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Vicinal Elimination from 2-Fluoroisopropyl Cation in the Gas Phase

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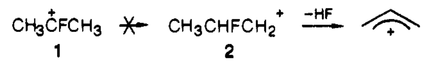
Abstract: An electron bombardment flow (EBFlow) reactor has been used to assay $C_3H_5^+$ isomer distributions from different sources. Quenching the ions by fluoride abstraction followed by ^{19}F NMR of recovered neutral C_3H_5F permits analysis of the ratio of $CH_3C{=}CH_2^+$ to allyl cation. Electron impact on 1-bromopropene yields predominantly allyl cation, in agreement with a previously reported mass spectrometric measurement. Ionization of isobutene yields an 80:20 mixture of $CH_3C{=}CH_2^+$ and allyl cation. Electron impact on *tert*-butyl fluoride yields only $CH_3C{=}CH_2^+$. The difference between the two latter results means that ionized isobutene is not an intermediate in production of $C_3H_5^+$ from *tert*-butyl fluoride. Therefore, the major fragment of *tert*-butyl fluoride, $(CH_3)_2CF^+$ (**1**), must be undergoing vicinal elimination of hydrogen fluoride to yield $C_3H_5^+$. Theoretical calculations provide evidence that this does not take place via an isolated, electronically excited state of **1**. Ab initio calculations on the ground-state $C_3H_6F^+$ potential energy surface reveal six stable isomers of **1**, **3**–**8**, all of which have stable, isoelectronic C_3H_6O analogues. Two of these, **7** and **8** (isoelectronic to allyl alcohol and acetone enol, respectively), correspond to ion–molecule complexes of $C_3H_5^+$ and hydrogen fluoride. More extensive calculations on **8** illustrate the difference between an ion–molecule complex and a hydrogen-bonded complex. Other isomers of **1**, $CH_3CHFCH_2^+$ (**2**) and $CH_3CH^+CH_2F$ (**11**), do not have stable, isoelectronic C_3H_6O analogues. Neither are they stable $C_3H_6F^+$ isomers. Ab initio calculations show that **2** undergoes barrier-free rearrangement to $CH_3CH_2CHF^+$ (**3**), while **11** represents one of the resonance structures of 2-methylfluoriranium, **4**. Ab initio results show good agreement with empirical estimates for ΔH_f° of **3**, of methylvinylfluoronium (**5**), and of methyl-2-propenylfluoronium (**9**). These lead to a calculated heat of formation of **8** that is 19 kcal/mol higher than that of **1**. Ion **1** corresponds to the global energy minimum, and its two lowest energy isomers are calculated to be **3** and fluoretanium (**6**). Together the experimental and theoretical results show that **1** undergoes a 1,3-hydrogen shift to **8** en route to elimination in preference to rearrangement to **6**.

Neutral products of gas-phase ion–molecule reactions reveal structural features of the reactants. In the mass spectrometer a given m/z value often corresponds to a mixture of isomeric ions that can be difficult to analyze by measuring ion masses, but which can be probed by quenching the ions via bimolecular fluoride abstraction in an Electron Bombardment Flow (EBFlow) reactor.[1–3] We report here experimental results for reactions that yield $C_3H_5^+$ ions. One of these reactions, expulsion of hydrogen fluoride from 2-fluoroisopropyl cation, **1**, yields only a single $C_3H_5^+$ isomer, $CH_3C{=}CH_2^+$.[2] A simple 1,2-hydride shift could, in principle, have led to the 2-fluoropropyl cation, **2**, which would, in turn, have easily expelled hydrogen fluoride to yield allyl cation, as reaction 1 depicts, but this does not take place.



(1)

The absence of reaction 1 strikes us as remarkable, since 1,2-hydride shifts are facile rearrangement pathways in cations and since allyl cation is reported to be 3–5 kcal/mol more stable than $CH_3C{=}CH_2^+$.[4] Reaction 2 takes place, instead, as the experimental results presented below demonstrate. Since the thermodynamic barrier to reaction 2 is ΔH = 26 kcal/mol, the barrier to reaction 1 must also be substantial. This is consistent with predictions by Frenking and Schwarz, who have discussed the surprisingly high activation barriers to 1,2-hydride shift in cations that are stabilized by adjacent lone pairs.[5] On the basis of semiempirical molecular orbital calculations, they have enunciated the principle that the barrier becomes greater as (a) the reactant LUMO is raised and becomes more delocalized or (b) the product LUMO is lowered and becomes more localized. Application of this principle predicts a barrier of appropriately high magnitude for the isomerization of **1**.

Background

We have previously reported that **1** does not scramble hydrogens between its two methyl groups.[2] This means that **1** expels hydrogen fluoride in preference to rearrangement to other isomers besides **2**. A list of plausible $C_3H_6F^+$ isomers can easily be drawn up by considering isoelectronic C_3H_6O structures, but the validity of such a list has not previously been explored. We have therefore examined minima on the $C_3H_6F^+$ potential energy surface using empirical and ab initio methods. We find that molecular orbital calculations confirm the simple picture based upon isoelectronic series.

$$\begin{array}{lcccc} & \mathrm{CH_3\overset{+}{C}FCH_3} & \longrightarrow & \mathrm{CH_3\overset{+}{C}{=}CH_2} & + \ \mathrm{HF} \qquad (2) \\ & \mathbf{1} & & & \\ \Delta H_f^\circ\ (\mathrm{kcal/mol}) & 139^6 & & 230^4 & -65^7 \end{array}$$

Ion **1** is isoelectronic with acetone and is a stable species that has been observed by NMR in solution.[8] Isoelectronic analogies would suggest that stable isomers of **1** should include **3** (isoelectronic with propionaldehyde), **4** (isoelectronic with propylene oxide), **5** (isoelectronic with methyl vinyl ether), **6** (isoelectronic with oxetane), **7** (isoelectric with allyl alcohol), and **8** (isoelectronic with acetone enol). Since **2** corresponds to a zwitterion rather

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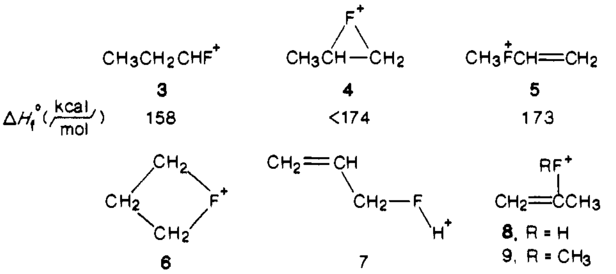
than a stable C_3H_6O structure, it might not be a stable ion structure. As reported here, ab initio calculations substantiate this.

