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Acidity Functions from ^{13}C-NMR[†]

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Abstract: A method of generating a thermodynamic acidity function from ^{13}C-NMR measurements is presented. An indicator base is sought in which two carbon atoms change their charge density very differently upon conversion to the corresponding conjugate acid. The difference between the chemical shifts of the signals for these atoms ($\Delta\delta$) is an acidity-dependent parameter from which other medium effects upon the chemical shifts have been canceled out. Unsaturated ketones like mesityl oxide (**1a**) and 4-hexen-3-one (**1b**) are sensitive probes for this approach because the signal for Cα changes very little, whereas the signal for Cβ undergoes a large shift upon hydronation to **2a** and **2b**. The $\Delta\delta$ parameter varies linearly with the concentration of indicator, at least below 1.5 M. A short extrapolation gives the chemical shift difference at infinite dilution and eliminates the problem of noncancelability of the activity coefficient term in the construction of an acidity function. Rather than establish still another acidity function, the $\Delta\delta^0$ parameters were correlated with H_0 values for sulfuric acid solutions. This correlation was then used to determine H_0 for other acids. The method was tested on two acids for which good literature values are available, $HClO_4$ and CH_3SO_3H, and then used to determine H_0 of H_3PO_4 and $BF_3{\cdot}xH_2O$, for which the literature data needed verification and correction, and of samples of industrial catalysts. The slope s of the correlation of $\Delta\delta$ with concentration of indicator varies with H_0, being the most negative at the acidity where the indicator is half-protonated. The pK_{BH^+} value for the indicator can then be easily determined ($pK_{BH^+} = H_{0.50\%}$) from the position of the minimum in the s vs H_0 plot.

Introduction

The acidity of a material is defined, manifested, and measured relative to a base, in the acid–base interaction. For Brønsted acidity, that interaction is the hydron transfer (eq 1).

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

Our group has been involved for some time with the development of methods for the evaluation of the acidity of strong acid and superacid catalysts.[1] Our initial efforts were prompted by the need of evaluating the acid strength of some nontraditional catalysts for hydrocarbon conversion[2] and describing the mechanisms of reactions in such media.[3] We soon found that the traditional Hammett measurements based on determination of the position of the hydronation equilibrium of a base (indicator) by UV–visible spectroscopy[4,5] are inapplicable to real-life catalysts for a number of reasons,[1d] including that we have yet to see a working catalyst which is not colored or even opaque.

Alternative approaches[5] are the determination of the heat of the acid–base reaction[6] and the measurement of the rates of chemical reactions[7] or conformational changes[8] which are controlled by acid–base equilibria. Calorimetry,[6] however, has uncertainties because thermal effects due to interactions other than hydron transfer can exist. In addition, acid–base interaction can involve more than one hydron transfer; thus, some molecules treated as simple bases in calorimetric studies[6] were later proven by NMR to be at least in part dihydronated in the acid used for calorimetry.[9] The main problem, of course, is not that acidity comparisons based on hydronation enthalpies may sometimes be in error but that one cannot know in advance when such pitfalls exist. Calorimetry needs a method like NMR spectroscopy to determine the nature of the interaction, and even then one cannot be sure that the heat evolved comes exclusively from the hydronation. Regarding kinetic measurements, the conversion of the rate data to a thermodynamic acidity function is, at best, tenuos.

At one time, we were interested in the reported use of voltammetry for acidity measurements,[10] but we found out that corrosion products usually present in industrial catalyst samples interfere with the measurements.

It was established early that the extent of hydronation of a base can be determined by NMR spectroscopy.[5,11] In previous work, we showed that superacid strength can be evaluated from the measurement of the equilibrium between an aromatic

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hydrocarbon and the corresponding Pfeiffer–Wizinger complex[12] (arenium ion) by ^{13}C-NMR.[1] Two features of the NMR method, however, prevented us[1] and others[5] from translating such results into a thermodynamic acidity function like H_0. First, the chemical shift is a function of other factors in addition to the extent of positive charge, particularly of the magnetic properties of the acid as a solvent. Second, NMR spectroscopy is a less sensitive method than UV–visible spectroscopy and requires a higher concentration of the indicator. These features are not too damaging when a limited range of concentrations of acid are studied in the same solvent[1] but affect the comparison between two acids. For these reasons, we expressed our results in terms of relative protonating abilities, RPA (better called relative hydronating abilities, RHA), rather than by an acidity function.[1d,13]

The solvent effect of the acid on the spectral properties of the indicator is an insoluble problem in the traditional Hammett measurements, where it is assumed that the extinction coefficients at a given wavelength for the indicator as well as for its conjugate acid are the same in the unknown acid as in the standard solvents,[4a] a proposition proven invalid at least in some cases.[11a,14] For NMR measurements, we proposed[15] that medium effects be eliminated or minimized by the use in correlations of the chemical shift difference between the signals of two carbons in the molecule of the indicator, whose charge densities change differently upon hydronation of the molecule.

In this paper, we discuss the method of determining acidity functions on the basis of this approach and the application of our method to some strong acids in solution.

Principle of the Method

The chemical shift difference was tested by us with aliphatic alcohols and unsaturated ketones as indicators.[15] We found the conjugated alkenones (**1**) to be superior to the primary alcohols. Hydronation of alkenones in superacids was shown by H-[16] and C-NMR[17] spectra to occur at oxygen (eq 2). Most of the charge is localized at Cβ, and very little is present at Cα (*cf.* **2**). The difference between the chemical shifts of these two carbons ($\Delta\delta$, eq 3) gives an acidity-dependent quantity largely free of solvent effects.

$$\underset{\mathbf{1}}{\mathrm{RCOCH{=}CR'R''}} + \mathrm{AH} \rightleftharpoons \underset{\mathbf{2}}{\mathrm{RC(OH){=}CHC^{+}R'R''}} + \mathrm{A^-} \quad (2)$$

