J. Am. Chem. Soc. **1993,** *115,* 3263–3269 3263

Isomers of $C_2H_4Cl^+$: Structures, Frequencies, and Energetics

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Received August 5, 1992

Abstract: High level ab initio molecular orbital calculations which include correlation energy, zero-point energies, and thermal corrections have been used to explore the $C_2H_4Cl^+$ hypersurface. The 1-chloroethyl cation is the global minimum with the chloronium ion lying 4.3 kcal mol^{-1} above it at the MP4SDTQ/6-311G(2df,p)//MP2/6-311G(d,p) level. The energy barrier for the conversion of the chloronium ion to the 1-chloroethyl cation was calculated to be 27.8 kcal mol^{-1} at the MP4 level and was found to be sensitive to electron correlation. The transition structure for interconversion of these two ions has been fully characterized with calculation of vibrational frequencies at MP2/6-311G(d,p). The 2-chloroethyl cation, which is a minimum with C_1 symmetry at the SCF/6-31G(d,p) level, collapses without a barrier to the 1-chloroethyl cation when zero-point energies are included. High-energy isomers, chlorine-protonated vinyl chloride, and an ion–dipole complex have also been found on the $C_2H_4Cl^+$ surface. Vinyl chloride protonates on the carbon of the CH_2 group and has a proton affinity of 171.4 kcal mol^{-1}. Calculated enthalpies of formation $\Delta H^\circ_{f,298}$ for the 1-chloroethyl cation and the chloronium ion are 198.1 and 202.0 kcal mol^{-1}, respectively. The difference (3.9 kcal mol^{-1}) in $\Delta H^\circ_{f,298}$ between these two isomers compares with experimentally determined differences of 5.6 and 2 kcal mol^{-1}. Calculated vibrational frequencies and intensities are compared with the experimental spectra, and if only one ion contributes to these spectra, the calculations favor the chloronium ion.

Introduction

The nonclassical bridged structure of halonium ions continues to be a topic of considerable interest in organic chemistry. In 1937, Roberts and Kimball[1] proposed a cyclic bromonium ion intermediate to explain the stereoselective bromination reactions with alkenes. Several decades later, the chloronium ion analogue was found by Fahey et al.[2] Since then the halonium ions have been heavily investigated in superacid media and in solvolytic reactions.[3] Experimental studies have shown that the structure of a halonium ion depends on the halogen, the substituent groups on the double bond, and the solvent.[4]

In the gas phase, the generation and detection of these halonium ions[5-8] has sparked controversy due to the method of producing the reactant ion[8] and to the inability of the experiment to provide structures.[6] Experimental enthalpies of formation are known for the nonclassical bridged and classical α-substituted structures.[8-10] In the case of $C_2H_4Cl^+$, Berman et al.[8] using the PIMS method found the difference between the enthalpies of formation for the bridged and open structures to be 5.6 kcal mol^{-1}. Holmes et al.[9] using appearance energies found a difference of 2 kcal mol^{-1}.

The $C_2H_4F^+$ and $C_2H_4Br^+$ potential surfaces[11,12] have been calculated at high levels of theory,[11d,12e] but the $C_2H_4Cl^+$ hypersurface[13-18] has yet to be subjected to such rigorous study. Ab initio calculations at SCF/6-31G(d,p) show that the 1-chloroethyl cation is the global minimum while the 2-chloroethyl cation is a transition structure which collapses to the chloronium ion.[18] The relative energies between the 1-chloroethyl cation and the chloronium ion are 2.48 and 0.38 kcal mol^{-1} from the IEPA and CEPA methods,[11b] respectively, while at the MP2/6-31G(d,p) level with zero-point energies included, the difference is 5.6 kcal mol^{-1}; MNDO[16] calculations show this difference to be 4.3 kcal mol^{-1}. The experimental IR spectrum of the 1-chloroethyl cation in a cryogenic solid matrix has been reported recently,[19] but to date there have been no calculated vibrational frequencies.

We are currently interested in reactions in the gas phase which will generate Cl^+ adducts of alkenes and alkynes. Previously,[15] we calculated the interconversion barrier between the 2-chloroethyl cation and the chloronium ion to be 6.3 kcal mol^{-1} at the SCF/4-31G level and studied substituent effects in $C_2H_4X^+$ isomers for X = NH_2, PH_2, AsH_2, OH, SH, and SeH.[20] As an extension of these interests we have chosen to study the $C_2H_4Cl^+$ hypersurface using the ab initio molecular orbital method up to the MP4SDTQ/6-311G(2df,p)//MP2/6-311G(d,p) level with calculated vibrational frequencies at the SCF/6-31G(d,p) and MP2/6-311G(d,p) levels to characterize the stationary points on the surface. These calculations also include thermal corrections

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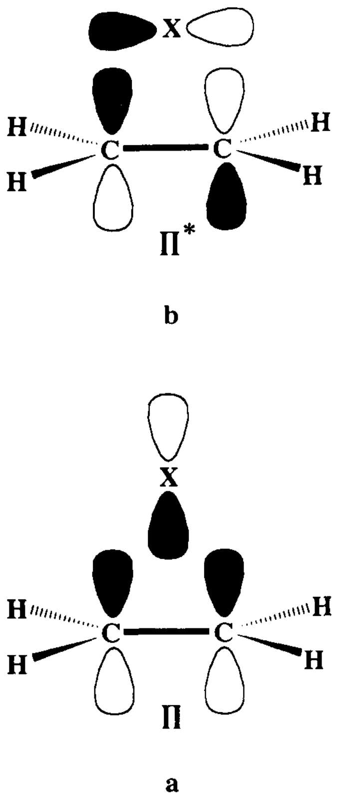
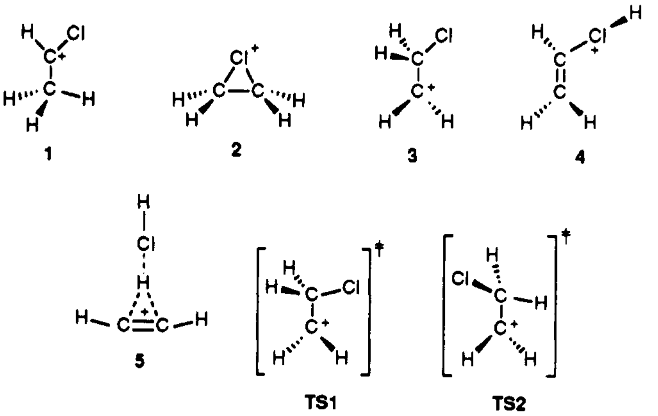


Figure 1. Orbital interactions: (a) π-donation from ethylene to the vacant p-orbital on X; (b) back-donation from X to π* on ethylene.

