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A Quantum Chemical Study on Electrophilic Addition

Part I. Reaction of Fluorine with Ethylene

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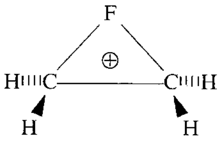
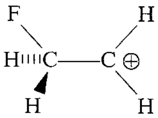
Non-empirical SCF-MO calculations were carried out on two limiting structures of $C_2H_4F^+$, corresponding to the cyclic and open valence tautomers, both of which are possible reaction intermediates of the electrophilic addition reaction of F_2 to $CH_2=CH_2$. It was found that both species had thermodynamic stability, corresponding to two distinct minima on the energy surface. However, the 2-fluoroethyl carbonium ion showed a greater stability than the fluoronium ion by about 10 kcal/mole.

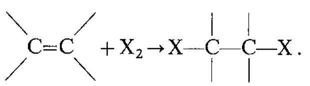




Key words: Fluorine, reaction with ethylene – Ethylene, reaction of fluorine with ~ – Electrophilic addition

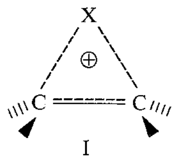
1. Introduction

The addition of halogens to olefins has long been known to be electrophilic [1]; producing an intermediate halonium ion which subsequently combines with a halide ion to form the dihalide.

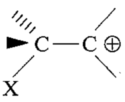


$$\rangle C=C\langle + X_2 \rightarrow X-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X. \tag{1}$$

The products of this type of reaction, depending upon the type of substituents attached to the double bond [2, 3], are often formed by a stereospecific anti addition and this has been interpreted as evidence for a cyclic or bridged halonium ion (I) as an intermediate instead of the open cation (II).



I

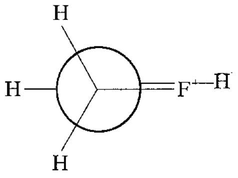


II

Recent nmr investigations of halonium ions in solvents of low nucleophilicity show that in solution these two cations are of similar energy with the position of the equilibrium varying with the halogen. Cations containing iodine and bromine are cyclic [4–8], and chloronium ions are also usually cyclic but with the parent (unsubstituted) cation existing as an equilibrium mixture of the open and cyclic ions [9]. Cyclic fluoronium ions have not been observed to date, but the fluorine in the open cations rapidly exchanges between the two carbon atoms of this ion [9, 10].

The simplest electrophilic reaction, addition of a proton to ethylene to form the ethyl cation, has been the subject of several molecular orbital investigations, both semi-empirical [11–13] and *ab initio*. Most predict the classical, or open cation to be the more stable, with the profile for their interconversion showing no transition state [14–16]. In the most extensive *ab initio* calculations however, Hariharan, Lathan and Pople [16] showed that inclusion of *d*-functions on the carbon atoms and a *p*-function on the bridging hydrogen stabilized the cyclic structure relative to the open one. Further they predicted that the cyclic ion would be the more stable for the Hartree-Fock wave functions.

Clark and Lilley [17, 18] have used *ab initio* molecular orbital calculations to show that the fluoroethyl cation *bridged by hydrogen* is of intermediate energy between the more stable 1-fluoroethyl cation and the 2-fluoroethyl cation. Again the profile for interconversion of these ions is without a transition state. The optimum conformation of the 2-fluoroethyl cation has been shown to be that in which fluorine eclipses a hydrogen atom as in the Newman projection (III).



III

This agrees with molecular orbital predictions of the effect of electronegative substituents on the conformation of substituted methyl groups adjacent to a planar carbonium ion centre [19].

We are currently carrying out a systematic study of the addition of halogens to carbon-carbon double and triple bonds. Initially we have examined the electrophilic addition of fluorine to ethylene (Eq. 1) as a model system, although in practice free radical reactions are energetically more favourable for these two molecules.

In the present work we have used a large basis set of Gaussian type functions to optimize the geometries of both the cyclic ethylfluoronium and 2-fluoroethyl cations.

2. Computational Details

Single determinant non-empirical SCF-MO calculations were used throughout this study. For geometry optimizations of both the 2-fluoroethyl and the fluoronium cations, in which many points had to be computed in order to establish

