Competing 1,3- and 1,2-Hydrogen Shifts in Gaseous Fluoropropyl Cations

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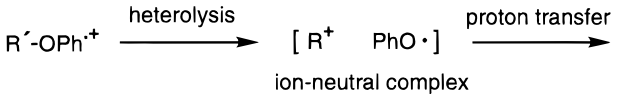
Abstract: An initial 1,2-hydrogen shift versus a 1,3-deuterium shift in emerging $FCD_2CH_2CH_2^+$ ions lead to differing patterns of deuteration in the neutral products that are recovered following reaction with a Brønsted base. Transient dideuterated fluoropropyl ions have been produced in $[C_3H_4D_2F^+$ PhO•] ion−neutral complexes by 70 eV electron impact on $FCD_2CH_2CH_2OPh$ and the resulting fluoropropenes collected in a specially designed electron bombardment flow (EBFlow) reactor. Under these conditions ion−neutral complexes greatly predominate over free fluoropropyl cations. Free ions afford products that are easily distinguished from those that result from ion−neutral complexes, in which the phenoxy radical serves as the Brønsted base. 1,2-Hydrogen shift yields ions containing CH_3-groups, while the ions from 1,3-shift have CDH_2-groups. Allyl fluoride and 1-fluoropropene arise from ion−neutral complexes, and the extent and positions of deuteration have been determined by ^{19}F NMR. Six deuterated variants of *trans*-1-fluoropropene can be resolved in the NMR spectrum of the neutral products collected from the EBFlow. The proportions of CH_3 and CDH_2 measured by integration imply a branching ratio of 1,2-hydrogen versus 1,3-deuterium shift of approximately 94:6.

Unimolecular hydrogen migration from an sp^3 center to a nearby carbon takes place frequently in carbocations[1] but only rarely in free radicals[2] or carbanions.[3] In positive ions 1,2-shifts correspond to an orbital symmetry-allowed thermal sigmatropic rearrangement. 1,3-Hydrogen shifts to sp^2 cationic centers occur in terpene biosyntheses[4] as well as in other reactions of natural products[5] where 1,2-shifts cannot happen. They also compete with 1,2-shifts in sterically constrained cyclohexyl[6] cations and operate to the exclusion of sequential 1,2-shifts in appropriately substituted cycloheptyl systems.[7] A recent upsurge of interest in 1,3-shifts within reactive intermediates[2,3,5,7,8] prompts the question as to how well they compete with 1,2-shifts in acyclic cations. This paper reports a study of neutral products from such transpositions in the gas phase, an unbiased comparison between a 1,3-deuterium shift and a 1,2-hydrogen shift.

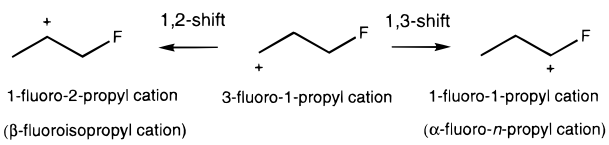
Over the past decade we have been examining monofluorinated cations formed by heterolysis of ionized, gaseous 1-phenoxyfluoroalkanes (R'-$OPh^{\bullet+}$).[9] This bond cleavage forms ion−neutral complexes containing a fluoroalkyl cation (R^+) plus a phenoxy radical, as schematically depicted in eq 1, in preference



(1)

to free R^+. The complex lives on the order of a nanosecond before undergoing proton transfer from the charged to the uncharged partner, yielding neutral alkene and ionized phenol as the observed products. The C−O bond heterolyzes with concomitant rearrangement of the alkyl group ($R' \rightarrow R^+$). The effects of fluorine (e.g., its capacity to stabilize positive charge when directly attached to a primary, positively charged carbon) have thus been revealed to an extent not hitherto observed in condensed phases. In the present case the starting structure, R' = 3-fluoro-1-propyl, would form a primary cation if it did not rearrange.

Equation 2 illustrates the cations (R^+) produced by competing



(2)

hydrogen migrations starting from a nominal 3-fluoro-1-propyl cation, the ion at the center of the equation. That structure corresponds to an unstabilized primary alkyl cation and does not represent a stable geometry. Hydrogen transpositions via 1,2-shifts or 1,3-shifts convert it to species that constitute local minima on the $C_3H_6F^+$ potential energy surface. Ab initio calculations[10] predict that the resulting cations have comparable stabilities. The ion to the left, 1-fluoro-2-propyl cation (or

(1) Shubin, V. G. *Top. Curr. Chem.***1984**, *116/117*, 267−341.

(2) (a) For an upper bound to 1,2- and 1,3-hydrogen shifts in simple alkyl radicals, see: Yamauchi, N.; Miyoshi, A.; Kosaka, K.; Koshi, M.; Matsui, H. *J. Phys. Chem. A* **1999**, *103*, 2723−2733. (b) Plausible 1,2- and 1,3-hydrogen shifts in photoexcited, matrix-isolated hexyl radicals have recently been reported by Takada, T.; Koizumi, H.; Ichikawa, T. *Chem. Phys. Lett.* **1999**, *300*, 233−256.

(3) For one of the rare examples of a unimolecular 1,3-hydrogen shift in gas-phase carbanion chemistry, see: Brauman, J. I.; Sannes, K. A. *J. Am. Chem. Soc.* **1995**, *117*, 10088−10092.

(4) Croteau, R. in *Biosynthesis of Isoprenoid Compounds*; Porter, J. W., Spurgeon, S. L., Eds.; Wiley: New York, 1981; Vol. 1 pp 225−282.

