Fluorine Shifts in Gaseous Cations. Analogues of Wagner-Meerwein Rearrangements

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Abstract: In the gas phase ionized (CH$_3$)$_2$CFCH$_2$OPh (where the asterisk designates a $^{13}$C-label) decomposes to yield ionized phenol via two competing pathways, both of which pass through intermediate ion-neutral complexes. One pathway involves methyl shift, which produces complexes that contain 2-fluorobutyl cations. The other pathway involves fluorine transposition, which forms complexes containing fluoro-tert-butyl cations. The distribution of $^{13}$C in the recovered neutral fluoroalkenes confirms that fluorine migration has indeed taken place, and SCF computations point toward a bridged, three-member cyclic transition state. Ab initio calculations provide an ordering of C$_4$H$_9$F$^+$ structures, some of which are isoelectronic with C$_4$H$_9$O epoxides and carbonyl compounds, as well as those that have no stable isoelectronic neutral counterparts.

Transposition of fluorine via bridging has so rarely been documented that it has been widely supposed to be impossible. Of the reports that have appeared in the experimental literature,$^1$-$^4$ the majority leave open questions that beg for resolution. In several examples of monofluorinated organic molecules the possibility of rearrangement by vic-elimination/readdition of hydrogen fluoride has not been definitively excluded, as in the latter example, in which isotopically substituted, free gaseous flcoronium ion, and unlabeled carbon atoms, could take place via either a bridged fluoronium ion, 1, or a proton-bound dimer of hydrogen fluoride and acetylene, 2, while the gas-phase heat of formation of 1 has been estimated to be 20-40 kJ mol$^{-1}$ (5-10 kcal mol$^{-1}$) lower than that of 2, relative stability differences of this magnitude do not necessarily provide a reliable guide for preference of one sort of reactive intermediate over another.

Five years ago we described an example of fluorine transposition in which vic-elimination/readdition could be ruled out. The molecular ions of primary alkyl phenyl ethers have been shown to decompose via the intermediacy of ion-neutral complexes that contain alkyl cations electrospectically bound to phenoxo radicals. When the alkyl group is $\beta$-fluoroisobutyl, as drawn in eq 1, the neutral products reveal that rearrangements have taken place in the course of the decomposition. Among the products are fluoroisobutenes. Deuterium labeling, as depicted, rules out the formation of these products by fluorine transposition via vic-elimination/readdition. Had vic-elimination taken place, the positive charge within the complex would have been carried by a methallyl cation. This would have led, in turn, to chemical equivalence between a deuterated and an undeuterated carbon, and readdition ought to have given rise to CH$_3$=C(CD$_3$)CD~F among the neutral products. Since the products portrayed in eq 1 are the only fluorinated C$_4$-neutrals expelled from ionized $\beta$-fluoroisobutyl-d$_6$ phenyl ether, a bridged structure has to intervene in a fluorine transposition. Here we present experimental data to prove that a fluorine transposition does indeed take place.

$$\text{(CD$_3$)$_2$CFCH$_2$OPh}$^{+} \rightarrow [\text{C}_4\text{H}_7\text{D}_6\text{F}^+ \text{PhO}]^{-}\text{phenol}^{+}$$

$$\text{CD}_2=\text{CFCH}_2\text{CD}_3 + \text{CD}_4\text{CF}^- = \text{CHCD}_3 +$$

$$\text{(CD$_3$)$_2$C}=\text{CHF} + \text{CD}_2=\text{C}$(CD$_3$)CH$_2$F (1)$$

In 1991 we reported the neutral products expelled from ionized $\beta$-fluoro-$n$-propyl phenyl ether. In those experiments isotopic ($^2$H, $^13$C) double labeling confirmed the role of fluorine bridging.$^5$ However, facile hydride shift occurs, as well, in the intermediate 1-fluoropropyl cations (7 and 8) within the ion-neutral complexes. The back-and-forth arrows in eq 2 represent this reversible isomerization. In free 1-fluoropropyl ions (both in solution$^9$ and in the gas phase$^3$) further rearrangement to 2-fluorosopropyl cation, 9, takes place. Among possible mechanisms for the overall skeletal rearrangement is methyl shift followed by hydride shift, as eq 2 depicts. The net result is to move fluorine from position

