J. Am. Chem. Soc. 1994, 116, 2481–2485 2481

Experimental Evidence for the Existence of Fluoroformic Acid and Its Ionized and Protonated Forms in the Gas Phase

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Received August 16, 1993[⊗]

Abstract: Protonated fluoroformic acid, $FC(OH)_2^+$, is produced in the gas phase upon dissociative ionization of ethyl fluoroformate, via $FCOOCH_2CH_3^{\bullet +} \rightarrow FC(OH)_2^+ + {}^{\bullet}CH{=}CH_2$ (McLafferty + 1 rearrangement). Sequential decomposition of $FC(OH)_2^+$ by loss of $^{\bullet}H$ provides access to the radical cation $FCOOH^{\bullet +}$, from which neutral fluoroformic acid can be generated by neutralization. Reionization ~0.4 μs later shows that solitary fluoroformic acid represents a stable molecule with an appreciable barrier for dissociation to FH + CO_2. This result is consistent with ab initio theory predictions and confirms that the spontaneous decay of FCOOH observed in condensed phases is an intermolecular, not intramolecular process. The major dissociations of cations $FC(OH)_2^+$ and $FCOOH^{\bullet +}$ involve cleavages of their F–C and C–OH bonds, ultimately leading to structurally characteristic losses of FH and H_2O from $FC(OH)_2^+$ and of $F^{\bullet}$ and $^{\bullet}OH$ from $FCOOH^{\bullet +}$. The eliminations of FH and $F^{\bullet}$ are associated with substantially larger reverse activation energies than the eliminations of H_2O and $^{\bullet}OH$.

Fluoroformic acid (FCOOH), the monofluoro derivative of carbonic acid, is a proposed intermediate in the oxidation of fluorocarbenes and ozonolysis of fluoroalkenes.[1,2] There are no experimental data available for this simple molecule, since all attempts to isolate it in solution have failed. According to chemistry textbooks, fluoroformic acid cannot exist in condensed phases because of autocatalytic decay to CO_2 + HF.[3] In contrast, solitary FCOOH is prediced by ab initio MO calculations to be a bound species with a high barrier (210 kJ/mol) for unimolecular decomposition to CO_2 + HF.[4] Consequently, in the absence of any intermolecular interactions, FCOOH should be capable of surviving long enough for experimental observation. This study describes the first generation and characterization of fluoroformic acid in the gas phase using neutralization–reionization mass spectrometry (NRMS).[5]

In NRMS experiments, an isolated neutral species is initially produced by neutralization from the corresponding gaseous ion[6] and subsequently identified by the mass spectrum obtained via reionization.[5] This method has led to the characterization of many elusive neutrals,[7] including hypervalent species,[8,9] diradicals,[10–12] carbenes,[10,13,14] and molecules susceptible to immediate intermolecular tautomerization (e.g., carbonic and carbamic acid).[15,16]

The investigation of a specific neutral by NRMS presupposes that the corresponding cation or anion is accessible and stable.[5,6,17] For the synthesis of fluoroformic acid, the radical ions $FCOOH^{\bullet +}$ or $FCOOH^{\bullet -}$ would be necessary, but have never been characterized. Here, tandem mass spectrometry methods (MS/MS)[18] are employed to prepare the radical cation $FCOOH^{\bullet +}$ and ascertain its unimolecular reactions, before it is used as precursor for neutral FCOOH. First data are also presented on protonated fluoroformic acid, $FC(OH)_2^+$, and the related radical $FC(OH)_2^{\bullet}$, neither of which has been documented experimentally.

Experimental Section

The experiments were performed with a modified VG AutoSpec tandem mass spectrometer that has been described in detail.[19] The instrument is of EBE geometry and contains three collision cells (Cls), one (Cls-1) in the field-free region following the ion soure (FFR-1) and two (Cls-2, Cls-3) in the field-free region following the magnet (FFR-3). Metastable ion (MI),[20] collisionally activated dissociation (CAD),[21] and neutralization–reionization ($^+NR^{+,-}$)[5] mass spectra were acquired in FFR-3 by utilizing the first two sectors as MS-1 and the second electric sector as MS-2. In regular MS/MS experiments, the precursor ion was produced in the ion source by electron ionization (EI) of the appropriate sample at 70 eV. In MS/MS/MS experiments, the precursor ion was formed by CAD with He in FFR-1 and later subjected to MI, CAD, or $^+NR^+$ in FFR-3. Unless otherwise noted, all ions exiting the ion source were accelerated to 8 keV.

MI spectra were acquired at a background pressure of $\sim 8 \times 10^{-8}$ mbar. Kinetic energy releases were calculated from peak widths at half height ($T_{0.5}$) and (for flat-top or dish-top signals) across the top (T_{top}) using established procedures.[20,22] For Gaussian peaks, *n* values were also determined on the basis of the ratios of peak widths at different heights.[23] The given *n* values are from the upper part of the peaks (≥50% height); the peak bottoms have smaller *n* values, presumably due to the presence

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[⊗] Abstract published in *Advance ACS Abstracts.* March 1, 1994.

(1) Gordon, R. J.; Lin, M. C. *Chem. Phys. Lett.* **1973**, *22*, 107–112.