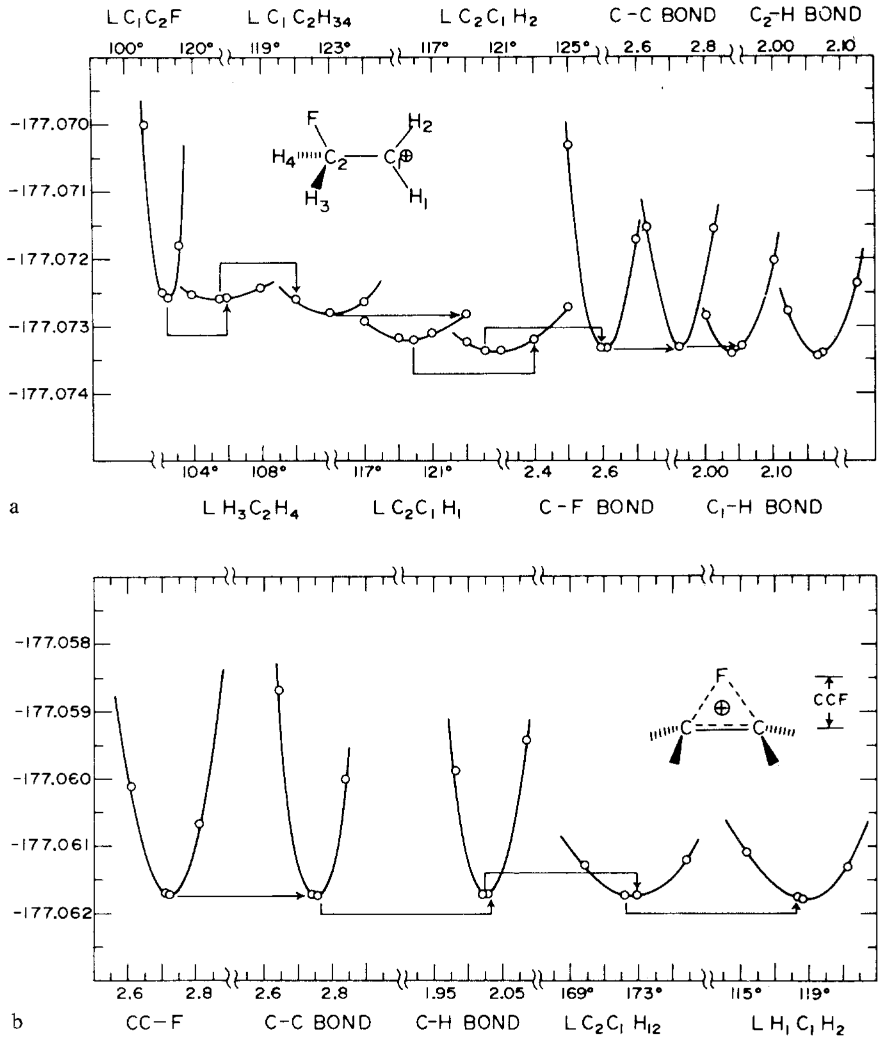


Fig. 1. Geometry optimization of 2-fluoroethyl cation and fluoronium ion

the minima, we decided to employ the less expensive but equally reliable 6-31G split valence shell basis and performed the quantum mechanical calculations using the GAUSSIAN 70 computer program [20]. The optimized geometries were then applied to estimate more accurately the relative stabilities of the various species using a series of extended basis calculations. The near molecular Hartree-Fock energies were computed using a 38 double-zeta basis set which in turn was obtained by contraction from a set of 88 primitive Gaussian type functions[1] through a modified [22] POLYATOM II Program [23]. To compare the results

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[1] The fluorine and carbon basis sets used were that of Dunning [21] ($(9^s, 4^p)$ contracted to $[4^s, 2^p]$), while in the case of the basis orbitals associated with the hydrogens (5^s) primitive GTF were contracted to $[2^s]$.

Table 1. Variation of total energy with molecular geometry as computed with a 6-31G split valence basis set for 2-fluoroethyl cation (see structure VI for numbering of atoms)

	Bond length (Bohr)				Angles (degree)					Total energy
	C_2–F	$\frac{1}{2}$(C–C)	C_1–H_1	C_2–H_3	$\angle C_1C_2F$	$\angle H_3C_2H_4$	$\angle C_1C_2H_{3,4}$	$\angle C_2C_1H_1$	$\angle C_2C_1H_2$	(Hartree)
1	2.5988	1.3634	2.0505	2.0746	105.4	105.9	121.0	123.0	123.0	−177.070012
2					110.4					−177.072501
3					115.4					−177.071875
4					112.1					−177.072620
5						107.9				−177.072473
6						103.9				−177.072551
7						105.5				−177.072624
8							119.0			−177.072219
9							123.0			−177.072767
10							125.0			−177.072650
11								125.0		−177.072119
12								121.0		−177.073117
13								119.0		−177.073166
14								117.0		−177.072914
15								119.7		−177.073183
16									125.0	−177.072710
17									121.0	−177.073361
18									119.0	−177.073241
19									120.8	−177.073362
20	2.4988									−177.070304
21	2.6988									−177.071713
22	2.6134									−177.073382
23		1.4134								−177.071538
24		1.3134								−177.071548
25			2.0005							−177.072843
26			2.1005							−177.072007
27			2.0396							−177.073437
28				2.0246						−177.072795
29				2.1246						−177.072349
30[a]	2.6134	1.3634	2.0396	2.0681	112.1°	105.5°	123.3°	119.7°	120.8°	−177.073457

[a] Optimized parameters.

from the previous computations, we also completed the Gaussian 70 calculation for the STO-3G basis functions.

