Strength of liquid acids in solution and on solid supports. The anion stabilization by solvent and its consequences for catalysis

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Abstract

The effect of solvents upon the effective strength of acids in solution was studied in the strong acid range by the measurement of the $\Delta\delta$ parameter for mesityl oxide at stoichiometric acid/base ratio ($\Delta\delta^1$) and in the weak superacid range by the measurement of the hydronation of hexamethylbenzene (HMB). The approach is applicable to acids which cannot be described by an acidity function (non-Hammett acids). For sulfuric acid, the strength given by the $\Delta\delta^1$ parameter changes with solvent in the order: sulfolane < neat acid < SO_2 < hexafluoroisopropanol (HFIP). Thus, sulfolane behaves like a basic solvent toward H_2SO_4. The small effect of SO_2 is a result of its being a polar solvent. The large acidity enhancement observed in HFIP solution results from its ability to form strong hydrogen-bonded complexes with the acid anion (anion stabilization). The extent of hydronation of HMB by trifluoromethanesulfonic acid (TFMSA) changes with solvent in the order: SO_2, SO_2ClF < trifluoroacetic acid (TFA) < HFIP. As TFA is more basic than SO_2, this finding demonstrates that TFA and HFIP are particularly good anion stabilizing solvents. Basicity of a solvent is not well described by the pK_{BH^+} measured for that compound as a solute, but can be assessed from the decrease in the extent of hydronation of a probe base by an acid in the solvent. For hydrogen-bond donor solvents, a correction has to be made for the anion stabilizing effect (acidity-enhancing). An empirical relative solvent basicity parameter (SB) was developed from the examination of hydronation of HMB by TFMSA (3 mol) in TFA-$CHCl_3$ solutions, and its suppression by the addition of an amount of solvent i equal to the acid (SB(i, TFA)). TFA is thus taken as the standard, non-basic, solvent, and also provides the anion stabilization. Values of SB(i, TFA) for some carboxylic acids and one nitroalkane are listed. The effect of anion stabilizing solvents as promoters for strong acid catalysts was shown by the acceleration of the transalkylation of p-di-$tert$-butylbenzene (p-DTBB) with toluene catalyzed by H_2SO_4, upon addition of small amounts of TFA or HFIP (most effective) to the acid. © 1997 Elsevier Science B.V.

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1. Introduction

A number of studies of strength of liquid acids in the strong acid to superacid range by $^{13}C\,NMR$ have been reported from our laboratory. Thus, we found that an acidity function can be determined with the use of an indicator in which the positive charge acquired upon hydron attachment is very unevenly distributed, such that one carbon atom carries most of the charge, whereas another carries very little [1,2]. Particularly suitable indicators were found to be α,β-unsaturated ketones, exemplified in Eq. (1) by mesityl oxide (4-methyl-3-penten-2-one, **1**). The difference between chemical shifts measured for the two atoms [3–8] $\delta_{C(\beta)} - \delta_{C(\alpha)}$ ($\Delta\delta$) is a measure of the extent of conversion of **1** to its conjugate base, **2**; extrapolated at infinite dilution (the $\Delta\delta^0$ parameter), it was correlated with the acidity function H_0 [1]. We applied then this approach to the determination of the acidity function of a number of chemically pure acid systems, as well as of some industrial catalysts [2,9–13]. We also obtained information about the structure of complex acids [10,11], the mechanism of ionization of polybasic acids (stepwise or concurrently) [11], intervention of simple or double hydronation of certain organic compounds [14] and hydrogen bond donor ability of solvents and solid surfaces [15]. Acid strengths (H_0) measured by our method were correlated with rates and used to establish reaction mechanisms [16]. The technique and its applications have been reviewed [17].

$$Me_2 \overset{\beta}{C} = \overset{\alpha}{C}H-CO-Me + AH$$
$$\mathbf{1}$$

$$\rightleftarrows Me_2 \overset{\beta}{C}{}^+ - \overset{\alpha}{C}H=C(OH)-Me + A^- \qquad (1)$$
$$\mathbf{2}$$

