Cyclization and rearrangement of monofluoroallylic cations from halonium metathesis in the gas phase

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Received 29 January 2002; accepted 11 March 2002

Dedicated to Yannik Hoppilliard on the occasion of her 60th birthday.

Abstract

Products of the F+–for-O metathesis between a variety of fluorinated cations and α,β-unsaturated ketones have been examined using FT-ICR and sector mass spectrometry. The reactant ions CF3+, C3F7+, and CFO+ all undergo ion–molecule reactions with carbonyl compounds to replace oxygen with F+. In principle, the simple transposition of atoms corresponds to the transformation C=O → C=F+ and ought to produce monofluorinated allylic cations, which DFT calculations predict to be highly stable. The metathesis, however, is so exothermic that cationic rearrangements take place, as attested by several experimental data, including: (1) unimolecular loss of HF from the ion created by methacrolein; (2) the Brønsted acidity of the ion created by methacrolein in its subsequent ion–molecule reactions; and (3) unimolecular loss of ethylene from the ion created by senecialdehyde. DFT calculations suggest that cyclization of unsaturated cations takes place, even though that mechanism removes the positive charge from conjugation with double bonds. Evidence for cyclization is to be found in CF3+-adduct ions as well as the metathesis ions (for instance, the reaction of sorbitol with CF3+, which forms CH2=OCF3+, as well as the metathesis ion). Electrocyclic ring closure of fluoroallylic ions creates cyclopropyl cations, which represent transition states rather than stable structures on the DFT potential energy surface. Calculated energy barriers to forming monofluorinated cyclopropyl cations range from ΔH = 160 to 266 kJ mol⁻¹. The exothermicities of metatheses with CF3+ are calculated to be >50 kJ mol⁻¹ higher than the respective barrier heights. (Int J Mass Spectrom 219 (2002) 525–535) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ion-molecule reactions; Collisionally activated decomposition; Isomerization; Resonance delocalization

1. Introduction

Allylic stabilization of carbocations is one of the best-established principles of organic chemistry. Both experiment and computation confirm that the allyl cation has the lowest heat of formation of any C3H5+ structure, being substantially favored over the only other stable isomer, 2-propenyl cation. The cyclopropyl cation lies much higher and is calculated to correspond to a transition state, which undergoes disrotatory ring opening to allyl cation without a potential energy barrier [1,2]. Eq. (1) lists the 0 K enthalpy

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PH S1387-3806(02)00705-4
difference and 300 K entropy difference between the two stable C_3H_5^+ isomers estimated using density functional theory (DFT) at the B3LYP/6-311G** level.

\[
\text{CH}_2=\text{CH}-\text{CH}_2^+ \leftrightarrow \text{allyl cation (3-propenyl cation)} \quad \Delta H=26 \text{ kJ mol}^{-1} \quad \Delta S=17 \text{ J mol}^{-1} \text{ K}^{-1}
\]

\[
\text{CH}_2=\text{C}^+\text{CH}_3 \quad \Delta H=26 \text{ kJ mol}^{-1} \quad \Delta S=17 \text{ J mol}^{-1} \text{ K}^{-1}
\]

\[
\text{In accordance with these two principles, DFT calculations predict 3-fluoroallyl cations to be more stable than the 2-fluoroallyl cation, as listed in Table 1. Also the isomeric 1-fluorocyclopropyl cation corresponds to a stable geometry (in contrast to the unsubstituted analogue), even though its ring opening to 2-fluoroallyl cation is exothermic by nearly 90 kJ mol}^{-1}. \text{ The 2-fluorocyclopropyl cation does not correspond to a stable structure on the DFT potential energy surface. Efforts to minimize that geometry indicate that, as in the case of the unsubstituted cyclopropyl cation, no barrier prevents its disrotatory ring opening to a 3-fluoroallyl cation.}
\]

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\]

Less widely known, but also well-established, is the stabilization of an sp^2-hybridized cation by substitution of a single fluorine. For instance, an \(\alpha\)-fluorinated primary carbocation has a lower heat of formation than does the isomeric \(\beta\)-fluorinated secondary cation \cite{3}. Eq. (2) gives the 0 K enthalpy and 300 K entropy changes calculated at B3LYP/6-311G** for one of the simplest examples, the 1-fluoropropyl system. Overlap of a fluorine lone pair with the vacant p-orbital of the cation gives the \(\alpha\)-C–F bond partial double bond character.

