Strength of Solid Acids and Acids in Solution. Enhancement of Acidity of Centers on Solid Surfaces by Anion Stabilizing Solvents and Its Consequence for Catalysis

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Abstract: A comparison of acidity of two solids, a poly(styrenesulfonic acid) (Amberlyst 15) and a perfluoroinated ion exchange polymer (Nafion-H, PFIEP) with the structurally related liquid acids methanesulfonic, sulfuric, and trifluoromethanesulfonic acid (TFMSA), was conducted with mesityl oxide as probe base (determination of the $\Delta\delta$[1] parameter) and for the fluorinated materials also with hexamethylbenzene as the probe base. It was found that Nafion-H is similar in strength to 85% sulfuric acid, whereas Ambelyst 15 is much weaker than 80% methanesulfonic acid or 60% sulfuric acid. Thus, the solids are much weaker acids than their liquid structural analogs. This seems to be a general property, because the rigidity of the solids prevents the acid groups/sites from cooperating in the transfer of a hydron, an essential feature in the manifestation of superacidity. The postulation of superacidity for a number of solid acids appears to have no basis in fact. On the other hand, the acidity of the groups/sites on the surface can be increased by the interaction with a nonbasic solvent, capable of forming strong hydrogen bonds with the anion of the site (anion-stabilizing solvent). The anion-stabilizing solvent generates a new liquid phase around the acid site; for appropriate structures of the solid acid and solvent this phase can be superacidic. The acidity-enhancing effect of the anion-stabilizing solvent was found to have an important effect in boosting the catalytic activity of the solid for carbocationic reactions.

Introduction

In the acid-catalyzed conversion of an organic compound, the acid strength of the catalyst has to be appropriately matched with the basic strength of the substrate. For instance, carbocationic reactions of alkenes can be induced in trifluoroacetic acid solution (H_o −3), as shown in the formation of trifluoro-acetates,[2] or on slightly acidic solids. Addition of acetic acid, however, requires the use of a small amount of stronger acid as catalyst; otherwise, a molecular addition may occur (at higher temperature).[3] A further increase in acidity is not beneficial, however, because it can lead to the conversion of the organic acid to its cation, thus removing the nucleophile, and the unwanted reaction of the carbocation with the olefin excess can occur. This loss of olefin is the fastest at the acidity at which the olefin is half-hydrated and leads to the formation of ill-defined oligomeric cations with cyclopentenyl structure.[4] At an even higher acidity level, particularly in the superacid range (assuming that the olefin can be dispersed fast enough into the acid to avoid polymerization during mixing), the olefin is fully converted to a persistent[5] alkyl cation and no further reaction is possible. On the other hand, a saturated hydrocarbon requires superacidic strength of the catalyst, to initiate a carbocationic

reaction by cleavage of a C−H[6] or a C−C bond.[1c,d,7] This matching of strength requires a good understanding of acid strength of various catalysts.

Mechanistic representations for the main classes of reactions in solutions have been secured for a long time.[8] As the chemistry of heterogeneous catalytic processes developed, the same representations were applied, sometimes after a study of the mechanism, but other times by simple analogy.[9] For acid catalysts, it was generally accepted that the carbocationic mechanisms established in solution should intervene on the solid surfaces as well.[9] It was also accepted that the manifestation and measurement of acidity should be the same for liquid and solid acids. Consequently, the application of the Hammett acidity function to solids was proposed and parameters H_o were reported, based on the change of color of indicators adsorbed on the surface,[10] or on the change in position of the indicator absorption band in the visible spectrum.[11,12]

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It was noted, however, that the Hammett approach was developed for acids-as-solvents, and it is not generally applicable even for acids in solutionn.[13,14] It was shown that acidity function studies are theoretically inapplicable to solids,[15] which explains the widely different H_o values obtained for the same material in different studies (*e.g.* Nafion-H: ≤ -12,[16ab] -10 to -12,[17] and -6.5;[18] sulfated zirconia: < -16[19] and -12[11]), as well as the lack of correlation of catalytic activity with H_o.[15b]

Alternative methods of acidity evaluation have been reported, but they are not adequately calibrated relative to known liquid acids, as discussed previously.[12] To elucidate the relationship between solid acidity and acidity in solution, we conducted experiments to determine the hydronating ability of structurally similar solid and liquid acids, toward the same probe bases under similar conditions, and we report our finding here. (In this study we concern ourselves with Brønsted acid.)

