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Theoretical Study of the Reaction of Cl^+ with C_3H_2

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A theoretical study of the $(ClC_3H_2)^+$ species has been carried out. Two different models, the complete MP4 at MP2 geometries and the QCISD(T) at B3LYP geometries, have been employed. Our calculations predict that the global minimum is a cyclic isomer with a three-membered carbon ring, $ClC_3H_2^+(^1A_1)$, whereas two different open-chain structures, $ClCCCH_2^+(^1A_1)$ and $ClHCCCH^+(^1A')$, lie ∼19 and 15 kcal/mol, respectively, higher in energy. The lowest-lying triplet state is an open-chain structure, $ClCCCH_2^+(^3A'')$, which lies >57 kcal/mol above the global minimum. These theoretical results allow the development of thermodynamic arguments about the reaction pathways of the process $Cl^+ + C_3H_2$. For the reaction of Cl^+ with vinylidenecarbene (l-C_3H_2), the production of $ClCCCH^+$ is both thermodynamically and kinetically favored, and even the formation of ClC_3H^+ is also more exothermic than the charge transfer. In the reaction of Cl^+ with cyclopropenylidene (c-C_3H_2), the production of both cyclic and open-chain chlorine−carbon compounds seems to be severely hindered; hence, charge transfer should be the dominant process. Consequently, only the reaction of Cl^+ with l-C_3H_2 seems to be a possible source of chlorine−carbon compounds in space, and the preferred product should be linear $ClCCCH^+$, which could be a precursor to ClCCC.

Introduction

Gas-phase chlorine chemistry is very interesting mainly because of its relevance to atmospheric studies. In addition, it is also relevant to interstellar chemistry. In the case of chlorine, only HCl has been conclusively 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 may be found in space. Several binary carbides containing other second-row elements, such as sulfur, silicon, or phosphorus, have been observed in space.[3] These compounds can be formulated as C_nX, with X being a second-row element and n varying from 1 to 4.

Previous studies predict that carbon−chlorine compounds could also be found in the interstellar medium. Both experimental[4−7] and theoretical studies[8,9] on the reaction of C^+ ions with HCl showed that CCl^+ could be synthesized in space. Furthermore, a theoretical study[10] has shown that $HCCl^+$, a precursor to neutral CCl, may be formed in the reaction of carbon atoms with H_2Cl^+ (protonated HCl). Another ab initio study of the reaction of C_2H^+ with HCl[11] concluded that $HCCCl^+$, a precursor to C_2Cl, may also be synthesized under interstellar conditions. C_2Cl, a possible interstellar candidate, is predicted[12,13] to be linear with a $^2\Pi$ ground state. On the other hand, a recent theoretical study[14] predicts that the global minimum for C_3Cl to be a cyclic C_{2v} species, although a quasilinear CCCCl structure lies quite close in energy (∼3−5 kcal/mol above the ground state).

In the present paper, we consider a possible process for the synthesis of precursors to C_3Cl, namely, the reaction of Cl^+ with C_3H_2. It is worth noting that two different C_3H_2 isomers have been detected in the interstellar medium. Cyclopropenylidene, c-C_3H_2, is one of the most abundant interstellar hydrocarbons and was observed for the first time in space several years ago.[22] On the other hand propadienylidene (singlet vinylidenecarbene), l-C_3H_2, with a linear carbon backbone and two hydrogens bonded to a terminal carbon atom, has been observed more recently in space.[16]

Theoretical studies of this type of reaction are particularly valuable, since experimental studies are difficult to carry out due to the difficulty of preparing C_3H_2 species. So far, we have carried out similar studies for the reactions of P^+, Si^+, and S^+ with C_3H_2 species.[17−19] Therefore, the present work allows a comparison of the reactivity features of chlorine with those of other second-row elements. Although the reaction of Cl^+ with C_3H_2 should proceed in principle along the triplet surface, both singlet and triplet $(ClC_3H_2)^+$ species will be considered, since we are not aware of any complete study of these species.

Computational Methods

The present work employs the same methods used in our previous studies on the reactions of P^+, Si^+, and S^+ with C_3H_2.[17−19] The geometries of the different species in this work were obtained at the second-order Møller−Plesset (MP2) level with the split-valence plus polarization 6-31G* basis set.[20] In addition, for comparative purposes, the density functional theory (DFT) was also employed for obtaining optimized geometries. For the DFT calculations, we selected the B3LYP exchange−correlation functional[21] and the 6-311G** basis set[22] for carbon and hydrogen atoms, whereas the McLean and Chandler basis set[23] (supplemented with a set of d functions) was employed for chlorine. We must emphasize that our previous calculations on C_3Cl and C_3Cl^+[14] 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 level with the 6-311G** basis set, as well as B3LYP calculations with the cc-pVTZ basis set).

Harmonic vibrational frequencies have been computed on each optimized geometry at its corresponding level of theory.

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To estimate the zero-point vibrational energy (ZPVE) at the MP2 level, we scaled the vibrational frequencies by a factor of 0.94.

On the MP2 geometries, single-point calculations at the fourth-order Møller−Plesset (MP4) level[24,25] were carried out to compute electronic energies. For the B3LYP geometries, we performed subsequent single-point calculations at the QCISD(T) level,[26] which stands for a quadratic CI calculation with single and double substitutions followed by a perturbative treatment of triple substitutions. In both cases, MP4 and QCISD(T), we employed the 6-311G** basis set and the frozen-core approximation. It is worth noting that in our previous calculations on related systems,[14,27] the QCISD(T)/6-311G** level seemed to be a reasonable compromise between cost and quality of the results, since it provides relative energies very similar to the more expensive CCSD(T)/cc-pVTZ method.

