Dear Dr. Glaser,

Sincerest thanks for your response and reviewer’s comments on our proposal on November 30th. We were pleased with their suggestions and have taken them all into consideration during our revision. Based on the reviewers’ recommendation, we have made changes to our proposal. The changes are described as follows:

Major Revisions.

1. Describe the meaning of values in preliminary data section
2. Change the spacing issue on the proposal

Response to Reviewer 1

1. *The only thing can be improved is to state how the preliminary results support your hypothesis with more details.*
   As the reviewer suggest we have describe the data in preliminary data section and discussed what those data means and what we can conclude from them.

2. *The idea of the space before each specific aim is not necessary*
   As the suggestion, we have change the space issue in the whole proposal and specifically spacing in the specific aim section.

3. *There is a lot of unnecessary space in the whole proposal. There’s no need to have space between two paragraphs. More information can be provided with the same limit of page*
   Thank you. The issue solved.
4. The font of the text seems not correct. It should be 12, Times New Roma, and single space
   The font is appeared to be 12pt except for titles. (we have used larger font size for titles). Note that we have changed the font size of the reference section which is now times new roman (12pt)

5. Some of the first letters of the first words in a sentence are not capitalized
   Corrected.

6. Pay attention to the consistency. If you use “Scan coordinate one”, you should also use “Scan coordinate two” in the following text, instead of “Scan coordinate 2”
   Corrected

7. The figure legend of Figure 2 is not finished.
   Completed the figure legend 2

8. C.3: “one way of identify the ...” should be “One way of identifying the
   Changed.

9. In Table 1, the unit should be kcal·mol⁻¹ instead of kcal mol⁻¹
   Changed.

Response to Reviewer 2

1. Grammatical errors
   We have change the grammatical errors in the proposal. Please note that I have explained why I wanted to do these specific calculations and what it means.

2. “the big questions here are why these are of interest and how you relate the significance of reactions of pentene with fluorine through these calculations”
   Explained this in background and significance.

3. “in the first scheme, those structures in the middle and the right are not isomers of pentene.”
   For the clarification, all the isomers of pentene are active compounds. The two other compounds appear in the scheme one a butene and pentane. Which has studied previously. They are reference compound.

4. “Furthermore, those structures that you have put on Figure 2 should be illustrated in the same orientation”
   I have changed the figure 2. Now you can see the double bond of each pentene.
5. **one thing that is missing in your project timeline is that there is not a firm evidence on your calculation time**
   Please not that there are at least five pentene isomers exist and each of the have different abstraction and different addition sites which give me so many combinations at two different levels. There is a large difference between the computational time at G2 level and DFT. To calculate the enthalpy changes involves lots of small calculation. Therefore it is practically impossible to include time for one calculation type and make the calculation time based on it.

Response to Reviewer 3.

1. **specific aim 3 is ill-defined.**
   We have updated C3 section and D3 section. It will clarify importance of specific aim 3.

2. **section B is a little weak,**
   We have not change much in Sec B. But we have improved the other sections to see the importance of these calculations.

3. **it seems to me, according to section B, that the author wants to study two topics instead of just one**
   We are thinking you are referring to PES and enthalpy changes. So finding the minimum energy structures are important. They is a high possibility of exist them as structures in the environment than other high energy structures.

4. **table legend should be put at ahead of the table, and the legend for table and scheme should be title case**
   We have changed the table legend. Now it is top of the table.

5. **C.2 just contain a table, no explanation or data analysis given. Again, the IR spectrum of C. 3 didn’t have any explanation, the author could analyses a little what the enthalpy difference tells us, and why the enthalpy difference determine with two methods is important to study.**
   Revised version includes explanation of the table and IR spectrum.

6. **different basis sets are used to the potential energy scan, and geometry optimization, but no explanation is given to justify the change of the basis sets. And the legend for figure 2. Is not completed**
   I have changed the basis set in C1 to make the calculation faster. I have included the reason now in C1 section. Fig 2 legend is now completed.

7. **In Section C, the author didn’t clearly specify which specific aim are those preliminary results serve for**
   C1 refers to specific aim 1, C2 refers to specific aim 2 and C3 refers to specific aim 3.

