J. Am. Chem. Soc. **1991**, *113*, 6771–6779

on the reactivity of OH^- due to the water ligands is observed as shown in Figure 1. Furthermore, by studying the reaction kinetics based on a Lindemann-type mechanism, we found that the solvation effect is caused by the increase of the unimolecular dissociation rate constant k_{-1} and by the decrease of the intermolecular conversion rate constant k_r as cluster size increases. Thus, from the present experiments, we obtain a similar conclusion as Jönsson et al. that since the reactivity of OH^- in the presence of CA is about 4 orders of magnitude higher than in basic aqueous solution without CA, and the higher degree of hydration causes more of a drop in the reactivity of the OH^- anion, *the enzymatic effect of CA is likely to be accomplished by decreasing the hydration of OH^-*. Hence, despite the rather different conditions, the present experiment provides some experimental support for the proposed mechanism, and offers an example of how cluster research can bridge the gap between the gas and condensed phases.

Conclusion

Studies of the reaction kinetics of large hydrated anion clusters $X^-(H_2O)_{n=1-59}$ with CO_2 in the gas phase at different temperatures and pressures reveal the following.

(1) The reactions of small hydrated anionic clusters $OH^-(H_2O)_n$ and $O^-(H_2O)_n$ with CO_2 show no large dependence on the flow tube pressure and temperature due to the nature of the ligand-switching reaction mechanism and the lack of a permanent dipole of carbon dioxide, which is similar to what has been reported in the literature. However, the present work demonstrates that the reaction rate constants drop very quickly as the cluster sizes increase, due mainly to the solvation effect caused by the weak bonding of CO_2 to the anion clusters.

(2) Hydration has a large effect on the reaction thermodynamics of O_2^- and O_3^-. Only one and two water ligands make the reactions endothermic even at low temperatures.

The results yield experimental evidence in support of the mechanism which has been proposed to account for the enzymatic hydrolysis of CO_2, one that is believed to be catalyzed by carbonic anhydrase. The hydrolysis of CO_2 in many biological systems may occur by the creation of a hydrophobic environment so that the hydration of the OH^- ion is greatly reduced, which enhances the interaction between CO_2 and the anion, and increases the intermolecular conversion rate constant for the formation of $HCO_3^-(H_2O)_m$.

It is well established that CO_2 plays an important role in many atmospheric and environmental processes both physically, e.g., the green house effect, and chemically like in the negative ion chemistry of the stratosphere.[3] Since more hydration occurs in lower parts of the atmosphere, the reactivity of large hydrated clusters, charged or neutral, is of interest in understanding the chemistry of CO_2 in the atmosphere. In another paper,[28] the chemistry between large hydrated clusters and CO_2 with regard to the atmospheric and environmental applications will be discussed.

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[28] Yang, X.; Castleman, A. W., Jr. To be published.

Isotopomer Distributions of Neutral Products from a Doubly Labeled Cation in the Gas Phase. Interconversion of 1-Fluoro-1-propyl Cation and 1-Fluoroisopropyl Cation on the $C_3H_6F^+$ Potential Energy Surface

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Abstract: The title cations $CH_3CH_2CHF^+$ (**3**) and $CH_3CHCH_2F^+$ (**4**) are formed as transient intermediates in the gas phase. These are labile on the millisecond timescale as free ions but can be intercepted in ion–neutral complexes. When **3** is generated as a free cation by reaction of CF_3^+ with propionaldehyde, it rearranges to $(CH_3)_2CF^+$ (**1**), as shown by recovery of 2-fluoropropene as a neutral product from its deprotonation in an EBFlow experiment. The same neutral product is recovered when **1** is produced directly by reaction of acetone with CF_3^+ in the EBFlow. Neutral products indicative of **3** and **4** (allyl fluoride and 1-fluoropropene) are recovered when these cations are formed in $[R^+ PhO^•]$ ion–neutral complexes by electron bombardment of CH_3CDFCH_2OPh (**6**). Analysis of the isotopic distribution in the recovered neutrals from EBFlow radiolysis of $CH_3CDF^*CH_2OPh$ (where the asterisked carbon is ^{13}C-labeled) allows an assessment of the primary rearrangement pathways. The distribution of label is assayed by using ^{19}F NMR. Rearrangement of the R^+ moiety to form deuterated **1** occurs in about half of the complexes formed. In the remainder, methyl transfer (to form deuterated **3**) is 2–3 times faster than fluoride transfer (to form deuterated **4**). Scrambling of deuterium in the neutral products provides evidence that **3** and **4** interconvert within the ion–neutral complexes.

Double isotopic labeling, using ^2H and ^{13}C specifically incorporated into a single molecule, has been employed for at least two decades as a mass spectrometric tool to investigate rearrangments of gaseous cations.[1] In addition to being heavier than the more common isotopes, both nuclei have nonzero spin. It is therefore conceivable to use magnetic resonance to probe the positions of labeled atoms in the reaction products in situations where mass spectrometry is unable to distinguish alternative pathways. Such an experiment can yield a wealth of information, provided that it is possible to resolve positional isomers in a product mixture.

We have reduced this idea to practice. This paper reports the use of the electron bombardment flow (EBFlow) technique[2] to

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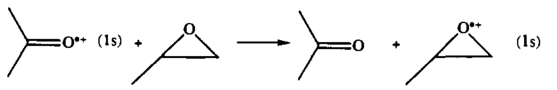
collect neutral products from a unimolecular ion decomposition of a doubly labeled cation, followed by NMR analysis to identify the products and determine the position and extent of labeling in every isotopomer. Elucidation of gaseous ion structures by neutral product analysis has been demonstrated,[2,3] but it turns out that some questions (even for comparatively simple systems) cannot be unraveled with fewer than four different NMR-active nuclei to probe molecular rearrangements. The effects of substituting a single fluorine into a carbocation represent such a case. While these effects can be computed ab initio, there are too few published data to confirm (or refute) predictions based on theory. The computational results often show great sensitivity to the choice of basis set or inclusion of election correlation, and there is no assurance that calculation necessarily becomes more accurate as it becomes more expensive.

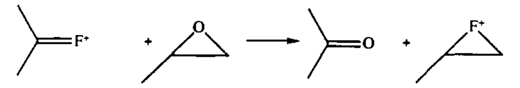
One objective of experiment is to test surmises based on theory. This paper presents new ab initio calculations of the local minima on the $C_3H_6F^+$ energy surface and experimental results that pertain to the same surface. The experimental design involves producing labeled cations in the gas phase, allowing them to be quenched by acid-base reactions, and examining the NMR of the resulting neutrals. By using ^{19}F as a probe nucleus and measuring the spin-spin couplings with ^1H, ^2H, and ^{13}C, we can determine the relative abundance of all of the isotopomeric products. These data permit an assessment of rearrangement pathways of $C_3H_6F^+$ cations and provide a test of theory.

Only one simple monofluorinated cation, 2-fluoroisopropyl (**1**), has been so well studied that its structure in solution[4] can be securely inferred to be the same as in the gas phase. Unlike isopropyl cation (which scrambles its hydrogens rapidly in both media), **1** shows no transposition of hydrogen between the two methyls,[5] even when it is produced with considerable internal energy at pressures on the order of 10^{-3} Torr. It is tempting to suppose that **1** is not labile because it possesses no low-lying isomers. This supposition leads, in turn, to the question of what will happen when isomeric structures are generated.

The $C_3H_6F^+$ potential energy surface was first examined ab initio by Hehre and Hiberty,[6] but the energetics of several structures can also be probed empirically by considering X-ray photoelectron spectra (XPS) of the isoelectronic C_3H_6O molecules. The method of equivalent cores[7] assumes that cations containing 1s-ionized oxygen atoms behave like F^+-containing cations. The energy difference between the two core-ionized species in eq 1 can be equated to the energy difference between the two fluorinated cations in eq 2.



(1)



(2)

1 2

We estimate the relative energies of ion **1** (whose gas-phase heat of formation is known,[8] $\Delta H_f° = 580$ kJ mol^{-1}) and the hypothetical bridged ion **2** as follows. Taking ΔH for eq 1 to be the difference in experimental oxygen core ionization energies (from XPS), we equate that difference to ΔH for eq 2. Gauged in such a straightforward fashion, the heat of formation of **2** is $\Delta H_f° \geq 750$ kJ mol^{-1}, but (as we have discussed elsewhere[9]) this direct approach is not foolproof. The most serious defect is that ion **2** is likely not to correspond to a potential energy minimum. SCF calculations with a small basis set (3-21G) show a stable geometry corresponding to **2**,[10] but this structure is not stable when a larger basis set (6-31G**) is used.[9] The higher level computations predict ions in which the fluorine is coplanar with the three carbons, with heats of formation on the order of $\Delta H_f° = 670$ kJ mol^{-1}. In other words, theory predicts stable 1-fluoroisopropyl cations (which are not isoelectronic to any stable C_3H_6O isomer). Moreover, the SCF calculations predict that 1-fluoroisopropyl cations have stabilities comparable to several other isomers. The picture that emerges is that 2-fluoroisopropyl cation (**1**) represents the global minimum for $C_3H_6F^+$ and that there are a half-dozen isomers 60–90 kJ mol^{-1} higher in energy, with no other structures intermediate between these and **1**.