A quantitative formulation for isoelectronic series has been presented by Jolly and co-workers as the equivalent cores approximation.[9] Peremptory assessment of stabilities of some of the structural isomers of **1** can be made empirically on the basis of this approximation, which equates ΔH for reaction 3 when X

$$R_1XR_2^+ + (CH_3)_2O \rightarrow (CH_3)_2X^+ + R_1OR_2 \qquad (3)$$

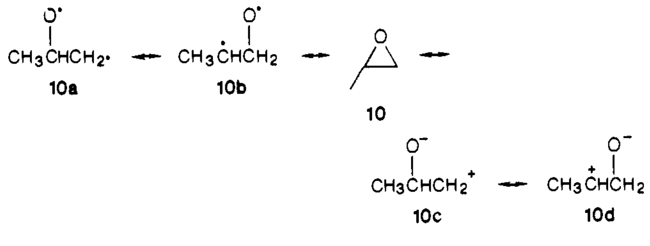
is a fluorine to the value of ΔH when X is an oxygen with a 1s vacancy (measurable by ESCA). The analogous equivalent cores estimate for $\Delta H_f°$ of **1** is based upon the ESCA of acetone[10] and uses CH_3CHO and CH_3CHF^+ in reaction 3 in place of dimethyl ether and dimethylfluoronium. This estimate lies within the reported error of the experimental measurement.[6] The major source of uncertainty in estimates based on reaction 3 is the $\Delta H_f°$ value used for dimethylfluoronium, $(CH_3)_2F^+$, 145 ± 2.5 kcal/mol.[11] Equivalent core heats of formation of 1-fluoro-1-propyl cation (**3**), the epifluoronium ion **4**, and methylvinylfluoronium (**5**) are shown below. Since the ESCA of oxetane, allyl alcohol, and acetone enol have not been reported, there is no basis for estimating empirical heats of formation for fluoretanium (**6**), **7**, and **8**. Our survey omits the conjugate acids of fluorocyclopropane and the 1-fluoropropenes that would be isoelectronic to cyclopropanol and the 1-propen-1-ols.



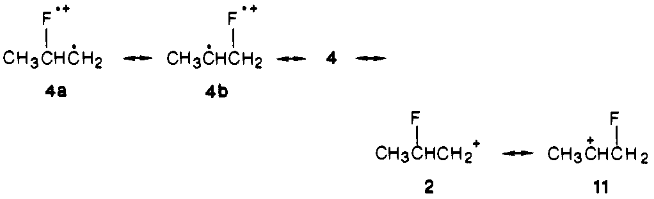
Theoretical investigations of portions of the $C_3H_6F^+$ energy surface have been previously reported at the semiempirical[5,12] and ab initio levels.[13] Ion **1** is the only isomer that has been studied using split-valence basis sets.[14] We present here a survey of potential energy minima with three questions in mind. (1) Can stable $C_3H_6F^+$ structures be predicted on the basis of their C_3H_6O isoelectronic analogues? (2) Are bond-length distortions qualitatively predicted by consideration of participating resonance structures? (3) Does a potential minimum exist along the reaction coordinate for reaction 2? The answer to all of these is affirmative. Ab initio results presented here provide a further explanation as to why reaction 1 is not observed: **2** is not a stable energy minimum, nor can it be viewed as making a major resonance contribution to its valence isomer **4**.

Distortions of $C_3H_6F^+$ structures relative to their C_3H_6O analogues are to be expected. Symmetrically substituted fluoronium ions such as **6** prefer to have two C-F bonds of equal length. As the two bond strengths, measured as D_0 (the bond dissociation energy at 0 K) or D_e (the quantum mechanical well depth), become unequal with unsymmetrical substitution, the stronger bond becomes shorter and the weaker bond longer. The relative contributions of $CH_3CHFCH_2^+$ (**2**) and $CH_3CH^+CH_2F$ (**11**) in a resonance hybrid will be reflected by the disparity between the two C–F bond lengths of **4**.

Heterolytic resonance hybrids can be viewed as making more important contributions to ground-state electronic structures of closed-shell ions than of most closed-shell neutrals. Consider propylene oxide (**10**) and its dissociative resonance structures **10a–d**. Homolytic structures (e.g., singlet diradicals **10a** and **10b**) will be much lower in energy than the heterolytic structures **10c** and **10d**, and there should not be a great energetic difference (<3 kcal/mol, the difference in $\Delta H_f°$ of between *n*-propyl and isopropyl radicals[15]) between **10a** and **10b**. The participation of heterolytic structures is greater for **10** than for acyclic ethers (hence the greater electrophilicity of epoxides) but ought not to have as much weight as the diradicals.



For an epifluoronium ion the relative contributions will be different. Homolytic structures will be higher in energy than heterolytic ones, since the adiabatic ionization potentials (IP's) of alkyl radicals with ≥2 carbons are <8.5 eV,[15] while the IP's of alkyl fluorides (where reported) are ≥9.5 eV.[4] The difference between the two lowest energy dissociative structures will also be greater than between two homolytic structures. The difference between **2** and **11** should be comparable to the difference in heats of formation between *n*-propyl and isopropyl cations, >30 kcal/mol.[15]



This description is rooted in valence bond theory, and it makes the following prediction regarding molecular orbital calculations. Restricted Hartree–Fock calculations, which emphasize the heterolytic contributions, ought to provide a satisfactory description of ions like **4**, where chemical intuition suggests their importance.

Bond-length distortions in some of the $C_3H_6F^+$ isomers turn out to be quite large. Reasons for this can be gauged by considering CH_3FH^+. Contrast the heat of formation of hydrogen fluoride plus methyl cation[4c] to fluoromethane[7b] plus a proton. The F–H heterolytic bond dissociation energy (i.e., the proton affinity of fluoromethane) is more than 110 kcal/mol greater than the F–C bond dissociation energy (i.e., the methyl cation affinity of hydrogen fluoride). As a consequence molecular orbital calculations predict the C–F bond of CH_3FH^+ to be unusually long and weak.[16] The general bond loosening in CH_3FH^+ is attested by the published ab initio vibrational frequencies,[17] which correspond to a zero-point energy that is nearly the same (within 10 cm^{-1}) as that of fluoromethane, even though CH_3FH^+ has 12 vibrations to fluoromethane's 9. This provides additional insight into the intermediacy of **8** in reaction 2. If the bond weakening and the disparity between bond strengths in **8** are great enough,

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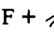
Table I. Energies (Based on 3-21G Optimized Geometries) in Atomic Units for $C_3H_6F^+$ Isomers[a]

	C–F bond lengths (Å)	rel energies (au)		ΔH for isomerization (kcal/mol)	
		3-21G//3-21G	6-31G//3-21G	3-21G//3-21G	6-31G//3-21G
1	1.290	0	0	0	0
3	1.287	0.02884	0.03343	19.2	22.1
4	1.458, 1.903	0.04978	0.04383	31.6	27.9
5	1.524 (sp 2), 1.554 (sp 3)	0.04523	0.05380	28.4	33.8
6	1.589, 1.589	0.02846	0.03675	20.2	25.4
7[b]	1.737	0.05556	0.05318		
8	1.928	0.04466	0.03701	25.6	20.8
HF + $CH_3C{=}CH_2^+$	∞	0.07497	0.05091	41.6	26.5
HF + 	∞	0.05156	0.02519	29.4	12.9

[a] Calculated bond lengths are in Å; relative 0 K enthalpies (in kcal/mol) based on zero-point energies from 3-21G normal modes calculations after scaling of vibrational frequencies by a factor of 0.9. [b] Constrained to C_s symmetry. Normal modes analysis gives a negative force constant.

the F–C bond will be sufficiently extended in the equilibrium geometry for **8** to correspond to a product-like energy minimum along the reaction coordinate for expulsion of hydrogen fluoride.

