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CASSCF Studies of 1,1-HF and 1,1-HCl Elimination Transition State Geometries of Haloalkanes

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Abstract

Elimination reactions are a possible degradation pathway of haloalkanes during their destruction in high temperature environments. Elimination reactions occur in two different pathways: a 1,2 elimination where a halogen and a hydrogen are eliminated from two different carbon atoms, or a 1,1 elimination where a halogen and a hydrogen are eliminated from the same carbon atoms. The highly multireference character of the 1,1 eliminations make it difficult to study these reactions using conventional Density Functional Theory (DFT) calculations, therefore the CASSCF, or Complete Active Space Self Consistent Field level of theory is utilized to optimize two propane molecules, 1,1 dichloro and 1,1 difluoropropane. Results are presented as transition state geometries with consideration of the optimum active space for generating reliable geometries and vibrational frequencies, and found that the 1,1 difluoropropane 1,1 HF elimination pathway had a threshold energy of 70.1 kcal/mol and matches with experimental data. However, the 1,1 HCl elimination transition state geometry from 1,1 dichloropropane produced a threshold energy of 121.6 kcal/mol which is too high of an energy for this reaction to take place. More research has been done on the 1,1 HCl elimination pathway including chloroform HCl elimination and 1,1 dichloroethane 1,1 HCl elimination in order to find a more reasonable transition state for 1,1 dichloropropane.

1. Introduction

CFCs, or chlorofluorocarbons, were developed in the early 1930s as refrigerants, solvents, and propellants. CFCs were used due to lack of toxicity, are chemically stable, not flammable, and reasonably priced[1]. In 1974, scientists began noticing the negative effect of CFCs on the atmosphere in the form of stratospheric ozone destruction[2]. This occurs when atomic chlorine diffuses from the troposphere to the stratosphere and reacts with ozone[2]. The reaction cycle of ozone with chlorine atoms is shown in reaction (1)[3].

$$\begin{aligned} Cl + O_3 &\rightarrow ClO + O_2 \\ ClO + O_3 &\rightarrow Cl + 2O_2 \end{aligned} \qquad (1)$$

In addition, CFCs contribute to the greenhouse effect by emitting infrared radiation back to the Earth instead of allowing it to diffuse out of the atmosphere, which in turn contributes to global climate change[2].

In 1987, the Montreal Protocol was signed which regulated the phasing out of CFCs by 1995, and replacing them with hydrochlorofluorocarbons, or HCFCs. HCFCs have similar chemical properties to CFCs in that they are not very flammable or toxic and they are chemically stable. However, these molecules have one major difference: they are easily reacted with OH radicals in the troposphere[2]. This process is shown in reaction (2)[3].

$$OH + RH \rightarrow H_2O + R \quad (2)$$

The hydroxyl radical reaction in (2) is the major pathway for stratospheric ozone degradation[3]. The hydroxyl radical is the most important oxidizer in the troposphere, and is the primary cleanser for the troposphere[4]. Understanding how gases like HCFCs react in the atmosphere or during remediation processes is important for both understanding how gasses affect the atmosphere and for possibly finding a suitable replacement.

HCFCs become chemically activated through the combination of radicals which are exothermic reactions. This process chemically activates the molecule over the energy barrier, which then proceeds through a unimolecular decomposition reaction, or an elimination reaction[5]. There are two elimination pathways the reaction could take: a hydrohalide could eliminate from two different carbon atoms in a 1,2 elimination, or it could eliminate from the same carbon in a 1,1 elimination. An example of a 1,2 elimination reaction is shown in (3).

$$CH_3CH_2CCl_3 \rightarrow CH_3CH{=}CCl_2 + HCl \quad (3)$$

Typically, a 1,2 elimination pathway is preferred, as seen in the case of HCl formation[6]. However, 1,1 elimination has been observed in various fluorochloro ethanes. An example of a 1,1 reaction can be seen in (4).