Chart I



which are essential for a direct comparison with gas-phase chemistry. Enthalpies of formation ($\Delta H^\circ_{f,298}$) have been calculated using methods employed by Pople's group.[21]

The criteria that determine whether or not a cyclic halonium ion is a three-membered ring or a π-complex are not clearly defined. In this paper we will use Dewar's model.[16,20] In a three-membered ring, two types of interactions are critical (Figure 1). If both donation from the π-orbital on ethylene to an empty p-orbital on chlorine (Figure 1a) and back-donation from a lone pair in a p-orbital on chlorine to π* (Figure 1b) are operative and approximately equal, then four electrons are involved in forming the two C–Cl bonds and the structure is best considered to be a three-membered ring. If there is negligible back-bonding, then the interaction is weaker and the combination is best considered as a π-complex.

In this work we report our high-level calculations on the 1-chloroethyl cation (**1**), the chloronium ion (**2**), the 2-chloroethyl cation (**3**), the chlorine-protonated vinyl chloride (**4**), and the ion–dipole complex (**5**). We also report the transition structure for the interconversion of the chloronium ion and the 1-chloroethyl cation (**TS1**) and the transition structure for the interconversion of the 2-chloroethyl cation and the 1-chloroethyl cation (**TS2**).

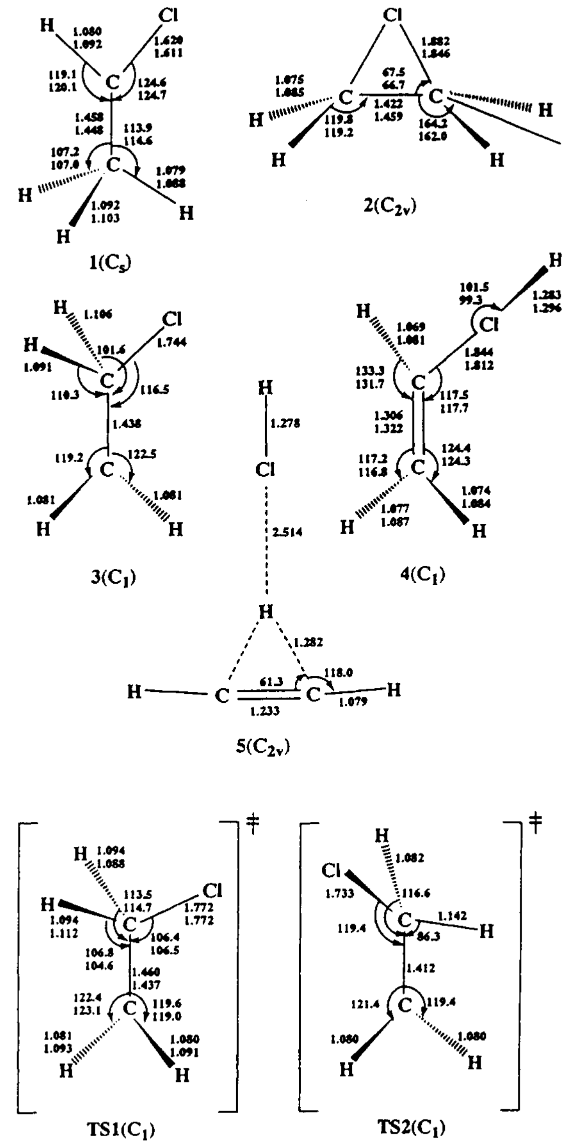


Figure 2. Optimized structures (lengths in Å, angles in deg). The upper numbers are from SCF/6-31G(d,p), and the lower numbers are from MP2/6-311G(d,p). **TS2** and **3** were examined only at SCF and **5** only at MP2.

Computational Method

All calculations were carried out using the Gaussian 82[22] and Gaussian 86[23] programs. Full structure optimizations were carried out on all critical points of the $C_2H_4Cl^+$ hypersurface using the 6-31G(d,p)[24] basis set at the SCF level (denoted SCF/6-31G(d,p)). Several of the more important structures (**1**, **2**, **4**, **5**, and **TS1**) were also optimized using the 6-311G-(d,p) basis set[25] and including electron correlation with second-order Moller–Plesset correction terms[26] (denoted MP2/6-311G(d,p)). All the structural details are shown in Figure 2. The critical points on the SCF/6-31G(d,p) surface were characterized by analytic frequency calculations

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Table I. Total Energies (hartrees) and Relative, Zero-Point, and Thermal Energies (all kcal mol^{-1}) from Structure Optimization Calculations

	SCF/6-31G(d,p)//SCF/6-31G(d,p)				MP2/6-311G(d,p)//MP2/6-311G(d,p)			
ions	total	relative	ZPE[a]	thermal	total	relative	ZPE[b]	thermal
CH_3CHCl^+ (**1**)	–537.22905	0	31.6	2.5	–537.76948	0	33.9	2.6
					–537.82901[c]	0		
$H_2CClCH_2^+$ (**2**)	–537.21885	6.4	33.0	2.2	–537.76655	1.8	35.9	2.1
					–537.82454[c]	2.8		
$CH_2CH_2Cl^+$ (**3**)	–537.19564	21.0	30.6	2.7				
CH_2CHClH^+ (**4**)	–537.18671	26.6	30.4	2.6	–537.73753	20.0		
$C_2H_3{\cdot}ClH^+$ (**5**)					–537.69855	44.5		
TS1, **2** → **3**	–537.19197	23.3	31.2	2.1	–537.71489	34.3	33.4	2.2
					–537.77648[c]	30.2		
TS2, **3** → **1**	–537.19543	21.1	30.4	2.2				
$CH_2CH_2 + Cl^+$			30.4	1.9	–537.61079[c]	136.9		
$CH_2CHCl + H^+$	–536.93908	182.0	25.6	2.1	–537.48671	177.4		
					–537.54803[c]	176.3		
$C_2H_3^+ + HCl$					–537.69110	49.0		

