# Fluorine Shifts in Gaseous Cations. Analogues of Wagner–Meerwein Rearrangements

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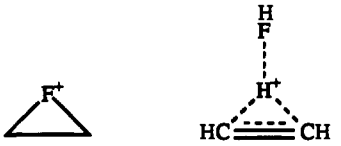
**Abstract:** In the gas phase ionized $(CH_3)_2C^*FCH_2OPh$ (where the asterisk designates a $^{13}C$-label) decomposes to yield ionized phenol *via* two competing pathways, both of which pass through intermediate ion–neutral complexes. One pathway involves methyl shift, which produces complexes that 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 $C_4H_8F^+$ structures, some of which are isoelectronic with $C_4H_8O$ epoxy 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[1-8] 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 1,5-migration reported by Peterson and Bopp in 1967[1] or the 1,2-shift demonstrated by Ciommer and Schwarz in 1983.[2] The latter example, in which isotopically substituted, free gaseous fluoroethyl cations exhibit fluorine transposition between labeled 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.

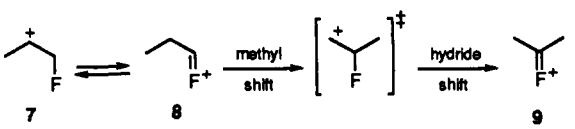


**1** **2**

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 electrostatically bound to phenoxy radicals. When the alkyl group is β-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 $CH_2{=}C(CD_3)CD_2F$ among the neutral products. Since the products portrayed in eq 1 are the only fluorinated $C_4$-neutrals expelled from ionized β-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.

$$(CD_3)_2CFCH_2OPh^{\bullet+} \rightarrow [C_4H_2D_6F^+\ PhO^\bullet] \xrightarrow{-\text{phenol}^{\bullet+}} CD_2{=}\underset{3}{CFCH_2CD_3} + CD_3\underset{4}{CF{=}CHCD_3} + \underset{5}{(CD_3)_2C{=}CHF} + \underset{6}{CD_2{=}C(CD_3)CH_2F} \quad (1)$$

In 1991 we reported the neutral products expelled from ionized β-fluoro-*n*-propyl phenyl ether. In those experiments isotopic ($^2H$, $^{13}C$) 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[3] and in the gas phase[5]) further rearrangement to 2-fluoroisopropyl 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




**7** **8** **9** (2)

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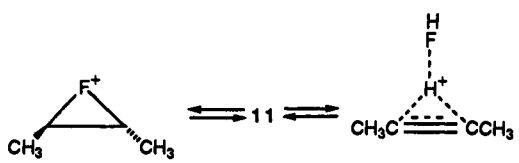
1 to position 2 by carbon transpositions, without any migration of fluorine. While this skeletal rearrangement does not occur within ion–neutral complexes,[5] it nevertheless raises the question as to whether a similar sequence of steps might occur in the higher homologue in eq 1. Were such a mechanism 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 $^{13}C$-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.

**10** **11** (3)

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, **10**. This is formed in ion–neutral complexes *via* eq 1 from a methyl shift that is analogous to the pinacol–pinacolone rearrangement. Does this ion interconvert with its isomer **11**, as eq 3 portrays? Such a rearrangement 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 4. It turns out that structures **12** and **13** should be energetically



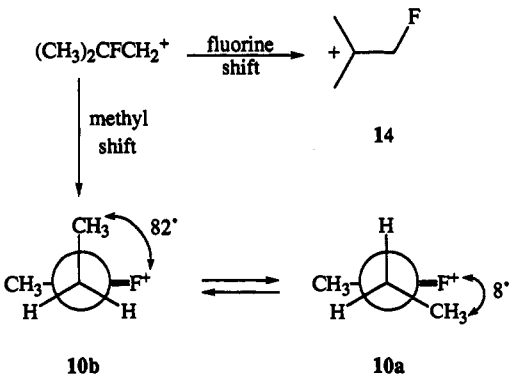
**12** **13** (4)

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).[10] We describe here the results of *ab initio* computations that permit estimation of the heats of formation of a variety of $C_4H_8F^+$ ions, including the hypothetical transition states **12** and **13**.

## Experimental Section

The EBFlow technique has been described in detail elsewhere.[4-6,9,11] EBFlow radiolysis products were analyzed by 282-MHz $^{19}F$ NMR on a Nicolet NT300 spectrometer, with corrections for relaxation time as previously outlined.[5] [1-$^{13}C$]-1-Phenoxy-2-fluoro-2-methylpropane was prepared from [2-$^{13}C$]-2-phenoxyacetic acid[5] 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 $^{13}C$–$^{19}F$ coupling constants: 2-fluoro-1-butene, <3 Hz; the 2-fluoro-2-butenes, 16 Hz; 1-fluoroisobutene, 247 Hz; methallyl fluoride, 167 Hz. Authentic samples of these compounds were prepared *via* reaction of 2-butanone, isobutyraldehyde, and methallyl alcohol with DAST. For the carbonyl-containing precursors the resulting *gem*-difluoroalkanes were converted to the corresponding vinyl fluorides by HF-elimination in a subsequent step. $^{13}C$–$^{19}F$ coupling constants in the fluoroalkene authentic samples were measured from their natural abundance $^{13}C$ NMR spectra.