(2) Cremer, D. *J. Am. Chem. Soc.* **1981**, *103*, 3633–3638.

(3) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980.

(4) Havlas, Z.; Kovár, T.; Zahradnik, R. *J. Am. Chem. Soc.* **1985**, *107*, 7243–7246.

(5) (a) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485–500. (b) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 808–815. (c) Holmes, J. L. *Mass Spectrom. Rev.* **1989**, *8*, 513–539.

(6) Gellene, G. I.; Porter, R. F. *Acc. Chem. Res.* **1983**, *16*, 200–207.

(7) McLafferty, F. W. *Science* **1991**, *247*, 925–929.

(8) Wesdemiotis, C.; Feng, R.; Danis, P. O.; Williams, E. R.; McLafferty, F. W. *J. Am. Chem. Soc.* **1986**, *108*, 5847–5853.

(9) Selgren, S. F.; Hipp, D. E.; Gellene, G. I. *J. Chem. Phys.* **1988**, *88*, 3116–3124.

(10) Wesdemiotis, C.; Leyh, B.; Fura, A.; McLafferty, F. W. *J. Am. Chem. Soc.* **1990**, *112*, 8655–8660.

(11) Srinivas, R.; Böhme, D. K.; Hrusák, J.; Schröder, D.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 1939–1942.

(12) Polce, M. J.; Wesdemiotis, C. *J. Am. Chem. Soc.* **1993**, *115*, 10849–10856.

(13) Wesdemiotis, C.; McLafferty, F. W. *J. Am. Chem. Soc.* **1987**, *109*, 4760–4761.

(14) Sülzle, D.; Drewello, T.; van Baar, B. L. M.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 8330–8333.

(15) Terlouw, J. K.; Lebrilla, C. B.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 354–355.

(16) Van der Berg, K.; Lebrilla, C. B.; Terlouw, J. K.; Schwarz, H. *Chimia* **1987**, *41*, 122–124.

(17) McMahon, A. W.; Chowdhury, S. K.; Harrison, A. G. *Org. Mass Spectrom.* **1989**, *24*, 620–624.

(18) Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry*; VCH Publishers, Inc.: New York, 1988.

(19) Polce, M. J.; Cordero, M. M.; Wesdemiotis, C.; Bott, P. A. *Int. J. Mass Spectrom. Ion Processes* **1992**, *113*, 35–58.

(20) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Mestable Ions*; Elsevier: Amsterdam, 1973.

(21) McLafferty, F. W.; Bente, P. F., III; Kornfeld, R.; Tsai, S.-C.l Howe, I. *J. Am. Chem. Soc.* **1973**, *95*, 2120–2129.

(22) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169–183.

(23) Holmes, J. L.; Terlouw, J. K. *Org. Mass Spectrom.* **1980**, *15*, 383–396.

of an additional Gaussian component arising from collisions with the background gases.

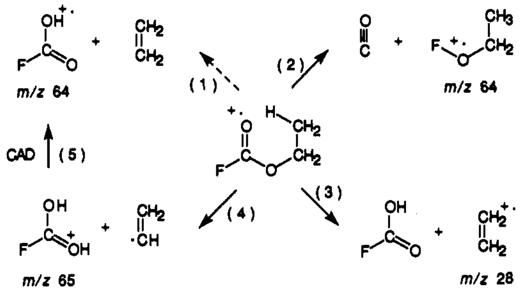
CAD spectra were obtained by introducing O_2 in Cls-3. The pressure of the collision gas was increased until the transmittance (T) of the precursor ion was reduced to 80%, corresponding to approximately single collision conditions.[22,24] For $^+NR^+$ spectra, the mass-selected precursor ion was neutralized by Xe in Cls-2 (80% T). After removal of the residual ions by electrostatic deflection, the remaining beam of fast neutrals was reionized by O_2 in Cls-3 (80% T). The newly formed ions were finally mass-analyzed and recorded in the $^+NR^+$ spectrum. The superscripts of N and R denote the charges of the precursor and the ultimate product ions, respectively. $^+NR^-$ ("charge-reversal") spectra were measured by combining neutralization and anionization with Xe in the same collision cell (Cls-2, 60% T). With polyatomic cations, such multicollision conditions form anions by stepwise addition of e^-, not simultaneous attachment of $2e^-$ and cogeneration of Xe^{2+}.[12,25]

The MS/MS and MS/MS/MS experiments were conducted with the slits of the instrument completely open in order to maximize the sensitivity and thus obtain spectra with acceptable signal/noise ratio. Under these conditions, the peak width at half height of the main beam is approximately 13 V. The spectra shown represent averages of >50 scans and are reproducible within ±10%.