All calculations were carried out with the Gaussian 94 program package.[28]

Results and Discussion

$(ClC_3H_2)^+$ Isomers. Only the more relevant $(ClC_3H_2)^+$ species will be briefly discussed. The optimized geometries for the different $(ClC_3H_2)^+$ structures are shown in Figure 1 (the corresponding harmonic vibrational frequencies and IR intensities are available upon request). The relative energies at different levels of theory are given in Table 1. All reported structures are true minima on the $(ClC_3H_2)^+$ singlet and triplet surfaces.

The $(ClC_3H_2)^+$ system can be viewed as the result of chlorine substitution on the $C_3H_3^+$ cation. The $C_3H_3^+$ ion is believed to play a key role in several combustion processes, such as in soot formation in fuel-rich flames. In $C_3H_3^+$, the most stable isomer is the cyclopropenyl cation,[30,31] c-$C_3H_3^+$, which is also the smallest aromatic molecule. c-$C_3H_3^+$ is stable both in the form of salts and in polar solvents. The propargyl cation, l-$C_3H_3^+$, has a linear carbon backbone with two hydrogens bonded to an end carbon and the third hydrogen atom bonded to the other terminal carbon. l-$C_3H_3^+$ is experimentally estimated to lie ~25 kcal/mol higher in energy than the cyclic isomer.[32] The structures of substituted cyclopropenyl and propargyl cations have also been discussed. Of particular relevance to the present study is the theoretical study[33] of the fluorine derivatives $(FC_3H_2)^+$.

Isomer **1**($^1A_1$) is the chlorine-substituted cyclopropenyl cation. Although the electronegativity of chlorine is higher than that of carbon and although chlorine is therefore expected to withdraw electronic charge from carbon, the fact that the vicinal C−C bonds are somewhat longer than the distal bond is an indication that there is a certain degree of π donation from chlorine. This is confirmed by the π populations obtained for this structure. However this delocalization has only a minor effect, since it is hindered by the participation of carbon in the b_1 orbital of the C_3 ring. In the case of the triplet isomer, two different structures corresponding to the same electronic state, $^3A''$, can be obtained. The first structure, **1a**($^3A''$), has a very long C−Cl distance, suggesting that this species can be viewed as an ion−molecule complex. The second structure, **1b**($^3A''$), corresponds to a much shorter C−Cl distance, suggesting a covalent interaction. At the MP2 level, **1b**($^3A''$) is a true minimum (all its vibrational frequencies are real), but at the B3LYP level, an imaginary frequency is obtained. Following the corresponding mode, an open-chain structure, **4**($^3A'$), is finally reached. It is interesting that both structures correlate in C_s symmetry with ground-state Cl^+ + c-C_3H_2.

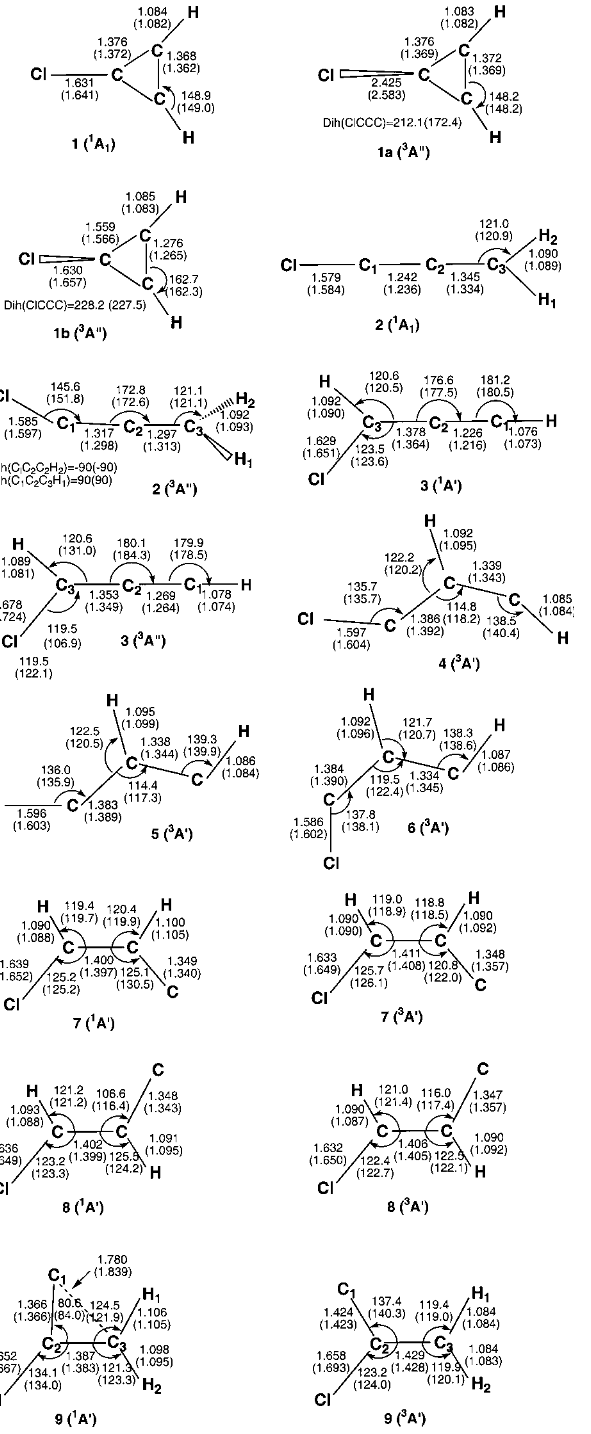
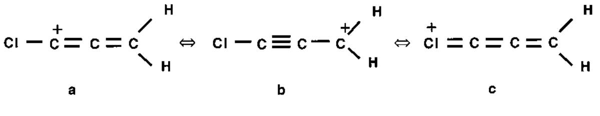