(5) For recent examples, see: (a) Alchanati, I.; Patel, J. A.; Liu, J.; Benedict, C. R.; Stipanovic, R. D.; Bell, A. A.; Yunxing, C.; Magill, C. W. *Phytochemistry* **1998**, *47*, 961−967. (b) Berrier, C.; Jacquesy, J.-C.; Jourannetaud, M.-P.; Lafitte, C.; Vidal, Y.; Zunino, F.; Duflos, A. *Tetrahedron* **1998**, *54*, 13761−13770.

(6) Maskill, H.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1462−1470.

(7) (a) Angle, S. R.; Mattson-Arnaiz, H. L. *J. Am. Chem. Soc.* **1992**, *114*, 9782−9786. (b) Angle, S. R.; Hossain, M. A. *Tetrahedron Lett.* **1994**, *26*, 4519−4522.

(8) (a) Coates, R. M.; Ho, J. Z.; Klobus, M.; Zhu, L. *J. Org. Chem.* **1998**, *63*, 9166−9176. (b) Hudson, C. E.; McAdoo, D. J. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 130−137.

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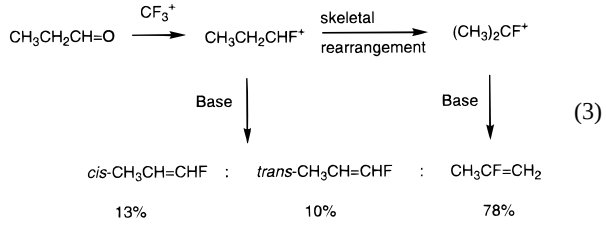
β-fluoroisopropyl cation), corresponds to a classical secondary cation, but the β-fluoro substituent destabilizes its positive charge. The ion to the right, 1-fluoro-1-propyl cation (or α-fluoro-*n*-propyl cation), is isoelectronic with propionaldehyde by virtue of the resonance structure $CH_3CH_2CH{=}F^+$. Here the α-fluoro substituent contributes a net stabilization of the positive charge. Consequently, the α-fluoro-*n*-propyl cation should be somewhat more stable than the β-fluoroisopropyl cation.[11] The α-fluoro-*n*-propyl cation can form from the 3-fluoro-1-propyl cation either by a 1,3-hydrogen shift, as depicted, or via successive 1,2-shifts. We describe experiments that reveal the relative rates of these rearrangements.

Stereochemical studies of diazonium ions in solution confirm[6] that the kinetics of 1,2- and 1,3-shifts within cyclic systems do not represent an unbiased measure of the competition between these pathways. By contrast, flexible acyclic precursors rapidly equilibrate among a range of conformations and provide a fairer test. In the gas phase fluoropropyl cations exhibit the following characteristics: (1) as mentioned above, the 1,3-shift product (α-fluoro-*n*-propyl cation) is calculated to be more stable than the 1,2-shift product (β-fluoroisopropyl cation),[10,11] (2) the two isomeric 1-fluoropropyl cations interconvert within ion−neutral complexes, transposing (but not randomizing) hydrogens between the central carbon and the one attached to fluorine,[12] and (3) free 1-fluoropropyl cations rearrange on the millisecond time scale to 2-fluoropropyl cations, $(CH_3)_2CF^+$, the global minimum on the $C_3H_6F^+$ surface. This last result has been ascertained by preparing 1-fluoropropyl ions from propionaldehyde via fluorine−oxygen metathesis[12] (the ion−molecule reaction depicted as the first step of eq 3) followed by deprotonation in a subsequent



(3)

collision with propionaldehyde.[13] Since a free $C_3H_6F^+$ ion formed as a fragment of 70 eV electron ionization of $PhOCH_2CH_2CH_2F$ (**1**) would be expected to have an internal energy at least as great as that of $CH_3CH_2CHF^+$ from the first step of eq 3, our previously published experimental data provide an unambiguous way to differentiate neutral fluoropropenes produced by free fluoropropyl ions from those formed via the intermediacy of ion−neutral complexes. Free fluoropropyl ions yield 2-fluoropropene as the predominant neutral product, while (as will be presented below) 1-fluoropropyl ions in ion−neutral complexes do not undergo skeletal rearrangement.

The second step of eq 1 affords the products observed from ion−neutral complexes: $C_6H_6O^{\bullet+}$ (seen in the mass spectrometer) and neutral alkenes, which are recovered in a specially constructed Electron Bombardment Flow (EBFlow) reactor. Over the past 30 years a number of research groups have devoted considerable effort to ascertaining which $C_6H_6O^{\bullet+}$ tautomer forms when an ionized phenyl ether expels alkene−phenol radical cation versus an ionized cyclohexadienone.[14] While some conflicting data remain to be resolved, the preponderance of evidence supports the former alternative. In other words, the proton transfers to the oxygen of the phenoxy radical, as depicted in the second step of eq 1.

