

A Strong Acid that Does Not Protonate Water

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The nature of solvated acids in benzene and chlorinated hydrocarbon solvents is sensitively revealed by IR spectroscopy. Two similarly strong, structurally related acids, triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) and the N–H acid bis(trifluoromethylsulfonyl) imide ($(\text{CF}_3\text{SO}_2)_2\text{NH}$), behave quite differently toward water in these media. Triflic acid protonates water at the one-equivalent level to give the hydronium ion, H_3O^+ . By contrast, bis(trifluoromethylsulfonyl) imide forms a simple hydrate, $(\text{CF}_3\text{SO}_2)_2\text{NH}\cdots\text{OH}_2$, even with water at the two-equivalent level. The difference arises from the differing abilities of the conjugate base anions to engage in H-bonding and ion pairing. It illustrates how acidity in low-dielectric media is critically dependent on the nature of the conjugate base anion. $\nu\text{O}-\text{H}$ and $\nu\text{N}-\text{H}$ stretching frequencies indicate that the H-bonding acceptor ability for solvents toward acidic protons increases in the order carbon tetrachloride < benzene \sim 1,2-dichloroethane < water. With benzene, a marked tendency for acidic protons to H-bond to the π -face of the arene ring is noted and an IR signature of this solvation mode is observed.

Introduction

Despite their importance to acid catalysis, the precise nature of the strongly acidic species present in organic solvents is frequently unknown and often goes unspecified. A catchall formulation, written as H^+ or $\text{H}_{\text{solvent}}^+$, often suffices for a description of the active protonating species in an acid-catalyzed reaction. The ubiquitous presence of trace water in organic solvents raises the inevitable question of whether a hydronium ion (H_3O^+ , H_5O_2^+ , etc.) or the added acid (HA) is the active protonating species. In this paper, we show that these contrasting possibilities can exist under the same conditions by simply changing the conjugate base anion (A^-).

We chose triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) for this study because of its widespread contemporary usage.¹ It has become the choice over sulfuric acid in many modern applications because under most conditions it is the stronger acid, it has better miscibility with a variety of solvents, and it is chemically less complicated. So-called 100% sulfuric acid is not a pure compound, and the bisulfate anion can get involved in unwanted byproduct chemistry as a nucleophile or oxidant. By contrast, triflate anion is essentially inert. We chose $(\text{CF}_3\text{SO}_2)_2\text{NH}$ to make comparisons of a typical oxyacid (i.e., an O–H acid) with a structurally related N–H acid. Trifluoromethylsulfonyl imides have attracted attention recently as the strongest gas-phase acids measured to date.^{2,3} Bis(trifluoromethylsulfonyl) imide is only a few orders of magnitude weaker than triflic acid when $\text{p}K_{\text{a}}$ values are measured in acetic acid solution.⁴ The neat acid strength of $(\text{CF}_3\text{SO}_2)_2\text{NH}$ cannot be compared to that of triflic acid using the familiar H_0 scale because $(\text{CF}_3\text{SO}_2)_2\text{NH}$ is a solid, not a liquid. Both acids are commonly used in dilute organic solvents, so these are the conditions we have chosen to investigate. We have recently investigated acidity in O-donor solvents and noted a strong predilection for dissolution of H^+ , i.e., the formation of

short, strong, low-barrier (SSLB) bridging H-bonds in $\text{H}(\text{solvent})_2^+$ type species.^{5,6} In the present work we investigate weaker donor, low-dielectric solvents, including benzene, 1,2-dichloroethane, and carbon tetrachloride.

Unexpected findings can result from considerations of strong acids in low dielectric solvent with water at the one-equivalent level. For example, the unexpected stabilization of the $[\text{Fe}(\text{H}_2\text{O})\text{-(TPP)}]^+$ ion (TPP = tetraphenylporphyrinate) rather than the formation of the very stable μ -oxo dimer, $(\text{TPP})\text{Fe}-\text{O}-\text{Fe}(\text{TPP})$, can be understood in terms of unusual solvation effects and acidity considerations in toluene solution.⁷

Experimental Section

Anhydrous triflic acid (Aldrich, 99% purity) and bis(trifluoromethylsulfonyl) imide (Fluka, $\geq 95\%$ purity) were used without further purification. Solutions of the acids were prepared by dissolving weighed amounts in benzene, 1,2-dichloroethane, or carbon tetrachloride. The defined $\text{H}_2\text{O}/\text{HA}$ ratio in solutions was obtained by mixing the calculated volumes of dry HA solutions with water-saturated solutions of benzene (0.032 M), 1,2-dichloroethane (0.1 M), and CCl_4 (0.0055 M).

All solutions for IR spectra were prepared in a glovebox (H_2O and O_2 level ≤ 1 ppm). IR spectra were obtained in the 4000–500 cm^{-1} range (32 scans, resolution 2 cm^{-1}) on a Shimadzu-8300 FT-IR spectrometer installed in the glovebox. A cell with Si windows was used. To avoid interference, the windows were wedge-shaped rather than coplanar.

