

Computational Study of the Oxidation of Volatile Organic Compounds by the OH Radical: An Exploration into the Molecular Realm

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Abstract

Volatile organic compounds (VOCs) present in the atmosphere are regulated by chemical processes and agents called ‘sinks’. These processes are poorly understood and most modeling of atmospheric reactions congregate and often ignore different individual reactions. These studies often ignore the behavior at the molecular level. This study attempts to understand the intermolecular and electrostatic interactions between the hydroxyl radical, the most important sink, and five VOCs. The study was performed in silico using Spartan '16, a computational chemistry software. Møller-Plesset and density functional models were used along two different basis sets, 6-311+G** and 6-31+G*, to generate the transition state geometry and thus the vibrational frequency of the transition state. These methods were used to generate a potential energy surface with the approaching distance and hydroxyl radical rotation as the parameters. The results suggest that as reaction reaches its transition state, electrostatic and intermolecular interactions become important in shaping the reaction's path. This behavior was rationalized by the interactions between the singly occupied molecular orbitals (SOMOs) of the hydroxyl radical and the highest occupied molecular orbitals (HOMOs) of the VOCs. This demonstrates that the often-ignored electrostatic interactions between neutral species influence reaction paths and therefore kinetics. This new understanding provides useful information for modeling of atmospheric chemical processes.

Keywords: VOCs, OH radical, atmospheric reactions

Introduction

The Earth's atmosphere is a complex mixture of different substances like nitrogen, oxygen, argon, and other trace gases. Some of these trace gases make about 1.92 % of dry air and are known as volatile organic compounds (VOCs).¹ A VOC is a carbon-based compound that is present in the atmosphere in its gaseous form. These VOCs consist of carbonyls, alcohols, alkanes, esters, aromatics, ethers, amides, etc. Some examples of these compounds are methane, acetone, chloroform, among others. Some of these compounds are shown in Figure 1.

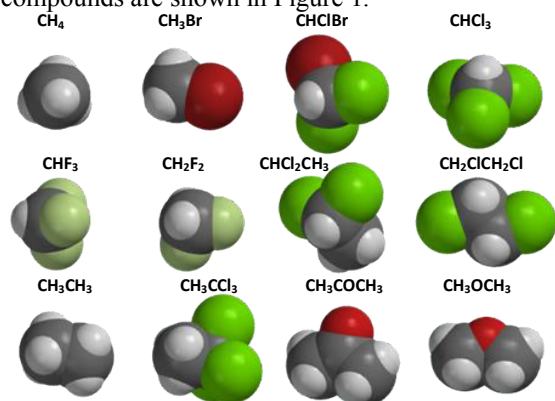


Figure 1. Common VOCs found in the atmosphere. Color legend: white H, dark red Br, gray C, green Cl, red O, light green F).

These organic gases have varied sources but being mainly produced by fossil fuel usage, biomass burning, terrestrial plants, oceans, anthropogenic and biogenic emissions.² These organic compounds have been found to be harmful to humans and the environment.³ In fact, these pollutants are not only found outdoors, but they are common indoors.⁴ However, the existence of these VOCs are regulated by chemical processes in the atmosphere. The agents and processes that reduce the concentration of these gases are called “sinks”.² The most important sink is the hydroxyl radical, $\cdot\text{OH}$.⁵ Other sinks such as ozone (O_3), the nitrate radical, $\cdot\text{NO}_3$, halogen radicals, photolytic fragmentation, and simple deposition also contribute to the reduction of VOCs levels.^{2,6} These sinks are shown in Figure 2.

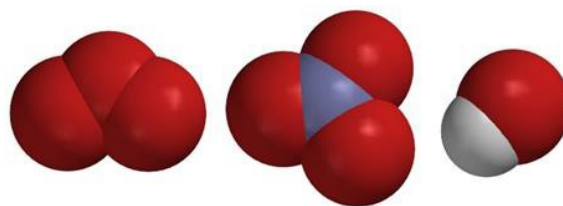
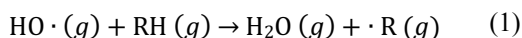


Figure 2. Common atmospheric sinks. From the left, ozone, nitrate radical, and hydroxyl radical. (Color legend: blue N, red O, white H).

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The hydroxyl radical is mainly generated by the photolysis of ozone by UV light in the presence of water vapor.⁷ This radical is the main initiator of the radical oxidation of VOCs in the atmosphere, turning them into different compounds that will either keep reacting and decomposing or will form final products like carbon dioxide and water.⁶ In VOCs, this radical oxidation is started by the hydroxyl radical in a process called hydrogen abstraction.² In this process, represented by equation 1, the radical approaches the VOC and a bond between the oxygen atom and the hydrogen from the VOC forms. The products of this process are water and a radical VOC.



Nevertheless, the chemistry of this or many other sinks is neither simple nor understood with the level of detail necessary to solve the problems caused by VOCs. In fact, the reactions that will occur depend significantly on the VOC reagent. In many cases, the intermediate species have physical and chemical properties that will affect adversely the removal process of the starting organic species.⁵ For example, the oxidation of VOCs with NO_x can produce O₃, which is toxic to humans.² The multitude of factors such as concentration, temperature, location, climate change, among others increase the difficulty when attempting to understand atmospheric chemistry. Climate change is becoming an increasing concern for researchers trying to study the atmospheric chemistry because as the symptoms of climate change begin to change the behavior of the atmosphere, this will have a large effect on the regulatory processes of VOCs.²

The importance of the hydroxyl radical and the aspects that affect the way it is regulated in the atmosphere make it a suitable target for study. In this study, hydrogen abstraction reactions between the hydroxyl radical and five VOCs are investigated. The purpose of this project is to explore the molecular behavior of these reactions. This behavior refers to the interactions between neutral species and the effects their mechanisms will have on kinetics. This work will consist of the study of structure, thermodynamics, and possible application to kinetics. The study will bring insight into the often-ignored molecular interactions in the microscopic world and their possible effects in the macroscopic level.

Background and literature review

Research on the kinetics of the hydrogen abstraction reactions by the hydroxyl radical is varied but is mainly focused on the experimental determination of reaction rates and the modeling of the reaction rates of these species in the atmosphere. However, the study

of these processes through computational methods is less common. The few studies that have in silico methods involve gas phase calculations used to determine the reaction rates for common reactions between the sink and a varied range of VOCs.

A good example of such research comes from the study by Petit et al., where computational calculations were performed on a list of different organic compounds to determine the rate coefficients for the hydrogen abstraction reactions.⁶ However, Petit's study focuses on the kinetics and computational methods to determine the rates exclusively and does not inquire in any other direction to further explain the results.

A possible direction in which to investigate is the more in-depth chemistry of the sinks, not only their respective reactions with VOCs but also their origins. Monks discussed the typical reaction rates for common sinks (among them the hydroxyl radical), the origin of these sinks, interactions with other sinks, and the factors that affect the presence of these sinks.⁷ However, this work is short and broad and it does not address some of the problems that were discussed earlier, such as intermediate chemistry and the new factors that affect kinetics such as climate change.

Climate change is becoming a concerning factor, especially with the conclusions from the Intergovernmental Panel on Climate Change, IPCC, in which it was declared that the last three decades to be the warmest in the last 800 years and possibly 1400 years.⁸ Therefore, the climate change factor must be an important aspect to be considered in the new research, since the atmosphere is a dynamic system and models are often static.