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**Table 1**

Relative 0 K heats of formation and 300 K entropies for C_3H_4F^+ isomers calculated using DFT at B3LYP/6-311G** (based on unscaled vibrational frequencies)

<table>
<thead>
<tr>
<th>C_3H_4F^+ isomer</th>
<th>(\Delta H_{0}^\circ) (kJ mol(^{-1}))</th>
<th>(S_{300}) (J mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-3-Fluoroallyl cation</td>
<td>0</td>
<td>278</td>
</tr>
<tr>
<td>Z-3-Fluoroallyl cation</td>
<td>6</td>
<td>278</td>
</tr>
<tr>
<td>2-Fluoroallyl cation</td>
<td>55</td>
<td>279</td>
</tr>
<tr>
<td>1-Fluorocyclopropyl cation</td>
<td>144</td>
<td>263</td>
</tr>
</tbody>
</table>

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\[
\text{This paper reports the formation and reactions of gaseous fluoroallyl cations by metathesis of acrolein with fluorinated electrophiles CF}_3^+ \text{ and CFO}^+. \text{ F}^+ \text{ and an oxygen atom are isoelectronic. The exchange of F}^+ \text{ for oxygen, } \text{C}=\text{O} \rightarrow \text{C}=\text{F}^+, \text{ by ion–molecule reactions of ketones with fluorinated methyl cations in the gas phase was discovered by Eyler and co-workers in the early 1970s} \cite{4,5}. \text{ The simple metatheses are very exothermic, as the B3LYP/6-311G** enthalpies in Eqs. (3) and (4) summarize. Given the background outlined above, it comes as a surprise to discover that the metathesis products of the higher homologues of acrolein display evidence for skeletal rearrangement. Those experimental data are the subject of this report.}
\]
2. Experimental

Mass-resolved ion kinetic energy (MIKE) spectra were recorded on a ZAB 2F two-sector (B-E) mass spectrometer at UC Riverside, with chemical ionization using CF₄ reagent gas. Metastable ion decomposition peaks were fitted with Gaussian functions using IGOR Pro software version 3.03 (WaveMetrics, Inc., Lake Oswego, OR, USA). CAD experiments were performed using an 8 kV beam selected from the first sector that was allowed to collide with helium gas in the second field-free region.

Ion–molecule reactions were studied in a Bruker CMS 47-X FT-ICR spectrometer equipped with an external ion source. CF₃⁺ (m/z 69) and C₂F₇⁺ (m/z 169) ions formed by electron ionization on 2-iodoperfluoropropane (Aldrich Chemical Co.) in the external ion source were transferred to the ICR cell and trapped there. In the same fashion, CFO⁺ ions (m/z 47) were produced by electron ionization of oxalyl fluoride (Oakwood Products, Inc.) in the external ion source and transferred to the ICR cell. Desired reactant ions were isolated in the cell by a series of rf ejection pulses to remove all other ions. Once isolated these ions were allowed to relax by collisions with argon bath gas at (2–3) × 10⁻⁷ mbar and then permitted to react with neutrals (2 × 10⁻⁸ mbar static pressure) in the presence of argon.

Density functional calculations (at B3LYP/6-311G**) were performed using GAUSSIAN98. Basis set superposition error for dissociation thermochemistry was estimated using counterpoise, with energies for individual fragments calculated both with and without ghost orbitals using the “Massage” option. Harmonic vibrational frequencies were computed for all optimized geometries and used without scaling to calculate zero point energy differences and entropies. As has been previously shown by comparison with experiment [6], vibrational frequencies ≤400 cm⁻¹ are well fitted by ab initio computation without scaling. Since those low frequencies make the major contribution to the vibrational entropy, no scaling should be used when calculated normal modes are used to estimate entropies. Calculated entropies are included in Tables 1, 2 and 4 in order to show that large differences are not seen among isomers nor between competing transition states.

3. Results

Metathesis reactions were observed in the FT-ICR between unsaturated carbonyl compounds and CF₃⁺, CFO⁺, and C₂F₇⁺. These same metathesis products were produced in the chemical ionization source of a double-focusing sector instrument (the ZAB) using CF₄ as reagent gas, and their MIKE spectra were examined. In favorable circumstances, the CF₃⁺ adducts of some of the aldehydes could be observed with sufficient intensities that their collisionally activated decomposition (CAD) MIKE spectra could be recorded.
3.1. Acrolein \([\ce{CH2=CHCH=O}]\)

Reaction of acrolein with \(\ce{CF_3^+}\) (\(m/z\) 69) in the FT-ICR produces the metathesis ion \(\ce{C_3H_2F^+}\) (\(m/z\) 59) as virtually the only ion–molecule reaction product. By contrast, reaction of acrolein with \(\ce{CFO^+}\) (\(m/z\) 47) forms not only the metathesis ion, but also a substantial amount of \(\ce{C_3H_3^+}\) (\(m/z\) 39), plausibly by elimination of HF from the metathesis ion (approximately 0.6 the intensity of \(m/z\) 59). As noted above in Eqs. (3) and (4), the metathesis reactions are extremely exothermic, and copious HF expulsion from metathesis ions was described in the original reports of the reactions of ketones with \(\ce{CF_3^+}\) [4,5].

