

Theoretical investigation of the transition states leading to HCl elimination in 2-chloropropene

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This paper describes *ab initio* electronic structure calculations on the planar transition states of 2-chloropropene leading to HCl elimination in the ground electronic state to form either propyne or allene as the cofragment. The calculations provide optimized geometries of the transition states for these two reaction channels, together with vibrational frequencies, barrier heights, and reaction endothermicities. The calculated barrier heights for the two distinct four-centre HCl elimination transition states, one leading to HCl and propyne and the other leading to HCl and allene, are 72.5 kcal mol⁻¹ (77.8 kcal mol⁻¹ without zero-point correction) and 73.2 kcal mol⁻¹ (78.7 kcal mol⁻¹) at the MP2/6-311G(d,p) level, 71.0 kcal mol⁻¹ (76.3 kcal mol⁻¹) and 70.5 kcal mol⁻¹ (76.0 kcal mol⁻¹) at the QCISD(T)/6-311+G(d,p)//MP2/6-311G(d,p) level, and 66.9 kcal mol⁻¹ (71.7 kcal mol⁻¹) and 67.3 kcal mol⁻¹ (72.1 kcal mol⁻¹) at the G3//B3LYP level of theory. Calculated harmonic vibrational frequencies at the B3LYP/6-31G(d) level along with transition state barrier heights from the G3//B3LYP level of theory are used to obtain RRKM reaction rate constants for each transition state, which determine the branching ratio between the two HCl elimination channels. Even at internal energies well above both HCl elimination barriers, the HCl elimination leading to propyne is strongly favoured. The smaller rate constant for the HCl elimination leading to allene can be attributed to the strong hindrance of the methyl rotor in the corresponding transition state.

1. Introduction

Numerous studies of the photodissociation of vinyl chloride near 200 nm have appeared in the literature [1–10]. Vinyl chloride, like ethene, has an excited state with $\pi\pi^*$ electronic character accessed near 200 nm [8]. Besides slightly decreasing the HOMO-LUMO gap, halide substitution opens new product channels (C–Cl fission and HCl elimination) that may proceed through an internal conversion mechanism or via an avoided crossing between diabatic excited states with $\pi\pi^*$ and $n\sigma^*$ electronic character.

After excitation near 200 nm, several product channels become energetically allowed in vinyl chloride. The primary dissociation reactions include CCl bond fission, CH bond fission, H₂ elimination, and HCl elimination. A comprehensive discussion of these and other channels appears in [1]. Here we briefly review the prior data and resulting interpretation of the mechanisms of HCl elimination of vinyl chloride, as the present work on 2-chloropropene sheds some light

on the prior work. Blank *et al.* studied the photofragment translation spectroscopy of vinyl chloride excited at 193.3 nm and considered HCl elimination through a four-centre mechanism and via two three-centre mechanisms (one leading to ¹A₁ vinylidene and one leading to ³B₂ vinylidene). One possible interpretation of the gas phase photofragmentation experiments is that after photoexcitation at 193.3 nm vinyl chloride internally converts to the ground electronic state and then undergoes three-centre HCl elimination producing singlet vinylidene, which isomerizes to acetylene. Since large translation energy release is observed in the HCl elimination products, it was proposed that HCl elimination proceeds via a three-centre mechanism to produce vinylidene with isomerization to acetylene synchronized with departure of the HCl product, giving additional recoil velocity to the HCl products beyond what one would expect from the exit barrier of this channel (5 kcal mol⁻¹) [1, 5]. Blank *et al.* observed a large red shift (~2.2 eV) in the photoionization onset of the HCl photoproduct, indicating internal excitation qualitatively consistent with the observation of vibrational excitation of the HCl photoproduct by others [1].

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Moss *et al.* [9], who studied the IR emission spectrum of the products from the dissociation of vinyl chloride at 193.3 nm, found a broad peak around 2900 cm^{-1} that extended to $\sim 2100\text{ cm}^{-1}$ and assigned it as rotationally excited HCl. Donaldson and Leone [7] studied the time resolved FT-IR spectrum of photoproducts of vinyl chloride dissociated at 193.3 nm. The HCl product exhibited a high degree of vibrational excitation with significant population in the $v = 4$ state (the highest state studied). Reilly *et al.* [6] investigated the state distribution of HCl from the photolysis of vinyl chloride using 2 + 1 REMPI with time-of-flight product detection. They found the HCl product to be vibrationally and rotationally excited: the ground vibrational state of HCl was described with populations having two distinct rotational temperatures, 340 K and 22 600 K, while HCl in the first and second excited vibrational states was described with temperatures of $2100 \pm 250\text{ K}$ ($v'' = 1$), and $1800 \pm 140\text{ K}$ ($v'' = 2$). Huang *et al.* [5] studied the HCl elimination channels of d_1 -vinyl chloride (H_2CCDCl) and determined a 3:1 branching ratio for three-centre versus four-centre elimination. The vibrational excitation of the HCl photoproduct following photolysis at 193 nm was studied using step-scan FTIR by Lin *et al.* [10], who concluded that the three-centre–four-centre branching ratio was 0.89:0.11 (or roughly 8:1).

Riehl and Morokuma [11] used *ab initio* electronic structure theory to exhaustively study the unimolecular dissociation reactions of vinyl chloride. Here we briefly reiterate their findings on HCl elimination via planar four-centre and three-centre transition states (TSs). The barrier height for four-centre elimination, leading to HCl + acetylene, is $77.36\text{ kcal mol}^{-1}$ at the highest level of theory {QCISD(T)/6-311+G(d,p)} with zero-point correction using scaled MP2/6-311G(d,p) vibrational frequencies. For the three-centre elimination mechanism studied, leading to HCl + singlet vinylidene, the barrier height is $69.06\text{ kcal mol}^{-1}$ at the same level of theory with zero-point correction. For the four-centre elimination reaction, the HCl separation at the TS is 1.79 \AA while the HCl separation is 1.44 \AA for the three-centre elimination TS, both at the MP2/6-311G(d,p) level. It is also interesting to note that the imaginary vibrational frequency corresponding to motion across the TS is 1844 cm^{-1} for the four-centre state and 575 cm^{-1} for the three-centre state at the MP2/6-311G(d,p) level.