The identity of the base affects the distribution of alkenes from gas-phase Brønsted acid−base reactions. In bimolecular proton transfers, for instance, the 2-methylbutene isomer ratio from deprotonation of $CH_3CH_2C(CH_3)_2^+$ depends on the proton affinity of the base.[15] That ratio turns out to be the same (within experimental uncertainty) regardless of whether the deprotonation takes place in an ion−neutral complex [$CH_3CH_2C(CH_3)_2^+$ PhO•] or in a bimolecular reaction with a neutral ether that has roughly the same basicity as phenoxy radical.[16] The experimental proton affinity of the phenoxy radical lies in the range 845−860 kJ mol^{-1} (owing to the uncertainty in the heat of formation of the neutral radical $-\Delta_f H°_{298} = 38-55$ kJ mol^{-1}, a range of values that ab initio calculations have not yet served to narrow),[17] comparable to the proton affinity of di-*n*-propyl ether, 846 kJ mol^{-1}.[18] The ion−neutral complex gives a 2-methyl-1-butene:2-methyl-2-butene isomer ratio of 1.3 ± 0.15,[16] while the bimolecular reaction with di-*n*-propyl ether gives a ratio of 1.2.[15] These ratios contrast to the nearly statistical ratio of 2.5 ± 0.5 that results from a bimolecular reaction in which a tertiary amine acts as base.[15]

Experimental Section

3-Fluoro-1-phenoxypropane (**1**) was prepared by reduction of 3-phenoxypropionic acid (Aldrich) with lithium aluminum hydride, followed by conversion of the resulting alcohol to the fluoride by means of diethylaminosulfur trifluoride (DAST): ^{19}F NMR (280 MHz, $CDCl_3$) −222.3 ppm (tt, J = 47.0, 25.2 Hz). The 3,3-dideuterated analogue (**1**-3,3-d_2) was synthesized in a similar fashion using $LiAlD_4$ to prepare the dideuterated alcohol, $C_6H_6OCH_2CH_2CD_2OH$: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.86 (br s, 1H), δ 2.04 (t, 5.9 Hz, 2H), δ 4.12 (t, 5.9 Hz, 2H), δ 6.85−7.0 (m, 3H), δ 7.2−7.4 (2H); GC/MS (70 eV) *m*/*z* (rel intensity, not corrected for ^{13}C natural abundance): 154 ($M^{\bullet+}$, 14), 95 (15), 94 (100), 77 (10), 66 (10), 65 (10), 51 (10), 43 (6), 40 (7). The dideuterated alcohol was converted to **1**-3,3-d_2 by dropwise addition of 0.81 g (5 mmol) of DAST to a −78 °C solution of 0.73 g (4.7 mmol) $C_6H_6OCH_2CH_2CD_2OH$ in CH_2Cl_2 under nitrogen, slow warming to room temperature, recooling to −78 °C, quenching by slow addition of saturated aqueous $NaHCO_3$ at that temperature, and separation and distillation of the organic layer to afford 0.71 g of **1**-3,3-d_2 (bp 45−50 °C, 0.2 Torr; 96% yield): ^{19}F NMR (280 MHz, $CDCl_3$) −222.6 ppm (t of I = 1 quintets, J = 25.2, 7.2 Hz); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (dt, J = 25.2, 5.9 Hz, 2H); δ 4.10 (t, 5.9 Hz, 2H), δ6.8−7.0 (m, 3H), δ 7.2−7.3 (2H); ^{2}H NMR (48 MHz, $CDCl_3$) δ 4.60 (d, J_{DF} = 7.2 Hz); GC/MS (70 eV) *m*/*z* (rel intensity, not corrected for ^{13}C natural abundance) 156 ($M^{\bullet+}$, 24), 96 (4), 95 (54), 94 (100), 77 (21), 66 (18), 65 (21), 63 (10), 51 (21), 43 (12), 41 (14), 40 (10). Within our limits of detection the labeled compounds were completely deuterated at the 3-position, i.e., >99 atom %D at that carbon.

EBFlow experiments[19] and NMR analyses were performed as previously described, with ^{19}F NMR integrations corrected for pulse

(9) (a) McAdoo, D. J.; Morton, T. H. *Acc. Chem. Res.* **1993**, *26*, 295−302 and references therein. (b) Shaler, T. A.; Morton, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9222−9226.

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

(11) Our most recent DFT calculations (B3LYP/6-311G**, including zero-point correction) place the 0 K heat of formation of 1-fluoro-1-propyl cation 15 kJ mol^{-1} below that of 1-fluoro-2-propyl cation.

(12) Shaler, T. A.; Morton, T. H. *J. Am. Chem. Soc.* **1989**, *111*, 6868−6870; **1990**, *112*, 4090.

(13) Eyler, J. R.; Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1974**, *96*, 3673−3675.

(14) (a) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195−3243 and references therein. (b) Weddle, G. H.; Dunbar, R. C.; Song, K.; Morton, T. H. *J. Am. Chem. Soc.* **1995**, *117*, 2573−2580. (c) Taphanel, M. H.; Morizur, J. P.; Leblanc, D.; Borchardt, D.; Morton, T. H. *Anal. Chem.* **1997**, *69*, 4191−4196.

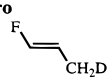
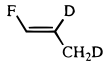
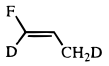
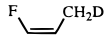
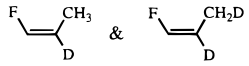
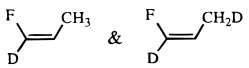
(15) Marinelli, W. J.; Morton, T. H. *J. Am. Chem. Soc.* **1978**, *100*, 3536−3539; **1979**, *101*, 1908.

(16) Morton, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 1596−1602.

(17) Wu, Y.-D.; Lai, D. K. W. *J. Org. Chem.* **1996**, *61*, 7904−7910.

(18) Lias, S. G.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, suppl. 1.