Acidity functions were determined by the NMR method both for molecular acids and for some composite acids, particularly systems made of Lewis acids dissolved in Brønsted acids [9,11]. Many of the latter systems are best described as solutions of a complex acid (Lewis–Brønsted compound) in the much weaker Brønsted acid [17]. It was observed, however, that many of the complex acids, particularly the systems containing a solid Lewis acid dissolved in a Brønsted acid cannot be studied at high dilutions of indicator. Indeed, such acids might not even exist in the absence of a rather large concentration of base [17–21]. In catalytic reactions, the substrates or some long-lived reaction intermediates are the bases in solution. An acidity function cannot be determined for such acids. Indeed, from the definition of the acidity function by Hammett, it follows (Eq. (2)) that H_0 measures the activity of hydrons in solution (the true acid strength) only if an activity term coefficient vanishes [22–24]. This requirement is fulfilled at infinite dilution [24,25] or with reasonable accuracy at high dilutions of indicator [24]. Another requirement, however, is that there be no interaction between the hydronated indicator and the acid anion. Indeed, the acid–base reaction was written by Hammett in an idealized form (Eq. (3)) neglecting the acid anion.

$$H_0 = -(\log a_{H^+}) + \log(\gamma_{BH^+}/\gamma_B) \qquad (2)$$

$$H^+ + B \rightleftarrows BH^+ \qquad (3)$$

An acid which satisfies the requirement for an acidity function was named a Hammett acid [17,26]. Based on Eq. (3), in Hammett's definition an ideal acid is a continuum in which hydrons float. A real acid, the reaction of which is described by Eq. (4), is a Hammett acid if the acid anion, neglected in Eq. (3), interacts strongly with the excess of acid (Eq. (5)) and not at all with the hydronated base.

$$AH + B \rightleftarrows A^- + BH^+ \qquad (4)$$

$$nAH + A^- \rightleftarrows (AH)_n A^- \qquad (5)$$

By contrast, acids like the composites discussed above, which do not satisfy the criteria for determination of an acidity function, were referred to as *non-Hammett acids* [17,26–28]. Acids in which the hydronated base and the acid anion are tightly ion-paired even at high dilutions, as it happens for strong acids in non-polar solvents [29], also belong to this class. Whereas no acidity functions can be deduced for such

systems, a pairwise comparison of the degree of hydronation of the same base, or closely related bases of known basicity ratio in different acids can be used to establish practically useful scales of *relative hydronating abilities* (RHA) [17,30]. For such a measurement, the indicator base is dissolved in the acid at a concentration close to stoichiometric [20,21,30]. The complex or composite acids are then related to molecular acids by examining the hydronation of the probe base by the 'standard' acids at the same acid to base ratio [17,21]. We demonstrated this approach for superacidic media, using benzene [20,2] and hexamethylbenzene (**3**, Eq. (6)) [30] as indicator bases and concluded that trifluoromethanesulfonic acid (TFMSA), 30:1 $HF–TaF_5$ and 4:1 $HBr–AlBr_3$ have RHA values of about 0 (i.e. anchor point), 11, and 12 on a logarithmic scale [17,30].

$$AH + C_6Me_6 \rightleftarrows A^- + C_6Me_6H^+ \qquad (6)$$
$$3 4$$
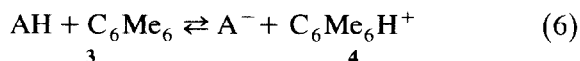
The complex acids mentioned above react as HTa_nF_{5n+1} ($n = 1, ..., 4$) and HAl_nBr_{3n+1} ($n = 1$ or 2) even though the latter does not exist, but its anions $(Al_nBr^-_{3n+1})$ are formed by reaction with bases. The usefulness of such materials is achieved in reactions with bases too weak to be hydronated to any significant extent by the excess of HF or HBr. Obviously, the indicators chosen to measure the strength of these and other composite acid are also bases too weak to be hydronated to any measurable extent by the Brønsted acid present in excess [17,21]. The latter thus behaves like a non-acidic solvent, but nonetheless it has an effect upon the hydronating ability of the medium [17]. There are also cases in which solutions of strong molecular Brønsted acids in nonacidic solvents are used as catalysts [16]. The acid strength of such materials has to be referred to a standard acid in the same solvent. Knowing the role of the solvent upon the acid strength of the solution is very important, especially because a fine-tuning of the acidity is often desired [16].

The first solvent property to be considered is basicity. Its usual definition consists of determi-

nation of the pK_{BH^+} value for the compound as a solute in another solvent. It is quite possible, however, that pK_{BH^+} does not describe adequately the behavior of the compound when used itself as a (basic) solvent. For example, there is evidence that the basicity of water changes from the pure liquid to a solution in another solvent and from one solvent to another [13,31,32]. An attempt was made to evaluate the relative basicities from the reduction of protonating ability of an acid by the basic solvents. For this purpose, the degree of hydronation of hexamethylbenzene (HMB, **3**) by TFMSA in the solvent investigated and in trifluoroacetic acid (TFA) were compared [33]. The solvent can, however, influence the acidity in more than one way, in some cases increasing the hydronating ability of the acid. We report here more extensive work on the measurement of acid strengths in solution and the effect of solvents on acidity and its consequences for catalysis.

