoring point has only the disadvantage that it stands far away from the stronger members of the scale. A reliable absolute pK_a value for a "well-behaved" strong acid would be very desirable. The other acids from Table 2 are not as suitable as references. **29** and **34** are cationic acids (see below), **19** is not a "well-behaved" compound, and **1** and **35** stand in far ends of the scale and the quality of their pK_a values is not as high as that of **13** (see refs 40 and 6). The agreement between the values from this work and those from the literature can be considered satisfactory. The most deviating result is that of **35**. As the experimental part of the original reference[6] does not describe the pK_a measurements, it is not possible to discuss this deviation thoroughly. Partially, it could be due to the "distance" between **35** and **13**.

The pK_a values for individual acids were found by minimizing the sum of squares of differences between directly measured ΔpK_a values and the assigned pK_a values.

$$u = \sum_{i=1}^{n_m} (\Delta pK_a^i - (pK_a(HA_2) - pK_a(HA_1)))^2 \quad (16)$$

The sum is taken over all the measurements whereby ΔpK_a^i is the result of a relative acidity measurement of acids HA$_1$ and HA$_2$ (HA$_2$ is the acid whose pK_a is higher). pK_a(HA$_1$) and pK_a(HA$_2$) are the absolute pK_a values for the two acids as found by the least-squares procedure. The precision and the consistency of the results can be assessed using a standard deviation as defined by eq 17,

$$s = \sqrt{\frac{u}{n_m - n_c}} \quad (17)$$

where n_m = 74 is the number of measurements and n_c = 36 − 1 = 35 is the number of pK_as determined. For our results, s = 0.04 pK_a units. This is a low enough value for the scale to be considered self-consistent. This value was also taken as the basis for giving the absolute pK_a values with two decimal digits in Table 1. This approach to estimate the precision of the results has a drawback however; the precision of the measurements is different for different classes of compounds, being dependent on the spectral properties of the compounds, namely the difference between the spectrum of the anion and the neutral and the wavelength(s) at which the measurements were carried out. The precision is highest for the phenylmalononitriles and phenols and lowest for acids **19** and **23**. The pK_a values for the latter two acids are given with lower precision in Table 1.

It is important to note that this estimate of precision must be interpreted as the precision of single measurements and not the precision of the absolute pK_a values. The reference compound **13** has an acidity that is about 7 pK_a units away from those for the strongest acids of the scale, and for obtaining their acidity, a large number (about 10) of ΔpK_a values has to be added, which significantly decreases the precision of the pK_a values for the compounds that stand far away from the reference compound. Still another point is the accuracy of the pK_a values, which is also significantly lower.

The spectra of the compounds (with the exception of the sulfonic acids **19** and **23**) in solutions of different acidity did not show any irregular behavior. The spectra of partially ionized acids could always be expressed as linear combinations of the spectra of the neutral and the anion. With most of the compounds, the spectra contained isosbestic points, and these were always sharp. These observations rule out the possibility that conjugation reactions take place to an appreciable extent under our experimental conditions as the homo- and heteroconjugation reactions are known to cause distortions in spectra.[44] The protonation−deprotonation process was reversible with all acids.

The spectra of **19** and **23** were slightly distorted, and the spectra of partially ionized acids could not be expressed as linear combinations of spectra of the anion and the neutral. The concentrations of **19** and **23** were sufficiently high to permit the homoconjugation reaction to occur. The homoconjugation constant K_{AHA} for **19** is 800 L/mol.[18] The same value was used for **23**, as the values of K_{AHA} do not differ very much within classes of acids as the acidities are not too different and steric factors are not involved. The resulting corrections to the ΔpK_a values were in the range of 0.05−0.2 pK_a units. The assumption in eq 9 is reasonable with **19** and **23** because the acidity center OH is not directly conjugated with the aromatic ring and no significant intramolecular charge transfer is involved in the anions on excitation. However, this assumption would probably not be valid for compounds with the acidity center conjugated

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directly to the aromatic ring (phenols, anilines) because the wavelengths and intensities of the spectral bands with intramolecular charge-transfer character of the deprotonated species are very sensitive to hydrogen bonding.[44,45]

Some of the measurements were made using $HClO_4$ instead of TfOH. Because of the procedure of preparing of solutions of $HClO_4$, substantial amounts of acetic acid (AcOH), a potential hydrogen bond donor, were introduced with this titrant. Two of the measurements were performed with both titrants, and the agreement is good (see Table 1). The rest of the measurements agree well with the overlapping measurements made with TfOH. Thus, we have reason to believe that AcOH does not interfere seriously. This is not unexpected because AcOH (pK_a in AN 22.3[18]) is a very weak acid compared to those studied in this work and the hydrogen bond donating ability of an acid in the conjugation reactions is directly related to its acidity.[46] Also, the basicity of AcOH (pK_a in AN 1.1[18]) as well as its concentration is too low to enable significant stabilization of the neutral acids by hydrogen bonding.