Ethyl fluoroformate was synthesized from ethyl chloroformate (Aldrich) according to the procedure of Tordeux and Wakselman.[26] Distillation of the product provided a sample with no detectable impurities based on the H-NMR spectrum. The EI mass spectrum, measured at a resolving power of ~2000, was identical within experimental error to the one reported.[27]

Results and Discussion

Attempt To Generate $FCOOH^{•+}$ from $FCOOCH_2CH_3^{•+}$. In order to access FCOOH by neutralization, it is necessary to find an appropriate precursor for the fluoroformic acid radical cation, $FCOOH^{•+}$ (m/z 64). Such acid ions are formed via the McLafferty rearrangement of esters containing the respective acid.[28] The EI mass spectrum of ethyl fluoroformate (Figure 1A) indeed includes a small peak at m/z 64, which could be the sought $FCOOH^{•+}$ (eq 1). However, a magnetic scan at increased resolution shows that >85% of the m/z 64 ion have the isobaric composition $C_2H_5FO^{•+}$. The fragments present in the corresponding CAD spectrum (Figure 1B) indicate that $C_2H_5FO^{•+}$ is the radical cation $FOCH_2CH_3^{•+}$, which can be produced from ionized ethyl fluoroformate by 1,1-elimination of CO (eq 2). Particularly characteristic for the structure $F–O–CH_2–CH_3^{•+}$ are the dissociations to $FOCH_2^+$ (m/z 49) + $^•CH_3$, FO^+ (m/z 35) + $^•C_2H_5$, and $FO^•$ + $^+C_2H_5$ (m/z 29); furthermore, the appearance of recognizable peaks at every m/z value between m/z 60 and 63 demonstrates that the precursor ion possesses at least 4 H atoms, which is true for $FOCH_2CH_3^{•+}$.



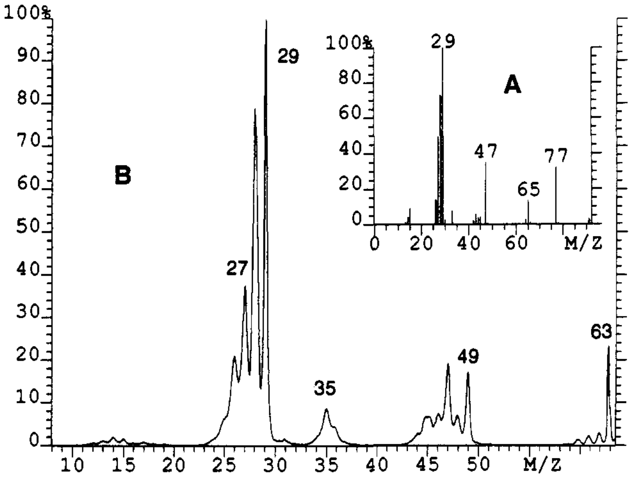


Figure 1. (A) EI spectrum of ethyl fluoroformate. (B) CAD spectrum of the cation at m/z 64 formed by EI of ethyl fluoroformate.

Although $FCOOH^{•+}$ (eq 1) is negligible in the EI spectrum of ethyl fluoroformate, the complementary fragment $CH_2{=}CH_2^{•+}$ (eq 3) appears with high abundance. According to Stevenson's rule,[28] the most favored product combination from a decomposing ion arises when the charge is retained on the piece of lowest ionization energy (IE). Thus, the EI spectrum of ethyl fluoroformate reveals that IE(FCOOH) > IE(C_2H_4) = 12.5 eV;[29,30] for comparison, IE(HCOOH) = 11.3 eV.[29] Fluorination has generally been found to raise the ionization energy due to the high electronegativity of the F atom.[29,31] Since $FCOOH^{•+}$ cannot be prepared directly from $FCOOCH_2CH_3^{•+}$, an alternative route is necessary, specifically one eliminating a neutral with IE ≫ 12.5 eV. This prerequisite is satisfied by the reaction $FC(OH)_2^+$ (protonated FCOOH) → $FCOOH^{•+}$ + $^•H$; IE($^•H$) = 13.6 eV.[29]

Generation of $FC(OH)_2^+$. Protonated fluoroformic acid (m/z 65) is formally generated from ethyl fluoroformate by the McLafferty + 1 rearrangement (eq 4), an important decomposition channel of ionized esters.[28] The MI spectrum of $FC(OH)_2^+$ contains fragments at m/z 45 and 47 resulting from dissociation to FH + ^+COOH and FCO^+ + H_2O, respectively (Figure 2A).[32] Water loss produces a Gaussian peak with $T_{0.5}$ = 43 meV (n = 1.4), while loss of FH gives rise to a flat-topped signal with substantially larger kinetic energy release ($T_{0.5}$ = 711 meV; T_{top} = 310 meV).

Since metastable precursor ions have narrow internal energy distributions (usually <50 kJ/mol), the two aforementioned processes must demand relatively similar critical energies in order to be able to compete against each other in the metastable time frame.[20,22,23] Formation of FH + ^+COOH ($\sum\Delta H^\circ_f$ = 316 kJ/mol)[29] and FCO^+ + H_2O ($\sum\Delta H^\circ_f$ = 427 kJ/mol)[29] over comparable barriers makes the reverse activation energy of FH loss significantly larger than that of H_2O loss. This indeed is reflected by the greater kinetic energy release associated with the generation of ^+COOH (*vide supra*).[20,22,33] The different peak shapes further indicate that the cleavages of hydrogen fluoride and water proceed through distinct mechanisms. The flat-top signal observed for $FC(OH)_2^+$ → FH + ^+COOH is characteristic for one-step four-center eliminations with a considerable energy for the reverse reaction.[22,33] On the other hand, the Gaussian

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(24) Todd, P. J.; McLafferty, F. W. *Int. J. Mass Spectrom. Ion Processes* **1981**, *38*, 371–378.