Experimental Section

Materials. Purification and handling of the liquid acids, solvents, and probe bases were described in a previous paper.[14c] Nafion-H (E. I. DuPont PFIEP resin 511X) was received as the potassium salt. To prepare the H form, the salt (25 g) was stirred with 10.5% HCl (133 mL) at 55−60 °C for 2 h, then the acid was decanted off and the exchange was repeated twice with fresh acid. The solid was filtered on a frit and washed with distilled water until the filtrate was neutral (1 L of water was needed). After being dried in air, the material contained 3.7% water (lost in the TGA below 150 °C). The residue was dried in a vacuum oven, with the air replaced by nitrogen as residual gas, for 11 h at 110−115 °C. Drying at higher temperature produces darkening of the polymer. Titration with NaOH gave for various batches of dry material an acidity content of 0.86−0.91 mequiv/g. Amberlyst 15, purchased as the H form, was dried in the same way. The catalytic substrates were used as purchased.

Analyses. NMR analyses of liquid and solid samples were conducted as described previously,[14] at 75.468 MHz and room temperature for mesityl oxide samples and at 22.5 MHz and 50−55 °C for hexamethylbenzene samples. The spectra of the probe bases on solid acids covered with solvents were acquired as for liquid samples.

Reaction of 1-Hexene with Toluene.[20] A mixture of 1-hexene (0.25 g, 2.97 mmol), toluene (3.33 g, 36.2 mmol), and tridecane (0.206 g, integration standard) was added to 1.02 g of Nafion-H (0.8625 mequiv acid groups/g) in a 10 mL round-bottomed flask, also containing a Teflon-coated stirring bar. A sample was taken and injected into the GC as a time zero mixture, then the flask was quickly stoppered and placed in a thermostated bath at 25.7 ± 0.3 °C. Samples were taken and analyzed at intervals.

In other experiments, the catalyst was soaked for 4 days in a 75:25 CF_3COOH−$CHCl_3$ mixture, then the solvent was evaporated on a vacuum line, until the solid remained only wet (10% weight increase,

with no liquid visible). The alkylation was conducted as above. At the end of the experiment, the liquid product was decanted off, fresh reactant mixture was addded, and the alkylation was repeated in the same manner.

All samples were analyzed by GLC on a 3 m × 3 mm o.d. column with 10% SP-1000 on Supelcoport. The progress of the reactions was monitored by the disappearance of 1-hexene, through conversion to products.

Isomerization of 1-Hexene.[21] Nafion-H (0.877 mequiv acid groups/g, 0.105 g) was placed in a 2-mL vial containing a Teflon-coated magnetic stirring bar, then a screw-cap with a Teflon-lined septum was tightened at the top of the vial, all inside a drybox. In the alternative approach, the catalyst was soaked for 6 days in trifluoroacetic acid (TFA) inside the drybox, then the liquid was removed by blowing nitrogen over the solid and the vial was capped as before. The vial was taken out of the drybox, 1-hexene (0.4 mL) was injected through the septum and the mixture was stirred in a thermostated bath, at 26 °C. Samples were taken through the septum and analyzed by GLC on a 30 m × 0.25 mm DB5 (95:5 methylphenyl-polysiloxane) capillary column with standard coating thickness. The column was held at 36 °C for 5 min, then heated to 140 °C at 40 °C/min.

Results and Discussion

1. Comparison of Acid Strengths of Solid Acids with Liquid Acid Analogs. If we choose two acids, I and II, which have the same acid site (XH) tied to a radical and backbone, respectively, of very similar structure, but one of them is a liquid and the other a solid, it is fair to say that the comparison of I and II gives a measure of the effect of "being a liquid" and "being a solid" upon acidity. It is also fair to say that if the nature and means of manifestation of acidity for liquids and solids are the same, I and II should be at least of comparable strengths.

