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Ab Initio/IGLO/GIAO-MP2 Studies of Fluorocarbocations: Experimental and Theoretical Investigation of the Cleavage Reaction of Trifluoroacetic Acid in Superacids[1a]

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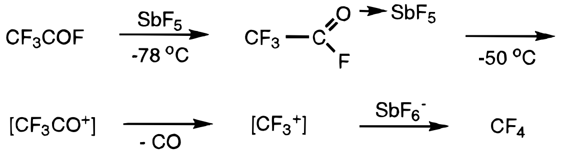
The structures of a number of fluorocarbocations were calculated at the correlated MP2/6-31G* level. ^{13}C and ^{19}F NMR chemical shifts of fluorocarbocations were calculated for the first time using IGLO and GIAO-MP2 methods. The data showed good correlation of calculated ^{19}F and ^{13}C NMR chemical shifts with the experimental chemical shifts of fluorocarbocations. The correlation for GIAO-MP2-calculated ^{19}F NMR chemical shifts with the experimental data is excellent. Using theoretical calculations as guidance, the protolytic cleavage of trifluoroacetic acid (CF_3COOH) in superacids forming CF_4 was also investigated experimentally and by *ab initio* calculations. This reaction is suggested to involve the gitonic $CF_3C(OH)(OH_2)^{2+}$ dication as an intermediate.

Introduction

Fluorocarbocations play an important role as intermediates in the electrophilic addition to fluoroolefins. The study of fluorocarbocations is of considerable interest because of the dualistic effect of a fluorine as a substituent. Due to its high electronegativity, a fluorine atom adjacent to a carbocationic center is inductively destabilizing. On the other hand, the nonbonded electron pairs on the fluorine atom can stabilize the positive charge through back-donation (n−p interaction). Numerous fluorocarbocations were observed as stable, long-lived ions by ^{13}C and ^{19}F NMR spectroscopy since the pioneering work of Olah, Chambers, and Comisarow,[2] although in some cases difficulties arose because of rapid fluoride ion exchange between superacid and fluorocarbocations. Attempts to directly observe CH_3CHF^+ [2] and CF_3^+ [3a] by NMR spectroscopy under superacid stable ion conditions were unsuccessful. The intermediacy of CF_3^+ was suggested,[3b] however, in the ionization and subsequent decarbonylation of trifluoroacetyl fluoride (CF_3COF) with SbF_5 at low temperature. Whereas no CF_3CO^+ and CF_3^+ cations could be observed directly, ^{19}F NMR spectroscopy showed already at relatively low temperature (−50 °C) the formation of tetrafluoromethane (CF_4). It was proposed that the great strength of the C−F bond in CF_4 (ca. 140 kcal/mol) leads to rapid quenching of CF_3^+ to CF_4 even in low-nucleophilicity fluorinated superacid media.



We wish to report now our *ab initio*/IGLO[4]/GIAO-MP2[5] studies of a series of fluorocarbocations which were earlier characterized by ^{19}F NMR spectroscopy under long-lived stable ion conditions. This permits comparison of calculated data with experimentally observed results. Such calculations have become increasingly useful to study electron deficient intermediates but were so far not reported for fluorocarbocations. We have also calculated the structures and ^{13}C and ^{19}F NMR chemical shifts for still elusive perfluorinated cations, such as CF_3^+. In addition, using theoretical calculations as a guide, we report the experimental and theoretical study of the protolytic cleavage of trifluoroacetic acid, CF_3COOH, in strong superacids giving CF_4. Based on *ab initio* calculations, it is suggested that the reaction involves the $CF_3C(OH)(OH_2)^{2+}$ dication as an intermediate.

Results and Discussion

Ab initio calculations were carried out by using the GAUSSIAN-94[6] package of programs. Optimized geometries were obtained at the MP2/6-31G* level, and selected parameters of the ions are given in Figures 1 and 2. Vibrational frequencies at the HF/6-31G*//HF/6-31G* level were used to characterize stationary points as minima. IGLO calculations were performed according to the reported method[4] at IGLO II level using MP2/6-31G* geometries. Huzinaga[7] Gaussian lobes were used as follows: Basis II, C, O, or F, 9s 5p 1d contracted to [51111, 2111, 1]; d exponent, 1.0; H, 5s 1p contracted to [311, 1]; p exponent, 0.70. GIAO-SCF and GIAO-MP2