(25) (a) Feng, R.; Wesdemiotis, C.; McLafferty, F. W. *J. Am. Chem. Soc.* **1987**, *109*, 6521–6522. (b) Griffiths, W. J.; Harris, F. M.; Barton, J. D. *Rapid Commun. Mass Spectrom.* **1989**, *3*, 283–285. (c) Leyh, B.; Wankenne, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *197*, 453–474.

(26) Tordeux, M.; Wakselman, C. *Synth. Commun.* **1982**, *12*, 513–520.

(27) McLafferty, F. W.; Stauffer, D. B. *Wiley/NBS Registry of Mass Spectral Data*; Wiley: New York, 1989.

(28) McLafferty, F. W.; Turecek, F. *Interpretation of Mass Spectra*, 4th ed.; University Science Books: Mill Valley, CA, 1993.

(29) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *24*, 579–590.

(30) The large abundance of $C_2H_4^{•+}$ in Figure 1A could partly be the result of an additional pathway(s) to this ion, for example via the rearrangement $H–CH_2CH_2–OC({=}O)–F^{•+}$ → $CH_2CH_2^{•+}$ + CO_2 + FH.

(31) Stams, D. A.; Thomas, T. D.; MacLaren, D. C.; Ji, D.; Morton, T. H. *J. Am. Chem. Soc.* **1990**, *112*, 1427–1434.

(32) A small peak for $^•H$ loss also appears in the MI spectrum of $FC(OH)_2^+$ but is barely resolved from the base of the much more intense precursor ion.

(33) Levsen, K. *Fundamental Aspects of Organic Mass Spectrometry*; Verlag Chemie: Weinheim, 1978.

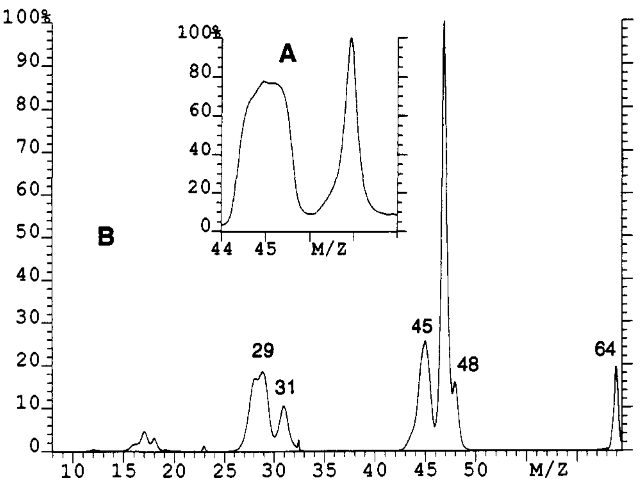
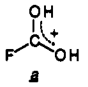


Figure 2. (A) MI and (B) CAD spectra of $FC(OH)_2^+$ formed by EI of $FCOOCH_2CH_3$.

shape obtained for $FC(OH)_2^+ \rightarrow FCO^+ + H_2O$ suggests a stepwise process,[22,33] possibly via rate-determining isomerization to $FC({=}O)OH_2^+$.[34] The MI characteristics of protonated fluoroformic acid agree well with structure *a*. They are incompatible with the isomeric ions *b* or *c* which resemble ion/molecule complexes and should lose HF or H_2O, respectively, in continuously endothermic dissociations with no appreciable reverse activation energies and thus very small kinetic energy releases ($T_{0.5} \leq 20$ meV).[22,33]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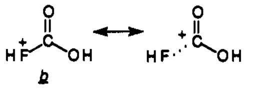
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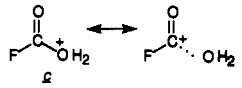
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Collisional activation of $FC(OH)_2^+$ gives rise to additional products (Figure 2B), among them the charge-stripping ions at m/z 32.5 ($FC(OH)_2^{\bullet 2+}$) and 23 ($^+HO{=}C{=}OH^+$; $^\bullet F$ loss). Particularly diagnostic for the connectivity of ion *a* are the fragments $FCOOH^{\bullet+}$ (m/z 64), $FCOH^{\bullet+}$ (m/z 48), FC^+ (m/z 31), and COH^+ (m/z 29). The structures $FCOH^{\bullet+}$ and $COH^{\bullet+}$ for m/z 48 and 29, respectively, were verified by comparison of the CAD spectra of these ions (MS/MS/MS) to reference CAD spectra of authentic $F{-}C{-}OH^{\bullet+}$ [14] and $C{-}OH^+$.[35] Most important for the present study is the fact that CAD of $FC(OH)_2^+$ provides access to the desired radical cation $FCOOH^{\bullet+}$ (eq 5). The unimolecular chemistry of this latter ion can be assessed by forming and isolating it in an MS/MS/MS experiment.

Generation of $FCOOH^{\bullet+}$ Via Sequential Dissociations. $FC(OH)_2^+$ cations formed from $FCOOCH_2CH_3$ in the EI source and subsequently subjected to CAD in FFR-1 yield *inter alia* $FCOOH^{\bullet+}$ (*vida supra*). These $FCOOH^{\bullet+}$ ions can be mass-selected by MS-1, thus allowing for the acquisition of their own MI and CAD spectra in FFR-3 (Figure 3).