(**a**) R = R′ = R″ = Me (**b**) R = Et, R′ = H, R″ = Me

$$\Delta\delta = \delta(\mathrm{C}\beta) - \delta(\mathrm{C}\alpha) \quad (3)$$

The problem of indicator concentration comes from the relationship (eq 4) between the acidity function H_0 and the activity

$$H_0 = -\log a_{\mathrm{H^+}} + \log \frac{\gamma_{\mathrm{BH^+}}}{\gamma_{\mathrm{B}}} \quad (4)$$

of hydrons in solution, which is the true measure of acidity. Thus, H_0 represents the true acidity only when the activity coefficient term vanishes. This condition is met at infinite dilution of indicator and in particular cases where the activity coefficients of the indicator and its conjugate acid are equal. One can, however, compare the acidities of two solutions of very similar properties (*e.g.*, different, but not by much, concentrations of the same acid) with the same indicator or closely related indicators because the activity coefficient terms are equal for the two experiments and eq 5 applies.

$$\Delta H_0 = \Delta(-\log a_{\mathrm{H^+}}) \quad (5)$$

There has been some debate as to whether hydronation of conjugated carbonyl compounds like **1** follows H_0 or some other acidity functions.[18] In fact, Hammett and Deyrup included some ketones (benzalacetophenone, β-benzoylnaphthalene, 4-benzoylbiphenyl, and antraquinone) in the set of indicators used to define the H_0 function.[4] The subsequent investigators concluded that only primary amines are proper indicators for the H_0 function. Hydronation of α,β-unsaturated carbonyl compounds in aqueous sulfuric acid[18a,b] showed a good correlation with H_0(amines) and H_A(amides), but for high acid concentrations correlation with H_0 was no longer satisfactory. Even if a Hammett-type acidity scale based on carbonyl compounds as indicator bases could be constructed, however, many of the carbonyl compounds do not have chromophores suitable for conducting hydronation studies by electronic spectroscopy techniques.[19]

The dispute on carbonyl compounds as Hammett indicators does not prevent, however, the quantitative comparison of acidities because various acidity functions are linearly related.[20] As a matter of fact, the existence of various acidity functions is due, as emphasized previously, mainly to the noncancelation of activity coefficient terms. Two main approaches have been tried to solve this problem, by Bunnett[20a] and by Marziano.[21] The latter showed that activity coefficient terms are to a good approximation linearly related. Later, Cox and Yates extended the activity coefficient correlations of Marziano to a large number of bases, treating the data by computer.[22] It has to be pointed out that the M_c function of Marziano (named excess acidity function by Cox and Yates) is bound to change all the time as more experimental values are collected.

Because NMR requires a larger amount of indicator than UV-visible spectroscopy, the presence of the indicator in solution reduces the acidity. Thus, the degree of hydronation of the indicator and the $\Delta\delta$ value should decrease when the concentration of the indicator increases. Therefore, the representation that the concentration of indicator in acidity measurements by NMR is of no importance[5b] is incorrect. The same error is apparent in an earlier attempt at determining p$K_{\mathrm{BH^+}}$ for alcohols by NMR.[23] Partial esterification with the acid[15,23] meant that the substrate concentration was different for each point of the correlation used to estimate the p$K_{\mathrm{BH^+}}$ values.[23]

From the examination of a large number of acid solutions, we found that $\Delta\delta$ varies linearly with the concentration of indicator (eq 6), at least for a range of indicator concentrations between 0.03 and 1.50 M. An example of such a correlation (valid for all acids studied by us) is shown in Figure 1.

$$\Delta\delta = s([\mathrm{B}] + [\mathrm{BH^+}]) + \Delta\delta^0 \quad (6)$$

The intercept of the line in eq 6 ($\Delta\delta^0$) represents the value of the $\Delta\delta$ parameter at infinite dilution of indicator. We chose $\Delta\delta^0$

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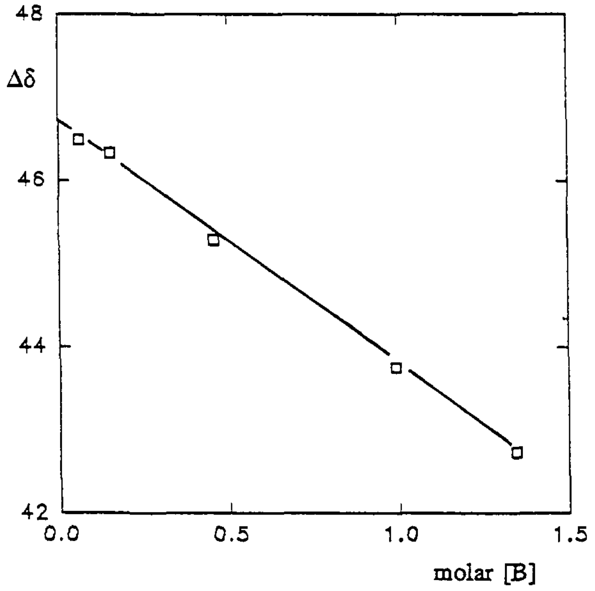

Figure 1. Variation of chemical shift difference $\Delta\delta$ with concentration of **1b** (in 75% H_2SO_4).

as the basis for the determination of an acidity function by NMR. It has the advantage over the quantites used previously for this purpose that examination of hydronation at infinite dilution largely eliminates or at least minimizes the problem of noncancelability of the activity coefficient term.

Considering the number of acidity functions already in existence, we decided not to contribute further to their proliferation. Instead, we anchored our measurements on the original Hammett acidity function, by calibrating $\Delta\delta^0$ with the H_0 values of sulfuric acid, a medium for which good literature data are available.[4c] Indeed, the strength of this acid had been determined many times by the traditional method[4c,24,25] and can be considered reliable. A calibration curve of $\Delta\delta^0$ *vs* H_0 was obtained, from which the acid strength of other acids can be established by determining $\Delta\delta^0$ of **1a** and **1b** in those acids. This method of evaluating the acidity function is therefore a secondary method.