$$CHF_2CH_2CH_3 \rightarrow {:}CFCH_2CH_3 + HF \quad (4)$$

The 1,1 elimination channel occurs in the presence of dihalogen substituents on the same carbon. This phenomenon is due to the decrease in energy that accompanies such a 1,1 disubstituted halogen molecule such as CH_3CHF_2. This reaction is divided into two steps. The first step is the HF or HCl elimination from Carbon 1 followed by a rearrangement to a cis carbene. After carbene formation, potential energy is released to form an alkene. An example of this phenomenon is the reaction shown in Holmes et al., which can be seen in (5)[7].

$$CDF_2CH_2F \rightarrow {:}CFCH_2F + DF \rightarrow CHF{=}CHF + DF \quad (5)$$

The 1,2 difluoroethene product has two different threshold energies. The 1,2 elimination pathway has a threshold energy of 67.8 kcal-mol-1, while the 1,1 elimination has a threshold energy of 69.8 kcal-mol-1. Holmes et al. determined that the 1,1 elimination pathway could not be neglected due to the contribution to the total rate of elimination for the molecule. In order to glean more information about this 1,1 elimination pathway, computational studies must be done to determine the transition states of 1,1 elimination degradations of HCFCs[7].

The method that has previously been using for determining transition state geometries, barrier heights, and rate constants for reactions is Density Functional Theory, or DFT. This calculation produces results that vary depending on which density functional was chosen, however is considered reliable for single-reference character calculations. A single reference calculation is when a single wavefunction is optimized. For multireference systems, like the reactions shown in (4) and (5), the calculated results were considered inaccurate. Therefore, one must use a multireference calculation in order to accurately determine transition state optimizations. A multireference calculation uses a linear combination of a single wavefunction to optimize a calculation[8].

Complete Active Space Self-Consistent Field (CASSCF) method is utilized for these multireference calculations. CASSCF calculates every combination of a chosen number of active electrons in a chosen number of active orbitals by moving one electron at a time until the lowest potential energy iteration is reached[9]. This calculation gives reliable transition state geometries, however still has systematic error in barrier height calculations[9, 10].

The second-order Moller Plesset theory, or MRMP2, calculation performs similarly to CASSCF through use of the active space and wavefunctions generated in the CASSCF calculation, in addition to dynamical electron correlation across the entire molecule since CASSCF involves the explicit calculation of electron correlation through the active space but neglects the entire molecule. A test was done by Tishchenko et al. compared this MRMP2 calculation to

DFT calculations, specifically MP2 and CCSD. They found that MRMP2 had the lowest mean unsigned error out of the methods tested for transition state geometry optimization. In addition, MRMP2 more accurately calculated the barrier heights, which is what CASSCF was missing[11].

For this research, CASSCF was utilized to optimize the transition state geometries of 1,1 difluoropropane and 1,1 dichloropropane and MRMP2 was used to calculate the threshold energies. These calculations were run using Gaussian 09 programs. Prior research performed by the research group include calculations and experimental data on the 1,2 elimination of these molecules, as well as on the ethane forms of the molecules. In addition, a current research group member is working on the experimental data for these molecules, and 1,1 elimination experimental data was published in 1976 by Holmes and Setser[7]. Other research groups have not used CASSCF calculations to optimize 1,1 elimination transition geometries to date, however the Donald Truhlar Group does extensive work with multireference computations. The lack of reliable computational information lead to the study of 1,1 elimination reactions in addition to explaining the phenomenon of molecules preferring the 1,1 elimination channel to the 1,2 elimination pathway.

2. Methods

The first step in CASSCF is determine the active space. Single point HF calculations generate the set of orbitals from which the orbitals that represent the reaction area in the molecule are selected first. Hartree-Fock calculations were done first on the initial geometry of the system as well as the predicted transition state of the carbene product. The molecules used were $CH_3CH_2CHF_2$ and $CH_3CH_2CHCl_2$. A single point calculation at a trial geometry was used to view the orbitals on Gaussian. The orbitals were then analyzed. The active space orbitals that were integral to the reaction area were determined for use in calculations.