$$\text{F} \rightarrow \text{F}^+ \rightarrow \text{CHF}$$

$$\text{F} \rightarrow \text{F}^+ \rightarrow \text{CHF}$$

(2)
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1 to position 2 by carbon transpositions, without any migration of fluorine. While this skeletal rearrangement does not occur within ion–neutral complexes, it nevertheless raises the question as to whether a similar sequence of steps might occur in the higher homologue in eq 1. Were such a mechanism to operate, it would not be necessary to invoke fluorine transposition to account for the fluoroisobutene products in eq 1.

This paper reports results of a 13C-labeling experiment to test whether fluorine migration necessarily happens in the course of eq 1. The results described below demonstrate that vicinal fluorine shift competes with methyl shift, as originally proposed. The relative migratory aptitudes (statistically corrected) favor methyl over fluorine by roughly a factor of 2.9. Vicinal methyl shifts in carbocations are often called Wagner–Meerwein rearrangements. Therefore, the fluorine shift can be considered as analogous to a Wagner–Meerwein rearrangement.

The experiments reported here make use of the EBFlow (electron bombardment flow) technique for collecting neutral products of ionic reactions in the gas phase, as well as conventional mass spectrometry. The data address another issue, as well: the lability of the 2-fluoro-2-butyl cation, which is homologous to the interconversion shown in eq 2. While we cannot at present answer this question, our experiments do permit us to rule out the further fluorine transpositions summarized in eq 3. It turns out that structures 12 and 13 should be energetically accessible but do not form within complexes. Reynolds has reported that bridged ion 12 ought not to be a stable intermediate, which sets fluorine shift apart from other halogen migrations (where the bridged ions are stable). Describe here the results of ab initio computations that permit estimation of the heats of formation of a variety of CH2F2+ ions, including the hypothetical transition states 12 and 13.

Experimental Section

The EBFlow technique has been described in detail elsewhere.4–6,11 EBFlow radiolysis products were analyzed by 282-MHz 19F NMR on a Nicolet NT300 spectrometer, with corrections for relaxation time as previously outlined.11 [1-13C]-1-Phenoxy-2-fluoro-2-methylpropane was prepared from [2-13C]-2-phenoxyacetic acids by addition of excess methylmagnesium bromide followed by reaction of the resulting tertiary alcohol with (diethylamido)sulfur trifluoride (DAST), as described below for the unlabeled analogue. The neutral products from its 70-eV EBFlow radiolysis exhibited the following 13C-19F coupling constants: 2-fluoro-2-butenes, 16 Hz; isobutylene, 17 Hz. Authentic samples of these compounds were prepared via reaction of 2-butanone, isobutyraldehyde, and methallyl fluoride to PhOCD2CF(CH3)20H was dissolved in 10 mL of methylene chloride and cooled to -78 °C. A slight excess of DAST (1.06 g, 6.6 mmol) was added dropwise via syringe to the magnetically stirred solution. The mixture was allowed to warm to room temperature with stirring over 8 h and then q chased to room temperature. Separation of the aqueous layer, drying the organic layer over MgSO4, and rotary evaporation of the methylene chloride afforded 0.96 g of crude product. Vacuum distillation (33–35 °C at 0.05 Torr) yielded 0.8 g of colorless liquid (80% yield). 1H NMR (300 MHz, CDCl3): δ 1.44 (d, J = 21.1 Hz, 6H), 3.97 (d, J = 18.4 Hz, 2H), 6.9–7.1 (m, 3H), 7.2–7.4 (m, 2H). GC/MS: m/z (relative intensity) 168 (M+, 25), 107 (10), 95 (8), 94 (100), 77 (28), 66 (6), 65 (5), 55 (21), 51 (13), 47 (17), 41 (6), 39 (19). 19F NMR (282 MHz, CDCl3; relative to CFCl3): δ 144.2 ppm (septet of triplets, J = 21.1 and 18.4 Hz). 13C NMR: δ -24.1 (d, JCF = 24.0 Hz), 73.2 (d, JCF = 27.1 Hz), 94.0 (d, JCF = 168.5 Hz), 114.7, 121.2, 129.5, 158.8.