The determination of the H_0 values consists of measurements of spectra for the indicator at three to five concentrations in each acid. The $\Delta\delta$ values measured are then fitted to a straight line (eq 6), the intercept of which gives the $\Delta\delta^0$ parameter. The intercept of the correlation with eq 6 is not dependent upon the units in which the concentration of indicator is expressed (molar, molal, or molar ratio of indicator to acid). We chose to use molal concentration because its calculation is easier.

The correlation of $\Delta\delta^0$ with H_0 gives a convenient method for ranking by strength strong acid catalysts by using ^{13}C-NMR spectra of calibrated indicators. To check the applicability of our method, we conducted the H_0 measurements on two acids for which good literature data are available, CH_3SO_3H and $HClO_4$. Further, we examined two acids for which the published data seemed questionable, $BF_3 \cdot xH_2O$ and H_3PO_4, and we demonstrated the usefulness of the method on some industrial strong acid catalysts.

Results and Discussion

Sulfuric Acid. Comparison of the spectra of **1a** and **1b** in H_2SO_4 of various strength from 40% to 100% and in $CHCl_3$ showed that the carbonyl signal shifts downfield by *ca.* 9–12 ppm, the signal for Cα shifts upfield by *ca.* 2–4 ppm, and that for Cβ moves downfield by 28–52 ppm. The ^{13}C-NMR spectra of **1a** and **1b** in the acid solutions were recorded at three to five concentrations of the indicator in the range of 0.05–1.5 M.

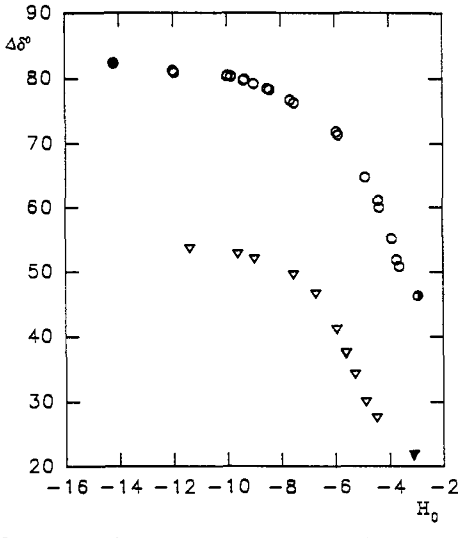

Figure 2. Chemical shift differences between Cβ and Cα of mesityl oxide (**1a**, ○) and 4-hexen-3-one (**1b**, ▽) at infinite dilution ($\Delta\delta^0$) as a function of the acidity of H_2SO_4 (●, **1a** in CF_3SO_3H and ◐ and ▼, **1a** and **1b** in CF_3COOH).

The results are presented in Tables I and II, respectively. The method is sensitive: $\Delta\delta^0$ of **1a** varies from 42.9 ppm in 46.09% H_2SO_4 ($H_0 = -3.05^{24}$) to 81.2 ppm in 100% H_2SO_4 ($H_0 = -12.0^{25}$), and $\Delta\delta^0$ of **1b** varies from 21.2 ppm in 49.77% H_2SO_4 ($H_0 = -3.39^{24}$) to 53.7 ppm in 99.98% H_2SO_4. The plots of the $\Delta\delta^0$ values of **1a** and **1b** *vs* H_0 of 40–100% H_2SO_4 gave the expected sigmoid-shaped curves (Figure 2). The same behavior was found for the other acids studied, for which H_0 was derived using the $\Delta\delta^0$ values calibrated in H_2SO_4. The inflection points of these curves are difficult to determine accurately, but they seem to be close to $H_0 = -4$ for **1a** and $H_0 = 6$ for **1b**. These values represent the respective pK_{BH^+} values.[4] Thus, 4-hexen-3-one requires an acid stronger by about 100 times (or 2 units on the H_0 scale) than mesityl oxide to be half-protonated.

The reactions of the ketones in the dilute acids (water addition)[26] or very concentrated acids[7b,15a] occurred to a too small extent during a run to alter the $\Delta\delta$ values.[11b]

The acidity measurements could not be conducted for low concentration of H_2SO_4 due to the insolubility of the two indicators in the acid (below 44% for **1a** and below 46% for **1b**, for 0.1 M indicator in the acid). For comparison, however, the $\Delta\delta$ values are shown in Tables I and II for less acidic or nonacidic media. Some changes in the $\Delta\delta$ values are observed even for acids in which no significant hydronation is to be expected (weaker than the acid where the indicator is half-hydronated by 3 H_0 units or more). The absence of the hydron transfer is shown by the zero value of the slope s in eq 6 (*cf.* entry for trifluoroacetic acid, TFA, in Table II), as will be discussed below. In such media, $\Delta\delta$ reflects the hydrogen bonding, which also increases with the acidity of the solvent. Thus, $\Delta\delta$ provides a means of comparing acid strength even for these media (but not H_0 values).

Perchloric Acid. The validity of the $\Delta\delta^0$ *vs* H_0 relationships established in Tables I and II and Figure 2 was tested by measuring the $\Delta\delta^0$ values for **1a** and **1b** in 47–70% perchloric acid. The results (Table III) are plotted in Figure 3 and show an excellent agreement with the literature data.[27a]

Surprisingly, clear solutions of **1a** and **1b** were obtained for concentrations of acid at which two phases were seen in sulfuric acid. As we do not have data for sulfuric acid weaker than $H_0 = -3.6$ (**1a**) and -4.45 (**1b**), the excellent agreement with the