**Scheme 1**



**14**

**10b** **10a**

**1-Phenoxy-2-fluoro-2-methylpropane.** A 1.0 g (6.0 mmol) sample of $PhOCH_2C(CH_3)_2OH$ 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 quenched by recooling to −78 °C, adding 6 mL of saturated aqueous sodium bicarbonate, and again slowly warming to room temperature. Separation of the aqueous layer, drying the organic layer over $MgSO_4$, 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, $CDCl_3$): 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 ($M^{\bullet+}$, 25), 107 (10), 95 (8), 94 (100), 77 (28), 66 (6), 65 (8), 55 (21), 51 (13), 47 (17), 41 (6), 39 (19). $^{19}F$ NMR (282 MHz, $CDCl_3$; relative to $CFCl_3$): −144.2 ppm (septet of triplets, $J$ = 21.1 and 18.4 Hz). $^{13}C$ NMR: δ 24.1 (d, $^2J_{CF}$ = 24.0 Hz), 73.2 (d, $^2J_{CF}$ = 27.1 Hz), 94.0 (d, $^2J_{CF}$ = 168.5 Hz), 114.7, 121.2, 129.5, 158.8.

A sample of $PhOCD_2CF(CH_3)_2$ was prepared by addition of methylmagnesium bromide to $PhOCD_2COOH$ 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 GC–MS.

**Computation.** *Ab initio* calculations were performed using the GAUSSIAN 92 program[12] 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] Isotopic effects on zero-point energies were computed from the GAUSSIAN 92 Cartesian force constant matrix.[14]

## 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 isoelectronic with 2-butanone. 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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(12) *Gaussian92*, Revision E.2, Frisch, M. J., Trucks, G. W., Head-Gordon, M., Gill, P. M. W., Wong, M. W., Foresman, J. B., Johnson, B. G., Schlegel, H. B., Robb, M. A., Replogle, E. S., Gomperts, R., Andres, J. L., Raghavachari, K., Binkley, J. S., Gonzalez, C., Martin, R. L., Fox, D. J., Defrees, D. J., Baker, J., Stewart, J. J. P., Pople, J. A., Eds.; Gaussian, Inc., Pittsburgh, PA, 1992.
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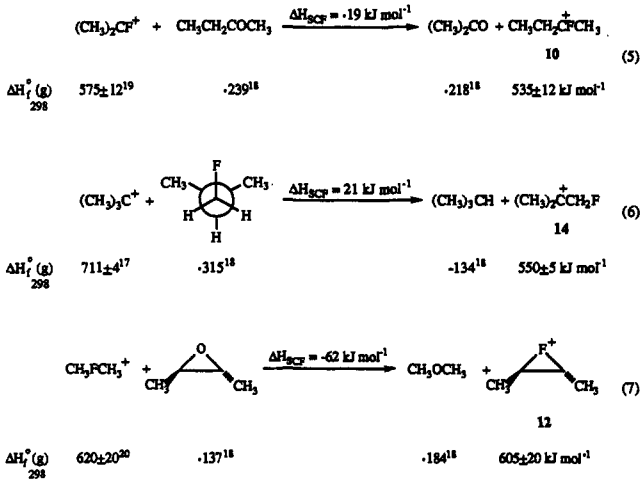
constrained to have planes of symmetry (by analogy to the most stable geometries computed for ions **7** and **8**[15]). While this corresponds to a stable conformation of **14**, the stable conformations of **10** turn out to be nonplanar (and chiral), as drawn.[9] The more stable conformer, **10a**, deviates only slightly from planarity, while the less stable one, **10b**, has a structure very similar to that calculated for 2-butanone, with the $CH_2$—$CH_3$ bond nearly perpendicular to the plane containing the C—F. Relative to **10a**, **10b** and **14** are 3 and 24 kJ mol$^{-1}$ 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 mol$^{-1}$ (including a 4 kJ mol$^{-1}$ 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 $C_3H_7F$ isomers[18]).

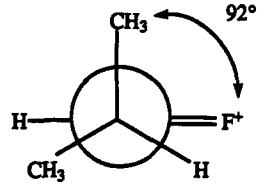
Other computational work on halogen-containing cations has presumed that relative energies of isomers may be gauged simply by comparing their relative electronic and zero-point energies,[10,16] but (as we have pointed out[15]) this can lead to large inaccuracies when comparing structures in which fluorine 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




formation for **10**, **12**, and **14** using experimental heats of formation[17–20] 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 mol$^{-1}$ greater for **10** than for **14**) is within experimental error of the SCF electronic energy difference between these two isomers.

