Theoretical Structures and Stabilities of $C_3H_5^+$ and $C_3H_2F_3^+$ Cations†

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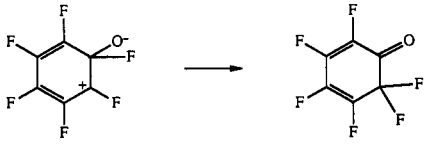
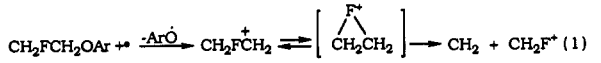
The structures and energies of $C_3H_2F_3^+$ isomers have been calculated, and at the MP4(SDQ)/6-31G**//HF/6-31G* + ZPVE level fluorine migration converting $CH_2{=}C^+CF_3$ (3) to the allylic cation $CH_2{=}CFCF_2^+$ (4) is exothermic by 31.5 kcal/mol, with a barrier involving a bridged fluoronium ion of only 6.1 kcal/mol. Rearrangement of 3 to $CHF{=}CHCF_2^+$ (16) is exothermic by 44.9 kcal/mol and occurs by a multistep process including a 1,3-fluorine migration with no barrier higher than 0.3 kcal/mol. Comparative studies of $C_3H_5^+$ are also reported. It is concluded that 3 is a good candidate for an experimental search for fluorine migration in carbocations.

Introduction

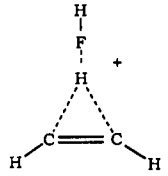
The intermediacy of cyclic halonium ions has been well documented in both the solution[1a] and gas phases.[1b] For the halogens bromine, chlorine, and iodine the bridged cyclic cations are in general lower in energy than the corresponding open-chain isomers.[1] In contrast, there is no definitive solution-phase example of either a cyclic fluoronium ion[1c] or of direct fluorine migration in a carbocation,[2] although a suggestion[3] of fluorine migration in the possible zwitterionic intermediate shown warrants further study.



Gas-phase results by Ciommer and Schwarz were suggested[4] to support fluorine migration in the fluoroethyl cation (eq 1). Beginning with singly ^{13}C-labeled precursor the product showed scrambling of ^{13}C into both the fragments shown. This result is in qualitative agreement with recent theoretical calculations (MP2/6-31G*)[5] which predict that the symmetric cyclic fluoroethyl cation is a minimum on the $C_2H_4F^+$ energy hypersurface. An important feature of this latter study was the conclusion that the energy surface could not be properly defined (even qualitatively) unless electron-correlation terms were included in the wave function. However, it has also been suggested[6a] that the results of Ciommer and Schwarz[4] can be explained by the ion molecule complex of HF and a vinyl cation depicted.

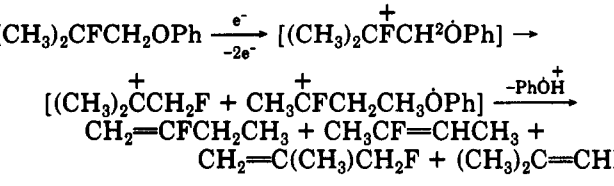


(1)



Fluorine migration was observed in the 2-fluoro-2-methyl-1-propyl cation (Scheme I)[6a] generated from the

Scheme I



† Dedicated to Professor P. v. R. Schleyer on the occasion of his 60th birthday.

phenyl ether by the electron bombardment flow technique,[6b] which permits isolation and direct observation of the neutral products resulting from the gaseous ions. The study of selectively deuterated precursors excluded processes besides 1,2-fluoride migrations for formation of the rearranged products.

Studies by Tedder et al.[7] of gas-phase addition of CF_3^+ to ethylene showed formation of fragment ions whose formation could be rationalized by 1,3-fluorine migrations as shown in eq 2.

$$CF_3^+ + CH_2{=}CH_2 \rightarrow CF_3CH_2\overset{+}{C}H_2 \rightarrow \overset{+}{C}F_2CH_2CH_2F \quad (2)$$

Our previous theoretical study suggested that 1,2-fluorine migrations in the cation $CF_3CH_2^+$ 1 should occur in the gas phase, as shown in eq 3, where 2 is the global minimum.[8]

$$\underset{1}{CF_3CH_2^+} \rightarrow \underset{2}{CF_2{}^+CH_2F} \rightarrow CHF_2\overset{+}{C}HF \quad (3)$$

Conversion of 1 to 2 has a calculated barrier of approximately 3 kcal/mol (HF/6-31G*//HF/6-31G*).[8] The fact that 2 is significantly more stable that 1 illustrates that fluorines β to a positive charge are destabilizing by σ electron-withdrawing effects, while fluorines bonded directly to a cationic center show a stabilizing π-electron donation,[2,9] as illustrated by the exothermicity of the reaction of eq 4.[10]

$$CHF_3 + CH_3^+ \rightarrow CH_4 + CF_3^+ \qquad \Delta H = -13.2 \text{ kcal/mol} \quad (4)$$

