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

G. K. Surya Prakash,* Golam Rasul, Arwed Burrichter, Kenneth K. Laali, and George A. Olah*

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661

Received June 14, 1996

The structures of a number of fluorocarbocations were calculated at the correlated MP2/6-31G* level. 13C and 19F NMR chemical shifts of fluorocarbocations were calculated for the first time using IGLO and GIAO-MP2 methods. The data showed good correlation of calculated 19F and 13C NMR chemical shifts with the experimental chemical shifts of fluorocarbocations. The correlation for GIAO-MP2-calculated 19F NMR chemical shifts with the experimental data is excellent. Using theoretical calculations as guidance, the protolytic cleavage of trifluoroacetic acid (CF3COOH) in superacids forming CF4 was also investigated experimentally and by ab initio calculations. This reaction is suggested to involve the gitanic CF3C(OH)(OH2)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 13C and 19F NMR spectroscopy since the pioneering work of Olah, Chambers, and Comisarow, although in some cases difficulties arose because of rapid fluoride ion exchange between superacid and fluorocarbocations. Attempts to directly observe CH2CHF+ and CF3+ by NMR spectroscopy under superacid stable ion conditions were unsuccessful. The intermediacy of CF3+ was suggested, however, in the ionization and subsequent decarbonylation of trifluoroacetyl fluoride (CF3COF) with SbF5 at low temperature. Whereas no CF3CO+ and CF3+ cations could be observed directly, 19F NMR spectroscopy showed already at relatively low temperature (–50 °C) the formation of tetrafluoromethane (CF4). It was proposed that the great strength of the C–F bond in CF4 (ca. 140 kcal/mol) leads to rapid quenching of CF3+ to CF4 even in low-nucleophilicity fluorinated superacid media.

\[
\begin{align*}
\text{CF3COF} & \xrightarrow{\text{SbF5}} \text{CF3CO}^+ \xrightarrow{-78^\circ \text{C}} \text{CF3C(OH)(OH2)2}^+ \\
\text{[CF3CO]+} & \xrightarrow{\text{CO}} \text{[CF3]+} \xrightarrow{\text{SbF5}} \text{CF4}
\end{align*}
\]

We wish to report now our ab initio/IGLO/GIAO-MP2


Results and Discussion

Ab initio calculations were carried out by using the GAUSSIAN-94® 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 at IGLO II level using MP2/6-31G* geometries. Huzinaga® Gaussian lobes were used as follows: Basis II, C, O, or F, 9s 5p 1d contracted to 31G* geometries. Huzinaga® Gaussian lobes were used as follows: Basis II, C, O, or F, 9s 5p 1d contracted to [31111, 2111, 1]; d exponent, 1.0; H, 5s 1p contracted to [311, 1]; p exponent, 0.70. GIAO-SCF and GIAO-MP2


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 application 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-\(\zeta\) 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-\(\zeta\)) 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\(^a\)