The MIKE spectrum of \(m/z\) 59 produced by Eq. (4) (\(R=R^{=}=\ce{H})\) shows that the dominant metastable ion decomposition of that ion is HF loss, with a flat-topped peak that suggests a translational kinetic energy release \(T_{\text{0.5}} \geq 1\) eV. This is reminiscent of the HF loss from \((\ce{CH_3})_2\ce{CF}^+\), which is known to expel HF by 1,2-elimination and which also displays a flat-topped peak in the MIKE spectrum [7]. The CAD spectrum of \(m/z\) 59, on the other hand, exhibits predominantly \(\ce{H_2}\) loss, with a Gaussian peakshape.

\[
\begin{align*}
\ce{H\u2013F &\rightarrow \ce{CH_2\equiv C\equiv CH}^+} \\
\text{\(m/z\) 59} &\rightarrow \text{\(m/z\) 39}
\end{align*}
\] (5)

Two alternative pathways may be envisaged for HF loss from \(m/z\) 59. A direct 1,2-elimination, as Eq. (5) portrays, would produce the propargyl cation. Alternatively, cyclization of \(m/z\) 59 to the unstable 2-fluorocyclopropyl structure drawn in Eq. (6) (\(R=\ce{H})\) could lead to the aromatic cyclopentenium ion, which is the more stable \(m/z\) 39 isomer [8,9]. Here, again, 1,2-elimination is required. Isotopic labeling could distinguish these two pathways, but the data in hand do not permit a choice to be made at this time.

\[
\begin{align*}
\ce{R\u2013F &\rightarrow \ce{CH_2\equiv C\equiv CH}^+} \\
\text{\(m/z\) 59 (\(R=\ce{H})\)} &\rightarrow \text{\(m/z\) 39 (\(R=\ce{H})\)}
\end{align*}
\] (6)

The ion–molecule reaction of \(m/z\) 59 with acrolein proceeds principally via hydride abstraction. While the metathesis reactions with \(\ce{CF_3^+}\) and \(\ce{CFO^+}\) exhibit rate constants \((1.1 \times 10^{-9} \text{ cm}^3 \text{ per molecule s}^{-1})\) that are not far from the ion–molecule collision rate, \(m/z\) 59 subsequently reacts with acrolein to form \(m/z\) 55 more slowly. A small amount of proton transfer also appears to be occurring to produce \(m/z\) 57 at \(\leq\) one fifth the rate of Eq. (7). The structure of the neutral \(\ce{C_3H_3F}\) product is not known, but the acylium ion shown in Eq. (7) seems most probable for \(m/z\) 55, which does not appear to react further with acrolein.

\[
\begin{align*}
\ce{CH_2\equiv CH\equiv CHF + CH_2=CHCH=O} &\rightarrow \text{\(m/z\) 59} \\
\rightarrow \text{\(m/z\) 55}
\end{align*}
\] (7)

3.2. Methyl vinyl ketone

The ion–molecule reaction of \(\ce{CF_3^+}\) (\(m/z\) 69) with methyl vinyl ketone in the FT-ICR produces the metathesis ion, \(\ce{C_4H_6F^+}\) (\(m/z\) 73) and the ion corresponding to subsequent HF loss, \(\ce{C_4H_5^+}\) (\(m/z\) 53), in approximately equal proportions. In order to examine its further reactions, \(m/z\) 73 was also produced by reaction of \(\ce{C_3F_7^+}\) (\(m/z\) 169), so as to prevent interference from the \(m/z\) 69 reagent ion. Metathesis of \(\ce{F^+}\) for \(\ce{O}\) with \(\ce{C_3F_7^+}\) is calculated to have nearly the same thermochemistry (within 5 kJ mol\(^{-1}\)) as for metathesis with \(\ce{CF_3^+}\) [10]. The reaction with \(\ce{C_3F_7^+}\) produces \(m/z\) 73 as the major reaction product and gives much less \(m/z\) 53.

The \(\ce{C_4H_6F^+}\) ion reacts with the parent ketone predominantly via proton transfer to give protonated methyl vinyl ketone, \(\ce{C_4H_7O^+}\) (\(m/z\) 71), as Eq. (8) depicts. There is no evidence for hydride abstraction to give \(m/z\) 69. Nor is there any evidence for addition of \(m/z\) 73 to the double bond.