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Table I. Correlation of the Chemical Shifts of Mesityl Oxide (**1a**) with the Acidity of Solvent

acid/solvent	conc of **1a** (mol/kg of acid)[a]	chemical shift diff $\Delta\delta$ (ppm)[b]	s^c	H_0^d
DMSO[f,g]		30.71		
$CHCl_3$[f,g]		30.70		
MeOH[f,g]		32.16		
AA[h]	0.523	33.90		0.00
DCA[h]	0.773	39.56		−0.75
DFCA[h]	0.773	44.72		−2.50
TFA[h]	0.719	46.55		
	0.342	46.58		
	0.029	46.74		
	0.000	46.72[e]	−0.27	−3.03
52.30% H_2SO_4	0.557	47.75		
	0.361	48.81		
	0.185	49.82		
	0.000	50.84[e]	−5.56	−3.63
53.32% H_2SO_4	0.735	47.60		
	0.361	49.66		
	0.110	51.28		
	0.000	51.86[e]	−5.85	−3.74
55.00% H_2SO_4	0.567	50.40		
	0.361	52.31		
	0.225	53.22		
	0.000	55.17[e]	−8.31	−3.91
58.77% H_2SO_4	0.695	54.83		
	0.323	57.5		
	0.205	58.49		
	0.000	60.00[e]	−7.45	−4.36
60.21% H_2SO_4	0.704	55.61		
	0.321	58.75		
	0.052	60.62		
	0.000	61.12[e]	−7.76	−4.50
62.51% H_2SO_4	0.668	59.99		
	0.321	62.47		
	0.085	64.09		
	0.000	64.70[e]	−7.04	−4.90
70.07% H_2SO_4	0.613	68.10		
	0.310	69.75		
	0.065	71.04		
	0.000	71.40[e]	−5.38	−5.91
70.22% H_2SO_4	0.641	68.91		
	0.361	70.23		
	0.039	71.69		
	0.000	71.88[e]	−4.62	−5.96
80.03% H_2SO_4	0.640	74.41		
	0.302	75.38		
	0.047	76.12		
	0.000	76.25[e]	−2.89	−7.50
80.82% H_2SO_4	0.594	75.12		
	0.277	75.93		
	0.031	76.64		
	0.000	76.70[e]	−2.70	−7.65
85.81% H_2SO_4	0.523	76.90		
	0.268	77.54		
	0.185	77.80		
	0.035	78.13		
	0.000	78.24[e]	−2.55	−8.41
86.35% H_2SO_4	0.574	76.90		
	0.294	77.61		
	0.062	78.25		
	0.000	78.40[e]	−2.64	−8.50
89.80% H_2SO_4	0.548	77.96		
	0.276	78.58		
	0.033	79.06		
	0.000	79.15[e]	−2.14	−9.00
92.10% H_2SO_4	0.574	78.93		
	0.261	79.45		
	0.032	79.84		
	0.000	79.89[e]	−1.67	−9.34
92.39% H_2SO_4	0.718	78.32		
	0.544	78.64		
	0.258	79.16		
	0.065	79.58		
	0.000	79.69[e]	−1.91	−9.38
95.77% H_2SO_4	0.353	79.78		
	0.277	79.74		
	0.031	80.26		
	0.000	80.31[e]	−1.46	
	0.545	79.61		
	0.269	80.00		
	0.039	80.29		
	0.000	80.35[e]	−1.34	−9.84
96.45% H_2SO_4	0.546	79.72		
	0.286	80.10		
	0.036	80.39		
	0.000	80.45[e]	−1.32	−9.96
96.70% H_2SO_4[g]	~0.273	80.00		
	~0.027	80.33		
	0.000	80.37[e]	−1.38	−10.00
99.95% H_2SO_4	0.536	80.45		
	0.267	80.68		
	0.047	80.88		
	0.000	80.91[e]	−0.86	−11.98
100.0% H_2SO_4	0.626	80.58		
	0.266	80.94		
	0.138	81.07		
	0.000	81.21[e]	−1.00	−12.00

[a] Molal concentration of base. [b] $\Delta\delta$ (eq 3) verifies eq 6, for molal concentration of base. [c] s verifies eq 6, for molal concentration of base. [d] Values from ref 24, with H_0 for 100% H_2SO_4 taken as −12.0 (ref 25). [e] $\Delta\delta$ extrapolated to infinite dilution ($\Delta\delta^0$, eq 6). [f] From internal TMS at 0.00 ppm. [g] Recorded at 22.65 MHz. [h] AA, acetic acid; DCA, dichloroacetic acid; DFCA, difluorochloroacetic acid; and TFA, trifluoroacetic acid.

established acidities for stronger perchloric acid suggests that we can extend the $\Delta\delta^0$ *vs* H_0 correlation down to $H_0 = -2$ (**1a**) and −3.45 or even −3.23 (**1b**) using perchloric acid as the reference acid. It is possible, however, that we deal with colloidal solutions here; therefore, caution is in order.

Methanesulfonic Acid. This compound was chosen as appropriate for testing our method on an organic acid. In terms of solvent properties, we expect this compound to be different from solutions of sulfuric or perchloric acids of the same acid strength.

Two concentrations, 100% and 80.5%, were studied with **1a** and **1b** (Table IV). The H_0 values which we obtained are in agreement with the literature values.[28]

Phosphoric Acid. Several Hammett acidity measurements have been reported for this acid.[4c,29] Some discrepancies and anomalies were noted for concentrations greater than 85%. It was concluded that for these concentrations, the published values may be in doubt.[4c] We found by ^{31}P-NMR that these solutions contain increasing amounts of polyphosphoric acids.

We reinvestigated phosphoric acid between 77% and 100% with **1a** as the indicator base. The results are shown in Table V. Our H_0 values are close to the literature values[4c] for acids weaker than 83%. For more concentrated solutions, our determinations give higher acidities (Figure 4). One data point in Figure 4 for 84.38% phosphoric acid was obtained with **1b**. The H_0 value obtained (−4.35) is in good agreement with the value obtained with **1a** (−4.20), both showing a higher acidity than the literature value, $H_0 = -3.72$.[4c,29a,b]

Boron Trifluoride Hydrates. There is a literature report on Hammett acidity measurements for $BF_3{\cdot}xH_2O$ (x = 1...3),[4c,30]

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(28) Bascombe, K. N.; Bell, R. P. *J. Chem. Soc.* **1959**, 1096.