Another example of the research done in the hydroxyl radical chemistry is the work by Wang et al. In their work, computational methods were used to understand a significant source of the hydroxyl radical. They focused their work around the formation of the hydroxyl radical from the O₃-H₂O complex.⁹ The aspect to notice from this work is the use of visualization that allows the reader to understand the meaning of the numeric information using 3D molecular modeling.

Although the sample studies hereby presented are strong in their own specific areas, they do not consider all the aspects that provide a more profound understanding of the problem of modeling the molecular behavior of atmospheric reactions. In fact, most studies ignore the molecular factors when they model atmospheric processes. Some cluster all the important aspects of a system and ignore the complexities in order to simplify the problem.² To truly obtain a complete understanding of the problem produced by VOCs and their effects in our health and environment, one must look farther. One must investigate the molecular realm. In this new world, hints are hiding everywhere. Therefore, the purpose of this study is to explore this

microscopic universe in order to understand the system in place.

This project will focus on studying five systems consisting of hydrogen abstraction by the hydroxyl radical from five VOCs, mainly organic compounds with halogens such as fluorine, chlorine, and bromine. The method is based on those used by Tzima, Chandra, Korchowiec, and Jursic, that computationally studied the hydrogen abstraction by the OH radical of different VOCs in the atmosphere.¹⁰⁻¹³ In this project, transition state geometry optimizations were used to determine the structure of the transition state. The transition state structure was used to generate potential energy surfaces that provided insights into the interactions at the transition state. Behaviors observed in the potential energy surfaces were rationalized using electrostatics and frontier molecular orbital theory.

This study has the purpose of revealing the interactions between the target species that are ignored by the fact the species are neutral. Furthermore, this project has the purpose of revealing the origins of molecular behavior as observed in potential energy surfaces.

Computational methodology

This project was carried *in silico* using the software Spartan '16.¹⁴ This software was used to carry out the geometry optimizations, transition state geometry optimizations, hydrogen abstractions simulations, among other calculations.

The first part of the experiment consisted of the collection of structural and energetic data for the unreacted VOCs. The geometry optimizations were carried using the following models: MP2/6-31G* and 6-311+G**, B3LYP/6-31G* and 6-311+G**, and EDF2/6-31G* and 6-311+G**. MP2 stands for second-order Møller-Plesset model, which provides great values in geometry calculations.¹⁵ B3LYP, which stands for Becke, 3-parameter, Lee-Yang-Parr, is a “hybrid” of density functional models and provides similar structural results to those of MP2.¹⁵ Finally, EDF2 stands for ‘Empirical Density Functional 2’, which is another density functional model that has a similar performance to MP2 and B3LYP.^{15,16} These models were chosen because of their performance in producing accurate structural values in geometry optimizations compared to other models. 6-31G* and 6-311+G** represent the basis sets of each model, these are functions that represent the overall state of a system.¹⁵

Data obtained from the geometry optimization consisted of infrared spectra, molecular orbitals, and their corresponding energies, thermodynamic values, vibrational frequencies, charges, bond orders, electrostatic potential maps, and images of the molecules and their highest occupied molecular orbitals

(HOMOs) and lowest unoccupied molecular orbitals (LUMOs).

The second part of the study consisted of constructing and calculating the transition states for the five hydrogen abstraction reactions. This was done by running transition state geometry calculations on all the guessed transition state complexes. The vibrational imaginary frequency was chosen for each transition state to represent the approaching radical to the hydrogen that will be abstracted. Using this vibrational mode for the transition state, a 2D potential energy surface was generated by selecting the 360° rotation of the hydroxyl radical with respect to the C-H (abstracted hydrogen) bond. Using the same vibrational mode, a similar 2D potential energy surface was generated for the distance between the oxygen in the radical and the hydrogen in the VOC.

The last of these experiments consisted of studying the LUMOs and HOMOs of each VOC and the sink to understand the structure of the transition state and provide further information about the sink-VOC interactions. In this part of the experiment, the degree of overlap between lobes of equal phase was taken as a source to rationalize the behavior observed in the potential energy surfaces.

Results and Discussion

Methane

Methane, CH₄, is a common VOC and the first target of this study. Its structure is shown in Figure 3. Methane has little to none electrostatic interactions with any other molecules. This is more clearly shown in its electrostatic potential map (EPM) in Figure 3. In blue are the areas of low electron density, that is the least negatively charged areas, and in red are shown areas with high electron density, which are the most negatively charged areas.

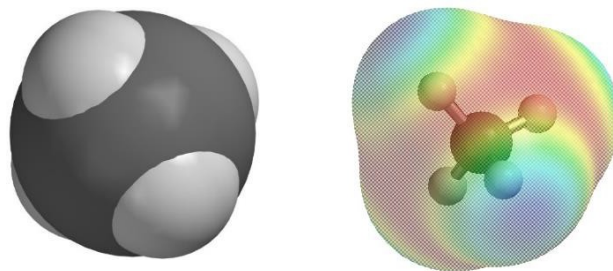
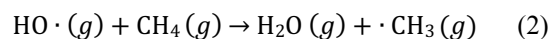


Figure 1. Space filling of CH₄ and EPM of methane. Model: B3LYP 6-311+G**.

The reaction of methane with the hydroxyl radical is shown below in equation 2.



To physically represent this reaction, the transition state was built by placing the OH radical at roughly 100° angle from the hydrogen that will be abstracted. The transition state for this reaction is shown in Figure 4. This image represents the transition state with a combination of electron density and EPM surfaces (mesh and color, respectively). Structural information about the transition state models for methane is summarized in Table 1. The different models show some structural similarities, but with some differences due to the model itself. This structural data showed great agreement with literature data with only a few deviations.^{12,13} However, the largest difference comes from the imaginary frequencies that represent the transition state.

Unfortunately, a single image of the transition state does not represent the full behavior of the reaction. For a better representation, is necessary to depict the energy of the system as a function of the approaching distance

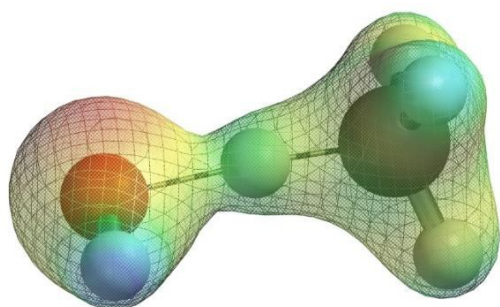


Figure 2. CH_4 -OH transition state represented by an EPM surface and an electron density gray mesh. Model: B3LYP 6-311+G**.

between the radical and methane and the energy of the system. This plot is shown in Figure 5 and is accompanied by snapshots of the reaction complex. This image shows the beginning of the hydrogen abstraction as the hydroxyl radical approaches hydrogen in methane. In the transition state, the electron density is observed in between the radical and methane. Finally, at the lowest point, water is formed along with the methyl radical.

