

# Quantum Chemical Studies on Electrophilic Addition

## II. Reaction of Chlorine with Ethylene

Alan C. Hopkinson and Min H. Lien

*Department of Chemistry, York University, 4700 Keele Street,  
Downsview, Ontario M3J 1P3, Canada*

Keith Yates and Imre G. Csizmadia

*Department of Chemistry, University of Toronto, 80 St. George Street,  
Toronto, Ontario M5S 1A1, Canada*

The geometries of the 2-chloroethyl and ethylenchloronium cations, two possible intermediates in the electrophilic addition of chlorine to ethylene, have been fully optimized using *ab initio* molecular orbital calculations employing the split valence shell 4-31G basis set.

These geometries were then used to compute more accurate wave functions using Dunning's double-zeta basis set. The bridged chloronium ion was found to be more stable by 9.35 kcal/mole, the opposite order of stability from the  $C_2H_4F^+$  ions. Interconversion of the two  $C_2H_4Cl^+$  cations was computed to have a barrier of 6.25 kcal/mole.

The activation energy for this chlorination reaction, using the ethylenchloronium cation and a chlorine anion at infinite separation as the model for the activated complex, was computed to be 128.7 kcal/mole, showing that this is not a feasible gas phase reaction.

**Key words:** 2-Chloroethyl and ethylenchloronium cations - Reaction profile for interconversion

### 1. Introduction

The electrophilic addition of molecular chlorine and bromine to olefinic double bonds has long been believed to proceed via a halonium ion as an intermediate [1, 2], with the product of this type of addition depending upon the nature of the substituent attached to the double bond. When only alkyl groups are present then the stereochemistry of the products indicates that the two halogen atoms have been added from *opposite* sides of the planar olefin (i.e. *trans* addition) [2b, 3]. This has been rationalized in terms of a cyclic halonium ion (I) in which the initial halogen atom



prevents the halide ion from attacking the same side as that approached in the formation of the halonium ion. The open chain cation, which in the case of the parent compound is a highly unstable carbenium ion (II), would be expected to lead to a mixture of both *cis* and *trans* addition when it combines with the halide ion.

Recently the ethylenchloronium ion has been prepared by the reaction of 1-chloro-2-fluoroethanol in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solutions at low temperatures [4]. Detailed analyses of the proton and  $^{13}\text{C}$  NMR spectra [5] have shown that the ion has the symmetric bridge form (I).

We have recently completed an extensive *ab initio* molecular orbital study of the electrophilic addition of fluorine to ethylene [6]<sup>1</sup>. Our calculations showed the open 2-fluoroethyl cation to be more stable than cyclic ethylenefluoronium ion by 10.3 kcal/mole, with an activation energy of 18.8 kcal/mole (relative to the more stable open cation) required for interconversion of these ions. It was computationally too expensive to construct a complete energy surface and this value of the activation energy will therefore necessarily be higher than the experimental value. Energy barriers of this magnitude permit rapid interconversion at room temperature and hence our model of  $\text{C}_2\text{H}_4\text{F}^+$  is for two rapidly interconverting open cations with the cyclic ion as an *intermediate* rather than an activated complex. This is in agreement with the interpretation of NMR results on the tetramethylethylenefluoronium ion, which has been observed at low temperatures in "magic acid" solutions. [7]. However in this open cation the positive charge is formally located on a tertiary carbon atom and this would be expected to further increase the stability of the open ion relative to the cyclic one.

The lack of experimental data on the parent ethylenefluoronium cation and the fact that our results on this ion predict the opposite stabilities from that found experimentally for the ethylenchloronium, bromonium and iodonium cations [8-13] (although not with the tetramethylethylenefluoronium cation), leaves some doubts as to the ability of the *ab initio* molecular orbital method to predict the correct order of stabilities of cyclic and open cations. We therefore decided to extend our studies to the ethylenchloronium cation, a species for which experimental data is available [13] but which is theoretically much more complex.

Previous *ab initio* molecular orbital treatments [14a, b, 15] have used smaller basis sets to study the relative energies of 1- and 2-chloroethyl cations and the two possible bridged structures (H or Cl bridging). In all studies the chlorine-bridged ion was found

<sup>1</sup> It should be noted that molecular orbital calculations are for gas phase reactions at 0°K, and that in the gas phase fluorine and ethylene react via a radical mechanism and not by the electrophilic mechanism followed in solution. Hence our calculations are not for the lowest energy process for reaction between these two molecules.

to be more stable than the 2-chloroethyl cation and the 1-chloroethyl cation was found to have almost identical energy to the chlorine-bridged ion. The 1-chloroethyl cation can be ruled out as a possible intermediate in chlorination reactions as there is no 1,1-dichloroethane produced. Consequently we have restricted our larger basis set calculations to only the 2-chloroethyl cation and the cyclic ethylenechloronium ion.