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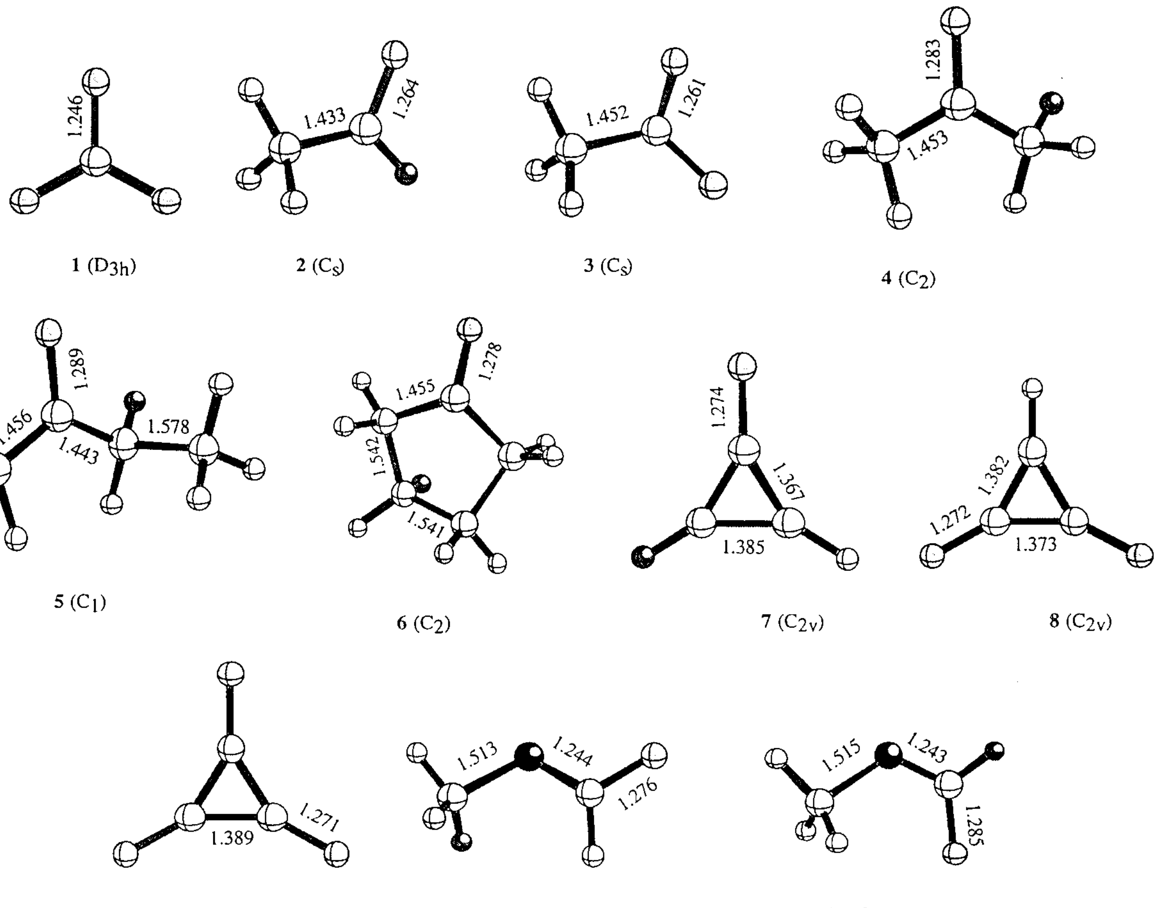
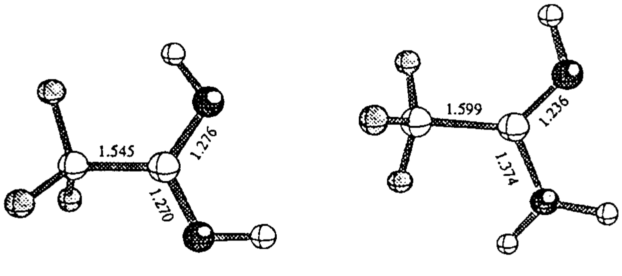


1 (D_{3h}) **2** (C_s) **3** (C_s) **4** (C_2) **5** (C_1) **6** (C_2) **7** (C_{2v}) **8** (C_{2v}) **9** (D_{3h}) **10** (C_s) **11** (C_s)

Figure 1. Selected MP2/6-31G*-optimized parameters of **1**-**11**.