[a] Scaled by 0.89. [b] Unscaled. [c] MP4SDTQ/6-311G(2df,p)//MP2/6-311G(d,p). Additional total energies (hartrees) at PMP4SDTQ/6-311G(2df,p) for C (–37.77544), Cl (–459.65714), Cl^+ (–459.18833), and H (–0.49981). Additional total energies (hartrees) at MP4SDTQ/6-311G(2df,p)//MP2/6-311G(d,p) for H_2 (–1.16773), C_2H_4 (–78.42246), and $C_2H_3^+$ (bridged) (–77.43002). At MP2/6-311G(d,p) for HCl (–460.29297), and $C_2H_3^+$ (–77.39839).

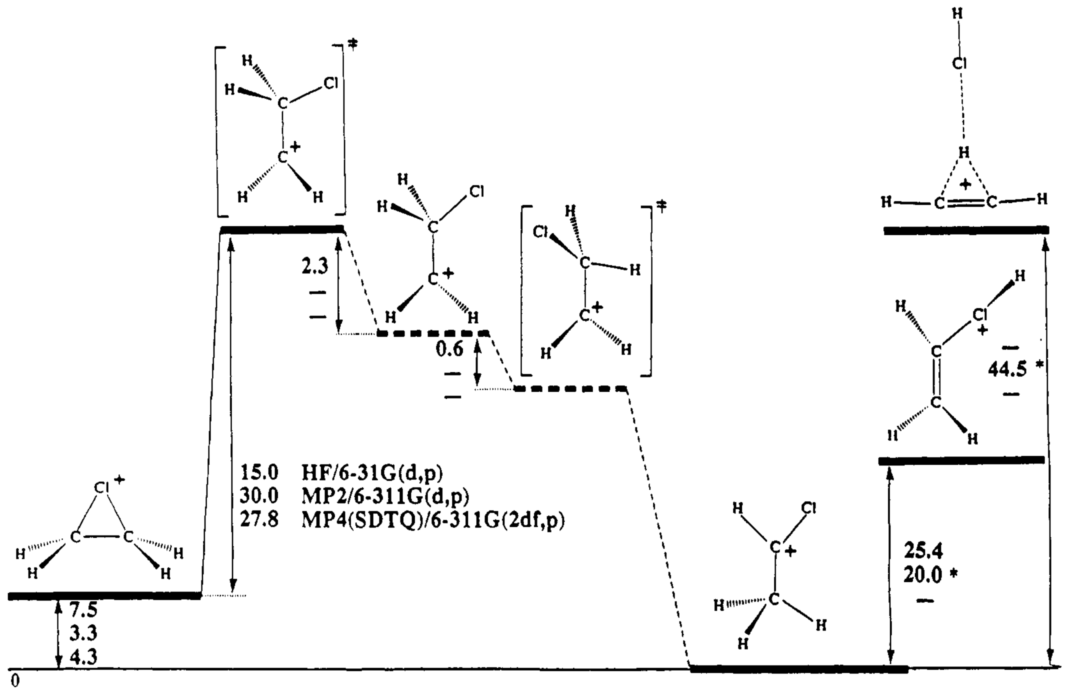

Figure 3. Relative energies (kcal mol^{-1}) of $C_2H_4Cl^+$ isomers at 298.15 K. Numbers marked with an asterisk do not include zero-point and thermal energies.

which yielded zero-point energies and thermal corrections. On the MP2/6-311G(d,p) surface numeric frequency calculations were used. Single-point calculations at fourth-order Møller–Plesset[27] theory were done with the 6-311G(2df,p) basis set at the optimized MP2/6-311G(d,p) geometry, denoted MP4SDTQ/6-311G(2df,p)//MP2/6-311G(d,p). Transition structures were found at the SCF/6-31G(d,p) level with the aid of the CALCALL routine in Gaussian 86, and these structures were then used to find their MP2/6-311G(d,p) counterparts.

Results and Discussion

Relative Energies. Table I lists the total energies and relative energies (not including zero-point energies and thermal corrections to 298.15 K). By contrast all these terms are included in the relative energy diagram in Figure 3. The global minimum on the $C_2H_4Cl^+$ hypersurface is the 1-chloroethyl cation and the nonclassical chloronium ion is also a minimum lying 7.5, 3.3, and 4.3 kcal mol^{-1} above structure **1** at the SCF, MP2, and MP4 levels, respectively. If we compare these results with the experimental difference in enthalpies of formation between the chloronium ion and the 1-chloroethyl cation, we find the 5.6 kcal mol^{-1} value of Berman et al.[8] closer to our calculated value of 4.3 kcal mol^{-1}. The other experimental value, 2 kcal mol^{-1} reported by Holmes et al.,[9] is slightly lower than our calculated value.

At the SCF level the 2-chloroethyl cation is a minimum with C_1 symmetry and lies 20.2 kcal mol^{-1} above the 1-chloroethyl cation. The transition structure for interconversion of these ions, **TS2**, is only 0.1 kcal mol^{-1} above the 2-chloroethyl cation, and when zero-point energy and thermal corrections are included, **TS2** becomes lower in energy than the 2-chloroethyl cation. Clearly then there is no barrier to interconversion between the 2-chloroethyl cation and the global minimum and the former isomer does not exist on the $C_2H_4Cl^+$ hypersurface.