Experimental Section

The EBFlow apparatus, operating techniques, and NMR analyses of neutral products have been previously described.[2,3] In the present experiments neat 2-methyl-2-fluoropropane-d_9 or a mixture of 2×10^{-4} torr of reactant (1-bromopropene or isobutene) with 2×10^{-4} torr of 2-methyl-2-fluoropropane-d_9 was bombarded with 70-eV electrons. The recovered reaction mixture was analyzed by 282-MHz ^{19}F NMR.

2-Methyl-2-fluoropropane-d_9. 2-methyl-2-propanol-d_{10} (Aldrich) was converted to the corresponding fluoride by reaction with (diethylamino)sulfur trifluoride (Carbolab);[2] ^{19}F NMR δ_F -131.4 ($J_{FD} = 3.2$ Hz).

Molecular orbital calculations were performed using MOPAC,[18] GAUSSIAN 80,[19] and the INDO-PSDCI program[20] as modified by Boldridge[21] on a VAX 11/785 at UCR and GAUSSIAN 82[22] on the Cray X-MP/48 at the San Diego Supercomputing Center. In computation of excited electronic states of **1** by PSDCI, INDO repulsion integrals were used, and the σ electron mobility constant was set to a value (0.95) such that the singlet energy of acetone was calculated to have its experimental value of 88 kcal/mol. Ab initio normal modes were computed using analytic second derivatives. Full MP2 treatments were performed in the MP2/6-31+G** calculations; core orbital contributions were not included in other Møller-Plesset calculations.

Results

EBFlow Experiments. When 1-bromopropene (cis:trans = 3:1; reaction 4) or isobutene (reaction 5) is bombarded in the EBFlow with 70-eV electrons in the presence of $(CD_3)_3CF$, NMR analysis of the products shows the indicated ratios of 2-fluoropropene to allyl fluoride. Both of these products have ^{19}F resonances that are well separated from those of the perdeuterated products from fragmentation of $(CD_3)_3CF$ that result from reaction 6. No 1-fluoropropene is observed among the neutral products of reaction 4, which argues against the intermediacy of vinylic radicals in formation of the recovered fluoroalkenes. As has been previously shown, 2-fluoropropene results from fluoride abstraction by $CH_3C{=}CH_2^+$, while allyl fluoride is the product from allyl cation.[2] The ratio observed from reaction 4 does not differ greatly from the reported ratio of $CH_3C{=}CH_2^+$ to allyl cation (0.37) from electron impact on 1-bromopropene determined by a collisionally activated decomposition (CAD) study.[23] Although $CH_3C{=}CH_2^+$ has been reported to undergo some structural isomerization under CAD conditions,[24] it does not isomerize detectably to allyl cation in the EBFlow.[2]

$$CH_3CH{=}CHBr \xrightarrow{70\ eV} C_3H_5^+ \xrightarrow{(CD_3)_3CF} CH_2{=}CFCH_3/CH_2{=}CHCH_2F = 0.25 \quad (4)$$

$$(CH_3)_2C{=}CH_2 \xrightarrow{70\ eV} C_3H_5^+ \xrightarrow{(CD_3)_3CF} CH_2{=}CFCH_3/CH_2{=}CHCH_2F = 4 \quad (5)$$

$$(CD_3)_3CF \xrightarrow[\text{electron impact}]{12\text{–}70\ eV} (CD_3)_2CF^+ \ \&\ CD_3C{=}CD_2^+ \xrightarrow{(CD_3)_3CF} (CD_3)_2CF_2 \ \&\ CD_3CF{=}CD_2 \quad (6)$$

Molecular Orbital Calculations. Semiempirical computations were performed as a prelude to ab initio calculations. Frenking and Schwarz have proposed a relationship between the barrier height for 1,2-hydrogen shift and a reactivity index α_n for the reactant ion, defined below, where ϵ_{LUMO} is the eigenvalue for the lowest unoccupied molecular orbital and $c_{i\mu}$ is the μth atomic orbital coefficient on the positive charge-bearing carbon (which bears the subscript i).[5]

$$\alpha_n = -\sum_{\mu} c_{i\mu}^2(\mathrm{LUMO})\epsilon_{LUMO}$$

Our MNDO calculations give a LUMO energy for **1** of −8.26 eV and a value of α_n of 6.50, from which Frenking and Schwarz's approximately linear relationship predicts an activation barrier of 28 kcal/mol for **1** → **2** (33 kcal/mol if only the two points for **3** → **11** and **11** → **3** are extrapolated). Since the isoelectronic analogy and the ab initio calculations described below predict that **2** is not a stable structure, further ramifications of this MNDO approach were not pursued.

Ion **1** is produced by electron impact ionization of *tert*-butyl fluoride, as illustrated in reaction 6. The possibility therefore exists that isolated, electronically excited states are responsible for the decomposition of this ion. We have explored whether **1** might have such a low-lying excited state by performing semiempirical INDO–PSDCI calculations[20] as modified by Boldridge.[21] These predict that the first excited singlet state of **1** ought to lie 113 kcal/mol above the ground state.[25] Electronically excited states of $C_3H_6F^+$ should thus have appearance potentials >15 eV. Since the product of reaction 2 is experimentally detected by FTMS at much lower ionizing energies, isolated states can be omitted from further consideration. Our ab initio calculations have been

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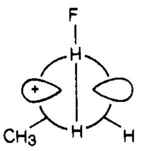
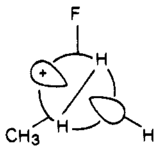
(25) Ab initio calculations of excited-state energies (based upon wave functions that are linear combinations of all singly substituted determinants from a GAUSSIAN 82 calculation) have been performed at Carnegie-Mellon University and give triplet and singlet energies for $(CH_3)_2CF^+$ of 123.4 and 140.1 kcal/mol, respectively (as compared to 79.6 and 103.2 kcal/mol calculated for acetone), using the STO-3G basis set. Split-valence (3-21G and 4-31G) basis sets give even higher values for excited-state energies. (Foresman, J. B.; Birge, R. R.; Pople, J. A., unpublished results, 1987).

confined to a search for ground-state potential energy minima.

Restricted Hartree–Fock calculations were performed on the $C_3H_6F^+$ isomers **1**–**8** with geometries optimized at the 3-21G level. Regardless of which starting geometry was chosen for **2** (conformations **2a**–**c**), no stable minimum was achieved for the 2-fluoro-1-propyl cation. Conformations **2a** and **2b** underwent 1,2-methyl shift in the course of a BERNY optimization[26,27] to give **3** as a stable minimum. Conformation **2c** underwent fluorine bridging to give **4** as a stable minimum.



2a



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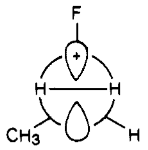

2c

The optimized geometry for **4** is not symmetrically bridged. The CH–CH_2–F bond angle is 78°, but, as given in Table I, the two C–F bond distances differ greatly. The structure is best described as a hybrid between a symmetrically bridged epifluoronium ion and **11**. Mulliken population analysis at 3-21G gives an overlap population for the methylene C–F bond that is nine times greater than for the methine C–F bond. Since both carbon–carbon bonds are short (1.46 and 1.48 Å for the methyl–methine and methylene–methine bond lengths, respectively) and have, to two significant figures, the same populations, **4** must have very little of the character of **2**.

