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Synthesis and Characterization of Trifluoromethylcarboxonium Salts

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The low-temperature protonation of trifluoroacetic acid with the superacids HF/SbF_5 and HF/AsF_5 resulted in the syntheses of the first examples of trifluoromethylcarboxonium salts. The less acidic trifluoromethylacetamide was also protonated in the same fashion, resulting in exclusive protonation of the carbonyl function. Their $[SbF_6]^-$ and $[AsF_6]^-$ salts were characterized by crystal structres, vibrational and multinuclear NMR spectra, and by electronic structure calculations. These salts are thermally unstable, colorless solids, stabilized by very strong hydrogen bonding. The proton NMR resonances of the $[CF_3C(OH)_2]^+[SbF_6]^-$ and $[CF_3C(OH)_2]^+[AsF_6]^-$ salts occur at an unprecedented 16.0 and 15.7 ppm, respectively, thus extending the upper limit of the range of observed proton NMR chemical shifts from 14 to 16 ppm.

Introduction

Protonated species are ubiquitous and of fundamental importance in a variety of processes and transformations, and even HeH^+ has been detected astrophysically in interstellar space representing the Universe's first molecularly bonded ion.[1-4] Superacids are ideal reagents for the protonation of bases.[5] When the difference in the proton activity H_o between the substrate and the superacid approaches a factor of about 10^{-6}, the strongest superacids, i.e., combinations of HF with strong Lewis acids, such as SbF_5 or AsF_5 with H_o values of about –21, can protonate even weaker superacids. Conventionally, sulfuric acid with a H_o value of –12.1 has been adopted as the border line between regular acids and superacids.[6, 7] Thus, the groups of Minkwitz and Kornath have demonstrated that HF/SbF_5 can protonate the weaker superacids H_2SO_4 (H_o = –12.1), HSO_3F (H_o = –15.1), and trifluoromethanesulfonic (triflic) acid (H_o = –14.6), respectively.[8-10] Trifluoroacetic acid, $CF_3CO(OH)$, (H_o = –2.7), has been utilized in various binary acid systems, such as with sulfuric acid, hydrofluoric acid, or triflic acid, without observing protonation of the weaker trifluoroacetic acid.[11, 12]

The equimolar adduct of acetic acid and trifluoroacetic acid forms molecular cyclic heterodimers instead of protonation of the weaker acid, acetic acid, through two hydrogen bonds at low temperatures.[13]

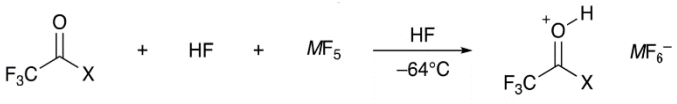
Herein, we report the successful protonation of trifluoroacetic acid and the more basic trifluoroacetamide, CF_3CONH_2. The protonation of trifluoroacetic acid and trifluoroacetamide yield the novel trifluoromethylcarboxonium cations, $[CF_3C(OH)_2]^+$ and $[CF_3C(OH)(NH_2)]^+$, respectively.

Results and discussion

Synthesis

The trifluoromethylcarboxonium ions were obtained in quantitative yield through the low-temperature protonation of trifluoroacetic acid and trifluoroacetamide with the binary superacids HF/AsF_5 and HF/SbF_5 in anhydrous HF solution (Scheme 1). Their MF_6^- salts (M = Sb and As) are thermally unstable, colorless solids that were characterized by their vibrational and multinuclear NMR spectra, electronic structure calculations, and the crystal structures of $[CF_3C(OH)_2][SbF_6]$ and $[CF_3C(OH)(NH_2)][SbF_6]$. To the best of our knowledge, trifluoromethylcarboxonium ions had previously been unknown. Furthermore, trifluoroacetic acid is a strong acid with a H_o value of –2.7. Trifluoroacetamide is considerably more basic than trifluoroacetic acid and, therefore, is easier to protonate.

