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Evaluation of Acidity of Strong Acid Catalysts

I. Derivation of an Acidity Function from Carbon-13 NMR Measurements

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The limitations of the Hammett indicator method for acidity measurements of liquid acid catalysts of practical importance and the inapplicability in principle of the Hammett acidity concept to solid acid catalysts are discussed. Evaluation of acidities from the hydronation equilibrium of two simple alcohols, methanol and ethanol, and an α,β-unsaturated ketone, 4-methyl-3-penten-2-one (mesityl oxide, **I**), by carbon-13 NMR is demonstrated for sulfuric acid–water mixtures. The latter compound is particularly useful because the signal for its carbon atom C-4 shifts downfield upon hydronation by almost 50 ppm, whereas the signal for C-3 moves upfield by 3 ppm. The comparison of the chemical shift difference δ(C-4)–δ(C-3) ($\Delta\delta$) for two different solutions allows a comparison of acidities of the two solutions from which other medium effects upon chemical shifts have been cancelled out. The variation of $\Delta\delta$ with concentration of **I**, or the ratio of base (**I**) to acid, is linear, at least between 1 and 0.05 M of **I**. Extrapolation of $\Delta\delta$ of **I** to [B]/[AH] = 0 ($\Delta\delta^0$) allows the use of ^{13}C NMR spectroscopy to establish a thermodynamically meaningful acidity scale, such as the traditional acidity function H_0. The slope of $\Delta\delta$ vs [B]/[AH] plot changes with acid strength; it is lowest (most negative) for the acidity at which **I** is half-protonated. The acidity required for half-protonation can thus be accurately determined from this slope. On the other hand, $\Delta\delta$ can be also measured at the stoichiometric ratio of the indicator base to acid molecules or sites. The latter approach must be used for comparison of strength of solid acids. © 1992 Academic Press, Inc.

INTRODUCTION

The problem of determining the strength of acids beyond the end of the pH scale was first addressed by Hammett and Deyrup (*1a*). Their H_0 acidity function, based on the determination of a protonation equilibrium (Eq. (1)) by electronic spectroscopy, was later extended to very high acidities by Gillespie *et al.* (*2*) and was also applied to evaluation of acidity of solid surfaces (*3*).

$$AH + B \rightleftarrows A^- + BH^+. \qquad (1)$$

Earlier we were interested in the measurement of Brønsted acidity of some superacid catalysts (*4*). As already pointed out (*5*), we realized quickly that the Hammett indicator method (*1*) cannot be applied to such media. A further elaboration on the reasons for this inapplicability pertaining to systems of actual or potential importance as catalysts is appropriate here:

1. Some Brønsted acid–Lewis acid composites that act as superacid catalysts cannot be generated in the absence of the substrate. For instance, a solution of TaF_5 in HF is saturated at the 1 : 108.6 molar ratio at 19.6°C (*6*), but the mixtures used as catalysts for hydrocarbon conversions in liquid phase were in the 1 : 30 to 1 : 15 molar ratio range (*4b, 7*), because the carbocations generated from the substrate helped to solubilize the Lewis acid. Likewise, it was established (*8*) that catalysts based on aluminum bromide are mixtures with a cocatalyst, usually HBr, which interacts with the Lewis

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acid to form a liquid phase. This active phase of a working catalyst had an HBr to $AlBr_3$ molar ratio of 1 : 1.14 (*9*) even though $AlBr_3$ is virtually insoluble in HBr (*10*) and the catalytic process was run at a temperature much above the boiling point of HBr (*9*). Formation of the liquid phase occurred because about an equivalent of carbocations were present, probably as heptabromodialuminates (*4a*).

2. One could, in principle, generate the actual catalyst systems and then determine their Hammett acidity, except that these measurements are based on UV-visible spectroscopy and most real-life catalysts are dark and often opaque; in our experience we have yet to see a working catalyst that is not colored.

3. The Hammett acidity measurement for a solid is normally based on observation of surface color changes upon contact with solutions of indicator (*3*), but in most cases it cannot be ascertained whether the color change results from hydron transfer. Thus, some sulfated metal oxides change color when covered with solvents like benzene, toluene, or chloroform even without an indicator being added (*11*). Recording spectra of indicators on solids (*12*) is an interesting idea, but the approach still does not give quantifiable results as to absorption coefficients.