Figure 1. MP2/6-31G* and B3LYP/6-311G** (in parentheses) optimized geometries for the different $ClC_3H_2^+$ structures. Distances are given in Å and angles in deg.

Isomer **2** is derived from the propargyl cation with chlorine substitution at C_1. Basically three different valence-bond structures may be proposed for this isomer.



The C−Cl bond distance is relatively short, indicating a strong C−Cl bonding. This is partly due to the delocalization of the b_1 electron pair of chlorine into the b_1 orbital of carbon, as suggested by structure c. The lowest-lying triplet state is a

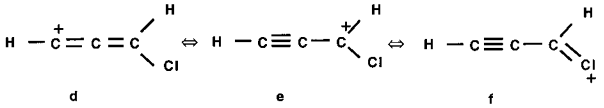
TABLE 1: Relative Energies (kcal/mol) for the $(ClC_3H_2)^+$ Species at Different Levels of Theory with the 6-311G Basis Set**[a]

	MP4	PMP4	B3LYP	QCISD(T)
1($^1A'$)	0.0	0.0	0.0	0.0
1a($^3A''$)	93.6	92.4	88.3	91.5
1b($^3A''$)	86.3	85.7	80.3	81.0
2($^1A'$)	19.3	19.3	16.5	19.5
2($^3A''$)	65.1	61.2	50.2	57.2
3($^1A'$)	15.1	15.1	14.8	15.5
3($^3A''$)	81.3	77.3	65.5	73.2
4($^3A'$)	82.1	79.6	75.0	77.2
5($^3A'$)	81.6	79.0	74.5	76.6
6($^3A'$)	84.4	81.7	76.7	78.8
7($^1A'$)	66.3	66.3	65.5	63.8
7($^3A'$)	106.9	102.1	101.9	98.6
8($^1A'$)	63.1	63.1	62.8	60.7
8($^3A'$)	103.9	99.3	99.5	96.0
9($^1A'$)	74.8	74.8	76.9	73.1
9($^3A'$)	120.4	119.2	115.4	115.4

[a] Zero-point vibrational energy differences have been included.

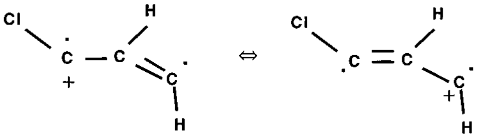
nonplanar structure with C_s symmetry. The CCCCl unit is slightly bent, with the hydrogen atoms on a plane perpendicular to this unit. The unpaired electrons are mainly located at carbons C_1 and C_3, and the main difference with the singlet state is the lengthening of the $C_1{-}C_2$ bond distance. This state also correlates with ground-state $Cl^+ + l\text{-}C_3H_2$.

Isomer **3** is the chlorine-substituted propargyl cation at C_3. This isomer can be also described by two valence-bond structures,

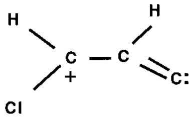


In this case, the shortening of $C_1{-}C_2$ and the lengthening of $C_2{-}C_3$, relative to those bonds in **2**($^1A_1$), suggest that structure d prevails over e. The longer C−Cl bond in this case, compared with isomer **2**, is an indication that delocalization of the electron pair of chlorine takes place to a lesser extent, and therefore, the contribution of structure f is somewhat smaller. For the corresponding triplet state, **3**($^3A''$), the C−Cl bond is considerably lengthened. Nevertheless the most important feature of this structure is that it is planar, with a C−C−C backbone quite close to linearity.

Structures **4**, **5**, and **6** are different isomers in which each carbon atom is bonded to either a hydrogen or a chlorine atom and can be considered as the result of the migration of a hydrogen atom from either structure **2** or **3**. All of them are planar triplet states of $^3A'$ symmetry. We also searched for the corresponding singlet states, but all our attempts collapsed into the cyclic **1**($^1A_1$) structure. The three isomers have very similar bond distances and bond angles, differing only in the relative positions of the hydrogen and chlorine atoms. There are several valence-bond structures contributing in this case, but the more important are the structures compatible with the population analysis.



Isomer **7**($^1A'$) was reached in an attempt to obtain structures with a four-membered ring similar to those obtained in $PC_3H_2^+$, $SiC_3H_2^+$, and $SC_3H_2^+$ [17−19]. This isomer can be mainly illustrated as



whereas the triplet state is very similar and results from the unpairing of the carbon lone pair. Therefore, the geometrical parameters for the singlet and triplet states are quite close.