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Inclusion of correlation energy is essential for the accurate determination of the barrier to interconversion of the chloronium ion and the 1-chloroethyl cation. At the SCF level the transition structure **TS1** for this interconversion is 15.0 kcal mol^{-1} above the chloronium ion but at the MP2/6-311G(d,p) level this barrier doubles to 30.0 kcal mol^{-1} and at our highest level of theory, MP4SDTQ/6-311G(2df,p)//MP2/6-311G(d,p), it is 27.8 kcal mol^{-1}. Inclusion of correlation energy usually favors nonclassical structures, and the chloronium ion is also stabilized by 3.2 kcal mol^{-1} relative to the classical 1-chloroethyl cation.

There are two high-energy minima on the $C_2H_4Cl^+$ hypersurface. Chlorine-protonated vinyl chloride lies 25.4 kcal mol^{-1} above the 1-chloroethyl cation at the SCF/6-31G(d,p) level and 20.0 kcal mol^{-1} above at MP2/6-311G(d,p). The other minimum is an ion–dipole complex structure **5** which lies 44.6 kcal mol^{-1} above the global minimum at the MP2/6-311G(d,p) level. We did not pursue these structures at higher levels of theory.

Structural Details. (a) 1-Chloroethyl Cation (1). On the $C_2H_4X^+$ hypersurfaces, the 1-haloethyl cation is the global minimum for X = F and Cl,[11d,19] while the bridged halonium ion becomes the most stable isomer when X = Br[12e] and I.[28] There are two rotamers of the 1-chloroethyl cation, the eclipsed 1-chloroethyl cation and the bisected 1-chloroethyl cation. The eclipsed rotamer is the more stable of the two, by 1.2 kcal mol^{-1} at the SCF level. Furthermore, the eclipsed 1-chloroethyl cation is a minimum (ν_1 = 104 cm^{-1}),[29] while the bisected 1-chloroethyl cation is a transition structure (ν_1 = −203 cm^{-1})[29] for methyl rotation. Inclusion of correlation in the eclipsed 1-chloroethyl cation causes the C–Cl and C–C bonds to shorten and the C–H bonds to lengthen slightly.

The experimental C–Cl bond length in ethyl chloride[30] is 1.789 Å, in comparison to 1.611 Å for the MP2/6-311G(d,p) calculated structure. This shows the interaction between the chlorine lone pair and the empty p-orbital on the positively charged carbon (Figure 4a). In ethyl chloride the experimental carbon–carbon single bond is 1.520 Å while the carbon–carbon double bond, taken from microwave data on vinyl chloride,[30] is 1.33 Å. Our MP2/6-311G(d,p) calculated carbon–carbon bond length of 1.448 Å is intermediate between a double bond and a single bond and is indicative of hyperconjugative π-donation[13,31] from the methyl groups (Figure 4b). Both of these interactions stabilize the eclipsed 1-chloroethyl cation enough to overcome the repulsion of the methyl hydrogen eclipsing with the chlorine atom and as a result the eclipsed structure is lower in energy than the bisected 1-chloroethyl cation. This preference for hydrogen to eclipse partly double-bonded molecules is well-known[13,31b] and is evident on the $C_2H_4F^+$ hypersurface[11d] but not in the case of $C_2H_4Br^+$.[12c]

(b) Chloronium Ion (2). This nonclassical $C_2H_4Cl^+$ isomer is a minimum with the lowest calculated vibrational frequencies of 442 cm^{-1} at the SCF level and 589 cm^{-1} at the MP2/6-311G(d,p) level (Table II).

Halonium ions have interesting structures which cannot be described satisfactorily without inclusion of correlation energy. We use structural parameters, charge distribution and the magnitude of coefficients involved in the interacting molecular orbitals in Figure 1 to assess whether the chloronium ion is best thought of as a π-complex or as a three-membered ring. Obviously any such discussion is subjective, but we follow the lead of previous studies[12e,20] in our analysis.

The C–C distance in the chloronium ion of 1.459 Å is intermediate between the experimental C–C single bond in cyclopropane (1.514 Å[32]) and the double bond in cyclopropene (1.296 Å[33]). Charge is also important in determining structure and perhaps the cyclopropyl and bridged ethyl cations are better species with which to compare the chloronium ion. The cyclopropyl cation can be viewed as a complex between ethylene and a doubly-excited state of CH^+ in which there is a π-donation to the vacant p-orbital on carbon (as in Figure 1a) and back-donation from a doubly-occupied orbital on carbon to π^* (Figure 1b). Both these interactions lead to elongation of the C–C bond in the "ethylene" fragment. The CH^+ group is expected to be a better back-donor than Cl^+ and this is reflected in the relatively short vicinal bonds (1.453 Å) and long distal bond (1.522 Å) of the cyclopropyl cation.[34] The cyclopropyl cation can then be considered as the prototype for a 3-membered ring carrying a positive charge. The other extreme structure is the bridged ethyl cation, where there is no possibility of back-donation, and in this π-complex the C–C distance is 1.385 Å (at MP2/6-311G(d,p)). In the chloronium ion the C–C distance then is halfway between that expected for a pure π-complex and that for a three-membered ring. The argument for considerable three-membered-ring character is strengthened by the C–Cl distance in the chloronium ion (1.846 Å), which is only slightly longer than the experimental value for the single C–Cl bond in ethyl chloride.[30]

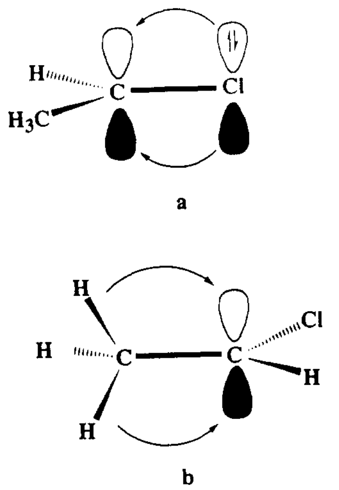

Figure 4. Donation into the "vacant" p-orbital of the 1-chloroethyl cations: (a) from the chlorine lone pair and (b) by hyperconjugation from methyl.