## 2. Computational Details

Single determinant non-empirical SCF-MO calculations were used throughout this study. The geometry optimizations for the 2-chloroethyl and ethylenechloronium cations required many calculations and we employed the split valence shell 4-31G basis set [16, 17] in the GAUSSIAN 70 program [18]. Near Hartree-Fock wave functions were then computed using Dunning's [19] double-zeta basis set with a modified [20] POLYATOM II program [21].

The calculations were carried out on the York University IBM 370/155 and University of Toronto IBM 370/165 computers.

## 3. Results and Discussion

### 3.1. Geometry Optimization

The ethylenechloronium cation has only recently been observed at low temperatures by NMR [13] and the 2-chloroethyl cation has never been detected, so there are no experimental geometries available. Consequently we had to optimize molecular geometries for both these cations. Prior to commencing this optimization we compared the experimental geometries of ethylene sulphide and ethylene oxide with those computed [15] using the minimal STO-3G basis set [22, 23]. For both these molecules this minimal basis set slightly underestimates the carbon-heteroatom bond length, overestimates the carbon-carbon and carbon-hydrogen distances and gives bond angles which are too small by  $4^{\circ}$ - $5^{\circ}$ . We then compared the geometry of the ethylenefluoronium cation as optimized with this minimal basis set with that obtained in our optimization [6] with the much larger 6-31G [24] basis set and found that the two geometries varied *in the same way and by almost the same amounts* as in the comparison between the minimal basis set calculations and experimental geometries on the ethylene oxide and ethylene sulphide. We therefore concluded that optimization with the larger 6-31G basis set gives considerably better geometries<sup>2</sup>. Furthermore we optimized the ethylenefluoronium cation with the intermediate 4-31G basis set and found good agreement with the geometry provided by the 6-31G basis set. This analysis led us to the conclusion that the 4-31G basis set would be adequate for the optimization of the ethylenechloronium and 2-chloroethyl cations.

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<sup>2</sup> Charge distribution is particularly sensitive to small changes in geometries and in basis sets. Using the geometry optimized with the STO-3G basis set, the fluorine atom in the ethylene fluoronium cation is found to have a charge of +0.048 [15]; with the geometry optimized with the 6-31G basis set and in a calculation with the even larger Dunning basis set, the fluorine atom in the same ion is computed to have a charge of -0.3096.

The optimized bond lengths and angles of the two  $\text{C}_2\text{H}_4\text{F}^+$  ions were taken as initial guesses at the carbon-hydrogen skeleton of the  $\text{C}_2\text{H}_4\text{Cl}^+$  ions. The distance of the chlorine atom from the carbon atoms was more difficult to estimate and was the first parameter which we chose to optimize. The remainder of the geometries of the two cations (I and II) were optimized one parameter at a time (bond lengths and then bond angles and torsional angle). A quadratic equation was fitted to the computed points in order to find the minimum energy as a function of each particular geometric parameter as described previously [6]. The whole optimization was done with the split valence shell 4-31G basis set, and the results are given in Tables 1 and 2.

As expected the C-C and C-H bond lengths are slightly shorter and the C-Cl bond is slightly longer than those found in the structures optimized with the smaller STO-3G basis set. These deviations are in the *same* directions and of *similar magnitude* to the differences between the calculated and experimental bond lengths for ethylene sulphide. Similar behaviour was also found for the bond angles so we are confident that our optimized structures are superior to those previously reported.

The carbon-carbon bond lengths in both cations are intermediate (1.44 Å) between the usual bond lengths of 1.54 Å and 1.34 Å for single and double bonds respectively. The carbon-chlorine bond length is considerably longer in the cyclic structure (2.08 Å) than in the open cation (1.84 Å) and both are longer than the experimental value for the bond in chloroethane (1.77 Å) [25]. These bond lengths are therefore consistent with the ions being intermediates in the conversion of a double bond into a single bond and with simultaneous formation of a carbon-chlorine bond.