Isomer **8** is the trans isomer of structure **7**, and consequently, the bond distances and bond angles are very similar to those found for the singlet and triplet states of **7**. The main difference between isomers **7** and **8** is that the C−C−C angle is greater for **7** whereas the C−C−H angle is greater for **8**, but this is only the consequence of the cis and trans arrangement relative to the chlorine atom. The valence-bond description of both structures is quite the same.

Finally, the last isomer that will be discussed is **9**, with two hydrogens bonded to the same carbon atom and a chlorine bonded to the central carbon. The most important difference between the singlet and triplet states is that the singlet appears to be a cyclic structure with a three-membered carbon ring. One of the C−C distances is large (~1.8 Å) enough to be considered a normal C−C bond, but the $C_1{-}C_2{-}C_3$ angle is $<90°$, supporting the cyclic nature of this structure. The $C_1{-}C_3$ bonding is mainly due to the delocalization of a C_1 lone pair into the vacant C_3 orbital. This interaction is hindered in the case of the triplet state, resulting in an open-chain arrangement.

The relative energies at different levels of theory of the $(ClC_3H_2)^+$ species are given in Table 1. It is readily seen that, as in the case of the $C_3H_3^+$ cation, all levels of theory predict that the global minimum is the cyclic species **1**($^1A_1$). Nevertheless, the energy difference with the open-chain structures is reduced compared with the structures of $C_3H_3^+$. The propargyl cation is experimentally estimated to lie ~25 kcal/mol higher in energy than the cyclopropenyl cation[32] (at the MP4 level, the energy difference is calculated to be ~29 kcal/mol[31]). In $(ClC_3H_2)^+$, the open-chain structures **2**($^1A_1$) and **3**($^1A'$) are respectively found to lie ~19 and 15 kcal/mol higher in energy at both MP4 and QCISD(T) levels. It is also interesting that, since **3**($^1A'$) is lower in energy than **2**($^1A_1$), chlorine substitution at the carbon atom bonded to two hydrogen atoms appears to be slightly favored over substitution at the terminal carbon bonded to just one hydrogen atom.

It seems that substitution by a more electronegative atom (Cl) favors an arrangement where the carbon atom may "extract" electronic density from another atom (H). The same trend is observed in the substitution by a fluorine atom.[33] In $(FC_3H_2)^+$, the cyclic isomer was also found to be the global minimum, whereas **3** was also preferred over **2**. Furthermore, in that case, a destabilization compared to $C_3H_3^+$ was observed for fluorine substitution, leading to H_2CCCF (isomer 2). The rest of structures lie all much higher in energy. Among the singlet states, the next lower-lying structure is **8**($^1A'$), ~61 kcal/mol at the QCISD(T) level, which is slightly favored over its cis isomer, **7**($^1A'$) (64 kcal/mol above the global minimum at the same level of theory). The cyclic isomer **9**($^1A'$) is the less stable singlet state lying ~73 kcal/mol above **1**($^1A_1$).

The lowest-lying triplet state is **2**($^3A''$), which lies ~57 kcal/mol higher than the global minimum at the QCISD(T) level of theory. The relative stability of structures **2** and **3** on the singlet surface is reversed for the triplets, since now **3**($^3A''$) lies ~16 kcal/mol higher than **2**($^3A''$). Perhaps the most important reason for this reversed stability order is the more difficult π donation from chlorine in **3**(^{3}A″), which results in a rather large C−Cl bond distance. Nevertheless, the most relevant feature is the relative instability of the triplet cyclic structures **1a**(^{3}A″) and **1b**(^{3}A″), which lie very high in energy, ~91.5 and 81 kcal/mol, respectively, above the global minimum. This is not surprising for **1a**(^{3}A″), being a long-distance complex, but it is more surprising for **1b**(^{3}A″), which is >20 kcal/mol less stable than **2**(^{3}A″). Even more stable than **1b**(^{3}A″) are the three related isomers **4**(^{3}A′), **5**(^{3}A′), and **6**(^{3}A′). All of them are quite close in energy and ~20 kcal/mol higher in energy than the lowest-lying triplet state. The rest of the triplet states, **7**(^{3}A′), **8**(^{3}A′), and **9**(^{3}A′), lie much higher in energy.

Compared with other similar species containing second-row elements, $(ClC_3H_2)^+$ is similar to triplet $(PC_3H_2)^+$,[17] where a cyclic structure was also found to lie below open-chain isomers. On the other hand, open-chain ground states were found for both silicon and sulfur analogues.[18,19] In that sense, chlorine seems to exhibit a behavior more related to fluorine or hydrogen (where cyclic ground states are found) than to other second-row elements.

Concerning the performance of the different levels of theory, it is worth noting that all levels of theory predict the same stability order. Furthermore, as a general trend, MP4 and QCISD(T) results are very close for singlet states, the largest discrepancy being observed for **7**(^{1}A′), namely, 2.6 kcal/mol. In the case of triplet states, where the convergency of the MP series may be affected by spin contamination, differences of up to 8 kcal/mol in the relative energies between MP4 and QCISD(T) are observed. Nevertheless, this is in part alleviated by employing approximate spin-projected MP4 values.[34,35] In all cases, the PMP4 values are closer to the QCISD(T) results than are the unprojected ones. The largest discrepancy between the PMP4 and QCISD(T) relative energies is found for **3**(^{3}A″), namely, 4 kcal/mol. Taking the QCISD(T) results as the most reliable ones, we calculate the mean absolute error of the PMP4 values to be just 2.5 kcal/mol. Even more interesting are the relatively good results obtained with the B3LYP method. In most cases, the B3LYP values are within 3 kcal/mol of the QCISD(T) values, the worst case being **3**(^{3}A″) with a discrepancy of 7.7 kcal/mol. The absolute mean error for B3LYP relative energies (taking QCISD(T) values as references) is 3.0 kcal/mol. The overall agreement between the relative energies at different levels gives further support to our conclusions.

