

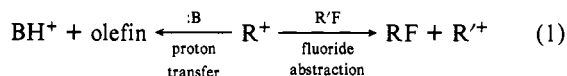
Structures of Organic Cations in the Gas Phase. Neutral Products from Fluoride Abstraction Examined by NMR¹

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Abstract: Structures of 2-fluoroisopropyl cation (**1**) and 2-propenyl cation (**2**) in the gas phase have been examined by quenching via ion-molecule reactions and examination of the neutral products by NMR. Both ions are produced by 70-eV electron bombardment of *tert*-butyl fluoride, and both react with the parent neutral to yield *tert*-butyl cation. The ion-molecule reaction of **1** yields 2,2-difluoropropane as >90% of the neutral product. The ion-molecule reaction of **2** yields 2-fluoropropene, as confirmed by preparing **2** from another source and examining the product from its reaction with *tert*-butyl-*d*₆ fluoride (**3**). Allyl fluoride is not detected among the reaction products. Since this product is observed when allyl bromide is bombarded with 70-eV electrons in the presence of *tert*-butyl fluoride, its absence in electron bombardment of *tert*-butyl fluoride alone implies that **2** is the only C₃H₅⁺ ion produced and that it does not rearrange to the allyl cation under the reaction conditions. The deuterated neutral products from electron impact on **3** alone or in the presence of diethyl ether indicate that **1** does not scramble its hydrogens, even when it contains enough internal energy to expel HF to form **2**. The use of deuterium isotope shifts in ¹⁹F NMR to study the position and extent of label in neutral products is exemplified as a new tool for probing structures of gaseous cations.

Investigations of gaseous ions represent an increasingly important aspect of organic chemistry. Although the reactivity of organic cations can be thoroughly studied by mass spectrometric techniques, their structures are often uncertain, since there is, as yet, no method for direct examination of polyatomic ions outside of condensed phases. One approach to structural characterization is exemplified by reaction 1, in which the cation is quenched by ion-molecule reactions to yield neutral products indicative of its structure. The two pathways shown can be likened to their analogues in solution, proton transfer from R⁺ to a base (:B) corresponding to an E1 reaction and fluoride abstraction by R⁺ corresponding to an S_N1 reaction.



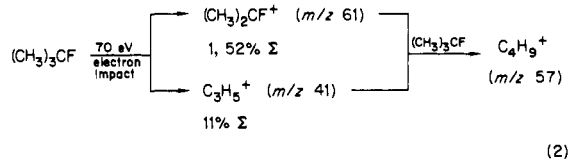
Several years ago we introduced the Electron Bombardment Flow (EBFlow) reactor as a technique for collecting the neutral products of ionic reactions in the gas phase.² We demonstrated the use of proton transfer to identify cation rearrangement pathways³ and, more recently, have discussed fluorinated compounds resulting from fluoride abstractions.⁴ In the present work we analyze neutral products from gas phase ion-molecule reactions of 2-fluoroisopropyl (**1**) and 2-propenyl (**2**) cations.

In an EBFlow experiment reactant gases flow the length of a cylindrical reaction vessel (with a steady-state pressure of $\leq 10^{-3}$ torr) and are bombarded with ionizing electrons that travel down the cylinder axis. Neutral products condense on a cold trap and are then vacuum transferred to an NMR tube, which is sealed off for subsequent spectroscopic examination. Under the reaction conditions, collisions between neutral molecules are comparatively infrequent. (For instance, at 2×10^{-4} torr the mean free path of a fluorine atom is >30 cm for colliding with a molecule whose collision diameter is 4 Å.) Homogeneous, second-order gas-phase reactions between neutrals are therefore improbable. Recovered products can thus be attributed to four sources: ion-molecule reactions in the gas phase, unimolecular reactions induced by electron impact, neutralization reactions of ions striking the walls, and condensed-phase reactions in the cold trap. Yields of neutral

products, normalized for the current of ionizing electrons, can be expressed as the percent conversion (relative to recovered, unreacted starting material) per milliamper. Normalized conversions from ion-molecule reactions increase in a predictable fashion as reactant pressure is increased, while normalized conversions of products from other sources will remain constant or decrease. Therefore, EBFlow experiments provide an empirical basis for deciding which products come from homogeneous gas phase ion-molecule reactions (even though <1% of the starting material is ionized in the reaction vessel).

