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Fluoronium metathesis and rearrangements of fluorine-stabilized carbocations

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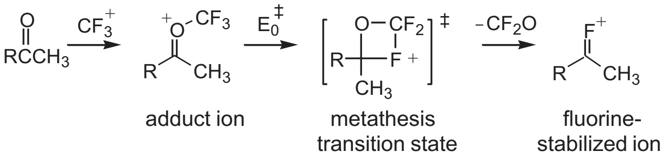
ABSTRACT

The ion–molecule reaction of gaseous trifluoromethyl cation with the conjugated enone 3-methylcyclopentenone yields the $C_6H_8F^+$ product from metathesis of F^+ with the ketone oxygen, along with concomitant formation of neutral carbonyl fluoride. Comparison of the infrared multiple photon dissociation (IRMPD) spectrum of the product ion with that predicted by anharmonic DFT shows a good match. The IRMPD action spectrum, monitored by expulsion of hydrogen fluoride to form $C_6H_7^+$ (*m/z* 79), shows that the ion–molecule reactions of CF_3^+ with two other isomeric, conjugated enones, cyclohexenone and 2-methylcyclopentenone, also yield the same product ion as results from 3-methylcyclopentenone. Although CF_3^+ is a comparatively soft Lewis acid (by comparison to the isoelectronic BF_3), formation of the most stable $C_6H_8F^+$ isomer (the one observed experimentally) cannot be accounted for by attachment of CF_3^+ to the C=C bond of a neutral enone. IRMPD of the $C_6H_7^+$ ion formed by reaction of CF_3^+ with 2-methylcyclopentenone, monitored by loss of H_2, indicates that the $C_6H_7^+$ ion consists of a mixture of protonated benzene and protonated fulvene. Neither of those $C_6H_7^+$ ions can be produced by unimolecular loss of HF from $C_6H_8F^+$ without prior rearrangement. Plausible pathways for reversible skeletal isomerization of $C_6H_8F^+$, probed by DFT, suggest the intervention of nonclassical, edge-protonated cyclopropane transition states, analogous to the rearrangement of the cyclohexyl cation to the 1-methylcyclopentyl cation.

The fluoronium metathesis reaction, first reported by Eyler et al. [1], represents a well-documented transposition of two isoelectronic atoms in the gas phase – F^+ and neutral O – as Eq. (1) illustrates for a methyl ketone [1,2]. Like its better known solution phase analogues (the Wittig reaction and olefin metathesis) it proceeds via a 4-membered ring. Unlike those analogues, the 4-membered cyclic structure intervenes as a transition state rather than as an intermediate.



(1)

Eq. (1) depicts the reaction of the trifluoromethyl cation, but a variety of halogenated cations can give rise to metathesis. Only recently has it proven possible to examine the vibrational structure of the adducts initially formed between fluorinated cations and neutral carbonyl compounds [3,4]. C=O stretching frequencies shift markedly to the red (170–320 cm^{-1}) upon attachment of CF_3^+ to carbonyl oxygen, a greater change than results from the attachment of H^+ [4,5]. The electronegativity of the CF_3 group accounts for the magnitude of the shift, but the examples studied to date suggest that the lowering of the C=O stretch correlates better with the empirical hardness or softness of the neutral carbonyl than with its ionization energy.

This paper describes rearrangements of fluorine-stabilized carbocations produced by fluoronium metathesis between CF_3^+ and cyclic enones. It begins by comparing the electronegativity and softness of small electrophiles. Experimental results for three isomeric starting materials then demonstrate the facility of interconversion among fluorine-stabilized carbocations and, with the assistance of DFT calculations, suggest an accessible pathway for rearrangement of the carbon skeleton.

CF_3^+ as a soft Lewis acid. As is well known, quantitative Lewis acidity scales depend on the identity of the nucleophile that attaches itself. Fluoride affinity represents one of the most widely used measures. Recently, Williams and Wenthold [6] reported gas phase fluoride affinities of trivalent aluminum compounds, giving the ordering $AlF_3 > AlHF_2 > AlH_2F > AlH_3$. AlF_3 and AlH_3 differ

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by roughly 100 kJ/mol in their experimental fluoride affinities. This not only matches theory, but it also agrees qualitatively with the ordering calculated for the fluoride affinities of trivalent boron, in which BF_3 and BH_3 differ by approximately 65 kJ/mol [7].