Reaction of Cl^+ with C_3H_2. We will consider the reaction of chlorine cations with either cyclopropenylidene or propadienylidene. In principle, there are three different channels for this reaction: production of $(HC_3Cl)^+$, production of $(C_3Cl)^+$, and charge transfer

$$\begin{aligned} & \rightarrow (HC_3Cl)^+ + H(^2S) \\ Cl^+(^3P) + C_3H_2(^1A_1) & \rightarrow (C_3Cl)^+ + H_2(^1\Sigma_g^{\ +}) \\ & \rightarrow Cl(^2P) + C_3H_2^{\ +}(^2A_1) \end{aligned}$$

The possible structures of $(C_3Cl)^+$ and $(HC_3Cl)^+$ have been reported in previous works.[14,29] We may briefly comment that the global minimum of $(C_3Cl)^+$ is predicted to be a linear singlet-state $ClCCC^+$.[4] However, the lowest-lying triplet state is cyclic, $ClC_3^+(^3B_2)$, with the triplet quasilinear state, $ClCCC^+$(^{3}A′), lying ~11 kcal/mol (QCISD(T) level) higher in energy than $ClC_3^+(^3B_2)$. In $(HC_3Cl)^+$, the global minimum is predicted[29] to be an open-chain structure $ClCCCH^+$(^{2}A′), but a cyclic ClC_3H^+(^{2}A′) structure is found to lie very close in energy (~1−2 kcal/mol at the G2 and CCSD(T) levels). Another open-chain structure, $ClHCCC^+$(^{2}A′), with both hydrogen and chlorine bonded to the same carbon atom, lies much higher in energy, ~37 kcal/mol above the ground state.

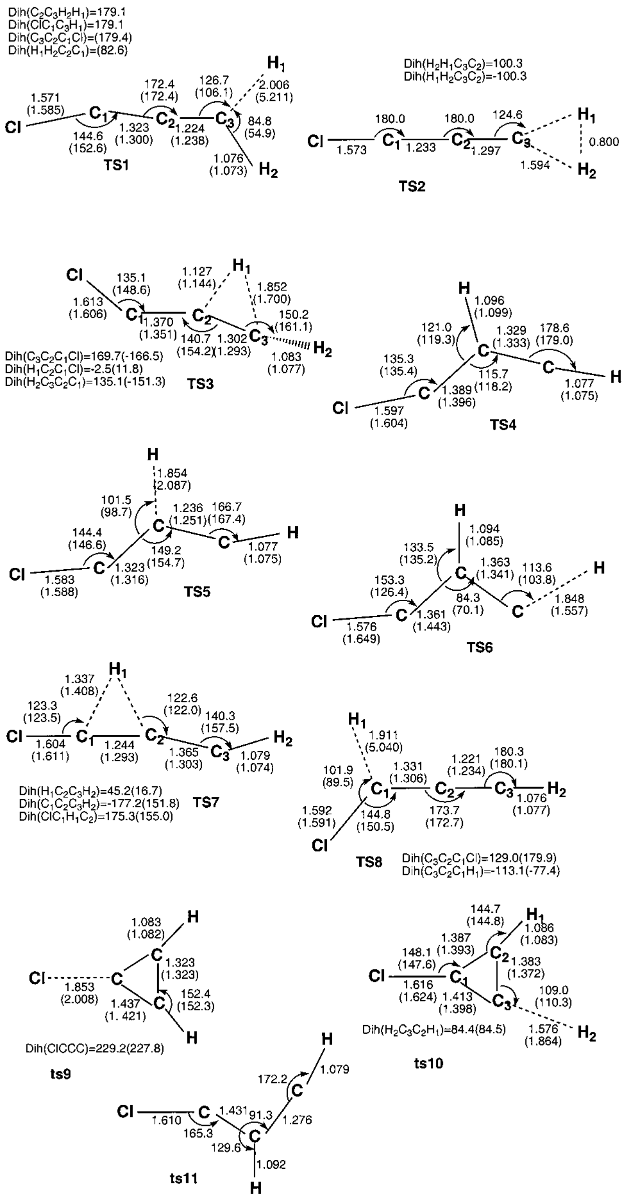


Figure 2. MP2/6-31G* and B3LYP/6-311G** (in parentheses) optimized geometries for the relevant transition states involved in the reaction of Cl^+ with C_3H_2. Distances are given in Å and angles in deg.

The relevant transition states on the triplet $(ClC_3H_2)^+$ surface are shown in Figure 2, whereas the energy profiles for the reactions of Cl^+ with l-C_3H_2 and c-C_3H_2 (taking Cl^+ + l-C_3H_2 as zero in energy) are given in Figures3 and 4, respectively, at the PMP4 and QCISD(T) levels. A reasonably good agreement between the PMP4 and QCISD(T) results is generally observed, giving further support to our conclusions. Intrinsic reaction coordinate calculations were used to establish that the different transition states connect the desired minima.