A sample of PhOC6F5CH2OH was prepared by addition of methylv magnesium bromide to PhOC6F5COOH followed by reaction of the resulting alcohol with DAST. The tertiary fluoride contained traces of elimination and rearrangement products, which proved difficult to remove (and which led to prominent m/z 95 and 96 peaks in the methane CI mass spectra). Therefore, the mass spectrometric data reported here were measured using GLC–mass spectrometry. Quadrupole mass spectra were measured using a Hewlett-Packard 5989A–MS.

Computation. Ab initio calculations were performed using the GAUSSIAN 92 program13 on the Cray C90 at the San Diego Supercomputing Center. Except where otherwise specified, ab initio computations will be described first. Scheme 1 outlines the competing Wagner–Meerwein shifts of a β-fluoroisobutyl cation. One of the stable ions, 10, is isolectronic with 2-butane. The other one, 14, is the tertiary ion homologous with 7. Previously, we have reported the electronic energies of both species

Scheme 1

by HF-elimination in a subsequent step. 13C-19F coupling constants in the fluoroalkane authentic samples were measured from their natural abundance 13C NMR spectra.

1-Phenoxy-2-fluoro-2-methylpropane. A 1.0 g (6.0 mmol) sample of PhOC6F5CH2OH was dissolved in 10 mL of methylene chloride and cooled to -78 °C. A slight excess of DAST (1.06 g, 6.6 mmol) was added dropwise via syringe to the magnetically stirred solution. The mixture was allowed to warm to room temperature with stirring over 8 h and then q chased to room temperature. Separation of the aqueous layer, drying the organic layer over MgSO4, and rotary evaporation of the methylene chloride afforded 0.96 g of crude product. Vacuum distillation (33–35 °C at 0.05 Torr) yielded 0.8 g of colorless liquid (80% yield). 1H NMR (300 MHz, CDCl3): δ 1.44 (d, J = 21.1 Hz, 6H), 3.97 (d, J = 18.4 Hz, 2H), 6.9–7.1 (m, 3H), 7.2–7.4 (m, 2H). GC/MS: m/z (relative intensity) 168 (M+, 25), 107 (10), 95 (8), 94 (100), 77 (28), 66 (6), 65 (5), 55 (21), 51 (13), 47 (17), 41 (6), 39 (19). 19F NMR (282 MHz, CDCl3; relative to CFCl3): δ 144.2 ppm (septet of triplets, J = 21.1 and 18.4 Hz). 13C NMR: δ -24.1 (d, JCF = 24.0 Hz), 73.2 (d, JCF = 27.1 Hz), 94.0 (d, JCF = 168.5 Hz), 114.7, 121.2, 129.5, 158.8.

A sample of PhOC6F5CH2OH was prepared by addition of methylv magnesium bromide to PhOC6F5COOH followed by reaction of the resulting alcohol with DAST. The tertiary fluoride contained traces of elimination and rearrangement products, which proved difficult to remove (and which led to prominent m/z 95 and 96 peaks in the methane CI mass spectra). Therefore, the mass spectrometric data reported here were measured using GLC–mass spectrometry. Quadrupole mass spectra were measured using a Hewlett-Packard 5989A–MS.