Fluorine-containing ion-molecule reaction products can be readily detected by ¹⁹F NMR spectroscopy of the crude reaction mixture. This is of special importance, for partially fluorinated compounds are often too reactive for reliable GLC analysis. The wide range of ¹⁹F chemical shifts and the dynamic range of Fourier transform methods permit the easy observation of <1 μmol of product, even in the presence of a 1000-fold excess of unreacted starting material. Moreover, a large deuterium isotope effect on fluorine chemical shifts allows the resolution of different isotopic variants of the same molecule. Identities of components in a mixture can usually be assigned on the basis of proton-fluorine spin-spin couplings.

This paper will focus on ions derived from 70-eV electron impact on *tert*-butyl fluoride. As reaction 2 depicts, the two major ions, *m/z* 61 (**1**) and 41, together compose >60% of the total ionization.⁵ Although reliable heats of formation have been determined for **1**⁶ and for *m/z* 41,⁷ structure identifications are based on the EBFlow data presented below. Both ions react with the parent neutral to yield *tert*-butyl cation (*m/z* 57). The *m/z* 61 cation reacts with a second-order rate coefficient of $k = 4.4 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, while *m/z* 41 reacts with $k = 1.5 \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹.⁸



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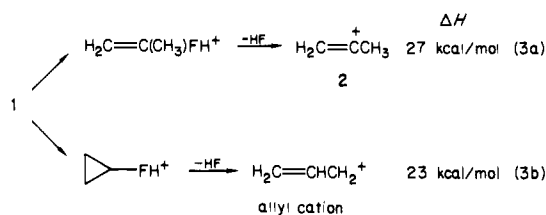
Table I. Fluoride Affinities ($D[R^+-F^-]$) of Selected Ions

	ΔH_f°	$D[R^+-F^-]$
$(CH_3)_3C^+$	166 ^a	180 ^c
$(CH_3)_2CF^+$ (1)	138 ^a	208 ^c
$H_2C=CHCH_2^+$	227 ^b	204 ^d
$H_2C=C^+CH_3$ (2)	230 ^a	210 ^d

^aReference 15. ^bTrager, J. C. *Int. J. Mass. Spectrom. Ion Proc.* **1984**, *58*, 259–271. ^cWilliamson, A. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5714–5718. Williamson, A. D.; LeBreton, P. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 2705–2709. ^dHeats of formation of corresponding neutral fluorohydrocarbons estimated from Benson [Benson, S. W. "Thermochemical Kinetics"; 2nd ed.; Wiley: New York, 1976] and from Whangbo et al. [Whangbo, M. H.; Mitchell, D. J.; Wolfe, S. *J. Am. Chem. Soc.* **1978**, *100*, 3698–3706].

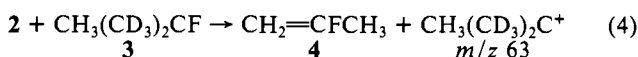
Ion **1** has been reported as a stable species in SbF_5-SO_2 solution,⁹ and the NMR data leave little doubt as to its structure. The heat of formation in the gas phase can be estimated with use of the method of equivalent cores¹⁰ from the ESCA O_{1s} ionization energies of acetaldehyde and acetone (which differ by 0.66 eV¹¹) and the heat of formation of 1-fluoroethyl cation (166 ± 1 kcal/mol¹²). The estimated value of 139 kcal/mol is the same, within stated uncertainties, as the experimental value in Table I, which was determined independently. Identification of ion **1** as the major fragment from *tert*-butyl fluoride (via loss of methyl radical from the molecular ion) is based on recovery of 2,2-difluoropropane as the neutral product from fluoride abstraction.

Existence of two stable isomers of the $C_3H_5^+$ cation (m/z 41) has been known for several years. Aue, Bowers, and co-workers determined that heat of formation of the less-stable isomer (e.g., from ionization of 2-bromopropene) is 5 kcal/mol greater than that of allyl cation,⁷ and the 2-propenyl structure **2** was proposed. Products consistent with this structure have been reported from γ -radiolysis studies in which **2** was produced via protonation of propyne or allene,¹³ and a growing body of evidence confirms the stability of other vinyl cations in the gas phase.¹⁴ The m/z 41 cation from *tert*-butyl fluoride could arise from two pathways, expulsion of HF from ion **1** or via loss of methyl radical from an intermediate $C_4H_8^+$ (m/z 56) ion. But since m/z 56 constitutes only 1% Σ (and the ratio of m/z 41 to m/z 56 in the mass spectrum of isobutene is only 3:2),⁵ the former pathway seems much more probable. Reaction 3 depicts two possible routes from **1**, one of which yields 2-propenyl cation, **2**, and the other of which yields allyl cation.