There are two possible conformers for the 2-haloethyl cations, one in which the halogen eclipses the hydrogens at the carbenium ion centre (III) and the other in which it bisects these hydrogen atoms (IV). So far we have only considered the eclipsed structure as



this is expected to be more stable for substituents X which are more electronegative than H [26, 27]. The 2-fluoroethyl cation should therefore have a larger barrier to rotation than the 2-chloroethyl cation and this is indeed found to be the case (Table 3). The results of this rotational study, assuming no other change in the molecular geometry, were computed using the extensive Dunning basis set and the resulting rotational profile is given in Fig. 1. Comparisons of computed rotational barriers with previously reported values for both the 2-fluoroethyl and 2-chloroethyl cations show the magnitude of this type of barrier to be very dependent on the size of the basis set. For both cations the barrier *increases* with improvement of the wave function and for the 2-chloroethyl ion our computed barrier is much larger than the literature values.

### 3.2 Interconversion of the Ethylenchloronium and 2-Chloroethyl Cations

Previous studies [14, 15] have shown the ethylenchloronium cation to be more stable than the 2-chloroethyl cation, with a monotonic decrease in the energy difference as the quality of the wave function is improved. However, we have used the same basis sets

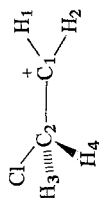
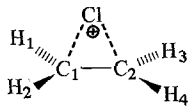


Table 1. Variation of total energy with molecular geometry as computed with the 4-31G basis set for the 2-chloroethyl cation

|                 | Bond Length (Bohr) |                   |                   | Angles (Degree) |   |   |  | Total Energy (Hartree) |   |   |
|-----------------|--------------------|-------------------|-------------------|-----------------|---|---|--|------------------------|---|---|
|                 | C-Cl               | $\frac{1}{2}$ C-C | C <sup>+</sup> -H | C-H             | $\angle$ C <sub>1</sub> C <sub>2</sub> Cl | $\angle$ H <sub>3</sub> C <sub>2</sub> H <sub>4</sub> | $\angle$ C <sub>1</sub> C <sub>2</sub> H <sub>34</sub> |                        | $\angle$ C <sub>2</sub> C <sub>1</sub> H <sub>1</sub> | $\angle$ C <sub>2</sub> C <sub>1</sub> H <sub>2</sub> |
| 1               | 3.3751             | 1.3593            | 2.0396            | 2.0681          | 113.9                                     | 105.54  | 123.0  | 119.7                  | 120.8   | -536.577256   |
| 2               | 3.4751             |                   |                   |                 |   |   |  |                        |   | -536.578229   |
| 3               | 3.5751             |                   |                   |                 |   |   |  |                        |   | -536.576957   |
| 4               | 3.4684             |                   |                   |                 |   |   |  |                        |   | -536.578238   |
| 5               |                    | 1.4093            |                   |                 |   |   |  |                        |   | -536.576404   |
| 6               |                    | 1.3093            |                   |                 |   |   |  |                        |   | -536.576368   |
| 7               |                    | 1.3590            |                   |                 |   |   |  |                        |   | -536.574509   |
| 8               |                    |                   | 2.1396            |                 |   |   |  |                        |   | -536.574139   |
| 9               |                    |                   | 1.9396            |                 |   |   |  |                        |   | -536.578240   |
| 10              |                    |                   | 2.0420            |                 |   |   |  |                        |   | -536.577470   |
| 11              |                    |                   |                   | 2.0181          |   |   |  |                        |   | -536.577241   |
| 12              |                    |                   |                   | 2.1181          |   |   |  |                        |   | -536.578240   |
| 13              |                    |                   |                   | 2.0649          |   |   |  |                        |   | -536.577954   |
| 14              |                    |                   |                   |                 | 111.90                                    |   |  |                        |   | -536.578093   |
| 15              |                    |                   |                   |                 | 115.90                                    |   |  |                        |   | -536.578244   |
| 16              |                    |                   |                   |                 | 114.22                                    |   |  |                        |   | -536.578006   |
| 17              |                    |                   |                   |                 |   | 107.54  |  |                        |   | -536.578279   |
| 18              |                    |                   |                   |                 |   | 103.54  |  |                        |   | -536.578110   |
| 19              |                    |                   |                   |                 |   | 101.54  |  |                        |   | -536.578291   |
| 20              |                    |                   |                   |                 |   | 104.20  |  |                        |   | -536.578147   |
| 21              |                    |                   |                   |                 |   |   | 121.0  |                        |   | -536.578192   |
| 22              |                    |                   |                   |                 |   |   | 125.0  |                        |   | -536.578292   |
| 23              |                    |                   |                   |                 |   |   | 123.19   |                        |   | -536.578095   |
| 24              |                    |                   |                   |                 |   |   |  | 118.70                 |   | -536.578409   |
| 25              |                    |                   |                   |                 |   |   |  | 120.70                 |   | -536.578448   |
| 26              |                    |                   |                   |                 |   |   |  | 121.70                 |   | -536.578409   |
| 27              |                    |                   |                   |                 |   |   |  | 122.70                 |   | -536.578461   |
| 28              |                    |                   |                   |                 |   |   |  |                        | 119.8   | -536.578396   |
| 29              |                    |                   |                   |                 |   |   |  |                        | 118.8   | -536.578465   |
| 30 <sup>a</sup> | 3.4684             | 1.3590            | 2.0420            | 2.0649          | 114.22                                    | 104.20  | 123.19   | 121.70                 | 120.14  | -536.578465   |