Computation. Ab initio calculations were performed using the GAUSSIAN 92 program13 on the Cray C90 at the San Diego Supercomputing Center. Except where otherwise specified, ab initio computations were performed using the 6-31G** basis set to obtain SCF-optimized geometries. Normal mode frequencies were computed for all SCF-optimized geometries by means of analytical derivatives. Corrections for basis set superposition error (BSSE) were estimated by means of the counterpoise method.13 Isotropic effects on zero-point energies were computed from the GAUSSIAN 92 Cartesian force constant matrix.

Results

In order to place the experimental results in perspective, ab initio computations will be described first. Scheme 1 outlines the competing Wagner–Meerwein shifts of a β-fluoroisobutyl cation. One of the stable ions, 10, is isolectronic with 2-butane. The other one, 14, is the tertiary ion homologous with 7. Previously, we have reported the electronic energies of both species.

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constrained to have planes of symmetry (by analogy to the most
stable geometries computed for ions 7 and 810). While this
corresponds to a stable conformation of 14, the stable confor-
mations of 10 turn out to be nonplanar (and chiral), as drawn.9
The more stable conformer, 10A, deviates only slightly from planarity,
while the less stable one, 10B, has a structure very similar to that
calculated for 2-butanone, with the CH2—CH3 bond nearly
perpendicular to the plane containing the C—F. Relative to 10A,
10B and 14 are 3 and 24 kJ mol1 higher (including zero-point
energy differences), respectively. The experimental data below
are consistent with the SCF results, but it is not easy to find
stability measurements that would provide benchmarks. At
6-31G* tert-butyl fluoride is lower than isobutyl fluoride by 33
kJ mol1 (including a 4 kJ mol1 zero-point energy correction),
but there are no experimental values available to calibrate this
(since the largest monofluoroalkanes whose heats of formation
are reported are the two C2H3F isomers18).1

Other computational work on halogen-containing cations has
presumed that relative energies of isomers may be gauged simply
by comparing their relative electronic and zero-point energies,10,16
but (as we have pointed out12) this can lead to large inaccuracies
when comparing structures in which fluorine has two ligands
with those in which fluorine has but one. Therefore, we have
used the isodesmic reactions in eqs 5-7 to estimate heats of

\[
\begin{align*}
(\text{CH}_3\text{CH}_2\text{CF})^+ & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{O} + \text{CH}_3
\rightarrow -10 \text{ kJ mol}^{-1} & \text{eq 5} \\
(\text{CH}_3\text{CH}_2\text{CF})^+ & \rightarrow \text{CH}_3\text{CH}_2\text{CFCH}_3
\rightarrow -21 \text{ kJ mol}^{-1} & \text{eq 6} \\
(\text{CH}_3\text{CH}_2\text{CF})^+ & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{F} + \text{CH}_3
\rightarrow -42 \text{ kJ mol}^{-1} & \text{eq 7}
\end{align*}
\]

formation for 10, 12, and 14 using experimental heats of
formation17-18 and SCF estimates of \(\Delta H \) (electronic energy change
corrected for zero-point energies). The difference in heats of
formation between 10 and 14 gauged in this fashion (including
the zero-point energy, which is 3 kJ mol1 greater for 10 than for
14) is within experimental error of the SCF electronic energy
difference between these two isomers.

This result justifies estimating the heat of formation of 11 on
the basis of its energy relative to 10.9 Ion 11 has a calculated
zero-point energy within 1 kJ mol1 of that calculated for 14, and
from the electronic energy difference between them,10,16 we estimate
\(\Delta H^\circ(11) = 595 \text{ kJ mol}^{-1} \) at room temperature. Since both 10
and 11 are stable, classical species,10 one effect of fluorine
substitution must be to destabilize nonclassical structures by
comparison. The sec-butyl cation, for example, enjoys either a
corner-protonated cyclopentane or a hydride-bridged species as
its only stable, calculated geometries.21 The effect of substituting
fluorine on one of the center atoms is to render bridging by carbon
or hydrogen less favorable.