Are any of the higher isomers accessible? Do they interconvert? To answer these questions, we turn to EBFlow experiments, which assess structures of gaseous ions in terms of neutral products recovered from their deprotonation.

Table I. ^{19}F NMR Chemical Shifts and T_1 Relaxation Times for C_3H_5F Isomers

C_3H_5F isomers	chemical shift (ppm)	T_1 (s)
2-fluoropropene	−87.5	3.3
(*E*)-1-fluoropropene	−129.5	4.3
(*Z*)-1-fluoropropene	−131.0	3.9
allyl fluoride	−215.6	7.6
cyclopropyl fluoride	−212.6[a]	*b*

[a] Rahman, M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1986**, *108*, 6296–6299. [b] Not measured.

Experimental Section

Spectra. GC/MS analyses were performed on a Finnigan 4000 quadrupole mass spectrometer equipped with a Hewlett-Packard 5890 gas chromatograph. Infrared spectra were recorded as neat films between NaCl plates on a Perkin-Elmer Model PE283. Routine ^1H and ^{13}C NMR spectra were recorded on a General Electric QE300 spectrometer. ^2H and ^{19}F NMR spectra were recorded on a Nicolet NT300 spectrometer, which was equipped with a home-built ^2H-decoupling unit. ^2H NMR spectra were recorded in $CHCl_3$ solution, with internal $CDCl_3$ as reference. ^{19}F NMR spectra were recorded in acetone solution, and chemical shifts are reported relative to $CFCl_3$.

The ^2H decoupler for the NT300 was designed and constructed around an existing replica of the standard ^1H decoupler, and it was necessary only to modify the decoupler for operation at the deuterium frequency, 46.062 MHz, which was generated by mixing the 10-MHz signal from the spectrometer with a 36.062-MHz signal generated by a PTS 160 frequency synthesizer. The mixer was a Model ZAD-3 purchased from Mini-Circuits, Inc. The output of the mixer was filtered through a low-power band-pass filter (Lark Engineering) having a center frequency of 46 MHz and a band gap of 3 MHz. The signal was then amplified by a broad-band power amplifier (ENI Model 400AP) capable of operating between 3 and 300 MHz with a power output of up to 3 W. The signal was filtered again through a high-power band-pass filter (Lark Engineering) before going into the probe. For ^2H–^{19}F decoupling, the spectrometer (whose magnet has a mean drift rate of 0.01 mT h^{-1}) was run unlocked, with the decoupling signal sent into the lock channel. The decoupler could be set to operate in the heteronuclear or the homonuclear decoupling mode. The ^{19}F probe contained a single, double-tuned coil for the lock and transmit/receive signals. It was found to be necessary to perform ^2H decoupling in the homonuclear (pulsed) mode in order to avoid introducing extraneous noise into the spectrum.

Table I lists the pertinent NMR parameters for the fluorine signal from every stable C_3H_5F isomer. The two isomers differing most in chemical shift, 2-fluoropropene and cyclopropyl fluoride, are separated by 35 500 Hz at 282 MHz. To ensure that all possible C_3H_4XF (X =

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(3) (a) Cacace, F. *Science* **1990**, *250*, 392–399. Cacace, F.; Speranza, M. In *Techniques for the Study of Ion-Molecule Reactions*; Farrar, J. M., Saunders, W. H., Jr., Eds.; *Techniques of Chemistry XX*; Wiley-Interscience: New York, 1988; pp 287–323.

(4) Olah, G. A.; Chambers, R. D.; Comisarow, M. B. *J. Am. Chem. Soc.* **1967**, *89*, 1268–1269.

(5) Redman, E. W.; Johri, K. K.; Morton, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 780–784.

(6) Hehre, W. J.; Hiberty, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 2665–2677.

(7) (a) Jolly, W. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1970**, *92*, 1863–1871. (b) Beach, D. B.; Eyermann, C. J.; Smit, S. P.; Xiang, S. F.; Jolly, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 536–539.

(8) Williamson, A. D.; Le Breton, P. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 2705–2709.

(9) Stams, D. A.; Thomas, T. D.; MacLaren, D. C.; Ji, D.; Morton, T. H. *J. Am. Chem. Soc.* **1990**, *112*, 1427–1434. The MP2 (FU)/6-31G** energy of the SCF-optimized 6-31G**//6-31G** geometry of **1** is given in Table II of this reference.

(10) Stams, D. A.; Johri, K. K.; Morton, T. H. *J. Am. Chem. Soc.* **1988**, *110*, 699–706.

Table II. Carbon–Fluorine Spin–Spin Coupling Constants (Hz) for C_3H_5F Isomers

C_3H_5F isomers	$^1J_{CF}$	$^2J_{CF}$	$^3J_{CF}$
2-fluoropropene	254.5	20.3[a]	30.5[b]
(*E*)-1-fluoropropene	253.9	5.3	7.1
(*Z*)-1-fluoropropene	249.2	11.0	11.1
allyl fluoride	162.2	16.8	12.1

[a] Coupling constant of vinyl carbon with fluorine. [b] Two-bond coupling constant of methyl carbon with fluorine.

H or D) isomers that might be formed are observed, a spectral width of 50 000 Hz was used.

It was found by calibrating the power spectrum of the pulse that pulse droop did not have a significant affect on the quantitation of the products in our analyses. Although it is desirable to allow a delay time of at least $5T_1$ between pulses for the most accurate quantitative results, in our experiments this would result in prohibitively long instrument time requirements. We have therefore chosen to perform the analysis using the optimum tipping angle (Ernst angle) for the species with the shortest T_1 in the sample and then to correct the results for differences in T_1 relaxation times. The accuracy of the correction was gauged by performing the analysis with a different delay time and comparing to the results after correction, with the original delay time.

The correction is applied in the following manner. The known, measured T_1 relaxation time for a product and the known tipping angle are inserted into eq 3 to yield a relative intensity, I_{rel}. The calculated relative intensity for a given resonance is then divided by the relative intensity calculated for the product with the shortest spin–lattice relaxation time to give a T_1 correction factor for each product. The measured integral

$$I_{rel} = \frac{\sin\theta(1 - e^{-\tau/T_1})}{[1 - (\cos\theta)(e^{-\tau/T_1})]} \qquad (3)$$

for each product is then divided by its T_1 correction factor to yield the actual relative amounts of products. For example, on the 282-MHz instrument, the analysis was performed by using a 63° pulse with a 3.3-s delay between pulses (3-s interpulse delay plus 300-ms acquisition time). 2-Fluoropropene, the product with the shortest T_1, is calculated to have an intensity, relative to that obtained by a 90° pulse with $\geq 5T_1$ interpulse delay, of $I_{rel} = 0.678$. The same calculation for allyl fluoride gives $I_{rel} = 0.447$. To correct for differences in T_1 relaxation times between these two products, the integral for allyl fluoride must be multiplied by 0.678/0.447 = 1.52. This kind of correction was applied to all the products listed in Table I. Values of the carbon–fluorine coupling constants were measured from ^{13}C NMR spectra of authentic samples of C_3H_5F isomers and are summarized in Table II.

Materials. CF_4 (stated purity 99.9%) was obtained from Liquid Carbonics and purified by vacuum transfer into a glass vessel followed by vacuum distilling half of it near its melting point into another liquid nitrogen cooled glass vessel. *tert*-Butyl fluoride (Aldrich Chemical Co.) was vacuum transferred into a glass vessel for use. Acetone and [d_6]-acetone (99.5% D atom) were obtained from Aldrich and used without further purification. (Diethylamino)sulfur trifluoride (DAST), 2-fluoropropene, and 2,2-difluoropropane were purchased from PCR Inc. and used without further purification. Authentic samples of other fluoropropenes were prepared by known procedures.