For the preparation of the $[AsF_6]^-$ salts, anhydrous HF (3.0 mL) and AsF_5 (1 mmol) were added to a poly-perfluoroethylene-propylene-polymer (FEP) ampule containing frozen samples of either trifluoroacetic acid or trifluoroacetamide (1.00 mmol) *in vacuo* at −196 °C. The mixtures were warmed to –64 °C and kept at this temperature



X = OH, NH_2; M = As, Sb

Scheme 1: Preparation of trifluoromethylcarboxonium ions through protonation of trifluoroacetic acid and trifluoroacetamide with hydrogen fluoride / pnicogen pentafluoride.

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for 15 minutes with intermittent agitation. The clear solutions were cooled to −78 °C and the volatile compounds were pumped off at −78 °C, leaving behind colorless solids. Single crystals were grown from concentrated HF solutions by slow evaporation of the solvent *in vacuo* at −78 °C.

For the preparation of the $[SbF_6]^-$ salts, anhydrous HF (3.0 mL) was condensed to an FEP ampule containing frozen samples of SbF_5 (1.00 mmol) at −196 °C. The mixtures were warmed to −20 °C to form a clear colorless solution. The solutions were cooled to −64 °C and using 18-gauge FEP tubing transferred at −78 °C into a second FEP ampule containing the samples of either trifluoroacetic acid or trifluoroacetamide (1.00 mmol). The mixtures were allowed to warm to −64 °C and kept at this temperature for 15 minutes with sporadic agitation. The clear solutions were cooled to −78 °C and the volatile compounds were pumped off at −78 °C, leaving behind colorless solids. Single crystals were grown from concentrated HF solutions by slow evaporation of the solvent *in vacuo* at −78 °C.

The resulting salts were isolated and characterized by multinuclear NMR and vibrational spectroscopy, and in case of the $[SbF_6]^-$ salts by their X-ray crystal structures.

X-ray crystallography

The complete crystallographic details for the structurally characterized $[CF_3C(OH)_2][SbF_6]$ and $[CF_3C(OH)(NH_2)][SbF_6]$ salts are given in the ESI.†

The $[CF_3C(OH)_2][SbF_6]$ salt crystallizes in the triclinic space group *P*-1 with 2 formula units per unit cell (V = 404.66(5) Å^3). The asymmetric unit is shown in Figure 1. The C–O bond lengths in the $[CF_3C(OH)_2]^+$ ion are 1.253(3) Å and 1.258(3) Å, respectively. The similarity in bond length suggests positive charge delocalization over the O–C–O fragment. The former carbonyl bond is slightly elongated compared to the C=O double bond length (1.197(10) Å) found in the crystal structure of the monohydrate of trifluoroacetic acid.[14] The C–C bond does not exhibit significant differences from the C–C bond distances in $CF_3COOH{\cdot}H_2O$. Both the C–O bond lengths and O–C–O/C–C–O band angles are consistent with values found in other protonated carboxylic acids.[15] As can be seen from Figure 2, the compound exhibits strong hydrogen bonds between the hydrogen atoms of the OH– groups and two of the fluorine atoms of the $[SbF_6]^-$ anion, resulting in a distortion of the $[SbF_6]^-$ octahedra and an elongation of two axial Sb–F bonds from about 1.87 Å to about 1.91 Å.

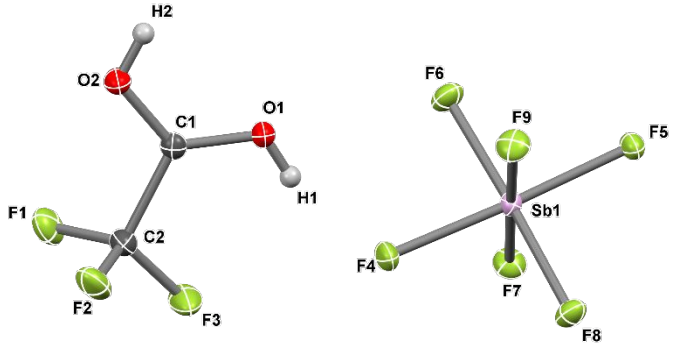

Figure 1: The crystal structure of $[CF_3C(OH)_2][SbF_6]$. Thermal ellipsoids are set at 50% probability, Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. Selected bond distances (Å) and angles (°): C1–O1 1.253(3), C1–O2 1.258(3), C2–C1 1.546(3), C2–F1 1.317(2), C2–F2 1.326(3), C2–F3 1.317(3) and O2–C1–O1 122.9(2), O2–C1–C2 114.4(2), O1–C1–C2 122.7(2), C1–C2–F1 110.3(2), C1–C2–F3 109.6(2), C1–C2–F2 108.2(2).