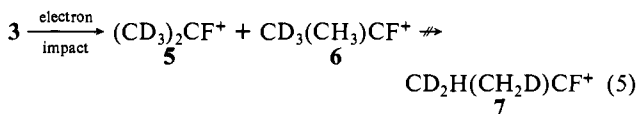


As Table I summarizes, the fluoride affinities of both m/z 41 ions are substantially greater than that of *tert*-butyl cation. Therefore, either isomer can react with *tert*-butyl fluoride to yield m/z 57. The neutral products, however, will be different. Allyl cation will product allyl fluoride, while **2** will produce 2-fluoro-

propene (**4**), as reaction 4 depicts.



The present study has sought to answer three questions. First, does fluoride abstraction predominate in reactions where it is thermodynamically possible for fluorine to act as a Brønsted base as well as a nucleophile? Second, can the structure of m/z 41 be characterized by intercepting it via fluoride abstraction? Third, is deuterated cation **6** stable with respect to scrambling of the isotopic label, as represented in reaction 5? The results below provide the affirmative answers to all three questions.



Experimental Section

General operating characteristics of the EBFlow reactor have been presented elsewhere.^{2,3} In the present design, 70-eV electrons (0.1–0.7 mA) from a directly heated rhenium filament are injected into an electrically grounded, stainless steel reaction vessel, 70 cm long \times 9 cm in diameter, along its central axis. The cylindrical reaction vessel is enclosed in a solenoid electromagnet maintained at a constant magnetic field in the range 0.2–0.3 T. At the collection end, electrons follow the diverging magnetic field lines and strike a conical Faraday plate. Neutral products (and unreacted starting material) are condensed into a glass, liquid nitrogen cooled trap in front of the Faraday plate, while unreacted positive ions are electrostatically extracted through a 2-cm-diameter aperture at the tip of the cone into a separate chamber, which is differentially pumped. For determination of normalized conversions, the total electron current striking the reaction vessel and the Faraday plate is averaged over the duration of the run. At the end of a run (0.5–1 h), contents of the cold trap are transferred via a vacuum line to a 5-mm NMR tube containing acetone- d_6 , which is then sealed and stored under liquid nitrogen until the product mixture is examined by NMR. Control runs (filament on but without ionizing electrons entering the reaction vessel) show zero yields of reported products. Other control experiments—EBFlow radiolysis of CF_4 with bromopropenes—were examined. Poor efficiency for collection of CF_4 prevented determination of percent conversions based on relative ^{19}F NMR integrals alone. Therefore a known standard, *o*-difluorobenzene, was added to samples after they had been transferred to the NMR tubes, and normalized conversions are reported relative to collected bromopropene, based on integral areas of both the proton and ^{19}F NMR spectra.

NMR spectra were recorded on the Nicolet 300 multinuclear instrument at UCR or on the Bruker 500 instrument at CalTech.¹⁶ In addition to reported products, variable levels of silicon tetrafluoride were detected in the reaction mixture and are attributed to reaction of hydrofluoric acid with the glass. Reported mass spectra were recorded on a VG ZAB 1F double-focussing B-E sector instrument or a Nicolet FTMS 1000 at 1.9 T, both at UCR.

2-Methyl-2-fluoropropane- d_6 (3). 2-Methyl-2-propanol- d_6 was prepared by addition of methylmagnesium iodide to acetone- d_6 (Aldrich, 99.5 atom % D) and dried by refluxing over calcium oxide. A 15-mL flask with a septum-capped sidearm was charged with 3 mL of *o*-dichlorobenzene and 1.85 g (0.023 mol) of freshly distilled 2-methyl-2-propanol- d_6 , equipped with a dry ice condenser, flushed with nitrogen, and cooled in a dry ice–acetone slush. The frozen solution was maintained under a static atmosphere of dry nitrogen while 3.5 mL (0.027 mol) of neat (diethylamino)sulfur trifluoride¹⁷ (Carbolab) was added slowly with a syringe via the rubber septum. The reaction mixture was allowed to warm to room temperature, magnetically stirred for 2 h, refrozen in a dry ice bath, and quenched with 3 mL of saturated aqueous sodium bicarbonate. The reaction was then allowed to return slowly to room temperature and gently warmed to distill the product, which was collected in a dry ice cooled trap to yield 1.63 g of 2-methyl-2-fluoropropane- d_6 (87% yield). Spectroscopic examination showed low but ineradicable levels of SO_2 , hydrofluoric acid, and deuterated isobutene