The angle θ between the bisector of HCH and the C–C bond is a measure of the hybridization at carbon; for ethylene it is 180° and for cyclopropane 150°. This angle, θ, decreases from 164.2° to 162° when electron correlation is included, showing an increased tendency for sp^3 character. Also, the ∠CCCl is 66.7° in the chloronium ion as compared to 60° for cyclopropane.

Although there are no C–C single bond stretching frequencies (~1600 cm^{-1}) indicated from the calculations, there is a vibrational frequency at 1471 cm^{-1} (after scaling the SCF/6-31G(d,p) frequency by a factor of 0.89) which consists of a carbon–carbon stretch coupled with CH_2 scissoring. This frequency is similar to that of three-membered rings containing weakly electronegative atoms.[16]

Finally, the Mulliken population analysis at the 6-31G(d,p) level gave a charge of +0.322 on Cl, −0.247 on C, and +0.293 on H, indicating that most of the positive charge is delocalized away from the chlorine, as expected in a π-complex. Moreover at the highest level of theory (6-311G(2df,p)) the positive charge on chlorine is only +0.185. Analysis of the highest filled a$_1$-type orbital (the interaction in Figure 1a) showed approximately equal contributions from both carbon and chlorine, indicating a strong

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Table II. Frequencies (in cm^{-1}) and Intensities (in Parentheses, units km mol^{-1}) Calculated for 1-Chloroethyl (**1**), Chloronium (**2**), and **TS1**

SCF/6-31G(d,p)//SCF/6-31G(d,p)			MP2/6-311G(d,p)//MP2/6-311G(d,p)		
1	**2**	**TS1**	**1**	**2**	**TS1**
3349 (A′) (23)	3456 (B_1) (62)	3412 (48)	3237 (A′) (20)	3326 (B_1) (51)	3278 (36)
3338 (A′) (5)	3444 (A_2) (0)	3300 (26)	3203 (A′) (8)	3313 (A_2) (0)	3210 (12)
3193 (A″) (23)	3332 (A_1) (1)	3287 (25)	3073 (A″) (35)	3201 (A_1) (3)	3153 (11)
3139 (A′) (66)	3328 (B_2) (23)	2754 (139)	3022 (A′) (125)	3199 (B_2) (24)	2948 (94)
1605 (A′) (28)	1653 (A_1) (8)	1633 (10)	1515 (A′) (44)	1546 (A_1) (2)	1543 (3)
1545 (A″) (27)	1593 (B_2) (14)	1482 (22)	1431 (A″) (28)	1503 (B_2) (13)	1411 (51)
1494 (A′) (15)	1335 (A_1) (9)	1428 (44)	1404 (A′) (38)	1273 (A_1) (4)	1362 (13)
1454 (A′) (96)	1317 (A_2) (0)	1368 (16)	1324 (A′) (94)	1232 (A_2) (0)	1306 (4)
1251 (A′) (25)	1283 (B_2) (32)	1255 (17)	1224 (A′) (101)	1213 (B_2) (33)	1226 (65)
1149 (A″) (1)	1219 (A_1) (0)	1131 (8)	1098 (A′) (206)	1162 (A_1) (0)	1051 (25)
1127 (A′) (226)	1057 (A_2) (0)	1061 (17)	1059 (A″) (0)	1025 (A_2) (0)	1018 (13)
855 (A′) (12)	1034 (B_1) (0)	790 (22)	847 (A′) (1)	1022 (B_1) (0)	752 (3)
834 (A″) (9)	904 (B_1) (3)	574 (2)	761 (A″) (13)	861 (B_1) (2)	699 (18)
423 (A′) (5)	567 (A_1) (108)	413 (26)	413 (A′) (3)	617 (A_1) (61)	438 (7)
104 (A″) (1)	442 (B_2) (47)	326i	126 (A″) (3)	589 (B_2) (17)	487i

interaction. In the highest-filled orbital of b_2 symmetry (the interaction in Figure 1b) the coefficient on the chlorine $3p_y$ was approximately four times larger than those on carbon $2p_z$ atomic orbitals and back-donation is clearly less effective.

(c) 2-Chloroethyl Cation (3). At the SCF level the structures of two rotamers of 2-chloroethyl cation are at critical points. As found by Reynolds,[18] the eclipsed conformation, in which the chlorine atom is coplanar with the CH_2^+ group, has one imaginary frequency ($\nu_1 = -120$ cm^{-1})[29] and is therefore a transition structure. The structure at the other critical point, **3**, has C_1 symmetry and is at a shallow minimum (lowest frequency is 104 cm^{-1}). In this structure, which was not previously found to be a critical point,[18] some geometric parameters indicate a tendency for one hydrogen atom to be bridging (a C–H bond in the CH_2Cl group is slightly longer than expected (1.106 Å) and ∠CCH for the same hydrogen is small (101.6°)). A further slight displacement of this hydrogen was found to result in a 1,2-hydride shift and formation of the 1-chloroethyl cation.

Both 2-chloroethyl structures are artifacts of the SCF level calculations and are not critical points when electron correlation is included. Indeed, inclusion of zero-point and thermal energies is sufficient to make **3** higher in energy than the transition structure for its rearrangement into the 1-chloroethyl cation. Structure **3** is of some interest, however, due to its structural similarity to the transition structure for interconversion of **1** and **2**.

(d) Chlorine-Protonated Vinyl Chloride (4). There have been no structural data reported for this isomer. The gauche structure is a minimum ($\nu_1 = 237$ cm^{-1})[29] and the two planar structures each have one calculated imaginary frequency at the SCF level and are transition structures for rotation about the carbon–chlorine bond. We have not attempted to find any transition structures between the chlorine-protonated vinyl chloride and structures **1** and **2** on the hypersurface. At the MP2 level the C–Cl bond length of 1.812 Å is longer than that in vinyl chloride while the C–C bond length in the chlorine-protonated vinyl chloride is shorter than in vinyl chloride by 0.011 Å. Dissociation of the chlorine-protonated vinyl chloride into $C_2H_3^+$ and HCl is endothermic by 29.0 kcal mol^{-1} at the MP2 level.