12 (C_s) **13** (C_s)

Figure 2. Selected MP2(FU)/6-31G*-optimized parameters of **12** and **13**.

calculations using tzp/dz basis set[5] have been performed with the ACES II program.[8] Chemical shifts are listed in Table 1.

So far the appplication of IGLO and GIAO methods to fluorocarbocations has not been explored. The IGLO method has been applied[9] only to calculate the ^{19}F NMR chemical shifts of a number of small neutral molecules. With the use of the large basis set TZP (triple-ζ plus polarization functions), satisfactory agreement between gas phase ^{19}F NMR chemical shifts with calculated ^{19}F NMR chemical shifts has been found. IGLO calculations with DZ (double-ζ) level were shown to be unreliable for ^{19}F NMR chemical shifts.[9] The application of the GIAO-MP2 method, which includes dynamic electron correlation in chemical shift calculations, to the chemical shifts

Table 1. ^{19}F **NMR and Selected** ^{13}C **NMR Chemical Shifts of Fluorocarbocations**[a]

no.	cations	atom	IGLO II//MP2/ 6-31G*	GIAO-SCF/ tzp/dz	GIAO-MP2/ tzp/dz	expt
1	$[CF_3]^+$	F	58.6	81.3	51.7	
		C^+	162.1	167.1	169.2	
2	$CH_3[CHF]^+$	F	215.0	230.8	258.8	
		C^+	277.5	279.0	279.7	
3	$CH_3[CFF]^+$	F	126.9	143.8	135.5	96.4[b]
		C^+	216.8	222.0	219.0	
4	$(CH_3)_2[CF]^+$	F	183.7	200.3	219.2	185.0[c]
		C^+	295.7	296.3	295.9	282.8[c]
5	$C_2H_5[CFCH_3]^+$	F	162.5			183.5[c]
		C^+	293.0			283.6[c]
6	$[c\text{-}C_5H_8F]^+$	F	159.1			149.4[c]
		C^+	311.4			294.0[c]
7	$[c\text{-}C_3H_2F]^+$	F	−56.5	−46.8	−50.2	−67.0[d]
		C(F)	168.2	170.3	181.2	
		C(H)	160.7	160.9	163.7	
8	$[c\text{-}C_3HF_2]^+$	F	−51.7	−42.1	−49.5	
		C(F)	154.0	156.0	163.3	
		C(H)	146.7	147.0	147.9	
9	$[c\text{-}C_3F_3]^+$	F	−50.6	−42.0	−55.4	−63.1[e]
		C	138.3	140.5	145.2	
10	$[t\text{-}CHF{=}OCH_3]^+$	F	73.3	90.4	72.8	49.9[f]
		C(F)	189.9	192.2	186.5	
		C(H)	75.0	76.5	83.1	
11	$[c\text{-}CHF{=}OCH_3]^+$	F	68.1	84.5	69.1	41.8[f]
		C(F)	184.3	188.0	180.9	
		C(H)	74.7	76.1	82.0	

[a] Both experimental and theoretical ^{19}F and ^{13}C NMR Chemical shifts are referenced to $CFCl_3$, TMS, respectively. [b] Reference 15. [c] Reference 18. [d] Reference 19. [e] Reference 20. [f] Reference 21.

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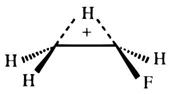
of ^{13}C, ^{17}O, ^{15}N, ^{19}F, etc.,[5] show, in some cases, significant improvements over the chemical shifts results computed at the SCF level.

CF_3^+, 1. In the gas phase, trifluoromethyl cation (**1**), is stable and has been observed as an abundant species.[10] We have recently reported the calculated energy and structure of **1**.[11] The MP2/6-31G*-optimized structure of **1** is a planar D_{3h} with a shorter C−F bond length of 1.246 Å compared to the C−F bond length (1.33 Å) of CF_4. Since fluorine possesses 2p nonbonded electron pairs, the back-donation 2p−2p overlap is maximum in ion **1**, resulting in the shorter C−F bond length. However, Reynolds[12] calculated the relative stability of CF_3^+ compared to other trihalomethyl cations (CX_3^+, X = Cl and Br). The calculated order of stability was found to be Cl > Br >> F. Therefore, the electron-withdrawing power of the three fluorine atoms in CF_3^+ surpasses their π-donating ability. The IGLO II- and GIAO-MP2-calculated ^{13}C NMR chemical shifts of **1** are 162.1 and 169.2 ppm, respectively, close to the predicted value of δ 140.0 obtained from comparison with other known trihalomethyl carbocations.[3] The GIAO-MP2-calculated ^{19}F NMR chemical shift of ion **1** is δ 51.7.