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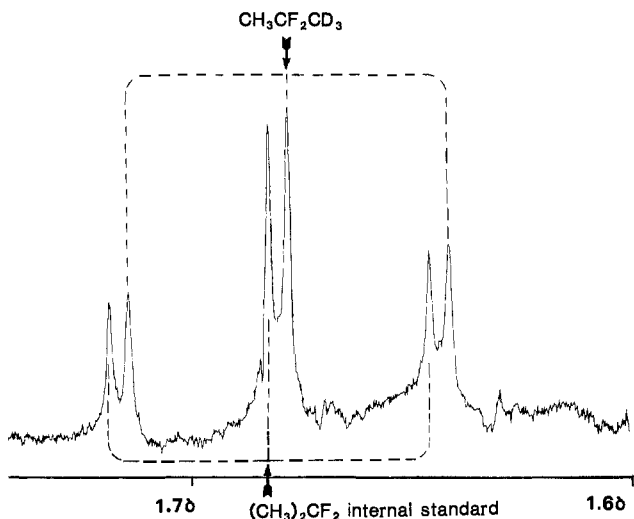
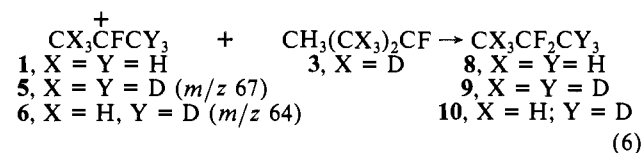


Figure 1. ^1H NMR (500-MHz) of deuterated 2,2-difluoropropane from EBFlow radiolysis of 2×10^{-4} torr of **3**. No peaks attributable to $\text{CD}_2\text{HCF}_2\text{CH}_2\text{D}$ can be discerned.

impurities. ^1H NMR (acetone- d_6) δ 1.37 (d, $J_{\text{HF}} = 21$ Hz); ^{13}C NMR δ_{CH_3} 28.7 (d, $J_{\text{CF}} = 9.8$ Hz), δ_{CF} 93.9 (d, $J_{\text{CF}} = 161$ Hz); ^{19}F NMR (CFCl_3 external standard) $\delta_{\text{F}} -131.3$ (^1H -decoupled spectrum shows a 13-line pattern from deuterium coupling; $J_{\text{HF}} = 21.2$ Hz, $J_{\text{FD}} = 3.2$ Hz); cf. $\delta_{\text{F}} -130.2$ for undeuterated *tert*-butyl fluoride. Mass spectrum (70 eV) m/z (rel intensity) 67.0832 (64), 64.0642 (100), 46 (8.4), 44 (13), 43 (6.5).

Results and Discussion

Previously reported EBFlow experiments have shown that electron bombardment of *tert*-butyl fluoride by itself yields two products, 2-fluoropropene (**4**) and 2,2-difluoropropane (**8**).⁴ The yield of the latter increases monotonically with pressure, being virtually negligible at 3×10^{-5} torr and rising from 1% mA^{-1} at 2×10^{-4} torr to 2% mA^{-1} at 4×10^{-4} torr. This product must arise via fluoride abstraction from the starting material by ion **1**, as reaction 6 depicts.



FTMS studies support this conclusion. All other plausible, thermodynamically accessible pathways for reaction of **1** with *tert*-butyl fluoride involve proton transfer from the cation (e.g., to yield product **4** plus HF). Typically, gas-phase proton transfers from electron-deficient carbocations have primary isotope effect on the order of $k_{\text{H}}/k_{\text{D}} \geq 1.3$,¹⁸ and ion **5** would be expected to react more slowly than ion **6**. We observe, however, that the m/z 64 and 67 ions from **3** react with parent neutral with the same rate constants (within the 10% uncertainty of the FTMS measurement due to the presence of m/z 64 from a sulfur dioxide impurity). Proton transfer therefore does not play a major role.