(e) Ion–Dipole Complex (5). As in the case of chlorine-protonated vinyl chloride, there has been no previous study of the ion–dipole complex. Dissociation of **5** into $C_2H_3^+$ and HCl is endothermic by 4.5 kcal mol^{-1} at the MP2 level. This calculated dissociation energy is inaccurate because the molecular orbital method cannot properly describe ions of this type (solvated ion complex). The complex has a long bond length (2.514 Å) between the two fragments and resembles $C_2H_3^+$ solvated by HCl. The geometry of the isolated $C_2H_3^+$ at the MP2 level (C–C 1.234 Å, and C–H(bridging) 1.281 Å) is almost identical with that of the $C_2H_3^+$ in the complex. Similarly, isolated HCl has a bond length of 1.274 Å at MP2/6-311G(d,p), compared with a distance of 1.278 Å in the complex.

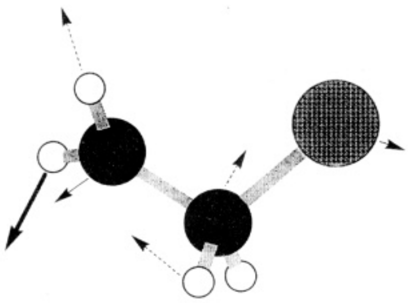

Figure 5. Motion of atoms in **TS1** from harmonic frequency calculations at MP2/6-311G(d,p).

(f) Transition Structure 1 (TS1). This is the transition structure for the interconversion of the chloronium ion to the 2-chloroethyl cation on the SCF/6-31G(d,p) hypersurface (Figure 3). When electron correlation was included, the C–C distance of **TS1** decreased, becoming similar to that calculated for the 2-chloroethyl cation at the SCF level. Furthermore, since inclusion of electron correlation resulted in both the 2-chloroethyl cation and **TS2** no longer being critical points, the energy hypersurface is simplified, with **TS1** being the transition structure for interconversion between chloronium and 1-chloroethyl cations.

The MP2/6-311G(d,p) structure was found by initially optimizing the geometry at fixed CCCl angles. A reaction profile was drawn, the maximum energy was found, and the corresponding critical point geometry was then used to calculate the vibrational frequencies. For this MP2/6-311G(d,p) structure there was one imaginary frequency (at −487 cm^{-1}) indicating a transition structure. From this structure we can see both the chlorine (∠CCCl = 106.5°) and a hydrogen (∠HCC = 104.6°) are slightly distorted in the direction required by bridging. Bridging by hydrogen leads to a 1,2-hydride shift and formation of the 1-chloroethyl cation, while bridging by chlorine is a structural feature of the chloronium ion. The motions associated with this transition structure (Figure 5) confirm the above analysis.

(g) Transition Structure 2 (TS2). It is well-known that the activation barrier for a 1,2-hydride shift in carbocations is small and **TS2**, for the conversion of the 2-chloroethyl cation into the 1-chloroethyl cation, is only 0.1 kcal mol^{-1} above the 2-chloroethyl cation at the SCF level and does not exist when electron correlation is included. Furthermore, at the SCF level, when zero-point and thermal energies are included, the barrier disappears. This structure then is an artifact of optimization at the SCF level and is of no physical significance. It is interesting to note that a transition structure analogous to **TS2** was also calculated at the SCF level for $C_2H_4Br^+$, but optimization at higher levels "proved insurmountable".[12e]

Table III. Comparison of Scaled Calculated and Experimental Frequencies[a] for 1-Chloroethyl Cation (**1**) and Chloronium Ion (**2**)

SCF/6-31G(d,p)[b]		MP2/6-31G(d,p)[c]		MP2/6-311G(d,p)[d]		
1	**2**	**1**	**2**	**1**	**2**	expt[e]
2981 (23)	3076 (62)	3094 (2)	3048 (3)	3075 (20)	3041 (3)	3040
2971 (5)	3065 (0)	3055 (10)	3048 (23)	3043 (8)	3039 (24)	
1428 (28)	1418 (14)	1449 (38)	1435 (13)	1439 (44)	1428 (13)	1410
1375 (27)						
1113 (25)	1142 (32)	1161 (88)	1140 (26)	1163 (101)	1152 (33)	1140
1023 (1)	1085 (0)	1042 (210)	954 (0)	1043 (206)	973 (0)	975
1003 (226)	941 (0)	1016 (0)	953 (0)	1006 (0)	971 (0)	940
	920 (0)					

[a] Frequencies in $\mathrm{cm^{-1}}$; intensities are in parentheses in km $\mathrm{mol^{-1}}$. [b] Scaled by 0.89. [c] Scaled by 0.94. [d] Scaled by 0.95. [e] Reference 19.

Table IV. Protonation Energies (kcal $\mathrm{mol^{-1}}$)[a] of Vinyl Chloride at Various Levels of Theory

site of protonation	SCF/ 6-31G(d,p)	MP2/ 6-311G(d,p)	MP4SDTQ/ 6-311G(2df,p)[b]
C of CH_2	176.8	172.3	171.4
C of CHCl	161.7		
Cl	156.2	158.2	

[a] At 298 K. [b] Using geometry optimized at MP2//6-311G(d,p).

Frequencies. It has been well-documented[35-37] that SCF harmonic frequencies are usually 10% too high. From experiments on cations generated from dichloroethanes, the most intense peak occurs at 1140 $\mathrm{cm^{-1}}$ and is attributed to a C–Cl stretch.[19] Our frequency calculations on the 1-chloroethyl cation show that the vibrational mode with the largest intensity (Table 2) is at 1127 $\mathrm{cm^{-1}}$ (intensity 226 km $\mathrm{mol^{-1}}$) and 1098 $\mathrm{cm^{-1}}$ (intensity 206 km $\mathrm{mol^{-1}}$) for the HF/6-31G(d,p) and MP2/6-311G(d,p) levels, respectively. Scaling these frequencies will make them much smaller than the reported experimental frequency, and this casts serious doubt on the assignment of the 1-chloroethyl cation structure (**1**) to the ion formed when dichloroethane and antimony pentafluoride were codeposited on a cesium iodide window at 77 K.[19] By contrast, one of the most intense peaks in the vibrational spectrum calculated for the chloronium ion (**2**) is at 1283 $\mathrm{cm^{-1}}$ (SCF level) and 1213 $\mathrm{cm^{-1}}$ (MP2 level). Scaling of this frequency results in a number close to the experimentally observed peak at 1140 $\mathrm{cm^{-1}}$.