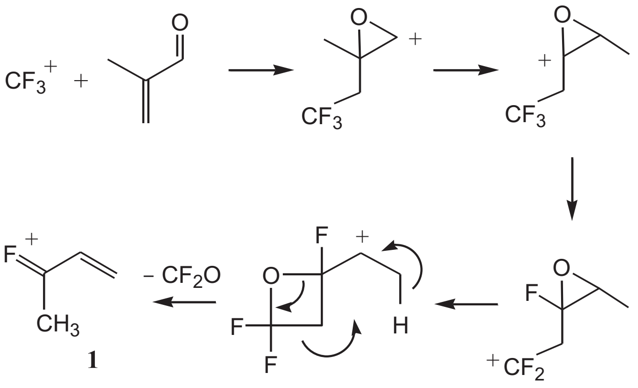
It therefore comes as a surprise to recognize that the experimental fluoride affinities of the CH_3^+ and CF_3^+ have virtually the same values (1080 and 1085 kJ/mol, respectively, within experimental uncertainty of one another),[1] even though they have different electron affinities. The vertical electron affinities of these planar cations are assumed to have nearly the same values as the vertical ionization energies of the corresponding radicals. The trifluoromethyl radical has a pyramidal geometry, and its vertical ionization gives a reported value 1.2 eV above the adiabatic ionization energy [12], which has been determined as 9.04 ± 0.04 eV [13]. The vertical electron affinity (EA) of CF_3^+ therefore has value close to 9.04 + 1.2 = 10.24 eV. The methyl radical is planar, and its adiabatic IE has the same value as the vertical value, 9.84 eV [17]. If EA of the cation provided by itself a correct gauge of Lewis acidity, this comparison would suggest, contrary to fact, that CF_3^+ ought to have a greater fluoride affinity than methyl cation.

As will be noted below, the two gaseous cations do turn out to have nearly the same empirical softness (defined as 1/[IE – EA], where IE stands for the vertical ionization energy). By contrast, monomeric borane behaves as a much softer Lewis acid than does BF_3. The reported IE of BH_3 is 12.03 eV [8], while its electron affinity is 0.04 eV [7]. Even taking into account that the literature reports adiabatic values, monomeric BH_3 has a softness >0.08 eV^{-1}. Since BF_3 has an adiabatic ionization energy (15.95 eV [9–11]) much higher than does BH_3, BF_3 behaves as a harder Lewis acid.

From the reported threshold for producing the CF_3^{++} dication from CF_4 [14], 40.7 eV, and the adiabatic appearance energy of CF_3^+ from CF_4 [15], 14.67 eV, the IE of planar CF_3^+ to form CF_3^{++} should be 40.7–14.67 = 26.03 eV, as compared with a CCSD/aug-cc-pVTZ value of 25.96 eV computed in the present work. Thus, the empirical softness of planar CF_3^+ is 1/(26.03 – 10.24) = 0.0633 eV^{-1}, versus the empirical softness of BF_3, <1/15.95 = 0.0627 eV^{-1} (because BF_3 has an electron affinity < 0). Using the calculated negative, adiabatic electron affinity of BF_3 [7], –0.56 eV, gives a softness of 0.0606 eV^{-1}. In other words, although planar CF_3^+ has a much greater electronegativity than does BF_3, the planar cation is softer than its isoelectronic neutral.

The evidence for a stable CH_3^{++} dication is equivocal, at best [16]; hence, it is not possible to gauge the softness of methyl cation experimentally. In the present work, electronic energy differences computed at the CCSD/aug-cc-pVTZ level give a vertical ionization energy of CH_3^+ equal to 25.64 eV, 0.32 eV lower than calculated at the same level for CF_3^+. Equating the EA of the CH_3^+ cation to the IE of the CH_3 radical gives a softness of 1/(25.64 – 9.84) = 0.0633 eV^{-1} for CH_3^+, virtually the same as for CF_3^+. If fluoride affinity of carbocations correlates with softness, then CH_3^+ and CF_3^+ ought to give the same values.

Rearrangements in the course of fluoronium metathesis. The exothermicity of attaching CF_3^+ to a carbonyl so greatly exceeds $E_0^{\ddagger}$, the barrier for metathesis (by at least 85 kJ/mol [4]), that adduct ions can access a variety of other competing pathways. In the case of propionaldehyde, the principal ion resulting from metathesis has the same structure as the product from acetone, $(CH_3)_2C{=}F^+$. ^{13}C labeling and collection of neutral products suggests that skeletal rearrangement occurs both in the initially formed $CH_3CH_2CH{=}OCF_3^+$ adduct ion and in the $CH_3CH_2CH{=}F^+$ metathesis product.[18,19] Similarly, metathesis between CF_3^+ and methacrolein ($CH_2{=}CMeCH{=}O$) yields a $C_4H_6F^+$ ion that acts as a Brønsted acid and which also undergoes a metastable ion decomposition that expels HF. Neither pathway should be possible for an ion with the structure $CH_2{=}CMeCH{=}F^+$ [20,21].



(2)

Given its vigorous reactivity, CF_3^+ might conceivably attack an α,β-unsaturated aldehyde at an sp^2 carbon instead of oxygen in the initial step. Electophilic addition of CF_3^+ to sp^2 carbon is well precedented [23]. The subsequent rearrangements depicted in Eq. (2) present a plausible isomerization pathway that could form the same product ion, **1**, as results from fluoronium metathesis of methyl vinyl ketone. The methyl group in **1** should exhibit Brønsted acidity, because deprotonation can produce 2-fluorobutadiene. Other mechanisms can also account for such a skeletal rearrangement, either from an initially produced adduct or after formation of $CH_2{=}CMeCH{=}F^+$. The present work looks at cyclic enones, where pathways analogous to those in Eq. (2) cannot occur.