<sup>a</sup> Optimized parameters.

Table 2. Variation of total energy with molecular geometry as computed with the 4-31G basis set for the ethylenechloronium cation



|                 | Bond Length (Bohr) |        |        | Angles (Degree)       |                    | Total Energy (Hartree) |
|-----------------|--------------------|--------|--------|-----------------------|--------------------|------------------------|
|                 | C-Cl               | C-C    | C-H    | $\angle C_1C_2H_{34}$ | $\angle H_3C_2H_4$ |                        |
| 1               | 2.3594             | 2.7377 | 2.0280 | 173.2                 | 118.3              | -535.776131            |
| 2               | 2.4416             |        |        |                       |                    | -535.934928            |
| 3               | 2.5250             |        |        |                       |                    | -535.065512            |
| 4               | 2.6096             |        |        |                       |                    | -536.172470            |
| 5               | 2.6953             |        |        |                       |                    | -536.259805            |
| 6               | 2.7819             |        |        |                       |                    | -536.330962            |
| 7               | 2.8693             |        |        |                       |                    | -536.388842            |
| 8               | 2.9576             |        |        |                       |                    | -536.435857            |
| 9               | 3.1363             |        |        |                       |                    | -536.504745            |
| 10              | 3.3174             |        |        |                       |                    | -536.549089            |
| 11              | 3.5005             |        |        |                       |                    | -536.576158            |
| 12              | 3.6854             |        |        |                       |                    | -536.590708            |
| 13              | 3.8718             |        |        |                       |                    | -536.596122            |
| 14              | 4.0595             |        |        |                       |                    | -536.594916            |
| 15              | 3.9352             |        |        |                       |                    | -536.596344            |
| 16              |                    | 2.6377 |        |                       |                    | -536.595081            |
| 17              |                    | 2.8377 |        |                       |                    | -536.593516            |
| 18              |                    | 2.7186 |        |                       |                    | -536.596454            |
| 19              |                    |        | 2.0787 |                       |                    | -536.594219            |
| 20              |                    |        | 1.9787 |                       |                    | -536.594658            |
| 21              |                    |        | 2.0260 |                       |                    | -536.596465            |
| 22              |                    |        |        | 175.0                 |                    | -536.595659            |
| 23              |                    |        |        | 170.0                 |                    | -536.597020            |
| 24              |                    |        |        | 167.0                 |                    | -536.596969            |
| 25              |                    |        |        | 168.7                 |                    | -536.597077            |
| 26              |                    |        |        |                       | 124.3              | -536.594858            |
| 27              |                    |        |        |                       | 112.3              | -536.594971            |
| 28              |                    |        |        |                       | 118.22             | -536.597077            |
| 29 <sup>a</sup> | 3.9352             | 2.7186 | 2.0260 | 168.7                 | 118.22             | -536.597077            |

<sup>a</sup> Optimized parameters.

Table 3. Barrier to rotation (kcal/mole) in 2-haloethyl cations

| Ion             | Double Zeta Basis set (Present Work) | Literature Values   |
|-----------------|--------------------------------------|---|
| $CH_2F-CH_2^+$  | 17.64                                | 8.4 <sup>a</sup><br>10.53 <sup>b</sup><br>9.31 <sup>c</sup> |
| $CH_2Cl-CH_2^+$ | 6.52                                 | 1.5 <sup>a</sup><br>0.91 <sup>b</sup>                       |

<sup>a</sup> Ref. [15].<sup>b</sup> Ref. [14b].<sup>c</sup> Ref. [26].