If propene is allowed into the ICR cell, \(m/z\) 73 adds to the alkene and then loses HF to give \(m/z\) 95, as Eq. (8) also depicts. As Table 2 summarizes, \(\ce{H_2C\equiv CHCFCH_3^+}\) (the product of simple metathesis on methyl vinyl ketone) is the most stable ion of that formula. Assuming that \(m/z\) 73 has that structure, then
the most straightforward explanation of its reaction with propene is that the intermediate adduct drawn in Eq. (8) (which comes from addition of propene to the more highly substituted end of the allylic cation) forms and then expels HF to produce a dimethylpentadienyl cation. Had the less highly substituted end of the allylic cation added to propene, then the fluorine would have been attached to an sp² carbon, and rearrangement (or else cyclization) would have been required in order for HF to be expelled. The greater reactivity of the more highly substituted end accords with the greater positive charge localization at that end, and it suggests that steric encumbrance does not outweigh the effects of electric charge.

When \( m/z \) 73 is produced in the CI source of the ZAB with CF₄ reagent gas, its MIKE spectrum shows loss of HF as virtually the only metastable ion decomposition, with a Gaussian peak shape, \( T_{0.5} = 0.055 \text{ eV} \). The CAD spectrum is essentially the same. This differs dramatically from the peak shape observed in 1,2-eliminations observed for HF loss from the metathesis peaks of acetone or acrolein.

3.3. Methacrolein [\( \text{CH}_2=\text{C}($\text{CH}_3$)$\text{CH}=$O$] and crotonaldehyde [\( \text{CH}_3\text{CH}=\text{CHCH}=$O$]

Two conjugated aldehydes are isomeric with methyl vinyl ketone, methacrolein and crotonaldehyde. Methacrolein reacts with CF₃⁺ or with C₃F₇⁺ in the FT-ICR to yield \( m/z \) 73 (\( \text{C}_4\text{H}_6\text{F}^+ \)) and \( m/z \) 53 (\( \text{C}_4\text{H}_5^+ \)) as the primary ion–molecule reaction products. The abundance of \( m/z \) 53 is greater than that of \( m/z \) 73, regardless of which perfluorinated ion is used. It is not obvious how HF might be expelled from the simple metathesis product, \( \text{CH}_2=\text{C}($\text{CH}_3$)$\text{CH}=$O$), since there is no hydrogen vicinal to the fluorine. Moreover, the subsequent reaction of \( m/z \) 73 with methacrolein proceeds principally via proton transfer to form \( m/z \) 71, giving only a small amount of hydride abstraction. Again, this is unexpected, since it is not clear how the simple metathesis product might act as a Brønsted acid.

Methacrolein and its isomers were chemically ionized with CF₄ in the ZAB source. The CI source mass spectra of methyl vinyl ketone, methacrolein, and crotonaldehyde differ from one another. The adduct ion from the ketone (\( m/z \) 139) is quite weak, while the aldehydes exhibit HF loss from the adduct ion (\( m/z \) 119) as well as the metathesis ion at \( m/z \) 73. The CI source spectra of the aldehydes give \( m/z \) 53:73:119:139 intensity ratios of approximately 100:60:3:9 for methacrolein and 100:55:14:16 for crotonaldehyde.

The MIKE spectrum of the \( \text{C}_4\text{H}_6\text{F}^+ \) (\( m/z \) 73) ions from methacrolein exhibits HF loss as the dominant metastable ion decomposition, with a Gaussian peak shape having a translational kinetic energy release (\( T_{0.5} = 0.09 \text{ eV} \)) significantly greater than that observed for HF loss from the \( m/z \) 73 from methyl vinyl ketone. The CAD spectrum of \( \text{C}_4\text{H}_6\text{F}^+ \) from methyl vinyl ketone shows only HF loss, while the CAD spectra of the ions from both of the aldehydes show half-dozen peaks with intensities on the order of 0.1–0.3 that of HF loss. The CAD patterns from the \( \text{C}_4\text{H}_6\text{F}^+ \) ions of the two aldehydes are the same. This leads to the question as to whether the \( m/z \) 139 adduct ions from the aldehydes also display the same CAD
patterns. While $m/z$ 73 is the major fragment in both CAD spectra, there are noticeable differences; for example the abundance of CF$_3^+$ ($m/z$ 69) relative to $m/z$ 73 is greater for the CF$_3^+$ adduct of methacrolein than for the adduct of crotonaldehyde.