When deuterated compound **3** is bombarded with 70-eV electrons in an EBFlow experiment, products **9** and **10** are seen in the ^{19}F NMR of the reaction product at -84.4 and -84.0 ppm (upfield from CFCl_3). These peaks stand well apart from the characteristic septet of **8** (at -83.6 ppm) and can be assigned on the basis of their splitting patterns, **9** appearing as a broadened singlet and **10** as a broadened quartet. The integral ratio is 1:1.6, the same as the intensity ratio of ions **5** and **6** in the mass spectrum. The combined yield of **9** and **10** is 1.1% mA^{-1} at a pressure of 2×10^{-4} torr, and the ^1H NMR of **10** can be observed, as shown in Figure 1. Apart from the triplet due to **8** (internal standard, from which **10** is shifted upfield by 0.004 ppm), there are no other

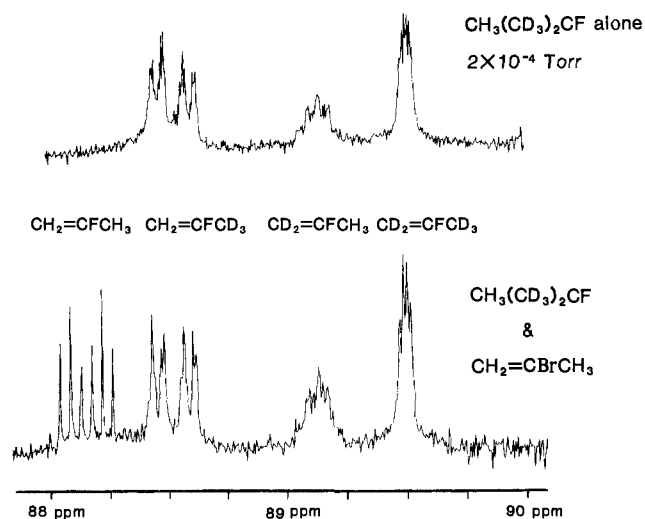


Figure 2. ^{19}F NMR (470 MHz) of 2-fluoropropenes from EBFlow radiolyses of neat **3** and of 2×10^{-4} torr of **3** plus 2×10^{-4} torr of 2-bromopropene. Undeuterated product **4** is seen only in the latter spectrum, while the deuterated products **11**–**13** are seen in both spectra.

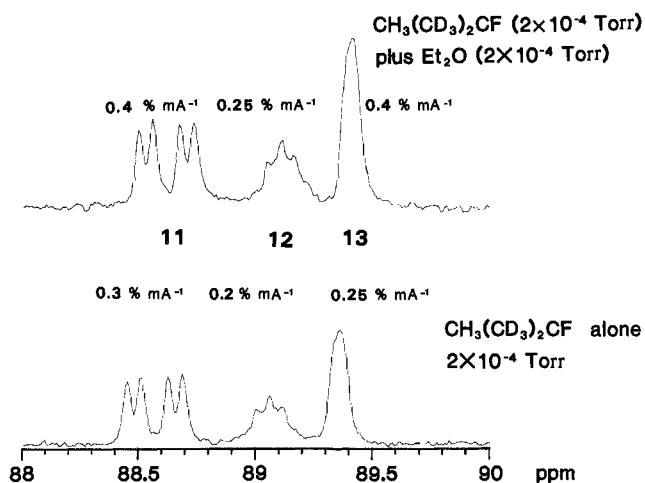


Figure 3. ^{19}F NMR (282 MHz) of deuterated 2-fluoropropenes collected from EBFlow radiolysis of **3** alone and of **3** plus diethyl ether. Normalized conversions are expressed as percent relative to recovered unreacted starting material divided by ionizing electron current (% mA^{-1}). Chemical shifts relative to CFCl_3 .

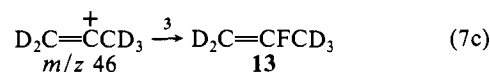
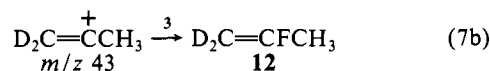
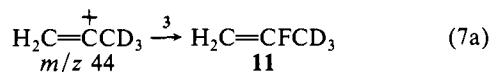
proton resonances attributable to other partially deuterated analogues. If, for example, $\text{CDH}_2\text{CF}_2\text{CHD}_2$ were present, it should have been detectable at levels above one-tenth the concentration of **10**.