CH_3CHF^+, 2. So far **2** has also not been observed in solution under stable ion conditions.[2] Structure **2** was found to be the global minimum on the potential energy surface. The hydrogen-bridged structure **2a** is not a minimum at the MP2/6-31G* level and converged into **2** upon optimization at the MP2/6-31G* level. C−H hyperconjugation is responsible for the shorter C−C bond (1.433 Å) in **2**. Structure **2** has previously been calculated by Reynolds[13] at MP2/6-31G**, and the results were similar to those obtained in the present study.



2a

Compared to **1**, the GIAO-MP2-calculated ^{13}C and ^{19}F NMR chemical shifts of **2** of δ 279.7 and 258.8, respectively, are much more deshielded. Correlation has little effect on ^{13}C NMR chemical shift calculations. Accordingly, both IGLO II (δ 277.5)- and GIAO-SCF (δ 279.0)-calculated ^{13}C NMR chemical shifts of **2** are very close to the corresponding GIAO-MP2-calculated value of δ 279.7.

$CH_3C(F)F^+$, 3. Methyldifluorocarbenium ion (**3**) was observed[14] as a long-lived ion by ionizing CH_3CF_3 in SbF_5/SO_2ClF solution at −80 °C and characterized by ^1H and ^{19}F NMR spectroscopy. The longer C−C bond (1.452 Å) of **3** compared to that (1.433 Å) of **2** can be accounted for on the basis that both fluorine atoms in ion **3** are capable of back-donation and thus stabilize the ion by resonance. The GIAO-MP2-calculated averaged ^{19}F NMR chemical shift of **3** is δ 135.5, which deviates from the experimental value (δ 96.4) by 39.1 ppm. However, the overall correlation of the GIAO-MP2-calculated ^{19}F NMR chemical shifts with the experimental chemical shifts of the fluorocarbocations is excellent as shown in Figure 3. The GIAO-MP2-calculated ^{13}C NMR chemical shift of **13** (δ