2. Experimental

2.1. Materials

Purification and handling of acids [1,30], silica gel [15], hexamethylbenzene (HMB) [30], and mesityl oxide [1,2] were described in previous publications. *p*-Di-*tert*-butylbenzene was dried over P_2O_5, under vacuum, for 20 h. The other hydrocarbons were stored on 3A molecular sieves and hexafluoroisopropanol (HFIP) was stored on 4A molecular sieves. Sulfolane was treated with $KMnO_4$ to remove possible traces of the more basic sulfoxide, washed, and distilled from P_2O_5 (b.p. 97–102°C at 0.5 mmHg), as described in the literature [34]. Sulfur dioxide was introduced through a column with P_2O_5 into the vacuum line, where it was condensed for use as solvent [30]. Trifluoroacetic acid (TFA) was dried by reaction with the appropriate amount (slight excess) of trifluoroacetic anhydride prior to use [35].

2.2. NMR analyses

The solutions of acids and indicators were prepared as described before; the tubes with solutions in SO_2 were sealed in flame [1,2,9–13,20]. The solvents for the hydronation of HMB were 75:25 SO_2–$CHCl_3$, 75:25 SO_2FCl–$CHCl_3$, 75:25 CF_3COOH–$CHCl_3$, and 90:10 HFIP–$CHCl_3$. The integrity of HMB after the NMR analyses was checked by quenching the sample in water, extracting in pentane, drying on $CaCl_2$, and analyzing by GLC on a 5 m × 3 mm OD column, with 5% Carbowax 20M on Gaschrom Q. For studying the strength of acids deposited on silica gel, the latter was slurried with Freon 11 in a small round-bottomed flask and the acid was added slowly in small drops, with vigorous stirring under nitrogen. For sulfuric acid, loadings of 2.5 and 5 mmol/g silicagel were employed; taking the surface area occupied by one molecule as 12.5 Å^2, it was calculated that full coverage of silica gel (675 m^2/g) is achieved at a loading of 10 mmol H_2SO_4/g. For methanesulfonic acid, the loading was 2.5 mmol/g of solid. After stirring for another 30 min, the solvent was evaporated under vacuum with slight warming. The batches of mounted acids were used for preparation of samples with variable ratios of acid to mesityl oxide (1). For that purpose, the weighed quantity of solid was covered with pentane or Freon-11 and the desired volume of mesityl oxide was injected from a microsyringe through a rubber septum. The quantity of probe base added was checked by weighing the syringe before and after addition. Coloring of the solid surface and discoloring of the supernatant liquid indicated that the probe base was adsorbed and reacted with the acid on the surface. No difference was seen between the results on samples prepared with either solvent for H_2SO_4, but for $MeSO_3H$ coloring of the liquid phase indicated that some of the acid had been extracted from the surface into pentane; therefore, Freon 11 was preferred as solvent. Vacuum evaporation gave a solid sample still containing traces of solvent. More extensive solvent removal led, however, to some loss of mesityl oxide. The sample was packed in a 7 mm MAS rotor under nitrogen and capped; a rotor cap without hole is used to avoid contact with air. The NMR spectra of solutions [1,2,9–13,30] and solid samples [15] were recorded as described before.

2.3. Reaction of p-di-tert-butylbenzene (p-DTBB) with toluene [36]

p-DTBB (3.58 g, 18.8 mmol) was dissolved in a mixture of toluene (10 ml, 94 mmol) and tridecane (1.68 ml), added as integration standard and also to reduce the solubility of acids in the organic solution. The reactant mixture was analyzed after dilution 1:50 with pentane, by GLC on a 3 m × 3 mm OD column with 10% SP-1000 on Supelcoport, at 120°C.

Sulfuric acid (0.3 ml), neat or mixed with 0.3 ml of anion-stabilizing solvent, was placed in a 5 ml round-bottomed flask with a Teflon-coated magnetic stirring bar. The flask was then capped with a rubber septum, placed in a bath at 27 ± 0.2°C, and stirred for 20 min. The reactant mixture (1.0 ml), equilibrated at the same temperature, was injected through the septum. Samples, 0.02 ml each, were withdrawn during the reaction from the hydrocarbon layer through the septum, diluted with pentane (1.0 ml) and analyzed by GLC as above. The same stirring rate was maintained for all runs. The progress of the reactions was monitored by the disappearance of p-DTBB, through conversion to the products.