Table 1. Proportions of Rearranged Monofluoropropenes from 70 EV EBFlow Radiolysis of $PhOCH_2CH_2CD_2F$, with Upfield Chemical Shifts ($\Delta\delta > 0$) Relative to Their Undeuterated Isotopomers[a]

	Δδ	Obsd (±5%)	Calcd
***trans*-1-fluoro**			
	-0.04 ppm	0.010	0.0045
	0.41 ppm	0.004	0.0024
	0.45 ppm	0.022	0.025
	0.66 ppm	0.008	0.012
	0.70 ppm	0.19	0.207
	1.06 ppm	0.095	0.095
***cis*-1-fluoro**			
	<0.01 ppm	0.014	0.011
	0.46 ppm	0.044	0.046
	0.64 ppm	0.39	0.42
	1.08 ppm	0.17	0.13
3-fluoro			
CH_2=CHCHDF & CHD=CHCHDF	0.74 ppm	0.01	0.01
CH_2=CDCHDF	1.06 ppm	0.04	0.04

[a] Calculated values reflect relative fractions 0.06 1,3-shift and 0.94 1,2-shift using Scheme 1 with $\gamma = 0.25$ and $\eta = 0.5$.

droop and relaxation time effects.[12] Total ionizing electron currents were on the order of 0.1−0.25 mA for run durations of 45−90 min. The total C_3H_5F recovery from EBFlow radiolysis of **1** was gauged by adding a known amount of hexafluorobenzene as an NMR integration standard to the reaction mixture following one EBFlow radiolysis, from which the fluoroalkene yield was measured as 4 μmol/A-sec. Reported relative yields are averages of duplicate runs.

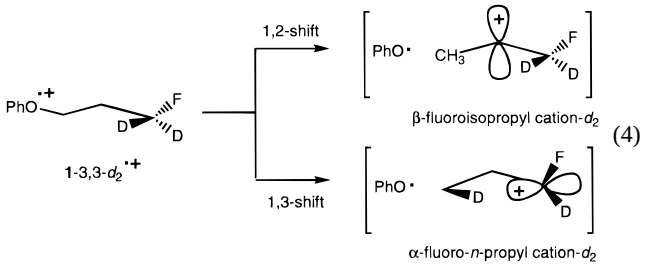
Density functional (DFT) calculations were performed using GAUSSIAN94 on the Cray C90 mainframe at the San Diego Supercomputing center. Normal modes calculations were performed on optimized geometries, and zero-point energy differences are based on unscaled harmonic vibrational frequencies.

Results

Bombardment of 3-fluoro-1-phenoxypropane ($FCH_2CH_2CH_2OPh$, **1**) with 70 eV electrons in a specially constructed electron bombardment flow (EBFlow) reactor[12,19] affords allyl fluoride as the major neutral product (0.7 of recovered C_3H_5F). Allyl fluoride could arise either from ionization or from thermal decomposition of the neutral starting material. The remaining isomers, however, result from rearrangments that only cations might have undergone: *cis*-CH_3CH=CHF, *trans*-CH_3CH=CHF, and CH_3CF=CH_2 in proportions of 0.16, 0.13, and 0.009, respectively. No fluorocyclopropane was detected. The yield of CH_3CF=CH_2 is so low that the 1-fluoropropene yields do not need to be corrected for the contribution from free fluoropropyl cations.

In the mass spectrometer ionized phenol (as produced by eq 1) accounts for more than half of the total ion current from 70 eV electron ionization of 3-fluoropropyl phenyl ether; about 20% of the total ion current comes from further decompositions of ionized phenol; and the molecular ion $\mathbf{1}^{\bullet+}$ represents 7% of the total ion current. Free $C_3H_6F^+$ constitutes only about 3% of the total ion current, a level consistent with the low recovery of CH_3CF=CH_2 in the EBFlow experiment. The intermediacy of [$C_3H_6F^+$ PhO•] ion−neutral complexes accounts for virtually all of the 1-fluoropropenes. While these experiments were performed at just one ionizing voltage, EBFlow studies of *n*-butyl phenyl ether have shown that isomer ratios do not vary as electron energy is decreased to 20 eV (although this does diminish the net yield).[19] Since CH_3CF=CH_2 is recovered only to the extent that one would expect on the basis of the proportion of free fluoropropyl fragment ions, it is clear that the ion−neutral complexes do not live long enough for skeletal rearrangement to take place, a result consistent with the absence of linear → branched rearrangement that we have found in EBFlow studies of *n*-butyl phenyl ether at all ionizing energies.

Assessing the relative contributions of 1,2- and 1,3-shifts requires the deuterium labeling experiment summarized in eq 4. Isotopic label that ends up on the methyl undergoes no further



(4)

transposition. Hydrons on the other carbons can move back and forth. The neutral product distribution was assayed using ^{19}F NMR. We find that EBFlow radiolysis of **1**-3,3-d_2 gave a mixture of C_3H_4DF and $C_3H_3D_2F$, 49± 2% of which was CH_2=$CHCD_2F$ (whose ^{19}F chemical shift is 1.24 ppm upfield from that of CH_2=$CHCH_2F$). That particular labeled allyl fluoride can come from vicinal elimination, some of which might have occurred from the neutral precursor. Our discussion focuses on the fluoropropenes that must have arisen via eq 4. Table 1 summarizes their relative proportions (and chemical shifts). Figure 1 reproduces the 467 MHz spectra of the *cis*- and *trans*-1-fluoropropenes. Isotopically induced chemical shift differences permit the resolution and quantitation of six different *trans* products. The position of the deuterium label was determined on the basis of observed coupling constants compared with those reported for the undeuterated analogue,[20] as well as by the splitting patterns observed under decoupling conditions. Some of the deuterated *cis* products and allyl fluorides (3-fluoropropenes) could not be resolved from one another, and they are grouped together in Table 1. The 1-fluoropropenes from the

(19) Morton, T. H. In *Techniques for the Study of Ion−Molecule Reactions, Techniques of Chemistry XX*; Farrar, J. M., Saunders, W. H., Jr., Eds.; Wiley-Interscience: New York, 1988; pp 119−164.

