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Isomers on the $C_2H_2Cl^+$ Surface. Calculated Enthalpies of Formation for Unsaturated Hydrocarbons and Monochloro Derivatives

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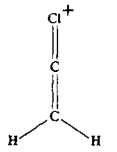
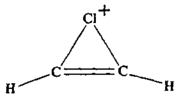
Ab initio molecular orbital calculations are reported for structures at minima and at saddle points on the $C_2H_2Cl^+$ surface. At SCF/6-31G(d,p), the 1-chlorovinyl cation (**1**), the chlorenium ion (**2**), the 2-chlorovinyl cation (**3**), and chlorine-protonated chloroacetylene (**4**) are all at minima, but inclusion of electron correlation at MP2/6-311G(d,p) eliminates the 2-chlorovinyl cation as a minimum and the transition structure for interconversion of **1** and **2** has a structure similar to **3**. At MP4/6-311G(2df,p)//MP2/6-311G(d,p) **1** lies 19.4 kcal mol^{-1} below **2**, and the barrier is 10.7 kcal mol^{-1} above **2**. The calculated proton affinity of chloroacetylene is 169.0 kcal mol^{-1}. For unsaturated molecules C_2H_4, C_2H_3Cl, $C_2H_3^+$, $C_2H_5^+$, and $C_2H_4Cl^+$ (two isomers), enthalpies of formation from MP4SDTQ/6-311G(2df,p) calculations are within 2 kcal mol^{-1} of experimental values. At the same level of theory, the calculated $\Delta H^\circ_{f,298}$ for the 1-chlorovinyl cation is 248.1 kcal mol^{-1}, and for the chlorenium ion it is 268.1 kcal mol^{-1}.

Introduction

Electrophilic addition of halogens to alkenes and alkynes occurs initially through the intermediacy of cyclic ions.[1] The halonium ions, formed in the reactions of alkenes, are relatively stable toward rearrangements, but the higher ring-strain energy of the unsaturated halenium ions leads to facile formation of vinyl cations.[2] There have been many theoretical studies of halonium ions,[3,4] but there are relatively few on $C_2H_2X^+$ species.[5-12] The surface for the $C_2H_2Cl^+$ ion was recently reported at high levels of theory, and it was noted that inclusion of electron correlation is essential for an adequate description of this surface and that consequently most of the earlier relatively unsophisticated molecular orbital calculations arrived at incorrect conclusions.[5] When electron correlation was included, the 1-chlorovinyl cation, **1**, was found to be the global minimum, the chlorenium ion, **2**, was at another minimum, while a third structure, the 2-chlorovinyl cation, **3**, was also believed to be at a minimum, although these stationary points were not characterized beyond the SCF level. A hydrogen-bridged structure, TS2, was located at the SCF level and was shown to be a transition structure for the interconversion of **1** and **3**. The transition structure, TS1, for interconversion of **1** and **2** was not reported.


1(C_{2v})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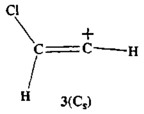
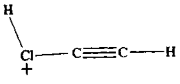

3(C_s)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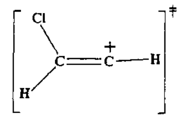
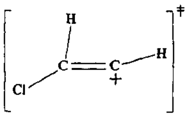

TS1(C_s)


TS2(C_s)

Our interest lies in generating ions $C_2H_4Cl^+$ and $C_2H_2Cl^+$ in the gas phase by reacting ethylene and acetylene with positive ions containing chlorine. In particular, we are interested in generating and characterizing the reactivities of different isomers of these ions. On each of these surfaces, the viabilities of the higher energy species depend on the height of the barriers to their rearrangement, and it therefore became important to have detailed knowledge of these surfaces. Here we present our work on the $C_2H_2Cl^+$ hypersurface, optimizing and characterizing all stationary points at both the SCF/6-31G(d,p) and MP2/6-311G(d,p) levels of theory. Our conclusions differ somewhat from Schaefer's recent work,[5] and we find the $C_2H_2Cl^+$ surface to be remarkably similar to that calculated for $C_2H_4Cl^+$, although the relative energy of the α-chloro-substituted and cyclic ions is much larger on the $C_2H_2Cl^+$ surface.[4]

Our gas-phase interests require a knowledge of enthalpies of formation for isomers of $C_2H_2Cl^+$. At the highest level of theory used here (MP4SDTQ/6-311G(2df,p)) we find that Pople's heat of atomization method[13] consistently gives calculated enthalpies of formation for unsaturated

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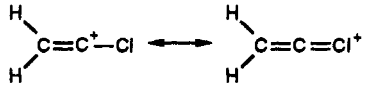
molecules and ions within 2 kcal mol^{-1} of the experimental values. We have applied this method to the $C_2H_2Cl^+$ ions, for which no experimental enthalpies of formation have been reported, and here we report $\Delta H^\circ_{f,298}$ values for the 1-chlorovinyl and chlorenium ions.