4. Most important, Hammett acidity measurements are *in principle* inapplicable to solids. In Hammett's approach, acidity is defined for the acid as a continuum, which hydronates the probe base without being significantly disturbed or altered by the latter. The anion from the acid molecule that transfers the hydron interacts strongly with other molecules of acid (cooperative effect[3] (*15*)); acidity is thus determined by anion stabilization, provided by excess acid or, in some cases, by the solvent (*15*, *16*) mainly through hydrogen bonding (*15*).

In contrast, on a solid surface each acid site interacts individually with the base, and other acid sites cannot give any assistance to the ionization (anion stabilization) because of the rigidity of the structure. The process occurring in a hydron transfer to a base is, therefore, an interaction of one AH with one B, even if the solid acid is taken in "excess" over the base. To obtain a meaningful measure of solid acidity one must devise a method that determines the position of the equilibrium in Eq. (1) for a stoichiometric ratio of base to acid sites. The reversibility of the acid–base reaction makes such a measurement feasible. Obviously, at any given moment a molecule of base can be either in neutral form, B, or in ionized form, BH^+; for a large ensemble of acid molecules or sites the $[BH^+]/[B]$ ratio will reflect at any moment the equilibrium constant of Eq. (1), even when there is no exchange of base molecules between acid sites. UV-visible spectroscopy is not useful at the concentrations of indicator needed for reaction with the acid sites in stoichiometric ratio, but NMR spectroscopy is perfectly suited to measure the concentration ratio of BH^+ to B for the large ensemble of AH and B pairs, by integration when the hydron transfer is slow and by chemical shift interpolation when the hydron transfer is fast.

By measuring the extent of conversion of some aromatic hydrocarbons to the corresponding arenium ions (Pfeiffer–Wizinger complexes (*17*)[4]) by ^{13}C NMR spectroscopy, we have related the hydronating ability of strong superacids like $HBr–AlBr_3$ and $HF–TaF_5$ to that of trifluoromethanesulfonic acid, previously established (*18*) to be 100 times stronger than 100% sulfuric acid (*4*, *5*). We report here the results of a study of calibration by ^{13}C NMR of acidities in the range of strength of 20–100% sulfuric acid. The accompanying paper reports on the application of our method to a liquid catalyst of practical importance, the boron trifluo-

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[3] The term cooperative effect is preferred over the previously used "homoconjugation" (*13*) because the older term has acquired a different meaning (*14*).

[4] Arenium ions are often improperly referred to as Wheland intermediates (*4b*).

ride–water system. Further applications of the approach to strong acid catalysts in solution or solid state will be reported.

EXPERIMENTAL

Materials

Commercial A.R. grade reagents were used throughout. Mesityl oxide was dried on molecular sieves. Sulfuric acid of various concentrations was prepared by mixing 95% acid with 18% oleum or with water, in appropriate proportions; each mixture was analyzed by titration with sodium hydroxide solution (a minimum of four titrations for each acid solution). About 1% trifluoroacetic anhydride was added to trifluoroacetic acid to remove adventitious water.

NMR Spectra

(*a*) *General.* Carbon spectra of the strong acid solutions were run at 75.468 MHz on a Bruker MSL 300 instrument at 25°C. A sweep width of 20 kHz, a pulse width of 5 μs, a receiver blanking delay of 20 μs, and a recycle delay of 10 s were employed. Some early measurements were run at 22.65 MHz, on a JEOL FX-90Q instrument, as indicated in Table 1.

(*b*) *Hydronation of ethanol.* The acid (1 ml) was weighed in a vial with polytetrafluoroethylene-lined screw-cap and cooled to 0°C. The quantity of alcohol required to give a 20% molar concentration in the mixture with acid and water was added. After the esterification equilibrium was reached (*19*) the solution was poured into an 8-mm-o.d./5.5-mm-i.d. tube, which was then placed inside a thin-walled 10-mm NMR tube containing deuterochloroform (*4a*).

