Reaction of $C_3H_2^+$ with Atomic Chlorine: A Theoretical Study

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A theoretical study of the reaction of atomic chlorine with the different isomers of $C_3H_2^+$ ($CCCH_2^+$, *c*-$C_3H_2^+$, and $HCCCH^+$) has been carried out employing different levels of calculations, namely, B3LYP, G2, and CCSD(T). These theoretical results allow the development of thermodynamic arguments about the reaction pathways of the process Cl + $C_3H_2^+$. One of the most important conclusions from our work is that the predicted predominant channel for the reaction with both $HCCCH^+$ and *c*-$C_3H_2^+$ is linear $CCCH^+$ + HCl. This channel is clearly exothermic and barrier-free for $HCCCH^+$, whereas for *c*-$C_3H_2^+$, it is predicted to be only slightly exothermic by the G2 method and is slightly endothermic at the CCSD(T) level. In the case of the reaction of Cl with the $CCCH_2^+$ isomer, production of $CCCCl^+ + H_2$ (which prevails over $HCCCCl^+$ + H) could be competitive with the $CCCH^+$ + HCl channel. Therefore, it seems that the role of the reaction of Cl with $C_3H_2^+$ as a possible source of chlorine−carbon compounds in space seems severely limited and eventually reduced only to the $CCCH_2^+$ isomer.

Introduction

The gas-phase chemistry of C_3H_2 is very interesting. There are two different isomers of this hydrocarbon which have been detected in space. Cyclopropenylidene, *c*-C_3H_2, is one of the most abundant interstellar hydrocarbons, as well as the first interstellar organic ring, and was detected in the interstellar medium[1] after its observation in the laboratory for the first time.[2] Another isomer, propadienylidene (singlet vinylidenecarbene), was also observed in space[3] after its characterization in matrices[4] as well as in the gas phase.[5] Propadienylidene has a linear carbon backbone and two hydrogens bonded to a terminal carbon atom and, therefore, will be represented as $CCCH_2$. In addition, a third isomer, triplet propargylene (HCCCH), was in fact the first C_3H_2 molecule identified in the laboratory. After some initial controversy about its actual structure, it seems that propargylene has a planar diradical structure.[7] Theoretical calculations[8,9] predict that singlet cyclopropenylidene is the C_3H_2 global minimum, whereas triplet propargylene and singlet propadienylidene lie about 8.7 and 13.5 kcal/mol, respectively, higher in energy.

Ion chemistry plays a crucial role in interstellar chemistry,[10,11] the initial ionization being produced either by photoionization or by cosmic-ray ionization,[12,13] and therefore, it is important to know the possible role of the different isomers of C_3H_2 or their cationic derivatives in the synthesis of interstellar molecules. Because the laboratory study of such reactions is not easy, theoretical studies may provide useful information about the ionic chemistry of C_3H_2 in the gas phase. So far, we have carried out several theoretical studies[14−17] of the reactions of C_3H_2 isomers with different second-row element cations, such as P^+, Si^+, S^+, or Cl^+. These studies have shown that ion−molecule reactions of the type $X^+ + C_3H_2$ might play an important role in the interstellar synthesis of precursors of binary carbides, and some of them (such as C_3S or C_3Si) already detected in space. However, reactions initiated by $C_3H_2^+$ cations might also be relevant in interstellar chemistry. $C_3H_2^+$ cations can be formed in the interstellar medium through different processes, such as $C_3H^+ + H_2$,[18−20] $CH^+ + C_2H_2$,[21] $C^+ + C_2H_4$,[22] $C^+ + C_2H_3$,[22] or $CH_2^+ + C_2H$.[22] Different $C_3H_2^+$ reactions have been experimentally studied by selection-ion flow tube (SIFT) and flowing-afterglow-SIFT techniques. For example, quite recently Scott et al.[23] have carried out a SIFT study of the reaction of $C_3H_2^+$ cations with atomic nitrogen. A theoretical study[24] on this reaction has also focused on its possible role in the synthesis of interstellar HC_3N and C_3N.

In the present work, we have carried out a theoretical study of the reaction of $C_3H_2^+$ with atomic chlorine, determining its energetics as well as characterizing the relevant transition states. Although the interstellar chemistry of chlorine remains rather uncertain, its volatility suggests that its gas-phase abundance in molecular clouds should be high.[25] The estimated abundance in chlorine relative to total hydrogen is about 4.0×10^{-9}, of the same order of magnitude than other second-row elements such as silicon or phosphorus.[22] We will consider the two species, *c*-$C_3H_2^+$ and $CCCH_2^+$, derived from the hydrocarbons detected in the interstellar medium and also $HCCCH^+$, which is obtained upon ionization of triplet propargylene. The reason for including the latter is that in some experimental studies of this kind of reactions the ions can be produced from propyne by electron impact,[23] and a mixture of $HCCCH^+$ and *c*-$C_3H_2^+$ is likely to be formed. Both experiments[26] and theoretical calculations[27] indicate that the lowest-energy isomer is the cyclic structure. The ab initio calculations[27] predict that the linear isomer $HCCCH^+$ should lie about 6 kcal/mol higher in energy, whereas the other isomer, $CCCH_2^+$, is more unstable and is predicted to lie about 46 kcal/mol higher than *c*-$C_3H_2^+$.