Recovered 2-fluoropropene (**4**) comes from more than one source. At 3×10^{-5} torr (where ion **1** lives, on average, >2 ms before undergoing a reactive collision with its parent neutral) **1** is likely to hit the wall before colliding with another molecule. At this pressure, product **4** must be produced by surface neutralization (e.g., loss of a hydrogen atom after **1** is converted to a radical). However, if this were the sole source of 2-fluoropropene, then the yield would be expected to decrease monotonically as pressure is increased. Experimentally the normalized yield of **4** decreases from 1.2% mA^{-1} at 3×10^{-5} torr to 0.4% mA^{-1} at 2×10^{-4} torr, but it increases to 0.6% mA^{-1} at 4×10^{-4} torr.

If the m/z 41 ion from *tert*-butyl fluoride possesses structure **2**, then fluoride abstraction from the parent neutral will also yield **4**. The corresponding ions from **3** would be expected to yield the three deuterated 2-fluoropropenes **11**–**13**, as reaction 7 depicts, in approximately the same ratio as the m/z 44, 43, and 46 ions are produced in the 70-eV mass spectra, 6:3:4. The ^{19}F resonances of neutral products **11**–**13** are easily resolved from one another, as shown by the upper NMR spectrum in Figure 2. The lower ^{19}F NMR spectrum in Figure 3 shows the same sample observed

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at a lower magnetic field, and the normalized conversions correspond roughly to the relative abundances of the proposed precursors.



To test this further, reaction 4 was examined in the EBFlow reactor. Ion **2** was generated by 70-eV electron impact on 2-bromopropene (from which it represents 33% Σ^5). Since EBFlow radiolysis of **3** yields only deuterated 2-fluoropropenes, it was anticipated that occurrence of reaction 4 would yield the undeuterated product, **4**, which could be resolved from its deuterated analogues. The lower NMR spectrum in Figure 2 shows that this is indeed the case. EBFlow radiolysis of 2×10^{-4} torr of 2-bromopropene plus 2×10^{-4} of **3** shows a pronounced yield of **4**, with a product ratio of **4**:**11**:**12**:**13** equal to 0.6:1.0:0.6:0.8. Since one-third of the total ionization from 2-bromopropene consists of ions with $m/z \leq 40$ (which are unlikely to yield $\text{C}_3\text{H}_5\text{F}$ products by reaction with **3**) and one-quarter of the total ionization consists of molecular ions (which we presume to be unreactive), we believe that reaction 4 must represent the major ionic pathway to product **4**.

One result warrants particular attention. No NMR peaks corresponding to isomers of **11**–**13** or **4** are observed. None of the spectra in Figures 2 and 3 show any evidence of other partially deuterated 2-fluoropropenes (e.g., $\text{CHD}=\text{CFCH}_2\text{D}$ or $\text{CHD}=\text{CFCHD}_2$). This means that if ion **2** comes from undergoing any process by which hydrogens interchange between carbon 1 and carbon 3, even though it must have ≥ 27 kcal/mol of internal energy in order to overcome the thermodynamic barrier to HF expulsion. By using double-focussing mass spectrometric techniques, the metastable ion decompositions m/z 67 \rightarrow m/z 46, m/z 64 \rightarrow m/z 44, and m/z 64 \rightarrow m/z 43 can be observed. The EBFlow results demonstrate that this decomposition occurs faster than any scrambling of isotopic label, and they therefore imply that species like the protonated fluorocyclopropane drawn in reaction 3b are not formed reversibly on the time scale of the fragmentation of 2-fluoroisopropyl cations.

The spectrum shown in Figure 1 implies that ion **6** does not scramble to form ion **7** on a longer time scale. In order to confirm this, a separate EBFlow experiment was performed in which **5** and **6** were quenched by a Brønsted base, diethyl ether. Ether (2×10^{-4} torr) and **3** (2×10^{-4} torr) were subjected to EBFlow radiolysis, and as the top spectrum in Figure 3 shows, no new isotopic variants can be discerned, even though the yield of **11**–**13** from Brønsted reactions of **5** and **6** can be estimated to account for approximately 65% of the recovered 2-fluoropropenes. This estimate is made as follows: the 70-eV-ionization cross sections of *tert*-butyl fluoride and diethyl ether are nearly the same, 1×10^{-15} cm².¹⁹ For EBFlow radiolysis of 2×10^{-4} torr of *tert*-butyl fluoride, the mean free path of 70-eV electrons is 1.5 m. Electrons travel helical paths that are several times longer than this in passing the length of the reaction vessel. This means that virtually all the electrons produce ionizations. When an equal pressure of diethyl ether is added, half of the electrons ionize the ether and the yield of 2-fluoropropenes from reaction 7 should drop by one-half. In other words, to compare normalized conversions between the two spectra in Figure 3, the values for the lower spectrum should be multiplied by 0.5 before they are subtracted from the values in the upper spectrum. This means that the ratio **11** plus **12** to **13** is roughly 1.5, which is close to the **6**:**7** primary ion ratio from **3**.