(20) Beaudet, R. A.; Baldeschwieler, J. D. *J. Chem. Phys.* **1962**, *9*, 30−41.

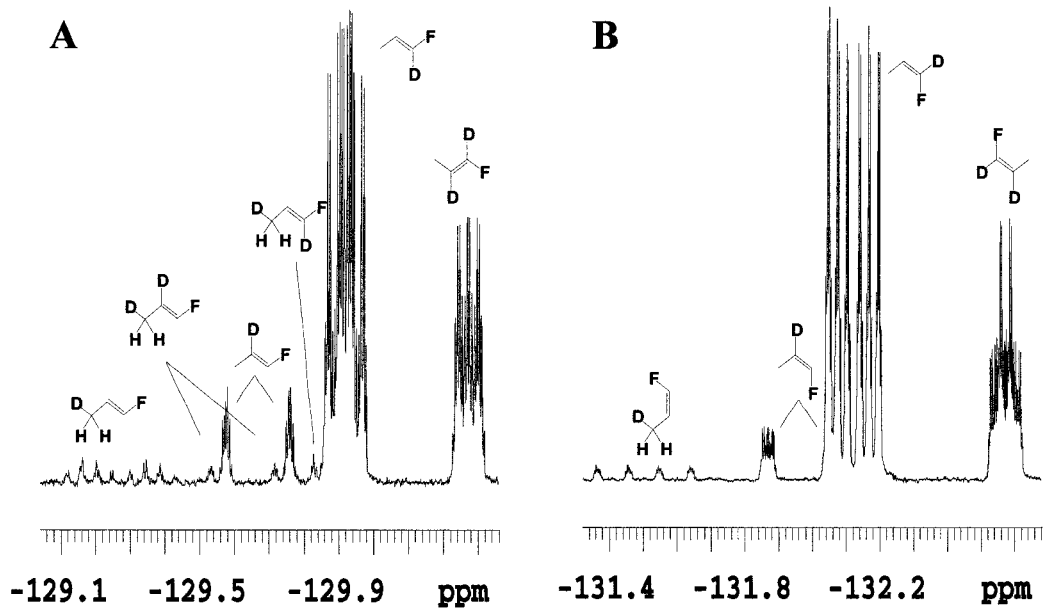


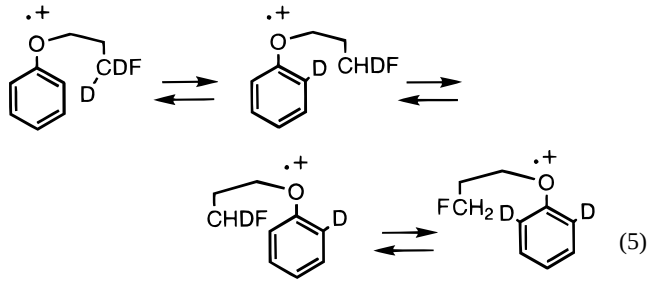
Figure 1. 467 MHz ^{19}F NMR spectrum of an acetone-d_6 solution of the neutral products recovered from 70 eV EBFlow radiolysis of 10^{-4} Torr **1**-3,3-d_2 (0.1 mA for 90 min) showing the deuterated *trans*- (spectrum A) and *cis*- (spectrum B) 1-fluoropropenes.

1,3-shift contain deuterium in their methyl groups. The peaks assigned to $CDH_2CH{=}CHF$ might overlap with those from small amounts of isotopomers with CD_2H-groups, but ^{1}H-decoupling of the *cis* isomer shows a 1:1:1 triplet, indicating that the methyl is predominantly monodeuterated.

The distribution of deuterium in the recovered neutral products agrees with the 2.1:1 $PhOH^{\bullet+}$:$PhOD^{\bullet+}$ ion abundance ratio observed in the 70 eV mass spectrum of **1**-3,3-d_2, provided we suppose that nearly all of the recovered $CH_2{=}CHCD_2F$ comes from molecular ion dissociation. The ratio of CDH_2:CH_3 in *trans*-1-fluoropropenes, 0.07, represents the contribution of 1,3-shift to the formation of those products. The proportion of CDH_2-containing products appears to be slightly higher in the *cis*-1-fluoropropenes (judging from the one isotopomer that can be well resolved), while 1,3-shift products constitute approximately 0.01 of the recovered allyl fluorides.

A substantial body of evidence suggests that 1,3-shifts in simple carbocations take place via the intermediacy of corner-protonated cyclopropanes, which randomize isotopic label via corner-to-corner proton shifts.[21] The distribution of neutral products in the present case argues against complete isotopic scrambling. Suppose, for example, randomization had taken place in the small percentage of ions that undergo a 1,3-shift. Subsequent ring opening to α-fluoro-*n*-propyl cation, **2** (the most stable linear cation) would have yielded a deuterium distribution corresponding to a statistical ratio $CD_2HCH{=}CHF$:$CDH_2CH{=}CHF$:$CH_2DCD{=}CHF$:$CH_2DCH{=}CDF$ equal to 2:2:2:1, which differs substantially from the distribution of those products among the *trans*-1-fluoropropenes.

One additional isotopic variant might arise via chain-ring exchange, as represented in eq 5. This is a minor process that has been observed to take place through distonic ions formed via six-member cyclic transition states.[22] In the present case chain-ring exchange would have to occur via seven-member cyclic transition states. A single exchange, followed by formation of ion−neutral complexes, would lead ultimately to



(5)

monodeuterated and undeuterated fluoropropenes. A double exchange would form undeuterated fluoropropenes. While we do not detect undeuterated *trans*-1-fluoropropene, the chemical shift of undeuterated *cis*-1-fluoropropene is the same as that of its 3-d_1-analogue. The splitting pattern that we observe for the four peaks in this region of the NMR (132.3−132.6 ppm) is more complicated than would be expected for $CH_2DCH{=}CHF$ and may result from the superposition of that signal with the signal from a small amount of the undeuterated analogue.

