Theoretical Study of the Reaction of HCl with $C_3H_2^+$: A Possible Source of Carbon−Chlorine Compounds in Space

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A theoretical study of the $(ClC_3H_3)^+$ species has been carried out. Two different models, G2 and QCISD(T) at the B3LYP geometries, have been employed. Our calculations predict that the global minimum is an open-chain isomer $ClHCCCH_2^+(^2A)$, whereas five different open-chain structures are also quite stable, lying about 5.9−13.1 kcal/mol above the ground state. The lowest-lying cyclic isomer, with a three-membered carbon ring, lies about 18.3 kcal/mol higher in energy. These theoretical results allow the development of thermodynamic arguments about the reaction pathways of the process HCl + $C_3H_2^+$. For the reaction of HCl with $CCCH_2^+$, formation of different chlorine−carbon compounds is exothermic and there are several mechanisms leading to these species that are barrier-free. However, production of carbocation compounds (cyclopropenyl cation, c-$C_3H_3^+$, and propargyl cation, l-$C_3H_3^+$) could be competitive with the formation of chlorine−carbon species. The predicted dominant channels for the reaction with both $HCCCH^+$ and c-$C_3H_2^+$ isomers are l-$C_3H_3^+$ and c-$C_3H_3^+$, respectively. Therefore, only the reaction of HCl with the $CCCH_2^+$ isomer seems to be a possible source of chlorine−carbon compounds in space.

Introduction

The chemistry of chlorine in dense interstellar clouds remains rather uncertain. To date, only HCl has been detected in the interstellar medium,[1] although several metal chlorides have been observed in circumstellar shells,[2] and there are indications that other chlorine compounds (essentially carbon−chlorine systems as CCl,[3] C_2Cl,[4] or C_3Cl[5,6]) may be found in space. Several binary carbides containing second-row elements, corresponding to the general formula XC_n, have been detected in the interstellar medium. To date, this family of molecules includes compounds such as SiC_2,[7] SiC_3,[8] SiC_4,[9] SC_2,[10] and SC_3.[11] In addition, gas-phase chlorine chemistry is very interesting because of its relevance in atmospheric studies.

One of the most abundant hydrocarbons observed in the interstellar medium is C_3H_2. In fact, there are two different C_3H_2 isomers, which have been detected in space: cyclopropenylidene, c-C_3H_2,[12] the first interstellar organic ring identified in space, and propadienylidene (singlet vinylydenecarbene), l-C_3H_2.[13] On the other hand, ion−molecule chemistry plays a crucial role in interstellar chemistry, and therefore it is important to know the possible role of the different isomers of C_3H_2 or their cationic derivatives, $C_3H_2^+$, in the synthesis of interstellar species. $C_3H_2^+$ cations can be formed in the interstellar medium through different processes, such as $C^+ + C_2H_4$, $C^+ + C_2H_3$, or $CH_2^+ + C_2H$.[14] In the last years, the possible role of the reaction of $C_3H_2^+$ cation with atomic nitrogen has been studied both theoretically[15] and experimentally.[16]

In the present work, we have carried out a theoretical study of the reaction of HCl with $C_3H_2^+$ to determine the reaction enthalpy as well as any possible activation barrier for the different paths that can be expected for this process. The aim of this study is to explain the possible role of this reaction in the synthesis of carbon−chlorine compounds in space. On the other hand, the abundance of HCl in the interstellar medium is lower than expected,[1] and this reaction could be considered as a possible degradation mechanism for HCl. We have considered, as in our previous studies of the reactions of Cl[6] and N[15] with $C_3H_2^+$, 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,[16] and a mixture of $HCCCH^+$ and c-$C_3H_2^+$ is likely to be formed. Both experimental[17] and theoretical[18] calculations indicate that the lowest-energy isomer is the cyclic structure, with the linear isomer $HCCCH^+$ lying about 6 kcal/mol higher in energy. The other isomer, $CCCH_2^+$, is predicted to lie about 46 kcal/mol higher than c-$C_3H_2^+$.

Given the multiplicity of the reactants, the reaction of HCl with $C_3H_2^+$ should proceed along the doublet $(H_3C_3Cl)^+$ surface. Nevertheless, given the lack of information about the structure and stability of $(H_3C_3Cl)^+$ species, in the first place a study of the most stable structures on doublet surface will be presented. The possible carbon−chlorine products of this reaction, $(HC_3Cl)^+$ and $(H_2C_3Cl)^+$, have been theoretically studied in previous works.[5,19]

Computational Methods

The geometries of the different species in this work have been obtained at the second-order Møller−Plesset level with the 6-31G(d) basis set[20] including all electrons in the calculations, which is denoted as MP2(full)/6-31G(d), and also using density functional theory (DFT). In particular, for the DFT calculations

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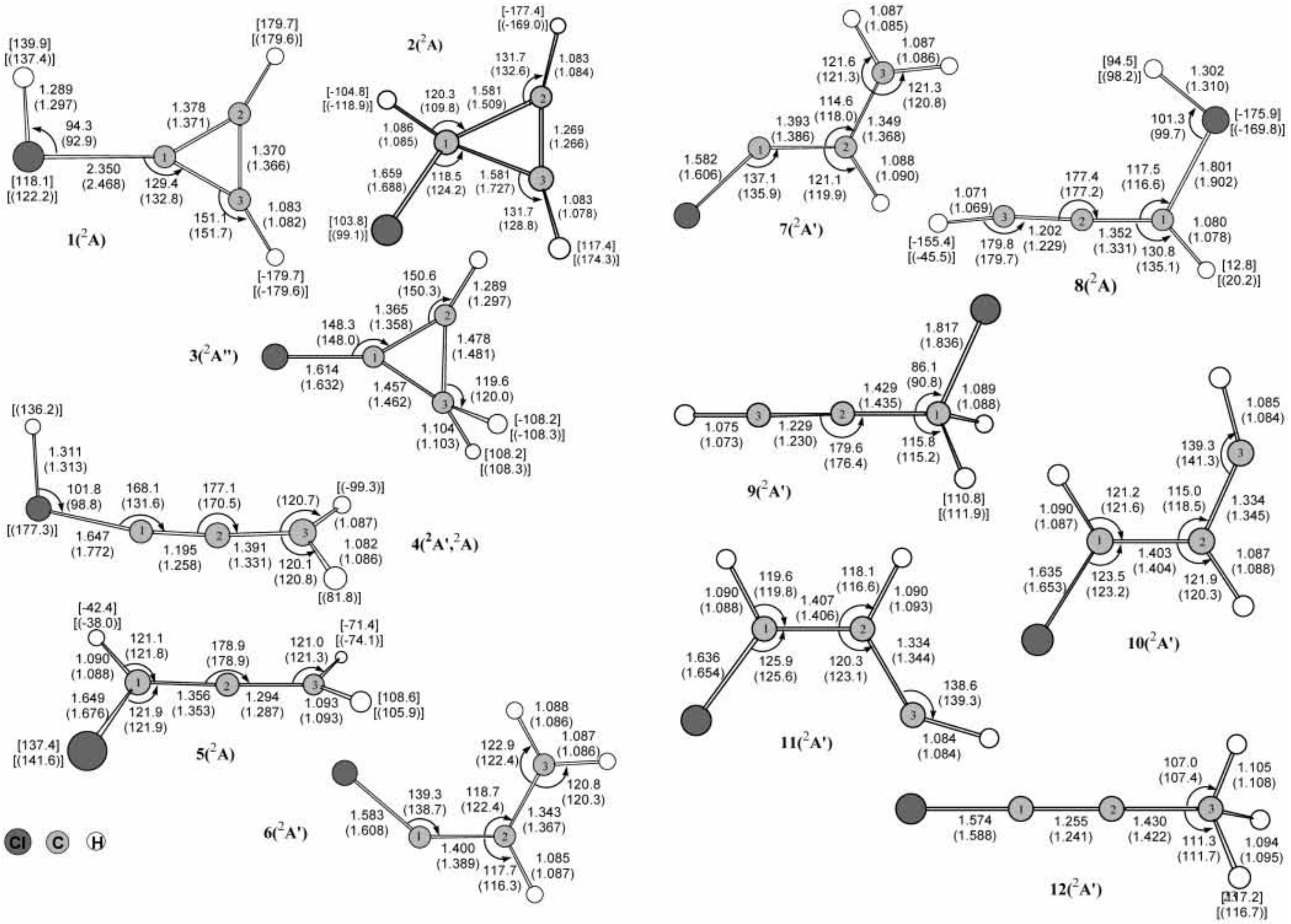