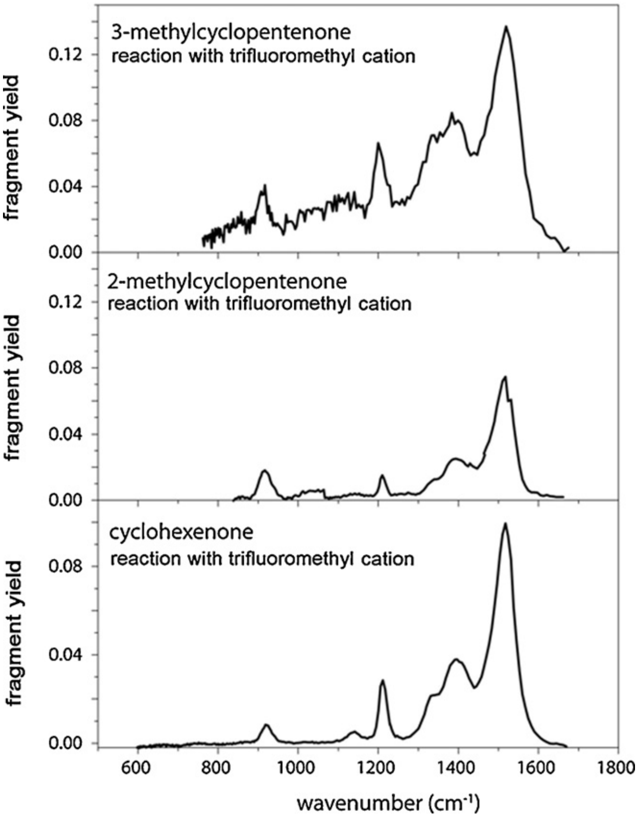


Fig. 1. IRMPD spectra of *m*/*z* 99 ions from reaction of the ketones in Chart 1 with CF_3^+.

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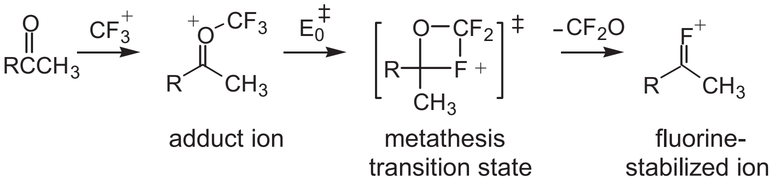
[1] Experimental heats of formation taken from webbook.nist.gov/chemistry.

1. Results

In order to explore the accessible pathways for isomerization, IR action spectroscopy has examined products from fluoronium metathesis of the three cyclic enones drawn in Chart 1. DFT (B3LYP/cc-pVTZ) provides an assessment of the relative stability of the corresponding metathesis product drawn beneath each ion. The ion–molecule reaction of CF_3^+ with each of the ketones yields a mixture of $C_6H_8F^+$ and $C_6H_7^+$: the metathesis ion (*m/z* 99) and the $C_6H_7^+$ ion (*m/z* 79) corresponding to loss of hydrogen fluoride from the metathesis ion.

Fig. 1 displays the room temperature IRMPD spectra of the products of fluoronium metathesis (*m/z* 99) of the unsaturated ketones shown in Chart 1. Infrared absorptions were monitored in all three cases by loss of hydrogen fluoride to yield *m/z* 79. Despite differences in signal-to-noise, it becomes apparent that all three starting materials yield, for the most part, the same product ion.



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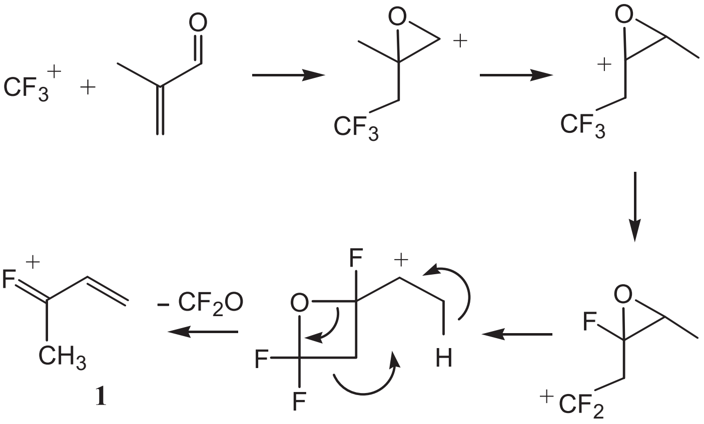