[2-d_1]-2-Fluoro-3-phenoxypropane, 6a. 1-Phenoxy[2-d_1]-2-propanol, obtained from the lithium aluminum deuteride reduction of phenoxyacetone (Aldrich), was treated with 1.2 equiv of DAST at −78 °C in dichloromethane. After aqueous workup and removal of the solvent, vacuum distillation (34–35 °C at 0.07 Torr) yielded the product. ^1H NMR (^2H-decoupled): δ 1.40 (d, $J_{HF} = 23.3$ Hz, 3 H), 4.09 (ABX pattern, $J_{HH} = 10.6$, $J_{HF} = 19.5$, 23.3 Hz, with the resonance further downfield having the smaller coupling to fluorine, 2 H), 6.8–7.0 (m, 3 H), 7.2–7.4 (m, 2 H). ^2H NMR: δ 5.04 (d, $J_{DF} = 7.5$ Hz). ^{13}C NMR (^1H-decoupled): δ 17.2 (d, $J_{CF} = 22.1$ Hz), 70.5 (d, $J_{CF} = 23.3$ Hz), 88.0 (doublet of $I = 1$ triplets, $J_{CF} = 168.6$, $J_{CD} = 23.4$ Hz), 114.5, 121.1, 129.4, 158.4. ^{19}F NMR: −179.6 ppm (quintet (23 Hz) of doublets (19.5 Hz) of $I = 1$ triplets (7.5 Hz)). GC/MS (70 eV): m/z 155 ($M^{\bullet+}$, 43), 107 (17), 95 (28.5. standard deviation (s.d.) = 1.5), 94 (100), 77 (28), 67 (6), 66 (17). 65 (15), 62 (10), 51 (26), 42 (17), 40 (16). IR (neat film): 3070, 3050, 2990, 2930, 2885, 2180 (ν_{CD}), 1602, 1592, 1495, 1455, 1385, 1300, 1255, 1225, 1175, 1150, 1080, 1055, 950, 920, 805, 752, 688 cm^{-1}.

[2-^{13}C]-2-Phenoxyacetic Acid. A 100-mL round-bottom flask and a 15-mL pressure-equalizing dropping funnel were dried in a 150 °C oven overnight. The apparatus was removed from the oven, a small amount of stopcock grease was applied to the joints, and the pieces were assembled while hot and allowed to cool under a stream of nitrogen. A 1.36-g (14.5 mmol) portion of dried phenol was dissolved in 10 mL of dry THF and added dropwise to a suspension of 0.70 g of NaH in 5 mL of dry THF. A solution of 2.01 g (14.5 mmol) of [2-^{13}C]bromoacetic acid (Cambridge Isotope Laboratories, 99% isotopic purity) in 10 mL of dry THF was added dropwise to the phenoxide/sodium hydride mixture at room temperature over the course of 30 min. After 2-h reflux, the contents of the flask congealed to a thick white solid mass, which required the addition of 30 mL more of dry THF to transform the mixture from a paste to a slurry that was more easily stirred, and the reaction mixture was refluxed for another 20 h, allowed to cool, poured into 30 mL of 10% aqueous HCl, and extracted with two 20-mL portions of ether. The combined ethereal layers were dried over Na_2SO_4, and solvent was removed under aspirator pressure to yield 2.13 g of solid residue (96% yield), which was sufficiently pure to use in the subsequent step. ^1H NMR ($CDCl_3$): δ 4.65 (d, $J_{CH} = 153$ Hz, 2 H), 6.8–7.4 (m, 5 H), 6.5 (br s, 1 H).

[1-^{13}C]-1-Phenoxy-2-propanone. A solution of 2.13 g (13.9 mmol) of [2-^{13}C]-2-phenoxyacetic acid in 30 mL of dry ether was cooled to −78 °C under a dry nitrogen atmosphere and 19 mL (28.5 mmol) of a 1.5 M solution of methyllithium in ether added dropwise over the course of 30 min with vigorous stirring. The mixture was allowed to warm to room temperature and stirring continued for an additional 24 h before the reaction mixture was cooled to 0 °C and quenched by the very slow addition of 20 mL of water over the course of 30 min. After the mixture had warmed to room temperature, the ether layer was separated, dried over Na_2SO_4, and, after removal of solvent, the residue distilled from calcium hydride to yield 1.27 g (8.42 mmol, 60% yield) of product. ^1H NMR ($CDCl_3$): δ 2.29 (d, $J_{CH} = 0.98$ Hz, 3 H), 4.54 (d, $J_{CH} = 144$ Hz, 2 H), 6.9–7.1 (m, 3 H), 7.2–7.4 (m, 2 H). Acidification of the aqueous layer and further extraction with ether yielded 0.2 g of unreacted phenoxyacetic acid.

[2-d_1]-2-Fluoro-[1-^{13}C]-1-phenoxypropane, 6b. [1-^{13}C]-1-Phenoxy-2-propanone was converted to **6b** by the same procedure as used for the preparation of **6a** above. ^1H NMR (^2H-decoupled): δ 1.42 (dd, $J_{HF} = 23.4$, $J_{CH} = 4.9$ Hz, 3 H), 4.07 (d, ABX, $J_{CH} = 143.3$ Hz, $J_{HH} = 10.6$ Hz, $J_{H_AF} = 19.1$ Hz, $J_{H_BF} = 23.3$ Hz, 2 H), 6.9–7.0 (m, 3 H), 7.25–7.35 (m, 2 H). ^2H NMR: δ 5.02 (d, $J_{DF} = 7.4$ Hz). ^{19}F NMR: −180.4 ppm (sextet of doublets of $I = 1$ triplets (23.3, 19.5, 7.4 Hz)). ^{13}C NMR (^1H-decoupled): δ 17.5 (d, $J_{CF} = 23.3$ Hz), 70.6 (d, $J_{CF} = 23.6$ Hz), 88.5 (dd of $I = 1$ triplets, $J_{CF} = 168.5$, $J_{CC} = 43.6$, $J_{CD} = 23.2$ Hz), 114.7, 121.2, 129.5, 159. GC/MS: m/z 156 ($M^{\bullet+}$, 44) 108 (13), 95 (24.9, s.d. = 1.8), 94 (100), 80 (9), 77 (37), 67 (7), 66 (16), 65 (14), 63 (11), 51 (29), 50 (10), 43 (29), 40 (26).

EBFlow. The EBFlow technique has been described elsewhere in detail.[2] After 70-eV electron bombardment for 1–2 h, the condensed EBFlow reaction mixtures were vacuum transferred to 5-mm NMR tubes containing degassed [d_6]acetone as solvent and sealed under vacuum for subsequent NMR analysis. For studies of free fluoropropyl ions, a mixture of 2 × 10^{-4} Torr of the carbonyl precursor and 3 × 10^{-4} Torr of CF_4 was bombarded with 70-eV electrons. For the experiment in which $C_3D_6F^+$ was quenched by fluoride abstraction, the EBFlow reaction mixture of [d_6]acetone and CF_4 also contained 3 × 10^{-4} Torr of *tert*-butyl fluoride. EBFlow radiolysis of acetone and CF_4 yielded $CH_3CF{=}CH_2$ and $(CH_3)_2CF_2$ in a ratio of 3:2. EBFlow radiolysis of propionaldehyde yielded a small amount of $CH_3CH{=}CHF$ as well as $CH_3CF{=}CH_2$, with a C_3H_5F:$C_3H_6F_2$ ratio of approximately 3:1.

Phenyl ethers **6a** and **6b** were subjected to 70-eV electron bombardment in the EBFlow apparatus at 1 × 10^{-4} Torr with no other added gases. Three repetitions of the radiolysis of **6a** were performed, along with a control in which the filament was turned on but no acceleration was supplied to the electrons. The average electron current in the reaction vessel during the experimental runs was in the range 0.1–0.2 mA. Two experimental runs and a control with **6b** were run under the same conditions. The normalized yield was measured by adding a known volume of C_6F_6 (measured value of $T_1 = 4.3$ s) to the reaction mixture as an NMR intensity standard. No fluorocyclopropane was observed under any conditions.

Computation. Ab initio calculations were performed on the 6-31G**//6-31G** optimized geometries[1] by using the GAUSSIAN 82 program, revision K, for MP2(FU)/6-31G** electronic energies[11] and The Cambridge Analytical Derivatives Package, issue 4.0, for normal modes at SCF 6-31G**.[12] A FORTRAN program was written to simulate the rearrangement kinetics and implemented on a VAX 8820. The program optimized the parameters in the kinetic models by using Powell's BOTM

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(11) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fleuder, E. M.; Pople, J. A. *GAUSSIAN 82*; Department of Chemistry, Carnegie-Mellon University: Pittsburgh, PA.

(12) Amos, R. D.; Rice, J. E. *The Cambridge Analytical Derivatives Package* (*CADPAC*), Cambridge, 1987.