The major decomposition pathway of metastable $FCOOH^{\bullet+}$ (Figure 3A) proceeds by loss of $F^\bullet$ to form ^+COOH at m/z 45 ($\Sigma D H^\circ_f$(products) = 668 kJ/mol).[29] This reaction leads to a broad, dish-topped signal with $T_{0.5} = 308$ meV ($T_{top} = 245$ meV). An additional, minor fragment in the MI spectrum of $FCOOH^{\bullet+}$ arises from decay into FCO^+ (m/z 47) + $^\bullet OH$ ($\Sigma \Delta H^\circ_f = 708$ kJ/mol)[29] and gives rise to a much narrower, Gaussian peak ($T_{0.5} = 35$ meV; $n = 1.7$).[36] The large differences in peak shapes and widths between $F^\bullet$ and $^\bullet OH$ loss are not without precedent. A broad, dish-topped peak has also been observed for the elimination of $F^\bullet$ from ionized formyl fluoride, $FC({=}O)H^{\bullet+}$.[14] On the other hand, in analogy to the $^\bullet OH$ cleavage from $FCOOH^{\bullet+}$, the $^\bullet OH$ elimination from ionized acetic acid, $CH_3COOH^{\bullet+}$, yields a narrow, Gaussian signal.[38] The large kinetic energy releases accompanying the elimination of fluorine reveal that the reverse reaction, *i.e.* the addition of $F^\bullet$ to the carbon atom of an acylium cation, requires a high activation energy. In sharp contrast, the barrier for addition of $^\bullet OH$ to an acylium ion must be substantially smaller. The exact reason for this divergence is not known.[39]

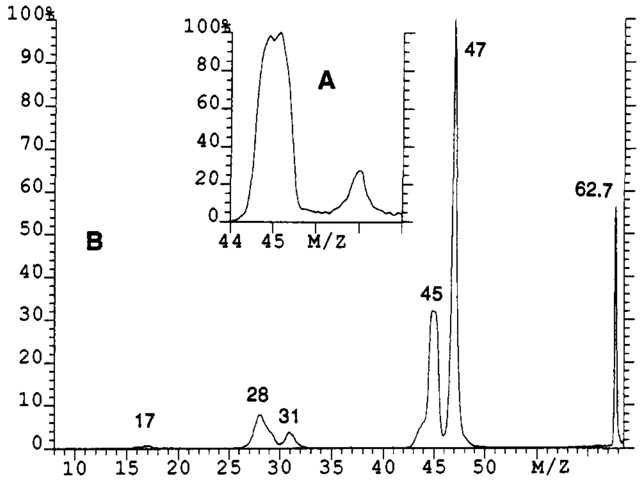
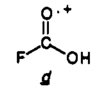


Figure 3. (A) MI and (B) CAD spectra of $FCOOH^{\bullet+}$ formed by CAD of $FC(OH)_2^+$. The narrow peak at m/z 62.7 results from metastable dissociations in front of the magnetic sector.[37]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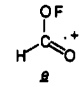
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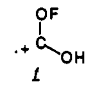
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According to the CAD spectrum of $FCOOH^{\bullet+}$ (Figure 3B), the structurally characteristic losses of $F^\bullet$ and $^\bullet OH$ remain as the principal dissociations upon collisional excitation. Most noteworthy among the new fragments are FC^+ (m/z 31) and OH^+ (m/z 17), which are in keeping with the presence of these substructures in the precursor ion. The combined MI and CAD data provide strong evidence that the m/z 64 ion generated by the MS/MS sequence $FCOOCH_2CH_3^{\bullet+} \rightarrow FC(OH)_2^+ \rightarrow FCOOH^{\bullet+}$ indeed is the radical cation of fluoroformic acid (*d*); any isomeric structures, such as *e* and *f*, are highly unlikely. If the FO substituted isomers *e* or *f* were present, then FO^+ (of m/z 35) should be observed in the CAD spectrum of Figure 3B, which is not the case. For example, ion $FO{-}CH_2CH_3^{\bullet+}$, which contains the FO group, does produce such a fragment (Figure 1B). It is concluded, therefore, that ion *d* is formed from $FC(OH)_2^+$ in pure form and exists as a stable species in the gas phase.

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(34) Theoretical calculations on the related ion $HO{-}C(OH)_2^+$ (protonated carbonic acid) predict that its MI dissociation to H_2O + ^+COOH proceeds after rate-determining isomerization to $HO{-}C({=}O)OH_2^+$. This process also produces a Gaussian peak: Egsgaard, H.; Carlsen, L. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 3403–3411.

(35) Burgers, P. C.; Holmes, J. L.; Mommers, A. A. *J. Am. Chem. Soc.* **1985**, *107*, 1099–1101.

(36) Metastable $FCOOH^{\bullet+}$ also loses $^\bullet H$, giving rise to a weak fragment at m/z 63. This ion overlaps with an adjacent artefact peak (see the CAD spectrum of Figure 3B), which prevents the exact measurement of abundance and kinetic energy release. The intensity of the artefact signal relative to the $FCOOH^{\bullet+}$ main beam is 0.7%; the intensity of $FCOOH^{\bullet+}$ with respect to that of its $FC(OH)_2^+$ precursor is 1.5%.[37]

(37) The narrow peak at m/z ~63 has the same width as the main beam (13 V) and is the only signal remaining in the MI (or CAD) spectrum of $FCOOH^{\bullet+}$ when the sample is pumped out. It most likely originates from hydrocarbons present in the instrument background: metastable $C_5H_7^+$ (m/z 67) dissociating to $C_5H_6^{\bullet+}$ (m/z 66) in FFR-1 and subsequently to $C_5H_5^+$ (m/z 65) in FFR-2 (region in front of the magnet) can account for the observed artefact.