(29) (a) Heilbronner, E.; Weber, S. *Helv. Chim. Acta* **1949**, *32*, 1513. (b) Gel'bshtein, A. I.; Shcheglova, G. G.; Temkin, M. I. *Dokl. Akad. Nauk SSSR* **1956**, *107*, 108. (c) Gel'bshtein, A. I.; Shcheglova, G. G.; Temkin, M. I. *Zh. Neorg. Khim.* **1956**, *1*, 282. (d) Downing, R. G.; Person, D. E. *J. Am. Chem. Soc.* **1961**, *83*, 1718. (e) Gel'bshtein, A. I.; Airapetova, R. P.; Shcheglova, G. G.; Temkin, M. I. *Russ. J. Inorg. Chem.* **1964**, *9*, 816.

Table II. Correlation of the Chemical Shifts of 4-Hexen-3-one (**1b**) with the Acidity of Solvent

acid/solvent	conc of **1b** (mol/kg of acid)[a]	chemical shift diff $\Delta\delta$ (ppm)[b]	s[c]	H_0[d]
$CHCl_3$	0.647	10.64		
	0.166	10.62		
MeOH	0.325	12.23		
AA[f]		~16		0.00
TFA[f]	0.627	21.64		
	0.332	21.80		
	0.237	21.80		
	0.114	21.77		
	0.000	21.74[e]	~0.0	−3.03
59.64% H_2SO_4	0.715	25.20		
	0.339	26.49		
	0.109	27.24		
	0.000	27.62[e]	−3.37	−4.47
62.44% H_2SO_4	0.728	26.93		
	0.496	27.85		
	0.336	28.63		
	0.000	30.04[e]	−4.31	−4.87
65.67% H_2SO_4	0.659	30.74		
	0.102	33.77		
	0.000	34.33[e]	−5.45	−5.28
67.92% H_2SO_4	0.661	33.97		
	0.340	35.52		
	0.054	37.33		
	0.000	37.55[e]	−5.52	−5.61
70.11% H_2SO_4	0.647	37.14		
	0.337	39.05		
	0.105	40.60		
	0.000	41.24[e]	−6.38	−5.94
75.07% H_2SO_4	0.845	42.73		
	0.610	43.74		
	0.307	45.28		
	0.088	46.33		
	0.035	46.49		
	0.000	46.70[e]	−4.73	−6.72
80.16% H_2SO_4	0.592	48.15		
	0.303	48.91		
	0.067	49.50		
	0.000	49.67[e]	−2.56	−7.55
89.77% H_2SO_4	0.569	51.47		
	0.289	51.76		
	0.073	52.02		
	0.000	52.09[e]	−1.11	−9.00
94.12% H_2SO_4	0.567	52.38		
	0.298	52.62		
	0.072	52.76		
	0.000	52.83[e]	−0.79	−9.61
99.89% H_2SO_4	0.551	53.41		
	0.279	53.54		
	0.985	53.67		
	0.000	53.71[e]	−0.55	−11.40

[a–e] See the same footnotes under Table I. [f] See footnote *h* under Table I.

but the hydronation curves shown there for the indicators studied were not overlapping properly, and each indicator was useful only over a narrow range of acidity.[30] We undertook a detailed study of this acid and reported it elsewhere.[15b] We found boron trifluoride hydrates to be stronger than previously reported. Indeed, the hydrates with $x < 1.4$ gave $\Delta\delta^0$ greater than those for 100% sulfuric acid, which means they are superacidic. The $\Delta\delta^0$ values for these solutions were compared to those obtained for trifluoromethanesulfonic acid ($H_0 = -14.2$[31]). The change in $\Delta\delta^0$ at an acidity so far above the half-protonation point was rationalized by a second hydronation;[9b,32] therefore, we cannot rigorously assign an H_0 value to these solutions.

Table III. H_0 Values for $HClO_4$

conc of $HClO_4$ (%)	H_0[a]	H_0[b] with **1a**	H_0[b] with **1b**
34.94	−1.85		
44.01	−2.75		
47.69	−3.23	−3.25	
48.98	−3.40	−3.55	
50.19	−3.45	−3.76	−3.40
51.63	−3.70	−3.88	
52.67	−3.85	−4.10	−3.77
55.18	−4.30	−4.57	−4.27
56.54	−4.53	−4.92	
56.89	−4.60		−4.85
58.75	−4.95	−5.35	−5.18
59.84	−5.20	−5.53	−5.25
60.85	−5.50	−5.78	−5.73
62.58	−5.60	−6.00	−5.82
63.41	−6.05	−6.13	−6.07
65.08	−6.51	−6.46	−6.40
66.62	−6.90	−7.00	−6.75
69.81	−7.70	−7.85	−7.60

[a] H_0 values for $HClO_4$ from ref 27a. [b] Experimental values.

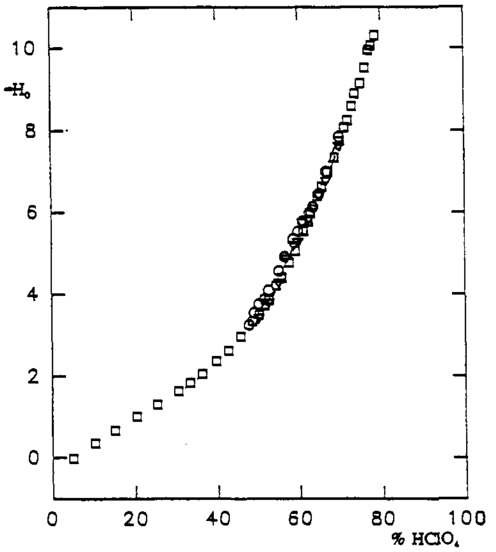

Figure 3. Variation of acid strength with concentration of $HClO_4$ (□, literature; ○, with **1a**; and ▽, with **1b**).