It appeared immediately that the only solid acids that have close liquid analogs are those in which the acid site is bonded as a substituent to a backbone (Type A solid acids). Their strength is determined by the nature of the acid group (*e.g.* $-SO_3H$ > $-COOH$) and the electronic properties of the backbone. An increase in the number of acid groups (reduction in the distance between acid groups) increases the strength for the first hydron transfer. With the exception of the acid group-grafted[22] layered metal phosphates,[23] all acids in this class are organic polymers carrying acid groups, such as sulfonic,[22b,24,25] phosphonic,[26] and carboxylic,[22a,27,28] as substituents. The second group of solid acids (Type B), in which the acid site is part of the crystalline lattice, and the acidity is determined by the ability of the lattice to provide a tridimensional delocalization of the negative charge in the corresponding anion, like silica−alumina or zeolites, do not have liquid analogs. Here, the reduction in the distance between acid sites (*e.g.* by the increase in the Al/Si ratio in zeolites) was said to decrease the acid strength.[29,30]

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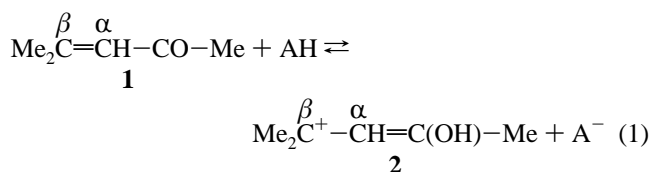(29) For example: Mortier, W. J. *J. Catal*. **1978**, *55*, 138.

(30) The existing data on the structure of acid sites of sulfated metal oxides (Arata, K. *Appl. Catal., A* **1996**, *146*, 3) does not allow a secure assignment of these catalysts. If the acid group is either a bisulfate molecule bonded to the surface through one oxygen atom (possibly with secondary coordination S=O→M) or a water molecule bonded to an adjacent Lewis site, the material is a Type A acid. If the acidic proton is bonded to a lattice oxygen and its strength is enhanced by an adjacent sulfate group, the material should be considered a Type B solid acid.

An increase in the distance between acid sites beyond a certain limit should in all cases eliminate their mutual interaction and the acid should have the same strength in the n-th ionization as in the first. Such independent, rather than consecutive ionization of acid groups was observed even in solution, for polybasic acids with very large molecules.[31]

We selected for investigation two pairs of acids: methanesulfonic (MSA) and Amberlyst-15, a poly(styrenesulfonic acid) cross-linked with *p*-divinylbenzene,[32] and trifluoromethanesulfonic acid (TFMSA) and Nafion-H (also referred to as perfluorinated ion exchange polymer, PFIEP), in which sulfonic acid groups are connected to a perfuoropolymer backbone by short perfluoroether chains. To widen the basis for comparison, several concentrations of sulfuric acid were also examined.

Nafion-H has been repeatedly referred to as a solid superacid and quantitative assessments of its acid strength were reported.[16a,b] The numbers given did not carry, however, any reference to an actual experiment, so it is likely that they were postulated on the basis of the presumption of superacidity (see also the work of Childs et al.[18]). The same presumption was accepted *a priori* in the evaluation of acid strength of Nafion-H and other solid acids from the broad-band NMR spectrum of adsorbed water at 4 K,[33] and from the IR spectra of adsorbed water or acetonitrile.[34] A subsequent study has shown, however, that water is a particularly unfortunate choice of probe base.[35] Also, both equilibrium[36a] and rate measurements[36b] have shown that there is no correlation between hydrogen bond donor ability and acid strength, except for a series of closely related materials.

In the present work, we used probe bases for which the positive charge in the conjugate acid is found mostly at carbon atoms, which makes them reasonable models for the substrates reacting with these acids in catalytic reactions.[31] The probe bases were used at near-stoichiometric ratio to the acid molecules or sites, providing a measure of *relative hydronating abilities* (RHA), rather than acidity functions.[14] The first series of experiments used mesityl oxide as the probe base (**1**, eq 1).[12]

$$Me_2C\!\!\!\overset{\beta}{=}\!\!\!\overset{\alpha}{CH}-CO-Me + AH \rightleftharpoons$$
$$\textbf{1}$$

$$Me_2\overset{\beta}{C^+}-\overset{\alpha}{CH}=C(OH)-Me + A^- \quad (1)$$
$$\textbf{2}$$