3. Results and discussion

3.1. Acidity measurements with mesityl oxide (1); extension of the Δδ method to low acid to base ratios (details given in Ref. [37])

To determine acidity functions, the Δδ parameter is measured at concentrations of 1 below 1.5 M [1,2]. For sulfuric acid this represents
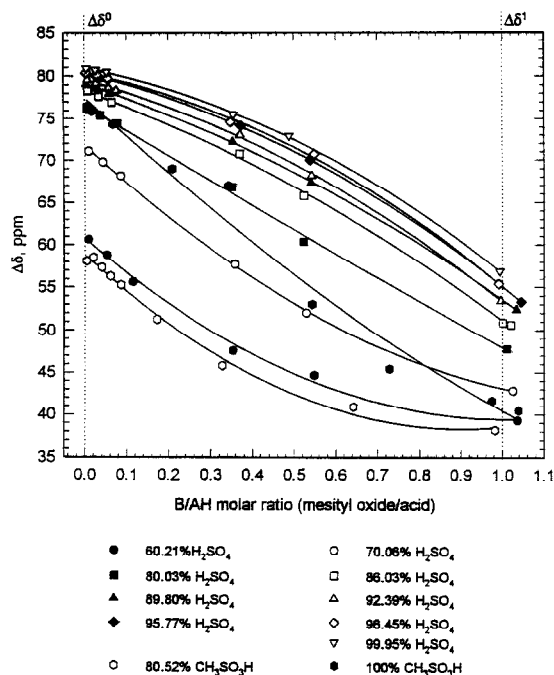
Fig. 1. Variation of $\Delta\delta$ for **1** in the range of acid to base ratios (B/AH) from 0 to 1.1. (triangle down) 99.95% H_2SO_4; (diamond) 96.45% H_2SO_4; (filled diamond) 95.77% H_2SO_4; (triangle up) 92.39% H_2SO_4; (filled triangle up) 89.80% H_2SO_4; (square) 86.03% H_2SO_4; (filled square) 80.03% H_2SO_4; (circle) 70.06% H_2SO_4; (filled circle) 60.21% H_2SO_4; (filled hexagon) 100% CH_3SO_3H; (hexagon) 80.52% CH_3SO_3H.

a base to acid ratio (B/AH) of about 0.08. Results of measurements at much higher concentrations of **1** in several sulfuric acid solutions and in two methanesulfonic acid solutions are represented in Fig. 1. From these data, values of the $\Delta\delta$ parameter at various B/AH ratios can be deduced. The values for B/AH = 1 are identified there as $\Delta\delta^1$. It can be observed that the $\Delta\delta^1$ scale is more compressed than the $\Delta\delta^0$

scale, but the ordering of acids remains the same within the errors of measurement. The exception is presented by 100% methanesulfonic acid, stronger than 80% H_2SO_4 at B/AH $\rightarrow$ 0 but similar to 60% H_2SO_4 at B/AH = 1.0. This change, which can be related to the fact that $MeSO_3H$ is not an aqueous system, is a clear manifestation of the medium effect on acid strength. Indeed, Fig. 1 shows that 80.5% $MeSO_3H$ behaves quite similarly with sulfuric acid solutions of the same strength.

3.2. The enhancement of hydronating ability of acids by solvents

The medium effects on acid strength were measured by determining the $\Delta\delta^1$ values for **1** in its reaction with 95.77% sulfuric acid in three solvents: sulfur dioxide, sulfolane, and HFIP, at a concentration of acid in solution of about 0.5 M. Sulfur dioxide (dielectric constant about 15 at room temperature [38]) has been long known to be a good solvent for carbocations [39,40]. Sulfolane (dielectric constant 43 at 30°C [41]) was described as a weakly basic solvent, appropriate for the generation of highly acidic solutions [42]. HFIP has been much used in carbocationic solvolyses, as a solvent with high ionizing power (for a discussion see Ref. [43]).