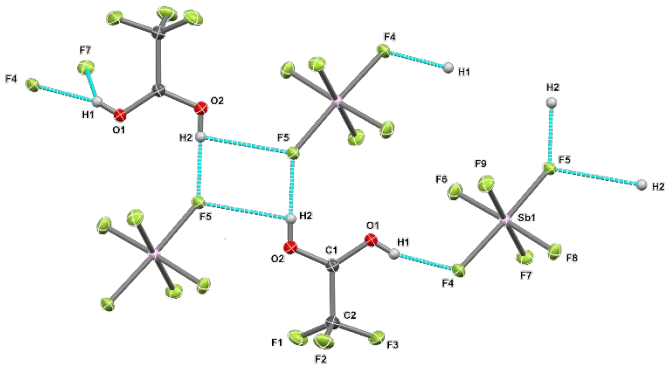

Figure 2: Hydrogen bonding in the crystal structures of $[CF_3C(OH)_2][SbF_6]$.Thermal ellipsoids are set at 50% probability. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. Selected distances (Å) and angles (°): O1–H1···F4 2.527(2), O2–H2···F5 2.561(2), Sb1–F4 1.915(1), Sb1–F5 1.904(1), Sb1–F6 1.869(1), Sb1–F7 1.867(1), Sb1–F8 1.872(1), Sb1–F9 1.864(1) and O2–H2···F5 176(3), O2–H2···F5' 100(3), F6–Sb1–F4 87.83(6), F6–Sb1–F9 91.70(6), F8–Sb1–F4 90.51(6), F8–Sb1–F9 90.11(6).

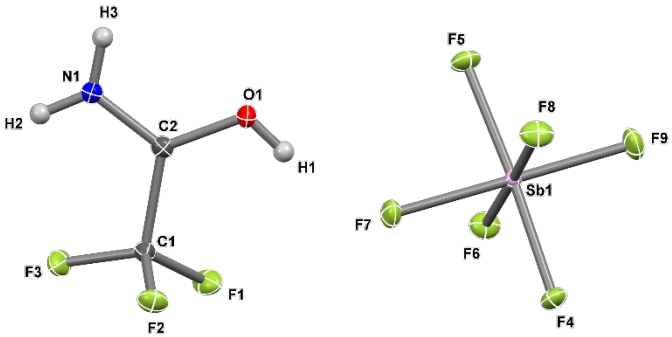

Figure 3: The crystal structure of $[CF_3C(OH)(NH_2)][SbF_6]$. Thermal ellipsoids are set at 50% probability, Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. Selected bond distances (Å) and angles (°): C2–O1 1.284(2), C2–N1 1.284(2), C1–C2 1.540(2), C1–F1 1.328(2), C1–F2 1.330(2), C1–F3 1.320(2) and N1–C2–O1 120.5(1), N1–C2–C1 118.8(1), O1–C2–C1 120.7(1), C1–F1–F2 35.87(7), C1–F3–F1 35.23(7), F3–C1–F2 109.0(1), C2–C1–F3 110.5(1), C2–C1–F1 109.9(1).

The $[CF_3C(OH)(NH_2)][SbF_6]$ salt crystallizes in the monoclinic space group *C*12/*c*1 with 8 molecules per unit cell (V = 1575.9(3) Å^3). The asymmetric unit is shown in Figure 3. As a result of protonation, the C–O bond is elongated to 1.284(2) Å; the C=O bond length in free trifluoroacetamide is 1.230(1) Å[16, 17]. Additionally, the C–N bond is shortened to 1.284(1) Å from 1.316(1) Å in $CF_3C(O)NH_2$, implying an increase in the double bond character of the amide bond. Similarly to the $[CF_3C(OH)_2]^+$ ion, the C–C bond in trifluoroacetamide does not significantly change upon protonation.