As Table I summarizes, **1** is the global energy minimum, with total energies of -215.053 91 au (3-21G//3-21G) and -216.158 80 au (6-31G//3-21G). The optimized conformation has no symmetry elements, although it approaches C_2 symmetry. Its energy lies 0.000 15 au below the energy that we calculate for the conformer with C_s symmetry, which had previously been reported as the minimum energy geometry.[14] The conjugate base, 2-fluoropropene, has calculated energies of -214.750 00 au (3-21G//3-21G) and -215.857 35 au (6-31G//3-21G). Normal mode calculations lead to a proton affinity (3-21G//3-21G) for 2-fluoropropene of 185 kcal/mol for protonation on the methylene carbon and 160 kcal/mol for protonation on fluorine. When compared with the proton affinity of propene (184 kcal/mol) that we calculate that 3-21G//3-21G, this agrees with a previously reported 3-21G//3-21G estimate that assessed the proton affinity of 2-fluoropropene to be only slightly greater than that of propene.[14] The 6-31G//3-21G proton affinities of 2-fluoropropene are 184 (on CH_2) and 159 kcal/mol (on F).

The isomers **3**–**8** all correspond to minima on the potential energy surface. Relative to **1**, isomers **3** and **5** have, at 6-31G//3-21G, calculated heats of formation that are within experimental error of the empirical estimates based on the method of equivalent cores. The ESCA of propylene oxide has not been reported, but we can take an equivalent cores estimate based on the O_{1s} ionization potential of oxirane as an upper bound for the heat of formation of **4**. The calculated heat of formation lies below this empirical upper bound.

Isomer **7** has a stable C–F bond if constrained to its extended conformation with the F–H bond and the three carbons coplanar. As can be inferred from Table I, **7** with this symmetry (C_s) is not thermodynamically stable with respect to free allyl cation and hydrogen fluoride. If the C–F bond is allowed to rotate out of the plane, 3-21G calculations predict that **7** undergoes heterolysis to yield an ion–molecule complex of allyl cation and hydrogen fluoride that is bound by 0.023 19 au.

Table II. Relative Energies of $CH_3C{=}CH_2^+$ vs Allyl Cation for Various ab Initio Methods[a]

method	ΔE^b	method	ΔE	$E(CH_3C{=}CH_2^+)$
6-31G**	0.025 68	MP3/6-31G**	0.020 91	−116.589 37
6-31+G**	0.026 65	MP4(SDTQ)/ 6-31G**	0.021 39	−116.609 52
6-311G**	0.025 04	MP2/6-311G**	0.020 04	−116.590 94
MP2/ 6-31G**	0.022 52	MP3/6-311G**	0.018 56	−116.622 51
MP2/ 6-31G**	0.022 57[c]	MP4(SDTQ)/ 6-311G**	0.029 66	−116.633 70

[a] Geometries optimized at HF/6-31G** unless otherwise noted. [b] The energies calculated for $CH_3C{=}CH_2^+$ corresponding to the left-hand column are given in Table III. [c] Geometry optimized at 6-31G* (from ref 28).

The calculated ΔH for reaction 2 at 6-31G//3-21G is in good agreement with experiment. However, the calculated overall ΔH for reaction 1 is too low. This is due to the fact that ab initio methods calculate too large an energy difference between $CH_3C{=}CH_2^+$ and allyl cation.[28] The problem does not appear to arise from insufficient basis sets, since geometry optimization of $CH_3C{=}CH_2^+$ at a higher Hartree–Fock level does not change the structure significantly beyond the one reported at the 6-31G* level.[29] Relative to $CH_3C{=}CH_2^+$, ab initio calculations on allyl cation at all levels give energies that appear to be too low, as Table II summarizes. Although inclusion of electron correlation narrows the gap between the two isomeric $C_3H_5^+$ ions, the gap begins to widen at the highest Møller–Plesset levels and the difference between them corresponds to $\Delta H > 9$ kcal/mol, based on vibrational frequencies computed at 6-31G**. For this reason we do not infer that the apparent instability of planar **7** or its bond lengths necessarily represent accurate predictions.

As Table I shows, the C–F bond in **8** is unusually long. There are other peculiar features of this ion. The calculated ΔH_f° for **8** at 6-31G//3-21G is nearly as great as that of the dissociated products, and its structure makes **8** appear as though it corresponds to an intermediate along the reaction coordinate for expulsion of HF from **1**. We have therefore examined calculations with larger basis sets in order to study these properties further. Three approaches can be used to estimate the stability of **8** from the calculations: the energy of **8** relative to **1**, the isodesmic[27] reaction 7, and the calculated energy change for expulsion of HF.

The level of calculation was chosen by considering results for simple fluoronium ions, for which there is already a body of published literature.[30] Our results are summarized in Table III. Del Bene has suggested that MP2/6-31+G** calculations are suitable for examining proton affinities and weakly bound complexes,[31] and we examined geometry optimization up to that level. Symmetry constraints were not imposed upon the optimization (except where noted in Table III as a cost-saving measure at the MP2/6-31+G** level).

In choosing which calculation is to be preferred, we make comparison with known reactions. The ab initio calculations at all of the levels in Table III underestimate the methyl cation affinity of fluoromethane, for which the experimental value is 59 kcal/mol.[11] The inclusion of electron correlation (MP2) substantially improves the agreement between experiment and theory. The MP2/6-31G** calculation gives the highest value for D_e(C–F), 56 kcal/mol.

At all of the levels in Table III the Hartree–Fock calculations overestimate the proton affinity of fluoromethane (estimated using published 6-31G* ab initio vibrational frequencies[17]). The MP2 calculations come closer to the experimental value. The MP2/6-31+G** calculations underestimate the proton affinity, while the MP2/6-31G** calculation gives the value (152 kcal/mol) that is closest to the reported experimental value. Likewise, the calculation at this level gives the best value for the methyl cation

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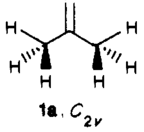
Table III. Ab Initio Results Used for Computation of Bond Strengths of Fluoronium Ions