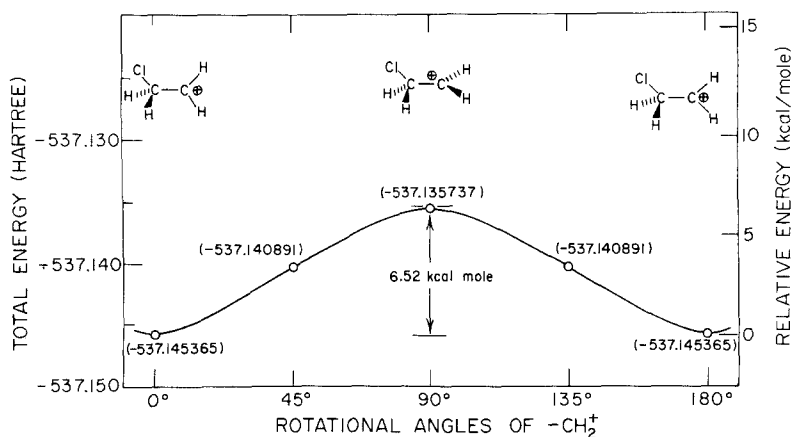


Fig. 1. The computed total energy as a function of the rotational angle in the 2-chloroethyl cation (Dunning basis set calculation)

as Hehre and Hiberty [15] but with the slightly different geometry as optimized by the 4-31G basis set and obtained energy differences of 13.82 and 11.69 kcal/mole with STO-3G and 4-31G basis sets respectively. These are markedly different from the literature values of 19.04 and 9.18 kcal/mole [15] for the *same* basis sets showing that small changes in geometry are very important when relative stabilities are being considered. Our calculations with the much larger (and therefore more reliable) Dunning basis set also gave the ethylenechloronium cation to be the more stable by 9.35 kcal/mole.

The profile for interconversion of the ethylenechloronium and 2-chloroethyl cations was of more fundamental interest to us. Three different types of behaviour have previously been reported for electrophilic additions to double and triple bonds. The addition of both  $F^+$  and  $Cl^+$  to acetylene results in stable vinyl cations with the cyclic fluorenium and chlornium ions being transition states in the interconversion of these  $\beta$ -halovinyl cations [28, 29]. Addition of  $SH^+$  to acetylene results in the cyclic ion being more stable than the corresponding vinyl cation and there is a barrier to interconversion of these ions [30]. We have recently reported a third type of profile obtained in the addition of  $F^+$  to ethylene [6]. Here the ethylenefluoronium cation was found to be an intermediate formed in the interconversion of two (equivalent) more stable 2-fluoroethyl cations. We have now constructed a reaction profile for the  $C_2H_4Cl^+$  ion by computing energies for three intermediate structures corresponding to 25%, 50% and 75% conversion from one optimized cation into the other. This method of choosing atomic coordinates assumes that the motion of all the atoms is occurring in a synchronized manner. Three different profiles, as computed with the different basis sets, are shown in Fig. 2. Each one has a barrier to interconversion with the most reliable Dunning basis set results predicting the energy of the transition state to be 15.6 kcal/mol above the more stable ethylenechloronium cation. This profile then is unlike that for the closely related reaction of  $F^+$  with ethylene, and is of the type found for the addition of  $SH^+$  to acetylene.

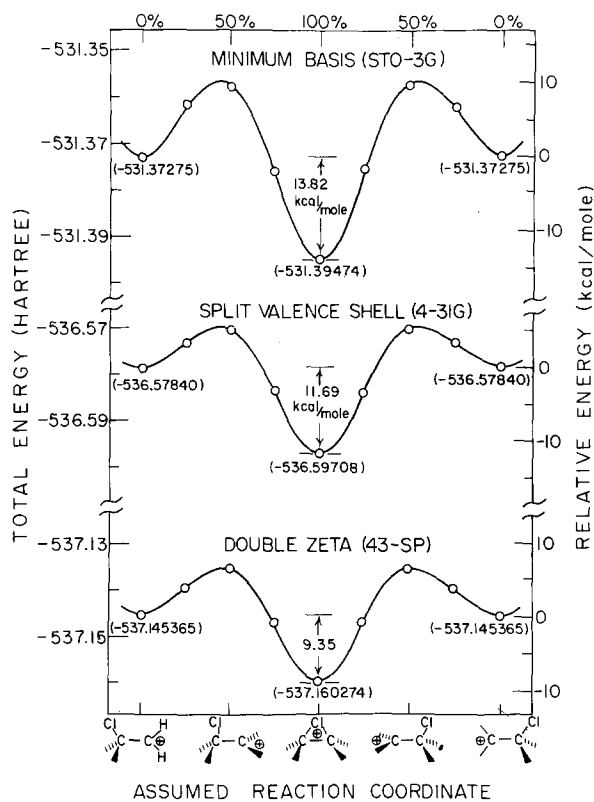


Fig. 2. Reaction profile for the interconversion of the 2-chloroethyl and the ethylenechloronium cations