(*c*) *Hydronation of I.* The mesityl oxide (**I**) solutions were prepared directly in the 8-mm tube. The acid (1.5 ml) was added from a Gilmont microburet, its weight was determined, and the tube was capped and sealed with paraffin film and then cooled inside a freezer at −15°C for 15 min, to minimize the extent of decomposition or other reaction upon addition of the indicator (*20*). The calculated volume of **I** was added quickly from a 100-μl syringe, the tube was capped, shaken well for mixing, analyzed by NMR, and reweighed. Chemical shifts were measured from the center line of the $CDCl_3$ in the outer tube, taken as 77.000 ppm, except for the solutions in nonacidic solvents, which were prepared directly in the 10-mm tube and referenced to internal TMS (δ 0.000). Decomposition (*20a*) and hydration (*20b*) of **I** were observed in the strongest and weakest sulfuric acid solutions, respectively. At variance with literature interpretations (*21*), these reactions should in principle alter the acidity of the medium, unless the reaction products have the same basicity as **I.** To check the effect of decomposition we measured the chemical shifts at various intervals after preparation of the sample. No variation was observed for moderate levels of decomposition, but chemical shifts could not be measured accurately at 0.05 *M* concentration of **I,** which requires a long accumulation time, for the solutions showing decomposition.

RESULTS AND DISCUSSION

Two types of indicator bases were investigated in this work: the simple alcohols exemplified by methanol (MeOH) and ethanol (EtOH), and the unsaturated ketone 4-methyl-3-penten-2-one (mesityl oxide).

Hydronation of primary alcohols (Eq. (2)) was an early subject of study in superacid chemistry (*22*). The signal for the carbon bearing the OH group (C-1) shifts downfield upon hydronation by 7 to 10 ppm, which makes possible the use of chemical shift interpolation (*23*) for measuring the ratio $[ROH_2^+]/[ROH]$.

$$R\text{–}CH_2OH + AH \rightleftarrows R\text{–}CH_2OH_2^+ + A^- \qquad (2)$$

$$\text{(a) } R = \text{H}, \quad \text{(b) } R = \text{Me}.$$

Correlation of chemical shifts with acidity is hampered by the dependence of the former upon factors other than the presence or absence of positive charge. Thus, hydrogen

TABLE 1

Correlation of ^{13}C Chemical Shifts[a] of Mesityl Oxide (**I**) with the Acidity of Solvent