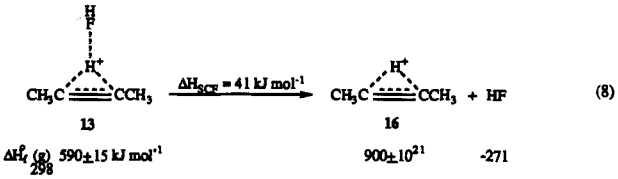
This result justifies estimating the heat of formation of **11** on the basis of its energy relative to **10**.[9] Ion **11** has a calculated zero-point energy within 1 kJ mol$^{-1}$ of that calculated for **14**, and from the electronic energy difference between them[4,10] we estimate $\Delta H_f°$(**11**) = 595 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 cyclopropane 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, $(CH_3)_2CHCHF^+$ (**15**), is also calculated as a stable species, 83 kJ mol$^{-1}$ above **10a** (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.




**15**

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 mol$^{-1}$ higher than that of **10a**. Therefore, vibrational effects cannot account for the discrepancy between the isodesmic estimate and the electronic energy difference.




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 $sp^2$ and one sp center), the optimized structure turns out to be bridged, with $C_{2v}$ symmetry. The electronic energy change (including BSSE) for eq 8 at MP2/6-311G** is 5 kJ mol$^{-1}$ greater than the SCF-calculated value at 6-31G**. For purposes of comparison, the hydrogen bond of **13** is only 11 kJ mol$^{-1}$ 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 $C_s$ symmetry constraint).

## EBFlow Experiments

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

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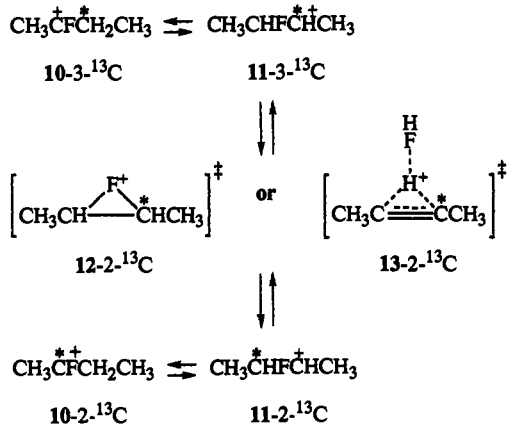
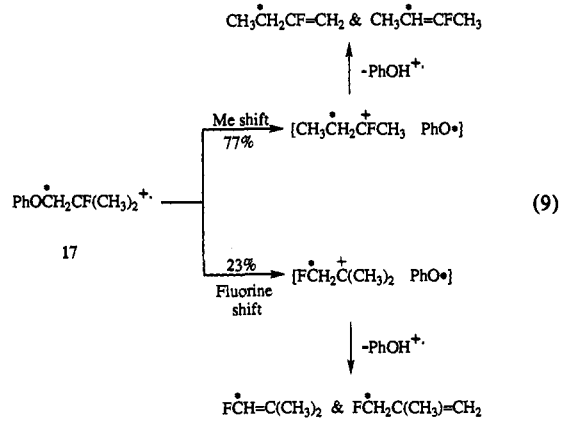
(22) Based on the gas-phase basicity of 2-butyne relative to methyl formate (Lias, S.G.; Ausloos, P. *Int. J. Mass Spectrom. Ion Processes* **1987**, *81*, 165–181) and the proton affinity scale of the following: Szulejko, J. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 7839–7848.

**Scheme 2**



of 70-eV electrons. Collection of the neutral fragments followed by NMR analysis 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 $C_4H_7F$ products recovered from the $^{13}C$-labeled precursor **17** all reflect transpositions characteristic of positive ions.



(9)

Isotopic labeling of the carbon at position 1 of β-fluoroisobutyl phenyl ether permits a further analysis of the cationic decomposition pathways beyond the deuterium labeling experiments we have previously reported.[4] In those studies, comparison between the 70-eV mass spectrum and the EBFlow results for $PhOCH_2CF(CD_3)_2$ confirmed that the recovered neutral fluorobutenes 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 $C_4H_7F$ 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 $^{19}F$ NMR spectrum we observe $^{13}C$–$^{19}F$ coupling constants that are >100 Hz, showing that fluorine shift to the labeled carbon has taken place. Examination of the $^{13}C$ NMR spectra of authentic samples of 1-fluoroisobutene and of methallyl 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 $^{13}C$-label was to be found in position 2. If the labeled carbon in 2-fluoro-1-butene were in that position, the $^{13}C$–$^{19}F$ coupling constant would have been much larger than we observe (<3 Hz). The small magnitude of the observed coupling rules out $^{13}C$-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 $^{13}C$ 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**.