Most of the calculations in this project were carried out on University of Toronto IBM 370/165 system, while some of them were performed on York University IBM 370/155 system.

3. Results and Discussions

3.1. Details of Optimization

The geometry optimization started with the values taken from Pople's calculations on both ethyl cation and protonated ethylene [16]. Only one geometrical parameter (bond length, bond angle, torsional angle) was varied at a time, while the rest were kept constant. A quadratic equation was fitted to the computed points in order to find the minimum of the energy as the function of the independent

Table 2. Variation of total energy with molecular geometry as computed with a 6-31G split valence shell basis set for the fluoronium ion (see structure V for numbering of atoms)

	Bond Length (Bohr)			Angles (degree)		Total energy
	CCF[a]	$\frac{1}{2}$(C–C)	C–H	$\angle C_2C_1H_{1,2}$	$\angle H_1C_1H_2$	(Hartree)
1	2.80930	1.36885	2.028704	172.85	118.3	−177.060652
2	2.90930					−177.057502
3	2.70930					−177.061690
4	2.60930					−177.060116
5	2.71956					−177.061695
6		1.31885				−177.058702
7		1.41885				−177.060029
8		1.375971				−177.061715
9			2.078704			−177.059475
10			1.978704			−177.059878
11			2.026233			−177.061725
12				175.85		−177.061215
13				169.85		−177.061520
14				172.21		−177.061741
15					121.3	−177.061322
16					115.3	−177.061076
17[b]	2.719560	1.375971	2.026233	172.21	118.64	−177.061747

[a] F to centre of CC bond; optimum C–F bond is 3.047836.

[b] Optimized parameters.

Table 3. Atomic coordinates (Bohr) for the optimized geometries of the 2-fluoroethyl cation and the fluoronium ion

Center	Coordinates			Charge
	x	y	z	
Fluoronium ion				
C1	1.36337900	0.0	0.0	6.0
C2	−1.36337900	0.0	0.0	6.0
H1	2.37392400	1.77167600	0.0	1.0
H2	2.40775000	−1.75194900	0.0	1.0
H3	−2.04485400	−1.04937900	1.64665800	1.0
H4	−2.04485400	−1.04937900	−1.64665800	1.0
F	−2.34661200	2.42141100	0.0	9.0
2-Fluoroethyl cation				
C1	1.37597100	0.0	0.0	6.0
C2	−1.37597100	0.0	0.0	6.0
H1	2.40030100	−0.14013400	1.74262200	1.0
H2	2.40030100	−0.14013400	−1.74262200	1.0
H3	−2.40030100	−0.14013400	1.74262200	1.0
H4	−2.40030100	−0.14013400	−1.74262200	1.0
F	0.0	2.71956000	0.0	9.0

variable (i.e. the geometrical parameter under investigation). The total energy value for this optimized geometry which was to be used as the first point for the optimization of the next parameter, was then recomputed by a new SCF-MO calculation. Figure 1 illustrates the overall optimization process for both the 2-fluoroethyl cation and bridged fluoronium ion. The numerical values for these

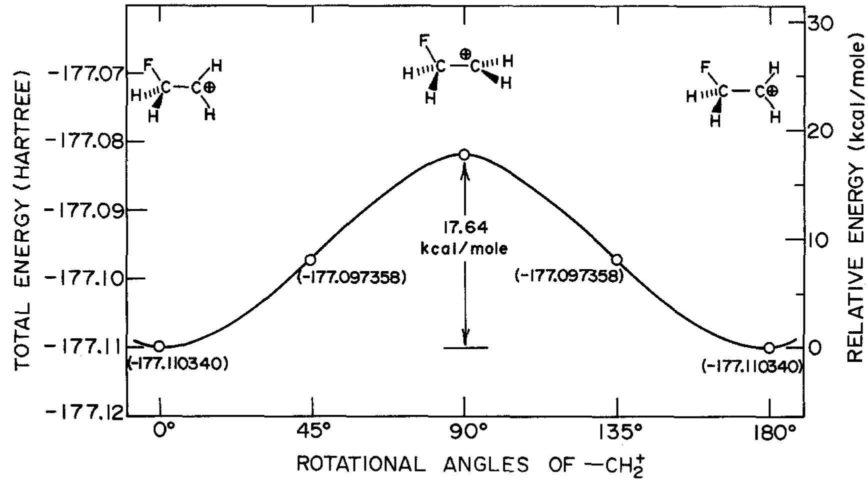


Fig. 2. The variation of total energy with the rotation along the C–C bond for 2-fluoroethyl cation

Table 4. Calculated barrier to internal rotation from different works

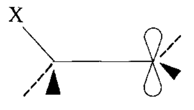
Authors	$E(B) - E(A)$	Number of basis functions
Hoffmann *et al.* [19]	– 8.4 kcal/mole	19 *sp*
Clark and Lilley [17]	– 10.53 kcal/mole	22 *sp*
Present study	– 17.64 kcal/mole	38 *sp*

two species are summarized in Tables 1 and 2 respectively. The optimized bond lengths, bond angles and total energies are listed as the last entries in these two tables. Table 3 shows the corresponding atomic coordinates of the optimized molecular structure. It perhaps should be pointed out that the initial values used for optimizing the bridged fluoronium ion were the optimized values of the parameters obtained from earlier much more extensive Dunning basis calculations.