Computational Methods

We have made a comparative study employing two different theoretical levels of theory. In the first place, we have employed the G2 method,[28] where the geometries are obtained at the second-order Møller-Plesset (MP2) level with the 6-31G(d) basis set,[29] including all electrons in the correlation calculation (MP2 = full/6-31G(d)). Electronic energies are computed in this

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method, making additivity assumptions, effectively at the QCISD(T)/6-311+G(3df,2p) level, where QCISD(T) stands for a quadratic configuration interaction calculation with single and double substitutions followed by a perturbative treatment of triple substitutions. On the other hand, we have also optimized the geometries of the different species using density functional theory (DFT); in particular, we have employed the B3LYP[30] exchange-correlation functional and the 6-311G(d,p) basis set.[31] Harmonic vibrational frequencies have been computed also at the B3LYP/6-311G(d,p) level in order to estimate the ZPVE, as well as to check the nature of stationary points. On the B3LYP geometries, we have carried out single-point calculations with the CCSD(T) method[32] (coupled-cluster single and double excitation model augmented with a non-iterative triple excitation correction) with the cc-pVTZ basis set. We must recall that the estimated uncertainty for G2 energy values is rather well established,[33] namely, about 1−2 kcal/mol (although for TSs of course there is no such an exact determination of uncertainties).

All calculations in this work were carried out with the Gaussian 98 program package.[34]

Results and Discussion

The reaction of $C_3H_2^+$ with atomic chlorine should take place along the singlet surface, given the multiplicity of the reactants. The more relevant $(ClC_3H_2)^+$ species, both on the singlet and triplet surfaces, have been described in a previous work,[17] and therefore, we will not discuss them further. Only two new species containing Cl−H bonds and lying higher in energy than the rest of $(ClC_3H_2)^+$ isomers appeared in the course of exploring the different reaction paths. The optimized geometries for all intermediates and products are available as Supporting Information.

The geometrical parameters for the relevant transition states for the title reaction are given in Figure 1. All reported structures are true transition states (with only one imaginary frequency, associated to the desired normal mode), with the exceptions of TS4 and TS10. TS4, which has been obtained at the MP2 level, is in fact a second-order saddle point because it has two imaginary frequencies, one of them associated to the elimination of a hydrogen molecule and the second one (b_2 normal mode) corresponding to rupture of C_{2v} symmetry. Our attempts to obtain a true transition state in C_s symmetry failed because in all cases finally we obtained the two separated fragments (H_2 and C_3Cl^+). Therefore, the relative energy of TS4 is only reported as a crude estimation of that corresponding to the true transition state and should be taken with caution. The relative energies and ZPVE values for all species involved in the reactions are given in Table 1.

We have considered several channels for this reaction:

$$Cl(^2P) + C_3H_2^+(^2A_1; ^2\Pi_g) \rightarrow C_3Cl^+(^1\Sigma; ^1A_1) + H_2(^1\Sigma_g^+) \quad (1)$$

$$\rightarrow HC_3Cl^+(^2A') + H(^2S) \quad (2)$$

$$\rightarrow C_3H^+(^1\Sigma; ^1A_1) + HCl(^1\Sigma) \quad (3)$$

Charge transfer has not been considered because of the much higher ionization potential for chlorine atoms than for any of the isomers of C_3H_2. It should be mention that in our previous study[17] $Cl^+ + C_3H_2$ was found to lie between 46 and 79 kcal/mol higher than $Cl + C_3H_2^+$, depending on the isomer considered for the hydrocarbon.

The discussion will be divided according to the isomeric identity of the reactant carbocation.