To further understand this reaction, it is necessary to bring the 3D potential energy surface. However, to understand its meaning it is necessary to view the behavior of the reaction complex. The 3D potential

energy surface for the hydrogen abstraction of methane is shown in Figure 6. The axis perpendicular to the energy of the system corresponds to the distance between the oxygen atom in the hydroxyl radical and the hydrogen that will be abstracted from methane. The second axis that is perpendicular to the energy corresponds to the rotation of the hydroxyl radical with respect to the C-H bond. The meaning of a potential energy surface is that it reveals the paths that a reaction can follow. This is done by following the valleys of lowest energy as one move from the reagents towards the products passing through the transition state.

The 3D potential energy surface represents the hydrogen abstraction of methane by the hydroxyl radical. To understand the plot, one starts at the region indicated by the blue arrow, this corresponds to the state where the reagents exist. The next important region is that indicated by the orange arrow, this is the transition state. Finally, the black arrow indicates the region where the products exist.

Given the information above, it is possible to discuss the most important aspects of this plot. The first aspect to notice in the small hump that characterizes the transition state. This hump only occurs in the angle of OH rotation between 100-200°. This means that as the OH radical rotates with respect to methane, at 100-200°, unfavorable electrostatic interactions between the radical and methane increase. Although the difference in energy is of a few kJ mol^{-1} , it is still significant. This small hump is also observed in the product region. This confirms that as the OH passes through that angle, unfavorable interactions increase. A possible rationale for this effect is that as the OH rotates, charges in the radical and/or methane interact unfavorably to increase the energy. To prove this rationale is necessary to monitor charges, distances, and the energy of the system as the OH rotates.

To rationalize the behavior observed in Figure 7, the system between the hydrogen atom in the radical and carbon is chosen. The reason for this choice is that as seen in Figure 5, the abstracted H has the highest positive electrostatic charge and C the most negative. Therefore, the interactions between two opposite-charged atoms will decrease the energy as they approach each other and vice versa. In Figure 7, as the

Table 1. Structural Analysis of CH_4 -OH Transition State.

Model	O-H _{abs} /Å	C-H _{abs} /Å	∠CHO	Imaginary Frequency /cm ⁻¹
B3LYP 6-311+G**	1.339	1.203	173.5°	-870
EDF2 6-311+G**	1.371	1.190	172.2°	-416
MP2 6-311+G**	1.337	1.176	170.8°	-1793

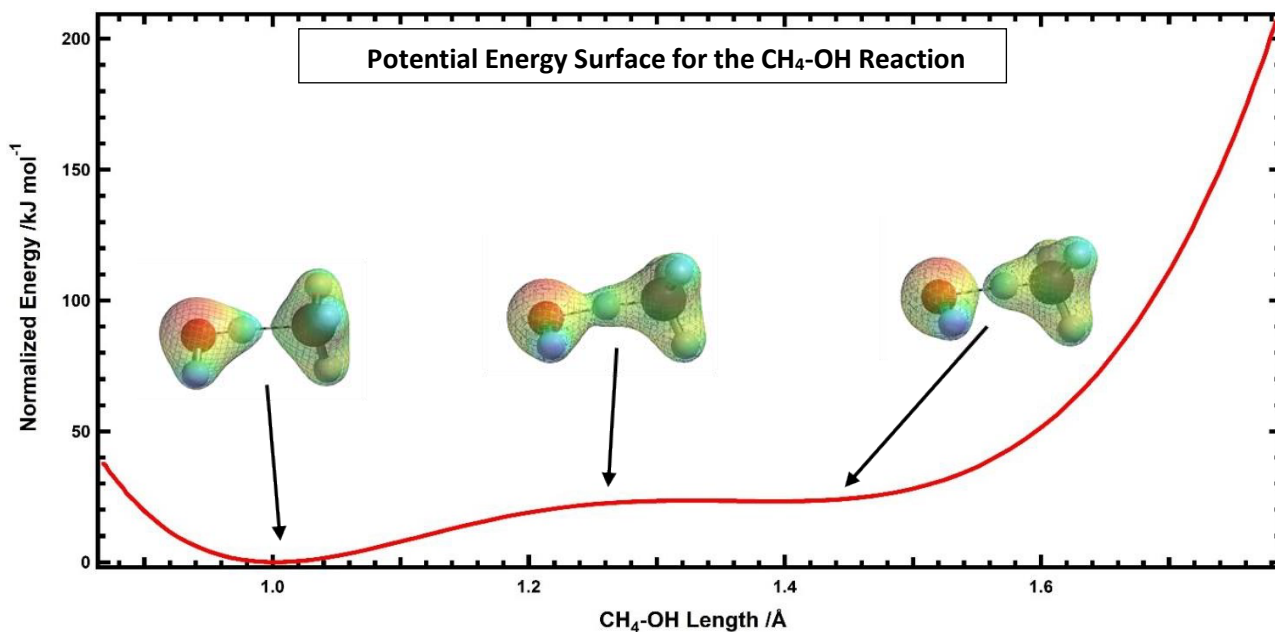


Figure 3. 2D potential energy surface for the reaction between methane and the hydroxyl radical. This plot has snapshots of the reaction that shows the formation and breaking of bonds. Model: EDF2 6-311+G**.

radical passes through the 100-200° angle, the distance between H and C increase rapidly. Therefore, as expected the energy will increase since C and H cannot interact favorably to decrease the energy of the system. The interactions between the inversely charged regions in the complex provides evidence on how electrostatic interactions, even in neutral species, affect the path of a reaction. However, to further understand the reaction pathway, it is necessary to introduce the interactions between molecular orbitals.

Frontier molecular orbital theory refers to the model that explain chemical behavior based on the interactions between molecular orbitals (MOs) in different molecules. Frontier MOs interact based on their geometry and their energy. The energy gap between them must be relatively small for bonding interactions to take place. Geometry is important to allow an adequate overlap between the lobes of a molecular orbital. When a good overlap occurs between

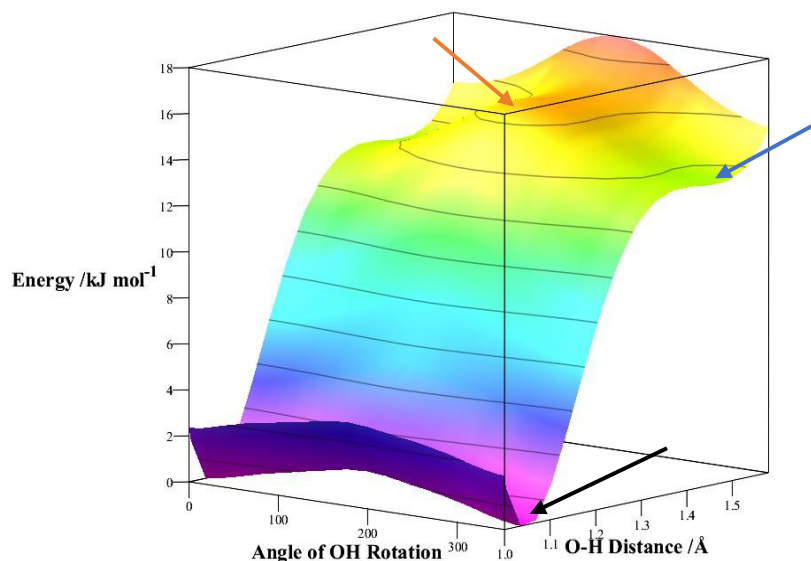


Figure 4. 3D potential energy surface for the hydrogen abstraction of methane. Model: EDF2 6-311+G**.