Fluorine substitution can stabilize primary cations, too. The
\(\alpha\)-fluoroisobutyl cation, (CH3)2CHCF3 (15), is also calculated
as a stable species, 83 kJ mol1 above 10 (including zero-point
correction). With such a large difference between 14 and 15, it
seems unlikely that these two isomeric ions rapidly interconvert
via hydride shifts within ion-neutral complexes.

Unlike the case of 10 versus 14, the isodesmic method estimates
12 to be more stable than would be predicted on the basis of the
electronic energy difference. The SCF-optimized geometry of
the epifluoronium ion 12 exhibits one negative force constant,
but its zero-point energy is still about 0.5 kJ mol1 higher than
that of 10A. Therefore, vibrational effects cannot account for
the discrepancy between the isodesmic estimate and the electronic
energy difference.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CF}^+ & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{O} + \text{CH}_3
\rightarrow -10 \text{ kJ mol}^{-1} & \text{eq 5} \\
\text{CH}_3\text{CH}_2\text{CF}^+ & \rightarrow \text{CH}_3\text{CH}_2\text{CFCH}_3
\rightarrow -21 \text{ kJ mol}^{-1} & \text{eq 6} \\
\text{CH}_3\text{CH}_2\text{CF}^+ & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{F} + \text{CH}_3
\rightarrow -42 \text{ kJ mol}^{-1} & \text{eq 7}
\end{align*}
\]

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(18) (a) Donalaski, E. S.; Hearing, E. D. J. Phys. Chem. Ref. Data 1993,
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affinity scale is based on the following: Ikuta, S. J. Chem. Phys. 1989, 91,
1376-1377. The uncertainty in \(\Delta H^\circ \) (CH3F) is taken from the following:

Similarly, we cannot gauge the stability of the proton-bound
dimer of 2-butyne with hydrogen fluoride, 13, by its electronic
energy relative to an isomeric structure. Rather than use an
isodesmic reaction, we compute \(\Delta H \) for its dissociation to
protonated 2-butyne, eq 8. This involves calculating not only the
zero-point energy difference but also the basis set superposition
error (BSSE). Species 13 exhibits one negative force constant,
while diagonalization of the Hessian for the bridged structure
for protonated 2-butyne, 16, gives all positive force constants.
Because this latter result was not anticipated, geometry optimizations
were performed at a higher level (MP2/6-311G**). Even if the
starting geometry for protonated 2-butyne is chosen to have a
classical structure (one sp2 and one sp center), the optimized
structure turns out to be bridged, with Csp symmetry. The
electronic energy change (including BSSE) for eq 8 at MP2/
6-311G** is 5 kJ mol1 greater than the SCF-calculated value
at 6-31G**. For purposes of comparison, the hydrogen bond of
13 is only 11 kJ mol1 weaker than that of 1 at the MP2/6-
311G** level (1 exhibits no negative force constants when its
geometry is optimized subject to a C symmetry constraint).

EBFlow Experiments

We have previously demonstrated the use of 13C-labeling in
neutral product studies using the EBFlow method.5 Just as in
a conventional mass spectrometer, a molecule is ionized by a beam

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between the 70-eV mass spectrum and the EBFLOW results for the 1-fluoroisobutenes in which W-label was to be found in position 2. If the labeled carbon in 2-fluoro-1-butene were in position 2, then we would have expected to collect linear 2-fluorobutenes in which 13C-label was to be found in position 2. If the labeled carbon in 2-fluoro-1-butene were in position 1, the 13C-labeled precursor, which is summarized in Table 1, the product distribution from unlabeled precursor should be 1.20 relative to its 70-eV electron impact source mass spectrum of PhOCD2F(CH3)2 gives a PhOH++/PhOD+ ratio in the range 1.4-1.5 for the deprotonation of 2-fluoro-2-butyl and of fluoro-tert-butyl cations within ion-neutral complexes. The mass spectrometric results have required that some assumptions be made regarding isotope effects (vide infra).