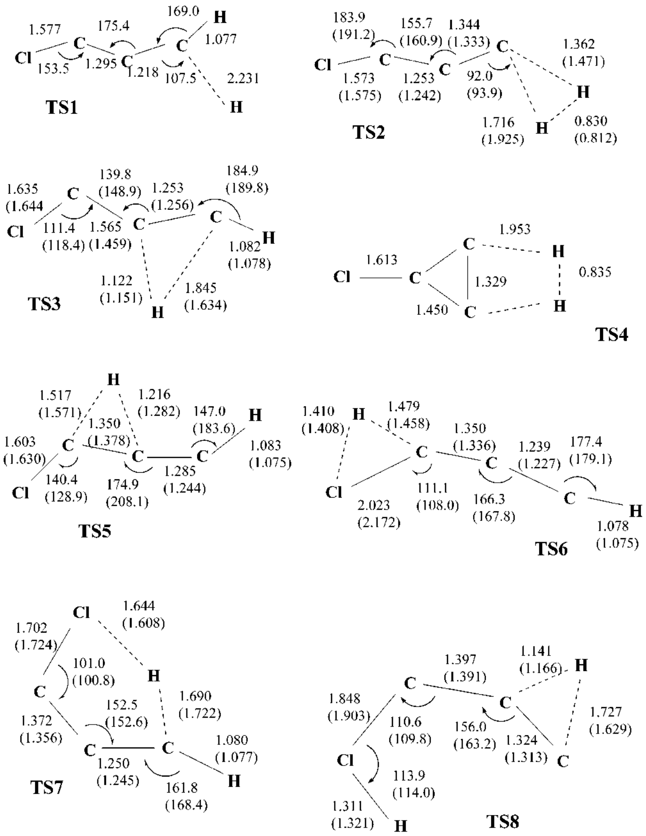

Figure 1. MP2=full/6-31G(d) and B3LYP/6-311G(d,p) (in parentheses) optimized geometries for the relevant transition states involved in the reaction of Cl with $C_3H_2^+$. Distances are given angstroms and angles in degrees.

TABLE 1: Relative Energies (in kcal mol^{-1}) with Respect to Cl + c-$C_3H_2^+$ and Zero-Point Vibrational Energies (in kcal mol^{-1})

	G2	CCSD(T)	ZPVE[a]
$Cl + c\text{-}C_3H_2^{+b}$	0.0	0.0	20.97 (20.51)
$Cl + CCCH_2^+$	+45.2	+42.3	19.67 (18.11)
$Cl + HCCCH^+$	+6.1	+6.8	18.72 (18.46)
$ClCCCH_2^+$	−88.2	−81.6	22.34 (21.87)
$ClC_3H_2^+$	−107.9	−102.1	23.45 (22.99)
$HCCCHCl^+$	−90.3	−84.3	22.78 (22.27)
$HCCCClH^+$	−20.1	−14.2	19.20 (18.77)
HC_3ClH^+	−17.7	−12.7	20.32 (19.55)
TS1	+9.9		15.93
TS2	+4.7	+11.9	16.03 (15.65)
TS3	−20.0	−11.8	18.52 (17.94)
TS4	+50.5		16.03
TS5	−4.3	+2.4	22.50 (17.21)
TS6	−5.3	−0.6	17.02 (16.85)
TS7	+3.8	+9.1	17.15 (17.02)
TS8	+36.1	+39.8	17.20 (16.15)
$ClC_3^+ + H_2$	+16.8	+24.5	14.25 (13.24)
$ClC_3H^+ + H$	+14.0	+17.6	15.71 (15.34)
$HCCCCl^+ + H$	+13.6	+16.3	16.38 (13.90)
$CCCCl^+ + H$	−1.0	+6.3	14.19 (14.06)
$c\text{-}C_3H^+ + HCl$	+13.6	+18.4	17.49 (16.01)
$CCCH^+ + HCl$	−2.1	+2.1	16.74 (16.64)

[a] MP2(full) values and B3LYP in parentheses. [b] Electronic energies (in hartree) for Cl + c-$C_3H_2^+$: −574.47739 (G2) and −574.44170 (CCSD(T)).

Cl + $CCCH_2^+$. The reaction of chlorine atoms with $CCCH_2^+$ will be considered first. The corresponding energy profile at the G2 and CCSD(T) levels is given in Figure 2. The reaction with $CCCH_2^+$ is initiated by formation of $ClCCCH_2^+$ through the interaction of chlorine with the terminal carbon atom. Two