<table>
<thead>
<tr>
<th>no.</th>
<th>cations</th>
<th>atom</th>
<th>IGLO II/MP2/6-31G*</th>
<th>GIAO-SCF/tzp/dz</th>
<th>GIAO-MP2/tzp/dz</th>
<th>expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[CF(_3)](^+)</td>
<td>F</td>
<td>58.6</td>
<td>162.1</td>
<td>167.1</td>
<td>169.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(^+)</td>
<td>277.5</td>
<td>279.0</td>
<td>279.7</td>
<td>279.7</td>
</tr>
<tr>
<td>2</td>
<td>CH(_3)(CHF)(^+)</td>
<td>F</td>
<td>215.0</td>
<td>230.8</td>
<td>258.8</td>
<td>258.8</td>
</tr>
<tr>
<td>3</td>
<td>CH(_3)(CFF)(^+)</td>
<td>F</td>
<td>126.9</td>
<td>143.8</td>
<td>135.5</td>
<td>135.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(^+)</td>
<td>216.8</td>
<td>222.0</td>
<td>219.0</td>
<td>219.0</td>
</tr>
<tr>
<td>4</td>
<td>(CH(_3))(_2)(CF(_3))(^+)</td>
<td>F</td>
<td>183.7</td>
<td>200.3</td>
<td>219.2</td>
<td>185.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(^+)</td>
<td>295.7</td>
<td>296.3</td>
<td>295.9</td>
<td>282.8</td>
</tr>
<tr>
<td>5</td>
<td>C(_2)H(_2)(CFCH(_3))(^+)</td>
<td>F</td>
<td>162.5</td>
<td>293.0</td>
<td>283.6</td>
<td>283.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(^+)</td>
<td>159.1</td>
<td>294.0</td>
<td>149.4</td>
<td>149.4</td>
</tr>
<tr>
<td>6</td>
<td>[c-C(_3)H(_2)F(_2)](^+)</td>
<td>F</td>
<td>-56.5</td>
<td>-46.8</td>
<td>-50.2</td>
<td>-67.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(F)</td>
<td>168.2</td>
<td>170.3</td>
<td>181.2</td>
<td>181.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(H)</td>
<td>160.7</td>
<td>160.9</td>
<td>163.7</td>
<td>163.7</td>
</tr>
<tr>
<td>7</td>
<td>[c-C(_3)H(_2)F(_3)](^+)</td>
<td>F</td>
<td>-51.7</td>
<td>-42.1</td>
<td>-49.5</td>
<td>-49.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(F)</td>
<td>154.0</td>
<td>156.0</td>
<td>163.3</td>
<td>163.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(H)</td>
<td>146.7</td>
<td>147.0</td>
<td>147.9</td>
<td>147.9</td>
</tr>
<tr>
<td>8</td>
<td>[c-C(_3)F(_3)](^+)</td>
<td>F</td>
<td>-50.6</td>
<td>-42.0</td>
<td>-55.4</td>
<td>-63.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>138.3</td>
<td>140.5</td>
<td>145.2</td>
<td>145.2</td>
</tr>
<tr>
<td>9</td>
<td>[t-CHF=OCH(_3)](^+)</td>
<td>F</td>
<td>73.3</td>
<td>90.4</td>
<td>72.8</td>
<td>49.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(F)</td>
<td>189.9</td>
<td>192.2</td>
<td>186.5</td>
<td>186.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(H)</td>
<td>75.0</td>
<td>76.5</td>
<td>83.1</td>
<td>83.1</td>
</tr>
<tr>
<td>10</td>
<td>[t-CHF=OCH(_3)](^+)</td>
<td>F</td>
<td>68.1</td>
<td>84.5</td>
<td>69.1</td>
<td>41.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(F)</td>
<td>184.3</td>
<td>188.0</td>
<td>180.9</td>
<td>180.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(H)</td>
<td>74.7</td>
<td>76.1</td>
<td>82.0</td>
<td>82.0</td>
</tr>
</tbody>
</table>

\(^a\) Both experimental and theoretical \(^{19}\)F and \(^{13}\)C NMR Chemical shifts are referenced to CF\(_2\)Cl\(_2\), TMS, respectively. \(^\circ\) Reference 15. \(^\circ\) Reference 18. \(^\circ\) Reference 19. \(^\circ\) Reference 20. \(^\circ\) Reference 21.
of $^{13}$C, $^{17}$O, $^{15}$N, $^{19}$F, etc., 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$_3$. Since fluorine possesses 2p nonbonded electron pairs, the backdonation 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 $\delta$ 140.0 obtained from comparison with other known trihalomethyl carbocations.$^{3}$ The GIAO-MP2-calculated $^{19}$F NMR chemical shift of ion 1 is $\delta$ 51.7.

**CH$_3$CHF$^+$, 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.

Compared to 1, the GIAO-MP2-calculated $^{13}$C and $^{19}$F NMR chemical shifts of 2 of $\delta$ 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 ($\delta$ 277.5) and GIAO-SCF ($\delta$ 279.0)-calculated $^{13}$C NMR chemical shifts of 2 are very close to the corresponding GIAO-MP2-calculated value of $\delta$ 279.7.

**CH$_3$C(F)F$^+$, 3.** Methyldifluorocarbenium ion (3) was observed$^{14}$ as a long-lived ion by ionizing CH$_3$CF$_3$ in SbF$_5$/SO$_2$ClF solution at $-80$ °C and characterized by $^1$H 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 $\delta$ 135.5, which deviates from the experimental value ($\delta$ 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

![Figure 3](image-url)

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.

fluorocarbocations is excellent as shown in Figure 3. The GIAO-MP2-calculated $^{13}$C NMR chemical shift of 13 ($\delta$
219.0) indicates a moderate shielding effect as compared to 2 (δ 279.7). However, no experimental 13C NMR chemical shift of 3 is available to make comparisons with the theoretical results.

(CH3)2CF+, 4. The C2 structure 4 is the most stable conformer of (CH3)2CF+ at the MP2/6-31G* level of calculations. A similar C2 structure was also shown to be the most stable conformer for the 2-propyl cation.15 Whereas the GIAO-MP2-calculated 13C NMR chemical shift of δ 295.9 agrees well with the experimental chemical shift of δ 282.8, the GIAO-MP2-calculated 19F NMR chemical shift of δ 219.2 again deviated by 34 ppm from the experimental value of δ 185.0.