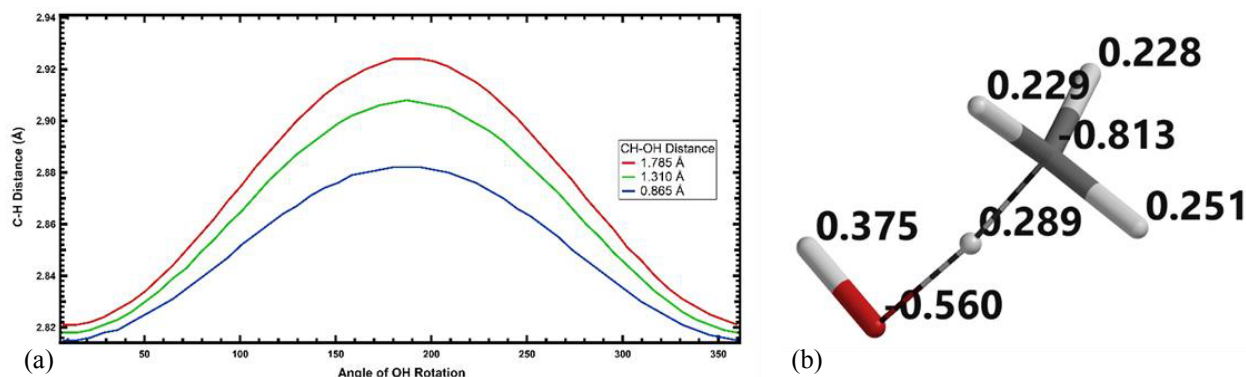


Figure 5. (a) As the OH radical rotates through 100-200°, the distance between the hydrogen in the radical and carbon in the VOC increases. (b) Carbon has the most negative atoms in the CH₄-OH complex and hydrogen is the most positive.

two lobes of the same phase (same color in diagrams) the energy of the system will decrease. However, when two lobes of different phases overlap or two lobes with the same phase do not overlap well the energy of the system increases.

In the CH₄-OH system, two MOs play an important role in shaping the transition state geometry and the path of the reaction. The electron of methane that will be part of the new O-H bond is in the HOMO. The electron of the OH radical that reacts with methane is located at the Singly Occupied Molecular Orbital, SOMO. A diagram

showing these MOs, their energies, and their interactions are shown in Figure 8.

The two SOMOs of OH with different energies correspond to the MOs with different electron spin. For methane, there are three degenerate HOMOs with different structures. The red lobe of the SOMO is not symmetrical under rotation with respect to the C-H bond. Additionally, only the red lobe of HOMO 2 is symmetrical under the rotation mentioned before. Therefore, when the OH radical approaches methane, the SOMO and HOMO will interact as shown in Figure

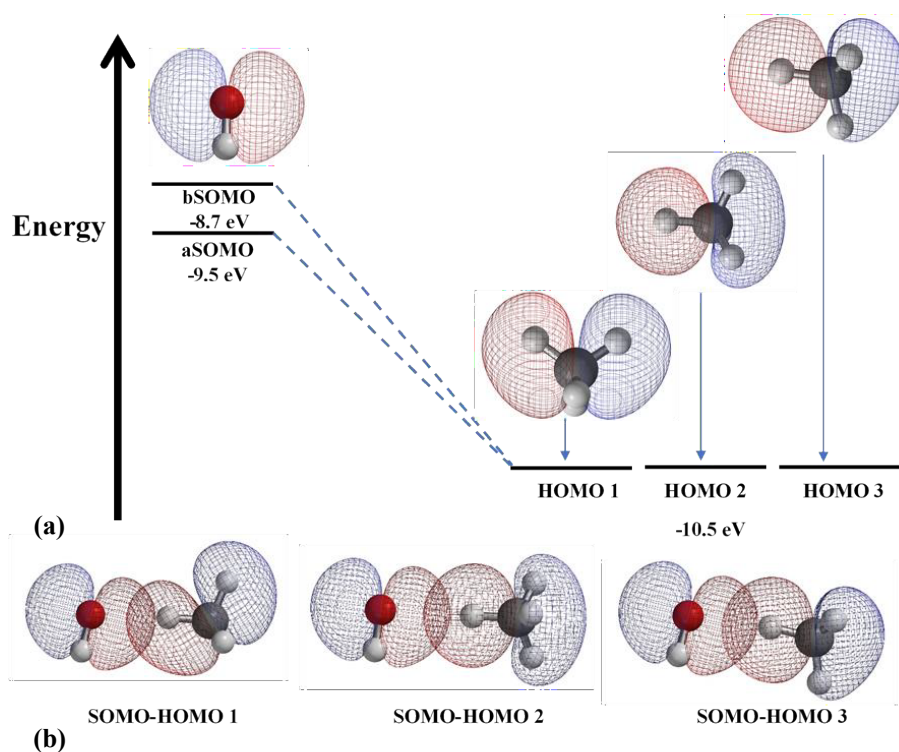


Figure 6. (a) Energy diagram representing the energy interactions between the SOMOs of the OH radical and the HOMOs of methane. The different shapes of the HOMOs of methane produce different degrees of overlap. (b) Interactions between the different HOMOs and SOMO.

8 (b). Figure 8 (b) shows the different degrees of overlap between the HOMOs and the SOMO. The rotation of OH produces fluctuations in the overlapping between the SOMO and the HOMO. These fluctuations in the overlapping will produce situations in which both MOs will constructively interfere well and thus reduce the energy of the system. Since the MOs are asymmetrical, there are angles in which the overlapping is reduced and thus increases the energy of the system. Therefore, the origin of the energy hump observed in the potential energy surface is caused by the change in the level of overlap of the MOs as the hydroxyl radical rotates with respect to methane.

Methyl bromide

Methyl bromide is the second molecule of interest in this project. Its structure is shown in Figure 9. In contrast to methane, methyl bromide is a polar molecule, as it is seen in its EPM in Figure 9, thus it is expected to have stronger molecular interaction produced by dipole-dipole interactions. Like methane, upon abstraction methyl bromide becomes a radical and the hydroxyl radical becomes water.

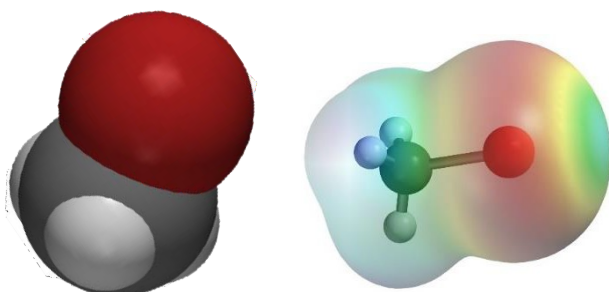


Figure 9. Space filling of CH₃Br and EPM of methyl bromide. Model: B3LYP 6-311+G**.

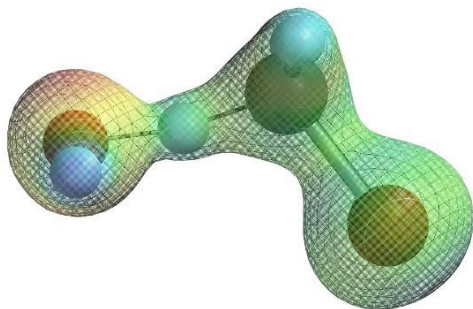


Figure 10. CH₃Br-OH transition state represented by an EPM surface and an electron density gray mesh. Model: B3LYP 6-31G*.