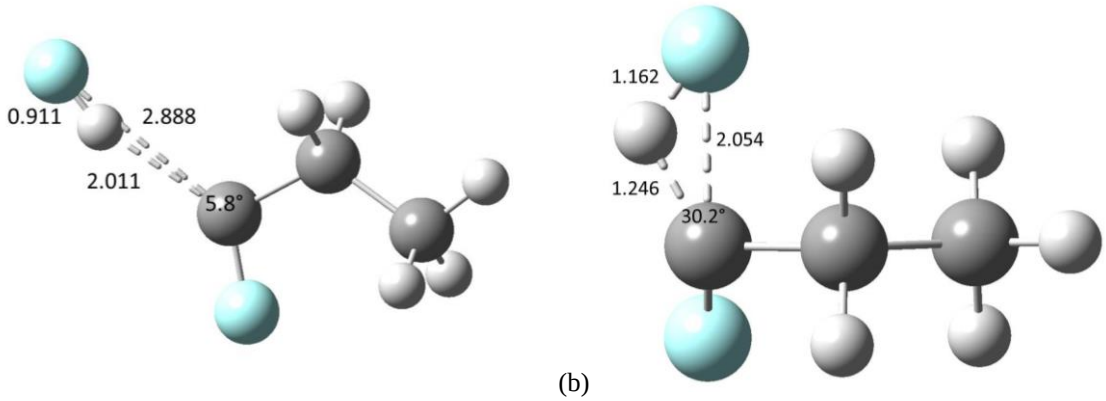
CASSCF optimization calculations were performed first on the $CH_3CH_2CHF_2$ system. The calculations were run at the 6-31G(d',p') basis set at varying active spaces. A CASSCF active space treats a subset of occupied and virtual orbitals as configuration interactions. For example, CASSCF(6,5) allows for configurations of 6 electrons in 5 orbitals (3 occupied, 2 virtual). For this calculation, the active space varied from (4,4) to (8,8). The $CH_3CH_2CHCl_2$ system had the same basis set as the 1, 1 difluoropropane system, and utilized an active space from (6,5) to (8,8).

Single Point MRMP2 calculations were begun in order to better calculate the threshold energies of the reaction. These calculations were run at the same basis set as the CASSCF calculations, as well as the same active spaces. The geometries produced from these calculations were then run using DFT to produce reliable threshold energies as well.

3. Results/Discussion

3.1 $CH_3CH_2CHF_2$

The calculations for the $CH_3CH_2CHF_2$ system came up with two different transition state geometries. The first geometry (Figure 1a), is the geometry found when $CH_3CH_2CHF_2$ is calculated at different levels of theory such as DFT and Hartree Fock, or when the chosen active space is too small. These calculations produce geometries with unreasonably low energies. The geometry was also tested with an intrinsic reaction coordinate (IRC) calculation, which follows the path of the reaction, showing that this geometry acts more as a fluorine atom abstracting a hydrogen atom as opposed to the elimination of hydrogen and fluorine. This geometry is the CASSCF calculation at the (4,4) active space. The second geometry is the more believable transition state geometry, with experimentally reasonable energies and an IRC that follows an elimination pathway (Figure 1b).



(a) (b)

Figure 1. Transition Stage Geometries of the 1,1 elimination pathway of 1,1 difluoropropane using CASSCF at the 6-31G(d',p') basis set. (a) Inaccurate transition stage geometry at CASSCF(4,4). (b) Believable transition state geometry, in this case CASSCF(6,5).

The energies, bond lengths, and bond angles of these geometries are found in Table 1. As one can see, the threshold energy for the CASSCF(4,4) geometry is considerably lower than the other geometries. In addition, the atoms that are eliminating from the CASSCF(4,4) molecule occur in an almost linear fashion as opposed to the average 31° angle between the H, C, and F atoms on the other active spaces.

Table 1. Bond lengths, angles, and threshold energies of 1, 1 difluoropropane transition state geometries at varying active spaces calculated with CASSCF at the 6-31G(d',p') basis set.