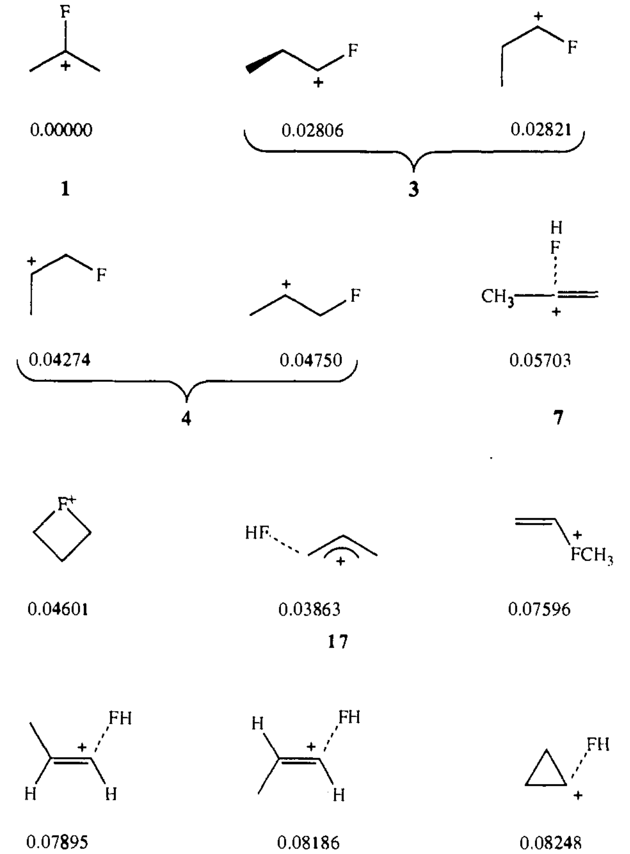

Figure 1. Stable $C_3H_6F^+$ geometries from SCF 6-31G** optimizations,[9] with MP2/6-31G** electronic energies (including core orbitals) in atomic units relative to **1**. These structures can be placed into a one-to-one correspondence with the stable C_3H_6O isomers (although there are some major structural differences).

algorithm.[13] A Runge–Kutta fourth-order routine was used to solve the set of differential equations to yield the final product proportions at each step in the optimization.

Results

A dozen different structures correspond to minima on the $C_3H_6F^+$ ab initio energy surface.[7] Figure 1 depicts them, along with their MP2/6-31G** electronic energies in atomic units. Acetone and **1** are isoelectronic and correspond to the global minima on their respective potential energy surfaces. At the MP2 level (by using SCF-optimized geometries), **1** is predicted to have a heat of formation approximately 80 kJ mol^{-1} below that of the next most stable isomer **3**, 1-fluoro-1-propyl cation. Propionaldehyde and **3** are isoelectronic. Both have planar and skew conformers of approximately equal stability.[9,14] While the two conformers of **3** possess nearly the same electronic energy, the SCF-calculated zero-point energy of the cis planar conformer at 6-31G** is 2.5 kJ mol^{-1} lower than that of the skew conformer.

Other predicted $C_3H_6F^+$ isomers include 1-fluoroisopropyl cation, **4**, whose planar conformers are calculated (at MP2) to have heats of formation 111 (s-cis) and 124 kJ mol^{-1} (s-trans) above **1**, when 6-31G** SCF zero-point energies are taken into account. As noted above, **4** possesses no stable isoelectronic analogue where O replaces F (since propylene oxide has a very different geometry). The MP2 calculations predict **3** to be 32 kJ mol^{-1} more stable than **4**. This is 4 times larger than the energy difference (8 kJ mol^{-1}) predicted by SCF calculations at the same level. Such a disrepancy is significant. If, on the one hand, SCF energies are correct, **3** and **4** are close enough thermodynamically for the two isomers to interconvert. If, on the other hand, the MP2 energies are correct, the difference is so large that while **3** may isomerize to **4**, the reverse reaction is improbable.

Free fluoropropyl cations can be prepared in the gas phase, as the first step of eq 4 portrays, by bombarding a mixture of CF_4 and the corresponding carbonyl compound with 70-eV electrons.[15] The metathesis of F^+ for O is very exothermic, and many of the product ions undergo subsequent unimolecular decomposition.

$$(CD_3)_2C{=}O \xrightarrow[-CF_2O]{CF_3^+} (CD_3)_2CF^+ \xrightarrow{(CH_3)_3CF} (CD_3)_2CF_2 \tag{4}$$

$$R^1CH_2COR^2 \xrightarrow[-CF_2O]{CF_3^+} R^1CH_2\overset{+}{C}FR^2 \xrightarrow{-H^+} R^1CH{=}CFR^2 \tag{5}$$

The fluoropropyl cations that do not decompose can be intercepted by acid–base reactions.[2,10] The fluorinated ion can be neutralized by a Lewis base, such as *tert*-butyl fluoride acting as fluoride donor.[5] Since *tert*-butyl fluoride also yields **1** under electron impact, we have explored 70-eV electron impact on a mixture of [d_6]acetone, CF_4, and *tert*-butyl fluoride to test whether the metathesis product can be captured by fluoride abstraction in the EBFlow. ^{19}F NMR of the product mixture shows both $(CH_3)_2CF_2$ (from reaction of **1** with *tert*-butyl fluoride) and $(CD_3)_2CF_3$ from reaction 4. (As we have previously shown, the ^{19}F resonances of the [d_0]- and [d_6]-2,2-difluoropropanes are easily resolved.[2,5]) The recovered neutral products observed by ^{19}F NMR were $CH_3CF{=}CH_2$, $CD_3CF{=}CD_2$, $(CH_3)_2CF_2$, and $(CD_3)_2CF_2$ in the ratio 6:4:3:2 (uncorrected for T_1).

The fluorinated ions can also be quenched by a Brønsted acid–base reaction, proton transfer to the starting material (represented by eq 5). Electron impact on a mixture of CF_4 and acetone yields the product expected from **1** (R^1 = H, R^2 = CH_3), 2-fluoropropene. Electron bombardment of a mixture of CF_4 and propionaldehyde under the same conditions also yields 2-fluoropropene as the principal recovered C_3H_5F isomer, with only traces of (*E*)- and (*Z*)-1-fluoropropene (both approximately 10% of the C_3H_5F yield). While ion **3** (R^1 = CH_3, R^2 = H) might have been formed initially from propionaldehyde, it rearranges extensively to **1** on the millisecond timescale of second-order reactions in the EBFlow.

This result suggests that isomers of **1** are to be sought under different conditions. We have recently described the formation of other fluoroalkyl cations in a gas-phase regime that is analogous to solvolysis.[16] As shown in a variety of previous studies, ionized alkyl phenyl ethers (X = O$^\bullet$) decompose unimolecularly via ion–neutral complexes, eq 6, where the ionic fragment R^+ undergoes rearrangements as though it were a free ion with a short (~10^{-10} s) lifetime.[17] Subsequent proton transfer to the phenoxy fragment yields phenol molecular ion and neutral alkenes. The structures of the collected fluoroalkenes reveal pathways by which the intermediate fluoroalkyl cations have isomerized. When deuterated starting materials are used, the positions and extents of isotopic substitution of each component in the recovered mixture can be assessed by ^{19}F NMR, in which every isotopic analogue is resolved.[2,10]

$$PhXR^+ \rightarrow [PhX \quad R^+] \rightarrow PhXH^+ + \text{alkenes} \tag{6}$$

Neutral products from 70-eV electron impact on fluoropropyl phenyl ethers were collected in the EBFlow. Fluorinated propyl cations in the corresponding ion–neutral complexes yield 1-fluoropropenes. We have paid particular attention to the deuterated 2-fluoro-*n*-propyl phenyl ether **6**, whose ionization provides a formal equivalent of the primary cation **5d**. This can rearrange either by a methyl shift or a fluoride shift, as depicted in eq 7. The neutral product distribution recovered from EBFlow radiolysis of the singly labeled ether **6a** is summarized in Table III. The normalized yield of fluoropropenes was 2.7 μmol A^{-1} s^{-1}. (A normalized yield of 9.65 μmol A^{-1} s^{-1} corresponds to one molecule of product for every electron entering the EBFlow reaction vessel.[2])

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(13) Powell, M. J. D. *Comput. J.* **1964**, *7*, 155–162.
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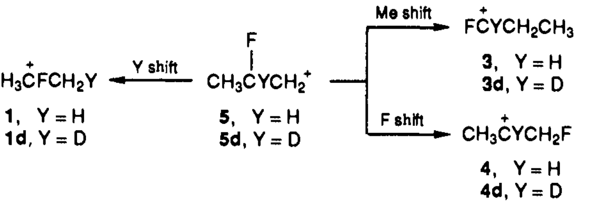
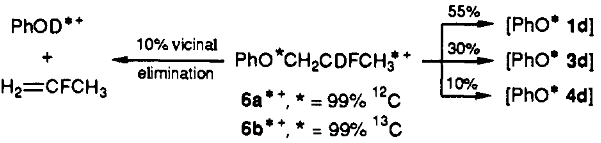
(17) Chronister, E. L.; Morton, T. H. *J. Am. Chem. Soc.* **1990**, *112*, 133–139 and references contained therein.