The transition state of this reaction is shown in Figure 10. The transition state structure of methyl bromide has similar structural characteristics to those of the transition state of methane. Details on the transition

state are summarized in Table 2. The main difference is the CHO angle. Like methane, the values obtained between different models differ by small fractions, except for the imaginary frequency that is drastically different as it was observed in methane. These structural values agree well with literature values.¹⁰

Given the structural changes of the methyl bromide system compared to that of methane, it is expected that the 3D potential energy surface is quite different from that of methane. The potential energy surface is presented in Figure 12. In this potential energy surface, the most particular aspect is the presence of two humps rather than one as in the case of methane. The two humps are produced by electrostatic interactions between different atoms in the reaction complex. These interactions are observed in Figure 11. The first plot shows that as positively charged atoms (solid lines) decrease their distance from the hydrogen in the radical (positively charged) the energy will increase. This effect occurs in the angles 100-250°, the approximate regions where the humps are observed in the potential energy surface. The second plot indicates that positively charged atoms reach their lowest charge between 140-260° and the negatively charged atoms reach their least negative charge. Therefore, an increase in energy is expected to occur in these angles because the charges are not interacting favorably. For those reasons, two humps with a region of high energy between them is observed in the transition state.

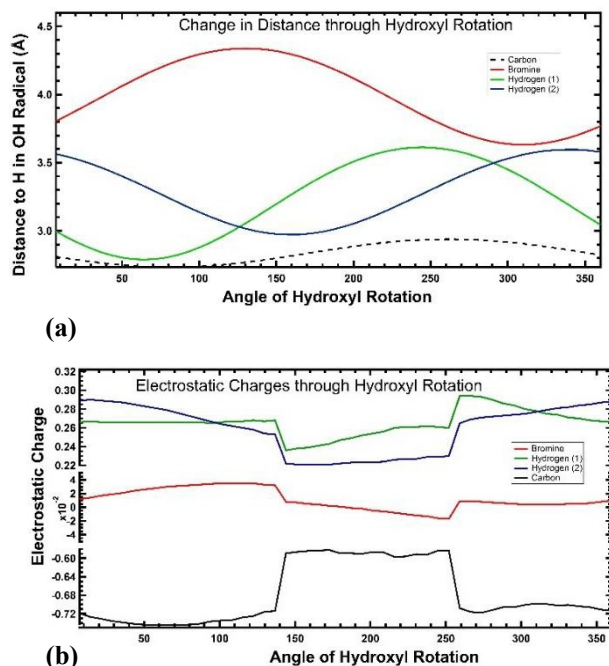


Figure 11. (a) Describes the distances between the H in the OH radical and different atoms as the radical rotates. (b) Describes changes in electrostatic charges as the OH radical rotates.

Table 2. Structural Analysis of CH ₃ Br-OH Transition State.				
Model	O-H _{abs} /Å	C-H _{abs} /Å	∠CHO	Imaginary Frequency /cm ⁻¹
B3LYP 6-31G*	1.296	1.225	165.7°	-1268
EDF2 6-31G*	1.335	1.198	161.8°	-801
MP2 6-31G*	1.280	1.209	170.0°	-2482

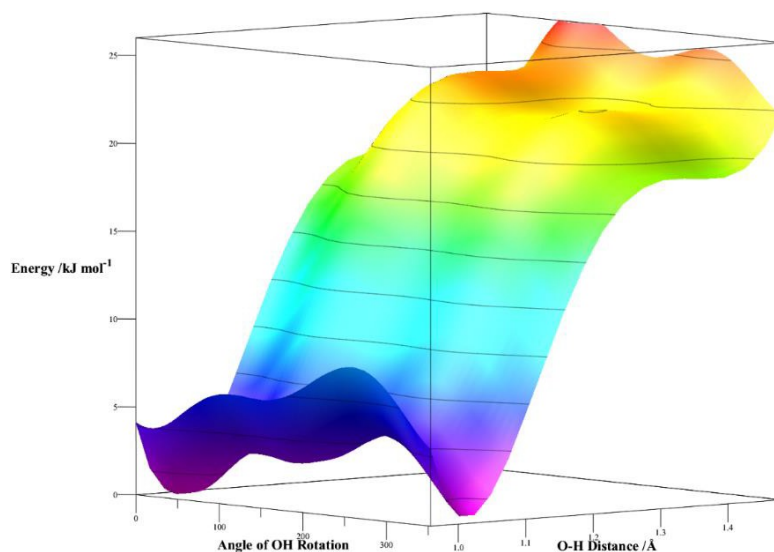


Figure 12. 3D potential energy surface for the hydrogen abstraction of methyl bromide. Model: EDF2 6-31G*.

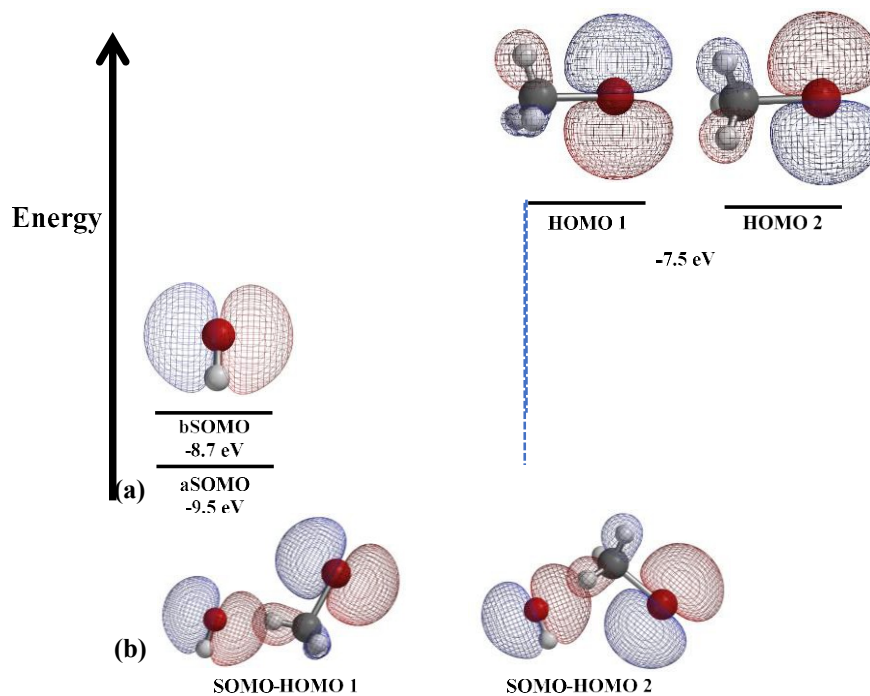


Figure 13. (a) Energy diagram representing the energy interactions between the SOMOs of the OH radical and the HOMOs of methyl bromide. The different shapes of the HOMOs of methyl bromide produce different degrees of overlap. (b) Interactions between the different HOMOs and SOMO.

A similar effect is observed in the regions where the products exist. However, this area is not of interest to this project. Nonetheless, the shape of the potential energy surface for the products and reagents have the same origins.