To design a system in which rearrangement to a more stable cation via a fluorine migration would be observable we considered the hexafluorobutenyl cation. Qualitative considerations suggested this cation could undergo a 1,2-

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Table I. Calculated Energies for $C_3H_5^+$ Cations

	total energy (hartrees)			
cation	6-31G*[a]	MP2[b]	MP3[b]	MP4SDQ[b]
6	-116.193213	-116.580638	-116.610258	-116.615486
5	-116.166650	-116.558076	-116.589329	-116.595690
7	-116.132165	-116.527342	-116.558168	-116.564055
8	-116.138066	-116.536383	-116.565091	-116.571207
9	-116.141229	-116.527842	-116.559645	-116.566661
10	-116.105329	-116.514872	-116.542521	-116.547497

[a] Hartree–Fock energy using 6-31G* basis set and 6-31G* optimized geometry. [b] Moller–Plesset energy using 6-31G** basis set and HF/6-31G* geometry.

fluorine shift to give the much more stable allyl cation, as shown in eq 5.

$$CF_3CH{=}C^+CF_3 \rightarrow CF_3CH{=}CFCF_2^+ \leftrightarrow CF_3CH^+CF{=}CF_2 \quad (5)$$

For economic reasons the hexafluorobutenyl system is too large for high-level theoretical calculations, so the 3,3,3-trifluoro-2-propenyl cation 3 was chosen for computational study. This mutation should not alter the significance of the results since the main reaction under consideration is still the 1,2-fluorine migration from a destabilized vinylic cation to an allylic cation (eq 6).

$$\underset{3}{CH_2{=}\overset{+}{C}CF_3} \rightarrow \underset{4}{CH_2{=}CFCF_2^+} \leftrightarrow CH_2^+CF{=}CF_2 \quad (6)$$

For comparison the analogous hydrocarbon rearrangement is also considered, namely the conversion of the 2-propenyl cation (5) to the allyl cation (6) (eq 7). Previous work[11] at the HF level shows the reaction of eq 7 has a barrier of about 17 kcal/mol. This system is of particular interest because 5 is the major product in the protonation of either propyne or allene in either gas[12a,b] or solution[12c] phase, despite the apparent greater stability of 6.

$$\underset{5}{CH_2{=}\overset{+}{C}CH_3} \rightarrow \underset{6}{CH_2{=}CHCH_2^+} \quad (7)$$

Methodology

Standard ab initio molecular orbital calculations were carried out using both the vectorized CRAY[13] version of the GAUSSIAN 86 package;[14a] and the MONSTERGAUSS[14b,c] program on several minicomputers, including Apollo DN10000 and DN3500, SUN 3-260, and IRIS 4D120. Geometry optimization was achieved by gradient techniques using either the Optimally Conditioned method[15] or the Berny Optimizer.[16] All such stationary points were optimized at the Hartree–Fock (HF) level using the split-valence 6-31G* basis set.[15] Moller–Plesset perturbation theory at full second, third, and partial fourth orders was used to recalculate the energy of critical points employing the 6-31G** basis set.[15] Force constants, harmonic frequencies, and zero-point vibrational energies (ZPVE) were determined at 6-31G* by numerically differentiating the analytical first derivatives of the restricted Hartree–Fock wave function. For all stationary points, localized molecular orbitals were obtained by employing the Boys criterion.[17] Bond orders and valence indices were calculated using Mayer's method.[18]

Table II. Calculated Energies for $C_3H_5^+$ Cations

	relative energy (kcal/mol)				
cation	6-31G*[a]	ZPVE[b]	MP2[c]	MP3[c]	MP4SDQ[c]
6	0.0 (0)	41.5	0.0	0.0	0.0
5	16.7 (0)	38.9	11.6	10.5	9.8
7	38.3 (1)	38.5	30.4	29.7	29.3
8	34.6 (1)	38.1	24.4	24.9	24.4
9	32.6 (0)	39.3	30.9	29.6	28.4
10	55.1 (1)	38.7	38.5	39.7	39.9

[a] Hartree–Fock energy using 6-31G* basis set and 6-31G* geometry The number of imaginary frequencies is given in parentheses. [b] Zero point vibrational energy, calculated at HF/6-31G* scaled by the factor 0.9. [c] Moller–Plesset energy using 6-31G** basis set and 6-31G* geometry, including correction for ZPVE.