(7)

Judging from the yields of [d$_1$]-2-fluoropropenes, we infer that roughly half of the parent ions yield ion–neutral complexes containing $CH_3CFCH_2D^+$ (**1d**). For a more precise determination, we compare the neutral product ratio C_3H_4DF:C_3H_5F, 2.6, to the $PhOH^{\bullet+}$:$PhOD^{\bullet+}$ ratio observed in the 70-eV mass spectrum, 4.6 (the standard deviations of both ratios are 0.3). It is clear that some of the recovered C_3H_5F must have come from a different reaction (such as thermal 1,2-elimination from unionized **6**). We assume that $CH_3CF{=}CH_2$ is the sole contaminant from nonionic reactions. Correcting the ion yield accordingly, we conclude that 2-fluoropropenes constitute 53 ± 7% of the recovered product from decomposition of $\mathbf{6}^{\bullet+}$. Thus corrected, the proportion of $CH_3CF{=}CH_2$, 0.14 ± 0.03, is still higher than would be expected from **1d**. Assuming a normal primary isotope effect ($k_H/k_D = 1.1-1.3$), we would have expected a proportion on the order of 0.06 and infer that a small fraction of $\mathbf{6}^{\bullet+}$ (estimated on the order of 8%) must be decomposing via a formal *vic* elimination, which need not involve an ion–neutral complex.

Double isotopic labeling provides additional information. We prepared the doubly labeled ether **6b** and subjected it to EBFlow radiolysis. The 2-fluoropropenes from the ^{13}C-containing precursor do not have any labeled carbon at position 2. The bulk of the recovered 2-fluoropropene must therefore come from the formal equivalent of a deuterium shift (Y shift in eq 7, where Y = D). While a literal 1,2-shift is certainly reasonable, intermediacy of the stable ion–molecule complex **7** (whose heat of formation is estimated to be 131 kJ mol^{-1} above that of **1**)[7,18] cannot be absolutely ruled out at this point.



(8)

The remaining 40% of $\mathbf{6}^{\bullet+}$ yields 1-fluoropropene and deuterated allyl fluoride, which we ascribe to the rearrangement in eq 7. We observe no formation of undeuterated allyl fluoride, but $CH_2{=}CHCHDF$ and undeuterated 1-fluoropropene are among the recovered products, which suggests that not only must the conversion **4** → **3** occur within the lifetime of the ion–neutral complex, but also the reverse shift **3** → **4**.

To test this supposition and to get an estimate of relative rates of interconversions, we measured the proportions of the ^{13}C label in various positions of the fluoropropenes from EBFlow radiolysis of **6b**. The ^{19}F NMR spectrum of the recovered (*Z*)-1-fluoropropenes is reproduced in Figure 2. The combined effects of isotopically induced chemical shift differences and ^{13}C–^{19}F spin–spin coupling permit the assignment and quantitation of every isotopomeric product. The observed distribution of label can be explained in terms of competition drawn in eq 8 (where the percentages have been rounded to the nearest 5%), in which methyl shift is 2.5 (s.d. = 0.6) times more likely than fluoride shift, followed by interchange of **3** and **4**. The proportions of isotopomeric fluoropropenes recovered in duplicate runs are summarized in Table IV and compared with results of a kinetic simulation, which is discussed below.

Table III. Neutral Fluoropropenes from 70-eV EBFlow Radiolysis of **6a**, Based on ^{19}F NMR Analysis (Intensities Corrected for T_1)

	proportion of recovered fluoropropene			
product	run 1	run 2	run 3	average ± s.d.
$CH_3CF{=}CH_2$	0.209	0.223	0.234	0.222 ± 0.013
$DCH_2CF{=}CH_2$	0.281	0.234	0.254	0.256 ± 0.024
(*Z*)-$CH_3CF{=}CHD$	0.077	0.060	0.067	0.068 ± 0.009
(*E*)-$CH_3CF{=}CHD$	0.061	0.069	0.062	0.064 ± 0.004
(*Z*)-$CH_3CH{=}CFD$	0.116	0.107	0.101	0.108 ± 0.008
(*E*)-$CH_3CH{=}CFD$	0.092	0.074	0.097	0.088 ± 0.012
(*Z*)-$CH_3CD{=}CFH$	0.044	0.057	0.047	0.049 ± 0.007
(*E*)-$CH_3CD{=}CFH$	0.036	0.047	0.040	0.041 ± 0.006
(*Z*)-$CH_3CH{=}CFH$	0.019	0.034	0.016	0.023 ± 0.010
(*E*)-$CH_3CH{=}CFH$	0.009	0.018	0.015	0.014 ± 0.005
$CH_2{=}CDCH_2F$	0.034	0.061	0.036	0.044 ± 0.015
$CH_2{=}CHCHDF$	≤0.02	0.016	0.030	0.02 ± 0.01

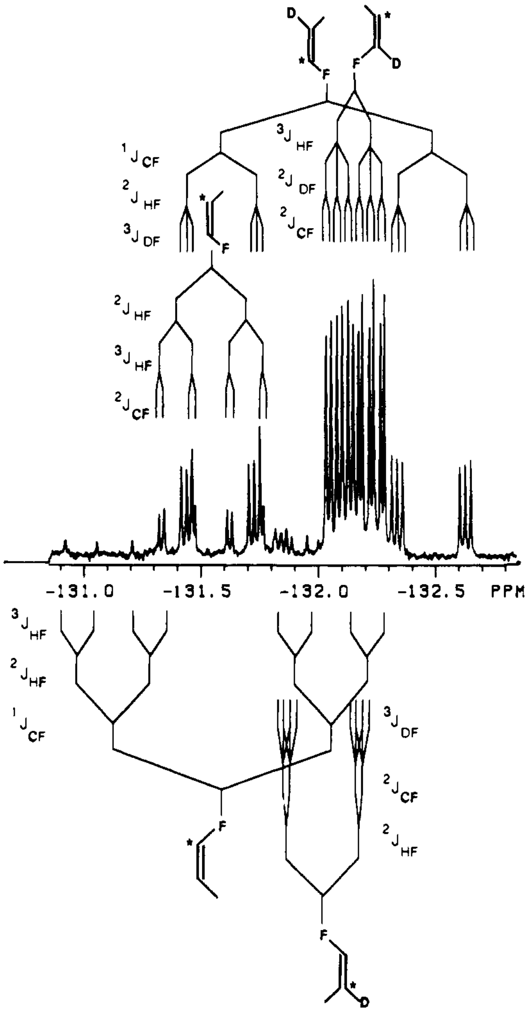


Figure 2. 282-MHz ^{19}F NMR spectrum (with selective ^1H decoupling of methyl protons) of (*Z*)-1-fluoropropenes from 70-eV EBFlow radiolysis of **6b**. Spin–spin splitting patterns were confirmed by means of ^1H and ^2H broad-band decoupling experiments.

Discussion

EBFlow experiments demonstrate that $C_3H_6F^+$ ions rearrange extensively to the global minimum, structure **1**, on the millisecond timescale. On the much shorter timescale of their existence in ion–neutral complexes, structures **3** and **4** do not isomerize to **1**, but they do interconvert with one another. The experimental results obtained here test our current theoretical understanding of fluorine-substituted carbocations. Three general questions can be addressed. First, how does fluoride 1,2-shift compare with methyl 1,2-shift? Second, what is the stability of a primary α-fluorocarbocation (e.g., **3**) relative to an isomeric secondary β-fluorocarbocation (e.g., **4**)? Third, how facile are hydrogen shifts that yield α-fluorocarbocations (such as **5** → **1** or **4** → **3**)?

Consider the first question. There are a few reports in the literature of ostensible intramolecular fluoride shifts. The cation **8** undergoes a rearrangement in solution (observed by NMR in

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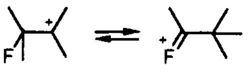
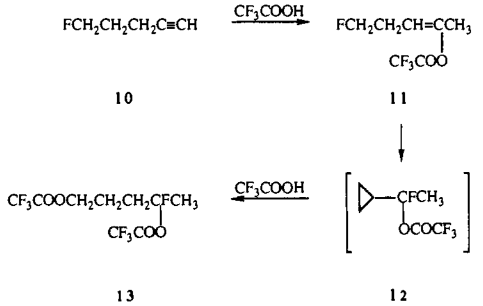
(18) Olah, G. A.; Bollinger, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 4744–4752.

SO_2–SbF_5) that renders all of the methyl groups equivalent.[18] While this could be consistent with a 1,2-shift via a bridged fluoronium ion, the ^{13}C NMR of **8** shows three resonances, which is taken to show that the rearrangement proceeds by the pinacol rearrangement-type pathway via ion **9** drawn in eq 9.[19]


(9)

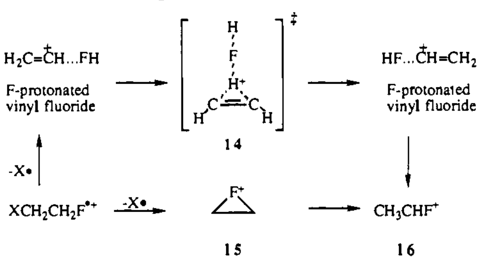
8 **9**

Another case of a putative fluoride shift has been proposed when acetylene **10** is treated with trifluoroacetic acid.[20] Here, the recovered product **13** might have arisen via a fluoride 1,4-shift to an initially formed vinyl cation. Alternatively, the homoallylic intermediate **11** might have undergone solvolytic rearrangement to the cyclopropylcarbinyl fluoride **12**, followed by rapid trifluoroacetolysis of the cyclopropane ring. Or else elimination and readdition of HF might have taken place. In the absence of additional results, the available data cannot be taken as a definitive example of an internal fluoride shift.