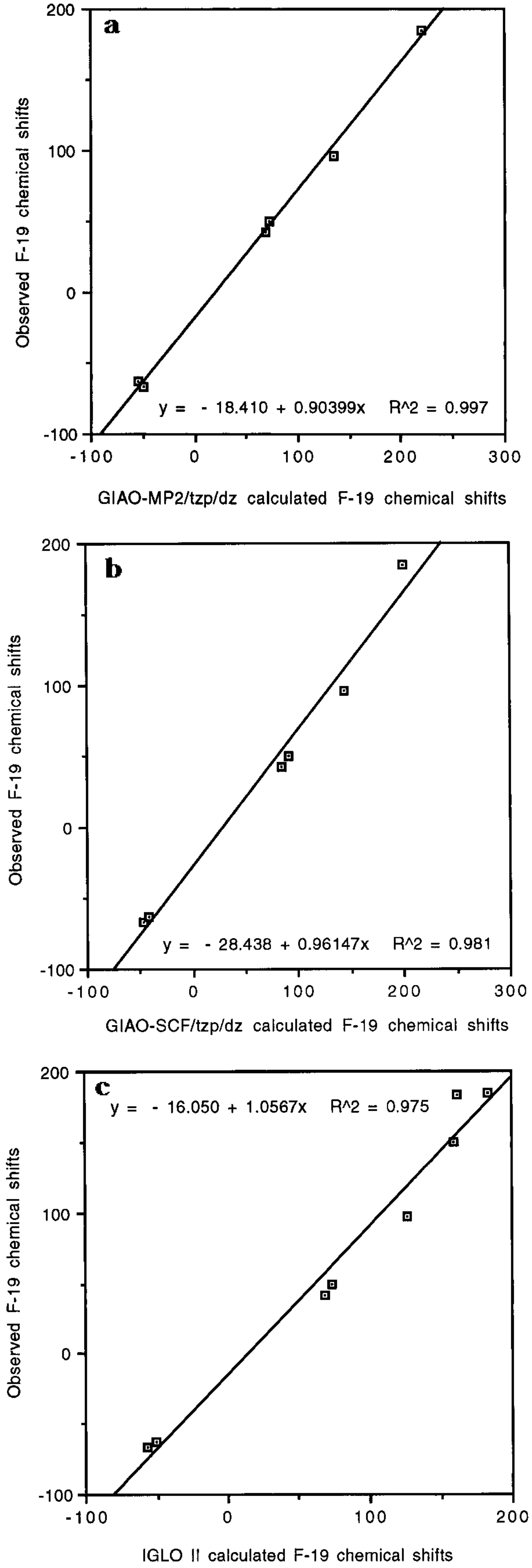


Figure 3. Plot of calculated vs experimental ^{19}F NMR chemical shifts of fluorocarbenium ions: (a) GIAO-MP2/tzp/dz vs experimental, (b) GIAO-SCF/tzp/dz vs experimental, and (c) IGLO II *vs* experimental.

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219.0) indicates a moderate shielding effect as compared to **2** (δ 279.7). However, no experimental ^{13}C NMR chemical shift of **3** is available to make comparisons with the theoretical results.

$(CH_3)_2CF^+$, 4. The C_2 structure **4** is the most stable conformer of $(CH_3)_2CF^+$ at the MP2/6-31G* level of calculations. A similar C_2 structure was also shown to be the most stable conformer for the 2-propyl cation.[15] Whereas the GIAO-MP2-calculated ^{13}C NMR chemical shift of δ 295.9 agrees well with the experimental chemical shift of δ 282.8, the GIAO-MP2-calculated ^{19}F NMR chemical shift of δ 219.2 again deviated by 34 ppm from the experimental value of δ 185.0.

$CH_3CH_2C^+FCH_3$, 5. The optimized structure **5** shows a long $C(CH_3)-C(CH_2)$ bond (1.578 Å) aligned parallel with the p-orbital of C^+ thus permitting maximum C−C hyperconjugation. This type of long bond has also been found in tertiary alkyl carbocations.[16] Ion **5** has also been observed in superacid solution under stable ion conditions.[17] Because of the size of the molecule, we were not able to calculate its chemical shifts at the GIAO-MP2 level. Experimental and IGLO-calculated chemical shifts are shown in Table 1.

c-$C_5H_8F^+$, 6. The twisted C_2 structure **6** is found to be the global minimum of 1-fluoro-1-cyclopentyl cation. The ion was previously prepared[17] by Olah et al. by treating 1,1-difluorocyclopentane with a SbF_5-SO_2ClF solution at −78 °C. The ^{19}F NMR spectrum of ion **6** contains a deshielded quintet centered at δ 149.4 and can be compared to the IGLO-calculated value of δ 159.1.

c-$C_3H_2F^+$, 7. The monofluorocyclopropenium ion (**7**) is the simplest substituted three-membered-ring Hückel aromatic system. The ion was studied by NMR and vibrational spectroscopy.[18] The two calculated C−C force constants obtained from vibrational spectroscopy of monofluorocyclopropenyl-d_0 and -d_2 cations correspond to a weaker C−C bond opposite to the fluorine-substituted carbon and a stronger C−C bond adjacent to the fluorine-substituted carbon. Our calculated structure **7** also shows that the longer (1.385 Å) C−C bond is opposite to the fluorine-substituted carbon and the shorter (1.367 Å) C−C bond is adjacent to the fluorine-substituted carbon. The interaction of the fluorine atom with the cyclopropenyl ring is substantial as shown by the shorter C−F bond (1.274 Å), which is even shorter than that of ions **4**−**6**. Both IGLO- and GIAO-calculated ^{19}F NMR chemical shifts of **6** agree well with the experimental data (Table 1).

c-$C_3HF_2^+$, 8. Difluorocyclopropenium ion (**8**) is not known experimentally. The calculated C−F bond length (1.272 Å) of **8** is very close to the C−F bond length of **7**. The two shorter C−C bonds (1.382 and 1.373 Å) indicate that the ion **8** also has substantial aromatic character. The calculated chemical shifts are also very close to those of monofluorocyclopropenium ion (**7**) (Table 1).

c-$C_3F_3^+$, 9. Trifluorocyclopropenium ion (**9**) is observed[19] experimentally by treating perfluorocyclopropene with an excess of SbF_5 at 0 °C. **9** is characterized by a single peak in the fluorine NMR spectrum at δ −63.1, which is deshielded by 57.8 ppm when compared to neutral perfluorocyclopropene (δ −120.9). The structural feature and calculated and experimental chemical shifts of this trifluoro-substituted cyclopropenium ion **9** are very similar to those of mono- and difluoro substituted cyclopropenium ions **7** and **8**, respectively (Figure 1).