Results and Discussion

Triflic Acid in Organic Solvents. The nature of triflic acid has been investigated in gaseous, liquid, and solid phases as well as in an argon matrix.⁸ These data provide an excellent basis for assigning the IR spectra of monomers and dimers of the acid in organic solvents. In addition, the calculated spectrum for an isolated molecule in vacuo by ab initio methods⁹ compares favorably with the experimental spectrum of the

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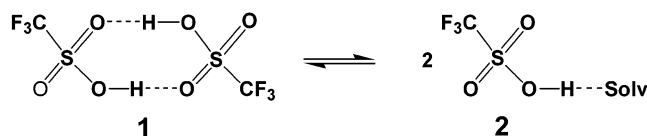
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TABLE 1: IR Frequencies for Monomeric and Dimeric Triflic Acid

| attribution ^{8,9} | dimer in CCl ₄ | liquid acid ⁸ | monomer | | | |
|----------------------------|------------------------------|--------------------------|------------------|------------|--------|------------------------|
| | | | CCl ₄ | benzene | DCE | Ar matrix ⁸ |
| ν OH | 3030 | 3040 br | 3442 | 3233 | 3205 | 3469 |
| ν_{as} SO ₂ | 1408 | 1414 | 1436, 1407 | 1427, 1409 | 1421 | 1444, 1412 |
| ν_s CF ₃ | 1251 | 1249 sh | 1251 | 1252 sh | 1251 | 1256 |
| ν_{as} CF ₃ | 1228–1215 | 1218 | 1221–1212 | 1214 | 1214 | 1226, 1208 |
| ν_s SO ₂ | 1149 | 1149 | 1150 | 1152 | 1150.5 | 1156 |
| ν S–OH | 919 | 925 | 867 | 884 | ~885 | 874 |

monomer, so these spectra provide a good point of departure for assigning the spectra of the monomeric acid perturbed by solvation in organic solvents.

The IR spectrum of triflic acid in CCl₄ solution is concentration dependent. At high concentrations (>0.1 M), ν O–H appears as a broad band at 3030 cm⁻¹, typical of H-bonded molecules. As the concentration is decreased, the intensity of this band decreases at the expense of a single new band growing in at 3442 cm⁻¹, becoming the only band at low concentrations (0.002 M). This band is therefore assigned to the free O–H group of monomeric acid. It is similar to that of dilute, monomeric, triflic acid in an Ar matrix (3469 cm⁻¹).⁸ The somewhat lower frequency in carbon tetrachloride is consistent with CCl₄ being a better H-bond acceptor than Ar. The existence of only one band for the H-bonded species and the absence of intermediates indicate that it arises from dimer in a monomer–dimer equilibrium.



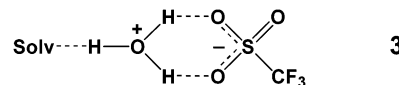
The spectrum of the dimer in the entire frequency range is not unlike that of the neat acid (Table 1), suggesting it, too, is a dimer.

In benzene and 1,2-dichloroethane (DCE) solutions, the spectra are no longer concentration dependent at triflic acid concentrations less than 0.1 M. Single ν O–H bands are observed at frequencies considerably higher than for dimers but distinctly lower than for monomers in CCl₄ solution or Ar matrix. This is consistent with the existence of monomers whose O–H bonds experience the stronger H-bonding acceptor properties of benzene and DCE. The data are compared in Table 1 along with prominent bands arising from the triflate anion. We note that the ν_s SO₂ and ν_s C–F stretching frequencies are practically insensitive to the degree of association and to the strength of solvation. On the other hand, when comparing the dimer and monomer in CCl₄ solution, ν S–OH differs by 52 cm⁻¹ and ν_{as} SO₂ differs by 28 cm⁻¹. Smaller changes are observed for different solvates of the monomer. As will be shown later, these bands are the most sensitive to the character of cation–anion interactions.

Formation of [H₃O][CF₃SO₃]. The addition of water to benzene or DCE solutions of triflic acid results in the immediate formation of a hydrated product. Figure 1a shows the IR spectrum of 0.0225 M triflic acid in DCE containing 0.0075 M water. Subtraction of the spectrum of monomeric triflic acid (0.03 M in DCE) with a coefficient $f = 0.5$ gave the spectrum of the hydrated species (Figure 1b). The concentration of the anhydrous acid is given by $f \times 0.03 = 0.015$ M, making the concentration of the hydrated form $0.0225 - 0.015 = 0.0075$ M. This corresponds to the concentration of added water, proving that the subtracted spectrum arises exclusively from a

1:1 hydration product. In a similar manner, the spectrum of a 1:1 hydrated product (Figure 1c) was obtained in benzene solution. It is essentially coincident with that in DCE. The hydration product could not be observed in CCl₄ solution due to low solubility.