There is an alternative pathway for interconversion in which the 2-chloroethyl cation rotates from the eclipsed (III) to the less stable bisected form (IV). One of the lone pairs on the chlorine atom then attacks the now adjacent empty *p*-orbital on the carbenium ion centre, resulting in a smooth transition to the cyclic ion, *without an energy barrier* [15]. The energy for rotation then would be the activation energy for this pathway. The Dunning basis set calculations gave almost the same energy for this rotational barrier (6.52 kcal/mole) as for the synchronous pathway (6.25 kcal/mole above the less stable 2-chloroethyl cation). However, these two pathways for converting the 2-chloroethyl cation into the cyclic ion are probably two extreme representations of the *same* pathway and it would appear therefore that the activated complex falls somewhere in between the two models tested here and that the activation energy will be slightly less than the 6.25 kcal/mole which we have calculated.

The energy barrier to interconversion of the  $C_2H_4Cl^+$  ions is too small to prevent formation of a small amount of the 2-chloroethyl cation at room temperature. Extrapolating to alkyl-substituted olefins our results therefore suggest that electrophilic addition of chlorine, assuming equal rates of combination with halide ion for both cations, should form predominantly, but not exclusively, the products of *trans* addition.



We have not included any  $d$ -functions on either the carbon or the chlorine atoms. Calculations on the  $C_2H_5^+$  cation using a split valence shell gave the open cation (VI) to be more stable than the bridged one (V) by 6.7 kcal/mole [31]. However inclusion of  $d$ -functions on the carbon atoms and  $p$ -functions on the bridging hydrogen atom reversed the order of stability. Thus inclusion of  $d$ -functions on the carbons and particularly on the chlorine would almost certainly result in a further stabilization of the



cyclic ion relative to the 2-chloroethyl cation. This effect is expected to be quite small, as shown in Clark's minimal basis set calculations [14], and we decided that inclusion of  $d$ -functions did not warrant expenditure of the excessively large amount of computer time required for such calculations.

### 3.3 Details of the Double-Zeta Basis Set Calculations

Detailed breakdown of the Dunning basis set calculations for the two cations and the intermediate structures used in construction of the profile for their interconversion are listed in Table 4. The virial coefficient deviates by less than 0.00032 from the theoretical value of  $-2$  required of a bound system, showing that the wave functions are indeed of high quality.

The energies of the occupied orbitals for the two cations are listed in Table 5, along with the appropriate irreducible representation from the  $C_{2v}$  and  $C_s$  point groups. Comparison of the eigenvalues for valence shell molecular orbitals (orbitals with energies less than  $-1.5$  Hartree) with those for the ethylenechloronium and 2-fluoroethyl cations [6] show that all the orbitals in the chlorine-substituted ions are more weakly bound by at least 0.12 Hartree. The largest deviation is for the  $Cl_{3s}$  orbital which is more weakly bound by greater than 0.4 Hartree than the  $F_{2s}$  orbital, thus reflecting the much larger electronegativity of the fluorine atom.

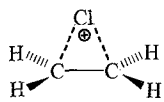
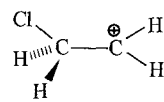
Comparison between the valence shell orbitals for the two  $C_2H_4Cl^+$  ions in Table 5 is more difficult due to the different molecular symmetries. In general, however, the valence shell orbitals of the more stable ethylenechloronium cation are the more tightly bound.

The energies for the inner electrons on the chlorine atoms also are quite different in the two  $C_2H_4Cl^+$  cations. All the inner orbitals, including the  $1s$  lone pair, on the ethylenechloronium cation are more stable by at least 2 eV than in the less stable 2-chloroethyl cation. Also the  $2p_x$ ,  $2p_y$  and  $2p_z$  atomic orbitals on the chlorine atoms are not degenerate in either of these two ions, providing further evidence that these inner electrons are involved in bonding.