Having observed the molecular behavior of the potential energy surface, it is time to rationalize it using frontier molecular orbital theory. A diagram like Figure 8 is shown in Figure 13. The MOs diagram shows a different energy behavior to the MO diagram of methane. In the case of methyl bromide, the energy of the HOMOs is higher than those of the SOMOs. Nevertheless, the energy gap between the two different MOs is small which is necessary for the MOs to interact.

The most important aspect of the MOs diagram is the shape of the lobes in the different MOs. In contrast to methane, the lobes for bromine are larger than those of the hydrogen atoms. This represents a source for new interactions between the OH radical and methyl bromide. As the radical approaches, the distance decreases between the lobes of different phase that surround bromine. Since the two lobes have different phases, there will be antibonding interactions caused by destructive interference. These interactions are unfavorable because as the wavefunctions destroy a node (a region with a 0% probability of finding an electron) is created, this reduces the volume of where the electrons can move thus increasing the energy of the system. Furthermore, these types of unfavorable interactions will occur between the other hydrogens (not abstracted) since the phase of their lobe is the opposite to that of the hydrogen that will be abstracted. Therefore, as the OH radical rotates it will encounter two lobes with opposite phases. The level of interaction is different between the two lobes (non-abstracted hydrogen and bromine) because of the relative size of the lobes. Therefore, the increase in energy due to these interactions will be different. The unequal interaction between the lobes of the MOs explains the presence of two unequally-sized humps in the transition state found in the potential energy surface.

Fluoroform

Fluoroform, CHF_3 , has the most halogen atoms compared to the previous two cases. Its structure is shown in Figure 14. Since fluorine is the most electronegative atom, it is expected that the hydrogen atom is highly electron deficient. This is confirmed based on the electrostatic potential map shown in Figure 14. Therefore, stronger interactions with other molecules are expected during a reaction.

The hydrogen abstraction of fluoroform by the hydroxyl radical occurs through the same process as the two previous molecules, thus there is not a drastic difference between the three transition state structures. The transition state structure is shown in Figure 15 along with its structural data in Table 3. These values agree well with literature.¹² The structural measurements of the transition state of fluoroform do not differ from the structures previously observed. Nevertheless, in order to understand the reaction better, the potential energy surface is required. The potential energy surface is shown in Figure 16.

The potential energy surface of fluoroform shows an identical behavior to that of methane. It will make sense given that, like methane, fluoroform has three identical atoms with which the hydroxyl radical may interreact. Nonetheless, it has been observed that the major cause of the shape of the transition state energy profile is the MO interaction. In order to understand the

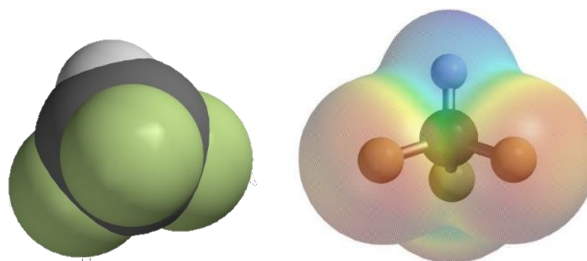


Figure 14. Space filling of CHF_3 and EPM of difluoromethane. Model: B3LYP 6-31G*.

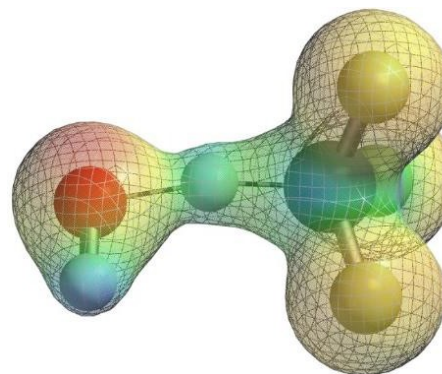


Figure 15. CHF_3 -OH transition state represented by an EPM surface and an electron density gray mesh. Model: B3LYP 6-31G*.

Table 3. Structural Analysis of CHF_3 -OH Transition State.

Model	O-H _{abs} /Å	C-H _{abs} /Å	∠CHO	Imaginary Frequency /cm ⁻¹
B3LYP 6-31G*	1.252	1.249	167.7°	-1455
EDF2 6-31G*	1.283	1.220	166.9°	-1061
MP2 6-31G*	1.244	1.229	162.3°	-2750

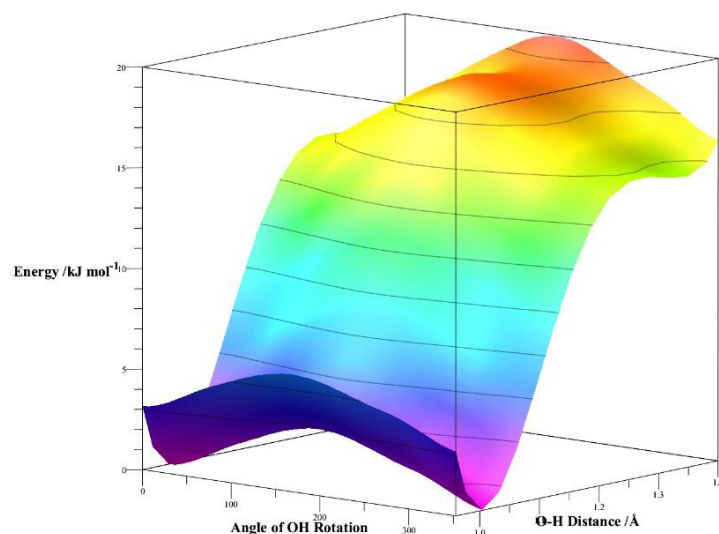


Figure 16. 3D potential energy surface for the hydrogen abstraction of fluoroform. Model: EDF2 6-31G*.

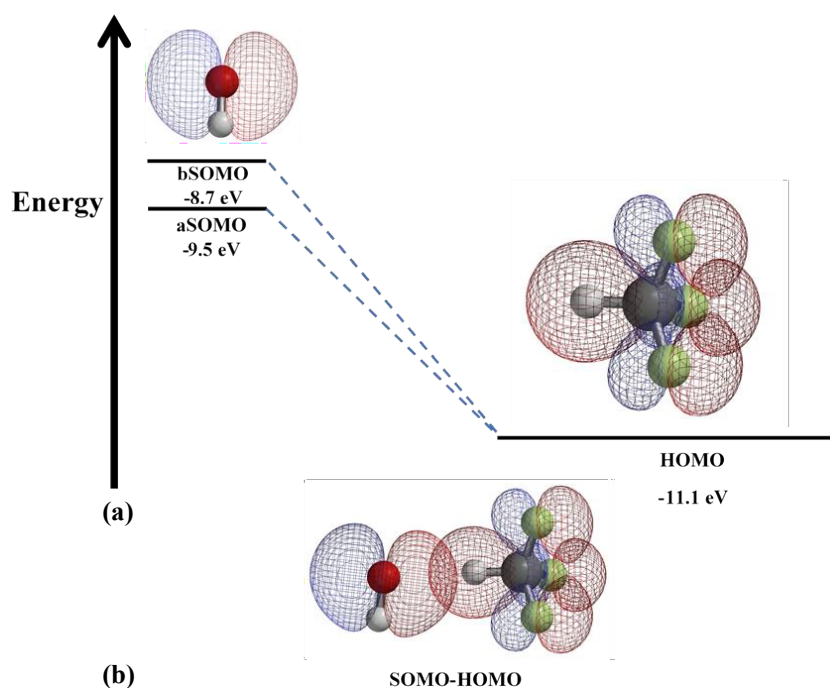


Figure 17. (a) Energy diagram representing the energy interactions between the SOMOs of the OH radical and the HOMO of fluoroform. The shape of the HOMO of fluoroform produce different degrees of overlap. (b) Interactions between the HOMO and SOMO.

reaction of fluoroform and the hydroxyl radical, the MO interactions are required. The diagram shown in Figure 18 represents the HOMOs and SOMOs of the reagents and their energy and interactions.