While the CF$_3^+$ adduct ions of the aldehydes appear to retain distinct identities, the similarities of the CAD spectra of their $m/z$ 73 ion–molecule products (as well as the unanticipated acidity of $m/z$ 73 from methacrolein) suggest that isomerization takes place in the putative metathesis ions, either in the course of their formation or afterwards. DFT calculations of relative stabilities, tabulated in Table 2, confirm the expectation that the metathesis ion from methyl vinyl ketone should have the most stable structure (1 or its geometric isomer) and that the ion expected from crotonaldehyde (2) is substantially favored over the metathesis ion from methacrolein (3).

3.4. Sorbital [CH$_2$CH=CHCH=CHCH=O]

Sorbital is a vinylogue of crotonaldehyde. It reacts with C$_3$F$_7^+$ in the FT-ICR to produce inter alia an ion corresponding to metathesis, C$_6$H$_8$F$^+$ ($m/z$ 99). This $m/z$ 99 ion reacts very rapidly with the neutral aldehyde to form the protonated parent ion, $m/z$ 97. The proton transfer reaction is so rapid as to make it hard to distinguish whether $m/z$ 79, which forms copiously, arises via expulsion of HF from $m/z$ 99 or via water loss from $m/z$ 97.

The reaction of sorbital with CF$_3^+$ introduces a new complexity. Two isobaric $m/z$ 99 ions are formed, which can be separated at high resolution. Exact mass measurement shows that the more abundant ion corresponds to C$_6$H$_8$F$^+$, while the less abundant one is CH$_2$OCF$_3^+$. It is not clear whether the expelled C$_3$H$_6$ neutral is cyclopentadiene or pentenyne. The internal energy of the initially formed CF$_3^+$ adduct is sufficient for trans–cis isomerization of the double bonds to take place rapidly via electrocyclic ring closure and reopening. If this geometrical isomerization occurs, the cis, cis adduct ion can adopt a conformation suitable for the thermally allowed, suprafacial 1,6-sigmatropic hydrogen shift drawn in Eq. (9), followed by a thermally allowed conrotatory electrocyclic ring closure that would lead to cyclization and subsequent expulsion of cyclopentadiene.

3.5. Ethacrolein [CH$_2$=C(C$_2$H$_5$)CH=O], senecialdehyde [(CH$_3$)$_2$C=CHCH=O], tiglaldehyde [CH$_3$CH=C(CH$_3$)CH=O], and their isomers

The expulsion of a hydrocarbon molecule from the CF$_3^+$ adduct, as described in the previous section, becomes a major pathway for the half-dozen C$_5$H$_8$O isomers studied here. CAD spectra were recorded for CF$_3^+$ adducts of the three isomers that display moderately intense M + 69 peaks in the ZAB source, as well as for the metathesis ions ($m/z$ 87) from all six carbonyl compounds. The M + 69 ion from ethacrolein exhibits ethylene loss ($m/z$ 125) as the most abundant ion in its CF$_4$ CI source mass spectrum. This $m/z$ 125 peak could be the CF$_3^+$ adduct of acrolein (CH$_2$=CHCH=OCF$_3^+$) or else protonated trifluoromethyl vinyl ketone, CH$_2$=CHC(CF$_3$)=OH$^+$. 

\[
\begin{align*}
\text{CF}_3^+\text{-adduct of sorbital} & \quad \text{ring closure} \\
\text{CH}_2\text{OCF}_3^+ & \quad \text{ring opening} \\
\text{cis, cis-geometry} & \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{OCF}_3 & \quad \text{ring closure} \\
\text{CH}_2\text{OCF}_3^+ & \quad \text{CH}_2\text{OCF}_3^+ \\
\text{m/z 99} & \\
\end{align*}
\]

\[
3.5. \text{Ethacrolein [CH}_2\text{=C(C}_2\text{H}_5\text{)CH=O], senecialdehyde [(CH}_3\text{)_2C=CHCH=O], tiglaldehyde [CH}_3\text{CH=C(CH}_3\text{)CH=O], and their isomers}
\]

\[
(9)
\]
Table 3
Relative intensities of major fragments in the CAD spectra of fluoroallyl cations produced by CF$_4$ chemical ionization of unsaturated carbonyl compounds