The intervention of ion-neutral complexes offers an economical explanation for the isomer distribution of the C4H7F products from 17. The fluoroisobutenes arise from the sequence CH3CHFCH2CH3 → CH3CHFCH2CH3

(CH3)2CF → CH3CHFCH2CH3

10-13C 10-13C

11-13C 11-13C

of 70-eV electrons. Collection of the neutral fragments followed by NMR permits an assessment of the competing pathways by which ions expel alkenes. In the case of ionized primary alkyl phenyl ethers the neutral products exhibit rearranged structures, as could not plausibly have arisen via radical or other uncharged intermediates. In the present case, the C4H7F products recovered from the 13C-labeled precursor 17 all reflect transpositions characteristic of positive ions.

Isotopic labeling of the carbon at position 1 of 2-fluorobutenyl phenyl ether permits a further analysis of the cationic decomposition pathways beyond the deuterium labeling experiments we have previously reported. In those studies, comparison between the 70-eV mass spectrum and the EBFLOW results for PhOCH2CF(CD3)2 confirmed that the recovered neutral fluoroisobutenes do indeed come from the molecular ion decomposition. In the present case, correlation of the EBFLOW with mass spectrometric results has required that some assumptions be made regarding isotope effects (vide infra).

The intervention of ion-neutral complexes offers an economical explanation for the isomer distribution of the C4H7F products from 17. Had the fluoroisobutenes arisen from the sequence 10 → 11 → 14 by means of methyl shift within the complex, the fluorine would have remained attached to an unlabeled carbon. But in the 19F NMR spectrum we observe 13C-19F coupling constants that are >100 Hz, showing that fluorine shift to the labeled carbon has taken place. Examination of the 13C NMR spectra of authentic samples of 1-fluoroisobuten and of methylallyl fluoride confirms that these are one-bond coupling constants and that the two-bond coupling constants are much smaller.

Having demonstrated that 14 is formed within the ion-neutral complex by a fluorine shift, we now ask whether 10 undergoes fluorine transposition during its brief lifetime, as exemplified by Scheme 2. If this were so, then we would have expected to collect linear 2-fluorobutenes in which 13C-label was to be found in position 2. If the labeled carbon in 2-fluoro-1-butene were in that position, the 13C-19F coupling constant would have been much larger than we observe (<3 Hz). The small magnitude of the observed coupling rules out 13C-label in either position 2 or position 1. In the same manner the observed coupling constant in the recovered 2-fluoro-2-butenes (20 Hz) rules out labeled carbon in positions 1, 2, or 4. As Table 1 summarizes, the 13C was detected in only a single position of each of the recovered products. Thus, fluorine transposition does not take place within 10, neither via 12 nor 13.

For the deuterium-labeled precursor in eq 1 the relative yields are (average of four independent runs; standard error values in parentheses) 3(E)-4(2)-5:6 = 0.36(0.01):0.18(0.01):0.28(0.02):0.11(0.03):0.08(0.01). From the distribution of these neutral products we would predict a PhOH++/PhOD+ ratio in the corresponding 70-eV source mass spectrum of [(4) + [5]] / [(3) + [6]] = 1.36(0.20), as compared to the reported ratio of 1.32 (after correction for 13C natural abundance). The corresponding proportions for an unlabeled precursor are (average of three independent runs) 2-fluoro-1-butene:(E)-2-fluoro-2-butene:(Z)-2-fluoro-2-butene:fluoroisobutene:methyl allyl fluoride = 0.41(0.01):0.14(0.01):0.23(0.01):0.11(0.02):0.12(0.02). These are virtually the same as the distribution of isomers for the 13C-labeled precursor, which is summarized in Table 1. The differences between the product distribution in eq 1 and those for undeuterated precursors can be ascribed to three isotope effects. One is the primary isotope effect on the acid-base reaction between the fluoroalkyl cation and the phenoxyl radical within the ion-neutral complex (proton transfer versus D+ transfer). From the neutral product distributions we calculate values for the primary isotope effect in the range 1.4-1.5 for the deprotonation of 2-fluoro-2-butyl and of fluoro-tert-butyl cations within ion-neutral complexes. The remaining isotope effects tend to enhance the migratory aptitude of CD3 relative to CH3: an a-secondary isotope effect that affects CD3 transfer relative to CH3 transfer and a a-secondary isotope effect that stabilizes 14 relative to its deuterated analogue.