We have included two cationic acids (**29** and **34**) in the scale. The log f values were in the range of 0.02−0.05. However, as there is no general procedure for calculating activity coefficients for ions in nonaqueous media, these cationic acids cannot be rigorously regarded as belonging in the scale.

The pK_a values determined in this work together with those from other authors[18,20,23−25] set up a continuous acidity scale in AN ranging from pK_a 4 to 27.

Discussion

Method. The presence of the acids in the same solution eliminates many possible sources of error or reduces their influence. (1) The disturbing effects (traces of water in the medium, concentration errors) affect both acids with the same magnitude and are expected to partially cancel out. Thus, we expect that the effect of traces of water on the measurements will be less pronounced than in such measurements where the pK_a of a single acid is measured at a time. (2) The solutions can be very dilute and consequently very weakly buffered with this method. If a minor acidity change of the solution occurs, it will affect both of the acids and its effect will cancel out. (3) An important point is that the method eliminates the need for quantitative measurement of acidity of the medium.

A disadvantage of the method is that only the acidity of such acids that absorb in the UV−vis spectral region and for which the spectra of the acid and the anion are different can be measured. Also, the pK_as of the acids must not be very different from each other (preferably not more than 1.5−2 pK_a units).

Sulfonimides and Sulfonic Acids. pK_a values for aromatic sulfonimides are almost lacking from the literature. One reason is that sulfonimides are strong acids and their acidity cannot be measured in nondifferentiating solvents. On the other hand, aromatic sulfonimides totally lack volatility, and therefore no gas-phase data

are available. To the best of our knowledge, there has been only one work[47] where pK_a data of some aromatic sulfonimides in water have been reported.

When the Hammett equation was applied to the aromatic sulfonimides **9**, **11**, **12**, **14**, **16**, **18**, and **20**, the following relationship was found:

$$pK_a = (11.25 \pm 0.05) - (1.97 \pm 0.07)(\sigma_1 + \sigma_2) \quad (18)$$

where $r^2 = 0.993$, $s = 0.11$, and σ_1 and σ_2 are the Hammett constants of the corresponding substituents (taken from ref 48).

The aromatic sulfonic acids **19**, **23−25** show a similar sensitivity toward substitution,

$$pK_a = (8.0 \pm 0.2) - (1.9 \pm 0.4)\sigma \quad (19)$$

where $r^2 = 0.92$ and $s = 0.3$, although the correlation is poorer. It is of interest to compare these data with those obtained for substituted benzoic acids. Applying the Hammett equation to a set of substituted benzoic acids (4-H, 4-Br, 4-NO_2, 4-COOH, pK_a values from ref 18) gives:

$$pK_a = (20.8 \pm 0.1) - (2.6 \pm 0.2)\sigma \quad (20)$$

where $r^2 = 0.987$ and $s = 0.12$. It can be seen that the acidity of benzoic acids is about 1.3 times more sensitive toward substitution in the aromatic ring than that of the acids with acidity center SO_2XH. The probable cause is that the $-SO_2-$ fragment in the anion is bigger, more polarizable, and more electronegative than the corresponding $-CO-$ fragment in carboxylates and can therefore "hold" more charge and has less of a tendency to delocalize it into the aromatic ring.