Portraying the isomerization of the fluoropropyl group as cationic rearrangements of free $C_3H_6F^+$ conveys a partial theoretical picture of 1,2- and 1,3-shifts. DFT calculations show that the primary 3-fluoro-*n*-propyl cation is unstable and enjoys two barrier-free pathways to stable isomers: a 1,2-hydride shift (to β-fluoroisopropyl cation) or closure to a corner-protonated fluorocyclopropane (which has a mirror plane of symmetry, with the C−F bond out of the plane of the ring). Geometry optimizations and normal modes calculations were performed at B3LYP/6-311G**, since this level has been reported to reproduce geometries of simple halogenated cations optimized at much higher computational levels.[23] The calculated 0 K heat of formation of corner-protonated fluorocyclopropane is 44 kJ mol^{-1} higher than that of the β-fluoroisopropyl cation. Subsequent isomerization of the corner-protonated fluorocyclopropane to α-fluoro-*n*-propyl ion is equivalent to a net 1,3-shift (except for the position of the isotopic label), for which the calculated barrier is $\Delta H^{\ddagger} = 20$ kJ mol^{-1} ($\Delta H^{\ddagger} = 22$ kJ mol^{-1} for the

(21) Corma, A.; Boronat. M.; Virula, P. *Appl. Catal. A* **1996**, 207−223 and references therein.

(22) Nguyen, V.; Cheng, X.; Morton, T. H. *J. Am. Chem. Soc.* **1992**, *114*, 7127−7132.

(23) van Alem, K.; Sudhölter, E. J. R.; Zuilhof, H. *J. Phys. Chem. A* **1998**, *102*, 10860−10868.

deuteration pattern corresponding to **1**-3,3-d_2). The observed kinetic preference for the 1,2-shift agrees qualitatively with our calculations, but it would be surprising if the 1,3-deuterium shift could operate to any detectable extent in competition with a barrier-free 1,2-hydride shift. A more accurate calculation would have to take into account the C−O bond heterolysis concurrent with the $R' \rightarrow R^+$ isomerization, which should introduce a barrier to 1,2-shift.

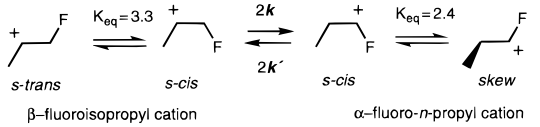
Discussion

EBFlow radiolysis of $PhOCH_2CH_2CH_2F$ (**1**) yields a product distribution that reflects kinetic control. Of the three principal isomers that are recovered—allyl fluoride, *cis*-1-fluoropropene, and *trans*-1-fluoropropene—allyl fluoride is the least stable thermodynamically,[24] yet it is the most abundant. *cis*-1-Fluoropropene is more stable than the *trans*, but the ratio recovered from 70 eV electron ionization of **1** (1.3) is less than the equilibrium ratio at temperatures ≤1000 K.

The results of EBFlow radiolysis of **1** show that eq 1 (where $R' = FCH_2CH_2CH_2$) operates in the gas-phase decomposition of $\mathbf{1}^{\bullet+}$. A vicinal alkene elimination via a four-member cyclic transition state (such as that which dominates the decomposition of ionized *sec*-alkyl phenyl ethers[25]) would have produced allyl fluoride as the only neutral product. While vicinal elimination does take place to some extent, production of 1-fluoropropene implies the intervention of $[C_3H_6F^+\ PhO\bullet]$ ion−neutral complexes. Since the *cis*:*trans* ratio is the same as has been reported from gas-phase deprotonation of free $CH_3CH_2CHF^+$ ions,[12] a pathway involving such ions is called for. As discussed in the Introduction, free ions cannot be contributing substantially to the EBFlow product yield, since the majority of them undergo the skeletal rearrangement depicted in eq 3. Nor could free fluoropropyl ions (which constitute only a small fraction of the total ionization from **1**) account for the comparatively high yield of neutral fluoropropenes. Ion−neutral complexes represent transient intermediates that reconcile the formation of ion−molecule reaction products with unimolecular kinetics of their production.

Isotopic substitution of the starting material at position 3 provides much more information. On one hand, intervention of a distonic intermediate (with subsequent expulsion of a neutral diradical) might conceivably account for the isomer distribution from unlabeled **1**. On the other hand, the deuterium distribution in the neutral products from EBFlow radiolysis of $PhOCH_2CH_2CD_2F$ (**1**-3,3-d_2) cannot be rationalized by any distonic pathway but is efficiently explained in terms of unimolecular cation rearrangements that find precedent in the previously published EBFlow radiolysis of CH_3CDFCH_2OPh.[12]

Within ion−neutral complexes intramolecular 1,2-hydrogen shifts operate reversibly between carbons that can bear a positive charge with comparable stability. In the case of ionized $PhOCH_2CH_2CD_2F$ this leads to deuteration of either or both vinylic carbons in the recovered 1-fluoropropene. We have observed this reversibility in ionized CH_3CDFCH_2OPh, as well. That prior study entered the 1-fluoropropyl cation potential surface via competing irreversible 1,2-methyl and 1,2-fluoride shifts, which form α-fluoro-*n*-propyl and β-fluoroisopropyl cations, respectively, with an initial ratio of approximately 2:1. Ionization of **1** enters the same manifold predominantly via an irreversible 1,2-hydride shift, which forms only the β-fluoroisopropyl cation initially. However, in both cases the isomeric cations interconvert as portrayed by eq 6 (with ***k*** symbolizing the first-order rate constant for shifting one hydrogen from position 1 of the β-fluoroisopropyl cation and ***k′*** the rate constant for shifting one hydrogen from position 2 of α-fluoro-*n*-propyl cation).