Sincerely,
Nureshan Dias
STUDY OF REACTIONS OF PENTENE WITH FLUORINE RADICAL

Nureshan Dias

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Abstract:

We present the proposal of theoretical study of reaction of fluorine atom with different isomers of pentene such as 1-pentene, 2-pentene. The reaction of pentene with fluorine atom are important to a detailed understanding of combustion chemistry, atmospheric, marine, and environmental chemistry. This proposal includes mainly the study metathesis reaction and addition reactions of pentene with fluorine. Addition to these two specific reaction types we have studied the global and local minimum geometries of pentene and vibrational analysis. The study was mainly conducted at two different levels G2 and ωB97XD using 6-311G** basis set. The enthalpy change of abstraction at C-1 is -24.52 kcal.mol\(^{-1}\) at G2 and -19.62 kcal.mol\(^{-1}\) at ωB97XD/6-311G**. The Enthalpy change for the addition reaction at C-1 position is -46.52 and -47.79 kcal.mol\(^{-1}\) at G2 and ωB97XD/6-311G** respectively. The energy we obtained from both the theoretical levels are comparable These results are compared with the previous studies and to the experimental data. Vibrational analysis suggests that abstraction at C-1 is the least favorable out of other possibilities of abstractions. The anharmonic and harmonic vibrational spectra looks exactly same for pentene. Further calculations necessary to have a better conclusion and compare both anharmonic and harmonic spectrums. The detailed description is included in the following proposal.
STUDY OF REACTIONS OF PENTENE WITH FLUORINE RADICAL

Reactions of halogens with alkenes have become an important benchmark in the study of polyatomic reaction dynamics. This is because these reactions are fast and nearly barrier less.\(^1\) They afford us to compare the reaction energies at different sites in different isomers. Radical addition and elimination reactions are a major pathway for transformation of unsaturated hydrocarbons. However, the detailed mechanism and dynamics for these reactions are unclear. To get a better understand about these systems we are doing some quantum chemistry calculations on pentene with fluorine. The interactions of Fluorine atoms with unsaturated hydrocarbons such as pentene are important in understanding the processes involved in combustion, atmospheric, marine, and environmental chemistry.

A. SPECIFIC AIMS

1. To calculate global and local minimum geometries

Pentene has different isomers and each isomer can have global and local minimum geometries. Our aim is to find these local and global minima.

Scheme 1. One form of the active compound, 1-Pentene (Left) where it can exhibit as different isomers, The 1-Butene (middle) and Pentane (Right) as the reference compounds.

![Scheme 1](image)

The first image of above scheme depicts the structures of pentene which we are interested. The H abstraction and addition reactions of butene with chlorine and H abstraction by chlorine in pentane was studied previously (Suits and coworkers)\(^2,3\). We use these two structures as our reference compounds.

2. To calculate and compare the reaction enthalpies of hydrogen abstractions and addition reaction for all sites for all conformers.

Our aim is to calculate the enthalpy values for different abstraction/addition sites and find the theoretical level dependency of energy at G2\(^4\) level and \(\omega B97XD\(^5\) functional.

3. Explore the effect of anharmonic/harmonic vibrational spectra upon addition and abstraction and mapped the electron density surfaces of reagents.
Relate the vibrational energy to bond dissociation of hydrogen abstraction and to identify the mechanism mapped the electron density surfaces.

B. BACKGROUND AND SIGNIFICANCE

Fluorine atom reactions with alkenes are an important prototype for the broad class of radical addition and elimination reactions. Fluorine sources literally cover the Earth with both oceanic and anthropogenic origins and alkenes are among the most abundant atmospheric hydrocarbons. These reactions play an important role in the oxidation of volatile organic compounds in marine boundary layers and the Polar regions, the burning of hazardous waste and possibly the aging of organic aerosols by heterogeneous processes. It is important to study the dynamics of these types of reactions since these kinds of reactions control so much of environmental process.

Scientists have studied different alkenes with chlorine but fluorine atom reaction with pentene is rarely studied. Pentene is a byproduct of thermal cracking of petroleum and it is classified as a volatile organic compound (VOC). Pentenes may be released during their manufacture and use in the chemical industry. They may also be released during the transport, storage of petrol, re-fueling of vehicles, vehicle exhausts and industrial and residential coal burning. Like other alkenes with halogens pentene with fluorine atom can undergo mainly abstraction reactions and addition reactions.