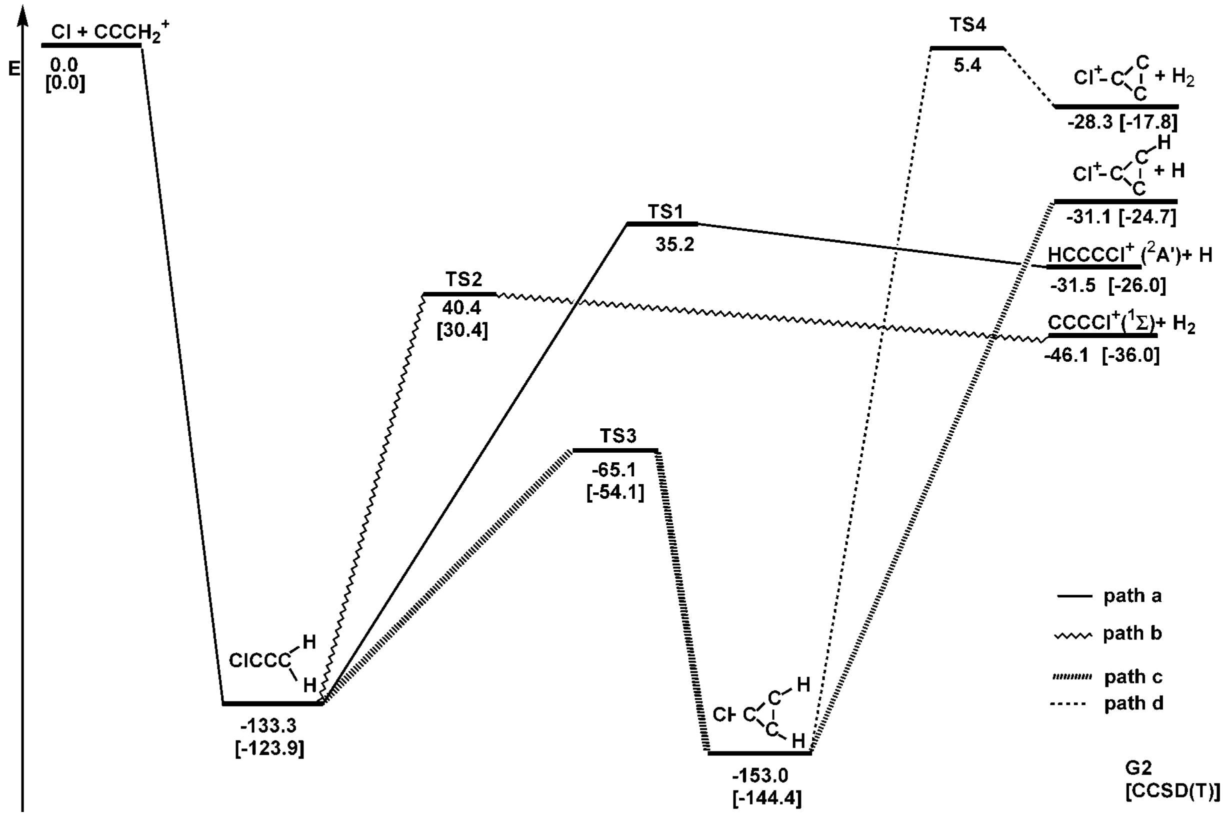

Figure 2. Energy profile, in kcal/mol, for the reaction of Cl with $CCCH_2^+$ at the G2 and CCSD(T) (in brackets) levels. ZPVE corrections have been included at the MP2=full/6-31G(d) and B3LYP/6-311G(d,p) levels, respectively.

different processes are then possible, abstraction of a hydrogen atom or elimination of a hydrogen molecule:

$$\mathrm{Cl} + \mathrm{CCCH_2}^+ \rightarrow \mathrm{ClCCCH_2}^+ \xrightarrow{\mathrm{TS1}} \mathrm{HCCCCl}^+ + \mathrm{H} \quad \text{(a)}$$

$$\mathrm{Cl} + \mathrm{CCCH_2}^+ \rightarrow \mathrm{ClCCCH_2}^+ \xrightarrow{\mathrm{TS2}} \mathrm{CCCCl}^+ + \mathrm{H_2} \quad \text{(b)}$$

Both processes are clearly exothermic because the corresponding products lie well below the reactants. (b) is more exothermic than (a) by more than 14 and 10 kcal/mol, respectively, at the G2 and CCSD(T) levels of theory. In the case of path a, the associated transition state for hydrogen elimination has only been obtained at the MP2 level, and consequently, only the G2 relative energy is reported. At the B3LYP level, no transition state is found for this process, and the corresponding scan for different C−H distances shows no sign of barrier at this level of theory. Furthermore, even though at the MP2 level TS1 lies higher in energy than the products (that is, the MP2 potential surface is topologically consistent), at the G2 level, TS1 is found to lie below the separated fragments. Therefore, it seems that at higher levels of theory it is quite likely that hydrogen elimination from $ClCCCH_2^+$ could be a barrier-free process, in agreement with the B3LYP result. In any case it can be concluded from our results that path b should be favored over path a not only thermodynamically but also from the kinetic point of view, because TS2 is placed below TS1 at the G2 level and, in any case, it lies below $HCCCCl^+$ + H.

Another possibility for the evolution of $ClCCCH_2^+$ is isomerization into the cyclic intermediate $ClC_3H_2^+$, and this opens up the possibility of formation of cyclic products. The cyclic intermediate, $ClC_3H_2^+$, may suffer either elimination of a hydrogen atom or elimination of a hydrogen molecule:

$$\mathrm{Cl} + \mathrm{CCCH_2}^+ \rightarrow \mathrm{ClCCCH_2}^+ \xrightarrow{\mathrm{TS3}} \mathrm{ClC_3H_2}^+ \rightarrow \mathrm{ClC_3H}^+ + \mathrm{H} \quad \text{(c)}$$

$$\mathrm{Cl} + \mathrm{CCCH_2}^+ \rightarrow \mathrm{ClCCCH_2}^+ \xrightarrow{\mathrm{TS3}} \mathrm{ClC_3H_2}^+ \xrightarrow{\mathrm{TS4}} \mathrm{ClC_3}^+ + \mathrm{H_2} \quad \text{(d)}$$

Path c involves only a transition state, TS3, which clearly lies below $Cl^+ + CCCH_2^+$. Elimination of a hydrogen atom from cyclic $ClC_3H_2^+$ is a direct process, because no transition state is found. We have made scans for different C−H distances at both MP2 and B3LYP levels, but in both cases, no sign of a barrier is observed. Although the relative energy of TS4 is doubtful (because it is not a true transition state), it seems clear from Figure 2 that production of ClC_3H^+ + H is both thermodynamic and kinetically favored over production of $ClC_3^+ + H_2$.