Figure 1. MP2 = full/6-31G(d) and B3LYP/6-311G(d,p) (in parentheses) optimized geometries for the different $(ClC_3H_3)^+$ isomers. Distances are given in angstroms and angles in degrees. Dihedral angles are given in brackets.

we selected the Becke's hybrid three-parameter functional combined with the Lee−Yang−Parr nonlocal correlation functional (B3LYP)[21] with the 6-311G(d,p) basis set.[22] Harmonic vibrational frequencies have been computed on each optimized geometry at its corresponding level of theory. This allows an assessment of the nature of stationary points, as well as an estimate of the zero-point vibrational energy (ZPVE) correction. We must point out that our previous calculations on C_3Cl and C_3Cl^+ [23] showed that the MP2 and B3LYP geometries and vibrational frequencies were rather insensitive to the basis set (in that work we also carried out optimizations at the MP2-(full) level with the 6-311G(d) basis set, as well as B3LYP calculations with the cc-pVTZ basis set).

To compute accurate relative energies, we have employed higher-level theoretical methods. The G1 and G2[24] methods were employed and, since we are dealing with open-shell states and spin contamination may affect the convergence of the MP series, approximate projected MP values were used to compute electronic energies. These results will be denoted as G1(P) and G2(P). In addition, on the B3LYP geometries we have carried out single-point calculations at the QCISD(T) level[25] (quadratic CI calculations with singles and doubles substitutions followed by a perturbative treatment of triplet substitutions) with the 6-311G(d,p) basis set. It is worth noting that in our previous calculations on related systems,[19,23] QCISD(T)/6-311G(d,p) calculations on B3LYP geometries were shown to provide very similar results to the most expensive CCSD(T)/cc-pVTZ level. Therefore, QCISD(T)/6-311G(d,p) seems a reasonable compromise between cost and quality for these systems.

All calculations reported in this work were carried out with the Gaussian 98 program package.[26]

Results and Discussion

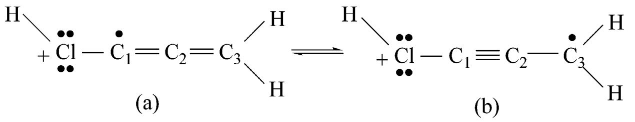
$(ClC_3H_3)^+$ Isomers. The more relevant $(ClC_3H_3)^+$ species will be discussed in this section. Given the multiplicity of the reactants, the reaction should take place in principle along the doublet surface. Therefore the optimized geometries for the different $(ClC_3H_3)^+$ structures on the doublet surface at the MP2-(full)/6-31G(d) and B3LYP/6-311G(d,p) levels are shown in Figure 1. All reported structures are true minima, since all their vibrational frequencies are real. The corresponding harmonic vibrational frequencies and IR intensities are not shown but are available upon request.

Structure **1** can be considered as the result of the interaction of HCl with the cyclic $C_3H_2^+$ through an apex. In this case the Cl−C bond distance is very long, suggesting that, in fact, **1**(^{2}A) is an ion−molecule complex. The geometrical parameters of the $C_3H_2^+$ unit are only slightly modified with respect to the cyclopropenylidene cation. The unpaired electron is mainly localized at the carbon bonded to chlorine and the positive charge is delocalized around the C_3 unit. Isomer **1** is a minimum at both levels of theory, and the IR spectrum should be dominated by symmetric stretching of the C_3 unit at 1276 cm^{-1} (MP2) or 1248 cm^{-1} (B3LYP).

Isomer **2** is obtained from **1** through migration of the hydrogen atom bonded to chlorine to carbon atom, C_1. This results in longer C_1−C_2 and C_1−C_3 bond distances and shorter

C_2-C_3 and C_1-Cl bond distances. At the MP2 level, C_1-C_2 and C_1-C_3 bond distances are very close, in contrast to B3LYP results where the value of the C_1-C_3 bond distance is too large for a typical single C−C bond distance. Isomer **2**(^{2}A) is a true minimum at the MP2 level, but has a small imaginary frequency (11i cm^{-1}, a symmetry) at the B3LYP level corresponding to C_1-C_3 stretching. The migration of the hydrogen atom from C_1 to C_3 gives the last cyclic isomer that we characterized, isomer **3**, which has a $^2A''$ lowest-lying state. The changes in C−C bond distances with respect to isomer **1** are smaller than in structure **2**. The most favorable π-donation from the chlorine atom toward the ring results in a shorter $Cl-C_1$ bond distance for structure **3**($^2A''$). This isomer is a true minimum on both the MP2 and B3LYP surface since all these frequencies are real. The infrared spectrum should be dominated by symmetric C−H stretching, at 3002 cm^{-1} (MP2) or 2964 cm^{-1} (B3LYP).

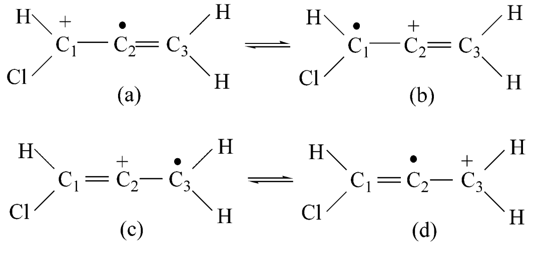
Structure **4** has a quasi-linear carbon backbone and can be viewed as the result of the interaction of HCl with vinylidenecarbene cation ($CCCH_2^+$) through the end carbon. Isomer **4** has a planar C_s structure ($^2A'$) at the MP2 level and a nonplanar C_1 structure (^{2}A) at the B3LYP level. The dominant valence-bond structures for this isomer, compatible with the population analysis, are the following:



The positive charge, which is formally located at the chlorine atom, favors p_π-d_π black-donation toward chlorine. According with geometrical parameters shown in Figure 1, structure (a) prevails at the B3LYP level, whereas (b) is the dominant at the MP2 level.

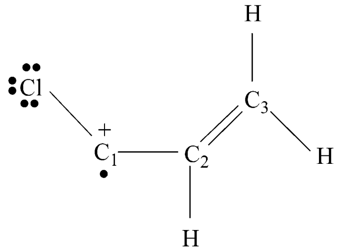
Structure **4** is a true minimum on the $C_3H_3Cl^+$ doublet surface at both levels of theory. The MP2 level predicts a line at 2621 cm^{-1}, corresponding to the C−C asymmetric stretching, as the most intense, but at the B3LYP level the IR spectrum is dominated by C−Cl stretching frequency (2702 cm^{-1}).

Structure **5**(^{2}A) is nonplanar with a C−C−C backbone quite close to linearity and can be considered as the result of the migration of the hydrogen atom bonded to chlorine from structure **4**. There are several valence-bond structures contributing in this case:



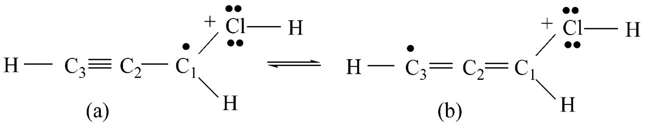
In accordance with the results of population analysis and geometrical parameters (see Figure 1), structures (a) and (b) seem to have a higher contribution than (c) and (d). A certain π-donation from a chlorine atom is also favorable. This structure is also a true minimum at both levels of theory and the IR spectrum should be dominated by C−C stretching which is predicted to be the most intense, and its fundamental is estimated at 2047 cm^{-1} (MP2) and 1856 cm^{-1} (B3LYP), respectively.