Mass Spectrometric Results

There is no way to check our yields of neutral products by directly comparing the isomer distribution from the EBFLOW of undeuterated precursors with the mass spectrum. In lieu of a direct comparison we have examined the mass spectrometry of PhOCD2F(CH3)2, assuming that the secondary isotope effects are the same for methyl shift and for fluorine shift and that the same primary kH/kD operates, as we have inferred from the neutral product studies in eq 1. The 70-eV electron impact source mass spectrum of PhOCD2F(CH3)2 gives m/z 94 and 95 as the two most intense peaks, corresponding (after correction for 13C natural abundance) to a PhOH++/PhOD+ ratio of 1.6. The PhOH++/PhOD+ ratio that we would predict on the basis of the neutral product distribution from undeuterated precursors should be 1.55 (standard error = 0.05).

Chemical ionization (CI) of 2-fluoroisobutyl phenyl ether has also been investigated. Whereas we had previously suggested9 that ion-neutral complexes of the form [C4H7F+ PhOH] might form in high yield from gas-phase protonation, a more careful examination shows that this is not so. When GC-MS is run with

Table 1. Proportions of C4H7F Products from 70 eV after Correction for Differences in T1 Relaxation Times

<table>
<thead>
<tr>
<th>product</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3CH2F=CH2</td>
<td>a</td>
<td>a</td>
<td>0.38</td>
<td>a</td>
</tr>
<tr>
<td>(E)-CH2F=CH2CCH3</td>
<td>a</td>
<td>a</td>
<td>0.14</td>
<td>a</td>
</tr>
<tr>
<td>(Z)-CH2F=CH2CCH3</td>
<td>a</td>
<td>a</td>
<td>0.22</td>
<td>a</td>
</tr>
<tr>
<td>(CH3)2CF=CHF</td>
<td>0.10</td>
<td>a</td>
<td>a</td>
<td>0.27</td>
</tr>
<tr>
<td>H3C=C(CH3)2CF3</td>
<td>a</td>
<td>a</td>
<td>0.17</td>
<td>a</td>
</tr>
</tbody>
</table>

* None detected.
CH₃ as the CI reagent, the most prominent peak results from HF loss from the protonated parent ion, and very little C₂H₅O⁺ ion (protonated phenol) is detected. Thus, the conjugate acid of β-fluoroisobutyl phenyl ether does not behave like protonated neopentyl phenyl ether, which yields ion in copious quantities. The m/z 95:m/z 94 ratio from 70-eV electron impact on (CH₃)₂CCD₂OPh is the same, within experimental error, as the m/z 96:m/z 95 ratio from methane CI on that same neutral precursor. The combined intensities of C₂H₅O⁺ and C₂H₅DO⁺ from methane CI on (CH₃)₂CFCDOPh are less than 2% of the base peak intensity.