Methods

Ab initio molecular orbital calculations were performed using the Gaussian 86 and Gaussian 90 programs.[14,15] Optimizations within the symmetry constraints were calculated at the Hartree–Fock level with the 6-31G(d,p) basis set[16] (SCF/6-31G(d,p)), and electron correlation was included by using Moller–Plesset perturbation[17] theory with second-order corrections in conjunction with the 6-311G(d,p)[18] basis set (MP2/6-311G(d,p)). The critical points were characterized by analytic frequency calculations at the SCF/6-31G(d,p) optimized geometries, and numeric frequency calculations were performed on the MP2/6-311G(d,p) optimized structures. Single-point calculations using fourth-order Møller–Plesset theory[19] with the 6-311G(2df,p) basis set at the MP2/6-311G(d,p) optimized geometries (MP4(SDTQ)/6-311G(2df,p)//MP2/6-311G(d,p)) were also carried out. Transition structures were found by using the eigenvector following routine of Baker.[20]

Results and Discussion

Structural Details. The structural parameters for all the $C_2H_2Cl^+$ ions are given in Figure 1. The 1-chlorovinyl cation, 1, is the global minimum at all levels of theory. In this ion the C–C bond distance of 1.281 Å is considerably shorter than the C–C double bond (1.333 Å)[21] in vinyl chloride, and the C–Cl distance of 1.555 Å is much shorter than the standard single bond length of 1.789 Å in ethyl chloride or the C–Cl distance of 1.726 Å in vinyl chloride.[21] This latter parameter indicates a substantial amount of double-bond character in the C–Cl bond and is the result of π-donation from chlorine to the formally vacant p-orbital on the cationic carbon. In valence bond terminology, two resonance structures, **1a** and **1b**, are both significant contributors.



1a **1b**

From the Mulliken population analysis with the 6-311G(2df,p) basis set the chlorine atom of the 1-chlorovinyl

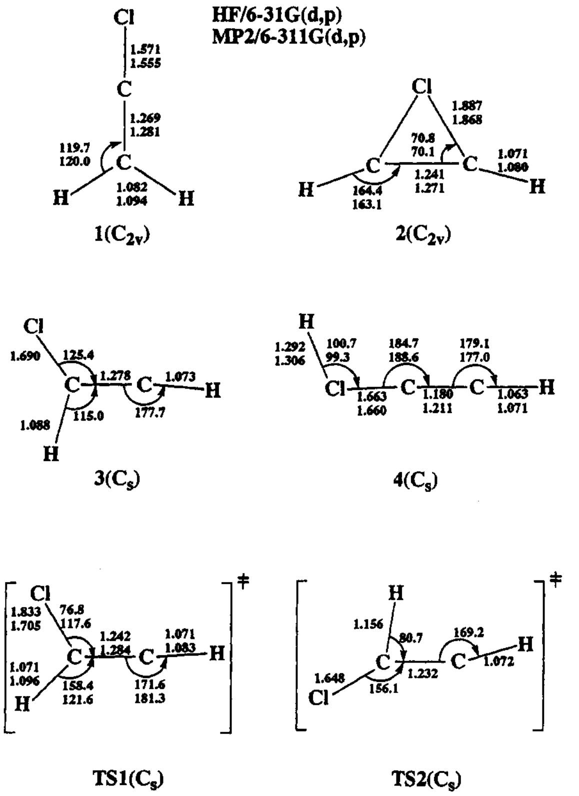


Figure 1. Optimized structures (lengths in Å, angles in deg). Higher numbers are from SCF/6-31G(d,p), lower numbers from MP2/6-311G(d,p). Data for 3 and TS2 are from SCF calculations.