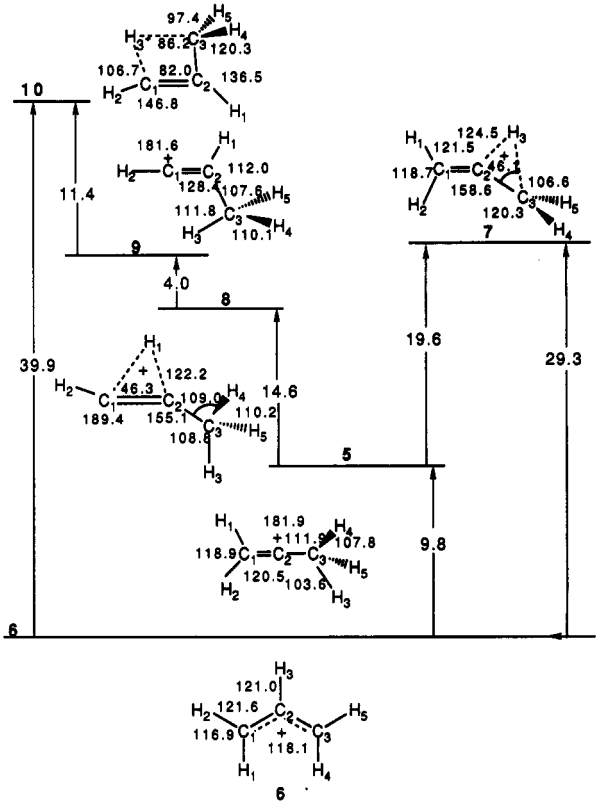

Figure 1. Calculated relative energies for $C_3H_5^+$ (kcal/mol) at MP4(SDQ)/6-31G**//HF/6-31G* + ZPVE.

Results

Calculated energies for structures 3–16 are presented in Tables I–IV. In each case the Hartree–Fock energy is followed by several Moller–Plesset energy calculations. The MP2 and MP3 wave functions are correct to full

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(13) Calculations run on the CRAY X-MP/24 Supercomputer at the Ontario Centre for Large Scale Computations (OCLSC).

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(18) Mayer, I. *Int. J. Quantum Chem.* **1986**, *29*, 477–483.

Table III. Calculated Energies for $C_3H_2F_3^+$ Cations

cation	total energy (hartrees)				
	3-21G[a]	6-31G*[b]	MP2[c]	MP3[c]	MP4SDQ[c]
16	-410.493487	-412.752362	-413.628986	-413.633347	-413.652764
17	-410.452699	-412.718473	-413.594963	-413.601117	-413.621673
14	-410.426191	-412.680910	-413.545466	-413.557573	-413.576903
13	-410.389162	-412.666740	-413.548350	-413.555811	-413.573472
3	-410.418940	-412.679438	-413.544111	-413.556400	-413.576171
3a	-410.418566	-412.679200	-413.543753	-413.556090	-413.575822
11	-410.394152	-412.650608	-413.541097	-413.544752	-413.567654
4	-410.468079	-412.727440	-413.604570	-413.610710	-413.630079
4a	-410.423497	-412.693688	-413.571628	-413.578227	-413.599582
12	-410.367998	-412.638883	-413.517847	-413.525613	-413.546083
15	-410.414852	-412.665055	-413.549199	-413.556972	-413.577713

[a] Hartree–Fock energy using 3-21G basis set and 3-21G geometry. [b] Hartree–Fock energy using 6-31G* basis set and 6-31G* geometry. [c] Moller–Plesset energy using 6-31G** basis set and 6-31G* geometry.

Table IV. Calculated Energies for $C_3H_2F_3^+$ Cations

cation	relative energy (kcal/mol)					
	3-21G[a]	6-31G*[b]	ZPVE[c]	MP2[d]	MP3[d]	MP4SDQ[d]
16	0.0	0.0 (0)	29.1	0.0	0.0	0.0
16a	25.6	21.3 (1)	28.5	20.8	19.6	18.9
14	42.2	44.8 (0)	26.3	49.6	44.8	44.8
13	65.5	53.7 (1)	24.5	46.0	44.1	45.2
3	46.8	45.8 (0)	25.9	50.1	45.1	44.9
3a	47.0	45.9 (1)	25.8	50.2	45.2	45.0
11	62.3	63.9 (1)	26.7	52.8	53.2	51.0
4	15.9	15.6 (0)	28.4	14.6	13.5	13.5
4a	43.9	36.8 (1)	28.1	35.0	33.6	32.4
12	78.8	71.2 (0)	27.2	67.9	65.7	65.0
15	49.3	54.8 (1)	27.1	48.1	45.9	45.1

[a] Hartree–Fock calculation using 3-21G basis set and 3-21G geometry. [b] Hartree–Fock calculation using 6-31G* basis set and 6-31G* geometry. The number of imaginary frequencies is given in parentheses. [c] Zero point vibrational energy as calculated at HF/6-31G* scaled by 0.9. [d] Moller–Plesset calculation using 6-31G** basis set and 6-31G* geometry, including ZPVE.