Structures **6** and **7** correspond to the cis and trans rearrangement, respectively, of the chlorine atom and a CH_2 unit with respect to the C_1-C_2 bond. Both isomers have a planar doublet state, $^2A'$, and the dominant valence-bond structure for these isomers is the following:

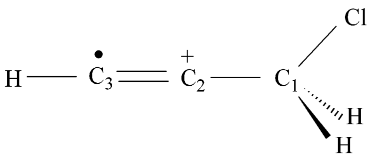


These structures favor the π-donation of the chlorine atom lone pair orbital into the C_1 vacant orbital, and the $Cl-C_1$ bond is considerably shortened. The two isomers, **6** and **7**, have very similar bond distances and bond angles. The main difference between **6** and **7** is that the $<C_1C_2C_3$ and $<ClC_1C_2$ angles are greater in **6** whereas the $<C_1C_2H$ angle is greater for **7**, but it is only the consequence of the cis and trans arrangement relative to the CH_2 unit. Isomers **6** and **7** are true minimum on the doublet potential surface. Both levels of theory, MP2 and B3LYP, agree in that the IR spectrum of **6** and **7** is dominated by the C−H bending frequency at 1455(1473) cm^{-1} and 1475(1476) cm^{-1} at the MP2(B3LYP) level, respectively.

Isomer **8** can be considered as the result of the interaction of HCl with the linear isomer, $HCCCH^+$. The interaction produces a considerable distortion of the hydrocarbon geometry. The dominant valence-bond structures for this isomer, compatible with the population analysis, are the following:



The positive charge is formally located at the chlorine atom and this favors $p_\pi-d_\pi$ back-donation toward the chlorine atom, as in the case of isomer **4**, which results in a C_1-Cl bond length for this isomer shorter than in structure **1**. Both levels of theory, MP2 and B3LYP, agree in that the IR spectrum of **8**(^{2}A) should be dominated by the C−C stretching frequency (2321 cm^{-1} (MP2) or 1995 cm^{-1} (B3LYP)). Structure **9**($^2A'$) is obtained from **8** through migration of the hydrogen atom bonded to chlorine to the C_1 atom. This results in a long C_1-C_2 bond distance and a short C_1-Cl bond distance. The unpaired electron is mainly located at the C_3, and the dominant valence bond structure is the following:



Structure **9** is a true minimum in the $(ClC_3H_3)^+$ doublet potential surface at both levels of theory. According to our MP2 and B3LYP results, the most intense line in the IR spectrum should be the asymmetric C−C stretching at 2531 cm^{-1} (MP2) or 2075 cm^{-1} (B3LYP).

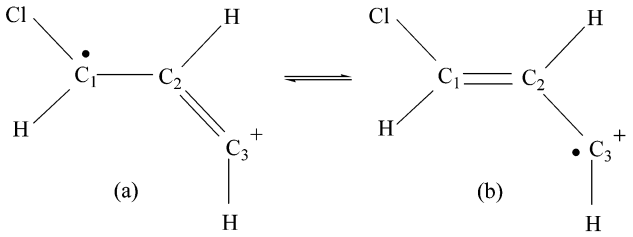
Structures **10** and **11** have planar doublet states, $^2A'$, and are obtained from **5** or **9** though migration of a hydrogen atom to C_2. The two isomers have very similar bond distances and bond angles, differing only in the relative positions of the chlorine

TABLE 1: Relative Energies (kcal/mol) for the $(ClC_3H_3)^+$ Species at Different Levels of Theory; Zero-Point Vibrational Energy Differences Have Been Included[a]

	1(^{2}A)	2(^{2}A)	3(^{2}A″)	4(^{2}A′,^{2}A)	5(^{2}A)	6(^{2}A′)	7(^{2}A′)	8(^{2}A)	9(^{2}A′)	10(^{2}A′)	11(^{2}A′)	12(^{2}A′)
					MP2(full)/6-31G(d) geometry							
MP4/6-311G(d,p)	30.3	18.9	14.4	53.3	0.0	10.0	5.9	35.1	22.0	13.9	15.7	4.3
QCISD(T)/6-311G(d,p)	31.8	21.0	16.0	51.7	0.0	9.0	5.6	32.0	21.4	12.5	13.6	6.0
G1	35.3	23.8	18.3	53.0	0.0	10.7	7.7	33.2	21.7	15.4	16.7	7.7
G2	34.6	22.8	17.7	52.2	0.0	10.3	7.4	32.6	22.4	15.2	16.5	7.3
G1(P)	35.5	24.4	18.9	48.8	0.0	8.9	6.1	27.6	21.1	12.5	13.2	8.3
G2(P)	34.8	23.4	18.3	48.1	0.0	8.4	5.9	27.1	21.7	12.3	13.1	8.0
					B3LYP/6-311G(d,p) geometry							
B3LYP/6-311G(d,p)	35.7	25.1	19.9	51.4	0.0	13.5	10.0	35.3	23.7	17.3	18.4	8.9
MP4/6-311G(d,p)	32.3	21.1	15.7	53.6	0.0	11.8	7.4	36.0	23.6	15.1	16.9	5.7
QCISD(T)/6-311G(d,p)	33.7	20.4	17.4	46.5	0.0	9.6	6.2	31.4	22.5	13.3	14.5	7.4
$\langle S^2\rangle$[b]	0.768	0.760	0.761	0.919	0.780	0.898	0.868	0.968	0.801	0.960	1.003	0.7588

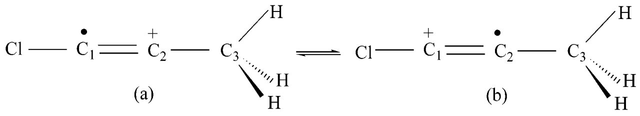
[a] ΔZPVE values have been scaled by 0.893 (HF/6-31G(d) level) and 0.94 (MP2=full/6-31G(d) level). [b] $\langle S^2\rangle$ expectation values for the HF/6-311G(d,p) wavefuction.

atom and the CH unit. These isomers can be described by the following two valence bond structures:



The shortening of the C_2-C_3 bond relative to the C_1-C_2 bond suggests that structure (a) prevails over (b). Structures **10** and **11** are true minimum on the doublet surface, since all their frequencies are real. For both a C−C stretching (near 1602-(1547) cm^{-1} and 1589(1554) cm^{-1}, at the MP2(B3LYP) levels, respectively) is predicted to dominate the IR spectrum.

Finally, we have considered isomer **12**, whose lowest-lying doublet is ^{2}A′. Structure **12** has a linear carbon backbone and can be obtained from structures **6** and **7** through migration of a hydrogen atom bonded to C_2 to C_3 atom. In contrast to the similar structure **9**(^{2}A′), the unpaired electron is almost equally distributed between C_1 and C_2, as a consequence of the following two dominant valence bond structures:



The C−Cl bond length is the shortest of all $(ClC_3H_3)^+$ structures. This is due to the possibility of π-donation from the chlorine atom toward C_1 in structure (b). Isomer **12** is also a true minimum on the $(ClC_3H_3)^+$ doublet potential surface at both levels of theory, and the IR spectrum would be dominated by the asymmetric C−H bending frequency (3029(2923) cm^{-1}, at the MP2(B3LYP) levels).

The relative energies at different levels of theory of the $(ClC_3H_3)^+$ species are given in Table 1. Since we are dealing with open shell states, we also provide G1(P) and G2(P) values, to alleviate spin-contamination problems. S^2 expectation values for the HF/6-311G(d,p) wave function are also shown in Table 1; the corresponding S^2 values for the B3LYP calculations are not shown since they are virtually coincident with the exact value. Concerning the performance of the different methods of calculation, it should be noted that unprojected G1 and G2 results are quite close to G1(P) and G2(P) values in most cases. The worst cases are **4**, **8**, **10**, and **11** as a consequence of their relative high spin contamination. It is also interesting to note that the QCISD(T) and G2(P) levels provide very close relative energies. The mean difference between both levels of theory for the twelve species, whose relative energy has been computed, is only 1.4 kcal/mol. Furthermore the B3LYP level provides also relative energies which compare reasonably well with the G2(P) method.