Cl + c-$C_3H_2^+$. $ClC_3H_2^+$ can also be reached from the reaction of atomic chlorine with cyclic $C_3H_2^+$, whose energy profile at the G2 and CCSD(T) levels is given in Figure 3. The further evolution of cyclic $ClC_3H_2^+$ could also lead either to ClC_3H^+ + H or to $ClC_3^+ + H_2$:

$$\mathrm{Cl} + c\text{-}\mathrm{C_3H_2}^+ \rightarrow \mathrm{ClC_3H_2}^+ \rightarrow \mathrm{ClC_3H}^+ + \mathrm{H} \quad \text{(e)}$$

$$\mathrm{Cl} + c\text{-}\mathrm{C_3H_2}^+ \rightarrow \mathrm{ClC_3H_2}^+ \xrightarrow{\mathrm{TS4}} \mathrm{ClC_3}^+ + \mathrm{H_2} \quad \text{(f)}$$

In any case, the most important conclusion is that production of both cyclic ClC_3H^+ and ClC_3^+ from c−$C_3H_2^+$ are clearly endothermic processes, and therefore its possible role in interstellar chemistry is severely limited. Of course, another possibility for the evolution of cyclic $ClC_3H_2^+$ is the isomerization into the open-chain isomer, $ClCCCH_2^+$, finally leading

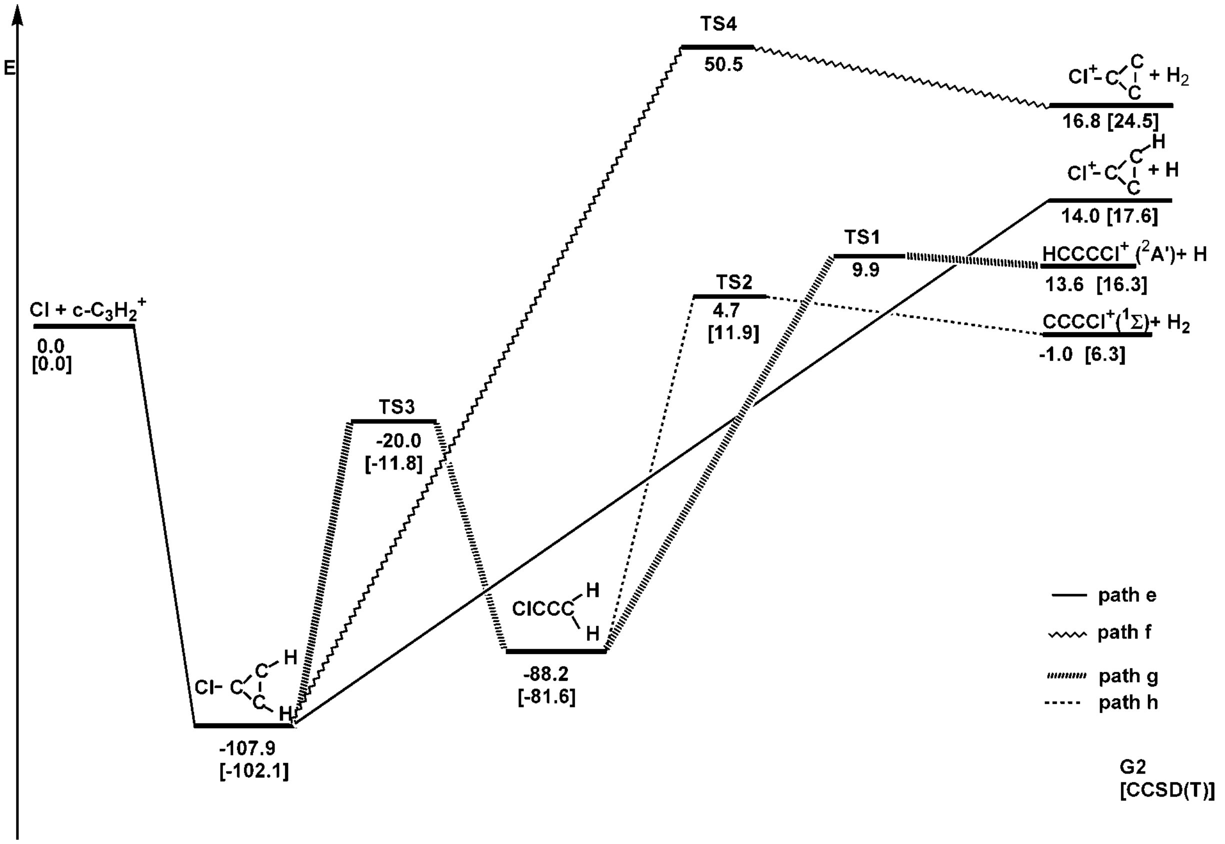

Figure 3. Energy profile, in kcal/mol, for the reaction of Cl with c-$C_3H_2^+$ at the G2 and CCSD(T) (in brackets) levels. ZPVE corrections have been included at the MP2=full/6-31G(d) and B3LYP/6-311G(d,p) levels, respectively.