(10)

Persuasive evidence for internal transposition of fluorine comes from gas-phase studies by Ciommer and Schwarz.[21] Decomposition of β-fluoroethyl-containing cations, as depicted in eq 11, leads ultimately to α-fluoroethyl cations. Isotopic double-labeling studies in the mass spectrometer show that the fluorine moves about half the time, which is consistent with a bridged ion, either HF hydrogen bonded to a bridged vinyl cation (structure **14**) or fluoriranium ion (**15**). The heat of formation of **15** and **16** can be estimated empirically by the method of equivalent cores. The estimated value ΔH_f(**16**) = 690 kJ mol^{-1} thus determined is in excellent agreement with the experimental value for the heat of formation of this 1-fluoroethyl cation. The estimated value ΔH_f(**15**) = 760 mol^{-1} agrees with ab initio estimates.[9]



(11)

The alternative pathway for fluorine transposition via **14** cannot be dismissed out of hand. This pathway involves a geminal elimination of hydrogen fluoride to yield a stable F-protonated vinyl fluoride with a C–F bond distance that we calculate (SCF optimization using the 6-31G** basis set) to be 1.89 Å. The electronic energy difference between this and free vinyl cation (which enjoys a symmetrical, bridged structure) plus HF is sensitive to the level of calculation: 0.021 76 au at SCF, 0.026 25 au at MP2, and 0.024 94 au at MP3. The symmetrical geometry **14** corresponds to a transition state that ranges from 3 kJ mol^{-1} (MP2) to 32 kJ mol^{-1} (SCF) higher in energy. Using the MP3 electronic energies (which place **14** only 14 kJ mol^{-1} above the stable geometries) and the known heats of formation of vinyl cation and HF, we estimate ΔH_f(**14**) = 780 kJ mol^{-1} for the symmetrical transition state.

There is additional evidence from the published mass spectrometric data regarding $PhOCH_2CH_2F^{\bullet +}$ and its dideuterated analogues, but it does not allow us to discriminate between the two pathways in eq 11. The published interpretations of those data antedate our understanding of ion–neutral complexes,[22] but the results can be reinterpreted in terms of the formation of [$C_2H_4F^+$ $PhO^\bullet$] complexes. If the ions in such complexes were exclusively of the structure **15** (or all passed through structures **14** or **15** en route to **16**), then the products from $PhOCD_2CH_2F$ (α-d_2) and $PhOCH_2CD_2F$ (β-d_2) would contain identical proportions of $PhOH^{\bullet +}$ and $PhOD^{\bullet +}$. This is not observed, neither for ions in the mass spectrometer source, nor for metastable ions, but some scrambling of α and β hydrogens does occur. Unfortunately, the mass spectrometer cannot distinguish which structures, **14**, **15**, or **16**, are being formed.

A similar problem exists for any effort to use mass spectrometry to assess whether structure **2** is accessible as a transition state in the case of the next higher homologue. Transposition of fluorine might plausibly occur by elimination–readdition via ion **17** (Figure 1), whose electronic energy is calculated to be lower than that of **4** and whose heat of formation must therefore be considerably lower than that of **2**. In order to assess definitively whether fluorine is capable of bridging, we must rely upon EBFlow experiments in conjunction with mass spectrometry.

Conclusive evidence for transposition via bridged fluoronium ions comes from our EBFlow studies of compound **18**, as portrayed in eq 12.[12] Methyl migration (not shown) competes with fluoride 1,2-shift, and the isotopic labeling results rule out elimination–readdition of DF as a possible pathway. The same type of isotopic

$$\underset{\mathbf{18}^{\bullet +}}{(CD_3)_2CFCH_2OPh^{\bullet +}} \rightarrow [(CD_3)_2\overset{+}{C}CH_2F \quad PhO^\bullet] \rightarrow$$
$$CD_2{=}C(CD_3)CH_2F + (CD_3)_2C{=}CHF \quad (12)$$

labeling study has been performed for **6**, and (as shall be treated more fully below) the result rules out **17** and implicates **2**. The ratio of methyl 1,2-shift to 1,2-shift from $\mathbf{18}^{\bullet +}$ is 4.4:1, which implies (after correcting for 2:1 statistical preference for methyl) that the migratory aptitude of fluoride is 0.45 that of a methyl group.

In the present study, we compare the relative migratory aptitudes of methyl, fluoride, and deuterium, as represented by eq 7. Relative to the methyl, the migratory aptitude of deuterium in $\mathbf{6}^{\bullet +}$ is 1.9, while that of fluoride is 0.45. The latter value agrees well with our result for **18**. Analysis of the distribution of deuterium among the neutral products from $\mathbf{6}^{\bullet +}$ shows no transposition of deuterium into the methyl group, which means that no vicinal elimination–readdition of HF via ion **17** is taking place within the ion–neutral complex. If **17** had been formed, a hydrogen would transpose every time the F moved, and $CH_2DCH{=}CHF$ would have been seen. This product is not detected. The data, however, cannot be used definitively to rule out geminal elimination to form ion **7**, since anti-Markovnikov readdition of DF to the double bond would not result in any net transposition of deuterium. However, such a pathway is not possible in eq 12, yet the migratory aptitudes of fluoride (relative to methyl) are the same for both $\mathbf{6}^{\bullet +}$ and $\mathbf{18}^{\bullet +}$. In our view, this comparison weighs against the intermediacy of **7** in the transposition of fluorine and argues that the fluoride 1,2-shift proceeds via structure **2** as a transition state.

In answer to the second question posed at the beginning of this discussion, we can give only a qualitative answer with regard to the relative stabilities of **3** and **4**. The fact that both ions interconvert within ion–neutral complexes suggests that they must be of comparable stability. The first ab initio computations using geometries optimized at STO-3G set *cis*-**4** approximately 20 kJ mol^{-1} lower than *skew*-**3**.[6] Better theoretical estimates are now

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Table IV. Neutral ^{13}C-Labeled Fluoropropenes from 70-eV Electron Impact on **6b**

	proportion with ^{13}C at								
	C1			C2			C3		
	run 1	run 2	sim	run 1	run 2	sim	run 1	run 2	sim
$CH_2DCF{=}CH_2$	*a*	*a*	0	*a*	*a*	0	0.27	0.26	0.26
(*Z*)-$CH_3CF{=}CHD$	0.075	0.065	0.070	*a*	*a*	0	*a*	*a*	0
(*E*)-$CH_3CF{=}CHD$	0.065	0.066	0.066	*a*	*a*	0	*a*	*a*	0
$CH_3CF{=}CH_2$	0.25	0.24	0.105[b]	*a*	*a*	0	*a*	*a*	0
$CH_2{=}CDCH_2F$	*a*	*a*	0	*a*	*a*	0	0.032	0.033	0.027
$CH_2{=}CHCHDF$	*a*	*a*	0	0.016	0.017	0.021	*a*	*a*	0
(*Z*)-$CH_3CH{=}CDF$	*a*	*a*	0	0.11	0.12	0.11	*a*	*a*	0
(*E*)-$CH_3CH{=}CDF$	*a*	*a*	0	0.078	0.10	0.089	*a*	*a*	0
(*Z*)-$CH_3CD{=}CHF$	0.025	0.031	0.038	0.008	0.009	0.004	*a*	*a*	0
(*E*)-$CH_3CD{=}CHF$	0.027	0.025	0.027	0.005	0.005	0.003	*a*	*a*	0
(*Z*)-$CH_3CH{=}CHF$	0.003	0.004	0.004	0.018	0.014	0.013	*a*	*a*	0
(*E*)-$CH_3CH{=}CHF$	0.003	0.003	0.004	0.012	0.011	0.009	*a*	*a*	0

[a] Below the detection limit (<0.001) in both runs. [b] Expected from $6^{\bullet +}$ only. All other stimulated proportions are corrected for the contribution of nonionically produced $CH_3CF{=}CH_2$.