Table 4. Components of the total energy (Hartree) for points on interconversion profile

|                           | 2-Chloro Cation | $\frac{3}{4}$ (2-Chloro)<br>+ | $\frac{1}{2}$ (2-Chloro)<br>+ | $\frac{1}{4}$ (2-Chloro)<br>+ | Bridged Cation |
|---------------------------|-----------------|-------------------------------|-------------------------------|-------------------------------|----------------|
| $V_{nn} = E_{nuclear}$    | 94.17080565     | 94.33645804                   | 94.93636382                   | 96.08068661                   | 98.05110629    |
| $T$                       | 537.07886720    | 537.06462057                  | 537.03159532                  | 536.97918501                  | 537.02468601   |
| $V_{ee}$                  | 286.69072215    | 286.83952236                  | 287.11757361                  | 287.83147542                  | 289.55331919   |
| $V_{ne} = E_{attraction}$ | -1455.08576031  | -1455.38005857                | -1456.22092714                | -1458.03850232                | -1461.78938206 |
| $E_{electronic}$          | -631.31617096   | -631.47591564                 | -632.071758221                | -633.22784190                 | -635.21137686  |
| $E_{repulsion}$           | 917.94039500    | 918.24060097                  | 919.08553275                  | 920.89134704                  | 924.62911149   |
| $E_{total}$               | -537.14536531   | -537.13945761                 | -537.13539439                 | -537.14715528                 | -537.16027057  |
| $V_{total}$               | -1074.22423251  | -1074.20407817                | -1074.16698971                | -1074.12634019                | -1074.18495658 |
| Virial coefficient        | -1.999876201    | -1.999860675                  | -1.999806754                  | -1.999687292                  | -1.999747590   |

Table 5. Orbital energies (Hartree) for the ethylenechloronium and 2-chloroethyl cations as computed with the Dunning double zeta

| <br>( $C_{2v}$ point group) |                            | <br>( $C_s$ point group) |                            |
|--|----------------------------|---|----------------------------|
| Energy   | Irreducible Representation | Energy  | Irreducible Representation |
| -105.1388  | $a_1$                      | -105.0588   | $a'$                       |
| -11.5984   | $a_1$                      | -11.6614  | $a'$                       |
| -11.5975   | $b_1$                      | -11.5565  | $a'$                       |
| -10.8407   | $a_1$                      | -10.7631  | $a'$                       |
| -8.3166  | $a_1$                      | -8.2396   | $a'$                       |
| -8.3132  | $b_1$                      | -8.2356   | $a'$                       |
| -8.3122  | $b_2$                      | -8.2354   | $a''$                      |
| -1.4405  | $a_1$                      | -1.4033   | $a'$                       |
| -1.2577  | $a_1$                      | -1.2742   | $a'$                       |
| -1.1251  | $b_1$                      | -1.1186   | $a'$                       |
| -0.9716  | $b_2$                      | -0.9612   | $a'$                       |
| -0.9036  | $a_1$                      | -0.8926   | $a'$                       |
| -0.8332  | $a_2$                      | -0.8764   | $a''$                      |
| -0.7489  | $a_1$                      | -0.7423   | $a'$                       |
| -0.7215  | $b_1$                      | -0.6503   | $a'$                       |
| -0.7096  | $b_2$                      | -0.6434   | $a''$                      |

The gross atomic populations for the  $C_2H_4Cl^+$  ions are shown in Fig. 3. As with the  $C_2H_4F^+$  ions, which are also included for comparison, there is a marked difference between the charges computed in our large basis set calculations and those previously reported by Hehre and Hiberty [15]. As discussed earlier this will result from differences in optimized geometries and also in basis set differences. Of more interest is the marked difference between the two pairs of cyclic and open cations. In the ethylenechloronium

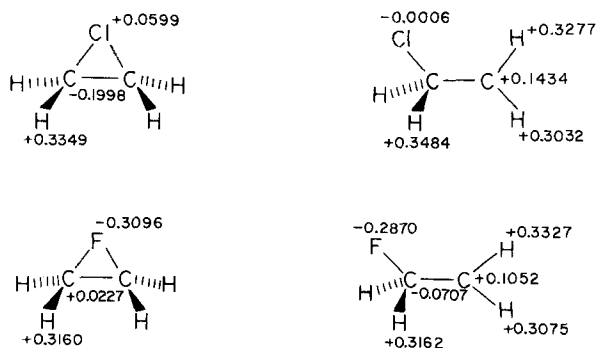


Fig. 3. Gross atomic populations for the 2-haloethyl and ethylenehalonium cations, as calculated by the Dunning basis set

cation the chlorine carried a small *positive* charge compared with a large negative one on the fluorine of the ethylenefluoronium cation. The carbon atoms also have charges of opposite signs in these two cations, with those in the chloronium ion carrying a substantial amount of negative charge. As usual for carbonium ions most of the positive charge is located on the hydrogen atoms in both ions.