It is readily seen that at all levels of theory, the most stable species is the open-chain structure **5**(^{2}A). The next lowest-lying structures are **7**, **12,** and **6** lying 5.9, 8.0, and 8.4 kcal/mol, at the G2(P) level, respectively, higher in energy than the global minimum. Structures **10** and **11** lie also rather close in energy, about 12.3 and 13.1 kcal/mol, at the G2(P) level, respectively, above isomer **5**. In both pairs of conformational isomers (**6**−**7** and **10**−**11**), the trans isomer is slightly favored over its cis counterpart. The most stable cyclic structure **3** lies about 18.3 kcal/mol at the G2(P) level, higher in energy than the global minimum. This isomer is about 5 kcal/mol more stable than the other cyclic isomer **2**, which has a hydrogen and a chlorine atom bonded to the same carbon. The open-chain isomer **9** is relatively close in energy to isomers **2** and **3**, lying 21.7 kcal/mol at the G2(P) level, higher in energy than isomer **5**. Finally, isomers **1**, **4**, and **8**, which have a Cl−H bond, are the least stable structures.

The $(ClC_3H_3)^+$ system can be viewed as the result of chlorine substitution on the $C_3H_4^+$ cation. In $C_3H_4^+$, an experimental study[27] has shown that the global minimum is the open-chain structure $H_2CCCH_2^+$, similar to isomer **5**, with H_3CCCH^+ (similar to structures **9** and **12**) and CH_2CHCH^+ (corresponding to isomers **6**, **7**, **10**, and **11**) lying about 13.8 and 25.4 kcal/mol, respectively, higher in energy. A theoretical study[28] has shown that the cyclic structure c-$C_3H_4^+$, similar to isomers **2** and **3**, lies about 28 kcal/mol, at the MNDO/6-31G* level, above the global minimum. Therefore, substitution of a hydrogen atom for chlorine retains the global minimum, the stability order (except in the case of isomer **9**), and reduces the energy difference between isomers. It is also interesting to note that **3** is lower in energy than **2**, **6** and **7** are lower than **10** and **11**, and **12** is lower than **9**. Therefore, chlorine substitution at the carbon bonded to just a hydrogen atom appears to be slightly favored over substitution at the carbon atom bonded to two hydrogen atoms.

Reaction of HCl with $C_3H_2^+$. In this section we will discuss the reaction of HCl with the different isomers of $C_3H_2^+$

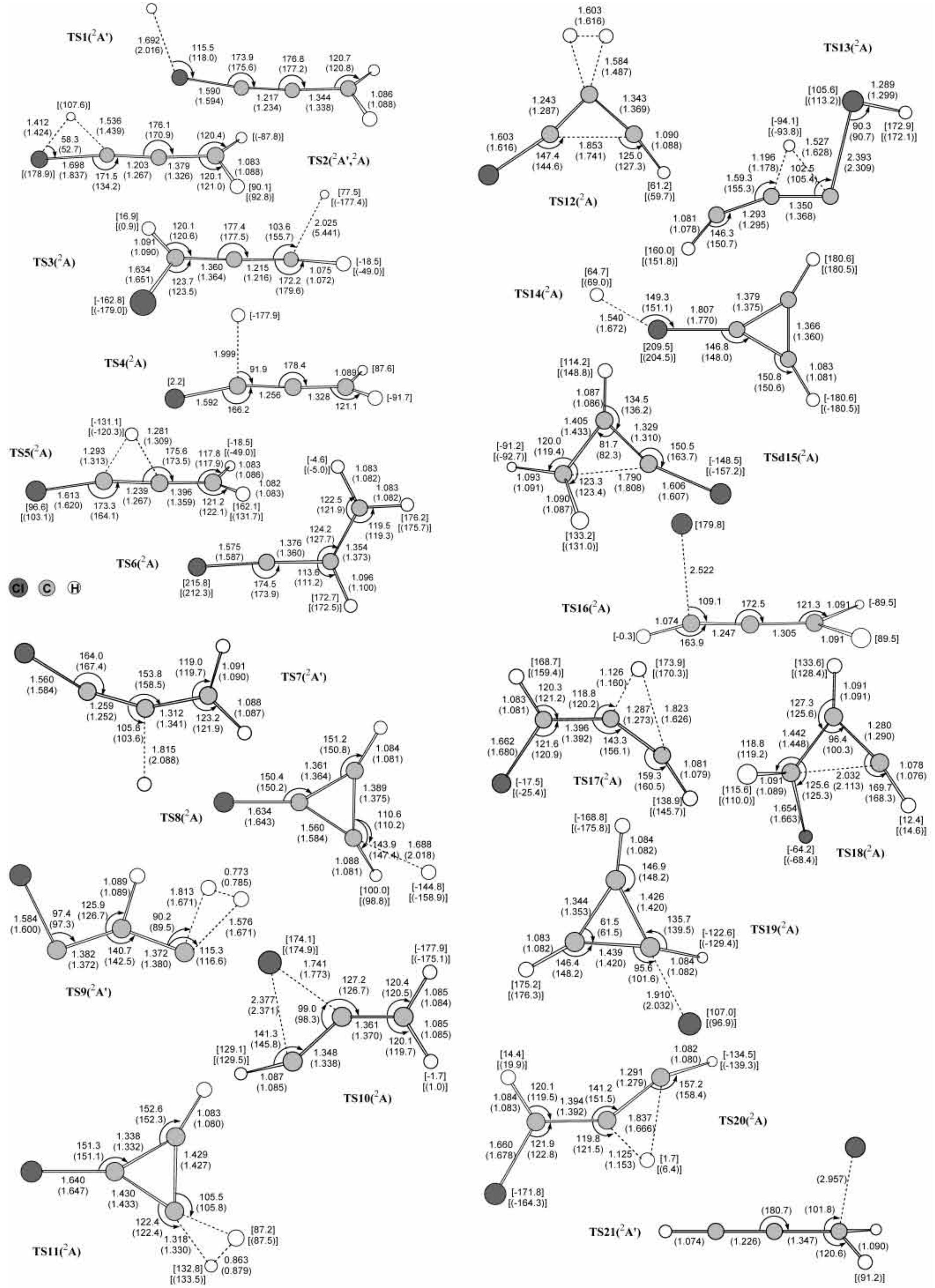

TS1(^{2}A')
TS2(^{2}A',^{2}A)
TS3(^{2}A)
TS4(^{2}A)
TS5(^{2}A)
TS6(^{2}A)
Cl C H
TS7(^{2}A')
TS8(^{2}A)
TS9(^{2}A')
TS10(^{2}A)
TS11(^{2}A)
TS12(^{2}A)
TS13(^{2}A)
TS14(^{2}A)
TSd15(^{2}A)
TS16(^{2}A)
TS17(^{2}A)
TS18(^{2}A)
TS19(^{2}A)
TS20(^{2}A)
TS21(^{2}A')

Figure 2

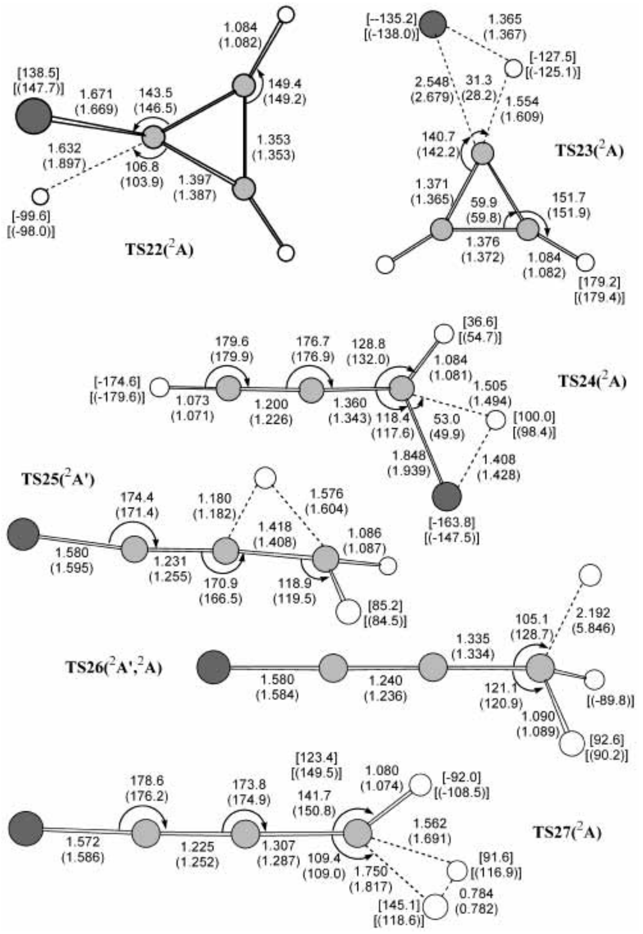


Figure 2 (continued). MP2 = full/6-31G(d) and B3LYP/6-311G(d,p) (in parentheses) optimized geometries for the relevant transition states involved in the reaction of HCl with $C_3H_2^+$. Distances are given in angstroms and angles in degrees. Dihedral angles are given in brackets.