The chemical shift differences $\delta_{C(\beta)} - \delta_{C(\alpha)}$ ($\Delta\delta$) for acid–base ratios close to stoichiometric and the values, measured or interpolated, for the base in the 1:1 mixture ($\Delta\delta^1$) for a few acids are given in Table 1.[37] It appears immediately that the solid acids are much weaker than expected on the basis of the strength of their liquid analogs. Thus, Amberlyst15 is much weaker than neat MSA and even than 80% aqueous MSA or the similarly strong 60.21% H_2SO_4. As for Nafion-H, far from being a solid superacid as consistently claimed in the literature,[16,17,38] it is similar in strength to 85% H_2SO_4. We should point out that the heat of neutralization of amines and pyridines

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Table 1. Values of the $\Delta\delta$ Parameter for **1** Dissolved in Liquid Acids or Adsorbed Solid Acid Surfaces[a]

no.	acid	H_o	**1**/AH[b]	$\Delta\delta^b$
1	Nafion-H		1.0	50–51[c,d]
			1.5	45.5
2	Amberlyst15		0.368	33.6
			1.000	32.4[c,e]
			1.070	32.3
3	100% MSA	−7.60	0.728	45.42
			1.000	41.0[c,e]
			1.038	40.44
4	80.52% MSA	−4.35	0.643	40.86
			0.982	38.11
			1.000	38.0[c,f]
5	89.80% H_2SO_4	−9.00	0.540	67.35
			1.000	53.0[c,e]
			1.033	52.39
5	86.35% H_2SO_4	−8.50	0.523	65.72
			1.000	51.0[c,e]
			1.020	50.62
5	80.03% H_2SO_4	−7.50	0.522	60.33
			1.000	48.3[c,e]
			1.010	47.78
5	60.21% H_2SO_4	−4.50	0.548	44.64
			1.000	39.5[c,e]
			1.036	39.27

[a] For a collection of more extensive data, see ref 37. [b] Molar ratio of **1** to acid or to the number of acid sites. [c] $\Delta\delta^1$. [d] Broad signal. [e] Interpolated value. [f] Extrapolated value.

with a poly(styrenesulfonic acid) was also found consistently lower than the heat of neutralization with *p*-toluenesulfonic acid in solution.[39] These findings are understandable, because the acid–base reaction is not represented by eq 2, but by eq 3, instead.[5,13,14c,40]

$$AH + B \rightleftharpoons A^- + BH^+ \quad (2)$$

$$nAH + A^- \rightleftharpoons (AH)_nA^- \quad (3)$$
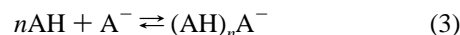
The clustering of the acid anion with excess acid was named "homoconjugation".[41] Since this term has been used for years to describe π-electron conjugation in systems with an interuption of the σ skeleton (*cf.* homoaromaticity[42]), we have been using "coperative effect" instead.[5,43] Its importance for the hydron transfer, particularly to carbon bases, has been discussed.[14c,43] The rigidity of the backbone prevents the acid groups of Nafion-H and Amberlyst15 from interacting in this manner. Swelling in certain polar solvents, notably water, leads to chain distortion and formation of clusters of sulfonic acid groups imbedded in pools of solvent.[44] The acidity of these pools, however is leveled by the basicity of the solvent. It follows, necessarily that acidity of solids is significantly lower than that of structurally similar liquid acids.

2. Effect of Solvents on Solid Acidity. The comparison of Nafion-H (PFIEP) with its structural analog, TFMSA, was also conducted with hexamethylbenzene (**3**) as probe base (eq 4).[5,14a,c] It has been determined that **3** is converted to **4** in $CHCl_3$–SO_2 solution to the extent of 5%, 16%, and 33%, for acid to base ratios of 1.2, 2.4, and 3.6, respectively.[5,14a,c] By contrast, the ^{13}C NMR chemical shifts for the signals of **3**