(38) Schwarz, H.; Williams, D. H.; Wesdemiotis, C. *J. Am. Chem.* **1978**, *100*, 7052–7055.

(39) Our result is related to findings of Bouma et al., who demonstrated that $H^\bullet$ addition to the oxygen atom of $HC{\equiv}O^+$ (yielding $HC{\equiv}OH^{\bullet+}$) demands a much higher activation energy than $H^\bullet$ addition to its carbon atom (yielding $H_2C{=}O^{\bullet+}$): Bouma, W. J.; Burgers, P. C.; Holmes, J. L.; Radom, L. *J. Am. Chem. Soc.* **1986**, *108*, 1767–1770. In a more recent study, Lifshitz et al. showed that $H^\bullet$ addition to the tropylium cation requires overcoming a barrier, but $H^\bullet$ addition to the isomeric benzyl cation does not: Lifshitz, C.; Gotkis, Y.; Ioffe, A.; Laskin, J.; Shaik, S. *Int. J. Mass Spectrom. Ion Processes* **1993**, *125*, R7–R11.

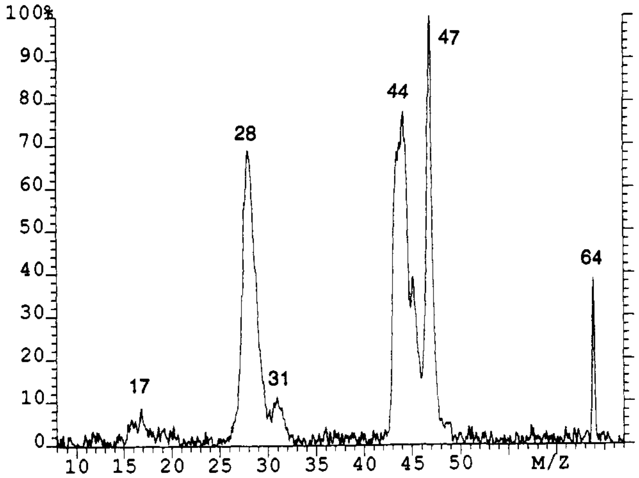

Figure 4. $^{+}\mathrm{NR}^{+}$ spectrum of $\mathrm{FCOOH}^{\bullet +}$ formed by CAD of $\mathrm{FC(OH)_2}^{+}$.[40]

Generation and Characterization of Neutral FCOOH. The $^{+}\mathrm{NR}^{+}$ spectrum of $\mathrm{FCOOH}^{\bullet +}$ contains an abundant recovery peak at *m/z* 64 (Figure 4), indicating that a large fraction of the FCOOH molecules generated upon neutralization of $\mathrm{FCOOH}^{\bullet +}$ have survived undissociated until reionization (average lifetime >0.4 μs). Further, all structurally indicative fragments of $\mathrm{FCOOH}^{\bullet +}$ (viz. CAD spectrum of Figure 3B) are included in the $^{+}\mathrm{NR}^{+}$ spectrum of Figure 4, consistent with preservation of the original FCOOH structure upon neutralization–reionization.[40] Consequently, solitary fluoroformic acid exists as a stable species and must surmount a finite barrier to dissociate into FH + $\mathrm{CO_2}$, in agreement with the theoretical prediction.[4]

The increased abundances of $\mathrm{CO_2}^{\bullet +}$ (*m/z* 44), $\mathrm{CO}^{\bullet +}$ (*m/z* 28), $\mathrm{FH}^{\bullet +}$ (*m/z* 20), and F^{+} (*m/z* 19) in the $^{+}\mathrm{NR}^{+}$ spectrum of $\mathrm{FCOOH}^{\bullet +}$ vis à vis the corresponding CAD spectrum can be attributed to partial formation of FCOOH above its dissociation threshold. These FCOOH molecules decay to FH + $\mathrm{CO_2}$, which after reionization contribute to the aforementioned ions thus raising their intensities.[41] Other, smaller differences between the $^{+}\mathrm{NR}^{+}$ and CAD spectra of $\mathrm{FCOOH}^{\bullet +}$, e.g., in the relative abundances of FC^{+} and OH^{+}, could be due to internal energy effects, as collisional reionization and CAD do not necessarily deposit the same internal energy distributions.[5,12,42]

The Radical $\mathrm{FC(OH)_2}^{\bullet}$. The $^{+}\mathrm{NR}^{+}$ spectrum of protonated fluoroformic acid, $\mathrm{FC(OH)_2}^{+}$, looks strikingly similar to that of the fluoroformic acid radical cation, $\mathrm{FCOOH}^{\bullet +}$ (Figure 5 vs Figure 4). Apparently, the majority of the incipient $\mathrm{FC(OH)_2}^{\bullet}$ radicals accessed in the neutralization step decompose to FCOOH + $^{\bullet}$H before reaching the reionization region. Further dissociation of FCOOH to FH + $\mathrm{CO_2}$ also occurs to some extent judging by the appreciable $\mathrm{CO_2}^{\bullet +}$/$\mathrm{CO}^{\bullet +}$ and $\mathrm{FH}^{\bullet +}$/F^{+} peaks in the $^{+}\mathrm{NR}^{+}$ spectrum of Figure 5.