CH3C(=F)CH3, 5. The optimized structure 5 shows a long C(=F)–C(=F) bond (1.578 Å) aligned parallel with the p-orbital of C=O, thus permitting maximum C–O hyperconjugation. This type of long bond has also been found in trialkyl 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 IGL-calculated chemical shifts are shown in Table 1.

-c-CsH3F+, 6. The twisted C2 structure 6 is found to be the global minimum of 1-fluoro-1-cyclopentyl cation. The ion was previously prepared18 by Olah et al. by treating 1,1-difluorocyclopentane with a SbF5–SO3ClF solution at −78 °C. The 19F NMR spectrum of ion 6 contains a deshielded quintet centered at δ 149.4 and can be compared to the IGL-calculated value of δ 159.1.

-c-CsH3F2+, 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-d8 and -d4 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 19F NMR chemical shifts of 6 agree well with the experimental data (Table 1).

c-CsH3F2+, 8. Diffuorocyclopropenium 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-CsF3+, 9. Trifluorocyclopropenium ion (9) is observed18 experimentally by treating perfluorocyclopropene with an excess of SbF5 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 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=OCH3+, 10 and 11. When α,α-difluoromethyl methyl ether was treated with SbF5–SO3ClF 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.

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(CH3)=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 19F 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 19F NMR chemical shifts. In the series CF3+, CH3C(=F)O+, and (CH3)2C(=F)–, both the calculated and experimental δ values indicate an increase in the deshielding effect at the carbocationic center with decreasing fluorene substitution. Presumably, this is due to an increase in fluorene back-donation into the carbocationic center. Both calculated and experimental 19F NMR chemical shifts indicate that this effect is more pronounced in the monoaluminated derivatives.

Protonolytic Cleavage of Trifluoroacetic Acid. We have previously attempted to observe the trifluoromethyl cation (1) by protolytic cleavage of trifluoroacetic acid (CF3COOH) or its esters with SbF5–H2O. However, only protonated trifluoroacetic acid was observed, and attempts to dehydrate it to trifluoroacetyl cation (CF3–CO+) 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 19F and 13C NMR spectroscopy.6 This is surprising, since protonated carboxylic acids in general readily dehydrate to yield the corresponding acyliminium cations.19 CF4 was not observed, but because of its volatility, small quantities of CF4 (bp = −128 °C) are difficult to observe in solution by 19F NMR spectroscopy. We have now reinvestigated the ionization of trifluoroacetic acid with Magic Acid by employing more sensitive gas IR spectroscopy to detect CF4 possibly formed during the reaction. Indeed, FT-IR analysis of gas samples taken after reacting trifluoroacetic acid with excess SbF5–SO3ClF at room temperature for 30 min in a autoclave showed a strong absorption band...
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\(_3\)CO\(^+\) 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\(_3\)H: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\(_3\)H 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 gitanic 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, gitanic dication (13), which is substantially more reactive than its parent monocation 12. 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 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.

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\(_2\)O and protonated trifluoroacetyl cation (CF\(_3\)CO\(^+\)), 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 CO\(^+\). Simultaneous dehydroxylation and deprotonation of dication 13 into CF\(_3^+\) (1), CO\(^+\), and H\(_2\)O was calculated to be exothermic by 37.0 kcal/mol at the MP2(fu)/6-31G* + ZPE level. This reaction is even more exothermic than the subsequent protolytic cleavage of CF\(_3\)COOH in superacid media involving the cleavage of proton(trifluoromethylcarbinoxonium) dication (CF\(_3\)C(OH)(OH\(_2\))\(^+\)), 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 protolytic cleavage of trifluoroacetic acid is energetically feasible, and dication 13 was found to be a stable minimum structure at the MP2(fu)/6-31G* level.

---

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$_3$COOH) in superacids giving CF$_4$ was also investigated, and the reaction mechanism is suggested to involve the intermediacy of the reactive gitonic CF$_3$C(OH)(OH$_2$)$_2$ dication (13).

Experimental Section

CF$_3$COOH, KF, CF$_4$, and H$_2$SO$_4$ 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$_3$COOH with Magic Acid. Trifluoroacetic acid (1 mL) was placed into a bomb (stainless steel) equipped with a magnetic stirrer and cooled to $-78 \degree$C. After the addition of 4 mL of FSO$_3$H/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$_3$COOH in various other acid systems (see text).

Acknowledgment. Support of our studies by the Loker Hydrocarbon Research Institute and the National Science Foundation is gratefully acknowledged. A.B. wishes to thank the Konrad-Adenauer Foundation for a scholarship.