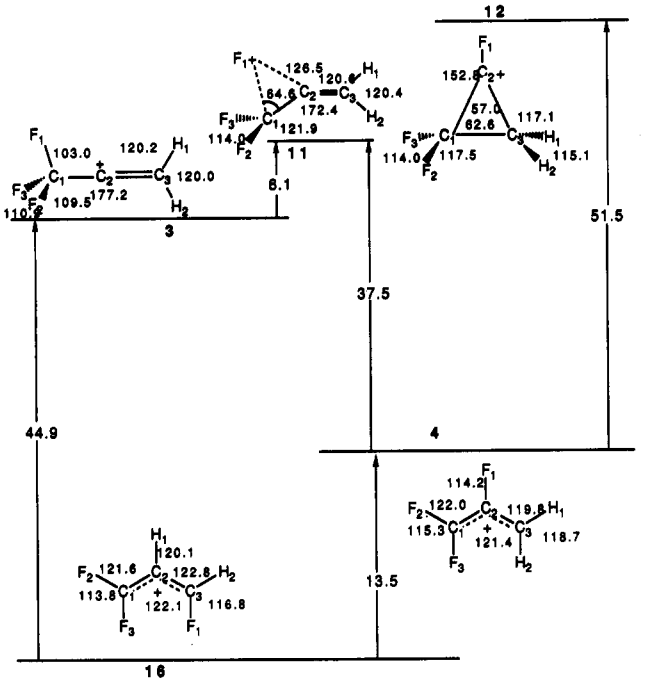


Figure 2. Calculated relative energies for $C_3H_2F_3^+$ (kcal/mol) at MP4(SDQ)/6-31G**//HF/6-31G* + ZPVE.

second and third orders, respectively. The MP4 wave function does not include triple substitutions. The basis set used for all Moller–Plesset calculations was 6-31G**. Correction for differences in relative zero-point vibrational energies was possible at the HF/6-31G*//HF/6-31G* level and are included (see Tables II and IV). The ZPVE were derived from calculated frequencies and scaled by a factor of 0.9.[15] Table V contains a summary of calculated activation energies for selected processes.

Table V. Calculated Activation Energies

reaction	E_A (kcal/mol)					
	3-21G[a]	6-31G*[b]	6-31G*[c]	MP2[d]	MP3[d]	MP4SD[d]
3 → 4	15.6	18.1	18.9	2.7	8.1	6.1
3 → 14	18.7	8.0	6.6	(-4.1)	(-1.0)	0.3
14 → 16	7.1	9.9	10.7	(-1.5)	1.1	0.3
5 → 6		21.6	21.3	19.0	19.3	19.6
5 → 9		17.9	17.2			
9 → 6		22.5	21.8	7.5	10.0	11.4

[a] Hartree–Fock energy using 3-21G basis set and 3-21G geometry. [b] Hartree–Fock energy using 6-31G* basis set and 6-31G* geometry. [c] Hartree–Fock energy after correction for differences in zero-point energies. [d] Moller–Plesset energy using 6-31G** basis set and 6-31G* geometry, including ZPVE.

Table VI. Calculated Bond Orders[a] for $C_3H_5^+$ Cations (6-31G*)

bond	cation					
	5	**6**	**7**	**8**	**9**	**10**
C_1C_2	2.06	1.44	1.94	2.31	2.10	1.85
C_2C_3	0.99	1.44	1.25	0.89	0.89	0.93
H_1C_1	0.84	0.91	0.90	0.17		
H_1C_2				0.69	0.81	0.86
H_2C_1	0.84	0.90	0.90	0.80	0.79	0.82
H_3C_1						0.60
H_3C_2		0.90	0.66			
H_3C_3	0.84		0.22	0.91	0.93	0.30
$H_{4,5}C_3$	0.89		0.86	0.91	0.91	0.95

[a] Bond orders calculated using the method of Mayer, ref 18.