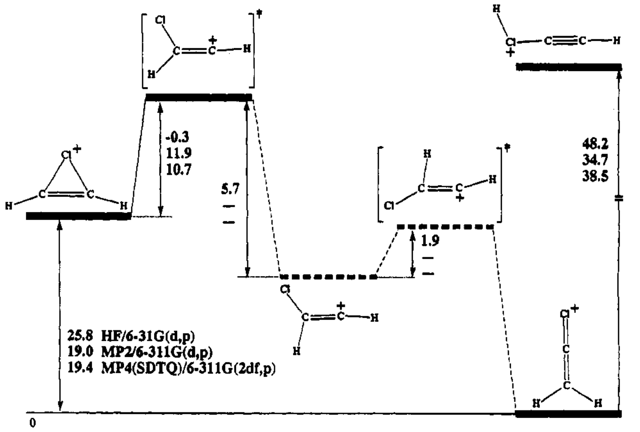


Figure 2. Relative energies (kcal mol^{-1}) including zero-point energies and thermal energies for $C_2H_2Cl^+$ isomers at 298 K.

cation has a charge of +0.267, and this compares with a charge of −0.091 in chloroacetylene.

The chlorenium ion, 2, is at a minimum at all levels of theory, although at the SCF level when zero-point and thermal energies are included it collapses without barrier into the 2-chlorovinyl cation (Figure 2). As with 1, inclusion of electron correlation results in a slight increase in the C–C distance and a slight decrease in C–Cl. The C–Cl distance of 1.868 Å is 0.079 Å longer than a normal single bond, indicating that the bonding is weak. We note, however, that dissociation of 2 into Cl^+ and C_2H_2 is endothermic by ~90 kcal mol^{-1} (Table I). Most of the positive charge of the chlorenium ion is on the hydrogen atoms (+0.301 on each), but the chlorine also has some positive charge (+0.220). The C–C distance of 1.271 Å is slightly shorter than the experimental double bond in

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Table I. Total Energies (Hartrees) of $C_2H_2Cl^+$ Isomers

	SCF/6-31G(d,p)			MP2/6-311G(d,p)			MP4SDTQ/6-311G(2df,p) electronic energy[a]
	electronic energy[a]	ZPE[b]	thermal[c]	electronic energy[a]	ZPE[d]	thermal[c]	
$H_2C{=}CCl^+$ (**1**)	−535.996 89 (0)	17.2	2.3	−536.514 17 (0)	18.1	2.4	−536.571 26 (0)
$HCClCH^+$ (**2**)	−535.955 77 (25.8)	17.0	2.5	−536.482 89 (19.6)	18.8	2.3	−536.539 38 (20.0)
$ClHC{=}CH^+$ (**3**)	−535.964 86 (20.1)	16.9	2.3				
$HC{\equiv}CClH^+$ (**4**)	−535.919 56 (48.5)	16.7	2.5	−536.458 47 (35.0)			−536.509 47 (38.8)
TS1	−535.955 72 (25.8)	17.2	2.0	−536.462 67 (32.3)	17.7	2.0	−536.521 03 (31.5)
TS2	−535.959 51 (23.1)	15.6	2.1				
$HC{\equiv}CH + Cl^+$							−536.368 22 (127.4)
$HC{\equiv}CCl + H^+$	−535.709 73 (180.2)	11.7	2.9	−536.241 30 (171.2)			−536.295 08 (173.3)

[a] The numbers in parentheses are relative electronic energies in kcal mol^{-1}. [b] Zero-point energies in kcal mol^{-1}, scaled by a factor of 0.89. [c] Sum of translational, rotational, and vibrational energies at 298 K. [d] Zero-point energies in kcal mol^{-1}, unscaled.

Table II. Harmonic Frequencies (cm^{-1}) and Intensities (km mol^{-1}) As Calculated at MP2/6-311G(d,p)

1			2			TS1		
3201	B_2	(145)	3382	A_1	(45)	3331	A′	(194)
3107	A_1	(283)	3309	B_2	(291)	3124	A′	(153)
1903	A_1	(352)	1762	A_1	(0)	1668	A′	(35)
1289	A_1	(35)	963	B_2	(18)	1148	A′	(8)
852	A_1	(49)	952	A_1	(3)	984	A′	(32)
816	B_1	(89)	699	B_1	(119)	786	A″	(70)
805	B_2	(7)	657	A_2	(0)	768	A′	(4)
356	B_1	(6)	643	A_1	(41)	550	A′	(68)
317	B_2	(6)	418	B_2	(18)	212i	A′	(34)

cyclopropene (1.296 Å)[22] and is considerably longer than the triple bond in acetylene (1.203 Å).[23] The CCH angle of 163.1° shows considerable distortion from the linear structure of acetylene.