(6)

Our kinetic analysis supposes that the conformers of the intermediate cations equilibrate rapidly but that the Brønsted acid−base reactions with the phenoxy radical inside the complex have rate constants with magnitudes comparable to ***k*** and ***k′***. Equation 6 summarizes the conformational equilibrium constants previously extracted from the experimental EBFlow product distribution from CH_3CDFCH_2OPh. Ab initio calculations predict that the β-fluoroisopropyl cation is planar, with stable *s-cis* and *s-trans* conformers, while the α-fluoro-*n*-propyl cation has only one stable planar (*s-cis*) and one nonplanar conformer (*skew*, which is chiral). Deprotonation of the *skew* can yield either *cis*- or *trans*-1-fluoropropene, while each planar conformer can form only one geometric isomer.

Our previously reported steady-state analysis of ^{13}C-labeled CH_3CDFCH_2OPh measured not only the two conformational equilibrium constants shown in eq 6, but also six branching ratios and three kinetic isotope effects. These give the relative rate constants corresponding to the numerical coefficients for the sequence of 1,2-shifts and deprotonation steps summarized in Scheme 1. We find that those relative rate constants cannot explain the product distribution recovered from EBFlow radiolysis of $PhOCH_2CH_2CD_2F$. This is not surprising, since the internal energy of the ion−neutral complex ought to depend on the structure of the precursor. However, if we assume that the Brønsted acid−base reaction rates are the only ones affected by changing the precursor, the relative rates from CH_3CDFCH_2OPh give a reasonable quantitative fit to the distribution of rearranged products recovered from $PhOCH_2CH_2CD_2F$. If we guess that deprotonations to form 1-fluoropropene are slowed by a factor of $\gamma = {}^1/_4$ and that deprotonations to form allyl fluoride are slowed by a factor of $\eta = {}^1/_2$, we calculate the product distribution summarized in the right-hand column of Table 1. According to this calculation, the proportion of $CH_2{=}CHCD_2F$ from interconverting ions should amount to 0.12 of the total fluoropropene yield and that a mixture of $CH_2{=}CDCH_2F$ and $CHD{=}CDCH_2F$ should represent a fraction of 0.0006. The former is recovered in much higher yield than predicted, while the latter isotopomers lie below our detection limit.

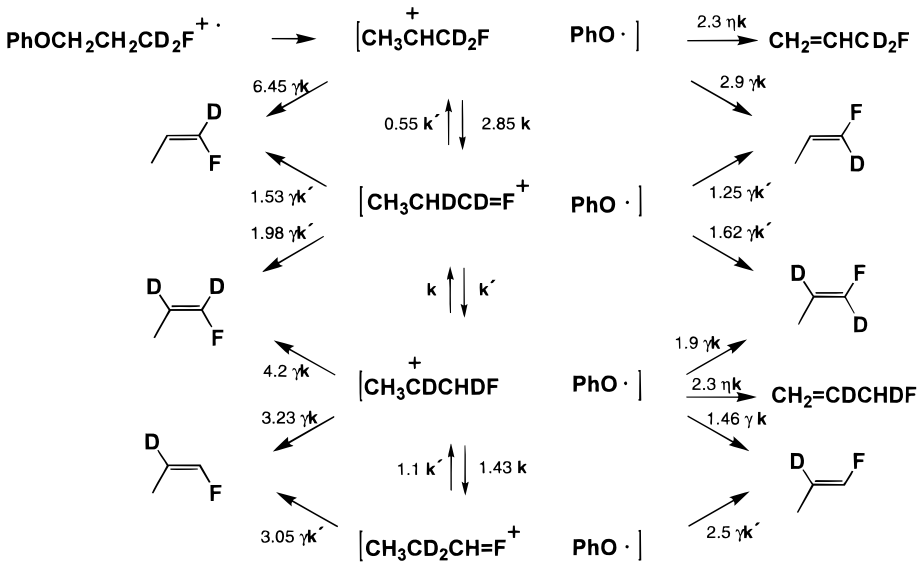
The relative proportions of H- versus D-transfer measured by EBFlow agree with the mass spectrometric intensity ratio (m/z 95 + m/z 67)/(m/z 94 + m/z 66) only if we suppose that all of the recovered $CH_2{=}CHCD_2F$ comes from decomposition of ionized $PhOCH_2CH_2CD_2F$. As a consequence, the mole fraction of ionized $PhOCH_2CH_2CD_2F$ decomposing via vicinal elimination to form $CH_2{=}CHCD_2F$ must be 0.42 ± 0.02 (as compared to a mole fraction of 0.1 for vicinal elimination from ionized CH_3CDFCH_2OPh[12]).

Neither Scheme 1 nor vicinal elimination (nor interconversions of distonic intermediates) can explain the formation of neutral products containing CH_2D-groups. We therefore infer that initial 1,3-deuterium shift competes with 1,2-hydride shift, as represented by eq 4. The 1,3-shift initially forms an α-fluoro-*n*-propyl cation, which is assumed to undergo the same sort of

(24) Dolbier, W. R., Jr; Medinger, K. S.; Greenberg, A.; Liebman, J. F. *Tetrahedron* **1982**, *38*, 2415−2420.