The 2-chloropropene molecule is structurally and electronically similar to vinyl chloride, but in this case the possibility of a three-centre HCl elimination has been removed because the H-atom α to the Cl is replaced by a methyl group. Both vinyl chloride and 2-chloropropene have C_s symmetry and a strong absorp-

tion excitation near 200 nm to a state with considerable $\pi\pi^*$ electronic character [8, 12]. Mueller *et al.* [12] have studied the photofragment translational spectroscopy after excitation at 193.3 nm using the ‘advanced light source’ for photoionization. That study reports the observation of several product channels, including both slow and fast CCl bond fission and HCl elimination.

In order to assist in the interpretation of those experiments, we report in this paper our *ab initio* calculations on the possible planar TSs leading to HCl elimination in the ground electronic state of 2-chloropropene. The present study finds two planar HCl elimination TSs: (i) a four-centre TS leading to HCl + propyne (similar to the four-centre TS leading to HCl + acetylene in vinyl chloride), and (ii) a four-centre elimination TS leading to HCl + allene.

2. Theoretical method

All calculations presented in this work were performed using either the Gamess-US electronic structure package [13] or the Gaussian98 package [14]. The structures presented in this paper have been optimized at three different levels of theory: HF/6-311G(d,p), MP2/6-311G(d,p), and B3LYP/6-31G(d). The former two geometries were optimized using Gamess-US while the latter geometries were optimized with Gaussian98 and used to obtain G3//B3LYP energies. Structures optimized at the MP2/6-311G(d,p) level were followed by single-point calculations at several higher levels, which were chosen to provide improved energetics and allow comparison with the results of Riehl and Morokuma. These were: MP4/6-311+G(d,p), QCISD(T)/6-311G(d,p) and QCISD(T)/6-311+G(d,p). Zero-point corrections for these additional single-point calculations were obtained from MP2/6-311G(d,p) frequencies scaled by 0.9748 [15]. The energetics for both G3 and G3//B3LYP are of similar accuracy; however, we selected the G3//B3LYP method because all the steps of the composite calculation are performed using the B3LYP/6-31G(d) optimized geometry, whereas G3 performs the frequency calculation (for zero-point energy correction) on the HF/6-31G(d) structure and all subsequent calculations on the MP2(full)/6-31G(d) geometry.

In order to ascertain that the calculated HCl elimination TSs indeed correspond to the desired HCl elimination channel(s), intrinsic reaction coordinate (IRC) calculations at the MP2/6-311G(d,p) level (using Gamess-US [13]) were performed. These used the Gonzalez–Schlegel second-order method with the step size (stride) set to $0.1\sqrt{(\text{amu})a_0}$.

Barrier heights and reaction endothermicities for the elimination channels studied were also determined with a G3//B3LYP calculation using the Gaussian98 pro-

gram package [14]. Clearly, the performance of G3//B3LYP for saddle points is likely to be worse than for true minima on the ground state electronic surface, since the parametrization implied in the higher level corrections has been derived from a set that includes species only from the latter group. However, for enthalpies of formation of stable species, this level of theory is known to give quite good agreement with experimental values (absolute average deviation of $1.25 \text{ kcal mol}^{-1}$ [16]).

3. Results

3.1. Reactant and products

As a convenient point of initial comparison, the optimized geometry of 2-chloropropene is shown in figure 1 (with MP2/6-311G(d,p) values in bold and B3LYP/6-31G(d) values—used in the G3//B3LYP sequence—underlined) together with the known experimental values (plain text) [17]. At either level of theory, the calculated geometry of 2-chloropropene agrees well with the experimental geometry; the largest deviation is in the CH bond lengths of the methylene group and the *cis* C=C—H bond angle. Similarly, the calculated geometries of the elimination products for both TSs (see table 1) agree well with the experimental and theoretical structures of allene [18–20], propyne [18, 20–22], and HCl [23, 24] that have been presented in the literature.

At the G3//B3LYP level, the calculated enthalpy of formation of 2-chloropropene is $-1.3 \text{ kcal mol}^{-1}$ at 0 K or $-4.6 \text{ kcal mol}^{-1}$ at 298 K (see table 2). The latter can be compared with the reported experimental value of $-5.9 \text{ kcal mol}^{-1}$ at 298 K [25, 26]. The G3//B3LYP value of $44.1 \text{ kcal mol}^{-1}$ for the 298 K enthalpy of formation of propyne is in superb agreement with the

reported experimental enthalpy of formation of propyne, $44.4 \pm 0.2 \text{ kcal mol}^{-1}$ at 298 K [27]. Similarly, the calculated enthalpy of allene at 298 K, $45.0 \text{ kcal mol}^{-1}$, agrees extremely well with the experimental value of $45.6 \pm 0.3 \text{ kcal mol}^{-1}$ [27]. For the relatively simple species HCl, G3//B3LYP produces $-21.7 \text{ kcal mol}^{-1}$ for the 298 K enthalpy of formation, in very good agreement with the well known experimental value of $-22.0_6 \pm 0.2_2 \text{ kcal mol}^{-1}$ [28].