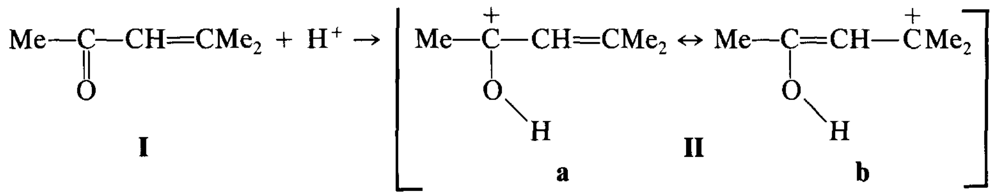
Solvent	H_0	Conc. **I**[b] (mol/liter)	[B]/[AH][c] × 10^3	Chemical shift			
				C-2	C-3	C-4	(C-4)–(C-3)
DMSO-d_6[d,e]	—	0.79	—	198.41	124.90	154.46	30.71
$CDCl_3$[d,e]	—	0.79	—	198.50	124.20	154.90	30.70
MeOH[d,e]	—	0.79	—	199.54	123.52	155.68	32.16
CH_3COOH	0.0	0.50[g]	43.5	200.84	123.69	157.56	33.87
$Cl_2CHCOOH$[d]	−0.75	0.85	69.9	205.36	123.90	163.46	39.56
$ClCF_2COOH$[d]	−2.5	0.85	(80.0)	206.46	122.78	167.50	44.72
CF_3COOH	−3.03	0.99	82.0	207.86	123.20	169.75	46.55
		0.49	39.4	207.89	123.16	169.75	46.58
		0.04	3.26	207.76	123.20	169.94	46.74
		0.00	0.00				46.7[f]
52.3% H_2SO_4	−3.63	0.75	104.0	208.31	123.55	171.30	47.75
		0.49	67.6	208.54	123.49	172.31	48.82
		0.26	34.7	208.79	123.52	173.34	49.82
		0.00	0.00				50.9[f]
53.3% H_2SO_4	−3.74	0.97	135.0	208.24	123.63	171.24	47.60
		0.50	66.3	208.67	123.45	173.11	49.66
		0.15	19.4	209.02	123.36	174.63	51.28
		0.00	0.00				51.8[f]
55.0% H_2SO_4	−3.91	0.78	101.0	208.67	123.36	173.76	50.40
		0.50	64.3	209.02	123.23	175.54	52.31
		0.31	40.1	209.18	123.16	176.38	53.22
		0.00	0.00				55.2[f]
58.7% H_2SO_4	−4.36	0.98	116.0	209.41	123.13	177.96	54.83
		0.47	54.1	209.83	123.03	180.61	57.58
		0.30	34.3	209.96	122.97	181.46	58.49
		0.00	0.00				60.0[f]
62.5% H_2SO_4	−4.90	1.02	111.0	210.93	122.48	182.82	59.99
		0.49	51.3	210.38	122.71	185.18	62.47
		0.13	13.9	210.51	122.64	186.73	64.09
		0.00	0.00				64.7[f]
70.2% H_2SO_4	−5.96	1.01	89.3	210.93	122.48	191.39	68.95
		0.58	50.5	210.96	122.39	192.62	70.23
		0.062	5.41	210.93	122.29	193.98	71.69
		0.00	0.00				71.9[f]
80.8% H_2SO_4	−7.65	1.02	71.9	211.03	122.23	197.34	75.12
		0.48	33.7	210.87	122.16	198.09	75.93
		0.054	3.80	210.77	122.06	198.70	76.64
		0.00	0.00				76.7[f]
85.8% H_2SO_4	−8.41	0.93	59.9	210.80	122.10	198.99	76.90
		0.48	30.8	210.70	122.06	199.61	77.54
		0.33	21.5	210.67	122.03	199.83	77.80
		0.063	4.01	210.60	122.00	200.12	78.13
		0.00	0.00				78.2[f]
92.1% H_2SO_4	−9.34	1.04	61.3	210.67	122.06	201.00	78.93
		0.48	27.8	210.45	122.00	201.45	79.45
		0.059	3.44	210.48	121.93	201.77	79.84
		0.00	0.00				79.9[f]
96.7% H_2SO_4[e]	−10.0	0.50	26.8	210.48	122.00	201.99	79.99
		0.05	2.68	210.51	121.98	202.31	80.33
		0.00	0.00				80.4[f]
100.0% H_2SO_4	−12.0	1.15	61.3	210.54	121.97	202.52	80.55
		0.48	26.1	210.48	121.93	202.87	80.94
		0.00	0.00				81.2[f]

[a] Measured at 75.468 MHz from external deuterochloroform (77.00 ppm), unless stated otherwise.
[b] Moles of total base (**I** + IH^+) per liter of solution (acid plus nonhydronated **I**).
[c] Moles of total base per mole of total acid (AH + A^-).
[d] From internal TMS at 0.0 ppm.
[e] Recorded at 22.65 MHz.
[f] Linearly extrapolated from the values at other [B]/[AH] ratios.
[g] Not concentration-dependent from 1 to 0.05 *M*.

bonding hindered determination of pK_a values of alcohols in aqueous acids by NMR (*24*). To minimize the medium effects we used the difference (*25*) between chemical shift changes of C-1 and C-2 as the acidity-dependent parameter. However, there was another complication for sulfuric acid, possible for other acids as well, namely partial esterification (*19*), shown for EtOH in Eq. (3). The acidity of ethyl hydrogen sulfate is similar to that of sulfuric acid and basicity of water is not greatly different from that of the alcohol. We found that chemical shift difference δ(C-1)–δ(C-2) can be used to determine the acid strength from the calibration curve shown in Fig. 1, but because of ester formation comparison of strengths of different acids is not straightforward (*26*).

$$H_3C\text{–}CH_2\text{–}OH + H_2SO_4 \rightleftarrows H_3C\text{–}CH_2\text{–}O\text{–}SO_3H + H_2O. \quad (3)$$

Hydronation of unsaturated ketones, such as mesityl oxide (**I**), had been studied in superacid solution (*28*). Both H-1 (*28*) and ^{13}C NMR (*29*) spectra indicated that the proton was attached to the oxygen (**II**, Eq. (4)). Transfer from chloroform solution to superacid moves downfield the signal for C-2 (carbonyl), by about 12 ppm, which is significantly less than the 30 ppm measured for saturated ketones (*29, 30*).