As can be seen from Figure 4, the compound exhibits three hydrogen bonds between the hydrogen atoms of the OH– and NH_2^- groups and three fluorine atoms of the $[SbF_6]^-$ anion,

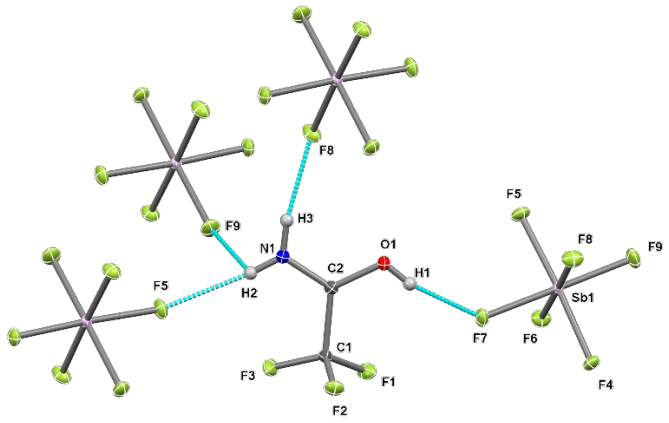

Figure 4: Hydrogen bonding in the crystal structures of $[CF_3C(OH)_2][SbF_6]$.Thermal ellipsoids are set at 50% probability. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. Selected distances (Å) and angles (°): O1–H1···F7 2.600(1), N1–H3···F8 2.884(2), N1–H2···F5 2.933(2), Sb1–F4 1.8717(9), Sb1–F5 1.881(1), Sb1–F6 1.8743(9), Sb1–F7 1.905(1), Sb1–F8 1.8891(9), Sb1–F9 1.867(1) andN1–H3···F8 170(2), N1–H2···F5 171(2), O1–H1···F7 164(2), F7–Sb1–F4 87.94(4), F7–Sb1–F6 89.45(4), F7–Sb1–F5 88.91(4), F5–Sb1–F8 89.99(4), F8–Sb1–F4 90.18(4) .

resulting in a distortion of the $[SbF_6]^-$ octahedra and an elongation of the Sb–F bond bridging to the OH hydrogen from 1.87 Å to 1.91 Å and of those bridging to the two NH_2 hydrogens from 1.87 Å to 1.88 and 1.89 Å, respectively. The differences in these Sb–F bond lengths suggests that the O–H···F bridge is stronger than the N–H···F bridges.

NMR spectroscopy

The ^1H ,^{13}C, and ^{19}F NMR spectra of trifluoroacetic acid and trifluoroacetamide together with their protonated $[AsF_6]^-$ and $[SbF_6]^-$ salts were recorded in SO_2 solution at −60 °C and are depicted in Figures S1-S20 in the ESI.† Since no NMR data had previously been reported for protonated strong acids, except for $[H_3SO_4][SbF_6]$ (δ = 12.1),[8] and the generally published proton NMR chemical shift tables covers only a range of −4 to 14 ppm, the ^1H NMR spectra of the protonated salts were of particular interest. Due to the very strongly electron withdrawing effect of a proton, we expected for the protonated salts increased deshielding and a significant shift of the resonances to higher energy.[18] This is indeed observed, showing the proton signals of the $[SbF_6]^-$ and $[AsF_6]^-$ salts of $[CF_3C(OH)_2]^+$ to occur at 16.01 and 15.67 ppm, respectively, thus significantly increasing the high frequency limit of the known proton NMR scales. Whereas the ^1H NMR spectrum of $[CF_3C(OH)_2][AsF_6]$ (Figure S4) shows only a single resonance at 15.67 ppm, that of the $[SbF_6]^-$ salt (Figure S7) shows a second weaker signal at 13.57 ppm which might be due to the presence of some $[Sb_2F_{11}]^-$ in the sample, plus an unknown resonance at 8.69 ppm. These impurities are attributed to the fact that SbF_5 is much less volatile than AsF_5 and therefore more difficult to pump off. This interpretation is also supported by the corresponding ^{19}F NMR spectra (Figures S6 and S9) which are very clean for the $[AsF_6]^-$ salt but show the presence of additional signals in the case of $[SbF_6]^-$.