At the SCF level the 2-chlorovinyl cation, **3**, is also at a minimum (lowest frequency, ν_1 = 230 cm^{-1}),[24] 6 kcal mol^{-1} below the chlorenium ion. The transition structure, TS1, for interconversion of these ions has almost identical electronic energy to the chlorenium ion, and when zero-point energy and thermal corrections are included, it is *lower* in energy (Figure 2). The second transition structure, TS2, for conversion of the 2-chlorovinyl cation into the 1-chlorovinyl cation by a 1,2-hydride shift is only 1.9 kcal mol^{-1} above **3**. At the SCF level then, although **1**, **2**, and **3** are all at minima, only the global minimum, **1**, would be expected to exist at ambient temperatures.

Inclusion of electron correlation has a dramatic effect on the reaction profile, and despite an extensive search, we were only able to locate three of the five stationary points found at the SCF level. Structures **1** and **2** are minima, but the only other structure which was a stationary point had a geometry resembling that of the 2-chlorovinyl cation and was found to be a transition structure. We examined the profile for interconversion of the 1-chlorovinyl cation and the chlorenium ion at MP2/6-31G(d,p) as a function of ∠CCCl, fixing this angle at 5° intervals over the range 90°–155° while optimizing all other geometric parameters. Around the maximum of the reaction profile, over the range 115°–125°, the surface was flat with the structure at 125° only 0.27 kcal/mol below the maximum at 117.2°. We refined the surface near the maximum, using intervals of 0.5° over the range 115°–120° and intervals of 0.1° around the maximum. Repeating the same point-by-point procedure at MP2/6-311G(d,p) over the range 116.8°–122.5° gave a maximum at ∠CCCl = 117.6°. Subsequent optimizations using these structures as initial guesses with the eigenvector-following routine[20] enabled us to quickly find the transition structures, and these were characterized by frequency calculations. This tedious point-by-point procedure should have revealed any high minimum on the surface; the only critical point we found had the structure given in Figure 1 for TS1 (υ = −142 cm^{-1}). The motions associated with the atoms in this imaginary frequency, given in the vector diagram in Figure 3, show that ring opening is accompanied by hydrogen migration.

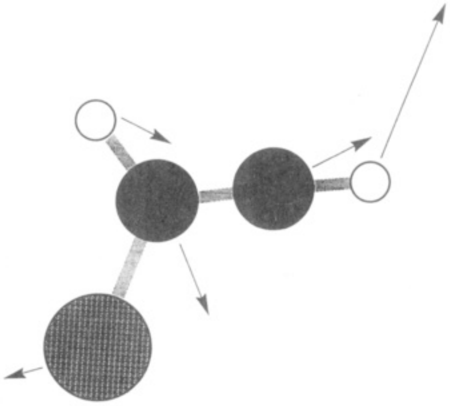

Figure 3. Motion of atoms in lowest vibrational mode of TS1 from MP2/6-311G(d,p).

Inclusion of electron correlation stabilizes the nonclassical chlorenium ion relative to the 2-chlorovinyl and 1-chlorovinyl cations. The barrier to rearrangement of the chlorenium ion through TS1 is ~11 kcal mol^{-1} and the product, the 1-chlorovinyl cation, is ~19 kcal mol^{-1} lower than the chlorenium ion. The reaction profile at both MP2/6-31G(d,p) and MP2/6-311G(d,p) then is simpler than the SCF profile with no 2-chlorovinyl cation as an intermediate, and the barrier for conversion of the chlorenium ion into the 1-chlorovinyl cation is much higher.

At the SCF level the structures and overall energetics from our calculations are almost identical to those reported by Hamilton and Schaefer.[5] Both studies found that, relative to the 1-chlorovinyl cation, inclusion of electron correlation results in stabilization of the chlorenium ion and destabilization of the 2-chlorovinyl cation. However, despite a rigorous search with post-Hartree-Fock wavefunctions, we were unable to locate a structure for the 2-chlorovinyl cation which was at a minimum; Hamilton and Schaefer reported a TZ2P CISD optimized structure for the 2-chlorovinyl cation which was "probably a high energy minimum" based on the fact that small geometric displacements resulted in small increases in energy, but

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(24) This is the calculated frequency for the lowest vibrational mode at the SCF/6-31G(d,p) optimized geometry.