The results of our measurements are shown in Table 1 and Fig. 2. In Table 1 the values for **1** as a free base in the same solvents and at the same concentrations, $\Delta\delta(B)$, and the differences $\Delta\delta^1 - \Delta\delta(B)$ are also given. The degree

Table 1

Effect of the solvent on the hydronation of mesityl oxide (**1**) by 95.8% sulfuric acid[a] evaluated by the $\Delta\delta^1$ parameter

No.	Solvent	$\Delta\delta^1$	$\Delta\delta(B)$[b]	$\Delta\delta^1 - \Delta\delta(B)$	$\{\Delta\delta^1 - \Delta\delta(B)\}/Q$[c]
1	—[d]	55.00	29.70	25.30	0.52
2	SO_2	58.40	32.42	25.98	0.57
3	Sulfolane	38.26	30.15	8.11	0.17
4	HFIP[e]	71.35	39.13	32.22	0.83

[a]Concentration ca. 0.5 M, equal to that of mesityl oxide (interpolated values).
[b]The $\Delta\delta$ value at the same concentration in the absence of acid; see Ref. [15].
[c]$Q = 78.00 - \Delta\delta(B)$, where 78.00 is the limiting $\Delta\delta$ value ($\Delta\delta^0$) at $H_0 -8.4$ (see text).
[d]Neat acid.
[e]HFIP = hexafluoroisopropanol.

Mesityl oxide - 95.77% H_2SO_4 in:

●   sulfolane (0.53M acid)

■   liquid SO_2 (0.43 ... 0.50M acid)

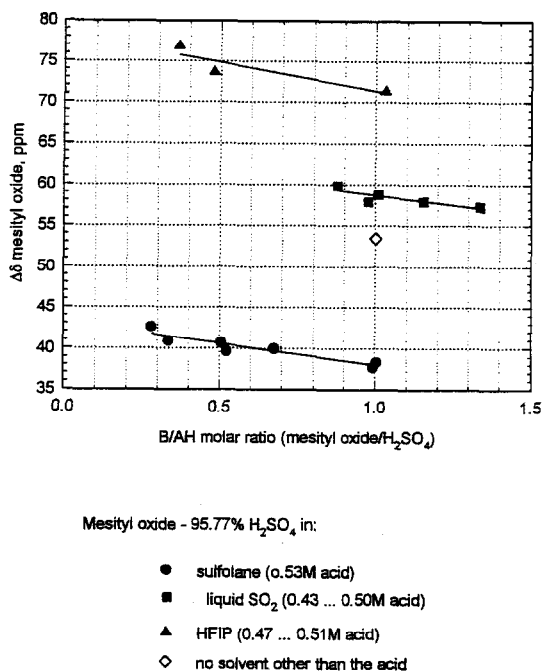▲   HFIP (0.47 ... 0.51M acid)

◇   no solvent other than the acid

Fig. 2. Variation of $\Delta\delta$ for **1** as a function of acid to base ratios (B/AH) and solvent. ● sulfolane (0.53 M acid); ■ liquid SO_2; ▲ HFIP (0.47–0.51 M acid); ◇ no solvent (other than the acid).

of hydronation of **1** in each solution could in principle be obtained from these values and the limiting $\Delta\delta$ value $(\Delta\delta^0)$ for the fully hydronated base, **2**. The latter value is not experimentally available because of the formation of a dication from **1** (**2**-H^{2+}) at very high acidities [14]. As a very rough estimate, the $\Delta\delta^0$ value of 78.00 determined in an acid of H_0 −8.4, four H_0 units stronger than the point of half-hydronation of **1** [2,17] was introduced in the calculation in the last column in Table 1, on the idea that in that medium the first hydronation is complete and the second hydronation should not be important. This being the case, the numbers calculated have only orientative values, but they can serve to compare the solvents studied.

It is seen immediately that the solution of acid in SO_2 has a somewhat higher hydronating ability toward **1** than the neat acid, which is not surprising, because the polar solvent, SO_2, stabilizes the ion pair resulting from Eq. (1). By contrast, the effective acid strength is very much diminished in sulfolane, which indicates that

contrary to the expectations based on earlier literature reports [42], the latter is not a good solvent for an acid of the strength of sulfuric acid in applications where the B/AH ratio is close to stoichiometric. On the other hand, the strength of the acid was significantly enhanced in HFIP solution.