The IR spectrum of the product has the characteristically broad ν O–H band (~600 cm⁻¹ width at half-height) at low frequency (~2750 cm⁻¹) of the H₃O⁺ ion.^{5,10} Such a low frequency can only arise if there is strong H-bonding of H₃O⁺ to the triflate anion, as seen in the crystal structure¹¹ and as proposed in triflic acid having 1:1 water content, where the frequency is also ca. 2750 cm⁻¹.¹² A strongly ion-paired structure is also consistent with the observation of minimal spectral differences between benzene and DCE solution. The doubly degenerate δ O–H bending deformation (E type in C_{3v} symmetry) is split into two components at 1774 and 1663 cm⁻¹. This indicates that H₃O⁺ is H-bonded to the anion in a nonequivalent manner, lowering its symmetry from C_{3v} to C_s . The most likely structure, **3**, has two of the three H-atoms interacting with the anion and the third interacting with a solvent molecule.



In the case of benzene as solvent, bands indicative of π -solvation are observed at 1810 and 1956 cm⁻¹ (marked with asterisks in Figure 1c). We have also observed these bands with water dissolved in benzene. Strong evidence has been accumulated for weak H-bonding between a water proton and the π -electrons of benzene using other indicators from IR, Raman,

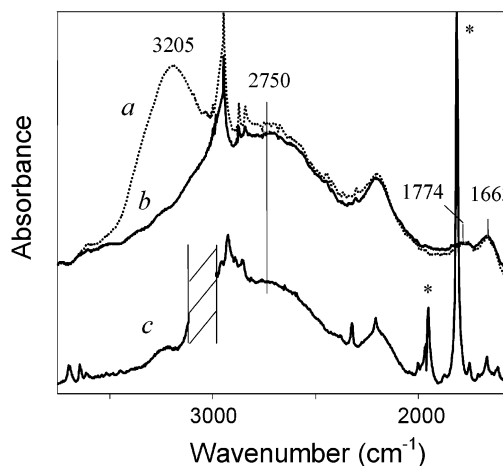


Figure 1. IR spectra of DCE solutions of 0.0225 M triflic acid containing 0.0075 M H₂O before (a) and after (b) subtraction of the remaining free acid. Spectrum c was obtained in the same way from IR spectra of benzene solution of 0.0667 M triflic acid + 0.01 M H₂O. Both spectra b and c belong to [H₃O][CF₃SO₃]. Nonsubtracted bands of benzene that form a π -complex are marked with an asterisk.

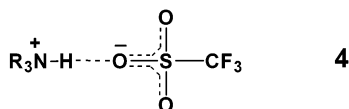
TABLE 2: IR Spectra of Triflate Anion in $[\text{H}_3\text{O}]^+$ and $[\text{H}_5\text{O}_2]^+$ Salts Compared with $[\text{Oct}_3\text{NH}][\text{CF}_3\text{SO}_3]$ and Crystalline $[\text{NH}_4][\text{CF}_3\text{SO}_3]$

| attribution (C_s) | $[\text{Oct}_3\text{NH}]^+$ salt in CCl_4 (Δ) ^a | attribution (C_{3v}) ^b | $[\text{H}_3\text{O}]^+$ salt in C_6H_6 or DCE ^c | $[\text{H}_5\text{O}_2]^+$ salt in DCE ^c | $[\text{NH}_4]^+$ salt |
|--|---|--|--|--|------------------------|
| $\nu_{\text{as}}\text{SO}_2(\text{A}'')$ | 1293 (143) | $\nu_{\text{as}}\text{SO}_3(\text{E})$ | ~ 1267 | ~ 1262 | 1260 |
| $\nu_s\text{CF}_3(\text{A}')$ | 1235 (16) | $\nu_s\text{CF}_3(\text{E})$ | ~ 1215 | 1198 | 1236 |
| $\nu_{\text{as}}\text{CF}_3(\text{A}'+\text{A}'')$ | 1214 | $\nu_{\text{as}}\text{CF}_3(\text{A})$ | | | |
| $\nu_s\text{SO}_2(\text{A}')$ | 1167 (-17) | | 1155 vw | 1198 | 1181 |
| $\nu\text{S}-\text{OH}(\text{A}')$ | 1027 (-160) | $\nu_s\text{SO}_3(\text{E})$ | 1034 | 1026 | 1035 |

^a Differences with monomeric triflic acid in CCl_4 . ^b Local symmetry for SO_3 and CF_3 groups. ^c Spectrum of SO_3 group is close to C_{3v} attribution despite lower actual symmetry in **3** or **5**.

and NMR data.^{13–17} These bands are assigned to combination modes because they do not belong to the fundamental transitions of benzene.¹⁸

Consideration of the IR spectrum of the triflate anion corroborates the assignment of structure **3** to the $[\text{H}_3\text{O}][\text{CF}_3\text{SO}_3]$ ion pair. The proposed bidentate H-bonding of the triflate anion in **3** can be contrasted to monodentate H-bonding in the tri-*n*-octylammonium triflate structure. At low concentrations, tri-*n*-octylammonium triflate dissolves in CCl_4 as a monomeric ion pair, **4**. As shown in Table 2, it develops a pattern of IR



bands similar to that of monomeric triflic acid in CCl_4 . This indicates that the symmetry of the triflate anion is the same, C_s . Compared to triflic acid in CCl_4 , the $\nu_{\text{as}}\text{SO}_2$ frequency of **4** decreases by 143 cm^{-1} and $\nu\text{S}-\text{O}$ increases by 160 cm^{-1} . This reflects a partial equalization of bonds in SO_3 groups of the ion relative to the covalent acid.