The 6-31G* fully optimized geometries for compounds 3–16 are given in Tables 8–11 (supplementary material). The bond distances are summarized in the structures in the text, while the bond angles are summarized on the structures in Figures 1–3. Bond orders appear in Tables

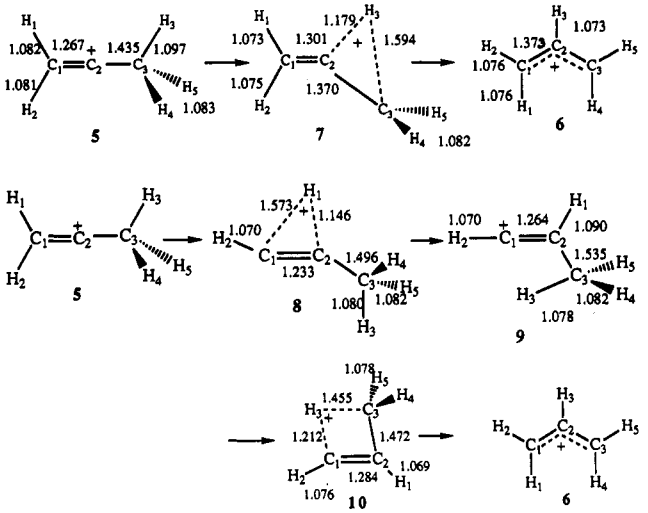
Table VII. Calculated Bond Orders for $C_3H_2F_3^+$ Cations (6-31G*)

	cation									
bond	3	3a	4	4a	11	13	14	15	16	16a
C_1C_2	0.76	0.76	1.09	0.86	0.88	0.70	0.82	1.02	1.23	0.94
C_2C_3	1.99	1.99	1.44	1.70	1.82	2.66	2.00	1.97	1.32	1.64
H_1C_2						0.37	0.75	0.82	0.82	0.80
H_1C_3	0.78	0.78	0.85	0.86	0.83	0.44				
H_2C_3	0.78	0.78	0.86	0.89	0.84	0.74	0.73	0.80	0.82	0.83
F_1C_1	0.90	0.96			0.49	0.94	0.89	0.60		
F_1C_2			0.91	0.90	0.53					
F_1C_3								0.31	1.01	0.93
F_2C_1	0.95	0.92	1.03	1.14	1.07	0.95	0.93	1.07	1.01	1.13
F_3C_1	0.95	0.92	1.02	1.14	1.07	0.95	0.93	1.97	1.03	1.13

VI and VII, and Tables 12 and 13 (supplementary material) contain the predicted IR vibrational frequencies (unscaled) calculated at the HF/6-31G*//HF/6-31G* level. Z-Matrices for all compounds are supplied as supplementary material.

Discussion

Although the $C_3H_5^+$ energy surface has been studied previously[11] higher level calculations were desirable. Structures **5–10** were fully optimized, and energies up to the MP4(SDQ)/6-31G**//HF/6-31G* + ZPVE level were calculated (Figure 1). Even though this is a very limited survey of the $C_3H_5^+$ energy surface, it is sufficient for comparison to the more in depth analysis of the $C_3H_2F_3^+$ surface.



The optimized geometries and Hartree–Fock energies for cations **5**, **6**, and **9** are in excellent agreement with those reported elsewhere.[11] Structure **7** represents the transition state for the 1,2-H migration from 2-propenyl cation (**5**) to the allyl cation (**6**). It contains a forming bond length of only 1.179 Å compared to the breaking bond length of 1.594 Å. Thus, the transition state is productlike. Similarly, at the Hartree–Fock level, **8** represents the transition state for the 1,2-H migration from the 2-propenyl cation (**5**) to the 1-propenyl isomer (**9**).

Evidence that **8** contains a true 3-center 2-electron bond is provided by a simple localized molecular orbital analysis which shows quite clearly the existence of a bonding orbital centered between the bridging hydrogen and the carbons of the double bond. The HF/6-31G* geometry of **8** shows extensive H_1C_2 bond formation (bond order 0.69) and almost complete H_1C_1 bond cleavage (bond order 0.17). Vibrational analysis shows that **8** has one negative frequency, characteristic of a first-order saddle point. The 6-31G*//HF/6-31G* calculated energies give **8** to be 0.7 kcal/mol less stable than **9**, consistent with **8** being a

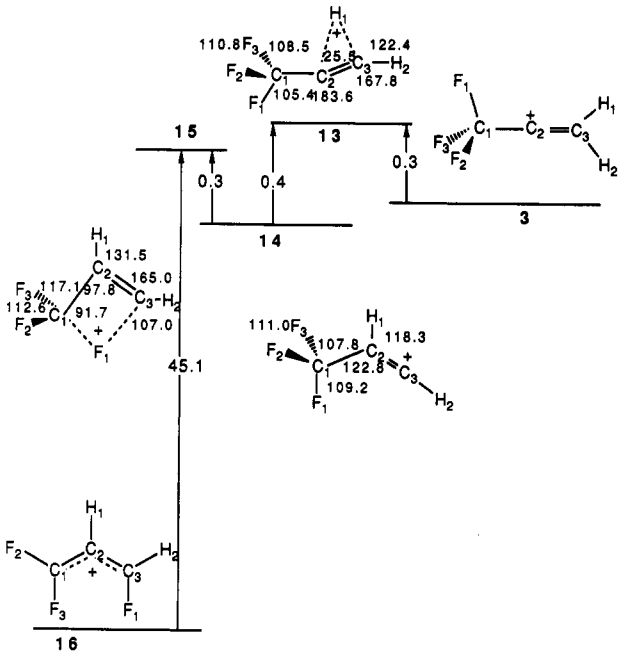


Figure 3. Calculated relative energies for $C_3H_2F_3^+$ (kcal/mol) at MP4(SDQ)/6-31G**//HF/6-31G* + ZPVE.