Table IV. H_0 Values for CH_3SO_3H

conc of CH_3SO_3H (%)	H_0[a]	H_0[b] with **1a**	H_0[b] with **1b**
85.52	−4.58	−4.35	−4.30
100	−7.86	−7.60	

[a] H_0 values for CH_3SO_3H from ref 28. [b] Experimental values.

Table V. H_0 Values for H_3PO_4

conc of H_3PO_4 (%)	H_0[a]	H_0[b] with **1a**
77.07	−3.00	−3.25
79.48	−3.25	−3.70
82.61	−3.55	−3.95
85.16	−3.87	−4.28
86.35	−3.95	−4.55
87.71	−4.05	−4.77
89.48	−4.25	−5.05
91.44	−4.45	−5.30
94.34	−4.70	−5.78
96.40	−4.85	−6.07
100.0	−5.25	−6.65

[a] H_0 values for H_3PO_4 from ref 4c. [b] Experimental values.

Industrial Catalysts. To demonstrate the utility of our method for practical applications, we collected various samples of strong acid catalysts from industrial installations. The materials received were colored, most often opaque, containing variable amounts of organic compounds and corrosion products in solution and

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(30) Vinnik, M. I.; Manelis, G. B.; Chirkov, N. M. *Russ. J. Inorg. Chem.* **1957**, *2*, 306.

(31) Kramer, G. M. Cited in ref 1d.

(32) The absence of leveling in the sigmoid curve presented in ref 11a may also be due to a second hydronation of *p*-fluorobenzamide.

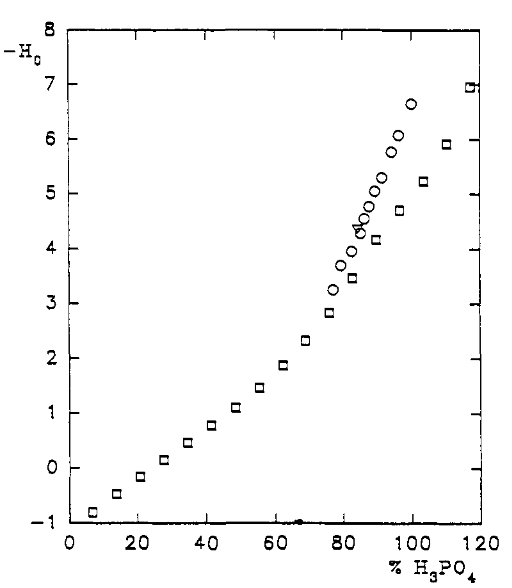

Figure 4. Variation of acid strength with concentration of H_3PO_4 (□, literature; ○, with **1a**; and ▽, with **1b**).

sometimes even solid particles in suspensions. Nevertheless, we were able in all cases to determine the $\Delta\delta$ and $\Delta\delta^0$ parameters using **1a** or **1b**. An example of a spectrum of a sample with added **1b** is shown in Figure 5. Thus, the NMR method can be applied to determine a thermodynamic acidity function for these catalysts.

Significance of Slopes *s* in Eq 6. As mentioned above, the variation of $\Delta\delta$ with the concentration of indicator is due to the decrease in acidity brought about by the increase in the concentration of base. For an acid so weak that no hydronation occurs, no such effect of the base is expected. Conversely, for an acid significantly stronger than that needed to hydronate the base fully, one can add to the solution more base and that is still fully hydronated. Therefore, there should be no effect of the base concentration on $\Delta\delta$ in that case either. This reasoning predicts that variation of $\Delta\delta$ with ($[B] + [BH^+]$) (slope *s* in eq 6) is the steepest at the acidity where the base is half-hydronated.

The values of *s* for **1a** and **1b** in the acids studied are listed in Tables I and II and in Tables VI–IX in the supplementary material. They are plotted *vs* H_0 in Figures 6 and 7, respectively. It can be seen that a minimum in the plot exists in all cases in the region where the hydronation curves (Figure 2) show an inflection. We have, thus, a method[15a] to determine pK_{BH^+} (equal to H_0 for 50% hydronation of the indicator) much easier than that from the sigmoid curve.[11a] The alternative approach, interpolation of the chemical shifts between the values for the nonhydronated (B) and fully hydrated (BH^+) forms of the indicator,[33] cannot be applied for unsaturated ketones because of hydrogen bonding at low acidity and double hydronation at high acidity. The difficulty in handling phosphoric acid is seen here again in that the minimum is broader and somewhat off the position of the inflection point in the $\Delta\delta^0$ *vs* H_0 plot for H_3PO_4, even though the latter is difficult to locate on the curve. Without H_3PO_4, we obtain pK_{BH^+} of -4.2 ± 0.3 for **1a** and -5.95 ± 0.05 for **1b**, close to some of the literature values.[18b]

Conclusions

The $\Delta\delta^0$ parameter provides a means to determine a thermodynamic acidity function of a solution by ^{13}C-NMR. The calculation of $\Delta\delta$ eliminates the medium effects, especially the effect of the magnetic susceptibility of solvent upon chemical shifts, whereas the extrapolation to infinite dilution solves the problem of noncancelability of the activity coefficient term. It has to be kept in mind that medium effects exist in the classical Hammett measurement because it is not possible to determine the molar absorptivity of the indicator and its protonated form in the medium where both are present, so it is assumed that the values determined for the former in a nonacidic solvent and for the latter in a different, much stronger acid are valid. It is known, however, that absorptivity is a function of the medium.[4,33] Even when an isosbestic point is observed, it is possible that the absorptivities of B and BH^+ at other wavelengths do change. The relative concentrations of B and BH^+ are obviously determined at other wavelengths than that of the isosbestic point. Nonetheless, it was most convenient to anchor our method on the H_0 acidity function determined for sulfuric acid by UV–visible spectroscopy. We felt that H_2SO_4 was studied before so extensively and carefully that there was little to be gained by trying to set up another acidity function.

The use of unsaturated ketones (**1**) as indicators allows accurate measurements over a large range of acidity because of the very large variation of $\Delta\delta^0$ with acidity. It is also possible to vary widely the basicity of indicators in this class by simply changing the substituents R, R′, and R″ in **1**. The syntheses of a variety of such materials have been published.