$$\underset{\textbf{I}}{Me\text{—}\underset{\underset{O}{\|}}{C}\text{—}CH{=}CMe_2} + H^+ \rightarrow \left[\underset{\textbf{a}}{Me\text{—}\overset{+}{\underset{O\text{—}H}{C}}\text{—}CH{=}CMe_2} \leftrightarrow \underset{\textbf{b}}{Me\text{—}\underset{O\text{—}H}{C}{=}CH\text{—}\overset{+}{C}Me_2} \right]_{\textbf{II}} \quad (4)$$

By contrast, we found that the signal for C-4 shifts downfield upon transfer from chloroform to superacid solution by almost 50 ppm, which indicates that this carbon carries a significant fraction of the positive charge (cf. **IIb**). The much smaller value reported in an earlier study (*29*) must have been in error. The large hydronation shift and the concentration of charge mainly in the carbon skeleton of **II** (hydroxyallyl cation (*28*)) made **I** an excellent prospect of a probe base for an acidity scale that can be correlated with catalytic activity in hydrocarbon conversions (*4, 5*).

We recorded the ^{13}C NMR of **I** in various solvents, including sulfuric acid up to 100% strong. The chemical shifts for C-2, C-3, and C-4 of **I**, as well as the difference $\Delta\delta = \delta$(C-4)–δ(C-3) for various media are given in Table 1. It is seen immediately that $\Delta\delta$ is a good measure of acid strength over a wide range of acidities. Table 1 also shows that $\Delta\delta$ is dependent upon concentration of **I**. The variation is most pronounced in the range of acidity where **I** is partially but significantly protonated. A similar behavior is shown by saturated ketones (*30*). Our findings thus contradict the literature statement that for acidity measurements by NMR "there is no need to use exactly equal

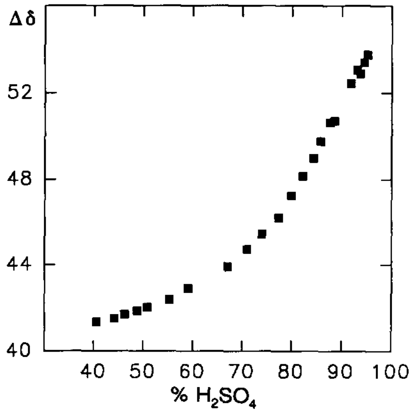


FIG. 1. The difference in chemical shifts of the carbon atoms of ethanol (20% M) in sulfuric acid as a function of acid concentration.

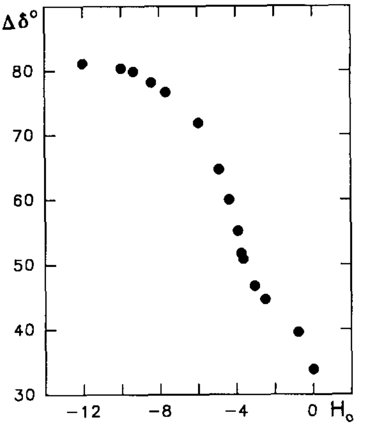


FIG. 2. Chemical shift differences between C-4 and C-3 of mesityl oxide at infinite dilution ($\Delta\delta^0$) as a function of solvent acidity (H_0).

amounts of substrate in each measurement" (*21*).

To relate the hydronation of the indicator base in solution at high dilution to the hydronation at stoichiometric ratio to the acid, expressing the quantity of base through its molar concentration is not convenient. In earlier work (*4, 5*) the degree of hydronation of organic bases was expressed as a function of the molar ratio of acid to base. For extrapolation to infinite dilution of base it is more convenitnt to use the molar ratio of total base (**I** + $\mathbf{IH}^+$) to acid, as done in Table 1, column 4. We found that $\Delta\delta$ varies linearly with this ratio, or with molar concentration, for solutions between 1 and 0.05 *M* in base. We estimated, therefore, the $\Delta\delta$ value at infinite dilution by linear extrapolation ($\Delta\delta^0$).

Even though the hydronation equilibria as normally determined by ^{13}C NMR (*4, 5*) can be used to determine quantitatively the relative hydronation ability of different acids by comparing the degrees of hydronation at the same concentration of base (*5*), such measurements cannot be used to generate an acidity function like H_0 (*1, 21*) because the activity coefficients cannot be expected to cancel out at the concentrations of base required by the NMR method. This limitation is removed, however, by the use of the extrapolation of the hydronation ratio to zero concentration, as applied in here.