Table III. Proton Affinities (kcal mol^{-1}) at 298 K from MP Level Calculations

molecule	site of protonation	MP2/6-311G(d,p)	MP4/6-311G(2df,p)	exptl
HC≡CCl	(a) C of CH	166.9	169.0	
	(b) C of CCl[a]	147.3	149.0	
	(c) Cl	132.3	130.5	
H_2C=CHCl[b]	(a) C of CH_2	172.3	171.4	
	(b) C of CHCl[a]	169.0	167.5	
	(c) Cl	158.2		
HC≡CH	triple bond	153.2	153.3	153.3[c]
H_2C=CH_2	double bond	164.7	163.4	162.6[d]

[a] Assumes cyclic ion is formed. [b] Data from ref 4. [c] Reference 27. [d] Reference 26.

they acknowledged that this procedure "in no way guaranteed that the 2-chlorovinyl structure is at a minimum." It is therefore possible, but not certain, that the CISD and MP2 hypersurfaces differ on whether the 2-chlorovinyl cation is at a high minimum. More importantly, both studies show that incorporation of electron correlation stabilizes the chlorenium ion relative to the 2-chlorovinyl cation and the existence of a barrier of ~11 kcal mol^{-1} to its rearrangement suggests that the chlorenium ion, if formed, will briefly retain its integrity under experimental conditions.

One additional minimum, chlorine-protonated chloroacetylene, 4, was located on the $C_2H_2Cl^+$ surfaces, but this isomer was high above the global minimum at all levels of theory.

Proton Affinities. The proton affinity of a base, B, is given by the exothermicity of the reaction in eq 1.

$$B + H^+ \rightarrow BH^+ \qquad (1)$$

In principle, there are three possible sites for protonation of chloroacetylene, both carbon atoms and chlorine. Proton affinities for each of these atoms, as calculated at various levels of theory, are given in Table III. Protonation at CH forms the 1-chlorovinyl cation, and this reaction has the highest proton affinity (169.0 kcal mol^{-1}). Protonation at the other carbon, *assuming* that it forms the chlorenium ion and not the 1-chlorovinyl cation, is exothermic by 149.0 kcal mol^{-1}. The chlorine atom is much less basic with a proton affinity of 130.5 kcal mol^{-1}.

For comparative purposes, and to establish the accuracy of the calculated proton affinities, we have included data for acetylene and ethylene, two molecules for which experimental proton affinities are firmly established.[25,26] Clearly, both MP2/6-311G(d,p) and MP4SDTQ/6-311G(2df,p) levels of theory give accurate values for the proton affinities, and at the higher level (MP4), the calculated proton affinities for both acetylene and ethylene are within 1 kcal mol^{-1} of the experimental values.

It is interesting to compare the effect of a chlorine atom on the proton affinities of acetylene and ethylene. In both chloroacetylene and vinyl chloride the favored site of protonation is the unsubstituted carbon atom and the product ion has the chlorine atom attached to the cationic carbon. The chlorine substituent enhances the proton affinities of acetylene by 15.7 kcal mol^{-1} and ethylene by 9 kcal mol^{-1}; i.e., the substituent effect is larger in the more unsaturated molecule.

In both chloroacetylene and vinyl chloride[4] the chlorine atom is the least favored site for protonation. The experimental proton affinity of ethyl chloride is known and, assuming that protonation of ethyl chloride is on chlorine, for molecules C_2H_nCl the relative basicities *at chlorine* as measured by the proton affinities (in kcal mol^{-1}) are C_2H_5Cl (169)[27] > C_2H_3Cl (158.2) ≫ C_2HCl (130.5). This sequence shows that the basicity of chlorine is strongly dependent on the hybridization of the carbon atom to which it is attached.

The Cl^+ affinities of ethylene and acetylene, assuming addition of Cl^+ (^3P) and formation of the cyclic chloronium and chlorenium ions, are 133.3 and 106.3 kcal mol^{-1}, respectively, at 298 K. The affinities follow the same order as the proton affinities but are lower, reflecting the higher stability of Cl^+ than H^+.