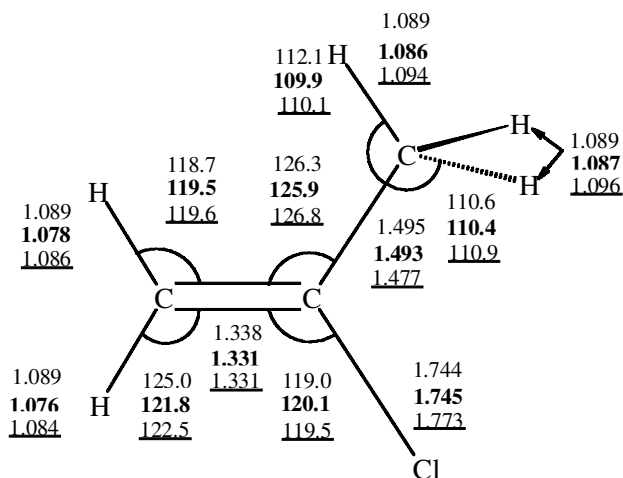


Figure 1. Ground state structure of 2-chloropropene. The experimental structural parameters appear in plain text while the corresponding parameters calculated at the MP2/6-311G(d,p) level of theory appear in bold. The structural parameters at the B3LYP/6-31G(d) level are underlined in the figure. The dihedral angles for the methyl group (not given in the figure) are assumed 60.0° for the experimental, 59.6° at the MP2 level, and 59.6° at the B3LYP level.

Table 1. Product and structural parameters calculated at the MP2 and B3LYP level. We also include the experimental structural parameters.

	MP2/6-311G(d,p)	G3//B3LYP	Experimental
Allene ^a			
C=C	1.307	1.307	1.308
C—H	1.079	1.088	1.087
C=C—H	121.0	121.5	118.2
Propyne ^b			
C...C	1.211	1.207	1.207
C—C	1.460	1.460	1.46
C—H (methyl)	1.087	1.097	1.112
C—H (terminal)	1.058	1.066	1.06
C...C—H	110.6	111.2	110.3
HCl ^c			
H—Cl	1.270	1.2899	1.2745

^a Experimental geometry taken from [19].

^b Experimental geometry taken from [21].

^c HCl bond length taken from [22].

Table 2. G3//B3LYP enthalpies of formation (kcal mol⁻¹) for the reactants and products of the TSs studied.

	0 K	298 K	Calc.-exp.
2-Chloropropene	-1.3	-4.6	1.3 ^a
Propyne	45.7	44.1	-0.3 ^b
Allene	46.8	45.0	-0.6 ^c
HCl	-21.6	-21.7	0.4 ^d

^a Exp. enthalpy of formation of 2-chloropropene at 298 K of -5.9 kcal mol⁻¹ from [25] (see also [26]).

^b Exp. enthalpy of formation of propyne at 298 K of 44.4 ± 0.2 kcal mol⁻¹ from [27].

^c exp. enthalpy of formation of allene at 298 K of 45.6 ± 0.3 kcal mol⁻¹ from [27].

^d Exp. enthalpy of formation of HCl at 298 K of -22.0₆ ± 0.0₂ kcal mol⁻¹ from [28].

3.2. TS A: HCl + propyne

TSA corresponds to the four-centre elimination of HCl to form propyne as the organic product. Figure 2 shows the parameters calculated at the RHF/6-311G(d,p) (*italics*), MP2/6-311G(d,p) (**bold**), and B3LYP/6-31G(d) (underlined) levels.

At both the RHF/6-311G(d,p) and MP2/6-311G(d,p) levels of theory, TS A closely resembles the four-centre HCl elimination TS of vinyl chloride calculated by Riehl and Morokuma [11]. (Both MP2 and RHF calculations to find the structures of the transition states discussed in this work were performed using Gamess-US while Riehl and Morokuma performed their calculations using Gaussian92. We found these transition states do optimize to slightly different structures using Gaussian98 but quote the values from the Gamess-US for the harmonic vibrational frequencies and structural parameters.) The CCl bond is 2.537 Å at the MP2/6-311G(d,p) level, an increase of 45% from the calculated ground state CCl bond length of 2-chloropropene (1.745 Å). For comparison, the CCl bond is 2.431 Å in the four-centre TS of vinyl chloride (MP2/6-31G(d,p)) [11]. The C=C bond shrinks by 0.082 Å at the MP2/6-311G(d,p) level with a length of 1.249 Å (exactly that of the four-centre TS of vinyl chloride). The *cis* CH bond is extended to 1.220 Å (compared with 1.256 Å in vinyl chloride), an increase of 0.144 Å. The C=C—Cl bond angle decreases to 93.0° at the MP2/6-311G(d,p) level (compared with 99.0° in vinyl chloride). The *cis* C=C—H bond angle decreases to 94.6° at MP2/6-311G(d,p) (76.9° in vinyl chloride). The *trans* CH bond contracts by 0.011 Å at MP2/6-311G(d,p), while the bond angle opens to 147.7° (1.069 Å and 153.7° in vinyl chloride). The C=C—C bond angle opens to 169.5° at the MP2/6-311G(d,p) level while the CC bond contracts to 1.449 Å. The other structural parameters of the methyl group remain relatively

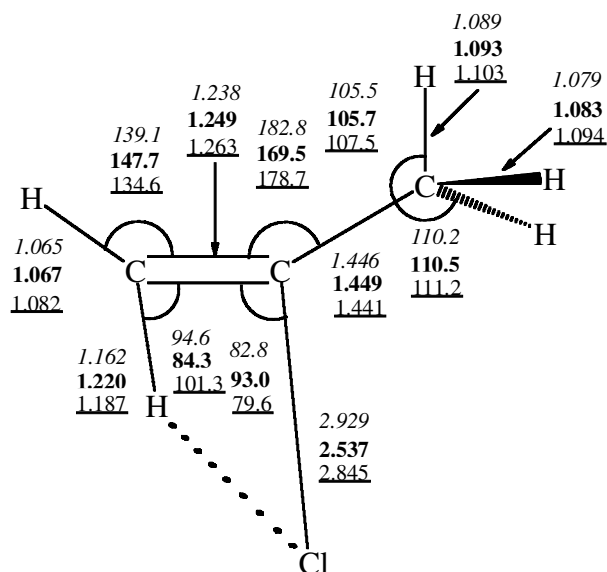


Figure 2. Calculated structure of transition state A corresponding to the four-centre elimination of HCl in 2-chloropropene resulting in propyne as the organic product. The one imaginary frequency plus the structural parameters calculated at the RHF/6-311G(d,p) level of theory appear in *italics* while those calculated at the MP2/6-311G(d,p) level of theory appear in **bold**. Finally, the structural parameters of the transition state using density functional theory (B3LYP/6-31G(d)) are underlined. The dihedral angles for the methyl group (not given in the figure) are 61.4° at the RHF level, 60.9° at the MP2 level, and 61.4° at the B3LYP level. The imaginary frequency corresponding to motion across the transition state is 794 cm⁻¹ (RHF), 1644 cm⁻¹ (MP2), or 1038 cm⁻¹ (B3LYP). Finally, the length of the forming HCl bond is 1.826 Å (MP2) or 1.907 Å (B3LYP).