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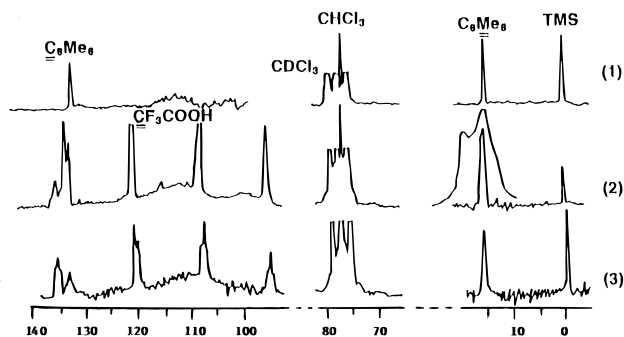
Figure 1. ^{13}C NMR spectra of hexamethylbenzene on Nafion-H (PFIEP), with CDCl$_3$ and TMS in the outer (coaxial) tube: (1) solvent, CHCl$_3$; (2) solvent, 75:25 TFA:CHCl$_3$; (3) sample of spectrum 2, after removal of the bulk solvent (see text).

deposited on Nafion-H in quantities as little as 1/4 molar to the acid groups, or at the same ratio in a chloroform solution just covering the solid (Figure 1, spectrum 1), were the same as on silica gel and in the pure solvent, respectively. The total inability of Nafion to hydronate **3**, first reported years ago,[43,45] is in line with the observations for mesityl oxide as base, discussed above.

$$AH + C_6Me_6 \rightleftharpoons A^- + C_6Me_6H^+ \qquad (4)$$
$$\qquad\quad \underset{\mathbf{3}}{} \qquad\qquad\quad \underset{\mathbf{4}}{}$$
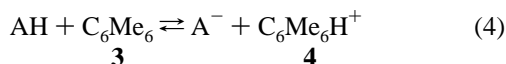
Having established that the anion-stabilizing solvents displace the acid−base equilibria in solution toward the ionized species,[14c,43] we checked then whether a similar effect would be seen here. Addition of **3** (0.039 g) as a solution in a 75:25 CF$_3$COOH−CHCl$_3$ mixture (0.7 mL) to Nafion-H (1.01 g), had a most remarkable consequence: each signal of **3** split in two. This splitting is seen clearly in Figure 1, spectrum 2, for the aromatic signal (132.66 and 135.80 ppm) and it is shown in the resolution-enhanced spectrum for the methyl signal (15.60 and 15.85 ppm). In each pair, one of the signals has the same chemical shift as for the system without TFA, whereas the other is shifted to lower field, as appropriate for the rapidly exchanging **3** $\rightleftharpoons$ **4** system.

The observation of equilibrium hydronation of **3** is the consequence of the interaction of TFA with the sulfonate anions, as shown previously for the reaction in solution.[14c] This *anion stabilization* by the solvent is described by eq 5. Different from

$$n\text{SOH} + A^- \rightleftharpoons (\text{SOH})_n A^- \qquad (5)$$
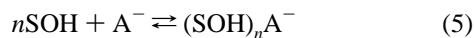
solution is the existence of two signals, which means that there are two types of molecules of free base **3**: one type exchanges rapidly with **4**, the other does not. The two cannot coexist in the same solution. Therefore, the anion-stabilizing solvent, TFA, has induced a phase separation in the system, from two phases (solid and liquid) to three phases, solid, bulk liquid, and the third phase, which we can call *the superacid phase*, because it is able to hydronate the hydrocarbon **3**. This representation of the process was also substantiated by the modifications observed in the spectrum upon cooling the sample to 0 °C (Figure 2, spectrum 4), when the low field signal for the aromatic carbon disappeared, because the intramolecular hydrogen shift within the ion **4** has slowed down at this temperature.[14a] Contrastingly, the upfield signal is somewhat sharper at 0 °C, indicating that there is exchange between the two signals, such that somewhere above 55 °C the signals would
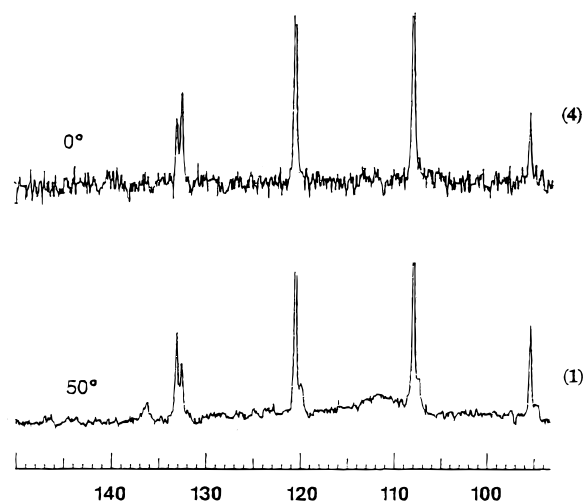
(45) Fǎrcaşiu, D.; Marino, G. M.; Kastrup. R. V.; Rose, K. D., presented at the 185th National Meeting of the American Chemical Society, Seattle, WA, 1983; Abstr. ORGN 160.
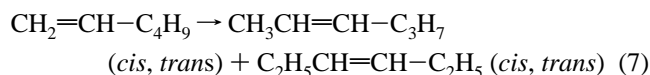