($CCCH_2^+$, $HCCCH^+$ and c-$C_3H_2^+$). Basically there are in principle four different channels for this reaction:

$$HCl(^1\Sigma) + C_3H_2^+(^2A_{1;}\ ^2\Pi_g) \rightarrow (ClC_3H)^+ + H_2(^1\Sigma_g^+)$$

$$\rightarrow (ClC_3H_2)^+ + H(^2S)$$

$$\rightarrow (C_3H_3)^+ + Cl(^2P)$$

$$\rightarrow C_3H_2(^1A_1) + HCl^+(^2\Pi)$$

Charge transfer can be discarded because of its endothermicity. $HCl^+ + C_3H_2$ was found to lie between 54.4 and 102.8 kcal/mol higher than $HCl + C_3H_2^+$, at the G2(P) level, depending on the isomer considered for the hydrocarbon. The possible $(ClC_3H)^+$ and $(ClC_3H_2)^+$ structures have been studied in previous works.[5,19] We will only consider in what follows the possible reaction mechanisms leading to exothermic products. The geometrical parameters for the relevant transition states for the reaction are given in Figure 2. All transition states, with the exceptions of TS7 and TS11, have an imaginary frequency associated with the corresponding reaction coordinate. TS7, at the MP2 level, and TS11, at both levels MP2 and B3LYP, are in fact second-order saddle points, since both have two imaginary frequencies. One of them corresponds to hydrogen atom elimination or hydrogen molecule elimination, respectively, and the second-imaginary frequency is associated with an out-of-plane bending, or with rupture of C−H bond-distance symmetry, respectively. All attempts to obtain true transition states in these two cases failed. Nevertheless, we have included the relative energies of these second-order saddle points as an estimation of the values for the true transition states.

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

(a) HCl + $CCCH_2^+$. The reaction of HCl with the linear isomer $CCCH_2^+$ will be considered first. The energy profile for this reaction is rather complicated because several possible reaction pathways. Therefore, it is divided into Figures 3 and 4, where the results for selected levels of theory, namely G2(P), which could be the most reliable one, and QCISD(T), are shown.

For the reaction of HCl with $CCCH_2^+$ the first step is formation of isomer **4** through the interaction of chlorine atom with the terminal carbon atom. Then hydrogen elimination through transition state TS1 would lead to the linear product $ClCCCH_2^+$

$$HCl + CCCH_2^+ \rightarrow \mathbf{4} \xrightarrow{TS1} ClCCCH_2^+ + H \qquad (a)$$

In the associate transition state for the hydrogen elimination, TS1, the C−H distance for the breaking bond is longer at the B3LYP level than at the MP2 level, a fact that is observed for all transition states corresponding to hydrogen elimination. At both levels of theory, MP2 and B3LYP, TS1 lies higher in energy than the products (that is, the potential surface is topologically consistent). TS1 is the case where we have found the largest energy difference between G2(P) and QCISD(T) results. This difference is mainly due to two factors. The first one is the geometry, since we have found that TS1 energy with respect to the reactants is about −16.5 and −12.8 kcal/mol at the QCISD(T)/6-311G(d,p) level calculated at the MP2 and B3LYP geometries, respectively. The second one is the extension of the basis set. We found that TS1 lies −22.3 and −29.4 kcal/mol at the MP4 level with the 6-311G(d,p) and 6-311G(2df,p) basis set, respectively, below the reactants. Therefore it seems that a large basis set is required in order to compute the electronic energy of TS1 at correlated levels and the G2(P) value could be the considered for this transition state. However, at the most reliable level, G2(P), TS1 is found to lie below the separate fragments. Therefore, it seems quite likely that hydrogen elimination could be a barrier-free process at higher levels of theory. In any case, since TS1 lies below reactants, path (*a*) is feasible under interstellar conditions.

Another possibility, which could be competitive with the preceding channel, is isomerization of **4** into the lowest-lying isomer **5**, through transition state TS2, which lies also below the reactants. In addition, at the G2(P) level TS2 lies above TS1. It is also interesting to point out that the B3LYP method, which is less sensitive to the basis set extension according to our calculations in these systems,[23] provides a relative energy for TS1 in qualitative agreement with the G2(P) level, that is a relative energy below TS2. The intermediate **5** may suffer either elimination of a hydrogen atom or elimination of a chlorine atom.

$$HCl + CCCH_2^+ \rightarrow \mathbf{4} \xrightarrow{TS2} \mathbf{5} \xrightarrow{TS4} ClCCCH_2^+ + H \qquad (b.1)$$

$$HCl + CCCH_2^+ \rightarrow \mathbf{4} \xrightarrow{TS2} \mathbf{5} \xrightarrow{TS3} ClHCCCH^+ + H \qquad (b.2)$$

$$HCl + CCCH_2^+ \rightarrow \mathbf{4} \xrightarrow{TS2} \mathbf{5} \xrightarrow{TS16} l\text{-}C_3H_3^+ + Cl \qquad (b.3)$$

The three processes are exothermic because the corresponding products lie well below the reactants, and production of $HCCCH_2^+$ + Cl is the most exothermic path. In the case of