(25) Traeger, J. C.; Luna, A.; Tortajada, J. C.; Morton, T. H. *J. Phys. Chem. A* **1999**, *103*, 2348−2358.

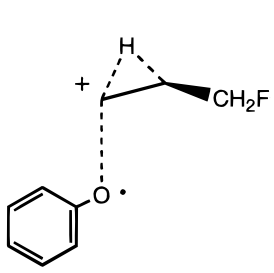
Scheme 1



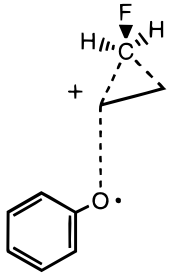
interconversions as drawn in Scheme 1. Relative proportions of 0.94:0.06 1,2-hydride shift:1,3-deuterium shift were used to derive the calculated product abundances in the right-hand column of Table 1, along with the relative rate constants for interconversion and Brønsted acid−base reactions summarized in Scheme 1. The normal isotope effect for the 1,2-hydride shift is $\boldsymbol{k}'_H/\boldsymbol{k}'_D = 1.8$, while the proton-transfer isotope effect is 1.3. If we guess that the isotope effect on 1,3-shift is the mean of those two values, then the ratio of 1,2-hydride shift to 1,3-hydrogen shift in ionized **1** should be 10:1.

We conclude that three decomposition pathways compete in fluoroalkene expulsion from ionized $PhOCH_2CH_2CD_2F$ (mole fractions in parentheses): formation of ion−neutral complexes via a 1,2-hydride shift (0.54), formation of ion−neutral complexes via a 1,3-deuterium shift (0.035), and vicinal elimination (0.42). Since **1** is a mixture of conformational isomers, one may inquire whether these mole fractions somehow reflect a conformational equilibrium in the neutral precursor. While there are some data showing that this might be the case in phenyl *n*-propyl ether,[26] there is no evidence for such an effect in $PhOCH_2CD_2F$, a shorter homologue of **1**-3,3-d_2.[27] With regard to compound **1 t**he answer to this question remains to be sought.

A qualitative picture of the transition state for the 1,2-hydride shift is easily imagined. The C−O bond of ionized **1** stretches until enough positive charge builds up on carbon to permit a sigmatropic rearrangement. The reaction coordinate has the character of a C−O bond heterolysis, in which the electron pairs that end up on the phenoxy oxygen lie in the same plane as the itinerant hydrogen, while the unpaired electron remains in an orbital parallel to the p-orbitals of the benzene ring. Maximum orbital overlap constrains both migration termini and the itinerant hydrogen to lie in the same plane as that of the benzene ring, as depicted by the transition state represented by structure **2**. The transition state for 1,3-shift is less evident. One alternative is that the shift occurs concurrently with fission of the C−O bond of $\mathbf{1}^{\cdot+}$, as suggested by eq 4. The other alternative supposes that the fluoromethyl bridges, forming an ion−neutral complex containing a corner-protonated cyclopropane. This transition



2



3

state is represented by structure **3**. Here all eight carbon atoms should be nearly coplanar with the oxygen. After this barrier is passed, rapid transfer of a proton from the fluorinated corner to one of the unfluorinated corners forms the much more stable α-fluoro-*n*-propyl ion, an exothermic isomerization ($\Delta H = -59$ kJ mol^{-1} by DFT) for which DFT calculations give a 20 kJ mol^{-1} barrier. If competition between the transition states represented by **2** and **3** determines the product ratio, then deuteration does not affect the branching ratio by virtue of the 2 kJ mol^{-1} difference that we compute for the barrier height difference between H- and D-transfer. Deuterium substitution would instead exert a secondary isotope effect on fluoromethyl bridging versus a 1,2-hydride shift. Methyl bridging without isotopic scrambling has been invoked as a minor pathway in expulsion of propene from ionized phenyl *n*-propyl ether.[28] Given the symmetry that we have calculated for corner-protonated fluorocyclopropane, this mechanism stipulates that the two undeuterated carbons of ionized $PhOCH_2CH_2CD_2F$ should become equivalent in the course of forming 1,3-shift products, an experimentally testable hypothesis. These reaction coordinates are the subject of ongoing computational exploration.

Conclusions

The competition between 1,2- and 1,3-shifts of hydrogen in an acyclic gaseous cation is reported here for the first time. While the 1,3-shift initially forms a cation (α-fluoro-*n*-propyl) that is more stable thermodynamically, it is kinetically less favorable than the 1,2-shift to form β-fluoroisopropyl cation

(26) Song, K.; van Eijk, A.; Shaler, T. A.; Morton, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 4455−4460.

(27) Kohler, B. E.; Morton, T. H.; Nguyen, V.; Shaler, T. A. *J. Phys. Chem. A* **1999**, *103*, 2302−2309.

(28) Traeger, J. C.; Morton, T. H. *J. Am. Chem. Soc.* **1996**, *118*, 9661−9668.

(which is less stable by 15 kJ mol^{-1})[11] by approximately a factor of 0.1. The cations produced by either shift interconvert with one another during the lifetime of their ion−neutral complexes with phenoxy radical. However, the complex formed from ionized **1** does not live long enough for skeletal rearrangement to 2-fluoroisopropyl cation (which occurs extensively in free fluoropropyl cations). The recovered neutral products from proton transfer within the complex exhibit the same *cis*:*trans* ratio of 1-fluoropropenes as do the neutral products from deprotonation of free $CH_3CH_2CHF^+$. As exemplified by the experiments described here, gas-phase cationic rearrangements within ion−neutral complexes provide a picture of fast isomerization processes that become obscured on longer observational time scales.

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