We have applied a scale factor of 0.89 to the frequencies calculated at SCF/6-31G(d,p) and factors of 0.94 and 0.95 to the two different sets of MP2 calculations.[35] The calculated frequencies which are closest to the experimental values are listed in Table III. The data calculated for the chloronium ion correlate particularly well with the experimental data. The most intense peak in the calculated spectrum for the chloronium ion is at 1152 $\mathrm{cm^{-1}}$. This proximity, however, does not permit unambiguous assignment of the spectrum to that of the chloronium ion as there is also a frequency of high intensity at 1163 $\mathrm{cm^{-1}}$ in the calculated spectrum of the 1-chloroethyl cation. The most intense transition in the 1-chloroethyl cation spectrum is calculated to be at 1043 $\mathrm{cm^{-1}}$ and coincides with a peak in the spectrum of the ion derived from 1,1-dichloroethane; this peak is not present in the spectrum of the ion generated from 1,2-dichloroethane and this difference in the two experimental spectra was not discussed previously.[19]

As noted earlier the experimental peaks at 975 and 940 $\mathrm{cm^{-1}}$ present a problem. They are absent in the spectrum calculated for the 1-chloroethyl cation, and although they are present in the chloronium ion spectrum, they have almost identical frequencies and are very weak.

In summary, the theoretical results do not unambiguously support the sole existence of either the 1-chloroethyl cation or the chloronium ion on the basis of the spectra obtained in the low-temperature experiments. The spectrum of the ion derived from 1,2-dichloroethane fits best with the data calculated for the chloronium ion, but the extra peak (around 1040 $\mathrm{cm^{-1}}$) in the spectrum formed with 1,1-dichloroethane as the precursor is more consistent with the harmonic frequency calculation on the 1-chloroethyl cation. The similarities in the two experimental spectra argue strongly for a common structure, but several features of the calculated spectra for the two ions are similar and it seems plausible that *both* ions are present, particularly in the 1,1-dichloroethane/SbF_5 mixture. If there is only one ion in the matrices, then the calculated spectral data favor the chloronium ion. This requires reversing the relative stabilities of the ions, but the small energy difference (4.3 kcal $\mathrm{mol^{-1}}$) between the two structures is for the gas phase and may well be reversed in the solid phase. However, the energy barrier of 27.8 kcal $\mathrm{mol^{-1}}$ is sufficiently high to prevent rapid interconversion at 77 K and the two dichloroethane precursors could result in different product ions at this temperature.

Proton Affinity of Vinyl Chloride. The three heavy atoms of vinyl chloride are all potential sites for protonation. Proton affinities, the enthalpy changes for the protonation reaction illustrated by eq 1, are given at various levels of theory in Table IV. For protonation on the carbon atom of the CHCl group the product, 2-chloroethyl cation, is not at a minimum and only an SCF-level proton affinity is reported.

$$C_2H_3Cl + H^+ \rightarrow C_2H_4Cl^+ \qquad (1)$$

The protonation reaction has the same number of electron pairs on both sides of the equation and inclusion of electron correlation might therefore be expected to be unimportant in the calculation of proton affinities. However, proton affinities at the SCF level are usually less accurate and are generally higher than values calculated from correlated wave functions. Proton affinities at MP4SDTQ/6-311G(2df,p) are usually within 2 kcal $\mathrm{mol^{-1}}$ of the experimental value, and MP2(full)/6-311G(d,p) calculations are of comparable accuracy.

Protonation on the CH_2 group produces the 1-chloroethyl cation and is calculated to be exothermic by 172.3 kcal $\mathrm{mol^{-1}}$ at MP2/6-311G(d,p) and 171.4 kcal $\mathrm{mol^{-1}}$ at MP4SDTQ/6-311G(2df,p). These values compare with an experimental proton affinity of 162.6 kcal $\mathrm{mol^{-1}}$ for ethylene,[38] showing that the chlorine enhances the basicity of alkenes by ~10 kcal $\mathrm{mol^{-1}}$. Protonation at the chlorine atom of vinyl chloride is exothermic by 158.2 kcal $\mathrm{mol^{-1}}$ (MP2/6-311G(d,p)). This value is surprisingly low when compared with the experimental proton affinities of methyl chloride (~163 kcal $\mathrm{mol^{-1}}$)[10] and ethyl chloride (169 kcal $\mathrm{mol^{-1}}$).[10]

The calculated proton affinity of the vinyl chloride can be combined with the experimental enthalpies of formation of C_2H_3Cl (5 ± 0.5 kcal $\mathrm{mol^{-1}}$)[10] and H^+ (365.7 kcal $\mathrm{mol^{-1}}$)[10] to calculate the enthalpy of formation of the 1-chloroethyl cation. Using this procedure $\Delta H°_{f,298}$ for the 1-chloroethyl cation is 198.4 kcal $\mathrm{mol^{-1}}$ (MP2/6-311G(d,p)) and 199.3 kcal $\mathrm{mol^{-1}}$ (MP4SDTQ/6-311G(2df,p)).