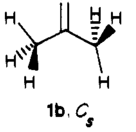
	HF	H_2F^+	CH_3F	CH_3FH^+	CH_3^+	$(CH_3)_2F^+$	$CH_3C{=}CH_2^+$	**8**
				HF/6-31G** Geometry				
bond length (Å)	0.901	0.944	(CF) 1.365	(CF) 1.690	1.080	(CF) 1.521	(C=C) 1.266	(HF) 0.097
bond angle (deg)		115.8	(FCH) 109.2	(HFC) 122.4	120.0	(CFC) 124.6	(CCC) 182.0	(CCC) 174.7
HF/6-31G** energy	-100.01169	-100.21518	-139.03974	-139.29013	-39.23630	-178.34155	-116.17640	-216.20651
HF/6-31+G** energy	-100.02430	-100.21672	-139.04906	-139.29387	-39.23668	-178.34484	-116.17711	-216.21668
HF/6-311G** energy	-100.04688	-100.24404	-139.07820	-139.32617	-39.24366	-178.38211	-116.19607	-216.26085
MP2/6-31G**[a] energy	-100.19412	-100.40111	-139.35956	-139.60254	-39.34657	-178.79517	-116.55814	-216.77266
MP2/6-31+G** energy	-100.21733	-100.40745	-139.38396	-139.61799	-39.35172	-178.81586		
				HF/6-31+G** Geometry				
bond length (Å)	0.902	0.945	(CF) 1.372	(CF) 1.751	1.080	(CF) 1.528	(C=C) 1.267	(HF) 0.908
bond angle (deg)		116.3	(FCH) 108.5	(HFC) 126.1	120.0	(CFC) 125.8	(CCC) 182.0	(CCC) 175.7
HF/6-31+G** energy	-100.02431	-100.21673	-139.04914	-139.29411	-39.23671	-178.34489	-116.17711	-216.21694
				MP2/6-31+G** Geometry				
molecular symmetry	$C_{\infty v}$	C_{2v}	C_{3v}	C_s	C_{3v}	C_{2v}		
bond length (Å)	0.969	0.969	(CF) 1.403	(CF) 1.627	1.084	(CF) 1.533		
bond angle (deg)		113.4	(FCH) 108.2	(HFC) 117.4	120.0	(CFC) 119.5		
MP2/6-31+G** energy	-100.21811	-100.40859	-139.38493	-139.61966	-39.35176	-178.81660		

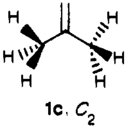
[a] Core orbitals not included.

affinity of hydrogen fluoride, 37.2 kcal/mol (which is within experimental error of the empirical value). Since the calculations at the MP2/6-31G**//HF/6-31G** level give the energies that replicate experimental values best of all, there seems little justification for performing geometry optimization for fluoronium ions beyond the 6-31G** level.

We have therefore used the 6-31G** basis set (split valence augmented with p orbitals on hydrogen and d orbitals on other atoms) to optimize geometries of selected larger ions. Three conformers of **1** were optimized: **1a**, subject to the constraint of two planes of symmetry; **1b**, subject to the constraint of only one mirror plane; and **1c**, subject to the constraint of a twofold rotation axis through the C–F bond. Conformer **1c** has the lowest energy of the symmetric structures. The C–F bond length for all of these is 1.25 Å, distinctly shorter than that for the 3-21G geometry. We find that isopropyl cation also adopts C_2 symmetry when optimized without imposed symmetry constraints, both at 3-21G and at 6-31G**.

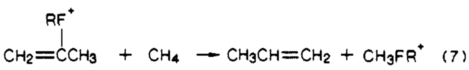

1a, C_{2v}


1b, C_s


1c, C_2

E6–31G**//6–31G** −216.255 70 au −216.256 81 au −216.257 09 au

The accuracy of isodesmic estimates based on geometries optimized at 6-31G** can be assessed for homologue **9**. From the ESCA of 2-methoxypropene, $IP(O_{1s}) = 538.84 \pm 0.03$ eV,[32] and its heat of formation,[33] we arrive at an equivalent cores estimate $\Delta H_f° = 162$ kcal/mol for **9**. Empirically, ΔH for reaction 7 is


$$CH_2{=}C(FR^+)CH_3 + CH_4 \rightarrow CH_3CH{=}CH_2 + CH_3FR^+ \quad (7)$$

9, R = CH_3

energy (au)			
6–31G**//6–31G**	−255 236 58	−40 201 70	−117 081 61
MP2/6–31G**	−255 955 18	−40 364 62	−117 503 37

8 kcal/mol when R = CH_3, while the ab initio calculation gives a value of 9.5 kcal/mol, and with post-SCF corrections (MP2) a value of 13.3 kcal/mol. Here the Hartree–Fock calculation gives a value within experimental error of the empirical value,[34] and inclusion of electron correlation overestimates the stability of **9**. To verify the greater accuracy of the Hartree–Fock calculation we compare calculated values for D_e of the sp^2 C–F bond of **9** with the empirical heterolytic bond dissociation energy, 12 kcal/mol. The Hartree–Fock value is 12.8 kcal/mol and, with MP2, 23.5 kcal/mol.

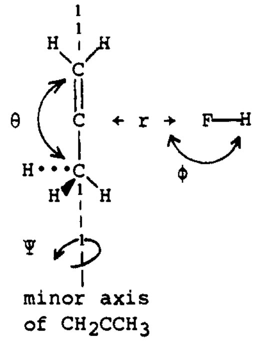


Figure 1. Optimized geometry computed for **8** at 6-31G**. C–C–C bond angle $\theta < 180°$ designates that the out-of-plane hydrogens are closer to the terminal methylene than the in-plane hydrogen. Angles ϕ and Ψ are defined in the text.

Based on calibration with **9**, the 6-31G** Hartree–Fock calculations are taken to be most likely to be accurate in estimating the heat of formation of **8**. The isodesmic calculation (reaction 7 where R = H) gives $\Delta H_f°(\mathbf{8}) = 158$ kcal/mol. In order to assess the variation of this estimate, the isodesmic calculation was performed at MP2 and at HF/6-311G**, yielding values of $\Delta H_f°(\mathbf{8}) = 161$ and 160 kcal/mol (based on 6-311G**//6-31G** energies for methane and propene of -40.209 01 and -117.103 42 au).

From Table I it can be seen that the ab initio energy change for dissociating **8** to $CH_3C{=}CH_2^+$ and hydrogen fluoride corresponds to $D_e = 8.7$ kcal/mol at 6-31G//3-21G, from which D_0 is calculated to be 5.7 kcal/mol. For the geometry optimized at 6-31G**, the energies correspond to $D_e = 11.6$ kcal/mol at HF/6-31G**, 9.6 at HF/6-31+G**, 11.2 at HF/6-311G**, and 12.8 at MP2/6-31G**. Table III summarizes the data.

At 6-31G** **8** exhibits an sp^2 carbon–fluorine bond length $r = 2.52$ Å, as drawn in Figure 1, which is longer than that at 3-21G//3-21G. The fluorine and carbons are coplanar ($\Psi = 0°$) and the HFC bond angle is virtually straight, $\phi > 178°$. Inclusion of additional diffuse functions in the basis set for optimization (6-31+G**) leads to additional elongation of the C–F bond to $r = 2.62$ Å. The energy at 6-31+G**//6-31+G** is only 0.17 kcal/mol lower than that at 6-31+G**//6-31G**, corresponding to a force constant <0.03 mdyn/Å for C–F stretching. The C-F bond length in **8** stands in contrast to the lengths of the C–F bonds in **9**, calculated to be 1.49 Å (sp^3 C–F) and 1.59 Å (sp^2 C–F) at 6-31G**, which are comparable to the C–F bond lengths computed for dimethyl fluoronium. The C–C–C bond angle of **8**, θ

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(34) Both the empirical and ab initio calculations use dimethylfluoronium as a reference, and the remaining experimental error in the empirical estimate corresponds to a standard error of 1.4 kcal/mol.