There has been some debate (*31*) as to whether hydronation of conjugated carbonyl groups follows H_0 (*32*) or some other acidity function (*33*), but this uncertainty should be of no consequence for the quantitative comparison of acidities, as various acidity functions are linearly related (*34*). One could, therefore, establish the relationship of $\Delta\delta$ with H_0 for **I** in an acid whose strength had been calibrated before by the traditional method, after which the acidity function H_0 of other acids can be determined by measuring the $\Delta\delta$ value in those acids.

A plot of $\Delta\delta$ values extrapolated to zero [B]/[AH] ratio ($\Delta\delta^0$) as a function of the acidity function H_0, which can be used as a calibration instrument, is represented in Fig. 2. The plot is a typical sigmoid curve. Noteworthy, however, is the scatter observed at the low-acidity end of the diagram, indicating that most of the chemical shift changes in that region are brought about by hydrogen bonding rather than by hydronation.

Basicity of the indicator base, expressed as acidity of its conjugated acid, pK_{BH^+}, is a necessary parameter for defining acidity functions (*1, 2*), and it is obtained from the acidity at which [B] = [BH^+] (generally true at concentration zero of the base). Conjugated carbonyl compounds have been a rather ill-behaved class, as various pK_{BH^+}

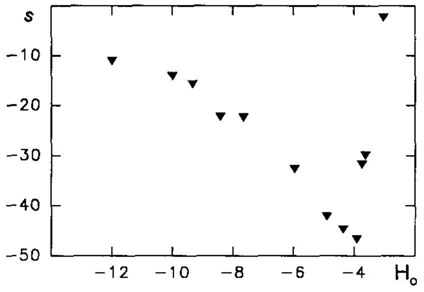


FIG. 3. Variation of slope of the linear correlation $\Delta\delta$ vs total concentration of base (**I** + $\mathbf{IH}^+$) with solvent acidity (H_0).

measurements gave widely different results (*31*). For **I**, a range of $\mathrm{p}K_{\mathrm{BH}^+}$ values from -2.4 (*31*) to -5.36 (*32*) has been reported. Even though the sigmoid curve of Fig. 2 looks much better than literature curves obtained from alternative measurements (see, for instance, Ref. (*33*)), it is still difficult to determine its inflection point accurately. Our work has given us a much better method for measuring acidity at which $[\mathrm{B}] = [\mathrm{BH}^+]$, as the acidity at which the slope (s) of the correlation of $\Delta\delta^0$ with the ratio of base to acid is the steepest (most negative). The representation of s as a function of H_0 (Fig. 3) shows a minimum at $H_0 = -4$, which represents the acidity at which **I** is half-hydronated.

It is interesting to note the asymmetric distribution of points in Fig. 3 around the minimum. On one hand, s increases rapidly at low acidity, again suggesting that chemical shift variations observed for acids with $H_0 > -3$ are due mainly to hydrogen bonding, rather than hydron transfer. On the side of greater acid strength s increases slowly and levels off, somewhat. This behavior is an indication of a second hydronation (formation of $\mathbf{I}\mathrm{H}^{2+}$) in the range of very strong acidity and superacidity (*35*).

CONCLUSIONS

Mesityl oxide (**I**) is a good indicator base for practical measurements of acid strength by ^{13}C NMR for acidities between H_0 -3 and -12; the parameter that measures the degree of hydronation of **I** and correlates with acidity is the chemical shift difference δ(C-4)–δ(C-3) ($\Delta\delta$).

The parameter $\Delta\delta$ varies linearly with the molar ratio of total base ($\mathbf{I} + \mathbf{I}\mathrm{H}^+$) to the acid, at least for total concentrations of **I** between 0.05 and 1 *M*. Extrapolation to zero leads to values that can be used to construct a thermodynamic acidity function, like H_0. This feature makes our approach different from, and qualitatively superior to, previous NMR-based acidity evaluations (*4, 5, 20a, 23, 36*). On the other hand, the degree of hydronation of **I** should be measurable at a stoichiometric ratio of acid to **I**, thus allowing strength comparisons between acids in solution and solid acids. The Hammett acidity function is in principle inapplicable to solids.

The slope of correlation of $\Delta\delta$ with the molar ratio of total base to acid, s, varies with acidity, being the steepest (most negative) in the acid in which **I** is half-hydronated.

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