On the other hand, the spectrum of the triflate ion in $[\text{H}_3\text{O}][\text{CF}_3\text{SO}_3]$ more closely approaches a structure having C_{3v} symmetry. As shown in Table 2, the set of bands is similar to those of $[\text{NH}_4][\text{CF}_3\text{SO}_3]$, whose solid-state structure is known from X-ray data to have more or less equivalent H-bonding to all three O-atoms.¹⁹ Thus, the bands at 1267 and 1034 cm^{-1} can be designated $\nu_{\text{as}}\text{SO}_3(\text{E})$ and $\nu_s\text{SO}_3(\text{A})$, respectively. However, the appearance of a weak band at 1155 cm^{-1} , which is forbidden by selection rules under C_{3v} symmetry, suggests that the actual symmetry is lower. As discussed below, the IR spectrum of the triflate ion in the H_3O^+ ion pair is very similar to that in the H_5O_2^+ ion pair. Since H_5O_2^+ ion can form only two geometrically equivalent H-bonds with a counterion, it cannot have a C_{3v} interaction with the triflate anion. Thus, the IR spectrum of $[\text{H}_3\text{O}][\text{CF}_3\text{SO}_3]$ is in accordance with the structure depicted in **3**, approaching, but not having, C_{3v} symmetry H-bonding interactions about the cation and anion.

Formation of $[\text{H}_5\text{O}_2][\text{CF}_3\text{SO}_3]$. Increasing water content in DCE solutions of triflic acid leads to the formation of $[\text{H}_5\text{O}_2][\text{CF}_3\text{SO}_3]$. The H_5O_2^+ cation is characterized by vibrations associated with (a) the terminal water molecules and (b) the unique O–H–O bridge, a prototypical short, strong, low-barrier (SSLB) H-bond.⁶ The water molecules show $\nu_s\text{OH}$, $\nu_{\text{as}}\text{OH}$ stretching and δHOH bending vibrations, whereas the central OHO fragment shows $\nu_{\text{as}}\text{OHO}$, $\nu_s\text{O}\cdots\text{O}$ stretching and δOHO , γOHO bending vibrations.^{5,20} In solution spectra, the two OH stretching vibrations of the water molecules are usually overlapped, giving one broad band.⁵ In the case of $[\text{H}_5\text{O}_2][\text{CF}_3\text{SO}_3]$, however, two well-resolved broad bands at 3460 and 3050 cm^{-1} are apparent and the δHOH band at 1739 cm^{-1} is distinctly

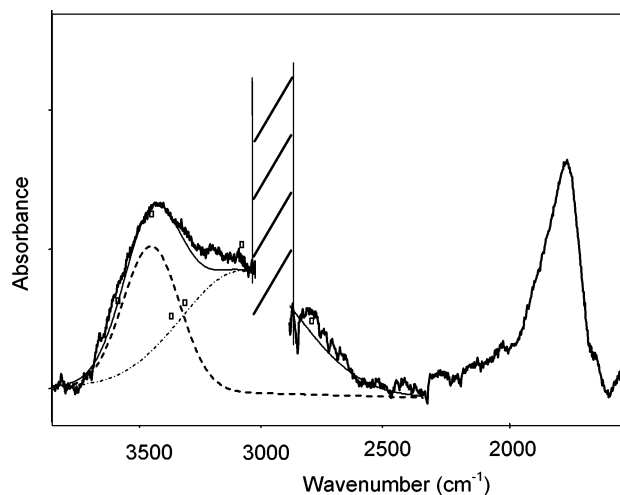
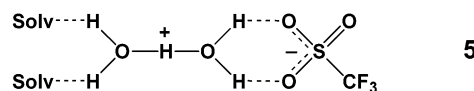


Figure 2. IR spectrum of H_5O_2^+ triflate in DCE showing deconvolution of $\nu\text{O}-\text{H}$.

asymmetric (see Figure 2). These peculiarities can be understood in terms of structure **5**, where one end of the H_5O_2^+ ion is



strongly ion-paired and the other end is more weakly H-bonded to DCE solvent molecules. The characteristic $\nu_{\text{as}}\text{OHO}$ of the H_5O_2^+ ion is observed as a broad band centered at 1085 cm^{-1} . The triflate anion bands are similar to those in **3**, but distinguishable (Table 2).

$[\text{H}_5\text{O}_2][\text{CF}_3\text{SO}_3]$ could not be observed in benzene solution due to low solubility.

IR spectroscopy has been used to study the ionization of neat triflic acid upon incremental additions of water.¹² At ca. 1:1 mole ratio of water and triflic acid, it was proposed that an acid hydrate, $\text{CF}_3\text{SO}_3\text{H}\cdots\text{OH}_2$, is in equilibrium with an ion-paired hydronium ion salt, $\text{CF}_3\text{SO}_3^-\cdots\text{H}_3\text{O}^+$. However, the IR spectra used to support this formulation are more simply interpreted in the same way as we have done in organic solvents, i.e., in terms of initial ionization to give the H_3O^+ ion, followed by the formation of the H_5O_2^+ ion as the water concentration increases.