transition state. However, Moller–Plesset single-point calculations predict that the bridged structure **8** is more stable than the classical 1-propenyl cation (**9**) by 4.0 kcal/mol. This reversal is due to the inclusion of electron correlation terms in the wave function. Such calculations favor nonclassical cations since they allow for a more favorable distribution of crowded electrons, and such a reversal in stabilities is well precedented.[9,11,19]

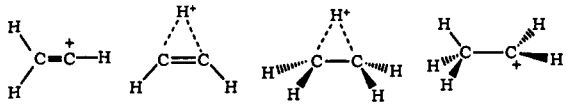
The last structure in this series, **10**, is the transition state for the 1,3-H migration of **9** to form **6**. This process is thermodynamically very favorable, being exothermic by 28.4 kcal/mol (MP4(SDQ)/6-31G**//HF/6-31G* + ZPVE). The geometry of **10** is productlike with a C_1H_3 bond-forming length of 1.212 Å and a bond breaking length (C_3H_3) of 1.456 Å, and LMO analysis shows the presence of a 2-electron 3-center bond.

An interesting feature of this surface is that the barrier to 1,3-H migration (**9** to **6**) is significantly lower (11.4 kcal/mol) than the barrier to the corresponding 1,2-H shift from **5** to **6** (19.6 kcal/mol) at MP4(SDQ/6-31G**//HF/6-31G* + ZPVE).

As mentioned earlier, the true nature of structures **8** and **9** is uncertain. Studies[11] on the $C_2H_3^+$ analogue show that the classical cation **17** is the only minimum at 6-31G*. However, upon MP2 optimization the bridged structure

(19) (a) Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 7325–7328. (b) Saunders, M.; Laidig, K. E.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652–7659.

18 also becomes a minimum. On the other hand, studies[11] on the ethyl cation showed that at 6-31G* both 19 and 20 are local minima, whereas, after MP2 optimization 20 collapses without barrier to give 19 as the only stable minimum. These results, coupled with our findings, indicate that compounds 5, 6, and 8 are all local minima, whereas 7 and 10 are true first-order saddle points. At this time it is fruitless to guess as to whether 9 is a saddle point or a local minimum. In order to determine this, full MP2 optimization followed by a vibrational analysis will be necessary.

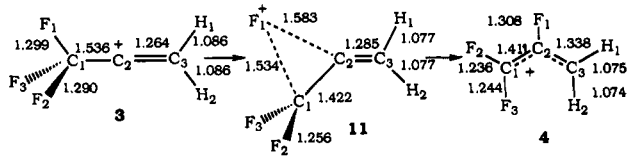


17 18 19 20

$C_3H_2F_3^+$. Structure 3 is the 3,3,3-trifluoro-2-propenyl cation, the so-called "reactant" for this study. It has essentially the classical vinylic cation geometry,[11] with a single bond length of 1.536 Å and double bond length of 1.264 Å. However, the in-plane fluorine atom has already begun to show signs of migration, with a $C_2C_1F_1$ bond angle of only 103.0° (versus 109.5° for F_2, F_3).

Structure 3a is a rotational isomer of 3 that is the transition state for rotation around the carbon–carbon single bond. Since this is the less stable of the two rotamers, it will not be considered further.

Structure 11 is the transition state for the 1,2-fluorine migration from 3 to 4. It exhibits a shortened carbon–carbon single bond length of 1.422 Å, consistent with the presence of a 2-electron 3-center bond. The migrating fluorine is bonded almost equally to both C_1 and C_2 (bond orders of 0.49 and 0.53, respectively). This is consistent with the study of $C_2H_4F^+$ which found that the lowest energy bridged structure was the one with C_{2v} symmetry,[5] but is in contrast to the hydrocarbon analogue 7 where the forming C–H bond is much more extensively developed. The CCC bond angle (172.4°) has decreased to reflect the changing state of hybridization of C_2.