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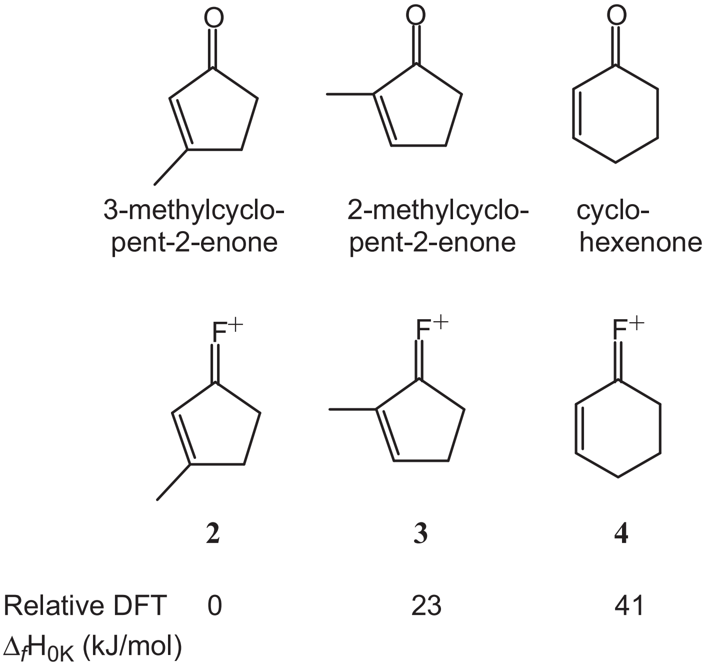


Chart 1. Three cyclic C_6H_8O enones and the corresponding fluoronium metathesis ions.

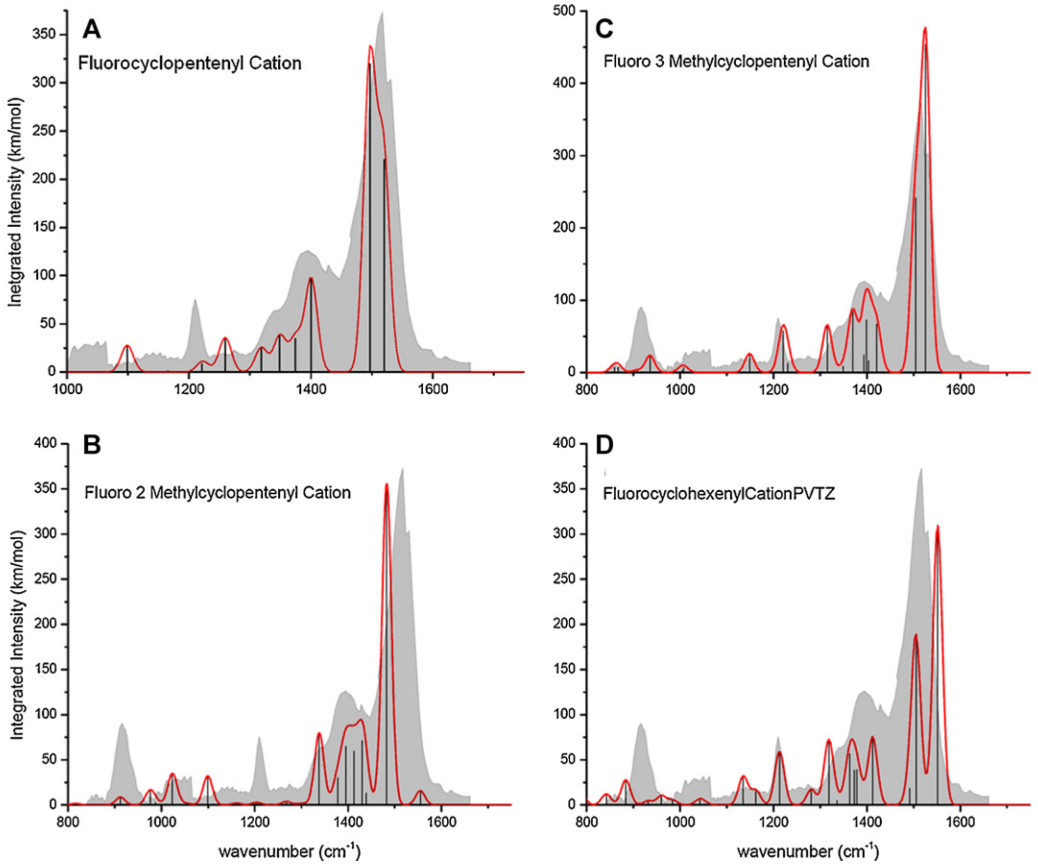
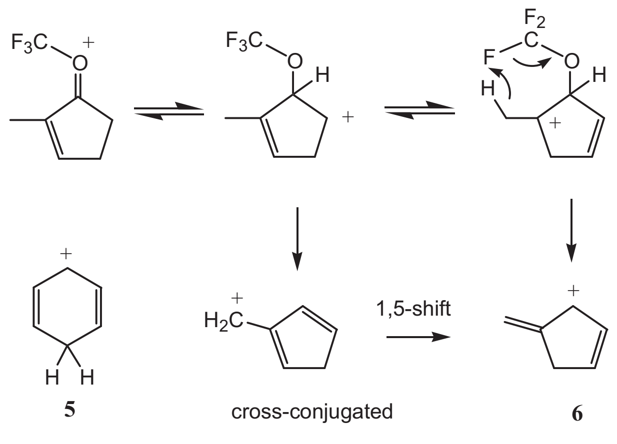


Fig. 2. Comparison of experimental IRMPD spectra with predicted anharmonic DFT infrared spectra (B3LYP/cc-pVTZ with 30 cm^{-1} Gaussian peak broadening) for 1-fluoro-2-cyclopentenyl cation (A) [22] and for 3 possible $C_6H_8F^+$ isomers (B–D). The silhouettes in B–D represent the experimental IRMPD spectra recorded for the ion-molecule reaction product from $CF_3{}^+$ and 2-methylcyclopentenone. The spectrum computed for ion **2** (upper right-hand panel) gives the best match. Note that the *x*-axis of panel A has a different scale from panels B–D.