unchanged at the TS. Finally, the distance between the eliminating H and Cl atoms is 1.826 Å, and the imaginary frequency corresponding to motion across the TS is 1644 cm⁻¹ at the MP2/6-311G(d,p) level. We found that these transition states do optimize to slightly different structures using Gaussian98, but quote the values from the Gamess-US for the harmonic vibrational frequencies and structural parameters. The products of this TS were explicitly confirmed to be HCl + propyne using an intrinsic reaction coordinate calculation.

The structure of TS A from the G3//B3LYP calculation for TS A appears in figure 2 as well (underlined structural parameters). The C=C—C structure is more open (∠178.7°) than at the MP2/6-311G(d,p) level but not as unrealistic as that predicted by RHF. The CCl bond (2.84 Å) lengthens at the B3LYP/6-31G(d) level compared with MP2 while the C=C—Cl bond angle (79.6°) closes somewhat. The eliminating CH bond shortens slightly to 1.187 Å while the H_{elim}—C=C

bond angle (101.3°) is more open than at either RHF or MP2. The HCl bond length at the TS changes by only 0.081 \AA compared with MP2, with a length of 1.907 \AA at the B3LYP/6-31G(d) level. The remaining structural changes at the B3LYP/6-31G(d) level compared with MP2 are relatively minor. It is interesting to note that the imaginary vibrational frequency corresponding to passage across the TS at the B3LYP level ($i1038 \text{ cm}^{-1}$) has a value intermediate between that produced at the MP2 level ($i1644 \text{ cm}^{-1}$) and that at the HF level ($i794 \text{ cm}^{-1}$), but closer to the latter.

A second possible four-centre TS leading to HCl + propyne was also considered. This TS has the methyl group rotated by about 60° , orienting the in-plane methyl hydrogen *cis* to the chlorine. A TS with this orientation of the methyl group was located at the RHF/6-311G(d,p) level of theory. However, an extensive search for this TS at the MP2/6-311G(d,p) level of theory with optimization tolerances set to $0.00001 E_h a_0^{-1}$ (one order of magnitude lower than the GAMESS-US default) and with recalculation of the force constant matrix after every step eventually converged to TS A. We therefore conclude that this second four-centre TS leading to HCl + propyne does not exist at the MP2/6-311G(d,p) level of theory.

3.3. TS B: HCl + allene

Another four-centre elimination TS, one leading to HCl + allene rather than HCl + propyne, exists in 2-chloropropene. The calculated geometry of this TS at the RHF/6-311G(d,p) level (*italics*), the MP2/6-311G(d,p) level (**bold**) and at the B3LYP/6-31G(d) level (underlined) is given in figure 3.

The structural parameters of TS B at the MP2/6-311G(d,p) level are as follows: the CCl bond length increases to 2.603 \AA (an increase of 49%). The C=C bond length is 1.295 \AA while the CC bond length is 1.375 \AA . The methylene CH bond lengths are quite similar with values of 1.073 \AA (*cis*) and 1.084 \AA (*trans*). The in-plane CH bond length of the methyl group is 1.236 \AA and the out-of-plane bond length is now 1.082 \AA . The bond angles have changed as follows: the C=C—C angle is now 168.9° , the C=C—Cl angle is 104.4° , and the CCH (in-plane) bond angle is 86.1° . The out-of-plane C=C—H bond angles for the methyl group are now 116.3° , with a dihedral angle of 72.5° . The methylene C=C—H bond angles change to 124.4° (*cis*) and 115.2° (*trans*). Finally, the bond length for the elimination product, HCl, at the TS is 1.779 \AA , and the imaginary frequency corresponding to motion across the TS is $i1698 \text{ cm}^{-1}$ at the MP2/6-311G(d,p) level. An intrinsic reaction coordinate calculation performed at the MP2/6-311G(d,p) level of theory confirmed explicitly that the product of this TS is allene + HCl.

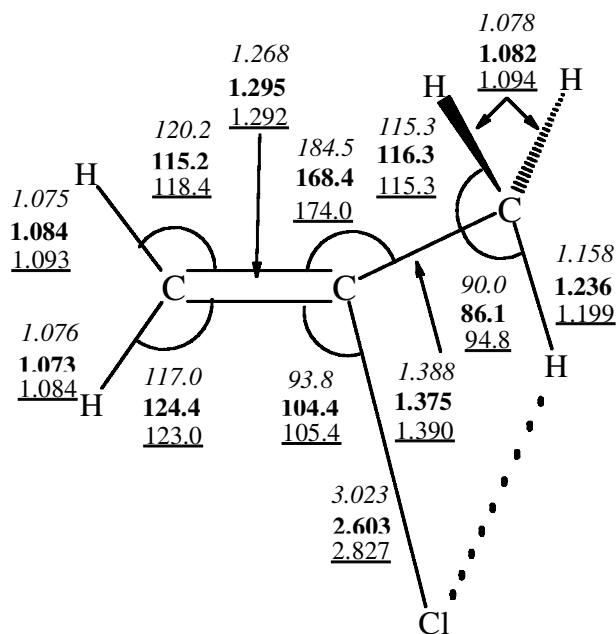


Figure 3. Calculated structure of transition state B corresponding to the four-centre elimination of HCl in 2-chloropropene resulting in allene as the organic product. The one imaginary frequency plus the structural parameters calculated at the RHF/6-311G(d,p) level of theory appear in italics while those calculated at the MP2/6-311G(d,p) level of theory appear in bold. Finally, the structural parameters of the transition state using density functional theory (B3LYP/6-31G(d)) are underlined. The dihedral angles for the methyl group (not given in the figure) are 110.1° at the RHF level, 72.5° at the MP2 level, and 68.6° at the B3LYP level. The imaginary frequency corresponding to motion across the transition state is 567 cm^{-1} (RHF), 1698 cm^{-1} (MP2), or 1080 cm^{-1} (B3LYP). Finally, the length of the forming HCl bond is 1.779 \AA (MP2) or 1.897 \AA (B3LYP).