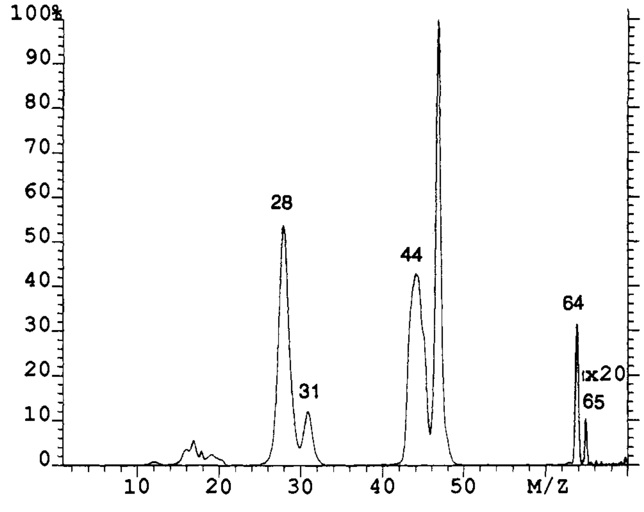

Figure 5. $^{+}\mathrm{NR}^{+}$ spectrum of $\mathrm{FC(OH)_2}^{+}$ formed by EI of $\mathrm{FCOOCH_2CH_3}$.

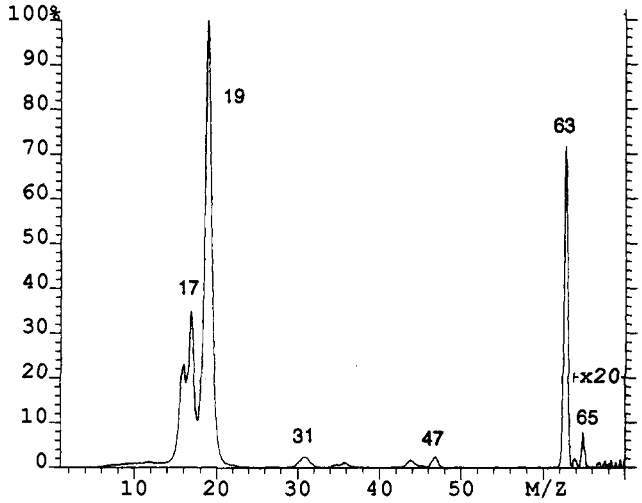

Figure 6. $^{+}\mathrm{NR}^{-}$ spectrum of $\mathrm{FC(OH)_2}^{+}$ formed by EI of $\mathrm{FCOOCH_2CH_3}$.

A small survival ion is observed in the $^{+}\mathrm{NR}^{+}$ spectrum of $\mathrm{FC(OH)_2}^{+}$. It is unlikely that this ion originates from an impurity because of the following facts: (1) The contamination of $\mathrm{FC(OH)_2}^{+}$ (*m/z* 65) with the ^{13}C-satellite of *m/z* 64 is negligible (<0.1%) based on the intensity of *m/z* 64 in the EI spectrum of ethyl fluoroformate (Figure 1A). Moreover, the ion of *m/z* 64 mainly is $\mathrm{FOCH_2CH_3}^{\bullet +}$ (*vida supra*) which produces abundant FO^{+} (*m/z* 35) and $\mathrm{FOH}^{\bullet +}$ (*m/z* 36) upon $^{+}\mathrm{NR}^{+}$; such fragments are, however, absent from Figure 5. (2) An isobaric hydrocarbon ion from the background should lead to extra peaks at, e.g., 62, 41, or 14 which is not the case for Figure 5. It is therefore tentatively concluded that the recovered precursor ion in the $^{+}\mathrm{NR}^{+}$ spectrum of $\mathrm{FC(OH)_2}^{+}$ results from the small fraction of $\mathrm{FC(OH)_2}^{\bullet}$ escaping dissociation to FCOOH + $^{\bullet}$H and that $\mathrm{FC(OH)_2}^{\bullet}$ is a weakly bound radical.

Corroborative evidence for the stability of the $\mathrm{FC(OH)_2}^{\bullet}$ radical is found by reionization into negative ions (Figure 6). The $^{+}\mathrm{NR}^{-}$ spectrum of $\mathrm{FC(OH)_2}^{+}$ (*m/z* 65) also contains a small recovered precursor ion at *m/z* 65. This anion cannot be due to an isobaric impurity with ≥2 carbon atoms (e.g., the ^{13}C-satellite of $\mathrm{FOCH_2CH_3}^{\bullet +}$ or a background hydrocarbon ion), because such admixtures would also produce $\mathrm{C_2}^{\bullet -}$ and $\mathrm{C_2H}^{-}$ fragments[43] which are not observed. Thus, the recovery peak must be the anion $\mathrm{FC(OH)_2}^{-}$;[44] its formation confirms that a finite part of radical $\mathrm{FC(OH)_2}^{\bullet}$ survives intact.