In the case of fluoroform, it is possible to observe a relatively complex HOMO compared to the other molecules that have been previously discussed. In fact,

the first aspect that may be noticed is the presence of three lobes with a different phase below the lobe that will react with the SOMO. Previous experience may suggest that the three lobes will provide for three increases in energy (or more) due to destructive interference. However, what is observed in the potential energy surface is one hump only. This is caused by

simple structural factors. First, the lobe of the HOMO that will be interacting with the SOMO is much larger, thus covering the space where the hydroxyl radical is rotating. This will reduce or not allow for any interactions between the opposite-phased lobes of the HOMO. Second, the distance between the abstracted hydrogen from the carbon atom is the largest in fluoroform when compared to the previous molecules. This increase in length suggests that the transition state occurs far away from the carbon center and thus from the opposite-phased lobes. The increase in energy is caused by the asymmetry of the lobes that will produce different degrees of overlap. This was the same behavior that was previously observed in methane.

Methyl chloride and difluoromethane

Having discussed methane, methyl bromide, and fluoroform, it is time to draw qualitative conclusions about the observed behavior. This section will serve the purpose of laying out the results for the rest of the molecules to compare with the molecules that have been discussed. The molecules that will be discussed in this section are methyl chloride and difluoromethane, shown in Figure 18.

The transition states shown in Figure 19 show similar patterns to those observed in previous transition state complexes. The structural information is presented in Tables 4 and 5. This data showed good agreement with literature values.^{11,12}

Methyl chloride and methyl bromide are structurally similar. Therefore, it is expected their potential energy surfaces are similar. Like in methyl bromide, methyl chloride showed two humps produced by the HOMO-SOMO interaction.

The potential energy surface of difluoromethane shows a different behavior from what has been previously observed. There is only one hump, but it appears to be deformed by the presence of more than one hump being combined/overlapped over each other. This combination of humps is because fluorine is the smallest halogen used in this experiment, therefore the bond angle between the atoms (and therefore the lobes)

is the smallest. Therefore, it is expected that the increases in energy occur closer to each other since the lobes are relatively close.

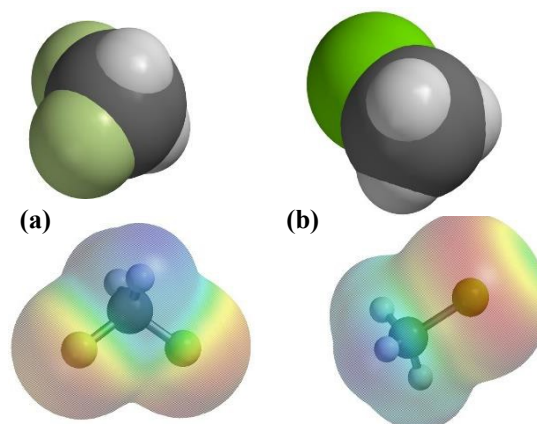


Figure 18. Space filling model and EPM of CH₂F₂ (a) and methyl chloride (b). Model: B3LYP 6-31G*.

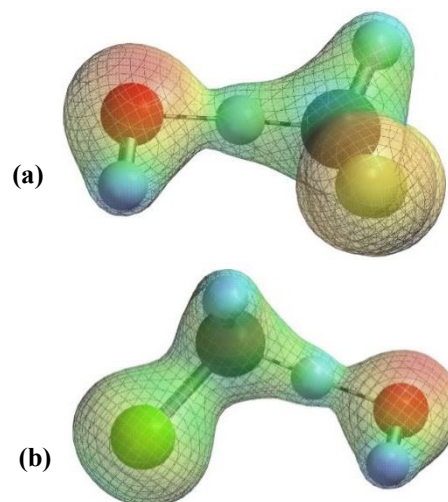


Figure 19. CH₂F₂-OH (a) and CH₃Cl (b) transition states represented by an EPM surface and an electron density gray mesh. Model: B3LYP 6-31G*.

Table 4. Structural Analysis of CH ₃ Cl-OH Transition State.				
Model	O-H _{abs} /Å	C-H _{abs} /Å	∠CHO	Imaginary Frequency /cm ⁻¹
B3LYP 6-31G*	1.323	1.212	166.1°	-1033
EDF2 6-31G*	1.355	1.197	163.5°	-427
MP2 6-31G*	1.285	1.209	159.2°	-2501

Table 5. Structural Analysis of CH ₂ F ₂ -OH Transition State.				
Model	O-H _{abs} /Å	C-H _{abs} /Å	∠CHO	Imaginary Frequency /cm ⁻¹
B3LYP 6-31G*	1.299	1.225	163.0°	-1269
EDF2 6-31G*	1.346	1.195	161.7°	-717
MP2 6-31G*	1.287	1.207	170.5°	-2459