Active Space	C-H Bond Length (Å)	C-F Bond Length (Å)	H-F Bond Length (Å)	HCF Bond Angle (°)	CASSCF Threshold Energy (kcal/mol)
(4,4)	2.011	2.888	0.911	5.8	67.936
(4,5)	1.246	2.054	1.162	30.2	90.716
(4,6)	1.217	1.986	1.210	34.9	91.381
(4,7)	1.217	1.986	1.210	34.9	92.899
(6,5)	1.246	2.054	1.162	30.2	89.548
(6,6)	1.253	2.067	1.153	29.4	98.566
(6,7)	1.252	2.049	1.152	30.1	86.936
(8,6)	1.246	2.056	1.160	30.1	96.774
(8,7)	1.247	2.055	1.160	30.2	90.590
(8,8)	1.256	2.033	1.164	31.4	83.662

Based on the information above as compared to experimental data and predictions that six electrons are involved in the reaction (H-C bond, C-F bond, and an F lone pair), the CASSCF(6,6) calculation seems to be the best active space. The geometries for the transition states of the CASSCF(6,6)/6-311+G(2d,p) 10f 6d are shown in Figure 2. The geometries were then optimized at DFT in order to get experimentally accurate threshold energies for both 1,1 elimination and 1,2 elimination reactions. The tables of these energies can be found in Tables 2 and 3. These energies, paired with the optimized geometries, match experimental data found by Wormack[12].

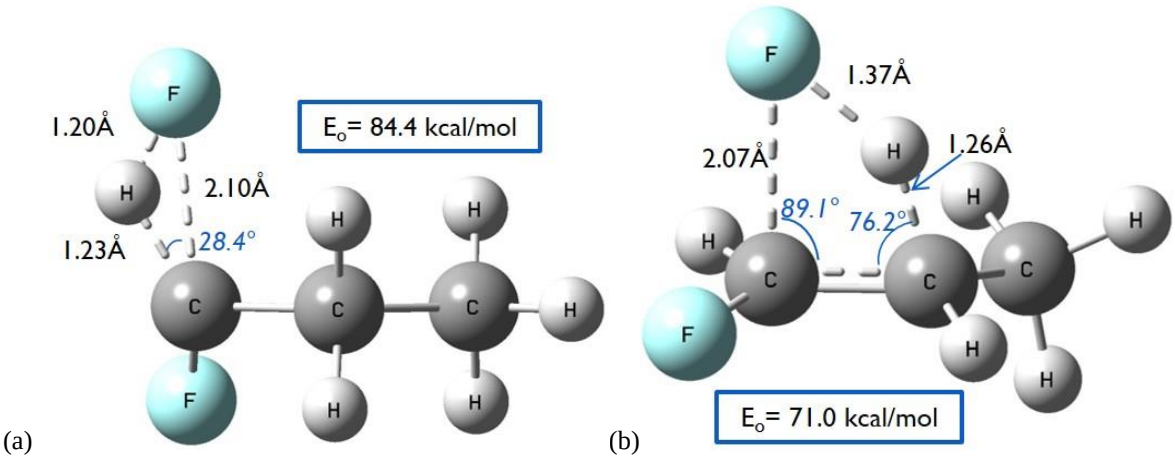


Figure 2. Transition state geometries at CASSCF(6,6)/6-311+G(2d,p) 10f 6d for (a) 1,1 elimination transition state geometry and (b) 1,2 elimination transition state geometry, in addition to the CASSCF threshold energies.

Table 2. Threshold Energies for CASSCF and DFT methods for the 1,1 elimination transition state geometries

Level of Theory	Basis Set	E_o (kcal/mol)
CASSCF(6,6)	6-311+G(2d,p) 10f 6d	84.4
B3PW91	6-31G(d',p')	72.2
B3PW91	cc-pvDZ	70.1

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Table 3. Threshold Energies for CASSCF and DFT methods for the 1,2 elimination transition state geometries.