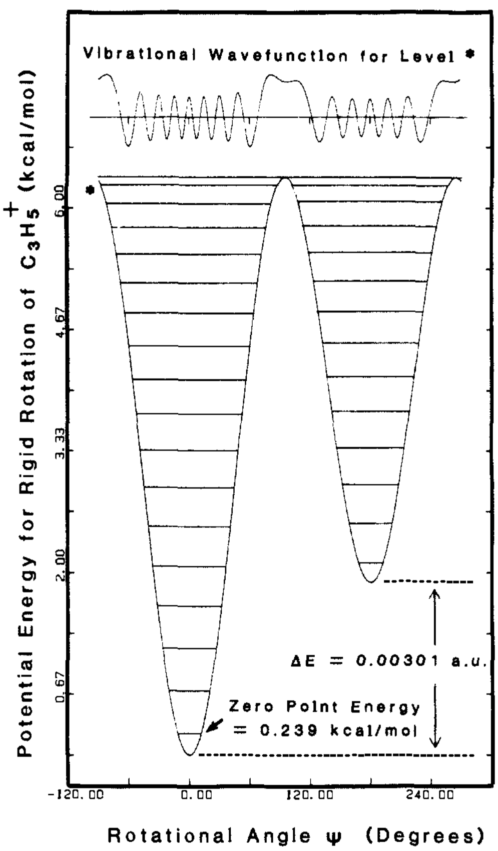


Figure 2. Rigid rotation of the $C_3H_5^+$ moiety of **8** about its minor axis treated as a hindered internal rotor. Potential function is a trigonometric fit of 6-31G** energies calculated at Ψ = 0, 90, and 180°: V (in kcal/mol) = 3.620 - 0.944 cos Ψ - 2.676 cos 2Ψ. Vibrational levels were computed using a basis set of 75 trigonometric functions by the method of: Lewis, J. D.; Malloy, T. B.; Chao, T. H.; Laane, J. *J. Mol. Struct.* **1972**, *12*, 427–449 (computer program written by Professor D. F. Bocian). The vibrational wave function for the asterisked level is drawn at the top of the figure.

= 175°, is nearly as close to linear as for free $CH_3C{=}CH_2^+$, θ = 182°. Mulliken population analysis at 6-31G**//6-31G** shows a total overlap population for the C–F bond in **8** equal to 0.004, as contrasted with a value of 0.074 for the sp^2 C–F bond in **9**. It is hard to avoid the suspicion that covalent character is largely absent from the C–F bond in **8** and that it is held together by electrostatic (ion–dipole) forces. Since the 6-31G** calculations (both at the Hartree–Fock level and with MP2) seem to *overestimate* the stability of **9**, we believe that the apparent lack of covalency in **8** is not a mere artifact of the basis set.

A classical electrostatic calculation of the attractive potential between $CH_3C{=}CH_2^+$ and HF in the 6-31G** optimized geometry gives a dissociation energy comparable to the ab initio value. Using the 6-31G** positive charge distribution of free $CH_3C{=}CH_2^+$ (distorted to the geometry it enjoys in **8**) and treating HF as a point dipole (with its 6-31G** dipole moment, 2.34 D) give a potential energy of ΔU = 12 kcal/mol for separation of ion and dipole.

The calculated barrier at 6-31G** for rigid rotation of the $CH_3C{=}CH_2^+$ portion of **8** around its minor axis by angle Ψ (leaving the hydrogen fluoride portion fixed) is 0.01003 au (0.00793 au at MP2) at Ψ = 90°. The ease of rotation further substantiates the notion that the C–F bond does not possess much covalent character. Treatment of this motion as a hindered internal rotor is summarized by Figure 2.

Discussion

The experimental results for 1-bromopropene (reaction 4) calibrate the EBFlow method for measuring the $C_3H_5^+$ isomer distribution from electron impact. Not only is there good agreement with an independent experimental measurement,[23] but there is also no evidence of contamination by alternative pathways. If, for instance, direct substitution of bromine by fluorine (either via fluorine atoms or F^+) had taken place, then 1-fluoropropene would have been detected. As this is not seen in the ^{19}F NMR of the product mixture, these reactions can be ruled out. For the same reason we also rule out the production of C_3H_5F from 1-propenyl radicals.

Table IV. Comparison of Empirical C–X and H–X Heterolytic (HET) and Homolytic (HOM) Bond Dissociation Energies (in kcal/mol) of $(CH_3)_nXH_m^+$ Ions[a]

	$[(CH_3)_3CH]H^+$ X = C		$(CH_3)_3NH^+$ X = N		$(CH_3)_2OH^+$ X = O		CH_3FH^+ X = F	
	HET	HOM	HET	HOM	HET	HOM	HET	HOM
H–X bond	163	93	225	92	192	107	150	125
C–X bond	66	92	122	86	84	108	36	178
Δ	27		6		23		89	

	$CH_3OH_2^+$		Neon[b] X = Ne		$(CH_3)_2SH^+$ X = S		CH_3ClH^+ X = Cl	
	HET	HOM	HET	HOM	HET	HOM	HET	HOM
H–X bond	182	119	48	231	201	88	168	114
C–X bond	67	132	33	303	100	91	62	129
Δ	52		15		−3		52	

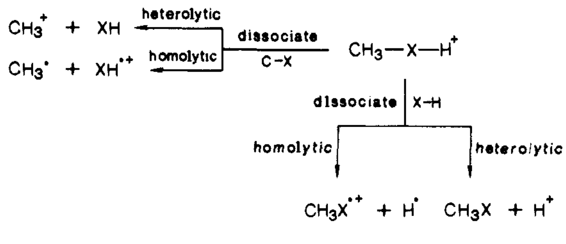
[a] The C–X heterolytic bond dissociation energy is equated to the methyl cation affinity of $(CH_3)_{n-1}XH_m$, and the H–X heterolytic bond dissociation energy is equated to the proton affinity of $(CH_3)_nXH_{m-1}$.[8a] The difference between the weaker H–X value and the weaker C–X value is represented as Δ. [b] Heterolytic bond dissociation energies taken as the proton affinity and methyl cation affinity of atomic neon. The latter was estimated by the method of equivalent cores from the reported ESCA of hydrogen fluoride and fluoromethane.

Reactions 4 and 5 stand in contrast to the formation of $CH_3C{=}CH_2^+$ as the sole $C_3H_5^+$ isomer from 70-eV electron impact on *tert*-butyl fluoride, which has been inferred from recovery of 2-fluoropropene with no allyl fluoride in previously reported EBFlow experiments,[2] and which is confirmed by our observation of the deuterated analogues from reaction 6. Fragmentation of *tert*-butyl fluoride to $CH_3C{=}CH_2^+$ requires two steps, methyl loss and hydrogen fluoride expulsion. There are two possible sequences in which these steps might occur, as reaction 8 depicts. If hydrogen fluoride expulsion were to come first, then

$$\mathbf{1}\ \xleftarrow[-CH_3]{a}\ (CH_3)_3CF^{\bullet+}\ \xrightarrow[-HF]{b}\ (CH_3)_2C{=}CH_2^{\bullet+} \rightarrow CH_3C{=}CH_2^+ + CH_3^{\bullet} \quad (8)$$

isobutene molecular ion would be an intermediate, as in reaction 8b. But since ionization of isobutene affords a mixture of $C_3H_5^+$ isomers (reaction 5), we infer that isobutene molecular ion cannot be an obligatory intermediate. We conclude that reaction 8a followed by reaction 2 must represent the predominant route to $CH_3C{=}CH_2^+$ cation.