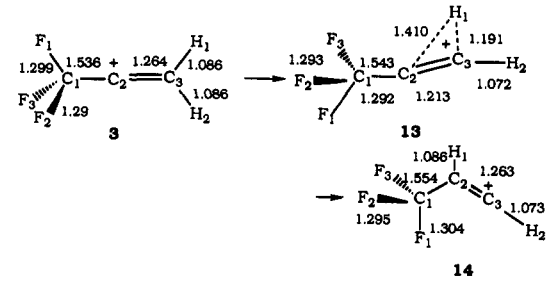


3 11 4

Cation 4 is the product of the 1,2-fluorine migration and is a local minimum 13.5 kcal/mol above the global minimum. Although this cation has an allylic structure the positive charge is concentrated on the CF_2 carbon (C_1) as shown by the longer C_1C_2 (1.411 Å) bond as compared to the C_2C_3 bond (1.338 Å). Both the C_1F_2 (1.236 Å) and C_1F_3 (1.244 Å) bonds are significantly shorter than C_2F_1 (1.308 Å), as a result of extensive π-donation from F_2 and F_3 towards the positively charged C_1.

Structure 4a is the perpendicular 1,1,2-trifluoroallyl cation and represents the transition state for rotation of the CF_2^+ in 4. It is 18.9 kcal/mol higher in energy than 4 and has C_1C_2 and C_2C_3 bond lengths of 1.494 and 1.305 Å, respectively, characteristic of single and double bonds, respectively. The C^+–F bond lengths in this ion are exceptionally short (1.227), implying a great deal of electron donation from fluorine to carbon. The calculated bond order of 1.14 is consistent with this analysis.

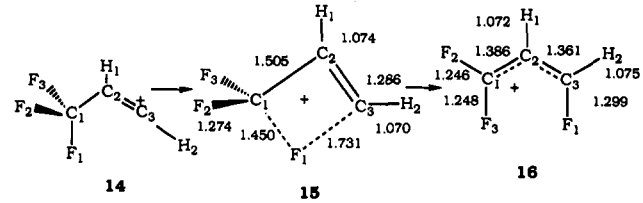
Structure 13 is believed to be the transition state for 1,2-hydrogen migration from 3 to 14. The H_1C_3 bond length (1.191 Å) is shorter than the H_1C_2 forming length (1.410 Å), suggesting this is an early, or reactant-like, transition state. The C_2C_3 bond order has increased to 2.66, showing the presence of extra electrons. LMO analysis predicts the existence of a 3-center 2-electron bond between H_1 and C_2C_3, and vibrational analysis gives one imaginary frequency.



3 13 14

In the 3,3,3-trifluoro-1-propenyl cation (14), the carbon–carbon bond lengths are almost identical with those in the 2-propenyl isomer (3). This is essentially a classical primary vinylic cation, with no special geometrical features.

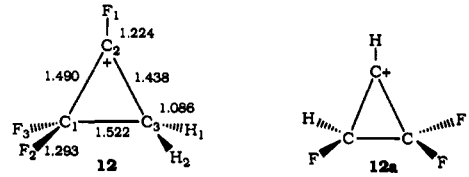
Structure 15 is the four-membered transition state for the 1,3-fluorine migration from 14 to 16. Once again, the migrating atom is coplanar with the carbon backbone. This structure is considerably reactant-like. The bond order for the breaking the F_1C_1 bond is 0.60, while the bond order for the forming the F_1C_3 bond is only 0.31. The carbon–carbon–carbon internal bond angle is a strained 97.8°.



14 15 16

The 1,1,3-trifluoroallyl cation (16) is the global minimum on the $C_3H_2F_3^+$ energy hypersurface. The geometry of 16 is typically allylic, with the C_1C_2 and C_2C_3 bond lengths being practically identical. Structure 16a, with the CF_2^+ group twisted out of plane, is 18.9 kcal/mol higher in energy, representing its loss of allylic conjugation.

The cyclopropyl cation 12 is formed by the disrotatory closing of cation 4. It is energetically quite unstable, lying 65.0 kcal/mol above the global minimum. Its structural features are interesting. The $C_1C_2C_3$ bond angle (57.0°) and short C_2C_3 bond length (1.438 Å) seem to imply extensive electron donation, or delocalization, from F_1. The bonds C_1C_2 and C_2C_3 are both much shorter than C_1C_3. This is most likely due to F_2 and F_3, which are strongly electron withdrawing. It should be noted that there was no attempt to find a "transition state" for the closing of 4 to 12. For the $C_3H_5^+$ analogue, no barrier was found[11] for the reverse process (ring opening), and hence the transition state is inconsequential. No minimum could be located for a product of a similar ring closing from cation 16 to give 12a in which all the fluorines would be destabilizing.