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An alternative approach to calculating enthalpies of formation is to use molecular orbital theory to provide heats of atomization[21,39] and to use experimental enthalpies of formation of the constituent atoms. We have recently found that using this procedure with MP4SDTQ/6-311++G(2df,p) calculations provides enthalpies of formation of silyl anions and radicals within ±3 kcal mol^{-1} of the experimental values.[40] In the current work our approach is slightly different; since we are dealing only with positive ions and neutral atoms, we have not included diffuse functions in the basis set. For the open-shell atoms we have used spin-projected UMP4 calculations[41] (PMP4) to remove spin contamination problems. Dissociation of $C_2H_4Cl^+$ into atoms is not isogyric, and in order to avoid potential problems due to incomplete calculation of correlation energy, we have used Pople's approach and added eight hydrogen atoms to make the overall reaction isogyric (eq 2). Molecular orbital calculations provided

$$8H + C_2H_4Cl^+ + e \rightarrow 2C + Cl + 4H + H_2 \qquad (2)$$

the energy of this reaction and then the experimental dissociation energy of hydrogen molecule (0.17447 au[42]) was used to correct this equation to the desired dissociation reaction (eq 3). Inclusion

$$C_2H_4Cl^+ + e \rightarrow 2C + Cl + 4H \qquad (3)$$

of the zero-point energy then gave the sum of the bond dissociation energies $\sum D_0$ for this reaction. Experimental heats of formation of the atoms[43] combined with $\sum D_0$ provided $\Delta H^\circ_{f,0}$, and addition of thermal corrections[43] and work terms enabled us to calculate $\Delta H^\circ_{f,298}$.[44] Using this procedure we calculated $\Delta H^\circ_{f,298}$ for 1-chloroethyl cation to be 198.1 kcal mol^{-1}, in reasonably good agreement with the two values, 198.4 and 199.3 kcal mol^{-1}, obtained from the proton affinity method above. The calculated enthalpies are in excellent agreement with the experimental values of 198.0,[9] 198.8,[8] and 199.0[10] kcal mol^{-1} but differ from the MNDO calculated value of 211.9 kcal mol^{-1}.[45]

The experimental enthalpies of formation for the chloronium ion vary over a wider range, from 200[9] to 204.4[8] kcal mol^{-1}. Using the heat of atomization method the theoretical $\Delta H^\circ_{f,298}$ is 202.0 kcal mol^{-1}, intermediate between the experimental values. Here again the MNDO method gives a higher value, 216.2 kcal mol^{-1}.[45]

Recently a $C_2H_4Cl^+$ ion has been found in the photoionization spectrum of the $C_2H_4{\cdot}HCl$ complex.[46] This ion has been estimated to have $\Delta H^\circ_{f,298} = 209 \pm 6$ kcal mol^{-1} and could conceivable be the chloronium ion. However, using the calculated proton affinity, the theoretical $\Delta H^\circ_{f,298}$ for chlorine-protonated vinyl chloride (**4**) is 212.5 kcal mol^{-1} and it seems more likely that this is the ion formed in the photoionization experiment.

Conclusion

Ab initio molecular orbital calculations show the 2-chloroethyl cation to be in a very shallow minimum but this is an artifact of the SCF method. When electron correlation is included, the 2-chloroethyl cation is no longer at a minimum, and a critical point with a similar structure is found to be the transition structure for interconversion of the 1-chloroethyl and chloronium ions. At the highest level of theory (MP4SDTQ/6-311G(2df,p)) the 1-chloroethyl cation is the global minimum and the chloronium ion is only 4.3 kcal mol^{-1} higher in energy. The transition structure for interconversion of these two ions is 27.8 kcal mol^{-1} above the chloronium ion and this is a sufficiently high barrier to permit both these ions to be observable in gas-phase experiments at ambient temperatures. This description of the $C_2H_4Cl^+$ hypersurface is very similar to that recently calculated for $C_2H_4Br^+$. There is one major difference; by optimizing at post-Hartree–Fock levels we have shown that a structure similar to the 2-chloroethyl cation is the transition structure for interconversion of the 1-chloroethyl and chloronium cations and that the H-bridged ion, **TS2**, is not at a critical point when electron correlation is included. That casts doubt on Hamilton and Schaefer's conclusion that a H-bridged ion similar to **TS2** is the transition structure for interconversion of the bromonium and 1-bromoethyl cations, and we note that they were unable to locate this transition structure at higher levels of theory.

The calculated infrared spectra for both the 1-chloroethyl and chloronium ions both have peaks at similar energies to those observed for ions derived from dichlorinated ethanes mixed with antimony pentafluoride at low temperatures. However, at the low energy end of the spectrum there are problems. The spectra from the experiments have peaks at 975 and 940 cm^{-1} and these are absent in the spectrum calculated for the 1-chloroethyl cation and are very weak in that calculated for the chloronium ion. Assuming that there is only one ion formed under experimental conditions, we can fit the experimental data better by assigning the chloronium ion structure, not the 1-chloroethyl cation as suggested in the initial assignments. However, one peak around 1040 cm^{-1} in the spectrum of the ion derived from 1,1-dichloroethane is absent in the spectrum of the ion from 1,2-dichloroethane, and this frequency coincides with an intense peak calculated for the 1-chloroethyl cation. It therefore seems possible that **both** ions are present in the 1,1-dichloroethane/SbF_5 mixture.

The carbon atom of the CH_2 group is the preferred site for protonation of vinyl chloride. The chlorine atom assists in delocalizing the positive charge and the basicity of vinyl chloride is about 10 kcal mol^{-1} greater than that of ethylene. By contrast, the chlorine atom of vinyl chloride is *less* basic than the chlorine in ethyl chloride, also by about 10 kcal mol^{-1}.

For the 1-chloroethyl cation the theoretical $\Delta H^\circ_{f,298}$ values calculated by two methods, one combining proton affinities with experimental enthalpies of formation and the other using heats of atomization, are within 1 kcal mol^{-1} of the experimental values. For the chloronium ion, where experimental values differ by 4.4 kcal mol^{-1}, the heat of atomization method gives a value halfway between the experimental values.

Acknowledgment. We thank Steven Quan, Chris Tan, and Daniel Bloom for technical assistance and the Natural Science and Engineering Research Council of Canada for continued financial support. We thank Dr. C. H. Reynolds for a preprint of his theoretical work on chloronium ions.

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