As expected for the electron density feeding NH_2 group, trifluoroacetamide is no longer an acid, and the ^1H NMR of its protonated salts (Figures S13 and S18) show clean single resonances at 13.18 and 12.12 ppm for the $[AsF_6]^-$and $[SbF_6]^-$ salts, respectively. In addition, they exhibit doublets in the 10.5 ppm region for the two non-equivalent protons of the NH_2 group. In no instance there was any evidence for a protonation of the NH_2 group, and the protonation occurred exclusively on the carbonyl oxygen atom. This situation contrasts that found for the related case of nitramine where both nitrogen and oxygen protonation was observed.[19]

The ^{19}F NMR spectra (Figures S5, S8, S11, S14, S17, and S20) are simple and straight forward, and only that of $[CF_3C(OH)_2][SbF_6]$ shows the above mentioned additional weak features in the Sb–F regions. Similarly, the ^{13}C NMR spectra (Figures S5, S8, S14, and S19) are in accord with the expectations of the carbonyl carbon being more deshielded upon protonation and hold no surprises.

Raman spectroscopy

The Raman spectra of all protonated species were recorded at −90 °C. The spectra and tables with observed frequencies and intensities are given in the ESI.†

The Raman spectra of trifluoroacetic acid and its protonated $[AsF_6]^-$ and $[SbF_6]^-$ salts are depicted in Figures S21–23. The observed and calculated frequencies and intensities are summarized in Table S1. As can be seen, the agreement between the observed spectra and those calculated at the B3LYP//aug-CC-pVTZ level of theory is very good and confirms the given assignment of the spectra. Similarly, the observed spectra of trifluoroacetamide and its protonated $[AsF_6]^-$ and $[SbF_6]^-$ salts are shown in Figures S24–26. The observed and calculated frequencies and intensities are summarized in Table S2. Again, the agreement between the observed spectra and those calculated is very good confirming the given assignments and the identity of the compounds.

The O–H stretching mode in a protonated species might be expected to exhibit a frequency shift to lower frequencies due to its increased bond polarity when compared to a normal O–H bond. However, the observed Raman spectra are not suitable for testing this prediction because of the inability to locate their exact band centers. The extreme broadness of these bands is mainly due to the very strong hydrogen bonding in the solid state.

Conclusions

The first-known examples of trifluoromethylcarboxonium salts were prepared by the low-temperature protonation of trifluoroacetic acid and trifluoroacetamide in anhydrous HF solution using the powerful protonating agent HF/MF_5 (M = As, Sb). In the case of trifluoroacetamide, the protonation occurred exclusively on the oxygen atom of the carbonyl group, and no evidence was observed for protonation of the NH_2 group. All these trifluoromethylcarboxonium salts are colorless, thermally unstable salts and are stabilized by strong hydrogen bridges. They were characterized by their crystal structures, multi-NMR

and Raman spectroscopy, and electronic structure calculations. The ^{1}H NMR spectra of the $[CF_3C(OH)_2][SbF_6]$ and $[CF_3C(OH)_2][AsF_6]$ salts in SO_2 solution show resonances at an unprecedented 16.01 and 15.67 ppm, respectively. This increases the upper limit of the range of observed ^{1}H NMR chemical shifts from 14 to 16 ppm.

Experimental details

Caution! Anhydrous HF, AsF_5, and SbF_5 can cause severe burns, contact with the skin must be avoided, and the compounds should only be handled in a well-ventilated fume hood. Appropriate safety precautions should be taken when working with these materials.