Bis(trifluoromethylsulfonyl) Imide in Organic Solvents. The IR spectra of $(\text{CF}_3\text{SO}_2)_2\text{NH}$ in dilute CCl_4 , DCE, or benzene solution ($<0.02\text{ M}$) are not concentration dependent and correspond to monomeric molecules. The structural analogy to triflic acid and the similarity of their IR spectra as monomers make assignments straightforward (Table 3).

The $\nu\text{N}-\text{H}$ frequency of $(\text{CF}_3\text{SO}_2)_2\text{NH}$ in the three solvents decreases in order $\text{CCl}_4 > \text{DCE} \sim \text{benzene}$, reflecting increasing H-bond acceptor ability: $\text{CCl}_4 < \text{DCE} \sim \text{benzene}$. This is

TABLE 3: IR Spectra of (CF₃SO₂)₂NH (HA) and Their Hydrates in Three Solvents

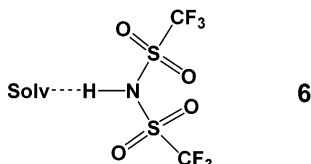
| freq | C ₆ H ₆ | | DCE | | CCl ₄ | | Oct ₃ NH ⁺ salt in CCl ₄ (Δ) |
|----------------------------------|-------------------------------|--------------------------------------|---------|-------------------------|-------------------|-------------------------|---|
| | HA | H ₂ O·HA (Δ) ^a | HA | H ₂ O·HA (Δ) | HA | H ₂ O·HA (Δ) | |
| ν _{as} H ₂ O | | 3605, [3617] ^b | | [3627] ^b | | 3682 | |
| ν _s H ₂ O | | 3536, [3542] ^b | | [3555] ^b | | 3596 | |
| νNH | 3155 | c, [2580] ^b | 3173 | 2580 br | 3292 | 2971–2674 | 3086 ^d |
| ν _{as} SO ₂ | 1447 | 1438 (9) | overlap | overlap | 1450 vs., 1430 vw | 1442 (8) | 1347 s (103), 1328 m |
| ν _s CF ₃ | 1229.5 | 1229 | ~1230 | overlap | 1234 | 1230 | } 1200 vs |
| ν _{as} CF ₃ | 1217 | 1214 | 1217 | 1219 | 1219 | 1214 | |
| ν _s SO ₂ | 1131 | 1134 | 1130 | 1134, 1060 vw | 1131 | 1134 | 1134 |
| νS–N | 857.5 | 894 (–37) | 861 | 895 (–34) | 855 | 889 (–34) | 1062 (–207) |

^a Frequency differences (Δ) with monomeric (CF₃SO₂)₂NH in the same solvent. ^b Bands due to dihydrate. ^c Maximum of very broad bands with low intensity not determined. ^d N–H from Oct₃NH⁺ not HA.

TABLE 4: Composition of (CF₃SO₂)₂NH (HA) Solutions with Differing Water Content

| solution | init HA concn (M) | hydrated·HA concn (M) | init H ₂ O concn (M) | free H ₂ O concn (M) | av H ₂ O:HA stoichiometry (n) |
|-------------------------------|-------------------|-----------------------|---------------------------------|---------------------------------|--|
| CCl ₄ | 0.010 | 0.00234 | 0.0018 | ~0 | 0.77 |
| | 0.010 | 0.0030 | 0.0036 | ~0 | 1.2 |
| C ₆ H ₆ | 0.015 | 0.0023 | 0.004 | 0.0018 | 0.96 |
| | 0.015 | 0.0033 | 0.008 | 0.00275 | 1.6 |
| | 0.015 | 0.0045 | 0.012 | 0.0024 | 2.1 |
| DCE | 0.010 | 0.0036 | 0.010 | 0.0035 | 1.8 |
| | 0.010 | 0.0048 | 0.0167 | 0.0066 | 2.1 |

similar to that seen with νO–H in triflic acid except that the small difference between DCE and benzene is reversed. These data are consistent with structure **6**, and the small reversal for benzene versus DCE must arise from a subtle peripheral steric or solvation effect.



Hydration of Bis(trifluoromethylsulfonyl) Imide. Solutions of this N–H acid with different H₂O mole ratios were obtained by mixing the dry (CF₃SO₂)₂NH solutions in CCl₄, C₆H₆, and DCE with corresponding water-saturated solvents. They contained three components: anhydrous acid, free water, and hydrated acid. The relative concentrations were determined by standard subtraction methods using standard spectra of the anhydrous acid and standard spectra of H₂O solutions in C₆H₆ (0.032 M)²¹ and DCE (0.10 M). The average stoichiometry (n) of the hydrated acid was determined as the concentration ratio of bound water to hydrated acid. The results are given in Table 4.

Sequential subtraction of the spectra of the solvent, free acid, and free H₂O from the composite gave the spectrum of the desired hydrated acid. Figure 3 shows a typical result for CCl₄ solution. The same spectrum was obtained at half the concentration of water. Both correspond to a hydrate with 1:1 stoichiometry (Table 4).