As can be seen in Figure 3, the production of both $ClCCCH^+$ and ClC_3H^+ from Cl^+ + l-C_3H_2 is clearly exothermic (~76 and 74 kcal/mol, respectively, at the QCISD(T) level). The production of $ClHCCC^+$ is also exothermic (~40 kcal/mol), but in this case, charge transfer may be competitive, since Cl + l-$C_3H_2^+$ is found at −51.4 kcal/mol (QCISD(T) level) below reactants. In the production of $ClCCC^+$ + H_2, the reaction

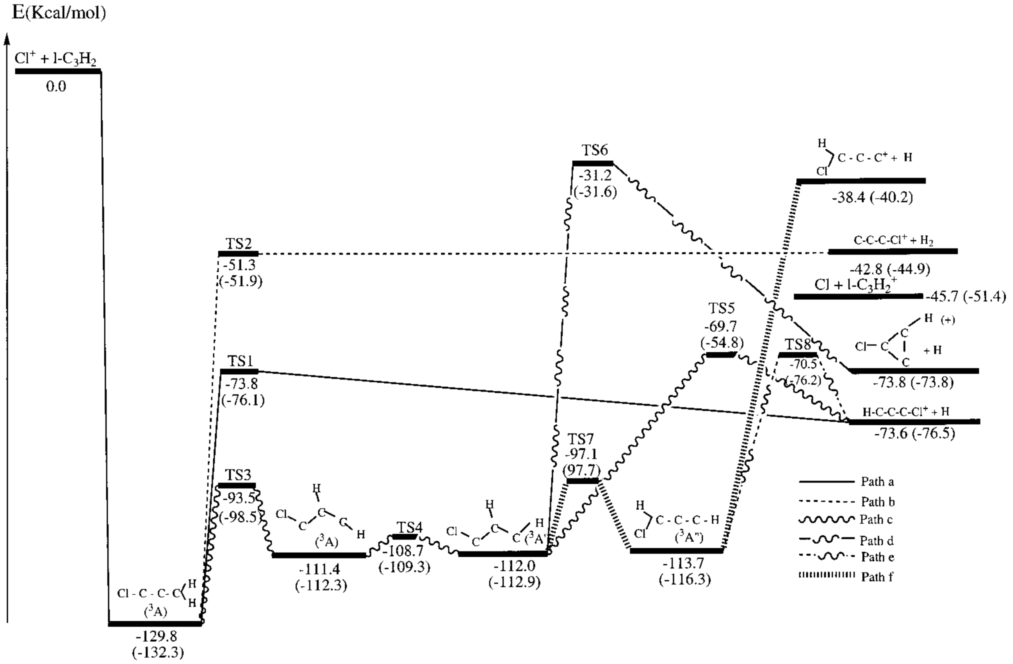


Figure 3. Energy profile, in kcal/mol, for the reaction of Cl^+ with l-C_3H_2 at the PMP4 and QCISD(T) (in parentheses) levels. ΔZPVE corrections have been included at the MP2/6-31G* and B3LYP/6-311G** levels.

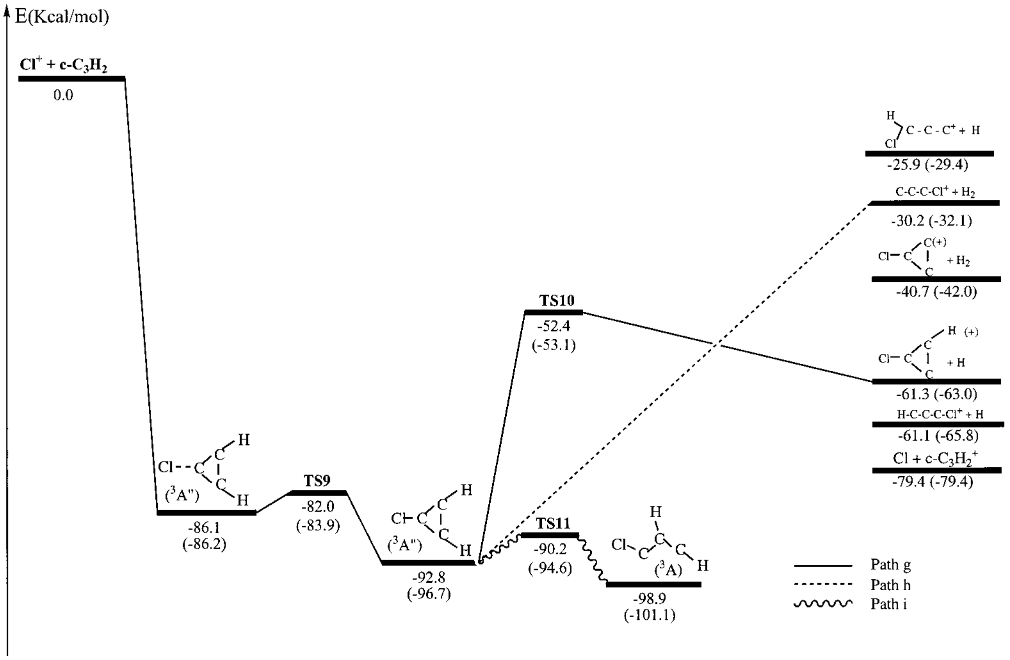


Figure 4. Energy profile, in kcal/mol, for the reaction of Cl^+ with c-C_3H_2 at the PMP4 and QCISD(T) (in parentheses) levels. ΔZPVE corrections have been included at the MP2/6-31G* and B3LYP/6-311G** levels.

enthalpy is near −45 kcal/mol, and therefore, charge transfer is also thermodynamically favored.