Enthalpies of Formation. There are no experimental enthalpies of formation for $C_2H_2Cl^+$, but a value can be obtained by using eq 1 with the experimental enthalpies of formation of the reactants, chloroacetylene (48.7 kcal mol^{-1}),[28] and the proton (365.7 kcal mol^{-1})[27] and the theoretical proton affinity. Using this procedure we obtain $\Delta H^\circ_{f,298}$ = 245.4 kcal mol^{-1}. The same method applied to acetylene, ethylene, and vinyl chloride led to theoretical enthalpies of formation (in kcal mol^{-1}) of 266.9, 214.9, and 199.3, respectively, all within 1 kcal mol^{-1} of the experimental values[27,29] (Table IV).

An alternative method of calculating the enthalpy of formation of a molecule or ion is to use molecular orbital theory to obtain the heat of atomization and to combine this with the sum of the experimental enthalpies of formation of the constituent atoms to calculate $\Delta H^\circ_{f,0}$. Dissociation of a molecule into atoms destroys several pairs of electrons, and in order to calculate such a reaction accurately it is necessary to recover most of the correlation energy. Pople[13] proposed a method of minimizing this problem by making the reaction isogyric by addition of the required number of H atoms on one side of the equation and the number of H_2 molecules required for balancing on the other. We have applied this method to both molecules and ions in Table IV, and we illustrate the method by giving the step-by-step results for 1-chlorovinyl cation. The reaction of interest is given in eq 2.

$$H_2C{=}C{=}Cl^+ + e \rightarrow 2C + 2H + Cl \qquad (2)$$

Here the reactants have one unpaired spin and the products have seven, so it is necessary to add six hydrogen atoms to the reactants as in eq 3.

$$6H + H_2C{=}C{=}Cl^+ + e \rightarrow 2C + 2H + Cl + 3H_2 \qquad (3)$$

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(25) Wagman, D. D.; Evans, W. H.; Parker, V. P.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. The NBS Tables of Chemical Thermodynamic Properties. *J. Chem. Ref. Data* 1982, Suppl. No. 2.

(26) McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 2612.

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(28) Estimated value taken from: Lauren, S. I.; Pimentel, G. C. *J. Phys. Chem.* **1989**, *93*, 2328.

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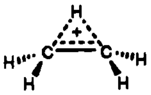
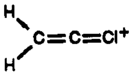
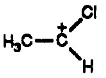
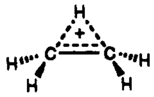
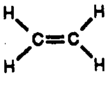
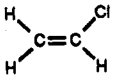
Table IV. Enthalpies of Formation $\Delta H^\circ_{f,298}$ (in kcal mol^{-1})

	MP4STDQ/6-311G(2df,p)	MNDO and AMI	experitl
	266.9,^{j} 264.2^k		265.9,^{f} 265.0^n
	214.9,^{j} 213.8^k	234.7,^{a} 226.5^d	215.6^f
	245.5,^{j} 248.1^k	256.9^b	
	268.1^k	278.9^b	
	199.3,^{j} 198.1^k	211.9^b	198,^{g} 198.9,^{h} 199^f
	202.0^k	216.2^b	200,^{g} 204.4,^{h} 204^f
$H{-}C{\equiv}C{-}H$	51.7,^{k} (55.7)^l	57.3,^{c} 54.8^d	54.55 ± 0.17
	11.5^k	15.3,^{c} 16.5^d	12.55 ± 0.10
$H{-}C{\equiv}C{-}Cl$	51.4^k		(48.7)^m
	3.7^k	5.9^e	5 ± 0.5^f

[a] Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783. Assumes bridged ion, which is a transition structure at this level of theory. [b] Reference 7. [c] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907. [d] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. [e] Dewar, M. J. S.; Zoebisch, E. G. *J. Mol. Struct.* **1988**, *180*, 1. [f] Reference 27. [g] Holmes, J. L.; Lossing, F. P.; McFarlane, R. A. *Int. J. Mass. Spectrom. Ion Proc.* **1988**, *86*, 209. [h] Berman, W.; Anicich, V.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 1239. [i] Reference 29. [j] Calculated from the theoretical proton affinity and experimental enthalpies of formation. [k] Calculated from theoretical heats of atomisation and experimental enthalpies of formation of atoms. [l] At MP4SDTQ/6-311++G(3df,3pd). Total energies in (hartrees) are H—C≡C—H, -77.189 36; H_2, -1.171 92; H, -0.499 82; C, -37.777 15. [m] Reference 28. [n] Hawley, M.; Smith, M. A. *J. Am. Chem. Soc.* **1989**, *111*, 8293.