It is conceivable that the ordering of acid strength for H_2SO_4 in the two solutions, HFIP > SO_2, result from a difference in basicity, the latter solvent being more basic of the two. In the light of the results obtained in trifluoromethanesulfonic acid (below) it is more likely, however, that the acidity-enhancing properties of HFIP as solvent result from its exceptional hydrogen-bond donor ability [33]. It has been known that hydronation of weak bases, particularly organic, require the participation of two or more molecules of acid per mole of base [29,44,45], the excess being used for generation of the complex anion as in Eq. (5) (cooperative effect [33], formerly named homoconjugation [29,46]). The interaction with the solvent, Eq. (7), displaces the equilibrium of Eq. (5), thus increasing the effective concentration of acid available for reaction with the base. Such a solvent has been referred to as an anion stabilizing solvent [33,47].

$$n\text{SOH} + \text{A}^- \rightleftarrows (\text{SOH})_n\text{A}^- \qquad (7)$$

At a much lower level of acid strength, it had been shown that the concentration of HCl in dioxane necessary to change the color of an indicator decreases upon addition of a phenol [48], a phenomenon also explained by the interplay of Eqs. (5) and (7).[3] We have demonstrated that the effect of solvent on acid strength is also manifested in the (weak) superacid range, by studying the hydronation of hexamethylbenzene (HMB, **3**) shown in Eq. (6), in trifluoromethanesulfonic acid (TFMSA). It was shown before that 0.5 M **3** in TFMSA solution (molar

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[3] This method of acidity evaluation was introduced by Hantzsch [49].

ratio TFMSA:**3** = 22:1) is fully hydronated. The equilibrium concentration of **3**–H$^+$ is plotted as a function of the TFMSA:**3** ratio in solutions in SO$_2$ and SO$_2$FCl with chloroform as co-solvent, in Fig. 3, showing that half-hydronation is achieved for an acid to base ratio of about 5 [30]. Replacing SO$_2$ or SO$_2$FCl with trifluoro-acetic acid (TFA, Fig. 3) increases the amount of **3**–H$^+$ present, such that half-hydronation is achieved for an acid to base ratio of 3.8. It has been reported that TFA is converted to its con-jugate acid by FSO$_3$H–SbF$_5$ in SO$_2$ solution, whereas the solvent itself is not hydronated [50], thus proving that TFA is the stronger base. It follows that HMB is hydronated to a greater extent by TFMSA *in the more basic solvent.* The acidity-enhancing effect of TFA must origi-nate, therefore, in its ability to interact with the acid anion as in Eq. (7) (anion stabilization).

Replacement of TFA by HFIP (Fig. 3) brings about another increase in the hydronating ability of the mixture: **3** is now half-converted to **3**–H$^+$ at an acid to base ratio of 2.9. HFIP is, therefore
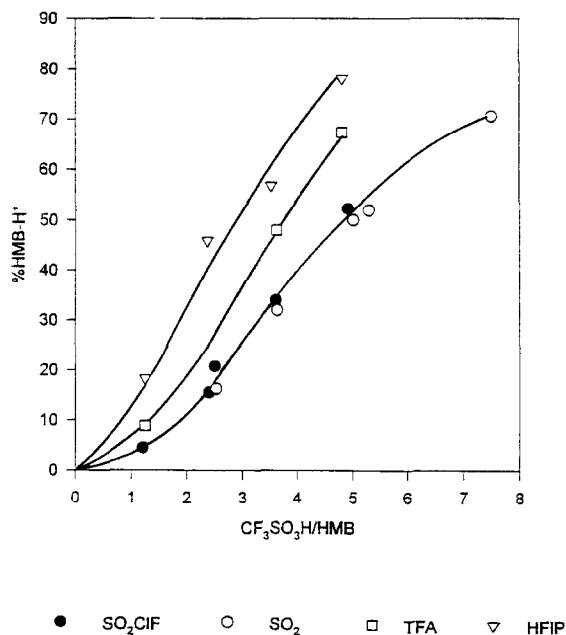
an even better anion stabilizing solvent than TFA, confirming that the hydrogen bond donat-ing ability does not necessarily parallel the acid strength of the solvent [15,51].

A similar increase in hydronating ability by the anion-stabilizing solvents TFA and HFIP was observed in the reaction of HMB (**3**) with 100% sulfuric acid. The experiments were less clean, because heating the solution of HMB in neat H$_2$SO$_4$ leads to some decomposition, which is almost entirely suppressed in the presence of the anion-stabilizing solvents. No measurable decomposition was seen by GLC in the HMB recovered from the solutions in TFMSA after recording the NMR spectra. The stability of HMB in the acids at much longer reaction times was not tested, however.

The anion stabilization by hydrogen bonding is essential for the hydronation of carbon bases, which cannot form hydrogen-bonded ion pairs like the nitrogen and oxygen bases, for example [29,52]. Similarly, in the composite Lewis–Brønsted superacids, the anion stabilization is provided by complexation with the Lewis acid. The cation is normally not specifically solvated, but it can be somewhat stabilized by ion pairing with the complex anion in addition to the minor stabilization by dielectric solvation. The hydro-gen bond energies are much lower than the bond strengths in the complex anions, but they are significant, nonetheless. For instance, com-plexation of the acetate anion with one, two, and three molecules of water in the gas phase liberates 15.8, 28.6 and 40.4 kcal/mol, respec-tively [53]. The energy evolved upon complexa-tion of a strong anion stabilizing solvent like TFA or HFIP with anions like trifluoromethane-sulfonate or hydrogen sulfate, which can form three primary hydrogen bonds, should be quite significant.