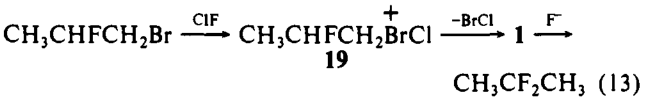
Table V. Equilibrium Constants and Relative Rate Constants for Scheme I Determined by Fitting to Experimental Product Ratios[a]

Conformational Equilibrium Constants	
trans-**4**/*cis*-**4**	$X = 0.3$
skew-**3**/*cis*-**3**	$Y = 2.4$
Deprotonation: $[C_3H_6F^+\ PhO^\bullet] \rightarrow PhOH^{\bullet +}$	
4 → allyl fluoride	$b = 2.3k$
4 → (*Z*)-1-fluoropropene	$c = 4.2k$
4 → (*E*)-1-fluoropropene	$s = 1.9k$
cis-**3** → (*Z*)-1-fluoropropene	$p = 0.5k'$
skew-**3** → (*E*)-1-fluoropropene	$v = 2.3k'$
skew-**3** → (*Z*)-1-fluoropropene	$t = 2.6k'$
Isotope Effects, k_H/k_D	
3 → **4**	$k'/w = 1.8$
3 or **4** → 1-fluoropropene	$q/v = 1.3$
4 → **3**	$k/z = 0.7$

[a] Relative to the hydride shift rate constants $\mathbf{4} \xrightarrow{2k} \mathbf{3}$ and $\mathbf{3} \xrightarrow{2k'} \mathbf{4}$.

available, based on geometries optimized by using 6-31G** SCF calculations. At the SCF level, **3** is 8 kJ mol^{-1} lower than **4**, while with energies computed at the MP2 level **4** is even higher (32 kJ mol^{-1}) relative to **3**. We have elsewhere argued that inclusion of electron correlation does not necessarily improve the quality of energetic estimates.[10] The experimental results agree best with the SCF calculations at 6-31G**.

The third question addresses the relative rate constants for $C_3H_6F^+$ isomerizations. As discussed below, we find experimentally that interconversion of **3** and **4** is more facile than expected from theory. We have described SCF geometry minimizations (using the 3-21G basis set) starting with various rotamers of the primary cation structure **5**. Barrier-free rearrangements to **3** (via methyl shift) or **4** (via fluoride shift) prevail over hydrogen 1,2-shift to **1** (regardless of which conformation of **5** is chosen as the initial geometry).[10] Previously reported semiempirical calculations for **4** → **3** predict a 70 kJ mol^{-1} barrier (as well as surprisingly high barriers for exothermic hydrogen 1,2-shifts in other conformationally mobile, electron-deficient cations).[23] While that theoretical result is consistent with our ab initio calculations on ion **5**, the computational results contradict a recent proposal that, in solution, species **19** (a formal equivalent of **5**) rearranges exclusively to **1**, as eq 13 portrays.[24] The EBFlow results for free ions are consistent with eq 13, but it turns out that there is more than one pathway to **1**.



$$CH_3CHFCH_2Br \xrightarrow{ClF} \underset{\mathbf{19}}{CH_3CHFCH_2\overset{+}{Br}Cl} \xrightarrow{-BrCl} \mathbf{1} \xrightarrow{F^-} CH_3CF_2CH_3 \quad (13)$$

Our EBFlow results for **6** show that the migratory aptitudes of deuterium, methyl, and fluorine are all of comparable magnitude, which is consistent with the chemical intuition that hydrogen shift barriers should be low. To discuss the fluoropropyl phenyl ether results in greater detail, it is worthwhile briefly to review what is known about the decompositions of propyl phenyl ether ions (eq 6, where R = *n*-propyl or isopropyl). It has been known for at least 15 years that neither the radical cation (X = O$^\bullet$) nor the conjugate acids (X = OH or OD) decompose in the gas phase via simple *vic* elimination.[25,26] The sequence of steps represented by eq 6 has been proposed and validated for larger alkyl groups by means of EBFlow studies,[27,28] and this mechanism has been described as a gas-phase analogue of solvolysis.[29] For propyl phenyl ether ions, mass spectrometric studies[17] have confirmed this pathway and rule out (at least for the conjugate acids) a competing mechanism involving reversible elimination–readdition.[30,31] This body of evidence, taken with the present result that ≥90% of the recovered neutrals from $6^{\bullet +}$ involve rearrangement of the fluoropropyl moiety, substantiates our conviction that the EBFlow product yields reflect the interconversion of $C_3H_6F^+$ isomers within ion–neutral complexes.

We have analyzed the proportions of the 1-fluoropropene products from the EBFlow in terms of the $C_3H_6F^+$ rearrangement/deprotonation pathways shown in Scheme I. The ratio of methyl shift to fluoride shift is calculated directly as the ratio of the isotopomers where fluorine is not bonded directly to ^{13}C to those where fluorine is attached to the ^{13}C, $a = 2.1$. The scheme portrays the subsequent product-determining steps for allyl fluoride and 1-fluoropropenes as occurring after the formation of ion–neutral complexes. The scheme illustrates the rearrangements occurring in $C_3H_5DF^+$ ions that behave as though they were free, and it has been analyzed in terms of first-order kinetics. We have previously demonstrated the importance of analyzing MIKE spectra in this fashion for the purpose of distinguishing mechanistic alternatives.[30] In the EBFlow experiment, though, we collect all of the products from precursor ions generated by 70-eV electron impact, so such an analysis in this case must be considered only as an approximation. It is possible that ion decay and rearrangement processes are multiexponential, although branching ratios are not likely to be greatly perturbed even if the disappearance of $6^{\bullet +}$ with time is not a single exponential function.[31]

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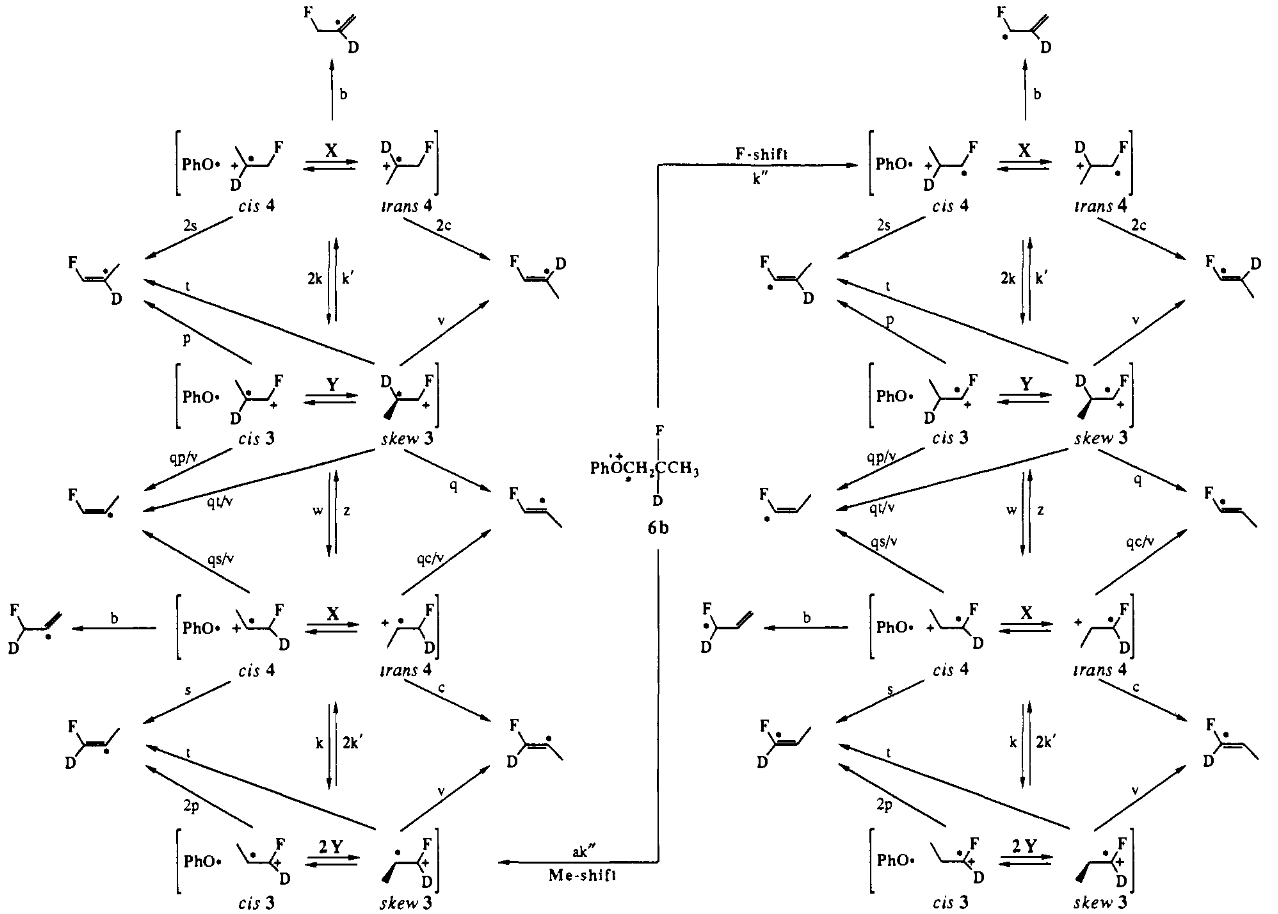
Scheme I. Rearrangements of 1-Fluoropropyl Cations within the Ion–Neutral Complexes Generated from $6^{\bullet+}$ (Only One Set of Epimers Is Shown) with Equilibrium Constants *X* and *Y* and Individual Steps Designated by Rate Constants *k*, *k'*, *k''*, *ak''*, *b*, *c*, *p*, *q*, *s*, *t*, *v*, and *w*[a]



[a] Key: • = ^{13}C.