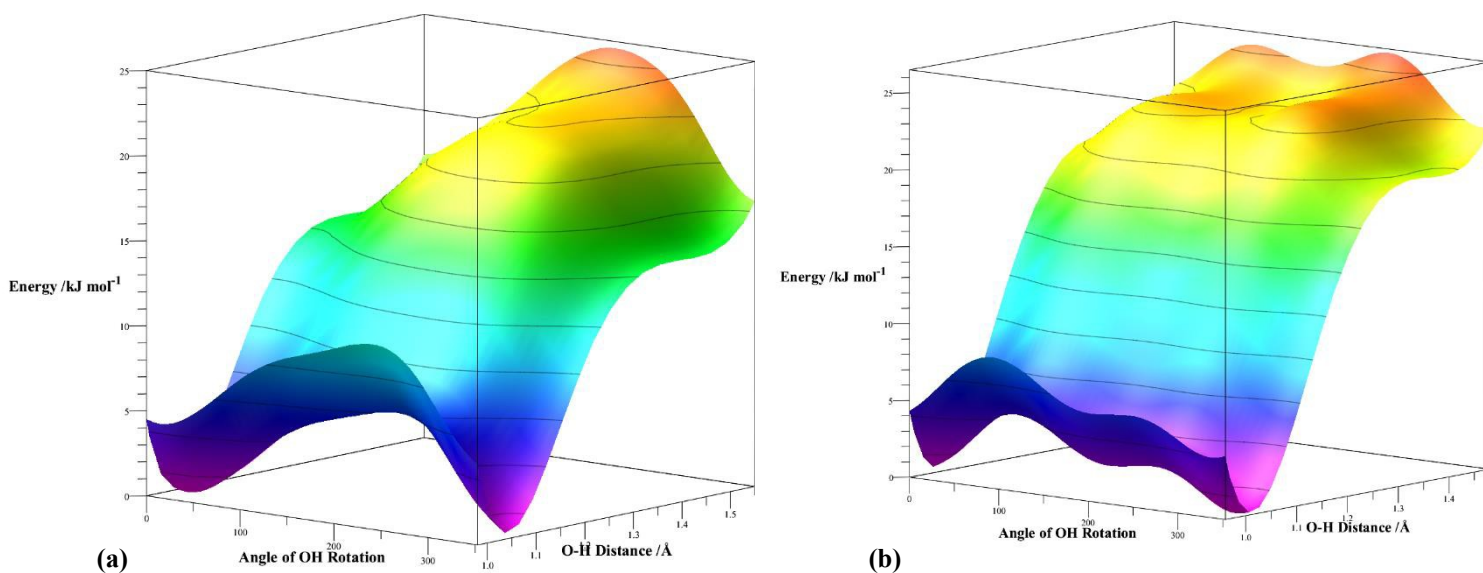


Figure 20. 3D potential energy surface for the hydrogen abstraction of difluoromethane (a) and methyl chloride (b). Model: EDF2 6-31G*.

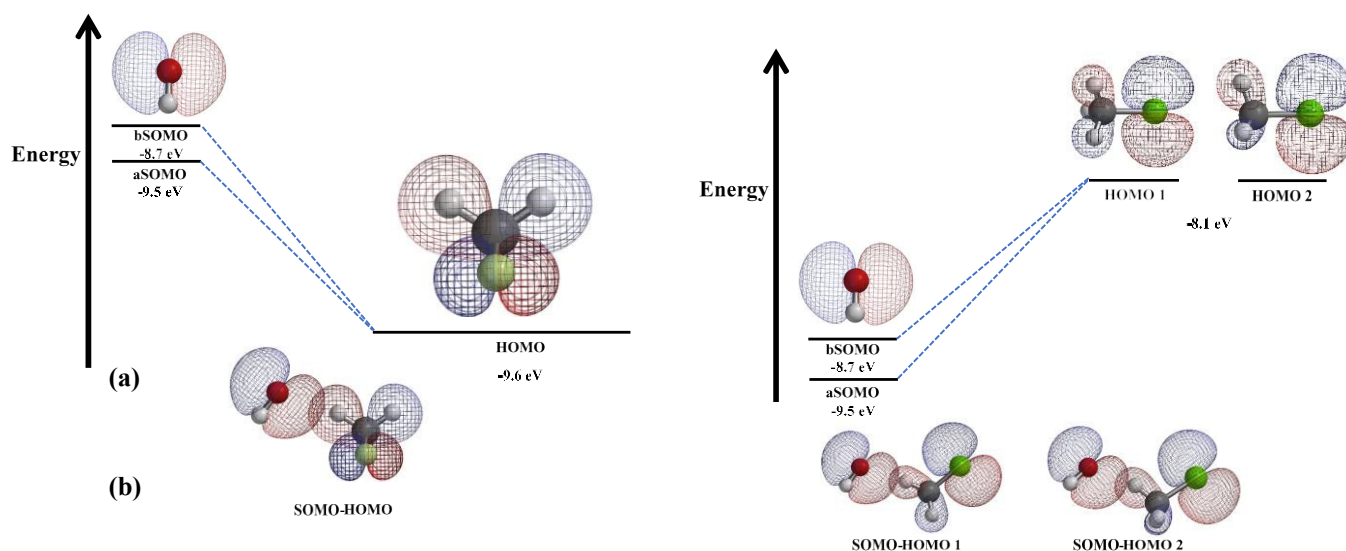


Figure 21. (a) Energy diagram representing the energy interactions between the SOMOs of the OH radical and the HOMO of difluoromethane (left) and methyl chloride (right). The shape of the HOMO(s) produces different degrees of overlap. (b) Interactions between the HOMO(s) and SOMO.

Summary and conclusions

The purpose of this project was to explore a set of different radical reactions in the atmosphere to better understand the aspects that affect them. The reactions covered discussed in this project occur between VOCs and the hydroxyl radical. Understanding what molecular factors affect these reactions is crucial to model and understand the presence and regulation of these VOCs in the atmosphere. These reactions are important processes that must be understood from a microscopic level. The VOCs discussed in this project are methane, methyl bromide, fluoroform, methyl chloride, and difluoromethane. When these molecules react with the hydroxyl radical the reaction will yield water and a radical derivative of the VOC.

The computational approach that was taken in this project had the main goal of generating potential energy surfaces for the reactions. These potential energy surfaces brought insight into how a reaction may proceed through one or several energy paths from reagents to products. The energy behavior observed in the potential energy surfaces was supported through the use of electrostatic molecular interactions between different atoms in the transition state complex. HOMO-SOMO interactions were used to rationalize the origin of these interactions and behavior.

It was observed that as the hydroxyl radical rotates with respect to the O-H(abtracted) bond, the energy increased in several regions represented as humps in the potential energy surfaces. These humps were caused when atoms with opposite or equal charge signs interacted unfavorably. However, the shape of these humps originated from the HOMO-SOMO interactions. It was observed that as lobes with opposite phases interacted closely there was an increase in energy due to the destructive interference between the HOMO and SOMO. This indicated that the degree of overlap played an important role in shaping the potential energy surface. The degree of overlap depended on the shape of the interacting lobes and the distances between them. Therefore, there is a direct qualitative relationship between the shape of a potential energy surface and the shape of the HOMO lobes in the VOC.

From the evidence presented in this project, it is possible to conclude that the MO interactions and electrostatic interactions play a crucial role in shaping the path of a chemical reaction and therefore the reactions rates that are observed through experimental measurements. However, it is important to mention that the potential energy surfaces only represent a very particular set of conditions and do not fully represent all the possibilities through which the same process can occur. The method that was used to generate the data limited the degrees of freedom of movement of the molecule. In fact, there is no reason for which the

molecules would not be allowed to approach in another direction other than the ones presented in this project. Nonetheless, the potential energy surfaces presented here represent the lowest energy interactions in a system of multiple possible energy paths. Therefore, although the results do not represent every possible process, they do represent an excellent sample of behavior to understand these chemical reactions.

Implications

The purpose of this project was to explore the aspects that influence chemical reactions at the microscopic level. This understanding is crucial in making accurate predictions of chemical processes at the macroscopic level. These predictions are useful tools in creating modeling that provides information about the presence and regulation of VOCs by sinks. This knowledge is central to understanding the complex chemistry that occurs in the atmosphere. The atmosphere is essential for humans and life in general. Therefore, obtaining new tools and understanding of processes that endanger the stability of the atmosphere must be a priority to scientists.

Future Work

There is still several questions and system that provide intriguing topics of investigation in this field. As it may be noticed from this project, all the molecules contained only three halogens F, Cl, and Br. It would be interesting to study molecules that contain other atoms. Additionally, all the molecules were limited to 5 atoms due to calculation costs. Larger molecules could provide interesting results as the molecule becomes more dynamic upon the addition of more carbon atoms or groups. Finally, the project that may provide the most interesting results will be one in which the behavior observed for the transition states is a mathematical model to then be introduced into a mathematical equation for the reaction rates of a specific reaction.

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