Anharmonic DFT calculations of vibrational frequencies (B3LYP/cc-pVTZ) provides a basis for assigning the structure of the product ion. Consideration of the three fits B–D shown in Fig. 2 leads to the conclusion that the fluoronium metathesis produces the ion predicted to have most stable $C_6H_8F^+$ structure, **2**, regardless of the identity of the starting enone. In order to test the validity of DFT predictions in the 1300–1600 cm^{-1} domain, panel A of Fig. 2 portrays the quality of fit at this level for the previously reported [22] 1-fluoro-2-cyclopentenium ion.

To probe the identity of ions arising by loss of hydrogen fluoride from $C_6H_8F^+$, the IRMPD spectrum of the *m/z* 79 ion from reaction of $CF_3{}^+$ with 2-methylcyclopentenone was examined. Protonated benzene, **5**, represents the most stable *m/z* 79 structure. IRMPD causes H_2 loss to yield $C_6H_5{}^+$ (*m/z* 77).[24] Further DFT calculations predict the 0K difference between two other *m/z* 79 ions, the isomers of protonated fulvene – the linearly conjugated tautomer **6** bottom right in Scheme 1 and the cross-conjugated structure to the left – as $\Delta H = 69$ kJ/mol in favor of **6**. Because these two $C_6H_7{}^+$ isomers can interconvert readily by suprafacial 1,5-sigmatropic hydrogen shifts, only **6** warrants further consideration.

No single $C_6H_7{}^+$ structure matches the observed spectrum, as Fig. 3 summarizes. Although the published IRMPD of protonated benzene, **5**, comes close [24], the band observed at 1080 cm^{-1} does not occur in the reported spectrum of **5**, nor does calculation predict its presence. DFT does predict a peak at that frequency in the spectrum of protonated fulvene **6**. Neither of the spin states (singlet or triplet) of methylcyclopentadienyl cation gives a good fit to the observed IRMPD spectrum of *m/z* 79. The closest match, shown in Fig. 4, corresponds to a mixture of **5** and **6**. Dissociation cross-sections for **5** and **6** may differ substantially from one another; hence, the proportions used to fit Fig. 4 represent only an approximation.



Scheme 1.

2. Discussion

This work has sought to explore whether $CF_3{}^+$ needs to attach to the C=C double bond of α,β-unsaturated carbonyl compounds, as depicted in Eq. (2), as a prelude to isomerization. Previous workers have noted that the trifluoromethyl cation does not exhibit a