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Metathesis ion</th>
<th>Loss of 20 (–HF)</th>
<th>Loss of 28 (–C$_2$H$_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$=C(CH$_3$)CHO</td>
<td>C$_4$H$_6$F$^+$ (m/z 73)</td>
<td>100</td>
<td>11</td>
</tr>
<tr>
<td>CH$_3$CH=CHCHO</td>
<td>C$_4$H$_6$F$^+$ (m/z 73)</td>
<td>100</td>
<td>8</td>
</tr>
<tr>
<td>CH$_2$=CHCOCH$_2$CH$_3$</td>
<td>C$_5$H$_8$F$^+$ (m/z 87)</td>
<td>93</td>
<td>100</td>
</tr>
<tr>
<td>CH$_3$CH=CHCOCH$_3$</td>
<td>C$_5$H$_8$F$^+$ (m/z 87)</td>
<td>93</td>
<td>100</td>
</tr>
<tr>
<td>CH$_3$=C(CH$_2$CH$_3$)CHO</td>
<td>C$_5$H$_8$F$^+$ (m/z 87)</td>
<td>100</td>
<td>34</td>
</tr>
<tr>
<td>CH$_3$CH=CHCH$_3$C=CHCHO</td>
<td>C$_5$H$_8$F$^+$ (m/z 87)</td>
<td>100</td>
<td>34</td>
</tr>
<tr>
<td>CH$_3$CH=C(CH$_3$)CHO</td>
<td>C$_5$H$_8$F$^+$ (m/z 87)</td>
<td>79</td>
<td>100</td>
</tr>
</tbody>
</table>

DFT calculations predict that these two isomeric ions have heats of formation within 0.2 kJ mol$^{-1}$ of one another.

Remarkably, the CF$_3^+$ adduct of senecialdehyde also exhibits ethylene loss (as confirmed by exact measurement) as the most intense peak in the CI source spectrum, even though the connectivity of its skeleton would not permit extrusion of a 2-carbon unit without a deep-seated rearrangement. The CAD spectra of the CF$_3^+$ adducts of ethacrolein, senecialdehyde, and tiglaldehyde all display m/z 125 as the most abundant fragment, being at least three times more intense than any other fragment ion.

Four conjugated C$_3$H$_6$O aldehyde structural isomers are possible, the three aforementioned and 2-pentenal (CH$_3$CH$_2$CH=CHCH=O). Their F$^+$-for-O metathesis ions give different CAD patterns, as noted in Table 3: all except 2-pentenal show more ethylene loss (m/z 59) than HF loss (m/z 67). The MIKE spectrum of m/z 87 from ethacrolein displays ethylene loss as a slightly more prominent metastable ion decomposition than HF loss (the former a Gaussian peak with $T_{0.5} = 0.1$ eV and the latter as a composite lineshape, with a small peak having $T_{0.5} > 0.4$ eV underneath a much larger Gaussian peak with $T_{0.5} = 0.03$ eV), but the relative intensities are reversed in the CAD. The m/z 87 ion from senecialdehyde displays Gaussian peaks for ethylene and HF loss, having $T_{0.5} = 0.04$ and 0.065 eV, respectively, with the latter slightly more intense than the former. The m/z 87 ions from the two unsaturated ketones studied show no other ions besides m/z 59 ($T_{0.5} = 0.08$ eV) and m/z 67. The m/z 87 peaks from the two ketones give the same relative CAD intensities, but that does not necessarily mean that they interconvert or decompose via common intermediates.

4. Discussion

At the outset of these experiments, it was anticipated that different α,β-unsaturated carbonyl compounds would undergo F$^+$-for-O metathesis to give discrete isomers of noninterconverting fluoroallylic ions. Several pieces of data contradict this expectation, among them:

1. Production of m/z 53 in the ion–molecule reaction of methacrolein with CF$_3^+$ (corresponding to loss of CF$_2$O and HF).
2. The Brønsted acidity of the m/z 73 ion produced by F$^+$-for-O metathesis of methacrolein.
3. Significant loss of ethylene in the metastable ion decomposition and CAD spectra of the m/z 87 ions produced by F$^+$-for-O metathesis of senecialdehyde.

Skeletal rearrangement must be converting one fluoroallylic cation to another. The most straightforward interpretation of the acidity of the metathesis peak from methacrolein would be that the initially formed ion 3 isomerizes to one of the other structures 1, 2, or 4, which could be readily deprotonated to give a fluoro-1,3-butadiene.
The question arises whether conjugate metathesis might take place (as illustrated in Eq. (10) to the right of the m/z 139 adduct ion of methacrolein). While the 6-member cyclic transition state may look appealing, the resulting vinyl cation has a calculated heat of formation 175 kJ mol\(^{-1}\) higher than that of the simple metathesis product (ion 3). Moreover, the calculated net enthalpy change for making the vinyl cation from m/z 139 is substantially higher than the activation barrier for the simple metathesis that produces 3 (which is drawn to the left of the m/z 139 ion in Eq. (10)). The optimized DFT structure of the vinyl cation has a peculiarly distorted geometry, with C–C–C bond angles of 91.5\(^\circ\) (methyl-C–CH) and 145\(^\circ\) (fluoromethyl-C–CH).