to the open-chain products, $HCCCCl^+$ and $CCCCl^+$. These are represented in Figure 3 as paths g and h:

$$Cl + c\text{-}C_3H_2^+ \rightarrow ClC_3H_2^+ \xrightarrow{TS3} ClCCCH_2^+ \xrightarrow{TS1} HCCCCl^+ + H \quad (g)$$

$$Cl + c\text{-}C_3H_2^+ \rightarrow ClC_3H_2^+ \xrightarrow{TS3} ClCCCH_2^+ \xrightarrow{TS2} CCCCl^+ + H_2 \quad (h)$$

As can be seen in Figure 3, production of $HCCCCl^+$ is clearly endothermic, whereas $CCCCl^+ + H_2$ is slightly exothermic at the G2 level and endothermic at the CCSD(T) level. Nevertheless both processes involve significant energy barriers, because both TS1 and TS2 lie above the reactants. Therefore, it seems that the production of carbon−chlorine compounds, either cyclic or open-chain, from the reaction of Cl atoms with c-$C_3H_2^+$ is severely hindered.

Cl + $HCCCH^+$. The energy profile for the reaction with the linear isomer, $HCCCH^+$, is shown in Figure 4. The reaction is initiated by formation of $HCCCHCl^+$ through interaction of the chlorine atom with one of the side carbon atoms. Several possibilities are then opened for the further evolution of this intermediate. One of them is isomerization into the cyclic isomer, $ClC_3H_2^+$, which may further evolve into $ClCCCH_2^+$:

$$Cl + HCCCH^+ \rightarrow HCCCHCl^+ \xrightarrow{TS5} ClC_3H_2^+ \xrightarrow{TS3} ClCCCH_2^+ \quad (i)$$

As can be seen in Figure 3, both TS5 and TS3 lie below the reactants, and therefore, conversion among these three species is feasible. Of course, once either $ClC_3H_2^+$ or $ClCCCH_2^+$ are formed they might give rise to the same final products obtained in channels a−h, i.e., cyclic or linear ClC_3^+ and ClC_3H^+. The production of the cyclic species from $ClC_3H_2^+$ has been omitted in Figure 3 in order to simplify the scheme. However, it is clearly seen that in both cases they are endothermic channels. In the case of production of ClC_3^+, there is in addition a high energy barrier (TS4 lies about 44.5 kcal/mol above the reactants). Therefore, it seems that the production of cyclic species from $HCCCH^+$ should be precluded.

The final evolution of $ClCCCH_2^+$ coincides with the previously considered paths a and b. Production of $CCCCl^+$ is slightly exothermic at both G2 and CCSD(T) levels, although it is subject to a small barrier (5.1 kcal/mol) at the CCSD(T) level. On the other hand, production of $HCCCCl^+$ is clearly endothermic at both levels of theory. It is then concluded that the production of open-chain chlorine−carbon compounds from the linear carbocation $HCCCH^+$ is also quite unlikely.

A second possibility for the evolution of $HCCCHCl^+$ is chlorine insertion into the C−H bond to give $HCCCClH^+$, which may further give linear $CCCH^+ + HCl$:

$$Cl + HCCCH^+ \rightarrow HCCCHCl^+ \xrightarrow{TS6} HCCCClH^+ \rightarrow CCCH^+ + HCl \quad (j)$$

Chlorine insertion into the C−H bond involves a transition state, TS6, and the resulting intermediate, $HCCCClH^+$, is characterized by a long C−Cl distance (1.963 and 2.018 Å at the MP2 and B3LYP levels, respectively). This intermediate is much more unstable than other $(ClC_3H_2)^+$ species (it lies about 87 kcal/mol above the lowest-lying intermediate, cyclic $ClC_3H_2^+$, at both G2 and CCSD(T) levels of theory) and can be viewed as the result of the interaction of $CCCH^+$ with HCl. Therefore,