Table V summarizes the results of a least-squares analysis of the EBFlow product distributions. Relative proportions of products corresponding to this simulation are given in Table IV.

The conformational analysis of **3** and **4** is based on our ab initio calculations. Ion **4** has two conformers, as Figure 1 depicts, both of which are nearly planar. The former leads to (*Z*)-1-fluoropropene, the latter to the *E* isomer. The s-cis conformer is predicted to have a lower electronic energy than the s-trans (at the SCF level as well as at MP2). Ion **3** also has two conformational isomers (just as does its neutral isoelectronic analogue propionaldehyde), an s-cis and a skew conformer. The energies of *cis*-**3** and *skew*-**3** are nearly the same. The s-cis isomer is presumed to yield only (*Z*)-1-fluoropropene, while the skew can give both geometrical isomers.

Scheme I depicts the isomerizations of doubly labeled 1-fluoropropyl cations in ion–neutral complexes with phenoxy radical. The complexity of this scheme is required by the experimental data. It portrays the conformational interconversions of **3** and **4** as taking place on a much more rapid timescale than hydride (or deuteride) shifts. One conformer of **3** yields (*Z*)-1-fluoropropene, while the other yields a mixture of *E* and *Z* isomers, and the equilibrium constant between cis and skew conformers is represented as *X*. Both conformers of **4** yield allyl fluoride. One yields (*Z*)- and the other (*E*)-1-fluoropropene. The equilibrium constant between *cis*- and *trans*-**4** is represented as *Y*. The kinetic analysis of this scheme with 11 experimental product ratios and 11 unknowns does not give a unique solution. We have selected the solution that gives positive values for all rate constants and does not demand unrealistic values for isotope effects.

The experimentally determined values of the relative rate constants (i.e., the branching ratios) in Scheme I show that **4** is deprotonated faster than it rearranges. The equilibrium between the s-cis and s-trans conformers favors the former by approximately a factor of 3. The skew conformer of **3** is favored over the s-cis conformer by roughly a factor of 2, but skew is also more rapidly deprotonated than s-cis. (This equilibrium constant takes into account the fact that the skew conformer is chiral.) The two geometrical isomers from deprotonation of *skew*-**3** are formed in the proportion *Z*:*E* = 53:47. Our analysis of Scheme I, however, does not allow us to calculate the equilibrium constant for interconversion of **3** and **4**, for which the algebraic expression is, taking into account all the conformers, $K_{eq} = k'/k$.

The most interesting relative rate constants are the isotope effects. The k_H/k_D values are close to unity. The primary isotope effect on deprotonation (taken to be the same for **3** and **4**) is $k_H/k_D = 1.3$, which is within experimental error of other primary isotope effects reported for proton transfers within ion–neutral complexes.[12,13,18,19] The isotope effect for isomerization of **4** to **3**, k/z, is calculated to be within experimental uncertainty of unity. The isotope effect for **3** → **4**, however, is significantly larger.

Though we cannot evaluate k'/k, the experimental data do permit us to examine the isotope effect on this equilibrium constant. Consider the β-monodeuterated isomer of **3**, $CH_3CHDCHF^+$, which has two diasteromeric forms of the skew rotamer, one where β-deuterium is gauche to fluorine and the other where β-hydrogen is gauche to fluorine. For racemic ions, equilibration of these plus *cis*-**3** with all the rotamers of monodeuterated **4**, $CH_3CHCHDF^+$, via deuteride shift has equilibrium constant $K_{eq} = w/z$. In both sets of ions, the deuterium is β to the positive charge. Therefore, the deuterium isotope effect on the **3** ⇄ **4** equilibrium, $K_H/K_D = zk'/wk = 1.8/0.7 = 2.5$, implies that deuterium prefers the β-position in **3** over the β-position in **4**. We interpret this isotope effect as a measure of the relative importance of hyperconjugation in 1-fluoropropyl ions. The magnitude of this secondary β-deuterium isotope effect is large, from which we conclude that the positive charge in **4** exerts a much

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greater electron demand than the charge in **3**. In other words, the lone pairs on fluorine mitigate the electron demand in the α-fluoro primary cation relative to the β-fluoro secondary cation. This is consistent with the view that monofluorination at a cationic center provides π-conjugative electron donation that outweighs the σ-withdrawing effect.[9]

Conclusions

The use of isotopic (^{2}H, ^{13}C) double labeling in neutral product studies of gas-phase ion chemistry has here been demonstrated for the first time. Analysis of fluorine-containing products by ^{19}F NMR reveals the position and extent of isotopic label in the reaction mixture, since the breadth of the fluorine chemical shift scale permits resolution of every isotopomeric product. The formal equivalent of $CH_3CDFCH_2^+$ rearranges by deuteride shift, methyl shift, or fluorine shift in the proportions 1.9:1:0.45. In ion–neutral complexes, the ions formed by the latter two shifts (deuterated analogues of **3** and **4**) interconvert, signaling that these ions are of comparable stability (as predicted by SCF calculations at 6-31G**). As free ions, these cations rearrange extensively to the more stable 2-propyl cations on the millisecond timescale. In ion–neutral complexes, however, the lifetimes are so brief that no rearrangement to this global minimum (deuterated **1**, which is also the ion formed by initial deuteride shift) can be detected. From the proportions of recovered neutral products, we can extract approximate values of conformational equilibrium constants, branching ratios, and isotope effects. The scope and range of isotopic double labeling are thus exemplified.

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Supplementary Material Available: Tables of Cartesian coordinates for the 6-31G** optimized geometry of *skew*-**3** and SCF normal modes for **1**, **3**, **4**, and **7** and a figure of the proton NMR of **6a** (2 pages). Ordering information is given on any current masthead page.

Partial Oxidation without Allylic C–H Bond Activation: The Conversion of Propene to Acetone on Rh(111)-p(2×1)-O

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Abstract: Propene is selectively oxidized to acetone by adsorbed atomic oxygen below 290 K on Rh(111)-p(2×1)-O ($\theta_0 = 0.5$) under ultrahigh vacuum conditions. The selectivity for acetone production over combustion is high, although the absolute yield is low, ~0.02 acetone molecules per Rh atom, because a large fraction of the propene desorbs prior to oxygen addition. An oxametallacycle, formed by a direct addition of oxygen to the 2-carbon, is proposed to be the intermediate that results in acetone formation. Isotopic labeling experiments demonstrate that the C–H bond at the 2-position of the carbon chain is selectively broken and transferred to the 1-position during acetone formation. This is supportive evidence for oxygen addition prior to dehydrogenation, since oxygen addition to the 2-carbon would decrease the C–H bond strength at the 2-carbon. Propene oxidation is dramatically different from reactions on Ag. Significantly, the allylic hydrogens of the propene are not activated during the oxidation. Furthermore, the ketone, not the epoxide or aldehyde, is formed on Rh. An important role of the surface oxygen is the inhibition of C–H bond activation. On clean Rh(111), propylidyne is formed. Propylidyne is totally oxidized into CO, CO_2, and H_2O when coadsorbed with oxygen. The inhibition of dehydrogenation allows oxygen addition to compete favorably with dehydrogenation on surfaces with oxygen coverages greater than 0.45 monolayers. For lower oxygen coverages, only combustion products are formed.

Introduction

The selective oxidation of hydrocarbons is an area of immense industrial importance because heterogeneous oxidation processes provide both large-scale petrochemical commodities and precursors for many specialty chemicals.[1] For example, the selective epoxidation of ethylene over silver-based catalysts is a large-scale process,[2] so that extensive efforts to understand the catalytic reaction mechanism have been made.[3]

It is well known that ethylene can be selectively epoxidized with oxygen adsorbed on Ag, whereas propene is mainly converted to carbon dioxide and water.[4] Indeed, under ultrahigh vacuum conditions, propene combusts to carbon dioxide and water on Ag(110).[5] The nonselective oxidation of propene on silver is largely attributed to the high acidity of the allylic protons. Norbornene and styrene, which contain no allylic protons, are oxidized to their respective epoxides by oxygen chemisorbed on Ag(110)[6] and Ag(111),[7] supporting the proposal that gas-phase acidity dictates oxidation selectivity on Ag. Because of the high reactivity of allylic protons on Ag, selective oxidation of propene is difficult.

Herein, we report that propene is selectively oxidized to acetone by oxygen chemisorbed on Rh(111)-p(2×1)-O. Surprisingly, allylic C–H bond activation does not occur in the propene oxidation to acetone. As a result, the product distribution and kinetics for propene oxidation are similar to those previously reported for styrene, which contains no allylic protons. Styrene is oxidized to acetophenone on Rh(111)-p(2×1)-O.[8,9] Indeed, we have widely observed that alkenes are oxidized to their corresponding methyl ketones on Rh(111)-p(2×1)-O.[10]

Furthermore, we have shown that an oxygen coverage of 0.5 is required for partial oxidation. Although the interactions of

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