The object of our theoretical calculations has been to consider the isomers accessible by rearrangement of **1**. As a prelude to discussing the ab initio results, let us review what chemical intuition might predict in terms of resonance structures. A covalent bond in an onium ion, RY^+, can be dissociated in two ways: heterolytically, to yield R^+ and Y, or homolytically, to yield $R^{\bullet}$ and $Y^{\bullet+}$. An unsymmetrically substituted onium ion therefore has four options for dissociating two different bonds, as represented by reaction 9. For electrically uncharged molecules bond homolysis



(9)

almost always has a lower thermodynamic barrier than bond heterolysis. But ions may favor dissociation one way or the other, depending upon the nature of their heteroatoms. In some cases an unsymmetrically substituted ion may favor homolytic dissociation of one bond and heterolytic dissociation of another. Empirical values for H–X and C–X bond dissociation energies for a series of onium ions are summarized in Table IV. The difference between the weaker X–H and the weaker X–C values is symbolized as Δ. Experimental values from which the bond strengths can be measured are not available for X = boron, but a difference in the heterolytic bond dissociation energies of 79 kcal/mol can be deduced from an isodesmic calculation,[35] which leads to a value of Δ = 6 kcal/mol when the ionization potentials of atomic hydrogen and trimethylborane are taken into account. Comparison of the values of Δ for the conjugate acids of dimethyl ether and of methanol shows that Δ can be as greatly affected by the extent of substitution of >two-coordinate onium ions as by the identity of the heteroatom X. Where experimental values are available, second-row elements exhibit smaller values of Δ than do their first-row counterparts. As can be seen from Table IV, the monosubstituted fluoronium ion exhibits by far the largest value of Δ. Based on this survey we expect that unsymmetrically substituted fluoronium ions will manifest the greatest degree of bond distortion that is to be observed. The extension of the C–F bond of fluoromethane upon protonation (and the fact that its magnitude is greater than the extension of the C–O bond of methanol upon protonation) has been remarked in previous theoretical studies.[13]

Since the value of Δ is so large for fluoronium ions, a large distortion of **8** relative to isoelectronic analogues is expected. Previous calculations have shown extremely long C–F bonds (>2.5 Å) in F-protonated alkyl fluorides.[30] With regard to reaction 2, a potential energy minimum corresponding to **8** is expected along the reaction coordinate. On the reactant side, transfer of hydrogen from carbon to fluorine in **1** is a 1,3-sigmatropic shift, for which a high potential energy barrier may be expected to exist.[36] On the product side, hydrogen fluoride will experience attraction toward any positive ion. Therefore **8** can be viewed as a local minimum between two maxima: on the one hand, the transition state for 1,3-shift and, on the other hand, infinite separation between ion and dipole.

The results of our Hartree–Fock calculations for symmetrically substituted fluoronium ions (H_2F^+, dimethylfluoronium, or **6**) predict equal bond lengths to fluorine, even though this was not imposed as a constraint of geometry optimization. An unsymmetrically substituted fluoronium ion can be anticipated to have unequal bond lengths. For CH_3FH^+ the ab initio calculations give bond strengths that vary with the level of the calculation, but which correspond to D_e in the range 150–160 kcal/mol for F–H and D_e in the range 20–40 kcal/mol for F-C. At the MP2/6-31G**//HF/6-31G** level the difference between these D_e's, 116 kcal/mol, is in good agreement with the experimental difference in heterolytic bond dissociation energies. As expected, the ab initio F-H bond length (0.922 Å at HF/6-31G**; 0.953 Å at MP2/6-31+G**) is shorter than the bond length in H_2F^+, while the F–C bond length is much longer than in dimethylfluoronium.

The variation of structure of simple fluronium ions with calculational method is instructive. Dimethylfluoronium and H_2F^+ are ions for which heterolytic dissociative resonance structures for the bonds to fluorine should be much lower in energy than homolytic ones. When electron correlation effects are included (MP2/6-31+G** geometry vs. HF/6-31+G** geometry) the bonds to fluorine elongate. For the F–H bond of protonated methyl fluoride, the homolytic resonance structure corresponds to a lower energy than does the heterolytic one. Accordingly the F–H bond exhibits greater elongation as a result of including electron correlation than does H_2F^+, while the C–F bond contracts substantially. This same trend has been reported using smaller basis sets, although the optimized bond distances are somewhat shorter (C–F = 1.602 Å at MP2/6-31G* and 1.682 Å at HF/6-31G*).[16] In terms of a valence bond picture, the addition of diffuse functions to the basis set for MP2 gives poorer agreement with experimental bond strengths because it appears to lead to excessive weighting of homolytic resonance structures. As noted in the Results, the MP2/6-31G** calculations give the best estimates of the methyl cation affinity and proton affinity of fluoromethane, as well as the best estimate of the methyl cation affinity of hydrogen fluoride.

The calculated heterolytic bond strengths of **8** are D_0 = 159 kcal/mol for F–H and <13 kcal/mol for F–C. Because there is a tradeoff between the strengths of the two bonds to fluorine, weakening of one will strengthen the other. To judge from the results for **9**, the homolytic resonance structures for the sp^3 C–F bond are too heavily weighted at the MP2 level, which weakens that bond and leads to a substantial overestimate of the sp^2 C–F bond strength.

With 6-31G** optimized geometries (which give a good match to the empirical bond strength of **9**), the calculated F–H bond length for **8** is only 0.006 Å longer than calculated for free hydrogen fluoride, while the F–C bond length is greatly elongated, at least 1 Å greater than that of dimethylfluoronium. If **8** is viewed as a fluoride shared between $CH_3C{=}CH_2^+$ and a proton, the virtually all of the covalency is directed toward the proton.

The three different methods of gauging the stability of **8** at 6-31G** are not in perfect agreement with one another. The isodesmic calculation (reaction 6, R = H) gives $\Delta H_f°(\mathbf{8})$ = 158 kcal/mol. The calculated dissociation into $CH_3C{=}CH_2^+$ and hydrogen fluoride gives $\Delta H_f°(\mathbf{8})$ = 156 kcal/mol (based on vibrational frequencies computed at 3-21G). These two values are close, but the calculated isomerization energy of **1** gives a much higher estimate, $\Delta H_f°(\mathbf{8})$ = 169 kcal/mol. This brings to mind the systematic overestimation of the gap between $CH_3C{=}CH_2^+$ and allyl cation, and we therefore feel justified in casting out the discrepant value.

The discrepancy between experiment and the values summarized in Table II constitutes a systematic error, which limits the confidence that can be placed in ab initio calculations. Pople has recently presented a series of computations that show that a nonclassical structure, bridged protonated acetylene, is a $C_2H_3^+$ isomer of lower energy than the classical vinyl cation.[37] A barrier is calculated to exist between these isomers, and it is conceivable that calculations on the $C_3H_5^+$ homologue err not because allyl cation is too low but because classical $CH_3C{=}CH_2^+$ is too high. If bridged protonated allene or bridged protonated propyne represents a deeper minimum, the energy difference between classical and nonclassical $C_3H_5^+$ structures is greater than the difference between classical and nonclassical vinyl cation. Comparison between the calculational methods that are common to Table II and Pople's survey suggests that the classical–nonclassical energy *difference* for $CH_3C{=}CH_2^+$ would have to be at least 1.5 kcal/mol *more* than that for $C_2H_3^+$ in order to bring the $CH_3C{=}CH_2^+$-allyl energy gap into line with experiment.