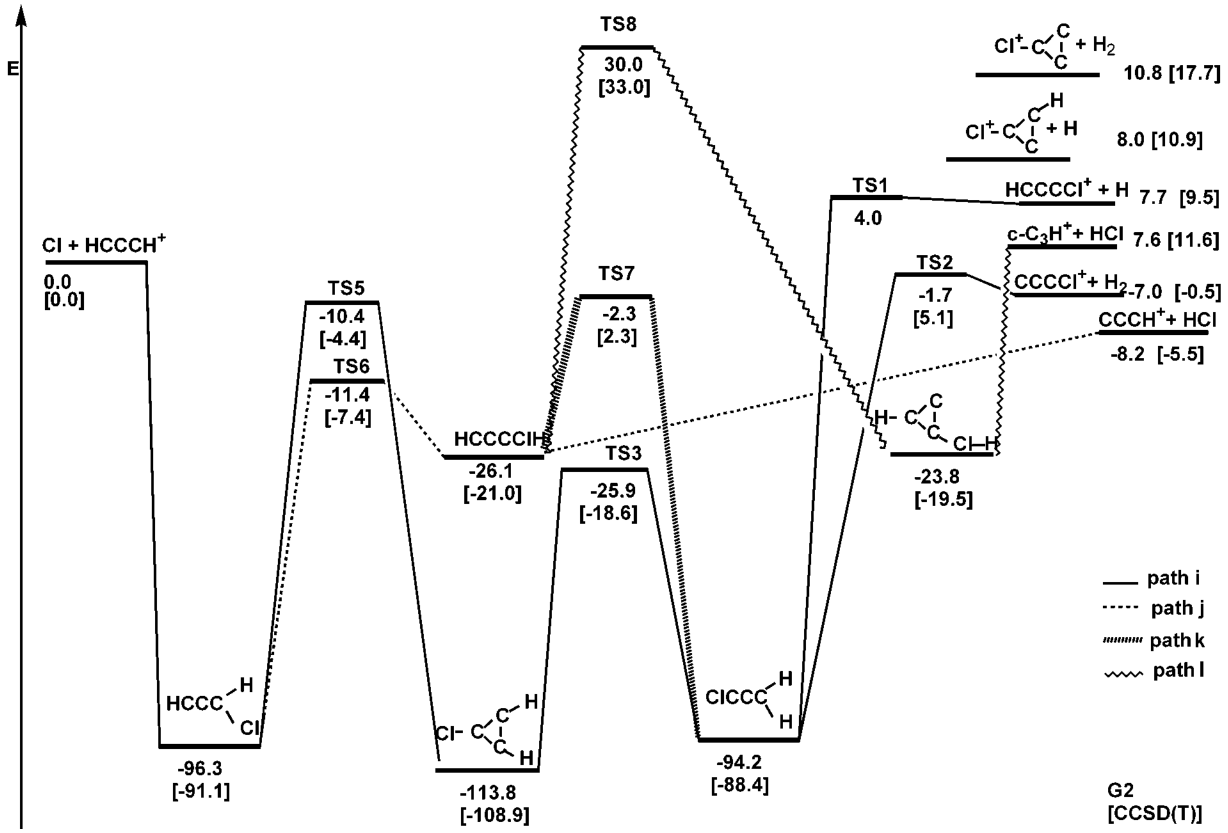

Figure 4. Energy profile, in kcal/mol, for the reaction of Cl with $HCCCH^+$ at the G2 and CCSD(T) (in brackets) levels. ZPVE corrections have been included at the MP2=full/6-31G(d) and B3LYP/6-311G(d,p) levels, respectively.

it is not surprising that the final step of path j, leading to linear $CCCH^+ + HCl$, does not imply any transition state. TS6 lies well below the reactants (about 11.4 and 7.4 kcal/mol, respectively, at the G2 and CCSD(T) levels), and therefore, this is a barrier-free path. In addition, it is clearly the most exothermic channel at both G2 and CCSD(T) levels and consequently should constitute the preferential path both from the thermodynamic and kinetic viewpoints.

Nevertheless, there are other possibilities for the evolution of $HCCCClH^+$ that should be discussed. One of them is migration of the hydrogen atom bonded to chlorine to the end carbon atom:

$$\text{Cl} + \text{HCCCH}^+ \rightarrow \text{HCCCHCl}^+ \xrightarrow{\text{TS6}} \text{HCCCClH}^+ \xrightarrow{\text{TS7}} \text{ClCCCH}_2^+ \quad (\text{k})$$

resulting in $ClCCCH_2^+$ and therefore leading finally to either $HCCCCl^+ + H$ (through TS1) or to $CCCCl^+ + H_2$ (through TS2). The isomerization takes place through a transition state, TS7, which lies slightly below the reactants at the G2 level, but is predicted to be about 2 kcal/mol higher in energy at the CCSD(T) level. Therefore, in any case, path j should prevail in principle over path k.

The last path shown in Figure 4 corresponds to hydrogen migration from the end carbon atom to the middle one. This is accompanied by cyclation of the C_3 unit, resulting in an intermediate, HC_3ClH^+, which can be viewed as the result of the interaction of cyclic C_3H^+ with HCl. This intermediate is also much more unstable than the lowest-lying $(ClC_3H_2)^+$ species, but it is relatively close in energy to the other intermediate resulting from the interaction of HCl with linear $CCCH^+$, $HCCCClH^+$. Similarly to the latter case, the final step of path l does not involve any transition state and leads directly to cyclic $C_3H^+ + HCl$:

$$\text{Cl} + \text{HCCCH}^+ \rightarrow \text{HCCCHCl}^+ \xrightarrow{\text{TS6}} \text{HCCCClH}^+ \xrightarrow{\text{TS8}} \text{HC}_3\text{ClH}^+ \rightarrow \text{C}_3\text{H}^+ + \text{HCl} \quad (\text{l})$$

Nevertheless, this path cannot compete with path j, because it is clearly endothermic and, more importantly, involves a high energy barrier, because TS8 lies more than 30 kcal/mol higher in energy than the reactants.