The variation of *s* in eq 6 with H_0 offers a very convenient way to determine pK_{BH^+} for our indicators.

Most important, the NMR technique is applicable for determining the H_0 values for industrial catalysts and other strongly acidic materials which could not be handled by previous methods of acidity measurement.

Experimental Section

Materials. Commercial AR grade **1a** and **1b** (minimum 97% purity by GC) were used as received. Storage on 4A molecular sieves was tried but did not change the results. When the GC analysis showed **1a** to be less than 97%, the indicator was redistilled under vacuum.

The acid solutions were prepared from the commercial 96% H_2SO_4, 70% $HClO_4$, and 85% H_3PO_4; for more concentrated sulfuric and phosphoric acids, fuming sulfuric acid (19% SO_3) and P_2O_5, respectively, were used to obtain the desired acid concentrations. A sample of methanesulfonic acid vacuum-distilled and thrice recrystallized under inert atmosphere was obtained from ATOCHEM and used as received. All manipulations involving this acid were conducted in a glovebag filled with dry nitrogen.

For sulfuric and perchloric acids, the solutions were analyzed by titration with 1 N NaOH (at least five titrations for each concentration). Phosphoric acid solutions were analyzed by potentiometric titration at 25 °C, after the titration curve for the whole range of pH values was established using the commercial acid. Alternatively, titrations in the presence of $CaCl_2$ with boiling under reflux were performed; H_3PO_4 formed $Ca_3(PO_4)_2$ and HCl which was titrated with NaOH in the presence of methyl orange.

NMR Spectra. The ^{13}C-NMR spectra of **1a** and **1b** in the acid solvents were recorded at 75.468 MHz on a Bruker MSL 300 instrument, at 25 °C. A 20-kHz spectral width, a number of 16-K points in the time domain, and a number of 16-K points for the Fourier transform gave a digital resolution of 0.03 ppm. A pulse width of 9 μs (90° pulse), a recycling delay 8.5 s, and a receiver blanking delay of 20 μs were used for the majority of the spectra. In order to avoid heating of the samples due to broad-band decoupling, which could cause decomposition of the indicator during long runs, an inverse gated decoupling program was used, with decoupling during the aquisition (49 ms) and a decoupling preirradiation of 1.5 s to establish NOE between the recycling delay and the excitation pulse. For faster accumulation, a WALTZ pulse sequence[34] with quadrature detection was used, in which case the excitation pulse was 4 μs, the 90° pulse for decoupling was 100 μs, and the total length of a scan was 2.5 s.

The chemical shifts were measured from the center line of the $CDCl_3$ signal (77.00 ppm) placed as an external standard and lock solvent in the 10-mm coaxial tube.[15]

The acid solutions of **1a** and **1b** were prepared directly in the 8-mm NMR glass tubes.[15] The acid (1.1 mL) was measured with a Gilmont pipet of 0.01-mL accuracy, and the quantity was checked by weighing on an analytical balance to 0.1 mg. The indicator was then added with

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(33) Edward, J. T.; Meacock, S. C. R. *J. Chem. Soc.* **1957**, 2000.

(34) Shaka, A. J.; Keeler, J.; Freeman, R. *J. Magn. Reson.* **1983**, *53*, 313.