Figure 2. Variable-temperature ^{13}C NMR spectra of hexamethylbenzene in 75:25 TFA:CHCl$_3$ on Nafion-H (PFIEP): (1) at 50 and (4) at 0 °C.

coalesce. The changes are reversed upon heating the sample back to 50 °C. (Note that both spectra, 1 and 4, in Figure 2 are expanded relative to those in Figure 1.)

The superacid phase could be separated from the bulk liquid phase by the following simple experiment: The tube with the mixture (0.071 g of **3**, 1.52 g of Nafion-H, 1.2 mL of mixed solvent) was moved into the drybox, its content was poured onto a frit, and the liquid was allowed to filter without suction. The solid, which was still wet (the particles tended to lump together, rather than flow freely), but with no liquid visible, was immediately introduced into another NMR tube, capped airtight, and its ^{13}C NMR was run. As seen in Figure 1, spectrum 3, the signals were weaker and somewhat broader than in the sample before the elimination of the bulk liquid phase. Of the aromatic carbon signals, only the low field peak (134.79 ppm) was present; of the two original solvents, the TFA signals were still present, but the signal of chloroform was gone. Thus, the superacid phase consists of a number of anion-stabilizing solvent molecules, associated with the acid group on the surface, containing dissolved, partially hydronated, base. It is not clear whether the superacid phase is continuous and covers all the surface or consists of isolated clusters ("droplets") of solvent molecules surrounding the individual acid groups.

In the continuation of the experiment, the tube was again moved into the dry-box and solvent of the same composition was added. The ^{13}C NMR spectrum of this mixture contained all the signals of the original spectrum for solvents and base in the two liquid phases ("bulk" and superacid) seen in Figure 1, spectrum 2, except that the signals for the base were much weaker because part of the base had been discarded with the original bulk solution.

The phase separation experiment helped also establish that the solvent effect observed was a surface phenomenon and was not connected to swelling of the polymer which would have increased the contact of the probe base with the acid groups inside the solid. Note also that there is not much difference in the degree of swelling by chloroform and by TFA (both are small, only solvents which are both basic and hydroxylic, like methanol, lead to a large degree of swelling) and there was no difference between the results in the presence of chloroform or with no solvent added. Only addition of TFA to the solvent generates the superacid phase. Most important, however, if the base had been brought inside the polymer by the solvent, filtration could not have removed so quickly all the chloroform and non-hydronated hexamethylbenzene (**3**); nor could simple
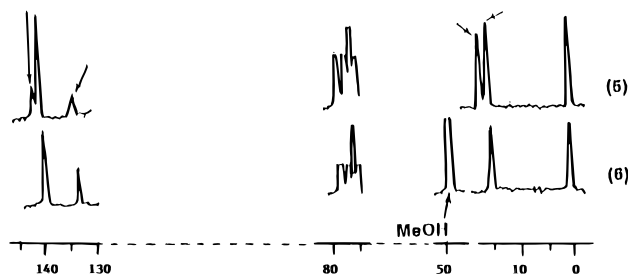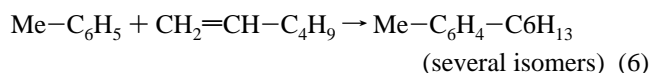
Figure 3. ^{13}C NMR spectra of hexamethylbenzene in 90:10 HFIP: CHCl$_3$ solution on Nafion-H (PFIEP), with CDCl$_3$ and TMS in the outer (coaxial) tube: (5) as prepared and (6) after addition of methanol.

addition of solvent afterwards reextract so quickly **3** into the liquid phase.