Expulsion of HF from the methylated fluoroallylic cations is endothermic (as noted in Table 2). As tabulated in Eq. (4), the metathesis reaction of methacrolein with CF\(_3\)\(^+\) (R=H, R’=CH\(_3\)) is sufficiently exothermic that either of the C\(_4\)H\(_5\)\(^+\) ions in Table 2 is thermodynamically accessible, but it seems highly likely that methylcyclopropenium (8) is the structure produced. The transition state for eliminating HF from 4 via a 5-member cyclic transition state to give the alternative structure 7 must lie very high, since the CH\(_2\) group of the allylic ion (which is not directly involved in the elimination) has to rotate 90\(^\circ\) to give the correct orientation of p-orbitals in the allenylen system. Metathesis probably does not form ions energetic enough to surmount the barrier to producing 7.

The internal energy of fluoroallylic ions created by metathesis of methacrolein is sufficient to cyclize to transition states 5 and 6. Isomerization of 3 to 4, for instance, could take place via closure to cyclopropyl cation 6 (activation energy \(\Delta H^\circ = 160\) kJ mol\(^{-1}\)), followed by a hydride shift to give cyclopropyl cation 5 and ring opening to 4. Cation 6 could also expel HF to give the 1-methylcyclopropenium ion 8. It is tempting to speculate that HF eliminations with large kinetic energy releases (flat-topped peaks in the MIKE spectra) take place via 1,2-eliminations of unrearranged ions, such as Eq. (5) represents, while the higher homologues eliminate HF via cyclized transition states to give cyclopropenium ions, as Eq. (6) represents (e.g., for R=CH\(_3\)), with smaller \(T\) values (Gaussian peaks in the MIKE spectra).

Elimination to form a cyclopropenium ion cannot take place from the ion formed by metathesis of sene- cialdehyde, 11, without further skeletal rearrangement. Closure of 11 to the 3,3-dimethyl-2-fluorocyclopropyl cation represents a mechanism by which methyl migration could occur, as Eq. (11) depicts. HF expulsion from the rearranged cyclopropyl structure produces dimethylcyclopropenium ion. Ring opening...
to the isomeric fluoroallylic ion 12 leads to a connectivity that would permit ethylene elimination. Table 4 summarizes the net thermochemistry of that isomerization. Interestingly, efforts to optimize the structure of 3,3-dimethyl-2-fluorocyclopropyl cation result in structure 14, the transition state for the methyl shift. The calculated activation energy, \( \Delta H^\circ = 266 \text{kJ mol}^{-1} \), is less than the exothermicity of formation of 11 by the metathesis reaction of senecialdehyde tabulated in Eq. (4) (R=CH \(_3\), R'=H).

The CAD patterns of the C\(_5\)H\(_8\)F\(^+\) (m/z 87) ions (Table 3) argue against rearrangement of the carbon skeleton prior to metathesis. The m/z 87 ion from senecialdehyde, 11, exhibits a greater proportion of ethylene loss than does m/z 87 from tiglaldehyde or ethacrolein (12 or 13). Hence, the isomerization that creates an extrudable 2-carbon unit from the senecialdehyde skeleton cannot have occurred by means of equilibration of the CF\(_3\)\(^+\) adducts of these aldehydes.

Ethylene expulsion in the CAD of 11 is related to the issue of ethylene expulsion from its precursor adduct ion, 9. As noted above, the connectivity of 9 does not permit extrusion of a 2-carbon fragment. Isomerization to the CF\(_3\)\(^+\) adduct of tiglaldehyde, 10, could give a structure with the right connectivity. DFT calculations on transition state 16 test the hypothesis that closure to a cyclopropyl cation provides a pathway for adduct ions analogous to Eq. (11). The DFT normal modes calculated for 16 show that the imaginary frequency corresponds to a motion that moves one of the methyls over to the positively charged carbon. In other words, 16 lies near the transition state for conversion of 9 to 10.