From molecular orbital calculations, using spin-projected UMP4 calculations (PMP4) for the atoms,[30] the electronic energy for the reaction in eq 3 is -0.140 70 au. Correction for the exact energy for the dissociation of hydrogen molecule (0.174 47 au)[30] gives the electronic energy, ΣD_e, for the dissociation reaction in eq 2 to be 0.382 70 au (240.14 kcal mol^{-1}). Correcting for the contribution from zero-point energy gives the heat of atomization, ΣD_0, to be 222.94 kcal mol^{-1}. From the CODATA thermochemical tables[32] the sum of the enthalpies of formation of the atoms is 471.8 kcal mol^{-1} and subtraction of ΣD_0 gives $\Delta H^\circ_{f,0}$ ($H_2C{=}CCl^+$) = 248.87 kcal mol^{-1}. The thermal correction of 0.73 kcal mol^{-1} required to correct the enthalpy to 298 K was calculated from the experimental heat capacities of the elements[32] and the thermal energy (from theory) plus the work term (*RT*) for $H_2C{=}CCl^+$. Here we use the "stationary electron" or "ion convention" in which the electron is taken to have zero kinetic energy. This procedure gives $\Delta H^\circ_{f,298}$ ($H_2C{=}CCl^+$) = 248.14 kcal mol^{-1}.

The calculated enthalpies in Table IV generally underestimate the experimental values by between 1 and 2 kcal mol^{-1}. The largest difference (2.75 kcal mol^{-1}) is for acetylene where deficiencies in the basis set create difficulties describing the highly anisotropic molecular environment. Extension of the basis set to 6-311++G(3df,3pd) improved the theoretical $\Delta H^\circ_{f,298}$(HC≡CH) to 55.7 kcal mol^{-1}, 1.15 kcal mol^{-1} higher than the experimental value.

The high level of agreement between experiment and theory at MP4SDTQ/6-311G(2df,p) for unsaturated molecules and cations indicates that theory at this level provides a reliable method for obtaining enthalpies of formation. The $\Delta H^\circ_{f,298}$ values of 248.1 kcal mol^{-1} for the 1-chlorovinyl cation and 268.1 kcal mol^{-1} for the chlorenium ion are therefore expected to be accurate within 2 kcal mol^{-1}.

Conclusion

At all levels of theory the α-chlorovinyl cation is the global minimum on the $C_2H_2Cl^+$ surface. At the SCF level we have located four minima, but when electron correlation is included the 2-chlorovinyl cation is no longer a minimum but rather the transition structure for interconversion of the α-chlorovinyl and chlorenium ions. The energy surfaces for $C_2H_2Cl^+$ and $C_2H_4Cl^+$ are similar, with three minima in the same order of relative energies, the α-substituted cation the lowest, followed by the chlorine-bridged ion, and the chloro-protonated acetylene and ethylene are the highest. The large ring-strain energy associated with an unsaturated ring results in the chlorenium ion being 19.4 kcal mol^{-1} higher than the α-chlo-

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(30) (a) Schlegel, H. B. *J. Phys. Chem.* **1988**, *92*, 3075. (b) Schlegel, H. B. *J. Phys. Chem.* **1986**, *84*, 4530.

(31) Kolos, W.; Wolniewiecz, L. *J. Chem. Phys.* **1968**, *94*, 404.

(32) Report of the CODATA Task Group, *J. Chem. Thermodyn.* **1978**, *10*, 93.

rovinyl cation, in contrast to the $C_2H_4Cl^+$ surface where the chloronium ion is only 4.3 kcal mol^{-1} above the α-chloroethyl cation. The barrier for conversion of the cyclic ion into the α-chloro substituted ion is smaller (10.7 kcal mol^{-1}) on the $C_2H_2Cl^+$ surface than that on the $C_2H_4Cl^+$ (27.8 kcal mol^{-1}) surface. Both the α-chloroethyl and chloronium ions have been characterized in the gas phase, but the lower barrier to rearrangement for the chlorenium ion will make experimental observation of this ion much more challenging.

Theory at MP4SDTQ/6-311G(2df,p) is capable of calculating enthalpies of formation within at least 3 kcal mol^{-1} even for the most unsaturated molecules. Here we have reported the first calculated $\Delta H^\circ_{f,298}$ values for the α-chlorovinyl cation (248.1 kcal mol^{-1}) and for the chlorenium ion (268.1 kcal mol^{-1}).

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