The two narrow bands at 3682 and 3596 cm⁻¹ are typical of a water molecule with free O–H groups and are assigned to ν_{as}OH₂ and ν_sOH₂, respectively. They are different from those of dissolved water (3707 and 3615 cm⁻¹) and appear at lower frequencies, indicating that the water molecule is bound via the O-atom to an acidic site. The set of bands at lower frequency (2600–3000 cm⁻¹) is assigned to νN–H, split by Fermi resonance of the 0 → 1 transition with overtones and combina-

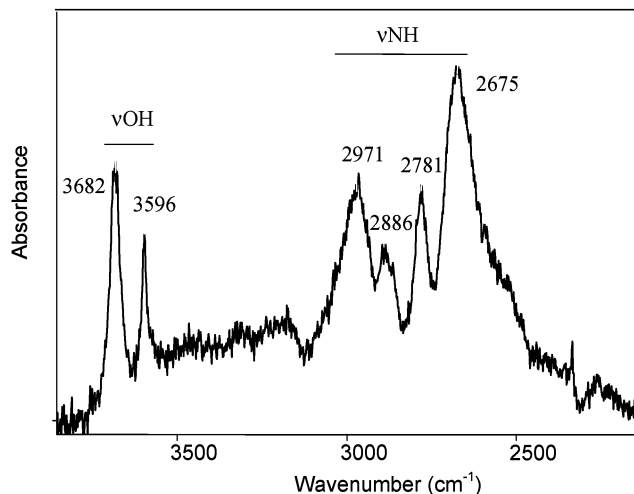
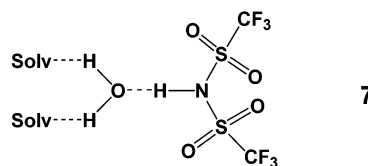


Figure 3. Spectrum of (CF₃SO₂)₂NH·OH₂ in CCl₄ derived from the spectrum of 0.01 M HN(SO₂CF₃)₂ solution containing 0.0036 M water after subtraction of the spectra of free water and anhydrous acid. The very broad νN–H band is split into several bands by Fermi resonance effects.

tions of low-frequency bands from the bis(trifluoromethylsulfonyl) imide moiety.²² Such strong Fermi resonance can only take place if the N–H bond of the acid remains intact. If proton transfer to water had occurred forming a hydronium ion pair, [H₃O][CF₃SO₂)₂N], the absorption would have to be assigned to O–H stretching vibrations of the H₃O⁺ ion. However, since Fermi resonance cannot occur between the vibrations of two electrostatically interacting moieties, assignment of the 2600–3000 cm⁻¹ bands to νO–H is untenable. Therefore, structure **7** is proposed for the monohydrated acid.



Similar conclusions are drawn from the IR spectrum of the hydrated acid in benzene and DCE solutions. In benzene at low concentrations of water, a 1:1 hydrate is formed (Table 3). The ν_{as}OH₂ and ν_sOH₂ bands are similar to those seen in CCl₄ but somewhat lower in frequency as expected for a stronger H-bond accepting solvent (Table 4). Thus, structure **7** is proposed with π-bound benzene weakly solvating the water molecule.

At higher concentrations of water, a 2:1 dihydrate is formed (Table 3). This same dihydrate is formed in DCE at all water concentrations studied. Figure 4b shows the spectrum of the

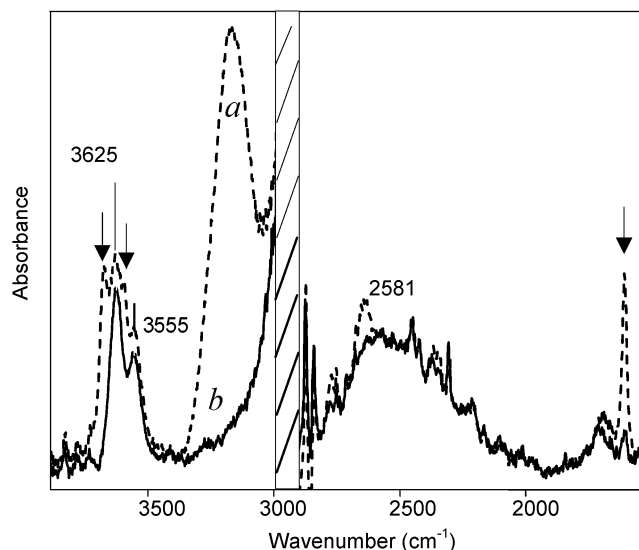


Figure 4. IR spectrum of 0.01 M $(\text{CF}_3\text{SO}_2)_2\text{NH}$ containing 0.01 M H_2O in DCE before (a) and after (b) subtraction of the spectra of free acid and free dissolved water molecules (marked by arrows). Spectrum b (solid line) belongs primarily to the dihydrated acid.