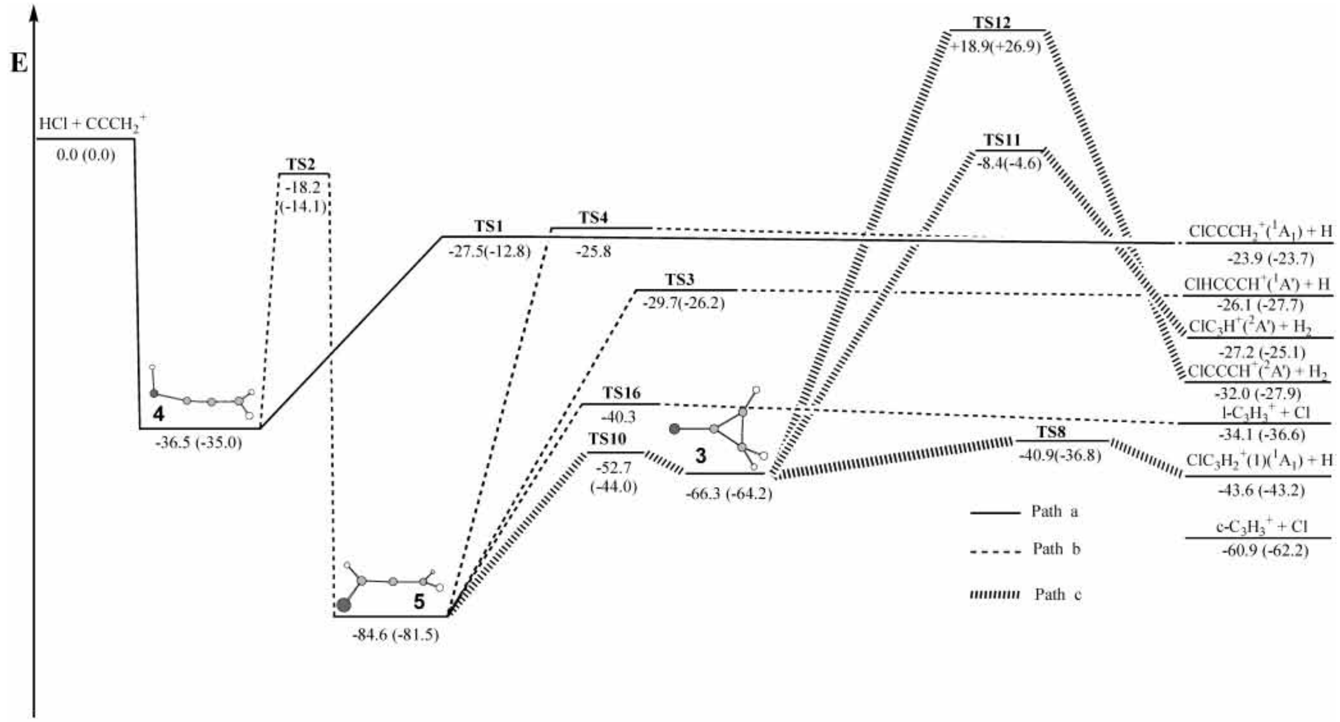


Figure 3. Energy profile (first part), in kcal/mol, for the reaction of HCl with $CCCH_2^+$ at the G2 and QCISD(T)/6311G(d,p) (in parentheses) levels.

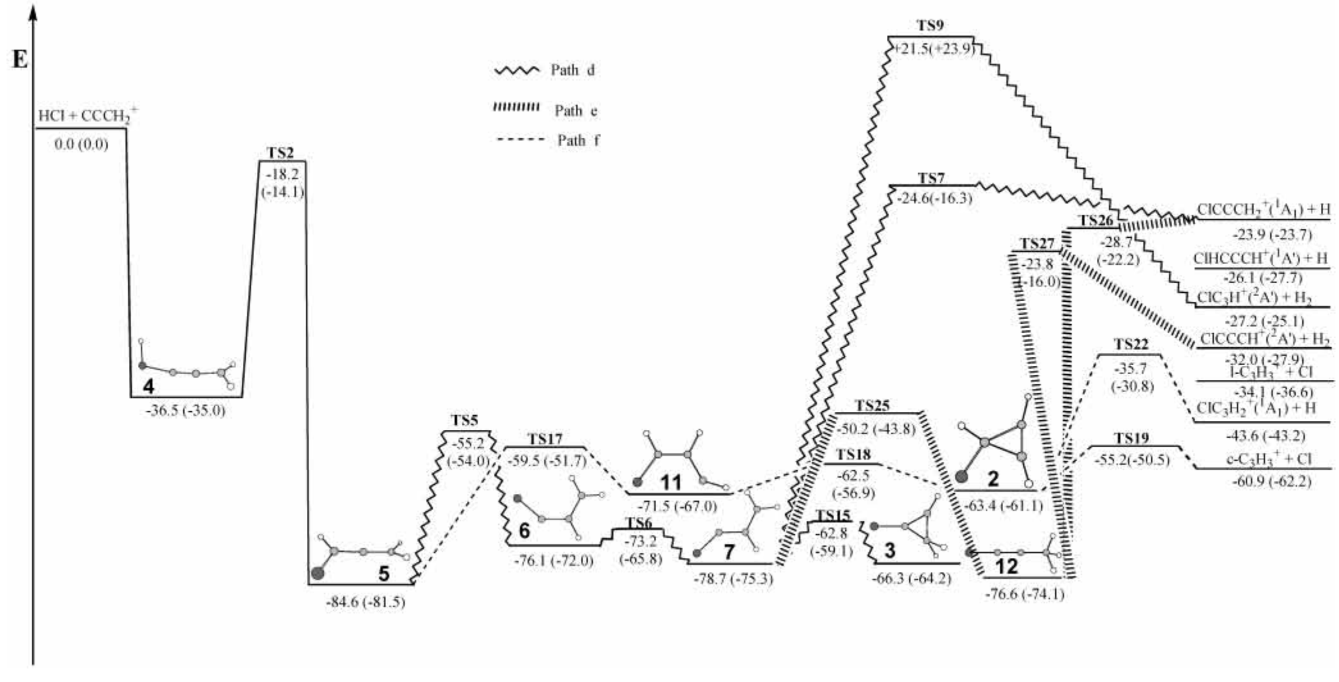


Figure 4. Energy profile (second part), in kcal/mol, for the reaction of HCl with $CCCH_2^+$ at the G2 and QCISD(T)/6311G(d,p) (in parentheses) levels.

path (*b.2*), at the B3LYP level, the C−H distance in TS3 is very long. On the other hand, in processes (*b.1*) and (*b.3*), the associated transition states for elimination of hydrogen or chlorine atom, TS4 and TS16, respectively, have only been obtained at the MP2 level, and consequently only the G2(P) energies are reported. At the B3LYP level, no transition states are found for these processes, and the corresponding scans for different C−H or C−Cl distances show no sign of barrier at this level of theory. Furthermore, at the G2(P) level, TS3, TS4, and TS16, are found to lie below the separated fragments. Therefore, it seems that at higher levels of theory it is quite likely that these processes could be barrier-free, in agreement with the B3LYP results. In any case, it seems clear from Figure 3 that production of $HCCCH_2^+ + Cl$ is both thermodynamic and kinetically favored over production of carbon−chlorine compounds, paths (*b.1*) and (*b.2*).

Alternatively, once structure **5** is reached, it might suffer migration of the chlorine atom and simultaneously cyclization, through transition state TS10, leading to isomer **3**. This process opens the possibility of formation of cyclic products. The cyclic intermediate, **3**, may suffer either elimination of a hydrogen atom, or elimination of a hydrogen molecule:

$$\mathbf{5} \xrightarrow{\text{TS10}} \mathbf{3} \xrightarrow{\text{TS8}} \mathrm{ClC_3H_2}^+ + \mathrm{H} \qquad (c.1)$$

$$\mathbf{5} \xrightarrow{\text{TS10}} \mathbf{3} \xrightarrow{\text{TS11}} \mathrm{ClC_3H}^+ + \mathrm{H_2} \qquad (c.2)$$

$$\mathbf{5} \xrightarrow{\text{TS10}} \mathbf{3} \xrightarrow{\text{TS12}} \mathrm{ClCCCH}^+ + \mathrm{H_2} \qquad (c.3)$$

Hydrogen atom elimination leading to the cyclic product $ClC_3H_2^+$ (path (*c.1*)), takes place through transition state TS8, which clearly lies below the reactants. Elimination of molecular hydrogen would lead to two different isomers, cyclic ClC_3H^+ (through TS11) or linear $ClCCCH^+$ (though TS12). In the case of linear $ClCCCH^+$, there is a high energy barrier (TS12 lies about 18.9 kcal/mol, above the reactants). Therefore, it seems that production of the linear isomer from path (*c.3*) should be precluded. Although, the relative energy of TS11 is doubtful (it is not a true transition state), it is clear that this process involves a transition state which lies below the reactants. In any case, it seems from Figure 3, that path (*c.1*) should be favored over path (*c.2*) not only thermodynamically but also from the kinetic point of view, because TS8 is placed below TS11 and lies below $ClC_3H^+ + H_2$.