The structure of TS B was also optimized at the B3LYP/6-31G(d) level as input for a G3//B3LYP calculation, figure 3 (underlined). Qualitatively, the structure of TS B follows the same trends as that of TS A. The C=C—C bond angle (174.0°) is more open at the B3LYP/6-31G(d) level compared with the MP2 level. The CCl bond length (2.827 \AA) lies between the length found at the RHF/6-311G(d,p) level and at the MP2/6-311G(d,p) level. The C—C—H_{elim} bond angle opens by about 8.7° compared with the MP2 level of theory while the C—H_{elim} bond length (1.199 \AA) shortens compared with MP2. Furthermore, the HCl bond length (1.897 \AA) increases by 0.118 \AA in the TS. The remaining structural parameters are relatively unchanged going from the MP2 level to the B3LYP/6-31G(d) level of theory. Again, the imaginary vibrational frequency for the normal mode corresponding to passage across the

TS, $i1080\text{ cm}^{-1}$, is intermediate between the values at the HF ($i567\text{ cm}^{-1}$) and MP2 ($i1698\text{ cm}^{-1}$) levels.

3.4. Reaction endothermicity and barrier heights

Table 3 lists the calculated reaction endothermicities (and also barrier heights) for the two elimination channels considered in the present work. All the values listed are relative to the ground vibrational state of 2-chloropropene. In addition, the values in parentheses list energies exclusive of the ZPE, i.e. relative to the bottom of the potential well of 2-chloropropene.

Based on the available experimental values [25–28], the experimental endothermicity for the HCl elimination leading to propyne is $28.2\text{ kcal mol}^{-1}$ at 298 K, which becomes $26.8\text{ kcal mol}^{-1}$ at 0 K. Similarly, the HCl elimination channel leading to allene is endothermic by $29.4\text{ kcal mol}^{-1}$ at 298 K, or $28.1\text{ kcal mol}^{-1}$ at 0 K. (In both cases the 298 K to 0 K transformation has been performed using the G3//B3LYP enthalpy increments for the reactant and the products. Effectively this introduces a relatively small error, at least in the present context, of treating the methyl hindered rotation as a quasi-vibration.) The difference between the two experimental exothermicities is quite small, and simply reflects the fact that experimental enthalpies of formation suggest that propyne is slightly ($\sim 1.3\text{ kcal mol}^{-1}$) more stable than allene. Using a previously calculated [29] (G3) value for the enthalpies of formation of 2-chloropropene and of allene and using the relative energetic difference between allene + H and propyne + H [30], the two 0 K exothermicities can be estimated as $25.0\text{ kcal mol}^{-1}$ and $26.1\text{ kcal mol}^{-1}$ [12]. These values are extremely close to the prediction based entirely on G3//B3LYP values given in table 2. In particular, the

G3//B3LYP values predict a difference in endothermicities of 1.0 kcal mol^{-1} , quite close to the experimental value of $1.2\text{--}1.3\text{ kcal mol}^{-1}$. Although at all levels of calculation the propyne channel appears slightly more stable than the allene channel, G3//B3LYP values come the closest to experiment, whereas at other levels the differences between the two product asymptotes are larger and range between 1.7 kcal mol^{-1} and 5.4 kcal mol^{-1} .

At all levels of calculation the height of the barrier associated with TS A appears to be very much the same as that associated with TS B, although the absolute heights differ substantially between various levels of calculations. This similarity between the two barrier heights holds even for those calculations that obtain an unrealistic value for how much lower the HCl + propyne asymptote is than the HCl + allene asymptote.

The simple Hartree–Fock calculation produces the lowest absolute values for the barriers ($\sim 64\text{ kcal mol}^{-1}$), but also differs the most from experiment in the predicted reaction endothermicities. These low barrier heights at the HF level go hand-in-hand with the relatively low imaginary frequencies ($i794\text{ cm}^{-1}$ and $i567\text{ cm}^{-1}$), reflecting a relatively small predicted curvature at the saddle point. On the other hand, the imaginary frequencies jump substantially at the MP2/6-311G(d,p) level, reflecting a significant increase in curvature at the saddle points, with the concomitant increase in barrier height (to $\sim 73\text{ kcal mol}^{-1}$). Although the introduction of polarization functions appears to very slightly increase the barrier heights, as the level of calculation increases from MP2 through MP4 to QCISD and QCISD(T), there seems to be a trend towards somewhat lower barrier heights.