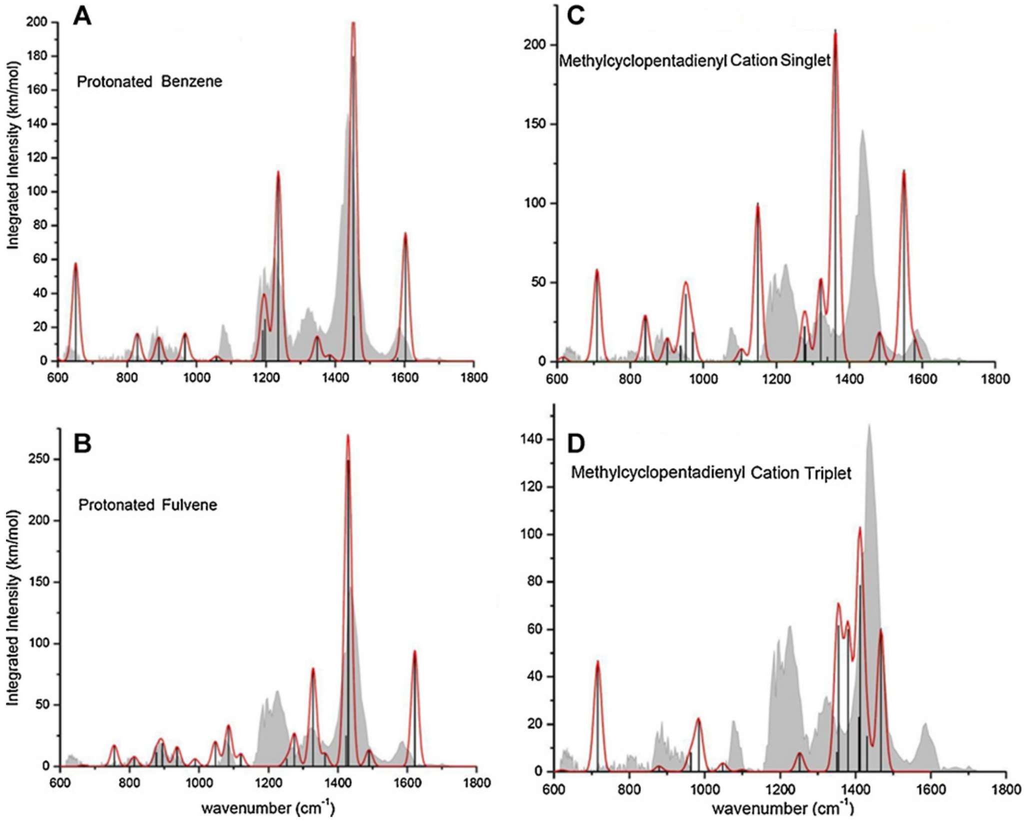


Fig. 3. Comparison of DFT-calculated anharmonic vibrational spectra (B3LYP/cc-pVTZ; 30 cm^{-1} Gaussian peak broadening) of four different structures with the observed IRMPD spectrum of the $C_6H_7^+$ ion (silhouette) formed by reaction of CF_3^+ with 2-methylcyclopent-2-enone: (A) ion **5**; (B) ion **6**; (C) singlet methylcyclopentadienyl cation; (D) triplet methylcyclopentadienyl cation. No single isomer gives all the predicted absorptions seen in the observed IRMPD spectrum.

high degree of selectivity in attacking heteroaromatic rings [23]. The conjugated enones studied in the present work were chosen because electrophilic addition to *sp*^{2} carbon does not provide an obvious pathway for rearranging the carbon skeleton. Nevertheless, isomerization does take place.

Computational evidence confirms the softness of the trifluoromethyl cation, relative to the hard acid BF_3. Comparisons between acetone and thioacetone ($Me_2C{=}S$) offer an apt example (Table 1 of the Supplementary data). While no experimental measure of the thermochemistry for protonating thioacetone is available, published *ab initio* calculations place its 0 K proton affinity (PA) about 28 kJ/mol greater than that of acetone [25]. Repetition of those calculations using DFT (B3LYP/aug-cc-pVTZ) gives the same PA difference. The same level of DFT calculation for acetone gives a 0 K CF_3^+ affinity of 280 kJ/mol, while the calculated gas phase BF_3 affinity of acetone has a value of 35 kJ/mol. By contrast, the calculated CF_3^+ and BF_3 affinities of thioacetone are 307 kJ/mol and 12 kJ/mol, respectively. The shift when the nucleophilic atom changes from a first-row to a second-row element represents a characteristic comparison between soft and hard Lewis acids: the affinity for the soft electrophile increases in going from oxygen to sulfur, while the affinity for the hard electrophile decreases [26].

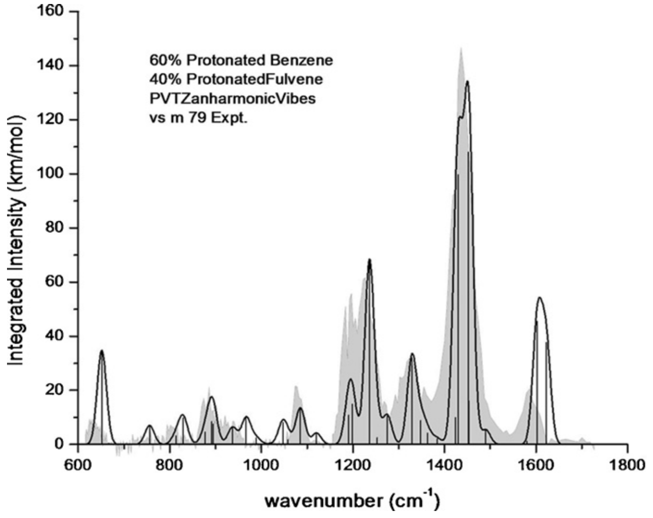
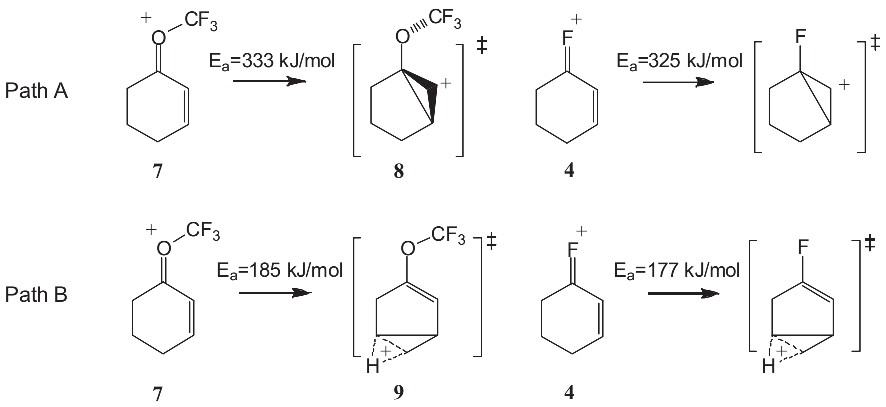


Fig. 4. Comparison of the observed IRMPD spectrum of *m/z* 79 with that predicted by anharmonic DFT (B3LYP/cc-pVTZ with 30 cm^{-1} Gaussian peak broadening) for a 60:40 mixture of ions **5** and **6**.