The other notable absence is that of allyl fluoride. No ¹⁹F NMR resonances are seen in the chemical shift range -215 to -217 ppm, where allyl fluoride is known to absorb.¹⁷ Because the thermochemistry of fluoride transfer from *tert*-butyl fluoride to allyl cation is favorable (cf. Table I above), it is at least plausible that production of allyl cation would have been detected by formation of allyl fluoride. Yet the yield is below the level of detectability, corresponding to a normalized conversion of $<0.01\%$ mA⁻¹. An EBFlow experiment was performed on a mixture of 2×10^{-4} torr of allyl bromide (from which m/z 41 constitutes 38% Σ at 70 eV⁵) plus 2×10^{-4} torr of *tert*-butyl fluoride to ensure that allyl cation does indeed abstract fluoride. Here, allyl fluoride was readily observable, corresponding to a normalized conversion of 0.3% mA⁻¹. In order to demonstrate that this product did not arise via some adventitious process, a sample of 2×10^{-4} torr of allyl bromide plus 2×10^{-4} torr of **8** was bombarded with 70-eV electrons in the EBFlow reactor. No allyl fluoride could be detected among the recovered material in this control experiment. The absence of allyl fluoride among products from reaction of **2** with *tert*-butyl fluoride implies that **2** does not rearrange to allyl cation on the millisecond time scale, as has been noted previously.⁷ Moreover, this rearrangement does not take place in the collision complex that leads to fluoride abstraction. Although rearrangements are known to occur when carbocations collide with neutral molecules that have large dipole moments,²⁰ fluoride abstraction is apparently much faster than rearrangement.

Another set of control experiments was performed to assess possible contributions from fluorine atom (F \cdot) and fluorine cation (F $^+$) reactions with bromopropenes. Electron bombardment of CF₄ is a copious source of F \cdot and F $^+$. The cross sections for production of these species by 70-eV-electron impact on CF₄ are ≥ 3.7 and 0.25 Å², respectively,^{5,19} more than an order of magnitude greater than the corresponding cross sections from 70-eV-electron impact on *tert*-butyl fluoride (for which we gauge the cross section for F \cdot production from the abundance of m/z 57 in the mass spectrum). Therefore the yields of fluoropropenes from EBFlow reactions of bromopropenes with CF₄ vastly overestimate (by a factor >10) the upper bounds for yields from F \cdot and F $^+$ reactions in mixtures of bromopropenes and *tert*-butyl fluoride. Experimentally we observe that the normalized conversion to 2-fluoropropene from 2×10^{-4} torr of CF₄ plus 2×10^{-4} torr of 2-bromopropene is 0.4% mA⁻¹, and the normalized conversion to allyl fluoride from 2×10^{-4} torr of CF₄ plus 2×10^{-4} torr of allyl bromide is 0.05% mA⁻¹. On the basis of these experiments, we infer that F \cdot and F $^+$ are not major contributors to our observed yields of fluoropropenes.

Conclusions

The 2-fluoroisopropyl cation (**1**) and the 2-propenyl cation (**2**) undergo ion-molecule reactions with *tert*-butyl fluoride to yield 2,2-difluoropropane (**8**) and 2-fluoropropene (**4**), respectively. Ionization of *tert*-butyl fluoride with 70-eV electrons yields **1** and **2** as primary ions in the ratio 100:22⁵ and, at 4×10^{-4} torr in the EBFlow reactor, neutral products **8** and **4** in the ratio 10:3. Therefore, less than 10% of **1** produces **4** in the EBFlow experiment.

Allyl cation is not formed under the reaction conditions. Otherwise, allyl fluoride would have been recovered, as it is when allyl bromide is bombarded with 70-eV electrons in the presence of *tert*-butyl fluoride. Ion **2** retains its structural integrity on the millisecond time scale of ion-molecule reactions, with no detectable rearrangement to allyl cation. The structure of **2** is confirmed by reaction 7.