The first step in the reaction of Cl^+ with l-C_3H_2 should be formation of isomer **2**. Hydrogen elimination would lead to $ClCCCH^+$, whereas the elimination of a hydrogen molecule results in the production of $ClCCC^+$

$$Cl^+ + l\text{-}C_3H_2 \rightarrow ClCCCH_2^+(\mathbf{2}) \xrightarrow{TS1} ClCCCH^+(^2A') + H \quad (a)$$

$$Cl^+ + l\text{-}C_3H_2 \rightarrow ClCCCH_2^+(\mathbf{2}) \rightarrow ClCCC^+(^3A') + H_2 \quad (b)$$

In the case of path a we obtained a true transition state (TS1). Nevertheless, it must be noted that at the B3LYP level the C−H distance is very long (5.211 Å). This fact and the very small energy difference between TS1 and the products suggest that process a could quite likely be barrier-free at higher levels of theory. On the other hand, in process b, we were only able to obtain a second-order saddle point (with two imaginary frequencies, one of them corresponding to the desired mode—that is, the elimination of a H_2 unit—and the other one leading to the loss of C_{2v} symmetry) at the MP2 level. All our attempts to obtain a true transition state allowing for a relaxed geometry failed, since the optimization finally led to TS1. Therefore, we have carried out a scan (at both MP2 and B3LYP levels) in C_s

symmetry for different C−X distances (X being the middle point of the H_2 fragment), optimizing all other geometrical parameters. This scan shows no sign of a barrier for this process. Furthermore, the energetic results obtained from employing the geometry of the second-order saddle point obtained at the MP2 level support this conclusion, since it is placed ∼8.5 and 7.0 kcal/mol below the products at the PMP4 and QCISD(T) levels, respectively. In any case, it is clear that both processes involve transition states which either lie below the reactants and are quite close in energy to the products or are barrier-free. In principle, process a seems to be kinetically favored over b, since TS1 is placed well below $ClCCC^+(^3A') + H_2$, although to establish a definitive conclusion about possible branching ratios, a nuclear dynamic treatment should be carried out.

Another possibility is the isomerization of **2** into **4** through the migration of a hydrogen atom which involves transition state TS2. Structure **4** may further isomerize into **5** through transition state TS3. Once **5** is formed, several processes may occur. Direct hydrogen elimination may take place, leading again to $ClCCCH^+$

$$\mathrm{ClCCCH_2^+}\ (\mathbf{2}) \xrightarrow{\mathrm{TS2}} \mathrm{ClCCHCH^+}\ (\mathbf{4}) \xrightarrow{\mathrm{TS3}} \mathrm{ClCCHCH^+}\ (\mathbf{5}) \xrightarrow{\mathrm{TS4}} \mathrm{ClCCCH^+}(^2A') + \mathrm{H} \tag{c}$$

Alternatively, once structure **4** is reached, it might suffer cyclization through transition state TS5, leading to isomer **1b**. Finally, elimination of a hydrogen atom results in cyclic ClC_3H^+

$$\mathrm{ClCCCH_2^+}\ (\mathbf{2}) \xrightarrow{\mathrm{TS2}} \mathrm{ClCCHCH^+}\ (\mathbf{4}) \xrightarrow{\mathrm{TS5}} \mathrm{ClC_3H_2^+}\ (\mathbf{1b}) \xrightarrow{\mathrm{TS6}} \mathrm{ClC_3H^+}(^2A') + \mathrm{H} \tag{d}$$

Another possibility is further isomerization into structure **3** through the migration of the hydrogen atom. Then hydrogen elimination may lead to either $ClCCCH^+$ or $ClHCCC^+$. In the first case, transition state TS8 is involved, whereas production of $ClHCCC^+$ seems to proceed without an energy barrier. To confirm that this is a direct process, we made a scan for different fixed C−H distances, optimizing the rest of the geometrical parameters, but found no sign of transition state

$$\mathrm{ClCCHCH^+}\ (\mathbf{5}) \xrightarrow{\mathrm{TS7}} \mathrm{ClHCCCH^+}\ (\mathbf{3}) \xrightarrow{\mathrm{TS8}} \mathrm{ClCCCH^+}(^2A') + \mathrm{H} \tag{e}$$

$$\mathrm{ClCCHCH^+}\ (\mathbf{5}) \xrightarrow{\mathrm{TS7}} \mathrm{ClHCCCH^+}\ (\mathbf{3}) \rightarrow \mathrm{ClHCCC^+}(^2A') + \mathrm{H} \tag{f}$$

It is not surprising that no transition state is found for the hydrogen elimination from **3** leading to $ClHCCC^+$, since the fragments are radicals and the energy difference between **3** and the products is very high (the reaction enthalpy for production of $ClHCCC^+(^2A') + H$ is the lowest of all possible products). In TS8, the C_1-H_1 distance at the B3LYP level is again very large (5.04 Å), and its energy is very similar to that of the final products (it is therefore a very late transition state), suggesting that this transition state could quite likely disappear at higher levels of theory.