A similar type of charge variation is found in the 2-chloroethyl and 2-fluoroethyl cations, with the fluorine again acquiring a much larger negative charge than the chlorine (the latter is negative also in this ion). The tertiary carbon atoms show the largest difference in these two cations, with that in the 2-chloroethyl cation having an abnormally large negative charge.

### 3.4 Reaction Profile for the Chlorination of Ethylene

We have used the Dunning basis set to compute wave functions for the reactants (ethylene and chlorine) using experimental geometries [25]<sup>2</sup>, and for the chloride ion and the energies of these species are listed in Table 6. These were then used, along with the computed energies for the  $C_2H_4Cl^+$  ions, to construct the reaction profile for this simple chlorination reaction. Computation of a wave function for 1,2-dichloroethane, the product of the reaction, using the extensive Dunning basis set was too expensive in computer time, so we have used the experimental heat of reaction ( $-43.6$  kcal/mole) [32, 33] to estimate the position of the product. Near Hartree-Fock calculations, such as those provided by the Dunning basis set, accurately reproduce heats of reaction for closed shell systems, so we are confident that the computed energy for the 1,2-dichloroethane would fall within the broad band used to represent this molecule on the profile in Fig. 4.

Analysis of the computed part of this profile showed that if the reaction proceeds *via* the cyclic cation, and the open cation is not on the reaction coordinate (as seems probable by formation of only *trans* addition products) then the calculations predict a minimum value of 128.7 kcal/mole for the activation energy. This is 4 kcal/mole smaller than that computed for the fluorination of ethylene [6] but both are unrealistically high and, even allowing for small inadequacies in the large basis set, it is clear that this mechanism is not a feasible one *for the gas phase*.

The chlorination of olefin in solution is known to be electrophilic and, at least at low halogen concentration, must have a mechanism similar to the one which we have examined. The major problem in attempting to correlate these calculations with the

Table 6. Computed total energies (Hartree) for other species involved in the electrophilic addition of  $Cl_2$  to  $CH_2=CH_2$

| Ion or Molecule  | Total Energy |
|--|--------------|
| Cl-Cl  | -918.870066  |
| $\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$ | -78.011636   |
| $Cl^-$   | -459.515906  |

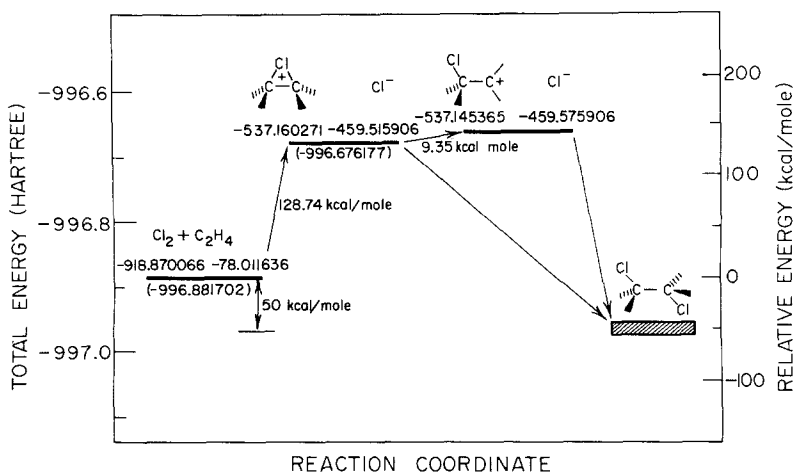


Fig. 4. Overall reaction profile for the electrophilic addition of Cl<sub>2</sub> to CH<sub>2</sub>=CH<sub>2</sub>

solution reaction is that the molecular orbital calculations produce energies for *isolated* ions and molecules. In solution the ions in particular would be heavily solvated and the cations and halides would not be at infinite separation as in the calculations.

The relevance of these calculations to the mechanism of chlorination of ethylene in solution then is in the comparison of the two possible intermediate cations. Solvation and the proximity of the halide ion should stabilize both these species by approximately the same amount and it seems reasonable to conclude that the ethylene-chloronium cation will be the more stable ion in solution (as also indicated by the NMR results), and that there will be a small barrier to interconversion of these ions.

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