***trans*- and *cis*-$CHF{=}OCH_3^+$, 10 and 11.** When α,α-difluoromethyl methyl ether was treated with SbF_5-SO_2 at −40 °C, two isomeric methoxyfluorocarbenium ions were obtained,[20] of which 70% is **10** and 30% is **11** as measured by integration of the ^1H NMR signals.

$$CH_3OCHF_2 \xrightarrow[-40\ ^0C]{SbF_5\text{-}SO_2} \mathbf{10} + \mathbf{11}$$

At the MP2/6-31G*//MP2/6-31G* level the ion **11** is only 3.2 kcal/mol more stable than the ion **10**. At the MP4(SDTQ)//6-31G*//MP2/6-31G* level the ion **11** is still 3.2 kcal/mol more stable than the ion **10**. This is, however, not in agreement with the experimental results where **10** was formed predominantly. The calculated structures of ions **10** and **11** show that the ions are predominantly carboxonium ions rather than carbenium ions as indicated from the calculated $C(CH_2)-O$ bond distances (1.24 Å) of **10** and **11**, which are close to the C═O distance in carbonyl compounds. The calculated chemical shifts are summarized in Table 1.

Chemical Shift Correlation. The GIAO-MP2-calculated ^{19}F NMR chemical shifts are in excellent agreement with the experimental data (Figure 3a) and are clearly superior to the GIAO-SCF (Figure 3b)- and IGLO II (Figure 3c)-calculated ^{19}F NMR chemical shifts. In the series CF_3^+, $CH_3C^+F_2$, and $(CH_3)_2C^+F$, both the calculated and experimental δ values indicate an increase in the deshielding effect at the carbocationic center with decreasing fluorine substitution. Presumably, this is due to an increase in fluorine back-donation into the carbocationic center. Both calculated and experimental ^{19}F NMR chemical shifts indicate that this effect is more pronounced in the monofluorinated derivatives.

Protolytic Cleavage of Trifluoroacetic Acid. We have previously[3] attempted to observe the trifluoromethyl cation (**1**) by protolytic cleavage of trifluoroacetic acid (CF_3COOH) or its esters with $FSO_3H{:}SbF_5$. However, only protonated trifluoroacetic acid was observed, and attempts to dehydrate it to trifluoroacetyl cation (CF_3CO^+) and subsequently via decarbonylation to cation **1** were unsuccessful.[3] In fact, even at 60 °C in neat "Magic Acid" no cleavage of protonated trifluoroacetic acid was observed by ^{13}C and ^{19}F NMR spectroscopy.[3b] This is surprising, since protonated carboxylic acids in general readily dehydrate to yield the corresponding acylium cations.[21] CF_4 was not observed, but because of its volatility, small quantities of CF_4 (bp = −128 °C) are difficult to observe in solution by ^{19}F NMR spectroscopy. We have now reinvestigated the ionization of trifluoroacetic acid with Magic Acid by employing more sensitive gas IR spectroscopy to detect CF_4 possibly formed during the reaction. Indeed, FT-IR analysis of gas samples taken after reacting trifluoroacetic acid with excess $FSO_3H{:}SbF_5$ (50 mol % SbF_5) at room temperature for 30 min in an autoclave showed a strong absorption band