When the base **3** was added as a solution in a 90:10 mixture of hexafluoro-2-propanol (HFIP) and CHCl$_3$ to Nafion-H, the signals of **3** were also split, but the exchanging signal in each pair was moved farther downfield than for the system with TFA. Complete separation is achieved even for the methyl signals, appearing at 15.01 and 16.47 ppm (Figure 3, spectrum 5; the signal between those for the aromatic carbons at 133.87 and 140.69 ppm is a spike of the HFIP quartet). This behavior was expected on the basis of our previous work, which showed that HFIP is a better anion-stabilizing solvent than TFA and gives a higher degree of hydronation by the acids in solution as well.[14c] Addition of an excess of methanol, a much stronger base than **3**, restores the spectrum of the non-hydronated **3** (Figure 3, spectrum 6).[43]

3. Effect of Anion Stabilizing Solvents on the Catalytic Activity of Solid Acids. The experiments described in the previous section have shown that an organic base moves from the bulk liquid to the superacid phase and back, slowly on the NMR time scale. It remained to be seen whether this transfer is fast enough on the chemical time scale to allow acid-catalyzed reactions to be influenced by the increase in strength of the acid sites by the anion-stabilizing solvent in the superacid phase. For that purpose, we have examined two reactions, the alkylation of toluene with 1-hexene (eq 6) and isomerization of the double bond in 1-hexene (eq 7) on Nafion-H, both at room temperature (26 °C).

$$Me-C_6H_5 + CH_2=CH-C_4H_9 \rightarrow Me-C_6H_4-C6H_{13}$$

$$\text{(several isomers) (6)}$$

$$CH_2=CH-C_4H_9 \rightarrow CH_3CH=CH-C_3H_7$$

$$\text{(cis, trans)} + C_2H_5CH=CH-C_2H_5 \text{ (cis, trans) (7)}$$

The progress of the first reaction, followed by GLC, is expressed in Table 1 by the quantity of unreacted hexene (limiting reactant) at a given time. In all cases, a small amount of dialkylated product (dihexylbenzene isomers) was observed as well. The conversion on the dry catalyst was much slower than that on the catalyst covered with TFA. Even after three batches of reactants had been converted with the same catalyst, the solid acid treated with the anion-stabilizing solvent was much better. Thus, in the reaction of Batch 4 on the latter, it took 3 h for the concentration of hexene to drop from 87.9% to 37.6%, whereas it took 18.5 h (20.8 − 2.25) for a decrease from 89.2% to 41.2% on the fresh, but untreated ("dry"), catalyst. In separate experiments we determined that TFA deposited on silica gel did not catalyze the alkylation reaction, but a slow addition with formation of trifluoroacetate esters[2] occurred. That the trifluoroacetate esters were not intermediates in reaction was tested by treating a mixture of 2- and 3-hexyl trifluoroacetates
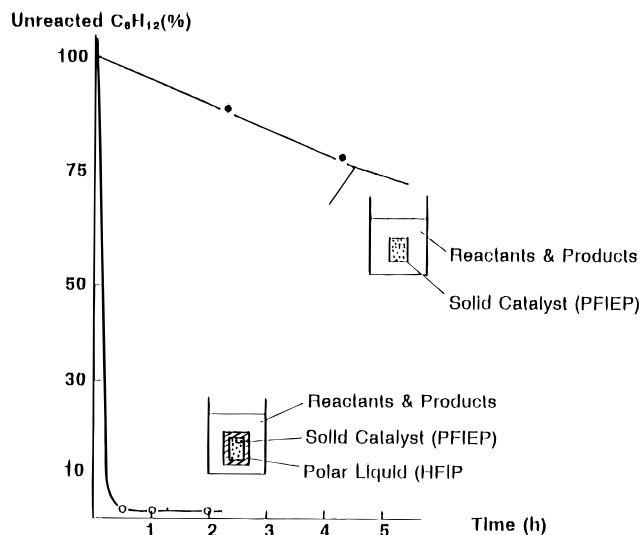

Figure 4. Conversion of 1-hexene by reaction with excess toluene, catalyzed by Nafion-H (PFIEP): (●) two-phase system (dry catalyst and hydrocarbon mixture) and (○) three-phase system (catalyst wet with HFIP and hydrocarbon mixture).