Table 3. Calculated energies (in kcal mol^{-1}) of transition states and product asymptotes relative to the reactant.^a

	TS A	Propyne + HCl	TS B	Allene + HCl
HF/6-311G(d,p) ^b	63.7 (68.6)	19.5 (24.6)	63.7 (68.3)	21.5 (27.1)
MP2/6-311G(d,p) ^c	72.5 (77.8)	23.1 (28.4)	73.2 (78.7)	28.5 (34.1)
MP2/6-311 + G(d,p)//MP2/6-311G(d,p)	73.1 (78.4)	24.2 (29.6)	73.6 (79.1)	29.2 (34.8)
MP4/6-311 + G(d,p)//MP2/6-311G(d,p)	71.9 (77.2)	24.8 (30.2)	71.7 (77.2)	27.6 (33.2)
QCISD/6-311G(d,p)//MP2/6-311G(d,p)	71.6 (76.9)	23.6 (29.0)	71.6 (77.1)	25.6 (31.2)
QCISD/6-311 + G(d,p)//MP2/6-311G(d,p)	72.1 (77.5)	24.8 (30.1)	71.9 (77.4)	26.5 (32.1)
QCISD(T)/6-311G(d,p)//MP2/6-311G(d,p)	70.4 (75.8)	24.1 (29.5)	70.2 (75.7)	25.8 (31.4)
QCISD(T)/6-311 + G(d,p)//MP2/6-311G(d,p)	71.0 (76.3)	25.3 (30.7)	70.5 (76.0)	26.9 (32.4)
G3//B3LYP ^d	66.9 (71.7)	25.5 (30.8)	67.3 (72.1)	26.5 (32.0)

^a Values include ZPE and are relative to the lowest vibrational level of 2-chloropropene. Values in parentheses do not include ZPE and are relative to the bottom of the potential for 2-chloropropene.

^b Scaled (0.9248 [15]) ZPE for 2-chloropropene is $43.7\text{ kcal mol}^{-1}$.

^c Scaled (0.9748 [15]) ZPE for 2-chloropropene is $43.8\text{ kcal mol}^{-1}$.

^d Scaled (0.96 [16]) ZPE for 2-chloropropene is $42.9\text{ kcal mol}^{-1}$.

Table 4. RRKM parameters.

	Harmonic vibrational frequencies/cm ⁻¹	Moments of inertia/amu Å ²
2-chloropropene	207.2, 345.1, 400.2, 444.3, 627.0, 713.2, 904.1, 936.4, 1030.0, 1085.8, 1202.7, 1432.6, 1455.8, 1498.9, 1518.2, 1727.7, 3053.2, 3112.6, 3137.7, 3181.6, 3271.6	53.9, 101.9, 152.7
HCl + propyne (TS A)	145.1, 150.9, 306.5, 331.4, 529.5, 580.9, 880.3, 887.9, 1030.8, 1069.6, 1081.1, 1406.1, 1448.1, 1487.5, 1861.0, 2032.0, 3008.9, 3108.8, 3153.3, 3279.9	56.2, 162.4, 215.4
HCl + allene (TS B)	183.3, 236.4, 301.6, 347.5, 524.9, 586.8, 863.8, 923.3, 1007.3, 1062.7, 1228.9, 1328.7, 1376.1, 1464.5, 1719.9, 1978.1, 3090.6, 3129.3, 3168.3, 3264.4	56.6, 159.7, 212.9

3.5. RRKM calculations

RRKM calculations were performed using the vintage Hase and Bunker code [31]. Branching ratios were calculated from the estimated rates by taking the barrier heights obtained at the G3//B3LYP level, along with unscaled B3LYP/6-31G(d) vibrational frequencies and moments of inertia (given in table 4) for 2-chloropropene, TS A, and TS B. The branching fractions for the two possible reaction paths correspond to the ratio of the estimated reaction rate constant for the desired TS to the sum of the reaction rate constants for both TSs. Although the branching ratio has a significant dependence on internal energy, it favours the propyne + HCl channel not only at total energy near the barrier height, but also at high internal energy where the branching is insensitive to the small difference in barrier heights. For example, at energies just above the barrier (70.0 kcal mol⁻¹) the branching fraction to the propyne + HCl channel is 78%. This somewhat declines as the internal energy increases, but at 147.9 kcal mol⁻¹ (193.3 nm) the branching fraction to propyne + HCl is still 67%.

4. Discussion

TS A, leading to HCl + propyne, closely resembles the four-centre elimination TS of vinyl chloride [11]. In both structures the CCl bond is greatly elongated (2.537 Å, 2 chloropropene; and 2.431 Å, vinyl chloride). In the MP2/6-311G(d,p) optimized structure, the incipient HCl bond length in vinyl chloride is 1.789 Å while the length of the incipient HCl bond is 1.826 Å in 2-chloropropene. At the same level of theory, the vibrational frequency for the normal mode corresponding to motion through TS A is 1644 cm⁻¹ (1844 cm⁻¹ for vinyl chloride [11]). For the allene + HCl channel, the H–Cl separation in the TS is 1.779 Å at this level of theory, while the frequency corresponding to motion across TS B is 1698 cm⁻¹.

At the MP2/6-311G(d,p) level, the barrier height for the 4-centre elimination through TS A is 77.8 kcal mol⁻¹

before zero-point correction and 72.5 kcal mol⁻¹ after zero-point correction. TS B lies very close (only ~0.7–0.9 kcal mol⁻¹ higher) in energy to TS A, with a barrier height of 78.7 kcal mol⁻¹ before zero-point correction and 73.2 kcal mol⁻¹ after zero-point correction (the preliminary barrier heights results in [12] were slightly different as the scaling factor used was of 0.93 for the MP2/6-311G(d,p) vibrational frequencies when calculating the zero-point energy correction).

However, at the same time the MP2/6-311G(d,p) calculation seems to favour the propyne + HCl asymptote by 5.4 kcal mol⁻¹ over the allene + HCl asymptote, quite far from the experimental value of ~1.3 kcal mol⁻¹. In this context, it is interesting to note that the calculated vibrational frequencies of allene at this level of theory agree relatively well with the experimental numbers: after scaling all frequencies by 0.9496 [15], all harmonic vibrational frequencies lie within 100 cm⁻¹ of their experimental value [32]. However, the vibrational frequencies of propyne found using MP2/6-311G(d,p) level of theory exhibit less agreement with the experimental vibrational frequencies (five of the scaled harmonic frequencies from our MP2/6-311G(d,p) calculation disagree with the experimental value [32] by more than 100 cm⁻¹). The disagreement in the harmonic vibrational frequencies suggests that the calculated force constants for propyne are not sufficiently accurate at this level of theory, and hence suggests that the relative energy of the propyne + HCl asymptote has to be used with caution.