Yagupolskii's Substituents. Compounds **30**, **33**, and **36** can be considered to be derivatives of **12**, **14**, and **18**, respectively, where an $=O$ fragment of a sulfonyl group adjacent to the NH acidity center is replaced by $=N-Tf$. The acidifying effects of the substitution are 5.8, 5.7, and 5.4 pK_a units for **12**, **14**, and **18**, respectively. The following values of pK_a have been found for $C_6H_5SO_2NH_2$, $CH_3C_6H_4SO(=N-Tf)NH_2$, and $CH_3C_6H_4S(=N-Tf)_2NH_2$ in DMSO: 16.0,[49] 8.0,[50] and 3.4.[50] It can be seen that the acidity increase is not additive; the first substitution increases the acidity by 8 pK_a units, while the second substitution increases it by 4.6 pK_a units (the small effect of the 4-methyl group can be neglected here). It has not yet been possible to measure the acidities of these compounds or the sulfonimides in the gas phase,[4] but there is a value of gas-phase acidity available for a "superacidic" aniline 4-($CF_3SO(=N-Tf)$)−$C_6H_4NH_2$, $\Delta G_{acid} = 313.4$ kcal/mol.[4] This compound is 13 orders of magnitude (!) more acidic in the gas phase than the corresponding unmodified aniline 4-Tf−$C_6H_4NH_2$ ($\Delta G_{acid} = 331.3$ kcal/mol[11]).

The sulfonimides **26**, **28**, and **32** can be considered to be derivatives of sulfonic acids in which an $=O$ fragment of the sulfonyl group is replaced with $=N-Tf$. These compounds can exist in two tautomeric forms:

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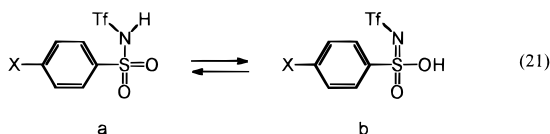
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Evidence (NMR) has been presented by one of us that **a** is the dominating form[9] in acetone and chloroform. The differences in acidities between **26**, **28**, and **32** and the corresponding sulfonic acids **19**, **23**, and **25** are 2.3, 1.8, and 2.2 pK_a units, respectively. These results can be regarded as evidence in favor of the structure **a** in AN, as otherwise the differences should be similar to the ones obtained for sulfonimides.

Phenols. A pK_a value of −1.0 for **31** has been reported in aqueous H_2SO_4.[51] This is about 1.3 pK_a units lower than the pK_a of picric acid.[51] In AN, according to Table 1, **31** is about 6 pK_a units more acidic than picric acid. This qualitatively higher difference leads to a conclusion that some solvent effect is in operation here. 2-nitro-phenols are known to give intramolecular hydrogen bonding[40] in AN. In water, on the other hand, this hydrogen bonding is absent due to the competition from water.[40] This intramolecular hydrogen bond causes considerable extrastabilization of the neutral in AN compared to water. There are no data in the literature on the hydrogen bond acceptor properties of the trifluo-romethanesulfonyl group, but it is likely that these are weak in comparison with those of the nitro group because the hydrogen bond basicity of sulfones is generally very low. Another factor might be that the picrate anion, due to its nitro groups, is likely to be more solvated in water than the deprotonated **31**.

Phenylmalononitriles. An interesting result with this class of compounds is that the pK_as of **6** and **7** in AN are practically equal, or that of **7** is even slightly lower. The same behavior of these two compounds has been

observed by one of us also in dimethoxyethane.[35] This is not completely unexpected. A similar effect is seen when comparing phenol to 4-fluorophenol; the latter is more acidic in water than the former by only 0.2 pK_a units.[17] The reason for this might be that although fluorine is an electronegative substituent, it is also a weak resonance donor.[48] The F is in the 4 position to the acidity center, which means that the inductive/field effect (but not the resonance effect) is weakened by the distance. The final factor is the strong electron deficiency of the ring that still weakens the inductive/field effect by saturation. These arguments have to be treated with caution however because the same is not observed in the gas phase, where **6** is more acidic by about 2 kcal/mol.

The correlation between the pK_as in AN and the gas-phase acidities[4] is poor,

$$pK_a = (-108 \pm 36) + (0.40 \pm 0.12)\Delta G_{acid} \quad (22)$$

where $r^2 = 0.69$ and $s = 0.91$. This is surprising because of all the compounds' classes in this scale, the phenyl-malononitriles should be relatively weakly influenced by solvation, and they are very suitable for measurements both in AN and in the gas phase.

Conclusion

The present results together with those from the other authors furnish a unified acidity scale in AN ranging from pK_a 4 to 27 and help to establish a solid basis for the reliable pK_a determinations of strong acids in AN. We have demonstrated that the acidities of strong acids are readily measurable and that AN is a suitable medium for this work.

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