Therefore, bearing in mind the results shown in Figure 4, it can be concluded that the predicted dominant channel for the reaction of Cl atoms with $HCCCH^+$ is path j, both from thermodynamic and kinetic arguments, and consequently, the preferential product should be $CCCH^+ + HCl$.

It is also interesting to point out that it is quite likely that production of linear $CCCH^+ + HCl$ could be as well the predicted dominant channel for the reaction of Cl with $c\text{-}C_3H_2^+$. One may propose the following path for this channel:

$$\text{Cl} + c\text{-C}_3\text{H}_2^+ \rightarrow \text{ClC}_3\text{H}_2+ \xrightarrow{\text{TS5}} \text{HCCCHCl}^+ \xrightarrow{\text{TS6}} \text{HCCCClH}^+ \rightarrow \text{CCCH}^+ + \text{HCl} \quad (\text{m})$$

This path is not shown in Figure 3, but its energetics relative to $\text{Cl} + c\text{-}C_3H_2^+$ can be summarized as follows (G2 values, CCSD(T) values in brackets):

$CCCH^+ + HCl$: −2.2 [1.3] kcal/mol

TS5: −4.3 [2.4] kcal/mol

TS6: −5.3 [-0.6] kcal/mol

Therefore, path m is predicted to be slightly exothermic and barrier free at the G2 level, whereas the CCSD(T) calculations predict that it is slightly endothermic and subject to a small energy barrier. In any case, these values are lower than those involved in any other path previously considered leading to either ClC_3H^+ or ClC_3^+.

The analogous path starting with $CCCH_2^+$:

$$\mathrm{Cl} + \mathrm{CCCH_2}^+ \rightarrow \mathrm{ClCCCH_2}^+ \xrightarrow{\mathrm{TS7}} \mathrm{HCCCClH}^+ \rightarrow \mathrm{CCCH}^+ + \mathrm{HCl} \quad \text{(n)}$$

involves only transition state TS7, whose energy is relatively close to that of TS2. Therefore, in this case, although production of $CCCH^+ + HCl$ is predicted to be slightly more exothermic, $CCCCl^+ + H_2$ cannot definitively ruled out as a possible competitive channel.

In addition to the previously discussed channels, other possibilities have also been explored. For example, other mechanisms for hydrogen molecule elimination, involving different previous migrations of hydrogen atoms, have been considered, but they have been discarded because they involve high-lying transition states that should preclude their possible competition with the paths already discussed.

Another interesting point is that for all isomers the reaction of $C_3H_2^+$ cations with atomic chlorine proceeds through rather stable intermediates ($HCCCHCl^+$, $ClC_3H_2^+$, and $ClCCCH_2^+$), because they lie well below the reactants and the products. This suggests that they could be long-living intermediates, and therefore, they could be observed in eventual experiments or even participate in other processes in the interstellar medium. Of course a more detailed dynamical treatment should be performed.

Conclusions

A theoretical study of the reaction of atomic chlorine with the different isomers of $C_3H_2^+$ ($CCCH_2^+$, c-$C_3H_2^+$, and $HCCCH^+$) has been carried out. We have employed two different levels of calculations, namely, G2 and CCSD(T). These theoretical results allow the development of thermodynamic arguments about the reaction pathways of the process $Cl + C_3H_2^+$. The most important conclusion from our work is that the predicted dominant channel for the reaction with both $HCCCH^+$ and c-$C_3H_2^+$ is linear $CCCH^+ + HCl$. This channel is clearly exothermic (−8.2 and −5.5 kcal/mol at the G2 and CCSD(T) levels, respectively) and barrier-free for $HCCCH^+$, whereas for c-$C_3H_2^+$, it is predicted to be only slightly exothermic (−2.2 kcal/mol) by the G2 method and slightly endothermic (1.3 kcal/mol) at the CCSD(T) level. The CCSD(T) calculations also predict a small energy barrier (2.4 kcal/mol) for the $Cl + c$-$C_3H_2^+$ reaction, whereas at the G2 level, it seems to be barrier free. It seems that chlorine−carbon compounds can only be formed in the reaction of Cl with the $CCCH_2^+$ isomer. In that case, our calculations predict that production of $CCCCl^+ + H_2$ could be competitive with the $CCCH^+ + HCl$ channel, and that should be dominant over $HCCCCl^+ + H$, both from thermodynamic and kinetic points of view. Therefore, on the basis of our theoretical results, it can be anticipated that the role of the reaction of Cl with $C_3H_2^+$ as a possible source of chlorine−carbon compounds in space seems severely limited.

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Supporting Information Available: Optimized geometries for all intermediates and products. This material is available free of charge via the Internet at http://pubs.acs.org.

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