Hydrogen abstraction reactions are called Metathesis reactions, in which a single atom is transferred from a stable molecule to an atom or radical, are the only truly bimolecular gas-phase reactions. Those involving hydrogen atom transfer arguably represent the most important subclass of this vast body of reactions, particularly for combustion dynamics. Free radical abstraction of hydrogen atoms in saturated hydrocarbons, for example, are reactions of great importance in combustion, and the differing propensities for reaction at different position of H atoms, as well as the different dynamics underlying these pathways, are important to a detailed understanding of combustion chemistry, atmospheric, marine, and environmental chemistry.

Scheme 2. The pathways for the addition, direct abstraction and addition elimination.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F + C_5H_{10}$</td>
<td>$C_5H_{10}F$</td>
</tr>
<tr>
<td>$F + C_5H_{10}$</td>
<td>$C_5H_9^\cdot + HF$</td>
</tr>
<tr>
<td>$F + C_5H_{10}$</td>
<td>$(C_5H_{10}F)^\cdot$</td>
</tr>
</tbody>
</table>
Kinetics studies of simple alkenes with halogens has shown Addition-elimination gives the same products but mechanism is different to direct abstraction. Moreover, other than to hydrogen abstractions fluorine with pentene can undergo addition reactions yielding fluoro-pentane radicals\textsuperscript{14}. Even though we know the possible pathways of these reactions the detailed mechanism is unknown. The mechanism may be change depending on the reaction site. Specially on the Hydrogen abstraction reactions. It is interesting to calculate the enthalpy change at different abstraction site to get a rough idea about the mechanism. Furthermore, these enthalpy changes are important in the combustion chemistry. One way of identify the mechanism is to identify the transition states. These transitions state can be change depending on the reaction sites.

**Scheme 3. The structure of the global minima (left) and a structure of the local minima (right)**

The pentene can have several local minima structures and a global minima structures. It is important to find the energies of these local and global minimum structures. Depending on these structures the abstraction of hydrogen may change. For the global minimum structure of pentene, considering the different hydrogen attached to the same carbon as chemically equal hydrogen is a good approximation. But for the local minimum structure of pentene the hydrogens attached to carbon 1 and 5 cannot be treated equally. It is interesting to find out the hydrogen abstraction enthalpies and reaction pathways for these local minimum structures. These hydrogen abstraction reactions can go through a transition state or it can have a roaming like pathway\textsuperscript{15}.

Density functional theories are good in calculating the excited state\textsuperscript{16}. The hybrid density functional with dispersions oB97xD is a better level of theory for calculating reactions enthalpies and finding the transition states of our system. By doing high calculation (G2) parallel to DFT level one can compare the accuracy of DFT method. Since this method accounts for dispersion\textsuperscript{17} terms and the system consists second raw atoms the Gaussian type orbitals\textsuperscript{18} are used in calculations.
C. PRELIMINARY RESULTS

C.1
The bonds in 1-pentene can rotate and gives structures with global minima and local minima. One way of identify the minimum energy structures are by doing a potential energy scan. We use Gaussian 09\textsuperscript{19} to perform our calculations. The potential energy scan was done using the density functional \omega B97XD and the basis set of 6-31G\textsuperscript{18} to minimize the time. By varying the two dihedral angles at once we obtained the 3D PES for 1-pentane. The minimum energy structures obtain of this can be further minimize using a better method.

![Figure 1. The surface of the 3-D potential energy scan of pentene. Color codes for the energy is given at the right side of the image. Scan coordinate one is the rotation of C2, C3 bond while scan coordinate two is rotation of the bond C3, C4. The deep wells (dark blue) corresponds to global minima, the peak (red) corresponds to global maxima, light blue areas correspond to local minima and greenish areas corresponds to transition states.](image)
To find the reaction enthalpies one needs to optimized the structure. We found the transition state at the level of ωB97XD/6-311G**. Transition state is needed to find the reaction mechanism and to obtained the IRC path.

![Chemical structures](image1)

**Figure 2.** The optimized structure of pentene (Top left), The transition state structure for Hydrogen abstraction at C-1 (Top Right), The optimized structure of pentene radical and Fluorine addition product respectively on bottom left and bottom right at the level of ωB97XD/6-311G**\textsuperscript{20}. The energies obtained from these structures are used to calculate the enthalpy changes.
Figure 3. The IRC scan obtained for both directions for the transition state. Where x coordinate at transition state being zero. The positive x direction is where abstraction of hydrogen by fluorine take place. IRC is important in predicting the reaction mechanism.