Calculations at all levels portray **8** as a bound species in which $CH_3C{=}CH_2^+$ is a major contributing resonance structure. We interpret the ab initio results for **8** as exhibiting a stable electrostatic bond.[38] Calculated properties of **8** exemplify an important feature of ionic bonding in the gas phase, namely, a low barrier to internal rotation perpendicular to a bond axis. As previously noted,[39] this degree of freedom distinguishes ion-molecule complexes from more conventional hydrogen-bonded complexes. The barrier height for 360° rotation about angle Ψ

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(35) Heat of formation of dimethylborane estimated from the isodesmic reaction $Me_3B + H_2 \rightarrow Me_2BH + CH_4$ using 3-21G//3-21G energies from: (a) Carmichael, I. *J. Phys. Chem.* **1986**, *90*, 2057–2060. (b) Budzelaar, P. H. M.; Kos, A. J.; Clark, T.; Schleyer, P. v. R. *Organometallics* **1985**, *4*, 429–437.

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(37) Pople, J. A. *Chem. Phys. Lett.* **1987**, *137*, 10–12.

(38) Although analogous local minima were reported in calculations on other closed-shell, gaseous cations several years ago (for example, Fois, E.; Gamba, A.; Suffritti, G. B.; Simonetta, M.; Szele, I.; Zollinger, H. *J. Phys. Chem.* **1982**, *86*, 3722–3728), their significance was not remarked at the time.

(39) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195–3243.

is comparable to the energy of a vibrational transition, but is lower than the ion–dipole bond energy. Intermediacy of analogous ion–molecule complexes has been demonstrated experimentally for a variety of unimolecular ion decompositions,[39,40] and **8** represents a potential energy minimum that conforms to the description of these intermediates.

The virtual lack of directed valence in the C–F bond of **8** is best illustrated by the potental energy curve for rigid rotation of the $CH_3C{=}CH_2^+$ moiety by angle Ψ in Figure 2. The central carbon is nearly linear ($sp^{1.004}$ hybridized) with its vacant p orbital pointed toward the fluorine along the HF bond axis. As the vacant orbital is rotated out-of-plane by angle Ψ, σ overlap with fluorine decreases and π overlap increases until there is only π overlap with a fluorine lone pair at $\Psi = 90°$. Energies at 90, 180, and 270° represent upper bounds for the values at these extrema since the structure has not been allowed to relax. Vibrational wave functions for the lowest levels are localized in one well or the other. Vibrational wave functions for the highest bound levels are delocalized. The wave function for the asterisked level in Figure 2 (which is 6.0 kcal/mol above the zero point of the lower well) is completely delocalized with nonzero amplitude at $\Psi = 90°$, signifying that in classical terms the ion and molecule orbit about one another while remaining electrostatically bound.

In Figure 2 the angular coordinate Ψ corresponds to a bending coordinate in the lowest vibrational levels. This transforms into hindered internal rotation perpendicular to the C–F bond axis at the highest bound levels.[41] It is not uncommon for high amplitude bending motions to correspond to internal rotation that abolishes directed valence, yet leaves the molecular fragments bound to one another (the thermal isomerization of methyl isocyanide is a good example). It is characteristic of ion–molecule complexes, however, that the barrier to this type of internal rotation is not only lower than the thermodynamic dissociation barrier for the molecular fragments but also that its magnitude is not substantially greater than one vibrational quantum of stretch or bend elsewhere in the molecule. If vibrational excitation in the organic or the HF moiety randomizes throughout the molecule, the energy is enough to set the two fragments into orbit about one another. Other calculations have described stable ion–molecule complexes.[42] Our results for **8** depicts a closed-shell case that does not possess any hydrogen-bonded isomers.

The two lowest energy isomers of **1** are 1-fluoro-1-propyl cation (**3**) and fluoretanium (**6**). Experimentally we know that fluoretanium is not accessible from **1**, for the hydrogens would scramble if the interconversion $\mathbf{1} \rightleftarrows \mathbf{6}$ took place. Our previously published studies of neutral products derived from $CD_3CFCH_3^+$ (**1**-d_3) have shown that hydrogens do not exchange between the two ends, neither in stable ions nor in those that expel hydrogen fluoride. For instance, when the different deuterated analogues from decomposition of **1**-d_3 are quenched by fluoride abstraction, the recovered neutral products have ^{19}F NMR spectra that are well resolved from one another. The splitting pattern of recovered $CH_2{=}CFCD_3$ is distinctive, and no $CDH{=}CFCD_2H$ can be detected.[2] Therefore the barrier separating **6** from **1** must be higher than the vicinal elimination barrier.

Interconversion of **1** with **3** cannot be excluded, for that reaction would not lead to hydrogen scrambling. The barrier to 1,2-hydrogen shift in **1** (estimated by the method of Frenking and Schwarz[5]) is not that much higher than the thermodynamic barrier from vicinal elimination. But our ab initio calculations show that the conformation that would result from hydrogen shift, **2b**, proceeds without any further barrier to yield **3** via methyl shift. Reaction 2 does not take place because the intermediate cation, **2**, is diverted by further rearrangement to an ion that cannot readily undergo elimination.

The ab initio calculations show that epifluoronium ion **4** is accessible from **3** via **2**. The interconversion of **1** and **4** need not lead to hydrogen scrambling, so it cannot be ruled out on the basis of the experiments that have been performed to date. Ion **4** has much more the character of resonance structure **11** than it does of **2**. Structure **2** would have one short C–C bond and one long C–C bond, while **11** should have two C–C bonds of approximately equal length. The C–C bond lengths of **4** are within 0.02 Å of one another.

By rules of orbital symmetry, thermal 1,3-elimination from **11** would have to proceed antarafacially to yield allyl cation. The geometry required for the antarafacial transition state is greatly distorted from the geometry of **4**. These arguments account for the failure to observe allyl cation from decomposition of **1**. Ions **5** and **7** could plausibly decompose to allyl cation, but they are high-energy isomers that would require unprecedented rearrangements to be accessible from **1**.

Conclusions

EBFlow experiments demonstrate that $CH_3C{=}CH_2^+$ from electron impact on *tert*-butyl fluoride is formed via vicinal elimination of hydrogen fluoride from ion **1**. Among the $C_3H_6F^+$ isomers surveyed, ab initio calculations show that there is a stable minimum for each one that corresponds to a stable isoelectronic C_3H_6O isomer. Structures **2** and **11**, which correspond to C_3H_6O zwitterions, are not stable; the former undergoes barrier-free isomerization and the latter is a contributing resonance structure of ion **4**. Ion **8** is an ion–molecule complex that corresponds to a product-like energy minimum along the reaction coordinate for vicinal elimination. Experimental consequences of calculational predictions are under active investigation.

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Supplementary Material Available: Listing of Cartesian coordinates of optimized geometries and unscaled vibrational frequencies from normal mode analyses (10 pages). Ordering information is given on any current masthead page.

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