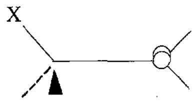
The adequacy of the 6-31G split valence shell basis is clearly demonstrated in light of the minor changes of the values in the last row from those in the first row.

3.2. Rotational Barrier in 2-Fluoroethyl Cation

The barrier to internal rotation, due to hyperconjugation, was studied for the cation $FCH_2–CH_2^+$ in the light of the recent paper of Hoffman *et al.* [19]. The results shown in Fig. 2 were in good agreement with their prediction: "In the cations $XCH_2–CH_2^+$ or anions $XCH_2–CH_2^-$, if X is more electronegative than H, then the cation will prefer conformation B, while the anion favours A. If X is less electronegative than H, then cation favours A while the anion prefers B" [19]. The barriers to internal rotation from different works are compared in Table 4.



A



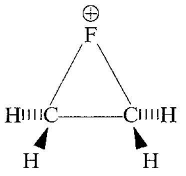
B

Table 5. Gross population or each atom for fluoronium ion (see structure V for numbering of atoms)

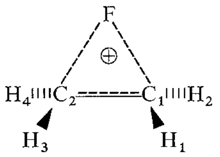
MC	C_1	C_2	H_1	H_2	H_3	H_4	F
1	−0.0000	−0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2	1.0000	1.0000	0.0000	0.0000	0.0000	0.0000	−0.0001
3	1.0000	1.0000	−0.0000	−0.0000	−0.0000	−0.0000	−0.0000
4	0.0870	0.0870	−0.0004	−0.0004	−0.0004	−0.0004	1.8276
5	0.7620	0.7620	0.0389	0.0389	0.0389	0.0389	0.3203
6	0.6431	0.6431	0.1173	0.1173	0.1173	0.1173	0.2447
7	0.4650	0.4650	0.0847	0.0847	0.0847	0.0847	0.7312
8	0.4830	0.4830	0.0945	0.0945	0.0945	0.0945	0.6558
9	0.1492	0.1492	0.0376	0.0376	0.0376	0.0376	1.5511
10	0.2248	0.2248	0.0740	0.0740	0.0740	0.0740	1.2543
11	0.5705	0.5705	0.2147	0.2147	0.2147	0.2147	0.0000
12	0.5926	0.5926	0.0225	0.0225	0.0225	0.0225	0.7247
Total	5.9773	5.9773	0.6840	0.6840	0.6840	0.6840	9.3096

3.3. Population Analysis and Charges

There are two possible electronic structures for the bridged fluoronium cation:



IV

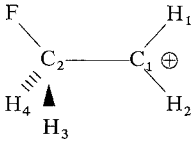


V

In Structure (IV) the fluorine atom forms two single bonds with two carbons and carries the positive charge, while in Structure (V), the positive charge is predominantly on the two carbons and the fluorine is loosely bonded to the carbon atoms. The population analysis as shown in Table 5 favors Structure (V).

3.4. Profile for Interconversion of Open and Cyclic Ions

Previous studies on the electrophilic addition of the hypothetical F^+ involving the two extreme Structures (V) and (VI) were reported by Clark [17] and Hehre [24] respectively. Hehre's 23*sp* split valence shell basis calculation revealed that the 2-fluoro cation was energetically favoured by 11.49 kcal/mole. However the



VI

opposite result, in which the bridged cation was found stabilized by 19.66 kcal/mole, was obtained also by Hehre in a 19*sp* minimum basis calculation. On the other hand Clark's 22*sp* basis calculation gave the bridged cation as being