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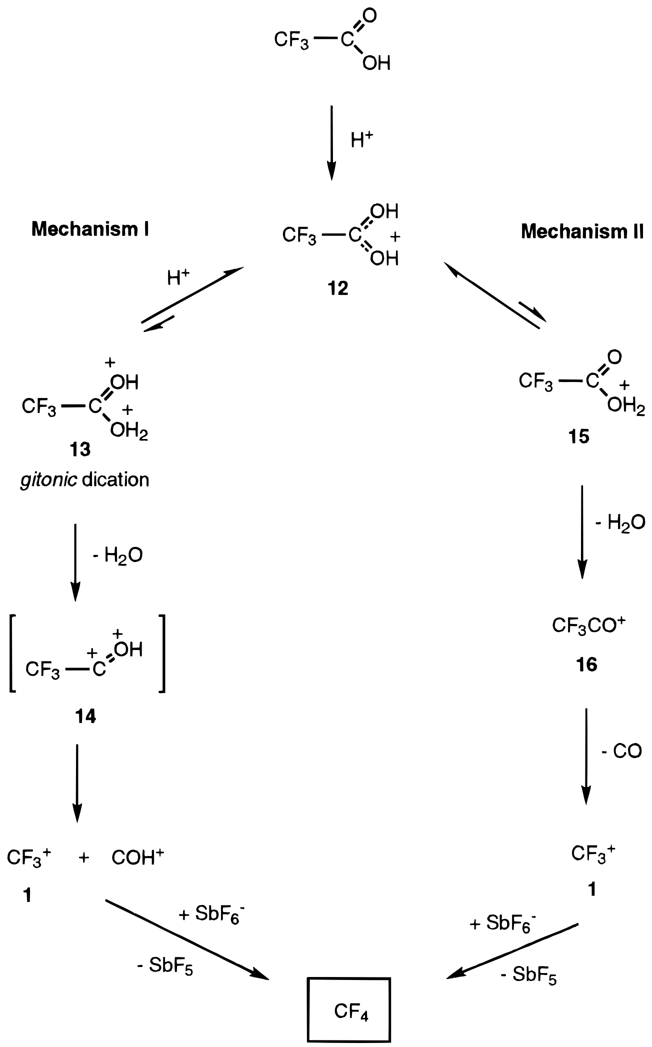
at 1277.3 cm^{-1} indicative of CF_4. The assignment of the peak to tetrafluoromethane was confirmed by adding pure CF_4 gas to the sample. The formation of CF_4 indicates protolytic cleavage of protonated trifluoroacetic acid to CF_3CO^+ and subsequent decarbonylation to the CF_3^+ cation which is then quenched by fluoride ion (from SbF_6^- or the acid system) to form CF_4.

Interestingly, no protolytic cleavage occurred when trifluoroacetic acid was reacted with superacid systems weaker than 1:1 M Magic Acid. For example, no formation of CF_4 was detected when mixtures of FSO_3H:SbF_5 containing only 1, 2, 5, and 10 mol %, respectively, of SbF_5 were used. There are two possible reasons for the lack of CF_4 formation in the latter acid systems: (a) The protolytic cleavage of trifluoroacetic acid is dependent on the acidity of the superacid employed, or (b) the fluoride concentration in these acid systems is not sufficient for the quenching of CF_3^+ cations to CF_4. We have also attempted to react trifluoroacetic acid with a mixture of FSO_3H and KF (ca. 1:1 M). This acid system generates HF *in situ* as a fluoride ion source for the quenching of CF_3^+ cations to CF_4. However, no CF_4 formation was detected under these conditions, indicating that the protolytic cleavage of trifluoroacetic acid is mainly dependent on the acidity of the superacid system. This acidity dependence can be rationalized by further protolytic (i.e., superelectrophilic) activation of protonated trifluoroacetic acid, involving a diprotonation equilibrium with a reactive gitonic dication (mechanism I) rather than direct cleavage of the monoprotonated trifluoroacetic acid (mechanism II).

Protolytic activation of protonated trifluoroacetic acid **12** (mechanism I) leads to a highly electron deficient, superelectrophilic, gitonic dication (**13**), which is substantially more reactive than its parent monocation **12**.[22] Its subsequent dehydration and decarbonylation leads to the CF_3^+ cation (**1**) which is then readily quenched by fluoride ion (from SbF_6^-) to form CF_4. Similar diprotonation equilibria have previously[23] been suggested in the ionization reactions of formic acid and acetic acid, respectively, in excess superacid. On the other hand, the direct cleavage of monoprotonated trifluoroacetic acid **12** (mechanism II) would involve tautomerization to form cation **15**, which subsequently would dehydrate and decarbonylate to yield the CF_3^+ cation (**1**).