The DFT heat of formation of 16, though, is extremely high, much higher than the cost of rotating the double bond out of conjugation with the positive charge, transition state 15. The calculated exothermicity of addition of CF\(_3\)\(^+\) to senecialdehyde is great enough (\( \Delta H = -341 \text{kJ mol}^{-1} \)) for 16 to be accessible, but the transition state for metathesis, 17, lies 100 kJ mol\(^{-1}\) lower (even though it corresponds to a substantially higher barrier than do the transition states for metathesis of saturated ketones and aldehydes with CF\(_3\)\(^+\)) [10]. If the calculated energies are correct, it is

<table>
<thead>
<tr>
<th>( \Delta H^\circ_{\text{rel}} ) (kJ mol(^{-1}))</th>
<th>( S_{300} ) (J mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E,E-9) 9</td>
<td>0</td>
</tr>
<tr>
<td>(10)</td>
<td>11</td>
</tr>
<tr>
<td>(11) + CF(_2)O</td>
<td>19</td>
</tr>
<tr>
<td>(12) + CF(_2)O</td>
<td>31</td>
</tr>
<tr>
<td>(Z-13) + CF(_2)O</td>
<td>96</td>
</tr>
<tr>
<td>(E-13) + CF(_2)O</td>
<td>107</td>
</tr>
<tr>
<td>( \dagger ) + CF(_2)O</td>
<td>285</td>
</tr>
<tr>
<td>( \dagger )</td>
<td>112</td>
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<tr>
<td>( \dagger )</td>
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<tr>
<td>( \dagger )</td>
<td>135</td>
</tr>
</tbody>
</table>
hard to imagine how isomerization via 16 could compete with metathesis.

The reactant aldehydes have predominantly trans geometries. The calculated barrier to interconverting cis and trans adducts (e.g., transition state 15) is sufficiently low that geometrical isomerization probably occurs rapidly prior to metathesis or rearrangement.

In general, the 1-fluoroallylic cations exhibit the same geometrical preferences as do the precursor aldehydes, as the comparison of E- with Z-13 in Table 4 indicates. The internal energy of metathesis ions is probably high enough for Z-E interconversion to take place even after expulsion of CF₂O, though it is not easy to see how any of the geometrical isomers of 11–13 could eliminate HF more easily than would a fluorinated cyclopropyl cation. Therefore, it seems a reasonable inference to conclude that cyclization plays a role in the rearrangement and decomposition chemistry of monofluorinated allylic cations, even though it appears unlikely to play a comparable role in the expulsion of ethylene from the CF₃⁺ adducts.

Since rearrangement of the CF₃⁺ adduct via cyclization seems improbable, other options must be weighed to account for ethylene loss. Eq. (12) depicts one alternative, starting with the adduct of CF₃⁺ to the alkene rather than the carbonyl. The most stable carbon adduct, 18, has an elongated C–CO bond and rotates the plane of the carbonyl nearly perpendicular to the plane of the sp² cation center. This geometry renders a 1,3-hydride shift plausible (though the transition state has not been calculated), to give the more stable acylium ion 19. A 1,2-shift of the CF₃ group, followed by a methyl shift and a hydride shift, gives the trifluoroacetyl ion 20, which has the requisite connectivity to lead to ethylene loss.

An even more complicated alternative might be imagined to start with 1,3-shift of a trifluoromethyl group in the Z,Z-rotamer of the carbonyl adduct 9, followed by 1,2-shift of a methyl to form ion 21. DFT calculations show that the initially formed CF₃-shift structure isomerizes to 21 without a barrier, and Eq. (13) tabulates the DFT enthalpy of 21 (relative to the adduct 9). The structure of 21 more closely resembles a complex of CHO⁺ with 2-trifluoromethyl-2-butene, with a C–CO bond length of 1.84 Å, than it does the conventional structure drawn in Eq. (13). Subsequent hydride transfer to give 22 is endothermic, but the sequence of further shifts illustrated in Eq. (12) can lead to ion 20, which (it should be noted) can also be formed from the CF₃⁺ adduct of tigaldehyde, 10.

5. Conclusions

When perfluorinated cations add to carbonyl compounds, the exothermicity is so great as to permit
reactions that have high energy barriers. These reactions include metathesis of \( \text{F}^+ \)-for-O and isomerization of the adduct itself. Isomerization does not necessarily precede metathesis. The metathesis products themselves form with such high internal energy content that they undergo skeletal rearrangement, too. Although the 3-fluoroallyl cation formed by metathesis of acrolein shows no evidence of rearrangement, its homo- and vinyllogues display fragmentations and ion–molecule reactions that cannot be explained without invoking unimolecular isomerization pathways, the most prevalent of which appears to operate via cyclopropyl cation transition states.

Pathways for isomerization of \( \text{CF}_3^+ \) adduct ions compass many more possibilities than do the rearrangements of metathesis ions. As of this writing, it is not easy to differentiate among possible mechanisms (except tentatively to discard those that, on the basis of calculated energies, appear unable to compete with metathesis). A clearer picture will emerge from a systematic study of a complete set of isomeric saturated ketones.

**Acknowledgements**

This work was supported by NSF Grant CHE 9983610 and the CNRS.

**References**