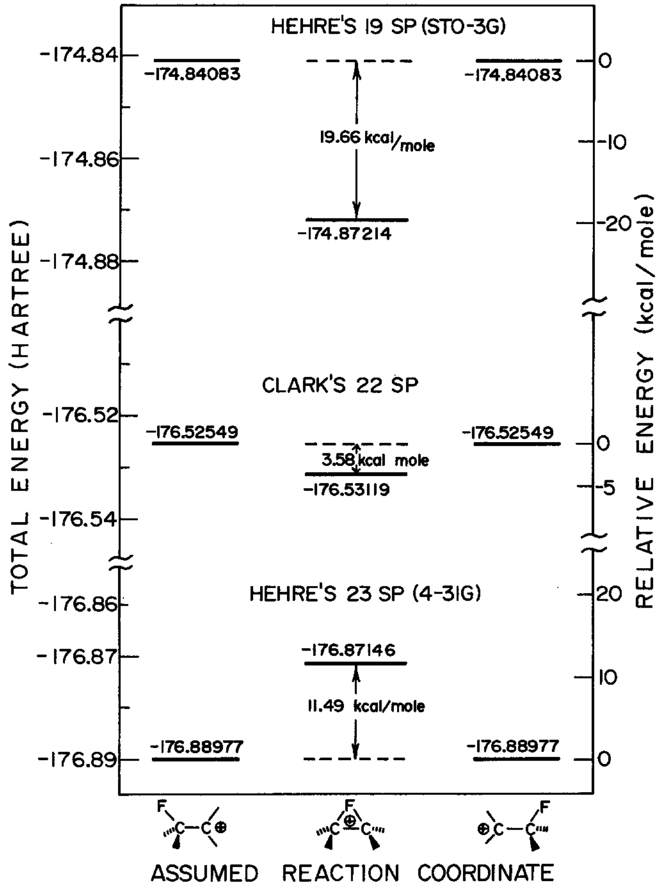


Fig. 3. Relative stabilities of 2-fluoroethyl cation and fluoronium ions as reported by earlier calculation

3.58 kcal/mole more favoured. It seems therefore that the larger basis set calculations tended to favour the open chain cation, as illustrated by Fig. 3.

In the present study we employed the optimized geometries of the two cations obtained from the 35*sp* split valence shell basis calculations for the 38*sp* double zeta calculations and for the 19*sp* minimum basis calculations. The results, as expected, confirmed that the extended basis favoured the 2-fluoro cation and the minimum basis the bridged cation (Fig. 4).

The optimized structures of the two cations were again used in a 38*sp* double zeta calculation to investigate the barrier associated with the transformation of V into VI. The energy profile for interconversion of the open and the cyclic cation was estimated by computing the total energy values at three intermediate structures corresponding to the nominal 25, 50, and 75% conversion. The atomic coordinates were chosen with the assumption that the motions of all the atoms were occurring in a synchronized fashion. Unlike in some of the previous studies, [14–18] the total energy values for these intermediate structures predict the presence of a transition state. However the existence of a transition state has

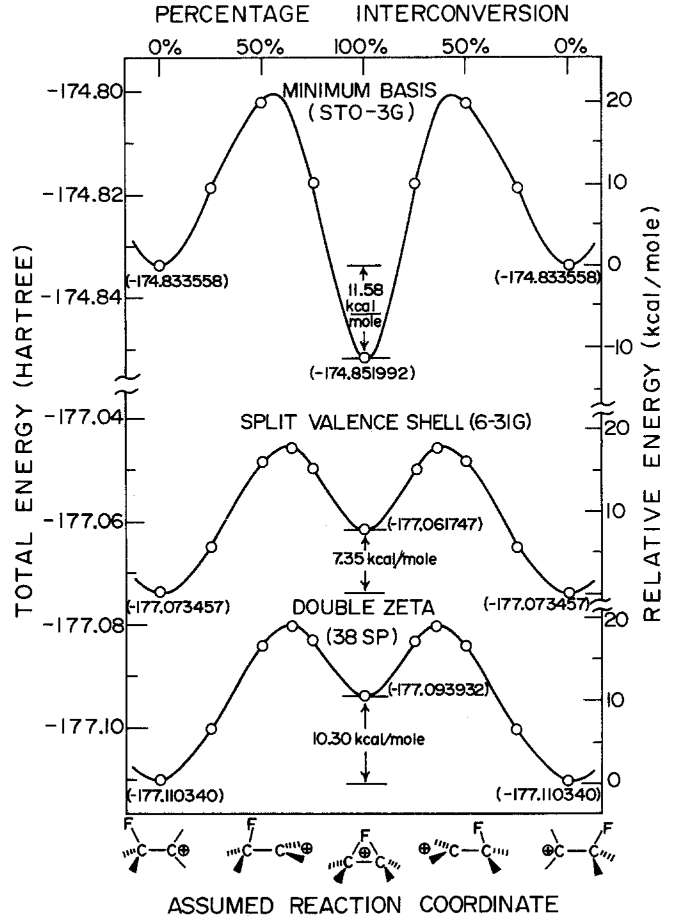


Fig. 4. Reaction profile for the 2-fluoroethyl cation and fluoronium ion interconversion

recently been indicated by Hehre and Hiberty [24]. The energy and geometry of this activated complex were estimated by using the computed total energies to fit a quadratic equation for each of the three basis sets. Calculations, using the appropriate geometry for each basis set, were then performed to determine the exact energies of the activated complex. For the largest basis set (double zeta) the barrier was found to be 18.8 kcal/mole above the more stable 2-fluoroethyl cation. The results of all the basis sets are shown in Fig. 4 and the numerical results obtained with the double zeta basis set are summarised in Table 6. The energy profile indicates that the non-classical cyclic cation is an intermediate between the two classical carbonium ions. The barrier is sufficiently low for a rapid interconversion at room temperature.