Table 2. Effect of the Anion-Stabilizing Solvent on the Alkylation of Toluene with 1-Hexene Catalyzed by Nafion-H[a]

			unreacted 1-hexene, %			
			treated catalyst[b]			
no	time h	dry catalyst[b]	batch 1	batch 2	batch 3	batch 4
1	0.0	100	100	86.7[c]	89.8[c]	87.9[c]
2	1.0		15.9[d]	31.1	59.3	67.5[e]
3	2.0		4.7			
4	2.25	89.2			18.2	
5	3.0		2.7			37.6
6	3.5				13.3	
7	4.25	79				
8	5.5				11.9	
9	19.0			2.5		
10	20.8	41.2	2.0			4.3
11	28.1	34.3				
12	48.6	25.1				
13	74.0				2.1	
14	117.9	16.2				
15	140.3	10.0				
16	189.3	6.6				

[a] The reaction conditions are described in the Experimental Section. See also ref 20. [b] With TFA. [c] The initial composition includes some material remaining from the previous batch. [d] At 1.05 h. [e] At 1.02 h.

prepared by addition, with toluene and dry, untreated, Nafion-H. No reaction took place.

The decrease in activity in Batches 1 to 4 was not caused by loss of TFA, because addition of TFA to the catalyst did not restore the activity. Instead, the catalyst was deactivated by water, because the reagents were used as purchased, without drying, and also the samples were taken by unstoppering the reaction flask without protecting it from the atmospheric moisture. To test this hypothesis, we added a small amount of trifluoroacetic anhydride to the catalyst after Run 4 and reacted another batch of hexene and toluene on it. The rate of conversion of hexene in this experiment was the same as in Batch 1.

Replacement of TFA with HFIP had similar results, only the catalyst was even more active: the unreacted hexene dropped below 5% in only 30 min. The comparison of the catalyst treated with HFIP with the untreated catalyst in the alkylation reaction is presented in Figure 4.

When the two types of catalysts were compared in the isomerization of 1-hexene, it was found that the dry catalyst

gave 12.1% conversion (87.9% unreacted 1-hexene) after 4.35 h, whereas the TFA-covered catalyst gave 78.0% conversion (22.0% unreacted 1-hexene) after 0.43 h and 88.0% conversion (12% unreacted 1-hexene) after 0.8 h. In both cases only double bond migration, with the formation of *cis* and *trans* isomers of 2- and 3-hexene, was observed, but no chain branching. Small amounts of trifluoroacetate esters were formed as side products on the treated catalyst.

Conclusions

The examination of two Type A solid acids together with their structurally related liquid analogs has demonstrated that the solids are much weaker acids than their liquid counterparts. This seems to be a general property, because the rigidity of the solids prevents the acid groups/sites from cooperating in the transfer of a hydron according to eq 3, an essential feature in the manifestation of superacidity. The postulation of super-acidity for a number of solid acids appears to have no basis in fact. On the other hand, the acidity of the groups/sites on the surface can be increased by the interaction with a non-basic solvent, capable of forming strong hydrogen bonds with the anion of the site (anion-stabilizing solvent), according to eq 5. The anion-stabilizing solvent generates a new liquid phase around the acid site; for appropriate structures of the solid acid and solvent this phase can be superacidic. Such liquid super-acidic phases, containing carbocations in solutions, described as "sludges", have been known to be formed at the surface of catalysts like the aluminum halides and to be the locus of the catalytic alkane conversion.[46] The acidity-enhancing effect of anion-stabilizing solvents was found to have an important effect in boosting the catalytic activity of the solid for carbocationic reactions. When such an assistance is not available or not possible, an alternative mechanism may intervene in the generation of the carbocationic or cationoidic intermediates from the less reactive precursors like alkanes, for example one-electron transfer,[15,47] or reversible dehydrogenation by the action of a noble metal cocatalyst.

(46) (a) Schneider, A. U.S. 3,128,316, **1964**. (b) Fărcaşiu, D.; Fisk, S. L.; Melchior, M. T.; Rose, K. D. *J. Org. Chem*. **1982**, *47*, 453 and references therein. (c) Fărcaşiu, D. *Acc. Chem. Res*. **1982**, *15*, 46. (d) Ghenciu, A.; Fărcaşiu, D. *Catal. Lett*. **1997**, *44*, 29.

(47) Ghenciu, A.; Fărcaşiu, D. *J. Mol. Catal. A*. **1996**, *109*, 273.