Level of Theory	Basis Set	E_o (kcal/mol)
CASSCF(6,6)	6-311+G(2d,p) 10f 6d	71.0
B3PW91	6-31G(d',p')	63.2
B3PW91	cc-pvDZ	61.0

3.2 $CH_3CH_2CHCl_2$

The calculations for the $CH_3CH_2CHCl_2$ system provide very similar results. For this system, the active space varies from CASSCF(6,5) to CASSCF(8,8). The geometry can be seen in Figure 2. The smaller active spaces do not work for 1, 1 dichloropropane for the same reason the CASSCF(4,4) did not work for 1, 1 difluoropropane. The system would not optimize at lower than CASSCF(6,5) and many of the incorrect (6,5) geometries looked similar to the CASSCF(4,4). Once again, the CASSCF(6,6) active space was chosen for the calculations. Images of the 1,1 and 1,2 transition state geometries are shown in Figure 3.

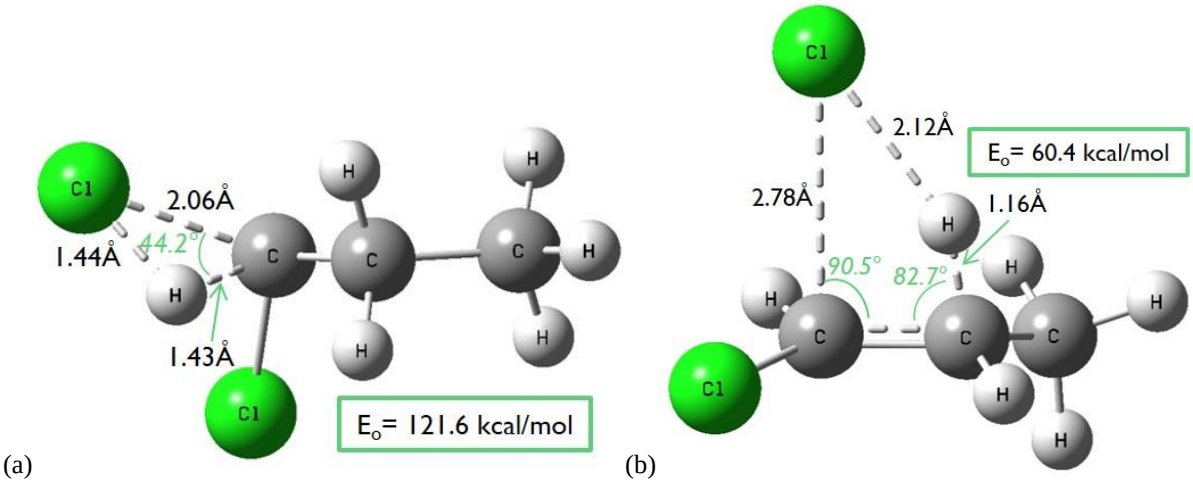

Figure 3. Transition stage geometry of the elimination pathways of 1,1 dichloro propane using CASSCF. (a) is the 1,1 elimination pathway, (b) is the 1,2 elimination pathway.

The 1,1 elimination transition state geometry has a threshold energy that is twice that of the 1,2 elimination transition state. The H-C-Cl bond angle is 15.8° larger than the H-C-F bond angle. In addition, the C-Cl bond distance of 2.06Å is shorter than the C-F bond distance (2.10Å), which does not follow the C-X bond length trends for 1,2 elimination reactions. The difference in geometry plus the unreasonably high energy causes questions to arise regarding the validity of this transition state.

In order to determine if there is a better transition state, the simplest 1,1 HCl elimination reaction, trichloromethane (chloroform) was optimized using CASSCF(6,6). The findings of this optimization are in the figure below. The threshold energy of 68.1 kcal/mol is a much more reasonable energy than 121.6 kcal/mol, both compared to experimental data from our research group and other literature[12]. This successful calculation means that there is quite possibly a better dichloropropane transition state than the one presented in Figure 3a.

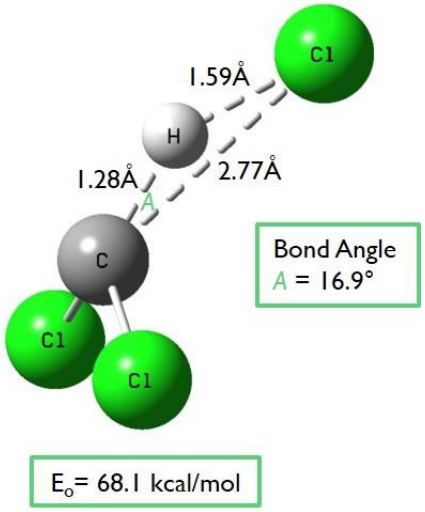

Figure 4. 1,1 HCl elimination transition state geometry for chloroform using CASSCF(6,6).