Perhaps at this stage we should consider the numerical reliability of our results. A double zeta basis set almost always gives fairly accurate results so that one may consider these reliable both qualitatively and semi-quantitatively. In other words one would expect the open cation to be more stable than the cyclic

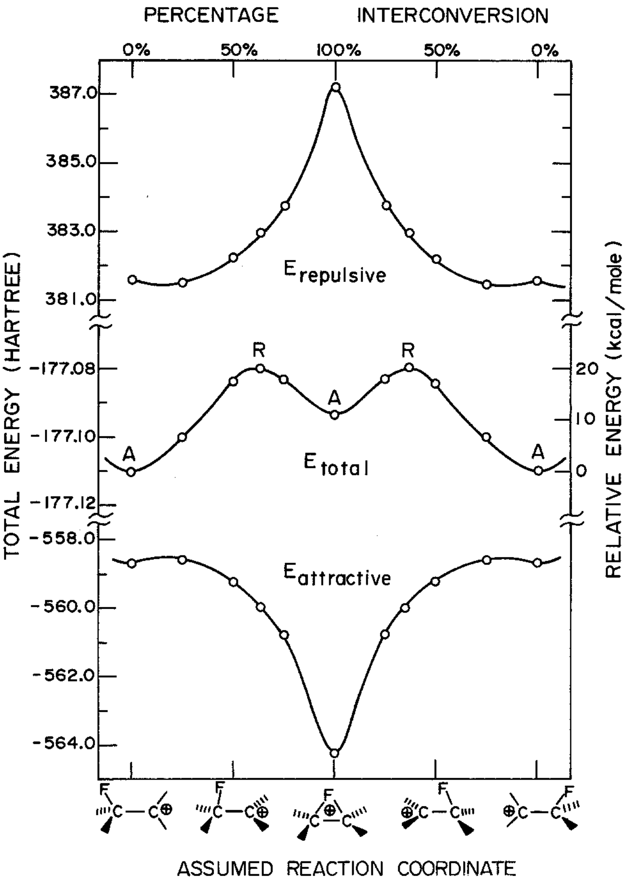
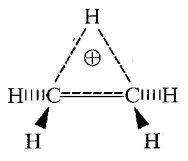
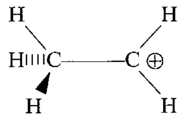


Fig. 5. The partition of the total energy reaction profile into repulsive and attractive components

valence tautomer even if the thermodynamic separation is different somewhat from the value computed here (+10.3 kcal/mole). Pople and coworkers [16] previously found that with a split valence basis set the cyclic ion VII was less stable than the corresponding open



VII



VIII

cation by about 6.7 kcal/mole. The inclusion of polarization functions for all the atoms *inverted* the relative stabilities so that VII became more stable than VIII by about 0.9 kcal/mole. Analysis of their tabulated results (Table 1 in [16]) indicated that the changeover occurred when a *p*-type polarization function was

Table 6. The components of the total energy (Hartree) for the different geometrical arrangement of $C_2H_4F^{\oplus}$ as computed with Dunning's DZ basis set

	2-Fluoro cation	$\frac{3}{4}$(2-fluoro) + $\frac{1}{4}$(Bridged)	$\frac{1}{2}$(2-fluoro) + $\frac{1}{2}$(Bridged)	0.3535 (2-fluoro)[a] + 0.6465 (Bridged)	$\frac{1}{4}$(2-fluoro) + $\frac{3}{4}$(Bridged)	Bridged cation
V_{nn}	73.03915118	72.98736308	73.37513083	73.85282964	74.33445101	76.19373107
T	177.24792151	177.21348337	177.19562491	177.16058781	177.13594415	177.20101728
V_{ee}	131.26525938	131.3216638	131.6152972	131.92381844	132.2681517	133.8276163
V_{ne}	−558.66267208	−558.62413209	−559.27016294	−560.01768530	−560.82163597	−564.31629673
E_{nuclear}	73.03915118	72.98736308	73.37513083	73.85282964	74.33445101	76.19373107
$E_{\text{electronic}}$	−250.14949120	−250.08898496	−250.45924083	−250.93327905	−251.41754010	−253.28766315
$E_{\text{repulsive}}$	381.55233207	381.5225103	382.1860529	382.9372358	383.7385469	387.2223646
$E_{\text{attractive}}$	−558.66267208	−558.62413209	−559.27016294	−560.01768530	−560.82163597	−564.31629673
E_{total}	−177.11034002	−177.10162188	−177.08410999	−177.08044941	−177.08308910	−177.09393207
V_{total}	−354.3582615	−354.3151053	−354.2797349	−354.2410372	−354.2190332	−354.2949494
Virial Coefficient	− 1.999223791	− 1.999368776	− 1.999370668	− 1.999547651	− 1.999701613	− 1.999395685

[a] Transition state complex.