Another possibility is the isomerization of **5** into isomer **6**, through the migration of a hydrogen atom, which involves transition state TS5. Structure **6** may further isomerize into **7**, through transition state TS6. Both transition states clearly lie below the reactants. Once **7** is formed, several processes may occur:

$$\mathbf{5} \xrightarrow{\text{TS5}} \mathbf{6} \xrightarrow{\text{TS6}} \mathbf{7} \xrightarrow{\text{TS7}} \mathrm{ClCCCH_2}^+ + \mathrm{H} \qquad (d.1)$$

$$\mathbf{5} \xrightarrow{\text{TS5}} \mathbf{6} \xrightarrow{\text{TS6}} \mathbf{7} \xrightarrow{\text{TS9}} \mathrm{ClC_3H}^+ + \mathrm{H_2} \qquad (d.2)$$

$$\mathbf{5} \xrightarrow{\text{TS5}} \mathbf{6} \xrightarrow{\text{TS6}} \mathbf{7} \xrightarrow{\text{TS15}} \mathbf{3} \qquad (d.3)$$

Direct hydrogen elimination, path (*d.1*), may take place through transition state TS7, leading again to the open-chain $ClCCCH_2^+$ isomer. The MP2 and B3LYP potential surfaces are topologically consistent, but at the G2(P) level, TS7 is found to lie below the products. Therefore, it seems that at higher levels of theory path (*d.1*) could be a barrier-free process. Elimination of molecular hydrogen from isomer **7** implies transition state TS9, which is associated with the molecular elimination and simultaneous cyclization. As can be see in Figure 4, TS9 is found to lie above the reactants at all levels of theory, suggesting that production of cyclic ClC_3H^+ from path (*d.2*) should be precluded in the interstellar medium. Another possibility once structure **7** is reached, is that it might suffer cyclization, through transition state TS15 (path (*d.3*)), leading to the cyclic intermediate **3**. The cyclic structure **3** may undergo the same process previously considered (path (*c*)), leading finally to $ClC_3H_2^+ + H$ (through TS8) or to $ClC_3H^+ + H_2$ (through TS11).

Alternatively, migration of a hydrogen atom in structure **7** leads to the isomer **12** with three hydrogen atoms bonded to the same carbon atom. This species may undergo hydrogen atom elimination or hydrogen molecule abstraction leading, respectively, to $ClCCCH_2^+ + H$ or to $ClCCCH^+ + H_2$:

$$\mathbf{7} \xrightarrow{\text{TS25}} \mathbf{12} \xrightarrow{\text{TS26}} \mathrm{ClCCCH_2}^+ + \mathrm{H} \qquad (e.1)$$

$$\mathbf{7} \xrightarrow{\text{TS25}} \mathbf{12} \xrightarrow{\text{TS27}} \mathrm{ClCCCH}^+ + \mathrm{H_2} \qquad (e.2)$$

Both processes are exothermic, and the associated transition states lie well below the reactants. At the G2(P) level, hydrogen atom elimination from isomer **12** could be a barrier-free process; this fact is in agreement with the C−H bond distance at the B3LYP level, which is very long (5.846 Å). Therefore, path (*e*) could play a role in interstellar chemistry. Chlorine atom elimination from isomer **12** has not been included because it is an endothermic process (about 49 kcal/mol, at the G2(P) level).

Finally, there is another path starting from **5**, which includes isomerization into **11** through migration of a hydrogen atom to the central carbon. Then cyclization may occur, leading to **2**. The cyclic intermediate, **2**, may suffer either elimination of a chlorine atom or elimination of a hydrogen atom:

$$\mathbf{5} \xrightarrow{\text{TS17}} \mathbf{11} \xrightarrow{\text{TS18}} \mathbf{2} \xrightarrow{\text{TS19}} c\text{-}\mathrm{C_3H_3}^+ + \mathrm{Cl} \qquad (f.1)$$

$$\mathbf{5} \xrightarrow{\text{TS17}} \mathbf{11} \xrightarrow{\text{TS18}} \mathbf{2} \xrightarrow{\text{TS22}} \mathrm{ClC_3H_2}^+ + \mathrm{H} \qquad (f.2)$$

As can be seen in Figure 4, all transition states involved in path (*f*) lie below the reactants, and therefore, formation of either c-$C_3H_3^+$ or $ClC_3H_2^+$ is feasible. In addition, it can be concluded from our results that path (*f.1*) should be favored over path (*f.2*), not only thermodynamically but also from the kinetic point of view, because TS19 is placed below TS22 and also below $ClC_3H_2^+ + H$. There is another possibility for isomerization of isomer **5** into **2** through intermediate **10**:

$$\mathbf{5} \xrightarrow{\text{TS20}} \mathbf{10} \xrightarrow{\text{TS18}} \mathbf{2}$$

This path is not shown in Figure 4, but its energies relative to $HCl + CCCH_2^+$ can be summarized as follows (G2(P) values and QCISD(T) values in parentheses):

$$\mathbf{10}\text{: } -72.2\ (-68.2)\ \text{kcal/mol}$$

$$\text{TS20: } -58.3\ (-51.2)\ \text{kcal/mol}$$

Therefore, the process of isomerization from **5** to **2** can take place with similar ease through isomer **10** or **11**.

We may conclude that for the reaction of HCl with linear $CCCH_2^+$ there are several mechanisms which lead to different cyclic and linear chlorine−carbon compounds ($(ClC_3H_2)^+$ and $ClC_3H)^+$), which are exothermic and barrier-free. However, formation of cyclopropenyl, c-$C_3H_3^+$, and propargyl, l-$C_3H_3^+$ cations, are also favorable, and therefore production of these carbocations could be competitive processes with formation of chlorine−carbon compounds.

(b) HCl + HCCCH⁺. The energy profile for the reaction with the linear isomer, $HCCCH^+$, at the G2(P) and QCISD(T) levels, is shown in Figure 5. For this reaction only the formation of the cyclic isomer $ClC_3H_2^+$ and the carbocations (l-$C_3H_3^+$ and c-$C_3H_2^+$) are exothermic processes. When a HCl molecule approaches $HCCCH^+$, structure **8** is initially formed. Then the cyclization with simultaneous hydrogen migration may occur, leading to cyclic isomer **1**. Once cyclic structure **1** is reached, $ClC_3H_2^+ + H$ or c-$C_3H_3^+ + Cl$ are obtained through transition states TS14 and TS23, respectively:

$$\mathrm{HCl} + \mathrm{HCCCH}^+ \rightarrow \mathbf{8} \xrightarrow{\text{TS13}} \mathbf{1} \xrightarrow{\text{TS14}} \mathrm{ClC_3H_2}^+ + \mathrm{H} \qquad (g.1)$$

$$\mathrm{HCl} + \mathrm{HCCCH}^+ \rightarrow \mathbf{8} \xrightarrow{\text{TS13}} \mathbf{1} \xrightarrow{\text{TS23}} c\text{-}\mathrm{C_3H_3}^+ + \mathrm{Cl} \qquad (g.2)$$

As can be seen in Figure 5, TS13 is found to lie more than 47 kcal/mol higher in energy than the reactants, suggesting that

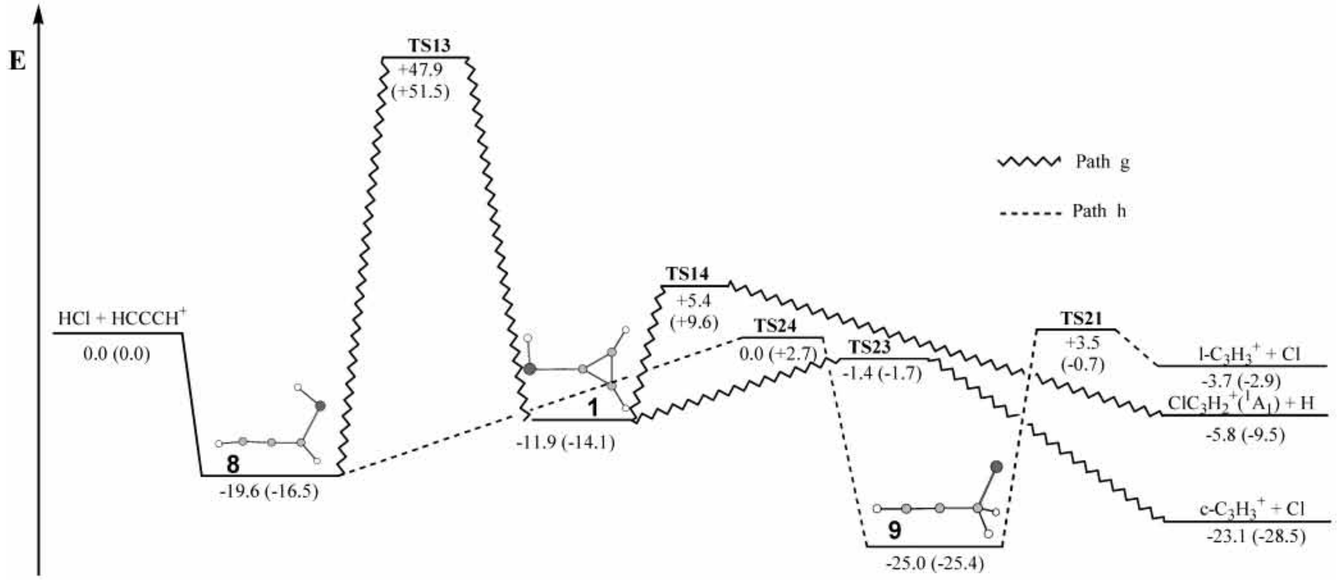


Figure 5. Energy profile, in kcal/mol, for the reaction of HCl with $HCCCH^+$ at the G2 and QCISD(T)/6-311G(d,p) (in parentheses) levels.