The differences in the two barrier heights calculated with fourth order Møller–Plessett perturbation theory and quadratic CI are smaller than in the case of the second-order Møller–Plessett calculation, and even show a reversal (to -0.5 kcal mol⁻¹) as the level of theory increases. Hence, one concludes that the two barriers are essentially the same, regardless of the level of calculation. However, the absolute height of the barrier is quite dependent on the level of calculation. Starting from MP2/6-311G(d,p), there seems to be a

more-or-less monotonic decrease in the absolute barrier height. The G3//B3LYP sequence produces energies effectively at the QCISD(T,fu)/G3Large level, which corresponds to the highest level employed here. Hence, although the performance of G3//B3LYP level of theory for transition states has not been thoroughly tested so far, one concludes that the current best estimate for the barrier height for both TS A and TS B is 67 kcal mol^{-1} including ZPE. Taking into account the next highest level of calculation, QCISD(T)/6-311+G(d,p)//MP2/6-311G(d,p) plus the trend towards lower barrier heights with increasing level of electronic structure methods, one additionally concludes that it is highly unlikely that the barrier is higher than 71 kcal mol^{-1} . Also, based on all available calculations, it seems highly unlikely that the two barrier heights, corresponding to TS A and TS B, differ appreciably. Another striking similarity between TS A and TS B is the HCl bond length. The optimized geometry for both TSs consistently yields an HCl bond length of about 1.8 \AA . As discussed above, this HCl bond length compares quite well with the HCl bond length for the four-centre TS of vinyl chloride [11] (about 1.79 \AA), while the HCl bond length for the three-centre elimination TS shows a substantially shorter HCl bond length (1.4 \AA). The curious similarities between TS A and TS B lead to the qualitative conclusion that it is experimentally very difficult to distinguish between HCl originating from either TS A or TS B in 2-chloropropene: the essentially identical barrier heights and HCl bond lengths in the TSs strongly suggest nearly identical vibrational excitation of the HCl photoproduct in both cases. This, of course, assumes that HCl vibrational excitation results largely from the extended length of the newly formed HCl bond in the TS, with very little exchange of energy with the other degrees of freedom in the exit channel. Based on the similarity of the four-centre TS in vinyl chloride and TS A and TS B in 2-chloropropene, one furthermore concludes that the vibrational excitation of HCl from the four-centre elimination TS of vinyl chloride should closely resemble that of HCl from 2-chloropropene.

Indeed, initial experiments using photofragment time-of-flight spectroscopy with photoionization detection could not distinguish between the two possible TSs leading to HCl elimination in 2-chloropropene [12]. Furthermore, the photoionization efficiency (PIE) curves for the HCl elimination product from 2-chloropropene and from vinyl chloride, figure 4, appear to be quite similar. Both PIE curves are red-shifted from the photoionization onset of vibrationally cold HCl (12.75 eV). Qualitatively, this is an indication of a similar degree of vibrational excitation for the HCl products from 2-chloropropene and a significant fraction of the HCl photoproducts from vinyl chloride.

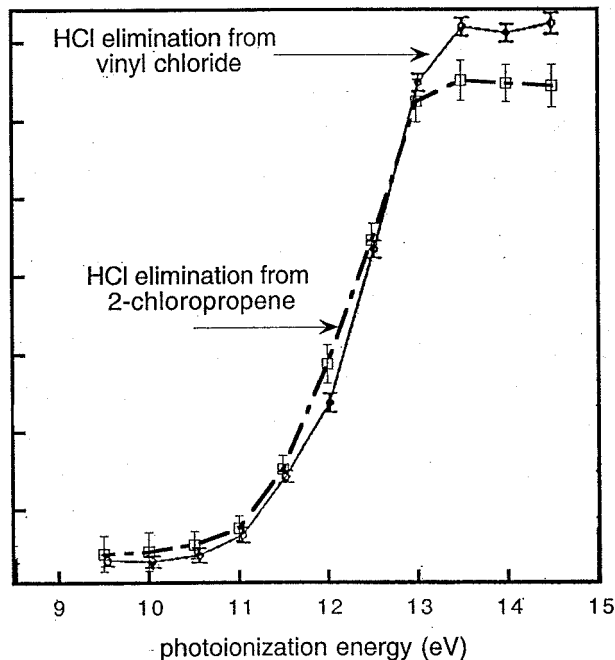


Figure 4. Photoionization efficiency curves for 2-chloropropene [12] and vinyl chloride [1]. Both curves appear to have a similar onset and rise, probably resulting from HCl formed via four-centre elimination in vinyl chloride and HCl formed in 2-chloropropene, which have similar H-Cl separation in the TS.

Experiments on the 193.3 nm photolysis of a related molecule, allyl chloride, show a less red-shifted HCl PIE curve, indicating less vibrational excitation of the HCl elimination product [34]. Given this, we found it surprising that the PIE curve of the HCl product from 2-chloropropene was so similar to that from vinyl chloride photodissociation (see figure 4), which has been assigned to two competing mechanisms, a dominant three-centre mechanism and four-centre mechanism similar to the HCl+propyne elimination in 2-chloropropene. (The shorter H-Cl distance in the transition state in the three-centre mechanism for vinyl chloride might lead one to expect a colder vibrational distribution of the HCl product than from the four-centre elimination in vinyl chloride or in 2-chloropropene.) However, recent work by Y. P. Lee and coworkers [10], identifying their high- J distribution of HCl product with the three-centre mechanism and the low- J product with the four-centre mechanism, concludes that the vibrational distributions of the HCl from the two mechanisms are quite similar. The similarity of the PIE curve of the HCl product from 2-chloropropene to that from vinyl chloride is consistent with their conclusions. Apparently it results from an accidental similarity of the statistical vibrational distribution of the HCl product from the three-centre mechanism in vinyl chloride to the HCl vibrational

distribution, determined largely by exit channel dynamics, from the four-centre elimination channel in both molecules.