Discussion

Reactions that pass through ion–neutral complexes in the gas phase provide access to cations that often cannot be examined by any other method. Instances where complexes result from bond heterolysis have been described as gas-phase analogues of solvolysis.¹² We have previously proposed that hydride shifts occur in a fashion concerted with such heterolyses,¹⁴ by analogy to traditional ideas regarding anchimeric assistance in solution. Other EBFlow studies have shown that 1,2-fluorine shifts occur in competition with 1,2-hydride shifts. In the case of FCH₂CH₃OPh, the epifluoronium ion 1 has been calculated to be a stable species,¹⁰ and EBFlow experiments confirm its stability within the short lifetime of [C₂H₅F⁺ PhO⁻] complexes. The heterolytic shifts that yield complexes containing the three-membered ring are independent of those that proceed via hydrogen shift, which yields [CH₃CHF⁺ PhO⁻] complexes. While this is strongly suggestive that the fluoride transposition in free C₂H₅F⁺ also occurs via 1,² that mechanism remains to be proved for the isolated ion.

In higher homologues fluorine shift takes place in competition with methyl shift. Three-way competition in CH₃CHFCH₂OPh⁺ has been measured: 1,2-hydride shift is more rapid than methyl shift, which is in turn about twice as likely as fluorine transposition. In that case the methylated three-membered cyclic fluoronium ion (methyl fluoriranium) is predicted to be a transition state rather than a stable species.¹⁴ Finally, in the present example, there is only a methyl shift in competition with fluorine shift. Here, too, methyl shift (when statistically corrected) is about twice as likely as fluorine migration. Thus, we have demonstrated 1,2-fluorine transposition from primary, secondary, and tertiary centers.

Equation 10 represents the transition state for the shift that creates 14 in a complex with phenoxy radical. Like every other epifluoronium ion except for 1, the three-membered ring in this transition state (gem-dimethylfluoriranium, 18) is unstable. As a free ion its zero-point energy (discounting the one negative force constant) is within 0.1 kJ mol⁻¹ of that of 12, and its SCF electronic energy is only 2 kJ mol⁻¹ higher than that of 12.

A secondary deuterium isotope effect leads to a greater proportion of CD₃ transfer in eq 1 than CH₃ transfer in undeuterated analogues. This can be attributed to the diminished role of eq 10 when the methyls are deuterated. We have examined a simplified computational model for this isotope effect by comparing the zero-point energy of the free ion, gem-dimethylfluoriranium (18), to that of tert-butyl fluoride (which is taken to stand for the reactant). The calculated zero-point energy difference is 0.4 kJ mol⁻¹ greater when the transition state has two CD₃ groups (as compared to tert-butyl-d₄ fluoride) than for the undeuterated case. This value of ΔZPE is of the appropriate magnitude to account for the experimental secondary isotope effect on the ratio of methyl to fluorine shift, kCD₃/kCH₃ = 0.82. The same computation for deuteriation of the methylene group predicts a ΔZPE of 1.2 kJ mol⁻¹. While this is much larger than for the effect of methyl deuteration, it is not observable in our experiments, since this kinetic isotope effect should decelerate methyl shift and fluorine shift to the same extent.

Finally we ask why further rearrangement of the fluorinated cations—e.g. degenerate rearrangement of 10 via 12 or 13 (eq 4), as portrayed in Scheme 2—does not take place within complexes. Since transition state 12 is calculated to be slightly more stable than gem-dimethylfluoriranium (18), we presume that there is enough energy within the complex to access 12. The transition state for transposition via elimination/readdition, 13, is calculated to be even more stable than 12.

The answer must be that formation of the ion–neutral complex is rate-limiting and that eq 4 cannot compete with proton transfer from the fluoroalkyl cation to the phenoxy radical. On the one hand, hydrogen transpositions do occur rapidly in the alkyl cations within ion–neutral complexes,⁵⁷,²³ though this may somehow be catalyzed by the neutral partner. On the other hand, the transition state in eq 10 has the phenoxy radical in a specific and stabilizing kind of geometry for 12 may be statistically improbable. These hypotheses can be tested experimentally. Future investigations of free cations (compared with those in complexes) will shed further light on the potential energy surfaces of positive ions that contain fluorine.

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References