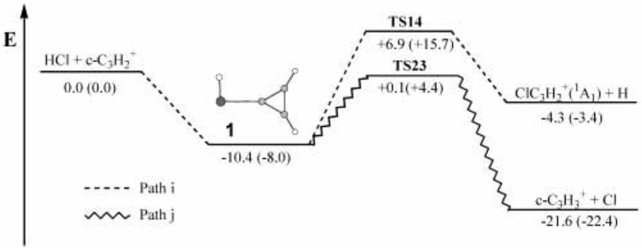


Figure 6. Energy profile, in kcal/mol, for the reaction of HCl with c-$C_3H_2^+$ at the G2 and QCISD(T)/6-311G(d,p) (in parentheses) levels.

production of both, $ClC_3H_2^+ + H$ and c-$C_3H_3^+ + Cl$, from the reaction of $HCl + HCCCH^+$ should be precluded in the interstellar conditions.

The other path, once structure **8** is reached, corresponds to isomerization into structure **9** through hydrogen migration from the chlorine atom to the near carbon atom. The final step of path (*h*) involves transition state TS21 and leads to l-$C_3H_3^+$ + Cl:

$$HCl + HCCCH^+ \rightarrow \mathbf{8} \xrightarrow{TS24} \mathbf{9} \xrightarrow{TS21} l\text{-}C_3H_3^+ + Cl \qquad (h)$$

The transition state for chlorine atom elimination, TS21, was only obtained at the B3LYP level, and the G2(P) energy was computed at the B3LYP geometry. Both transition states, TS21 and TS24, are predicted to lie very close in energy to the reactants. At the G2(P) level, TS24 has the same energy as the reactants and TS21 lies above the reactants only by 3.5 kcal/mol. Then it is quite likely that path (*h*) could be affected by a negligible barrier. As can be seen in Figure 5, in the reaction of HCl with linear $HCCCH^+$, production of $ClC_3H_2^+ + H$ is severely hindered; therefore, it seems that formation of l-$C_3H_3^+$ + Cl should be the dominant process.

(c) HCl + c-$C_3H_2^+$. The energy profile for the reaction with the cyclic isomer, c-$C_3H_2^+$, is shown in Figure 6. When the reactant is the cation cyclopropenylidene, only production of cyclic $ClC_3H_2^+ + H$ and c-$C_3H_3^+ + Cl$ are exothermic processes. The reaction of HCl with c-$C_3H_2^+$ should be initialized with the formation of the long-distance complex **1**. Once this structure is obtained, two processes may take place. Direct hydrogen atom elimination leads to the cyclic $ClC_3H_2^+$ and involves transition state TS14

$$HCl + c\text{-}C_3H_2^+ \rightarrow \mathbf{1} \xrightarrow{TS14} ClC_3H_2^+ + H \qquad (i)$$

As can be seen in Figure 6, production of $ClC_3H_2^+$ involves a significant energy barrier, because TS14 lies about 6.9 kcal/mol above the reactant. Therefore it seems that the production of $ClC_3H_2^+$ from this reaction is severely hindered.

Another possibility for the evolution of the cyclic intermediate **1**involves hydrogen atom migration and simultaneous chlorine atom elimination leading to c-$C_3H_3^+$, through transition state TS23, which are predicted to be very close in energy to the reactants (at the G2(P) level, TS23 lies above the reactants only by 0.1 kcal/mol). Therefore, path (*j*), which can be schematically represented as follows:

$$HCl + c\text{-}C_3H_2^+ \rightarrow \mathbf{1} \xrightarrow{TS23} c\text{-}C_3H_3^+ + Cl \qquad (j)$$

should be the most favorable one for this reaction. It seems that chlorine−carbon compounds cannot be formed in the reaction of HCl with c-$C_3H_2^+$, and therefore, formation of c-$C_3H_2^+ + Cl$, affected by a negligible barrier, should be the dominant process.

Conclusions

A theoretical study of the $(ClC_3H_3)^+$ species on the doublet potential surface has been carried out. Predictions for their geometries and vibrational frequencies have been made at both MP2 and B3LYP levels. All levels of theory employed predict that the lowest-lying species is a linear isomer $ClHCCCH_2^+$ (**5**), whereas five different open-chain structures, **7**, **6**, **10**, **11**, and **12**, lie quite close in energy (ranging from 5.9 to 13.1 kcal/mol, depending on the isomer considered). The lowest-lying cyclic structure is **3**, which lies about 18.3 kcal/mol above the global minimum. These species can be formally derived from the carbocation $(C_3H_4)^+$ upon chlorine substitution. Substitution of a hydrogen atom by chlorine retains the global minimum and reduces the energy differences between isomers, except in the case of isomer **9**. It also seems that isomers where chlorine substitution takes place at the carbon bonded to just a hydrogen atom appear to be slightly favored over substitution at the carbon atom bonded to two hydrogen atoms.

In addition, a theoretical study of the reaction of HCl with the different isomers of $(C_3H_2)^+$ has been carried out. These theoretical results allow the development of thermodynamic arguments about the reaction pathway of the process HCl + $(C_3H_2)^+$.

The reaction of HCl with the linear isomer $CCCH_2^+$ is exothermic for the production of different chlorine−carbon compounds ($ClCCCH_2^+$, $ClHCCCH^+$, $ClC_3H_2^+$, ClC_3H^+, and $ClCCCH^+$). In addition, there are several channels for their formation, which imply transition states that lie below the reactants, and therefore there are barrier-free processes. On the other hand, formation of cyclopropenyl and propargyl cations are also exothermic and barrier-free paths. Therefore, in this case production of chlorine−carbon compounds could be competitive with the formation of carbocations.

Our predictions show that in the reaction of HCl with both $HCCCH^+$ and c-$C_3H_2^+$ isomers, production of chlorine−carbon compounds seems to be severely hindered. For these reactions, formation of cyclopropenyl and propargyl cations, respectively, should be the dominant channels.

The main conclusion from this work is that only the reaction of HCl with the linear $CCCH_2^+$ isomer seems to be a possible source of chlorine−carbon compounds in space. In our previous studies on possible sources of carbon−chlorine compounds in space,[5,6] we have found that for the reaction of Cl^+ with C_3H_2, only the reaction with the linear isomer, $CCCH_2$, seems to be a possible source of chlorine compounds in space.[5] On the other hand, the results of the reaction of Cl with $C_3H_2^+$ show that carbon−chlorine compounds can only be formed in the reaction of Cl with the linear isomer, $CCCH_2^+$. In this case, our calculations predict that production of $CCCCl^+ + H_2$ could be competitive with the $CCCH^+$ + HCl channel.[6] Therefore, we could conclude that, for the three reactions considered in our studies, only those processes starting from the linear isomer $CCCH_2$ (neutral or cationic) of the C_3H_2 hydrocarbon are possible sources of carbon−chlorine compounds in the interstellar medium.

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