Fig. 3. Equilibrium concentration of hydronated HMB (**3**–H$^+$) in reaction of **3** (0.4 M) with TFMSA in solution (with CHCl$_3$ as co-solvent in all cases; see Section 2). ● SO$_2$FCl [30]; ○ SO$_2$ [30]; □ TFA; ▽ HFIP.

3.3. Comparison of basicities of weakly basic solvents

It was noted that the pK_{BH^+} may not de-scribe adequately the basicity of a liquid when it

is used as a solvent or part of a solvent mixture [17]. Instead, the relative basicities of weakly basic solvents can be evaluated from the reduction in hydronating ability of a strong acid toward a probe base by the solvent, relative to a standard solvent, considered non-basic. Indeed, if we consider the idealized description of the reaction of the base in the acid solution, Eq. (3), the equilibrium constant for the reaction is expressed by Eq. (8), in which γ are the activity coefficients.

$$K = \frac{[BH^+]}{[B]} \times \frac{\gamma_{BH^+}}{\gamma_B} \times \frac{1}{a_{H^+}} \qquad (8)$$

If the same probe base is placed in equal concentrations in two different acid solutions the acid strengths can be compared by Eq. (9):

$$\frac{a_{H^+}(2)}{a_{H^+}(1)} = \frac{[BH^+](2)}{[B](2)} \times \frac{[B](1)}{[BH^+](1)}$$

$$\times \frac{\gamma_{BH^+}(2)}{\gamma_{BH^+}(1)} \times \frac{\gamma_B(1)}{\gamma_B(2)} \qquad (9)$$

If the two media are in fact solutions of the same acid to which small amounts of two different basic solvents were added, the ratio of the hydron activity in the two media will provide a measure of the relative basicities of the two solvents. If the difference in basicities of the two is not large, the activity coefficient ratios for the probe molecule will cancel out to a good approximation. We can define a relative solvent basicity parameter, $SB(2, 1)$ as in Eq. (10):

$$SB(2, 1)$$

$$= \log\left(\frac{a_{H^+}(2)}{a_{H^+}(1)} \right)$$

$$= \log\left\{ \frac{[BH^+](2)}{[B](2)} \times \frac{[B](1)}{[BH^+](1)} \right\} \qquad (10)$$

The comparison is complicated, however, by the intervention of the anion-stabilizing properties of the two solvents, as demonstrated above by the behavior of SO_2 and TFA as solvents in the reaction of hexamethylbenzene (HMB, 3)

Table 2
Solvent basicity parameters relative to TFA, from the hydronation of HMB (3) by TFMSA[a,b]

No.	Basic solvent, i[c]	% 3–H$^+$	SB(i, TFA)[d]
1	—[e]	40.0	0
2	dichloroacetic acid (DCA)	24.4	−0.32
3	2-nitropropane	22.0	−0.37
4	chloroacetic acid (CAA)	18.3	−0.48
5	acetic acid (AA)	6.7	−1.00

[a] TFMSA = trifluoromethanesulfonic acid.
[b] 0.4 M 3 in 75:25 TFA–CHCl$_3$, molar ratio TFMSA:3 = 3.
[c] The basic solvent was added in an amount equimolecular to TFMSA.
[d] Solvent i, relative to TFA (Eq. (10)).
[e] Reference, no basic solvent added.

with trifluoromethanesulfonic acid (TFMSA). A correction is necessary to obtain a true comparison of basicities. Such a treatment was developed with HMB (3) as the probe molecule, dissolved (0.4 M) in TFA–CHCl$_3$ (75:25), reacting with TFMSA (3:1 molar ratio TFMSA/HMB). TFA is thus the reference, non-basic, solvent and it also provides the anion-stabilizing effect necessary for the acid–base reaction involving a hydrocarbon base like 3. The solvent basicity parameter of a solvent i is, therefore, defined as SB(i, TFA). The position of the hydronation equilibrium was determined by chemical shift interpolation between the values in the same solvent without addition of acid and the values in neat TFMSA. The basic solvents were compared pairwise; the principle and the operation of the experiments have been described [33]. For the definition of the SB parameters, mixtures with an equimolar amount of TFMSA and basic solvent were compared. The results are presented in Table 2.