**Table 1.** Proportions of $C_4H_7F$ Products from 70 eV after Correction for Differences in $T_1$ Relaxation Times

| | proportion with $^{13}C$-label at | | | |
|---|---|---|---|---|
| product | C1 | C2 | C3 | C4 |
| $CH_3CH_2CF{=}CH_2$ | *a* | *a* | 0.38 | *a* |
| (*E*)-$CH_3CF{=}CHCH_3$ | *a* | *a* | 0.14 | *a* |
| (*Z*)-$CH_3CF{=}CHCH_3$ | *a* | *a* | 0.22 | *a* |
| $(CH_3)_2C{=}CHF$ | 0.10 | *a* | *a* | *a* |
| $H_2C{=}C(CH_3)CH_2F$ | *a* | *a* | 0.17 | *a* |

[a] None detected.

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**:(*Z*)-**4**:**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 $PhOH^{\bullet+}$:$PhOD^{\bullet+}$ 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 $^{13}C$ natural abundance[4]). 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:1-fluoroisobutene:methallyl 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 $^{13}C$-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 phenoxy 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 $CD_3$ relative to $CH_3$: an α-secondary isotope effect that affects $CD_3$ transfer relative to $CH_3$ transfer and a β-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 spectrum of $PhOCD_2CF(CH_3)_2$, assuming that the secondary isotope effects are the same for methyl shift and for fluorine shift and that the same primary $k_H/k_D$ operates, as we have inferred from the neutral product studies in eq 1. The 70-eV electron impact source mass spectrum of $PhOCD_2CF(CH_3)_2$ gives *m/z* 94 and 95 as the two most intense peaks, corresponding (after correction for $^{13}C$ natural abundance) to a $PhOH^{\bullet+}/PhOD^{\bullet+}$ ratio of 1.6. The $PhOH^{\bullet+}/PhOD^{\bullet+}$ 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 β-fluoroisobutyl phenyl ether has also been investigated. Whereas we had previously suggested[9] that ion–neutral complexes of the form $[C_4H_7F^+\ PhOH]$ 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

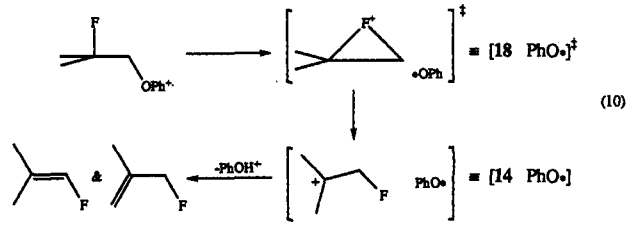
$CH_4$ as the CI reagent, the most prominent peak results from HF loss from the protonated parent ion, and very little $C_6H_7O^+$ ion (protonated phenol) is detected. Thus, the conjugate acid of β-fluoroisobutyl phenyl ether does not behave like protonated neopentyl phenyl ether, which yields that ion in copious quantities. (The *m/z* 95:*m/z* 94 ratio from 70-eV electron impact on $(CH_3)_3CCD_2OPh$ 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 $C_6H_7O^+$ and $C_6H_6DO^+$ from methane CI on $(CH_3)_2CFCD_2OPh$ 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.[9,23] We have previously proposed that hydride shifts occur in a fashion concerted with such heterolyses,[24] 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 $FCH_2CH_2OPh$, the epifluoronium ion **1** has been calculated to be a stable species,[10] and EBFlow experiments confirm its stability within the short lifetime of $[C_2H_4F^+\ PhO^\bullet]$ complexes.[6] The heterolyses that yield complexes containing the three-membered ring are independent of those that proceed *via* hydrogen shift, which yields $[CH_3CHF^+\ PhO^\bullet]$ complexes. While this is strongly suggestive that the fluorine transposition in free $C_2H_4F^+$ 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 $CH_3CHFCH_2OPh^{\bullet+}$ has been measured: 1,2-hydride shift is more rapid than methyl shift, which is in turn about twice as likely as fluorine transposition.[5] 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**.




(10)

A secondary deuterium isotope effect leads to a greater proportion of $CD_3$ transfer in eq 1 than $CH_3$ 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 $CD_3$ groups (as compared to *tert*-butyl-$d_6$ fluoride) than for the undeuterated case. This value of ΔΔZPE is of the appropriate magnitude to account for the experimental secondary isotope effect on the ratio of methyl to fluorine shift, $k_{CH_3}/k_{CD_3} = 0.82$. The same computation for dideuteration of the methylene group predicts a ΔΔZPE 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*-dimethylfluoranium (**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,[5,9,23] 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 orientation relative to the three-membered ring. Return to this 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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