Another interesting aspect of the HCl elimination from 2-chloropropene is that the RRKM calculations suggest that the propyne product is favoured over the allene product by almost a 3:1 margin at threshold, and still by a 2:1 margin after 193 nm excitation. Based on the very similar barrier heights of the two TSs and the considerable excess energy after photoexcitation at 193 nm, one would in the zero-order picture expect the branching ratio to be much closer to 1:1. Since the barrier heights and hence the amount of excess energy are practically the same for both elimination channels, the main difference must be arising from a difference in the vibrational frequencies of the two TSs, where the softest frequencies are those that will exert the highest influence. A closer comparison of the two TSs shows that the frequencies are very similar in both cases, with the exception of the two softest modes (and also the imaginary frequency, although the latter does not contribute to the RRKM rate). The softest frequency, which is $\sim 25\%$ stiffer in TS B, corresponds to a CCC bend. The next lowest frequency, which is $\sim 57\%$ stiffer in TS B, corresponds to the methyl hindered rotor. Clearly, in TS A this is close to a free internal rotation, while in TS B this corresponds to a highly hindered rotor, locked in by the incipient HCl bond. Consequently, the spacing of the levels of the internal rotor is expected to be denser in TS A than in TS B. Thus, the persistently high branching ratio favouring the propyne+HCl channel arises primarily from the loss (or, perhaps, significant increase in the hindrance) of the internal methyl rotor in TS B. Finally, one could conceive of distinguishing between the products of TS A and TS B by selective deuteration of the methyl group in 2-chloropropene, giving $\text{CH}_2\text{CClCD}_3$. Similar experiments, which were performed on vinyl chloride, indicated a branching ratio of 3:1 favouring four-centre elimination of HCl [5]. This should allow for the possibility of selectively detecting either HCl from TS A or DCl from TS B.

5. Conclusion

We have performed *ab initio* electronic structure calculations of the planar TSs leading to HCl elimination on the ground electronic state of 2-chloropropene. Two transition states were found: one leading to the propyne+HCl products, the other to allene+HCl products. The structure of both TSs, and particularly of TS A (leading to propyne+HCl), bear very interesting similarities to the four-centre elimination TS of vinyl chloride calculated by Riehl and Morokuma [11]. Both TSs in 2-chloropropene and the four-centre TS in vinyl chloride have a similar HCl bond length. The bar-

rier height for TS A is $72.9 \text{ kcal mol}^{-1}$ (with ZPE correction) compared with $81.2 \text{ kcal mol}^{-1}$ for the four-centre HCl elimination in vinyl chloride at the MP2/6-311G(d,p) level [11]. Furthermore, the barrier height for TS B leading to HCl+allene is quite similar, with a value of $73.8 \text{ kcal mol}^{-1}$ at the MP2/6-311G(d,p) level with zero-point energy correction. The difference between the barrier heights related to TS A and TS B is even smaller at higher levels of calculation. In addition, as the level of calculation increases, the absolute barrier heights tend to decrease further, becoming $71.0 \text{ kcal mol}^{-1}$ and $70.5 \text{ kcal mol}^{-1}$ for TS A and TS B, respectively, at the QCISD(T)/6-311+G(d,p)//MP2/6-311G(d,p) level and $66.9 \text{ kcal mol}^{-1}$ and $67.3 \text{ kcal mol}^{-1}$ at the composite G3//B3LYP level of theory. These two levels of theory also predict very similar overall endo-thermicities: $25.3 \text{ kcal mol}^{-1}$ (quadratic CI) or $25.5 \text{ kcal mol}^{-1}$ (G3) for the propyne channel and $26.9 \text{ kcal mol}^{-1}$ (quadratic CI) or $26.5 \text{ kcal mol}^{-1}$ (G3) for the allene channel. These endothermicities are in reasonably good agreement with the available experimental data.

RRKM calculations using the G3//B3LYP barrier heights along with the unscaled B3LYP/6-31G(d) harmonic vibrational frequencies for the two TSs and 2-chloropropene produce estimates of the reaction rate constants as a function of energy for each HCl elimination channel, from which one can obtain branching ratios for the two reaction paths. These appear to decisively favour the propyne+HCl channel over the allene+HCl channel by a margin of 2:1 even for internal energies near $150 \text{ kcal mol}^{-1}$. The dominance of the HCl+propyne channel is readily attributed to the difference in the internal methyl rotor of the two TSs, which is highly hindered in case of the TS leading to allene+HCl by the incipient HCl bond, but corresponds to nearly free rotation in the case of the TS leading to propyne+HCl products.

Finally, a comment should be made on the fact that the present study neglects HCl elimination channels resulting from atom migrations, i.e. intermediates such as $\text{H}_2\text{CCHClCH}_2$ or HCCHClCH_3 for H atom migration or $\text{H}_2\text{CClCCH}_3$ resulting from Cl atom migration. Transition states such as these were considered in the much more thorough study by Riehl and Morokuma for vinyl chloride; however, the calculations predicted that the HCl elimination transition state accessed after migration lie higher in energy than either planar HCl elimination transition states (the lowest HCl elimination TS resulting from atom migration lies over 8 kcal mol^{-1} above the four-centre elimination TS in vinyl chloride). Thus, although the migration may be a relatively easy process the HCl elimination barrier prevents this from making a significant contribution to the observed HCl

products [6]. Riehl and Morokuma make the important point, however, that these migration mechanisms may play a role in H atom scrambling (similarly, migration TSs may play a role in H atom scrambling for 2-chloropropene, and must be addressed before interpreting the results of experiments on the isotopically labelled compound). We expect that the migration TSs, of 2-chloropropene will also lie higher in energy than the simple planar TSs, and for this reason have not considered them in the current work; however, they are the subject of a continuing study of HCl elimination in 2-chloropropene as well as related compounds.

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