3.4. Acid strength of liquid acids supported on silicagel

In a quantitative study of hydrogen bonding ability it was found that silica gel is a hydrogen bond donor better than acetic acid and poorer than hexafluoroisopropanol (HFIP). Not surprisingly, the $\Delta\delta^1$ values for mesityl oxide in

Table 3
Strengths of liquid acids adsorbed on silica gel[a] evaluated by the $\Delta \delta^1$ parameter

No.	Acid	$\Delta \delta^1$	$\Delta \delta^1$ in the neat acid
1	99.95% H_2SO_4	—	56.0
2	99.40% H_2SO_4	61.0	—
3	95.77% H_2SO_4	60.0	55.0[b]
4	89.80% H_2SO_4	57.0	53.0
5	86.35% H_2SO_4	—	51.0
6	85.0% H_2SO_4	53.0	—
7	80.0% H_2SO_4	51.5	48.0
8	100.0% $MeSO_3H$	45.0	41.0

[a] 5 mmol/g of silica gel.
[b] 58.40 for the acid in SO_2 solution.

Table 4
Reaction of *p*-DTBB with toluene catalyzed by H_2SO_4 and mixtures thereof[a]

No.	Time (h)	Unreacted DTBB (%)		
		cat. A[b]	cat. B[c]	cat. C[d]
1	0.5	88	65	46
2	1.0	85	60	40
3	2.0	81	53	—
4	2.5	—	—	32
5	3.5	78	48	30

[a] The reaction conditions are described in Section 2. See also Ref. [37].
[b] Neat H_2SO_4.
[c] 1:1 (v:v) H_2SO_4–TFA.
[d] 1:1 (v:v) H_2SO_4–HFIP.

80–100% sulfuric acid and in 100% methane-sulfonic acid were greater when the acids were adsorbed at less than one monolayer coverage on silica gel than for the neat acids and, in one case (95.8% H_2SO_4) for which data were available, greater even than for the solution of the acid in SO_2. The results are shown in Table 3.

3.5. Role of acidity enhancement by anion stabilization in catalysis

The reaction studied was transalkylation of *p*-di-*tert*-butylbenzene (*p*-DTBB) with toluene (Eq. (11)), catalyzed by sulfuric acid.

$$Me-C_6H_5 + p\text{-}Me_3C-C_6H_4-CMe_3$$
$$\rightarrow m\text{- and } p\text{-}Me-C_6H_4-CMe_3$$
$$+ C_6H_5-CMe_3 \qquad (11)$$
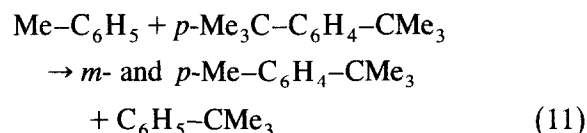
Transalkylation gives mainly *p*-*tert*-butyltoluene; the *meta* isomer was a minor product. Another minor product, *m*-di-*tert*-butylbenzene (*m*-DTBB), was formed by the isomerization of the starting material, but was not counted in the calculated conversion. Benzene, resulting from the transfer of both *tert*-butyl groups of the starting material, was also observed in trace amounts. In the simplest treatment, the reaction mechanism involves a reversible hydronation of *p*-DTBB as the first step (preequilibrium), followed by the transfer of a *tert*-butyl cation in the rate-determining step. The reaction rate increases with the amount of the conjugated acid of *p*-DTBB at equilibrium and is thus directly dependent upon the hydronating ability of the catalyst. Three catalysts were used: sulfuric acid (A), a 1:1 (v:v) mixture of sulfuric acid and TFA (B) and a 1:1 (v:v) mixture of sulfuric acid and HFIP (C). The progress of the reaction, expressed as the amount of unreacted DTBB as a function of time for the three catalysts, is shown in Table 4. It is seen that the addition of an anion-stabilizing solvent increases the rate of reaction and that HFIP, for which the transalkylation has nearly reached equilibrium at the end of the experiment, is more effective than TFA, exactly as it was in the measurements of acid strength presented above.

As another illustration, it was found that reactions catalyzed by strong acids like the hydrogen halides, sulfuric acid, *p*-toluenesulfonic acid, etc., are significantly accelerated when the acids are adsorbed onto the surface of silica gel [54]. Those findings are easily rationalized by the acidity enhancement through an anion-stabilizing effect of the silica gel surface found in our experiments.

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