Finally, we have also computed the reaction enthalpy for the production of $CCCH^+ + HCl$. Given the multiplicity of the reactants, we considered the lowest-lying triplet state for linear C_3H^+. We obtained enthalpy values of −47.8 and −51.2 kcal/mol at the PMP4 and QCISD(T) levels (including ZPVE differences), respectively. As in the production of $CCCCl^+ + H_2$, the results of the scan (at the MP2 and B3LYP levels) showed no sign of a transition state. Therefore, although this process could be slightly favored over the production of $CCCCl^+ + H_2$, it is not likely to be competitive with the production of $ClCCCH^+$.

In summary, in the results for the reaction of Cl^+ with l-C_3H_2, only formation of the cyclic ClC_3H^+ species and the open chain $ClCCCH^+$ isomer are predominant over charge transfer. Three different channels (all of them barrier-free, since they involve transition states which lie clearly below reactants), a, c, and e, lead to $ClCCCH^+$, whereas path d results in the formation of ClC_3H^+. In principle, on the basis of the relative energies of the transition states involved in each pathway, the production of $ClCCCH^+$ should be favored. The formation of other species that also involve barrier-free mechanisms, such as $ClHCCC^+$, $CCCH^+$, and $ClCCC^+$, seems less favorable, since their exothermicity is lower and even charge transfer should be competitive.

The reaction of Cl^+ with c-C_3H_2 should be initialized with the formation of the long-distance complex **1a**$(^3A'')$, which may lead to **1b**$(^3A'')$ through the transition state TS9. Once this structure is obtained, several processes may take place. Direct hydrogen elimination leads to cyclic ClC_3H^+, involving transition state TS6, which clearly lies below the reactants

$$\mathrm{ClC_3H_2^+}\ (\mathbf{1b}) \xrightarrow{\mathrm{TS6}} \mathrm{ClC_3H^+} + \mathrm{H} \tag{g}$$

Another possibility is elimination of a hydrogen molecule leading to cyclic ClC_3^+

$$\mathrm{ClC_3H_2^+}\ (\mathbf{1b}) \xrightarrow{\mathrm{TS6}} \mathrm{ClC_3^+} + \mathrm{H_2} \tag{h}$$

We have not found a transition state for this process, but a scan for H_2 elimination suggests that this is a barrier-free process. A similar conclusion is reached for the $C_3H^+ + ClH$ channel. Considering the triplet cyclic isomer for C_3H^+, we obtained reaction enthalpies of −67.8 kcal/mol (PMP4) and −66.7 kcal/mol (QCISD(T)). No transition state was obtained for this process, the corresponding scans showing no sign of a barrier.

Finally, ring opening may take place, leading to structure **4**$(^3A')$

$$\mathrm{ClC_3H_2^+}\ (\mathbf{1b}) \xrightarrow{\mathrm{TS5}} \mathrm{ClCCHCH^+}\ (\mathbf{4}) \tag{i}$$

The corresponding transition state was only obtained at the MP2 level, and the QCISD(T) energy was computed at the MP2 geometry. Once structure **4** is formed, the system may evolve in the same way as previously discussed, that is, open-chain products such as $ClCCCH^+$, $ClCCC^+$, or $ClHCCC^+$ may be formed. However, as can be seen in Figure 4, all these processes and even the production of the cyclic species ClC_3H^+, C_3H^+, and ClC_3^+ are less exothermic than charge transfer. Therefore, it seems that in the case of the reaction of Cl^+ with c-C_3H_2, charge transfer should be the dominant process.

Conclusions

A theoretical study of the $(ClC_3H_2)^+$ species on the singlet and triplet surfaces has been carried out. Geometries and vibrational frequencies for the different isomers have been obtained at the MP2/6-31G* and B3LYP/6-311G** levels. Electronic energies have been computed at the MP4/6-311G**//MP2/6-31G* and QCISD(T)//B3LYP/6-311G** levels. The two most reliable levels of theory employed, PMP4 and QCISD(T), predict that the lowest-lying species is a cyclic isomer with a three-membered carbon ring, **1**$(^1A_1)$, whereas two different open-chain structures (formally derived from the propargyl cation upon chlorine substitution), **2**($^1A_1$) and **3**($^1A'$), lie ∼19 and 15 kcal/mol, respectively, higher in energy. On the other hand, the lowest-lying triplet state is an open-chain structure, **2**($^3A''$), which lies >57 kcal/mol above the global minimum.

The reaction of Cl^+ with l-C_3H_2 is exothermic for the production of $ClHCCC^+$, $CCCH^+$, and $ClCCC^+$, but charge transfer should prevail, given its higher exothermicity. On the other hand, productions of both $ClCCCH^+$ and ClC_3H^+ are clearly more exothermic than charge transfer, and in addition, these are barrier-free processes, since the channels for their production imply transition states that lie below the reactants. Our prediction is that production of $ClCCCH^+$ should be thermodynamically and kinetically favored. In the reaction of Cl^+ with c-C_3H_2, the production of both cyclic (ClC_3H^+ and $ClC_3{}^+$) and open-chain ($ClCCCH^+$, $ClCCC^+$, and $ClHCCC^+$) chlorine−carbon compounds seems to be severely hindered, since charge transfer should be the dominant process.

Therefore, the main conclusion of our work is that only the reaction of Cl^+ with l-C_3H_2 seems to be a possible source of chlorine−carbon compounds in space and that the preferred product should be linear $ClCCCH^+$, which, upon dissociative recombination, could eventually lead to ClCCC.

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