The three enones drawn in Chart 1 all react with CF_3^+ to yield the same product, ion **2**. Because the rearrangements shown in Eq. (2) appear to be unavailable in the cyclic systems, the results would seem to rule out attack of a C=C double bond as the pathway for isomerization, even though electrophilic attack of *sp*^{2} carbon by CF_3^+ has literature precedent [23]. The elimination of hydrogen fluoride in the course of IRMPD implies that, given sufficient internal energy, ions **2**–**4** can interconvert. It is otherwise difficult to see how ion **2** could expel HF, except to yield methylcyclopentadienyl cation, for which neither spin state (which have high heats of formation, *cf*. Table 2 of the Supporting material) appears to contribute to the experimental IRMPD spectrum shown as silhouettes in Figs. 3 and 4. The reaction of CF_3^+ with 2-methylcyclopentenone yields *inter alia* a mixture of two $C_6H_7^+$ isomers, protonated benzene **5** and protonated fulvene **6**, neither of which could easily form from **2** without rearrangement. The most economical conclusion is that ions **2**–**4** interconvert prior to IRMPD dissociation.

As regards the result summarized by Fig. 4, isomerization of the carbon skeleton could take place either in the initially formed



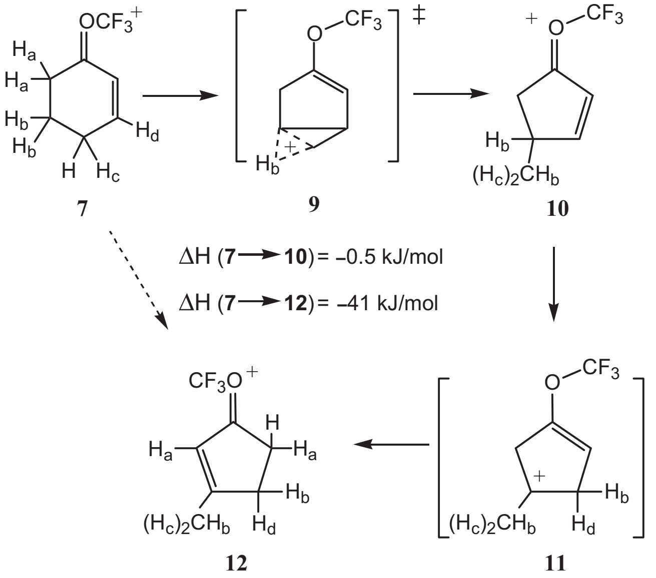
Scheme 2.

adduct ion (*e.g.* **7**) or else in the product of fluoronium metathesis (*e.g.* **4**). Paths A and B in Scheme 2 depict two alternative transition states for rearrangement of a substituted cyclohexenyl ring to a methylcyclopentenyl, with DFT calculated energy barriers (*cf.* Table 3 of the Supplementary data). In Path A the cationic *sp*^{2} carbon connected to the heteroatom attacks the C=C double bond to form a cyclopropyl cation. As previously noted [21], such species represent saddle points rather than stable intermediates. Transition state **8** has a calculated heat of formation greater than that of cyclohexenone plus CF_3^+, which argues against the operation of Path A. Similarly, the analogous transition state starting from **4** also represents a high barrier.

Path B provides a less energetically demanding alternative to Path A. These transition states mirror those discussed for the facile isomerization of cyclohexyl to methylcyclopentyl cation [27–29]. While the pathway for ring contraction of the parent cyclohexyl cation via nonclassical, protonated cyclopropane structures remains a subject of debate [30], DFT calculations for both **4** and the CF_3^+ adduct of cyclohexenone **7** (*cf.* Supplementary data Table 3) bring to light the saddle points illustrated in Scheme 2. Instead of adding to the C=C double bond intramolecularly, the less highly substituted end of the allylic cation attacks an *sp*^{3}-hybridized methylene group to form an edge-protonated cyclopropane. In these saddle points the negative force constants correspond to transit of the proton between carbons. For the CF_3^+ adduct **7** that motion initially leads to the carbocation **10**. DFT predicts the same sort of transformation starting from **4** (*cf.* Supplementary data Table 3). Subsequent hydrogen shifts within **10** would produce ion **12**, as Scheme 3 depicts. Perhaps surprisingly, the transition states represented in Path B lie lower in energy than those drawn in Path A.

The conversion of the CF_3^+ adduct of cyclohexenone, **7**, to intermediate **10** follows an interesting path, as the labeled hydrogens indicate in Scheme 3. DFT predicts that the proton on the edge of the 3-membered ring (one of the hydrogens labeled H_b) migrates without a barrier to a corner (the carbon with its hydrogens labeled H_c) to form a methyl group. Poised between two *sp*^{2} carbons (one attached to the remaining H_b and the other connected to H_d) that methyl group prefers to attach itself to the former, producing the CF_3^+ adduct of 4-methylcyclopent-2-enone, **10**. After the barrier-free conversion of **9**–**10**, a 1,2-hydride shift can convert **10** to the tertiary cation **11**, which can isomerize thereafter to ion **12**. The labeled hydrogens in Scheme 3 portray the outcome expected from a hypothetical deuterium labeling experiment.