Table 7. Orbital energies for the different geometrical arrangement of $C_2H_4F^+$ as computed with Dunning's DZ basis set

MO	Fluoronium ion	75 % 25 %	50 % 50 %	35.35 %[a] 64.65 %	25 % 75 %	2-Fluoro cation
1	−26.59586 (a_1)	−26.56205 (a)	−26.51580 (a)	−26.54178 (a)	−26.49845 (a)	−26.50540 (a')
2	−11.62894 (a_1)	−11.65571 (a)	−11.66996 (a)	−11.66394 (a)	−11.66852 (a)	−11.66399 (a')
3	−11.62810 (b_1)	−11.61018 (a)	−11.59673 (a)	−11.60337 (a)	−11.59347 (a)	−11.59422 (a')
4	− 1.88967 (a_1)	− 1.84343 (a)	− 1.80825 (a)	− 1.82654 (a)	− 1.80379 (a)	− 1.82476 (a')
5	− 1.34497 (a_1)	− 1.35080 (a)	− 1.35616 (a)	− 1.35318 (a)	− 1.36029 (a)	− 1.36505 (a')
6	− 1.16229 (b_1)	− 1.15314 (a)	− 1.14943 (a)	− 1.15131 (a)	− 1.14657 (a)	− 1.14379 (a')
7	− 1.02569 (b_2)	− 1.00684 (a)	− 0.99731 (a)	− 1.00232 (a)	− 0.99062 (a)	− 0.98947 (a')
8	− 0.96396 (a_1)	− 0.95687 (a)	− 0.95094 (a)	− 0.95506 (a)	− 0.94412 (a)	− 0.94774 (a'')
9	− 0.91429 (b_1)	− 0.89349 (a)	− 0.90427 (a)	− 0.89708 (a)	− 0.92090 (a)	− 0.93835 (a')
10	− 0.88533 (b_2)	− 0.88873 (a)	− 0.86181 (a)	− 0.87677 (a)	− 0.85950 (a)	− 0.87658 (a')
11	− 0.85207 (a_2)	− 0.84132 (a)	− 0.81678 (a)	− 0.83089 (a)	− 0.80896 (a)	− 0.80697 (a')
12	− 0.83887 (a_1)	− 0.81213 (a)	− 0.79453 (a)	− 0.80248 (a)	− 0.78847 (a)	− 0.78580 (a'')

[a] Transition state complex.

included in the basis set of the bridging atom. Clearly in our case the addition of polarization functions would affect the numerical value of the computed thermodynamic stabilities for example the 10.3 kcal/mole may be considerably less, perhaps as low as 5 or 6 kcal mole: however a changeover is not expected. This is because the bridging H atom in VII is very poorly represented using 5 nondirectional *s*-type orbitals only and the addition of the directional *p*-orbitals to the H atom makes a major improvement. However our bridging atom, F, already possesses a fairly large number of *s* and *p* orbitals; hence the inclusion of a *d*-type polarization function is expected to result in a relatively minor change. In other words it appears that our conclusion considering relative stabilities (i.e. VI > V) is basis set independent.

3.5. Detailed Analysis of the Double Zeta Calculation

The components of the total energy in the two limiting structures as well as those of the interconversion are summarized in Table 6. The expectation values of the kinetic (T), electron-electron repulsion (V_{ee}), nuclear-electron attraction (V_{ne}) and nuclear-nuclear repulsion (V_{nn}) operators were partitioned into two groups, the attractive and repulsive components of the total energy

$$E = \underbrace{V_{nn} + T + V_{ee}}_{\text{repulsive}} + \underbrace{V_{ne}}_{\text{attractive}} . \tag{2}$$

The attractive and repulsive components are plotted against the assumed reaction coordinates and the curvatures of these plots are compared to that of the reaction profile (the middle curve in Fig. 5). It is found that both the open and the cyclic structures are attractive (A) dominant; however, the transition state, connecting these two minima is repulsive (R) dominant.

3.6. Orbital Energies for $C_2H_4F^+$

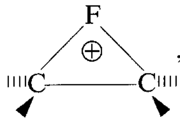
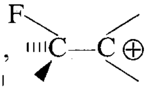
The orbital energies, as calculated by the double zeta basis set, for the bridged cation (V) and the 2-fluoro-cation (VII) are listed in Table 7 along with those of the intermediate geometries corresponding to the 25, 50 and 75 % interconversion.

3.7. Overall Reaction Profile for the Fluorination Reaction

Considering the overall addition reaction,

$$C_2H_4 + F_2 \rightleftarrows C_2H_4F^+ + F^- \rightarrow FCH_2 - CH_2F \tag{3}$$

it was necessary to carry out SCF calculations on all the species involved.