12 12a

Figures 2 and 3 are a qualitative energy level diagram for various $C_3H_2F_3^+$ isomers at the MP4(SDQ)/6-

31G**//HF/6-31G* + ZPVE level. The most striking contrast between this and the corresponding representations at HF/6-13G*//HF/6-31G* + ZPVE is that the higher level of theory favors bridged cations 11, 13, and 15. Thus, the calculated activation energy for the conversion of 3 to 4 is lowered from 19.0 kcal/mol at HF/6-31G*//HF/6-31G* + ZPVE to only 6.1 kcal/mol at MP4(SDQ)/6-31G**//HF/6-31G* + ZPVE. This process corresponds to the 1,2-fluorine shift from the 3,3,3-trifluoro-2-propenyl cation (3) to the 1,1,2-trifluoroallyl cation (4).

Similarly, the barrier to 1,2-hydrogen migration from 3 to 14 is reduced to a mere 0.3 kcal/mol when electron-correlation effects are accounted for. Interestingly, structure 13 is still predicted to be a saddle point. This is in contrast to the studies on smaller systems where the bridging nonclassical cation was found to be a local minimum and not a transition state, after inclusion of electron correlation.[11]

It is striking that the *primary* and *secondary* vinyl cations 3 and 14 are predicted to be of very similar stability. This illustrates a strong destabilizing effect of CF_3 relative to hydrogen both α and β to a vinylic carbocation center.

1,3-Fluorine migration from 14 via the four-membered transition state 15 leads to 16, the global minimum. Results at HF/6-31G**//HF/6-31G* + ZPVE predict the barrier for such a conversion to be 10.8 kcal/mol. However, at MP4(SDQ)/6-31G**//HF/6-31G* + ZPVE this barrier all but disappears. It is also remarkable that 3, 13, 14, and 15 are so close in energy as to be not energetically distinguishable. As noted by a referee "formation of 3 would lead to a species that is just a point on a potential energy hypersurface that immediately collapses to 16". Since the isomerization of 3 to 16 is exothermic by 40–50 kcal/mol, with little or no barrier, one would conclude that reaction of the 3,3,3-trifluoro-2-propenyl cation 3 in the gas phase should lead mainly to formation of the 1,1,3-trifluoroallyl cation 16, with competing formation of the less stable isomer 4. Solvation effects might result in a somewhat different pattern in solution.

Conclusions

Based on these calculations, the $C_3H_2F_3^+$ system should be ideal for observing fluorine migrations. It is predicted that the relatively unstable 3,3,3-trifluoro-2-propenyl cation 3 can readily rearrange to either the 1,1,2-trifluoroallyl cation 4 or the 1,1,3-trifluoroallyl cation 16. By analogy, rearrangement via 1,2- or 1,3-fluorine shifts to allyl cations should be favorable in the system $CF_3CH{=}C^+CF_3$ as well. Efforts to observe these reactions experimentally are underway.

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Supplementary Material Available: Z-Matrices for 3–16 and tables of bond lengths, bond angles, and IR frequencies (23 pages). Ordering information is given on any current masthead page.

Regiochemistry of the Coupling of Aryl Radicals with Nucleophiles Derived from the Naphthyl System. Experimental and Theoretical Studies

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We here report the photostimulated reaction of unactivated aromatic halides with ambident nucleophiles derived from the naphthyl system such as 1- and 2-naphthylamide, 2-naphthoxide, 2-naphthalenethiolate, and 2-naphthaleneselenate ions, by the $S_{RN}1$ mechanism of nucleophilic substitution. According to our experimental results, C-arylation in position 1 of the naphthyl moiety is the only reaction observed with 2-naphthoxide ions and it is favored over N-arylation with 1- and 2-naphthylamide ions. Heteroatom arylation is preferred over C-arylation with 2-naphthalenethiolate ions while it is the only observed reaction with 2-naphthaleneselenate ions. A theoretical study was carried out to explain the regiochemistry of the system. In competition experiments, 2-naphthalenethiolate ions proved to be 1.8 ± 0.2 times more reactive than 2-naphthoxide ions for C-substitution toward *p*-anisyl radicals in liquid ammonia.

The radical mechanism of aromatic nucleophilic substitution, or $S_{RN}1$, is a well-known process by which a substitution is produced on a nonactivated adequately substituted substrate.[1] This nucleophilic substitution mechanism is a chain process that involves radicals and radical anions as intermediates. The main steps of this mechanism are sketched in Scheme I.

Scheme I

$$(RX)^{\bullet-} \rightarrow R^{\bullet} + X^- \quad (1)$$

$$R^{\bullet} + Nu^- \rightarrow (RNu)^{\bullet-} \quad (2)$$

$$(RNu)^{\bullet-} + RX \rightarrow RNu + (RX)^{\bullet-} \quad (3)$$

Ambident behavior of anions in aromatic $S_{RN}1$ reactions is very rare. However, it has been found that aryl radicals

(1) For reviews, see: (a) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph 178; American Chemical Society: Washington, DC, 1983. (b) Bowman, W. R. *Chem. Soc. Rev.* **1988**, *17*, 283.

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