Materials and Apparatus

All reactions were carried out in Teflon-FEP ampules that were closed by stainless steel valves. Volatile materials were handled in grease-free Pyrex glass vacuum lines equipped with Kontes® HI-VAC® valves or in stainless steel/Teflon-FEP vacuum lines.[20] Reaction vessels and the stainless-steel vacuum line were passivated with ClF_3 prior to use. Non-volatile materials were handled in the dry nitrogen atmosphere of a glove box. HF (Galaxy Chemicals) was dried by storage over BiF_5.[21] AsF_5 was prepared from AsF_3 and F_2.[22-24] SbF_5 (Ozark Mahoning) was freshly distilled before use. Trifluoroacetic acid (Sigma-Aldrich) was distilled from P_2O_5, and trifluoroacetamide (PCR) was purified by sublimation.[25, 26] SO_2 (Matheson Tri-Gas) was dried by storage over CaH_2. The NMR spectra were recorded at 298 K unless otherwise stated on either a Bruker AMX-500 or Varian VNMRS-500 spectrometer. Spectra were externally referenced to 25% tetramethyl silane in dichloromethane-d_2 for ^{1}H and ^{13}C NMR spectra, and to 80% $CFCl_3$ in chloroform-*d* for ^{19}F NMR spectra. Raman spectra were recorded either directly in 9 mm Teflon-FEP ampules or J. Young NMR tubes in the range 4000–80 cm^{-1} on a Bruker Vertex 70/RAM II spectrophotometer, using a Nd-YAG laser at 1064 nm.

Crystal Structure Determination

Diffraction quality crystals were grown from anhydrous HF solution inside Teflon-FEP ampules by slow evaporation of the HF solvent in a dynamic vacuum at −78 °C. The FEP reactors were cooled to −78 °C, opened under a stream of N_2 gas and the crystalline content was dropped into the trough of a low-temperature crystal-mounting apparatus at −110 °C. A glass fiber that was attached to a magnetic CrystalCap™ and dipped into PFPE (perfluoropolyether) oil was used to mount the crystals on the goniometer with a magnetic base. The single-crystal X-ray diffraction data were collected on a Bruker SMART APEX DUO 3-circle platform diffractometer, equipped with an APEX II CCD, using Mo Kα radiation (TRIUMPH curved-crystal mono-chromator) from a fine-focus tube. The frames were integrated using the SAINT algorithm to give the *hkl* files corrected for Lp/decay.[27] The absorption correction was performed using the SADABS program.[28] The structures were solved by intrinsic phasing and refined on F^2 using the Bruker SHELXTL Software Package and ShelXle.[29-33] All non-hydrogen atoms were refined anisotropically. ORTEP drawings were prepared using the Mercury CSD program.[34]

Preparation of $[CF_3COH(X)][AsF_6]$ (X = OH, NH_2)

Anhydrous HF (3.0 mL) and AsF_5 (1 mmol) were added to a Teflon-FEP ampule containing a frozen sample of trifluoroacetic acid or trifluoroacetamide (1.00 mmol) in vacuo at −196 °C. The mixtures were warmed to −64 °C, kept at this temperature for 15 min and sporadically agitated. The clear solutions were cooled to −78 °C and the volatile compounds were removed *in vacuo* at −78 °C, leaving behind colorless solids.

Preparation of $[CF_3COH(X)][SbF_6]$ (X = OH, NH_2)

Anhydrous HF (3.0 mL) was condensed to a Teflon-FEP ampule containing frozen samples of SbF_5 (1.00 mmol) at −196 °C. The mixture was warmed to −20 °C to form clear colorless solutions. The solutions were cooled to −64 °C and, under a stream of dry nitrogen using an 18-gauge FEP tubing, transferred into a second Teflon-FEP ampule containing a sample of either trifluoroacetic acid or trifluoroacetamide (1.00 mmol) at −78 °C. The mixtures were allowed to warm to −64 °C, kept at this temperature for 15 min and sporadically agitated. The clear solutions were cooled to −78 °C and the volatile compounds were removed *in vacuo* at −78 °C, leaving behind colorless solids.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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