The total energies obtained by double zeta basis calculations of F_2, C_2H_4, F^-,  ,  and trans-CH_2FCH_2F are listed in Table 8. The geometries used of the above species are either experimental (25) or the optimized ones. Figure 6 shows the reaction profile for fluorination.

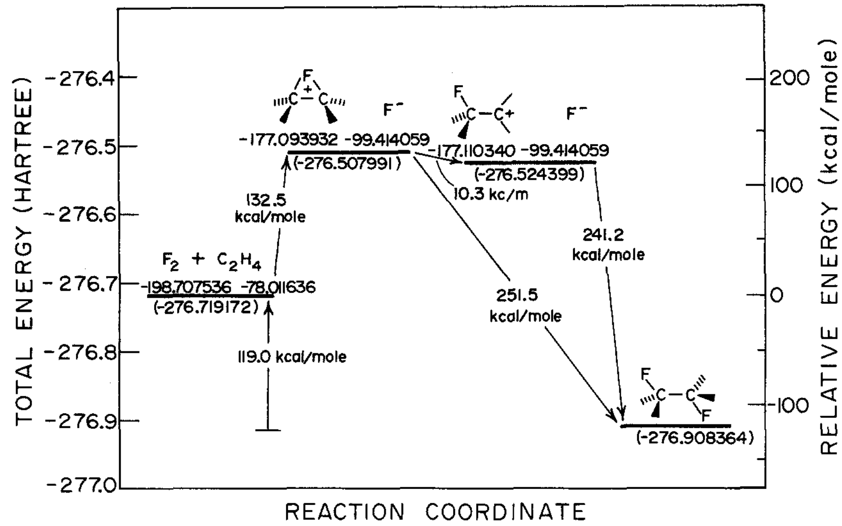
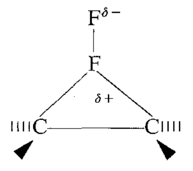


Fig. 6. Overall reaction profile for the addition reaction of F_2 to $CH_2=CH_2$

The energy separation between the reactants ($CH_2=CH_2+F_2$) and the products (FCH_2-CH_2F) is computed to be -119.0 kcal/mole. The experimental heat of this reaction is -126.8 or -131.3 kcal/mole, depending upon the heat of formation of the difluoroethane.[2]

If we assume that all the energy differences presented in Fig. 6 are computed with similar accuracy then we can be reasonably confident that the energy separation between the initial state ($CH_2=CH_2+F_2$) and one of the possible intermediate states (V or VI) is well over 100 kcal/mole. This unrealistically high value for an activation energy is a clear indication that in the gas phase the reaction does not proceed through separated ions but perhaps *via* some neutral addition complex such as IX and full



IX

ion separation to fluoronium ion V and fluoride ion (F^-) can only be stabilized by extensive solvation.

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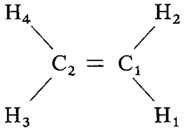
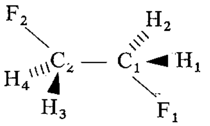
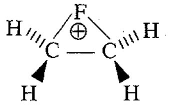
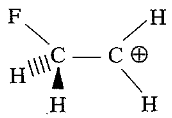
[2] This assumes that the heat of formation of 1, 2-difluoroethane is the same as that of 1, 1-difluoroethane (-114.3 kcal/mole [26] and -118.8 kcal/mole [27]). It has been shown that heats of formation of fluorochlorohydrocarbons can be obtained by bond energy additivities [27]. Further justification for this assumption comes from the heats of formation of the dichloroethanes, which differ by only 0.4 kcal/mole [27].

Table 8. Total energy values for species involved in the addition reaction of F_2 to $CH_2=CH_2$

Ion or molecule	Total energy (Hartree)	Atom	Coordinates (Bohr)		
			x	*y*	*z*
F_2–F_1	−198.707536	F_1	1.340000	0.0	0.0
		F_2	−1.340000	0.0	0.0
	−78.011636	C_1	1.275510	0.0	0.0
		C_2	−1.275510	0.0	0.0
		H_1	2.332838	1.725403	0.0
		H_2	2.332838	−1.725403	0.0
		H_3	−2.332838	1.725403	0.0
		H_4	−2.332838	−1.725403	0.0
F^-	−99.414059	F	0.0	0.0	0.0
	−276.908364	F_1	0.0	0.0	0.0
		C_1	0.0	0.0	2.629246
		C_2	2.788458	0.0	3.610656
		F_2	2.788458	0.0	6.239902
		H_1	−0.973568	−1.679205	3.318707
		H_2	−0.973568	1.679205	3.318707
		H_3	3.762026	−1.679205	2.921195
		H_4	3.762026	1.679205	2.921195
	−177.093932	See Table 3			
	−177.110340	See Table 3			

[a] Optimized geometry.

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