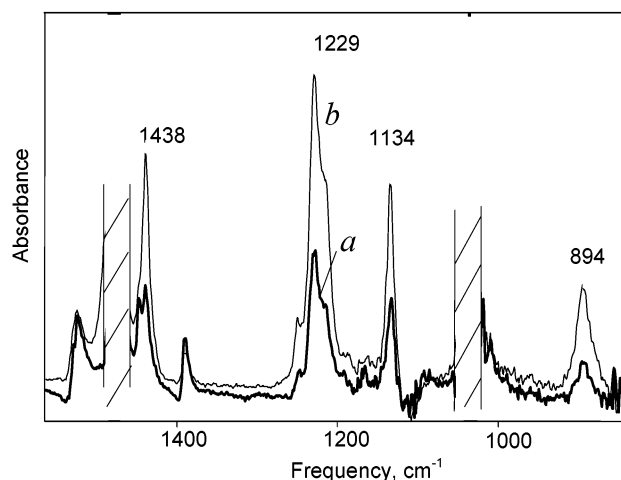
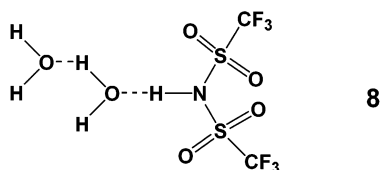


Figure 5. IR spectra of complexes (a) $\text{H}_2\text{O}\cdot\text{HN}(\text{SO}_2\text{CF}_3)_2$ **7** and (b) $\text{H}_2\text{O}\cdot\text{H}_2\text{O}\cdot\text{HN}(\text{SO}_2\text{CF}_3)_2$ **8** in benzene solution in the frequency range of anion vibrations.

dihydrate in DCE. It is generically related to the monohydrate, so structure **8** is proposed.



The vibrations assigned to the water molecules in the dihydrate, $\nu_{\text{as}}\text{OH}$ at 3625 cm^{-1} , $\nu_{\text{s}}\text{OH}$ at 3555 cm^{-1} , and δOH_2 at 1607 cm^{-1} , are typical of O-bound water molecules with relatively free O–H groups.

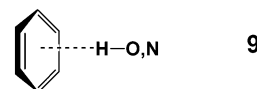
As shown in Figure 5, the IR spectra of the monohydrate and dihydrate are coincident in the region of the $\text{N}(\text{SO}_2\text{CF}_3)_2$ moiety vibrations. Hence, as reported by the heavy atoms of the anionic moiety, attaching the second H_2O molecule to the 1:1 complex via a relatively weak H-bond has rather little influence on the strength of the interaction of the first H_2O molecule with $\text{HN}(\text{SO}_2\text{CF}_3)_2$. This is consistent with structures **7** and **8**.

The data in Table 3 reveal that the $\nu\text{N}-\text{S}$ frequency increases by 37 cm^{-1} and the $\nu_{\text{as}}\text{SO}_2$ frequency decreases by 9 cm^{-1} in $(\text{CF}_3\text{SO}_2)_2\text{NH}\cdots\text{OH}_2$ relative to $(\text{CF}_3\text{SO}_2)_2\text{NH}\cdots\text{C}_6\text{H}_6$ (both in benzene solution). This reflects the movement of electron density from the N–H bond into the $\text{N}(\text{SO}_2\text{CF}_3)_2$ moiety in the hydrate arising from stronger H-bonding to water relative to benzene. Delocalization of charge into the N–S bonds increases their multiplicity and also affects the S=O bonds. This effect is much more dramatic in the $[\text{Oct}_3\text{NH}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ salt, representing complete proton transfer. The $\nu\text{N}-\text{S}$ frequency is higher by 207 cm^{-1} and the $\nu_{\text{as}}\text{SO}_2$ frequency is lower by 103 cm^{-1} relative to monomeric acid (Table 3). Thus, the nature of the $n\text{H}_2\text{O}\cdot\text{H}-\text{N}$ bonding in **7** and **8** is much closer to that of H–N in the monomeric acid than in the ion pair $\text{Oct}_3\text{N}-\text{H}^+\cdots\text{N}(\text{SO}_2\text{CF}_3)_2^-$.

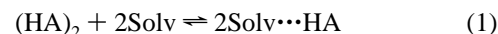
Summary and Conclusions

Both triflic acid and $(\text{CF}_3\text{SO}_2)_2\text{NH}$ experience a strong solvating influence from benzene and DCE. The influence on the anhydrous acids is roughly comparable for these two solvents. The change in frequency of $\nu\text{O}-\text{H}$ of triflic acid in benzene or DCE relative to that in carbon tetrachloride is quite large ($>210\text{ cm}^{-1}$).

We believe that benzene acts as a π -base in a manner similar to that proposed in benzene/water interactions,^{13–17} and we have identified IR bands at 1810 and 1956 cm^{-1} sensitive to this interaction. Their molar intensities and frequencies change relative to free benzene because of polarization in structure **9**.

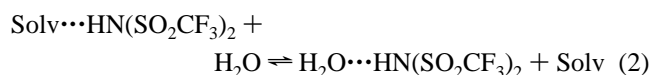


The relatively strong solvation of the anhydrous acids by benzene and DCE has a material effect on self-association equilibria (eq 1).