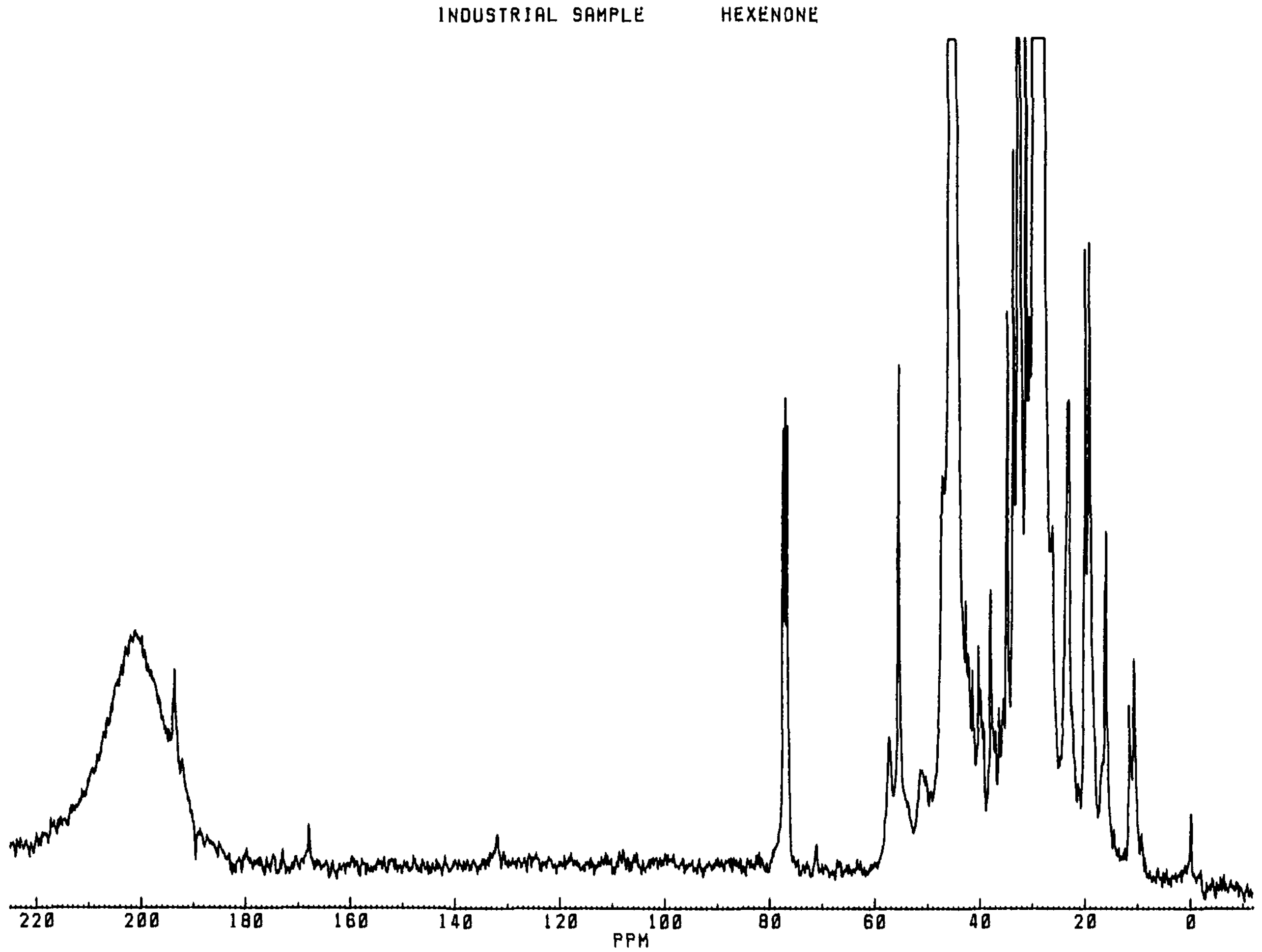

Figure 5. ^{13}C-NMR spectrum of **1b** in an industrial catalyst.

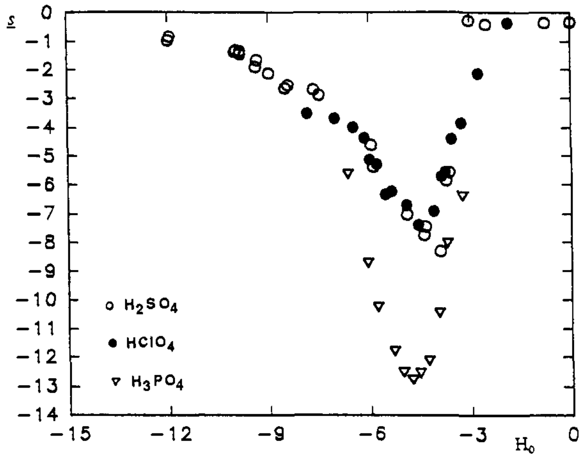

Figure 6. Variation of slopes of the linear correlation $\Delta\delta$ *vs* total concentration of **1a** (eq 6) with the acidity of H_2SO_4 (○), $HClO_4$ (●), and H_3PO_4 (▽).

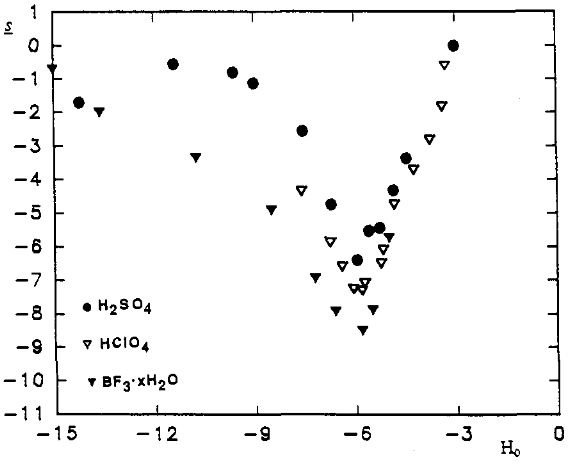

Figure 7. Variation of slopes of the linear correlation $\Delta\delta$ *vs* total concentration of **1b** (eq 6) with the acidity of H_2SO_4 (●), $HClO_4$ (▽), $BF_3 \cdot xH_2O$ (▼).

a 100-μL microsyringe in the necessary amount, also checked by weighing. For the strongly acidic media, the tube containing the acid was cooled in dry ice or a liquid N_2 bath, then the indicator was added, and the tube was shaken for mixing while warming to room temperature. This approach was not successful for H_3PO_4 because the high viscosity prevented mixing in the tube. Those samples were prepared in a round-bottomed flask with a magnetic stirrer, and the acid containing the indicator was then transferred to the 8-mm tube. Samples in 100% H_3PO_4 (mp = 42.35 °C[35]) crystallized in some cases; in others, they could be run as undercooled liquids.

The decomposition of **1a** in concentrated sulfuric acid[7b] is too slow to be observed during our runs. The addition of water (eq 7)[26] was observed, however, in the weaker acids. This reaction replaces two molecules of base in solution, **1** and H_2O, by one molecule with two basic sites, hydroxy ketone **3**.

$$\underset{\mathbf{1}}{\mathrm{RCOCH{=}CR'R''}} + \mathrm{H_2O} \rightleftarrows \underset{\mathbf{3}}{\mathrm{RCOCH_2CR'R''OH}} \qquad (7)$$

(**a**) R = R′ = R″ = Me (**b**) R = Et, R′ = H, R″ = Me

3a. ^{13}C-NMR (0.75 M **1a** in 52.3% H_2SO_4, $H_0 = -3.63$): δ 216.56 (C=O), 72.89 (C—OH), 53.55 (CH_2), 27.80 and 22.30 (CH_3-s).

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[35] *Handbook of Chemistry and Physics* 53rd ed.; CRC Press: Cleveland, OH, 1972–1973.

3b. ^{13}C-NMR (1.0 M **1b** in 62.4% H_2SO_4, $H_0 = -4.87$): δ 218.95 (C=O), 66.45 (C—OH), 48.79 (CH_2), 36.46 (CH_2), 20.87 and 7.15 (CH_3-s).

The effect of this reaction on our measurements was checked by measuring the chemical shifts of averaged signals for **1** and **2** at several lengths of time after mixing, that is, at various degrees of conversion to **3**. No significant difference between the measured values was observed.

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Supplementary Material Available: Tables of the correlation of chemical shifts for **1a** and **1b** with acidity (H_0) of perchloric, phosphoric, and methanesulfonic acids (8 pages). Ordering information is given on any current masthead page.