To summarize, the published IRMPD spectrum of protonated benzene, **5** [24], fits the predicted IR spectrum in Fig. 3A, but, as noted above, the band observed at 1080 cm^{-1} in the present work from HF expulsion is neither seen in the experimental spectrum of protonated benzene nor predicted by anharmonic DFT calculations. It is not easy to imagine a tautomer of protonated benzene, and the vibrational spectrum predicted for a mixture of the two most stable $C_6H_7^+$ ions, **5** and **6**, in Fig. 4 provides a satisfactory match to experiment. This mixture results from the reaction of CF_3^+ with 2-methylcyclopent-2-enone (which, so far as experiment is able to detect) produces only ion **2** as the concomitant $C_6H_8F^+$ isomer). Either (as mentioned above) **2**, **3**, and **4** must interconvert prior to expelling HF (since **2** cannot yield **6** directly because the methyl group is too far away from the fluorine), or else the CF_3^+ adduct of 2-methylcyclopentenone interconverts with ions **7** and **10** followed by hydrogen shifts and expulsion of HF and CF_2O.



Scheme 3.

3. Conclusion

The three enones in Chart 1 all undergo ion-molecule reaction with CF_3^+ to yield the same product, ion **2**, which is the most stable $C_6H_8F^+$ isomer, as revealed by vibrational action spectroscopy using IRMPD. The experiments cannot distinguish whether skeletal rearrangement takes place in the initially formed CF_3^+ adduct of the carbonyl oxygen or if isomerization occurs after expulsion of CF_2O resulting in fluoronium metathesis. Precedent [18,19] suggests that both pathways operate. Available evidence indicates that activation of $C_6H_8F^+$ leads to expulsion of hydrogen fluoride to form a mixture of protonated benzene **5** and protonated fulvene **6**, products that could not arise directly from ion **2** if it retains its structure. The most economical explanation is that **2** must undergo skeletal isomerization before expelling HF. DFT predicts that the preferred mechanism for rearrangement of the carbon skeleton takes place via nonclassical carbocation transition states (*e.g.* Pathway B in Scheme 2) analogous to those proposed for isomerization of the cyclohexyl cation.

IRMPD investigations [19,22,31] and theory [18,20,21,25,32–35] both attest to the partial CF double bond character of α-monofluorinated carbocations, as well as to the destabilization of carbocations in which fluorine substitution occurs further away. Nevertheless, the present study and its predecessors, as well as solution phase experiments [36], demonstrate that monofluorination does not abolish the tendency for electron-deficient ions to undergo facile rearrangement. Results presented here further suggest that 3-center 2-electron bonds remain accessible (at least as transition states such as illustrated by Path B) in fluorinated cations.

4. Experimental

The commercially available conjugated enones (Aldrich) were used for these experiments without further purification. Resonant IR multiple photon dissociation (IRMPD) action spectra were conducted using a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer coupled to the infrared beam line of FELIX, the free-electron laser for infrared experiments at Rijnhuizen. Details of the laser, the FTICR, and the multiphoton dissociation process have been described elsewhere [24,29,37–39]. Briefly, CF_4 was leaked into an external ionization chamber at a pressure of $\approx 3 \times 10^{-5}$ Torr and the fragment ions injected into the ICR cell. A He gas pulse was then used to capture ions and to cool them collisionally. The ionizer was a slightly modified Micromass EI/CI source with a tungsten filament using an electron energy typically around 60 eV. The fragment ions (principally CF_3^+). were injected into the ICR cell of a home-built 4.7 T FTICR mass spectrometer via a quadrupole deflector and a 1-m long RF octopole ion guide. A transient pressure of He from a gas bulb was then introduced into the ICR cell via a pulsed valve. The gas bulb contained approximately 1 atm of helium plus a few Torr partial pressure of enone. Partial pressures of enones in the gas bulb and the duration of the gas pulse were adjusted so as to optimize the abundance of m/z 99 or m/z 79 ions. After a 3 s pump and cooling delay, ions were mass isolated by the use of a SWIFT excitation pulse, which removed the remaining CF_3^+ and other unwanted ions. Subsequently, a mechanical shutter opened, which exposed the ions to the IR radiation of FELIX, in which 30 macropulses were typically accumulated (6 s of irradiation). When the laser wavelength is in resonance with an allowed vibrational transition in the ion, multiple photon absorption occurs by virtue of the high pulse energy of FELIX (typically 30 mJ in a 5 μs pulse). Incoherent IVR-mediated multiple-photon excitation allows each ion to absorb on the order of 10–100 IR photons. The ions thereby reach internal energies substantially above the dissociation threshold. A standard FTICR excite/detect sequence then determined the amount of parent and fragment ions (*i.e.* m/z 79 from m/z 99; m/z 77 from m/z 79), and an action spectrum was generated by plotting their ratio as a function of the IR wavelength.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2011.07.024.

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