The 1,1 HCl chloroform elimination optimization does not match the optimizations done by Zhu et al[13]. The Zhu et al calculations seem to have the same issue that was found with the 1,1 difluoropropane linear transition state where the reaction seems to be a hydrogen abstraction as opposed to an elimination. However, the CASSCF geometry of the chloroform follows the 1,1 difluoropropane trends, as well as known experimental data.

Building up from the chloroform, the 1,1-dichloroethane 1,1-HCl elimination transition state geometry was optimized using CASSCF(6,6). The calculated threshold energy is 78.2 kcal/mol, which compared to the chloroform is very reasonable since the 1,1 dichloroethane is the chloroform with an added methyl group. This is more proof that the 1,1 dichloropropane elimination transition state (Figure 3a) is most likely not the lowest energy transition state. The 1,1-dichloroethane 1,1-HCl elimination transition state is found in Figure 5, with a H-C-Cl bond angle of 10.7°, which is much closer to the 16.9° from the chloroform as opposed to the 44.2° angle from the dichloropropane.

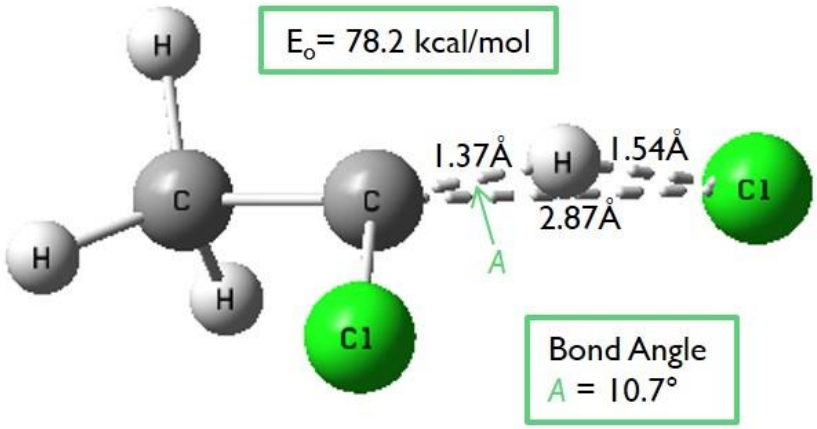

Figure 5. CASSCF(6,6) 1,1 HCl elimination transition state geometry of 1,1 dichloroethane.

4. Conclusion

The 1,1 HF elimination pathway from 1,1 difluoropropane has been computationally determined and found to be accurate based on the threshold energy found using first CASSCF methods followed by DFT calculations. The threshold energy of 70.1 kcal/mol corresponds to the experimental data, meaning that the geometry found is accurate. These results show that the 1,1 eliminations can be optimized by multireference calculations, providing important information about the 1,1 elimination mechanism that was previously unknown.

The 1,1-HCl elimination pathway for HCl elimination was more difficult to isolate. The 1,1 dichloropropane transition state geometry had a threshold energy that was too large to be reasonable, and further research through optimizing the simplest type of 1,1 HCl elimination transition state proved this as well. The optimization of chloroform and 1,1 dichloroethane transition states shows that there is a possible transition state with a lower, more reasonable threshold energy. It is possible that the reason a reasonable transition state geometry is because the energy between the transition state and the product is very small, causing the maximum of the reaction profile difficult to isolate.

For future work, the 1,1-HCl elimination of 1,1 dichloropropane will be optimized by using the 1,1-dichloroethane transition state as the starting geometry. In addition, 1,1-chlorofluoropropane will be optimized for both HF and HCl eliminations, along with 1,1-bromofluoropropane optimization calculations for HBr and HF eliminations. Finally, carbene geometries will be optimized to glean more information about their structures and information about their rates of reactions.

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