The principal products in the $^{+}\mathrm{NR}^{-}$ spectrum of $\mathrm{FC(OH)_2}^{+}$ originate from the major fraction of $\mathrm{FC(OH)_2}^{\bullet}$ which dissociates to FCOOH. Upon anionization, FCOOH yields no survival anion

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[40] The very low intensity of the artefact beam[36] prevents it from yielding any detectable ions in the $^{+}\mathrm{NR}^{+}$ spectrum of Figure 4.

[41] $\Sigma\Delta H^{\circ}_{f}(\mathrm{FH+CO_2}) = -666$ kJ/mol.[29] According to theory,[4] FCOOH is thermodynamically more stable than FH + $\mathrm{CO_2}$ by ~30 kJ/mol and separated from these products by a barrier of ~210 kJ/mol. Other possible fragmentations of FCOOH, such as the homolytic cleavages to $\mathrm{FCO}^{\bullet}$ + $^{\bullet}$OH ($\Sigma\Delta H^{\circ}_{f} = -136$ kJ/mol)[29] or to $\mathrm{F}^{\bullet}$ + $^{\bullet}$COOH (−111 kJ/mol),[29] require much more energy and lead to less stable products; therefore, they should not be competitive. ($\Delta H^{\circ}_{f}(^{\bullet}\mathrm{COOH}) = -190$ kJ/mol from: Holmes, J. L.; Mommers, A. A.; Terlouw, J. K.; Hop, C. E. C. A. *Int. J. Mass Spectrom. Ion Processes* **1986**, *68*, 249–264.)

[42] Burgers, P. C.; Drewello, T.; Schwarz, H.; Terlouw, J. K. *Int. J. Mass Spectrom. Ion Processes* **1989**, *95*, 157–169.

[43] All reported $^{+}\mathrm{NR}^{-}$ spectra of cations containing two or more C atoms contain $\mathrm{C_2}^{\bullet -}$ and $\mathrm{C_2H}^{-}$ fragments.[5,10,12,25a]

[44] Since a reference spectrum of pure $\mathrm{FC(OH)_2}^{-}$ is not available, we cannot exclude the possibility that, once formed, this anion isomerizes to a more stable structure. A known, stable $\mathrm{CH_2FO_2}^{-}$ isomer is $\mathrm{F}^{-} \cdots \mathrm{HOOCH}$, the hydrogen bonded adduct of fluoride and formic acid: Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *195*, 2944–2950.

(m/z 64) but several structurally diagnostic fragments, including $FCOO^-$ (m/z 63),[45] F^- (m/z 19), and ^-OH (m/z 17). The weaker ions in the $^+NR^-$ spectrum, namely FC^- (m/z 31), $FO^-/FOH^{\bullet-}$ (m/z 35/36), $CO_2^{\bullet-}$ (m/z 44), and FCO^- (m/z 47), are formed from $FC(OH)_2^\bullet$ or from FCOOH. Some of them arise by simple rearrangements, which are favored upon $^+NR^-$ if they can lead to stable anions.[10,12,25a]

Conclusions

Combined MS/MS and charge permutation experiments allow the tailored synthesis and characterization in the gas phase of fluoroformic acid (FCOOH), ionized fluoroformic acid ($FCOOH^{\bullet+}$), and protonated fluoroformic acid ($FC(OH)_2^+$). All three species are found to be stable and undergo unique unimolecular reactions.

The inability to generate $FCOOH^{\bullet+}$ by dissociative ionization of $FCOOCH_2CH_3$ is circumvented by producing this ion via the MS/MS sequence $FCOOCH_2CH_3^{\bullet+} \rightarrow FC(OH)_2^+ \rightarrow FCOOH^{\bullet+}$. Neutralization of the latter radical cation provides direct access to the elusive FCOOH. Alternatively, FCOOH is formed by $H^\bullet$ loss from the weakly bound radical $FC(OH)_2^\bullet$ which arises upon neutralization of $FC(OH)_2^+$. Only a small part of the gaseous FCOOH produced in these reactions decomposes to FH + CO_2. The spontaneous, complete decay observed in condensed phases must therefore be due to intermolecular effects.

The major dissociations of both $FCOOH^{\bullet+}$ and $FC(OH)_2^+$ yield FCO^+ and ^+COOH fragments. FCO^+ is formed by loss of $^\bullet OH$ or H_2O and ^+COOH by loss of $F^\bullet$ or FH, respectively. The eliminations of the neutrals containing fluorine have much larger reverse activation energies; this means that addition of $F^\bullet$ or FH to ^+COOH to form a new F–C bond commands a considerable amount of energy.

Acknowledgment. The National Institutes of Health and the Petroleum Research Fund, Administered by the American Chemical Society, are thanked for generous financial support. We are grateful to Dr. Michael J. Taschner and Alex M. Woo for experimental assistance in the synthesis of ethyl fluoroformate. We thank Michael J. Polce, Marcela M. Cordero, and Šárka Beranová for helpful suggestions and discussions.

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(45) McMahon, T. B.; Nothcott, C. J. *Can. J. Chem.* **1978**, *56*, 1069–1074.