C.2

Table 1. The enthalpy change of Hydrogen abstraction at C-1 and enthalpy change of addition of Fluorine to C-1 carbon in 1-pentene at G2 level of theory and \( \omega \text{B97XD}/6-311G** \).

<table>
<thead>
<tr>
<th>Method</th>
<th>Name</th>
<th>Type of the reaction</th>
<th>Enthalpy change/kcal.mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>G2</td>
<td>1-pentene</td>
<td>H-abstraction at C-1</td>
<td>-24.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F-addition to C-1</td>
<td>-46.52</td>
</tr>
<tr>
<td>( \omega \text{B97XD}/6-311G** )</td>
<td>1-pentene</td>
<td>H-abstraction at C-1</td>
<td>-19.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F-addition to C-1</td>
<td>-47.79</td>
</tr>
</tbody>
</table>

The enthalpy changes for the addition reaction at 2 different levels are almost same and enthalpy changes for the abstraction reaction at two levels are comparable. The hydrogen at C-1 is least favorable for the abstraction reaction since H has attached to a sp\(^2\) carbon. Further calculations are needed to conclude the accuracy of \( \omega \text{B97XD} \) functional.

C.3

One way of identifying the mechanism is mapping the electrostatic potential surface on electron density surfaces. ESP is a measure of the potential energy of a proton near a molecule, and its value differs for different region of the molecule. A negative electrostatic potential corresponds to high electron density and the ability to attract a proton. A positive electrostatic potential corresponds to low electron density and shielding of the nuclear charge, repulsing protons. An electron density isosurface is colored according to the value of electrostatic potential at each point on it.

Figure 4. The figure illustrates the optimized structures of \( \text{C}_3\text{H}_{10} \)(left) and \( \text{C}_3\text{H}_9^\circ \) with electrostatic potential (ESP) mapped on electron density (ED) surface (color spectrum range
from blue to red, with blue being the most electronegative, equivalent to a value of \(-6.21 \times 10^{-2}\). The density value used is 0.004.

Dissociation energies can be predicted from vibrational modes. For hydrogen abstraction reaction bond, must have to break. But since pentene has different hydrogen at different carbons it is near impossible to identify the specific IR bands. We are calculating the anharmonic vibrations for the reactants and products in abstraction reaction and try to distinguish them and identify the C-H vibrations that are missing from the spectra. Below we have calculated anharmonic spectra for pentene.

![IR Spectrum](image)

**Figure 5.** The anharmonic IR spectrum of pentene at the level of \(\omega B97XD/6-311G**\)(The harmonic vibrational spectrum is exactly like this)

The anharmonic and harmonic spectrums for pentene are exactly same. The only difference is anharmonic calculations are more expensive. We cannot conclude anything from the anharmonic and harmonic vibrational spectrums of pentene. More spectrums are needed to identify the differences in anharmonic spectrum to harmonic spectrum.

**D. PROPOSED RESEARCH**
We will be using the computer cluster available at the university of Missouri and Gaussian 09 to do our calculations.

**D.1**
We will find the local and global minima structures by doing a 3D dihedral angle potential energy scan at the level of \(\omega B97XD/6-311G**\) for 1-pentene, cis 2-pentene and trans 2-pentene. We will further optimized structures of local minima and global minima and be calculating the energy barrier for global minima to local minima.

**D.2**
We will find the enthalpy change for addition reactions for each isomer and we the enthalpy changes for each abstraction sites for each isomer including for both local and global minima structures at ωB97XD/6-311G** and the higher-level theory G2.

**D.3**
To get a better understand about the mechanism we optimized the transition state for each reaction and obtained the IRC path. Since our reactions includes radicals we would like to see the electron density surfaces for each product. Furthermore, vibrations are important in dissociation of bonds. we will account for both the anharmonic and harmonic vibrational spectra and relates vibrational energy to dissociation of hydrogen in the abstraction reactions. We will plot the electron density surfaces of the reactants and products to get the better understand about the mechanism. These calculations will be done at the level of ωB97XD/6-311G**.

**E. PROJECT TIMELINE**

Our projects is relatively less expensive but calculation of anharmonic spectrum takes time. The graphic below shows the time allocation for each specific task.

<table>
<thead>
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<th>Month 2</th>
<th>Month 3</th>
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F. REFERENCES