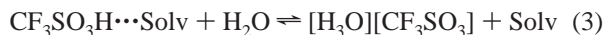
Thus, at triflic acid concentrations less than 0.1 M in benzene and DCE, the equilibrium favors solvated monomers on the right-hand side. On the other hand, in a more weakly solvating solvent such as CCl_4 , $\sim 98\%$ of the triflic acid molecules remain in dimeric form in 0.1 M solution. This portion decreases to 53% at 0.01 M concentration. For $(\text{CF}_3\text{SO}_2)_2\text{NH}$, self-association is less favorable, so only the solvated monomers are formed at the concentrations studied.

The interaction of water molecules with triflic acid and $(\text{CF}_3\text{SO}_2)_2\text{NH}$ in low-polarity organic solvents differs dramatically. In the case of $(\text{CF}_3\text{SO}_2)_2\text{NH}$, there is simply a solvation competition between the water and solvent molecules for H-bonding with the N–H proton. In CCl_4 solutions (a very weakly solvating agent), the equilibrium is shifted completely to the right-hand side (eq 2).



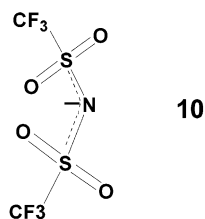
In benzene solution, with 0.015 M acid and 0.004 M H_2O , ca. 15% of the acid is hydrated, accounting for about half the water available. The uncomplexed water is stabilized by $\text{H}_2\text{O}\cdots$ benzene π -interactions. At higher water concentrations, $(\text{CF}_3\text{SO}_2)_2\text{NH}\cdot\text{H}_2\text{O}$ simply begins forming a dihydrate, $(\text{CF}_3\text{SO}_2)_2\text{NH}\cdot(\text{H}_2\text{O})_2$.

In contrast, triflic acid readily ionizes in the presence of trace water to give a hydronium ion pair $[\text{H}_3\text{O}][\text{CF}_3\text{SO}_3]$ (eq 3).



The differing behavior of triflic acid and $(\text{CF}_3\text{SO}_2)_2\text{NH}$ lies in the different properties of the CF_3SO_3^- and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ anions. The triflate anion stabilizes the H_3O^+ ion by forming two (or possibly three) H-bonds with oxygen atoms of SO_3^- group in an ion pair. This allows proton transfer from triflic acid to water in the $\text{CF}_3\text{SO}_3\text{H}\cdots\text{OH}_2$ presumptive precursor complex. On the other hand, the $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ anion is less able to stabilize the H_3O^+ ion, probably because it can form only one H-bond, via the N-atom. As a result, the $(\text{CF}_3\text{SO}_2)_2\text{NH}\cdots\text{OH}_2$ complex is stable to proton transfer. These results have implications for other acids in organic solvents. Oxyacids having anions structurally similar to the SO_3^- group in the triflate anion (e.g., HClO_4 , HFSO_3) should display high acidity toward water in low dielectric organic solvents, forming H_3O^+ and H_5O_2^+ cations, while acids such as $(\text{CF}_3\text{SO}_2)_2\text{NH}$ having anions less suited to making multiple H-bonds may remain un-ionized.

It follows that if H_2O is used as an indicator base for measuring the strength of acids in low dielectric media, triflic acid will behave as a strong acid, but $(\text{CF}_3\text{SO}_2)_2\text{NH}$ will behave as a weak acid. The inapplicability of water as an indicator for determining acid strength has been commented on by Fărcașiu.²³ If a stronger base which cannot engage in multiple H-bonding is used as an indicator, such as tri-*n*-octylamine, then both acids will appear strong. Oct_3NH^+ salts will be formed, and as discrete ion pairs in CCl_4 solution, the N–H stretching frequencies in these salts will be sensitive indicators of the proton acceptor properties of the anions. Indeed, they should reflect the intrinsic acid strength difference of the monomeric acid molecules.³ The $\nu\text{N-H}$ frequencies of $[\text{Oct}_3\text{NH}][\text{CF}_3\text{SO}_3]$ and $[\text{Oct}_3\text{NH}][(\text{CF}_3\text{SO}_2)_2\text{N}]$ ion pairs in dilute CCl_4 solution are 3030 and 3086 cm^{-1} , respectively, indicating that triflate is the *stronger* base. This surprising conclusion is counter to the prevailing wisdom that triflic acid is a stronger acid than $(\text{CF}_3\text{SO}_2)_2\text{NH}$, and contrary to the present results with water as the indicator base. At the individual molecule level, however, this reversal is quite understandable. The $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ anion is better able to delocalize the negative charge than triflate, and we have provided IR evidence supporting this in terms of increasing $\nu\text{N-S}$ frequencies. This is represented by the electronic description 10.



The conclusion that an individual molecule of $(\text{CF}_3\text{SO}_2)_2\text{NH}$ is an intrinsically stronger acid than $\text{CF}_3\text{SO}_3\text{H}$ is consistent with gas-phase acidity rankings.² In the gas phase, acidity correlates with the ability of the anion to carry negative charge, so the larger, better-delocalizing $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ anion is a considerably weaker base than triflate. This highlights the omnipresent role that solvation takes in determining acid strength in condensed media. The dramatic reversal of acid strength of these acids toward H_2O , to the extent that the intrinsically stronger acid will not even protonate water (in low dielectric organic media), is a powerful illustration of this fundamental tenet of acidity.

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