Deuterium-labeling experiments show that neither **1** nor **2** exchanges hydrogens internally between carbon 1 and carbon 3. Vibrationally excited **1** expels HF to form **2**, presumably via reaction 3a, which requires a formally forbidden 1,3-hydrogen shift. Reversible rearrangement to protonated fluorocyclopropanes, as shown in reaction 3b, does not take place. If it did, isotopic

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scrambling would have been observed (even in the absence of production of allyl cation). The heat of formation of protonated fluorocyclopropane is unknown, but it can be crudely estimated from the calculated heat of formation of fluorocyclopropane (-28 kcal/mol)²¹ by taking the proton affinity of fluorocyclopropane to be the same as that of 1-fluoropropane. Estimating this latter value to be equal to the proton affinity of fluoroethane plus the difference in ionization potentials of fluoroethane and 1-fluoropropane,¹⁵ we gauge the ΔH_f° for F-protonated fluorocyclopropane to be on the order of 160 kcal/mol. The fact that vibrationally excited **1** neither yields allyl cation nor scrambles isotopic label en route to **2** testifies to the kinetic inaccessibility of protonated fluorocyclopropane.

These results show the utility of fluoride abstraction for assigning ion structures. The use of ¹⁹F NMR to determine the extent and position of deuterium label in neutral products opens

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new avenues for explorations of ion rearrangement pathways and reactivity in the gas phase.

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Registry No. 1, 14665-81-7; 2, 50457-57-3; 3, 61207-57-6; D₂, 7782-39-0; F⁻, 16984-48-8; *t*-BuF, 353-61-7; *t*-Bu⁺, 14804-25-2; (CH₃)₂CF₂, 420-45-1; CH₂=CFCH₃, 1184-60-7; (CD₃)₂C(OH)CH₃, 53853-65-9; MeMgI, 74-88-4; (CD₃)₂CO, 666-52-4; (Et₃N)SF₃, 38078-09-0.

Electron Spin-Echo Modulation Studies of Doxylstearic Acid Spin Probes in Sodium and Tetramethylammonium Dodecyl Sulfate Micelles: Interaction of the Spin Probe with D₂O and with Deuterated Terminal Methyl Groups in the Surfactant Molecules

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Abstract: Electron spin-echo studies have been carried out for a series of *x*-doxylstearic acids (*x* = 5, 7, 10, 12, and 16) in frozen aqueous solutions of sodium dodecyl sulfate and tetramethylammonium dodecyl sulfate in D₂O and of sodium dodecyl sulfate and tetramethylammonium dodecyl sulfate deuterated in their terminal methyl groups. Modulation effects due to interactions of the nitroxide groups with water deuterium and terminal methyl group deuterium have been measured as a function of *x*. The results are discussed in terms of the distributions of water and of terminal methyl groups measured separately in these micelles. In addition information is deduced about the probable conformations of the spin probe and surfactant molecules in the micelles. There is a profound influence of the counterion on all these factors as shown by the great difference between the sodium dodecyl sulfate and tetramethylammonium dodecyl sulfate micelles.

In several recent papers we have shown how electron spin-echo modulation (ESEM) spectrometry can be utilized to obtain information about the structure of micellar systems.¹⁻⁵ Electron spin-echoes originating from the photogenerated *N,N,N',N'*-tetramethylbenzidine (TMB) cation radical and from *x*-doxylstearic acid spin probes in rapidly frozen micellar solutions show deuterium modulation for samples prepared in D₂O or with surfactants deuterated in their head group or counterions. We have demonstrated that micellar structure is retained in these rapidly frozen solutions by electron spin resonance observation of TMB⁺ in the thawed solutions, since in bulk solution TMB⁺ has only a lifetime of microseconds! We have found that micellar structural factors play an important role in the photoionization efficiency of TMB. Substitution of the tetramethylammonium

cation for the sodium cation in dodecyl sulfate micelles brings about enhanced interaction between the TMB cation and water as measured by ESEM. This was accompanied by a marked increase in the photoionization efficiency of TMB. We have postulated that the surfaces of sodium dodecyl sulfate (SDS) and tetramethylammonium dodecyl sulfate (TMADS) micelles differ on the molecular level.⁴ While SDS micelles have a relatively compact head group structure, the head group structure of TMADS micelles seems to be more disordered or rougher perhaps

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