Scheme 1



In order to investigate the two mechanistic possibilities, we have carried out *ab initio* calculations. Diprotonated trifluoroacetic acid **13** (mechanism I) was found to be a stable minimum structure at the MP2/6-31G* level and can be viewed as a donor−acceptor complex of H_2O and protonated trifluoroacetyl dication (CF_3COH^{2+}, **14**) with a long C−C bond of 1.599 Å (Figure 2). Protonation of **12** to form dication **13** was calculated to be slightly endothermic by only 2.6 kcal/mol at the MP2(fu)/6-31G* + ZPE level. Attempts to find a stable minimum for protiotrifluoroacetyl dication (**14**) failed because of its spontaneous dissociation into CF_3^+ (**1**) and protonated carbon monoxide COH^+. Simultaneous dehydration and deprotonation of dication **13** into CF_3^+ (**1**), COH^+, and H_2O was calculated to be exothermic by 37.0 kcal/mol at the MP2(fu)/6-31G* + ZPE level. This reaction is even more exothermic if the subsequent protonation of water to H_3O^+ ($\Delta H = -167.0$ kcal/mol at the MP2(fu)/6-31G* + ZPE level) in the superacid media is considered. Finally, fluoride abstraction by CF_3^+ (**1**) from SbF_6^- leads to the formation of CF_4.

Tautomerization of **12** to form cation **15** (mechanism II), on the other hand, is endothermic by 15.9 kcal/mol at the MP2(fu)/6-31G* + ZPE level. Subsequent dehydration of cation **15** to form trifluoroacetyl cation (CF_3CO^+, **16**) was calculated to be endothermic by 26.8 kcal/mol at the same level. Decarbonylation of **16** to form CF_3^+ (**1**) is also endothermic by 19.6 kcal/mol; the latter two reactions become exothermic, however, if the subsequent protonation of H_2O and CO to H_3O^+ ($\Delta H = -167.0$ kcal/mol) and COH^+ ($\Delta H = -97.6$ kcal/mol), respectively, is considered. As in mechanism I, fluoride abstraction by CF_3^+ (**1**) from SbF_6^- leads to the formation of CF_4.

Based on the calculated data, it is suggested that the protolytic cleavage of CF_3COOH in superacid media involves the cleavage of protio(trifluoromethylcarboxonium) dication ($CF_3C(OH)(OH_2)_2^+$, **13**) (mechanism I) rather than the direct cleavage of monoprotonated trifluoroacetic acid **12** (mechanism II). This is in accord with the observed acidity dependence of the reaction. In addition, theoretical calculations have shown that diprotonation of trifluoroacetic acid is energetically feasible, and dication **13** was found to be a stable minimum structure at the MP2(fu)/6-31G* level.

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Conclusions

The structures of a series of fluorocarbocations were calculated at the correlated MP2/6-31G* level. ^{13}C and ^{19}F NMR chemical shifts of these structures were calculated using IGLO and GIAO-MP2 methods. The data showed good correlation of calculated ^{19}F and ^{13}C NMR chemical shifts with the experimental chemical shifts of the fluorocarbocations. The correlation for GIAO-MP2-calculated ^{19}F NMR chemical shifts with the experimental data is excellent. The protolytic cleavage of trifluoroacetic acid (CF_3COOH) in superacids giving CF_4 was also investigated, and the reaction mechanism is suggested to involve the intermediacy of the reactive gitonic $CF_3C(OH)(OH_2)^{2+}$ dication (**13**).

Experimental Section

CF_3COOH, KF, CF_4, and H_2SO_4 are commercially available products (Aldrich) and were used as received. Antimony pentafluoride (Allied-Chemical) and fluorosulfonic acid (3 M) were double distilled prior to use. IR spectra were obtained on a Nicolet 800 FT-IR spectrometer using a gas IR cell equipped with NaCl windows.

Protolytic Cleavage of CF_3COOH with Magic Acid. Trifluoroacetic acid (1 mL) was placed into a bomb (stainless steel) equipped with a magnetic stirrer and cooled to −78 °C. After the addition of 4 mL of FSO_3H/SbF_5 (1:1 molar ratio) the reactor was closed and allowed to warm up to room temperature under continuous stirring. A gas sample was taken from the reactor after about 2 h. FT-IR analysis showed a strong absorption band at 1278 cm^{-1}. The assignment of this peak to CF_4 was confirmed by adding pure CF_4 gas to the sample. The same experimental procedure was used for the attempted protolytic cleavage of CF_3COOH in various other acid systems (see text).

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