Theoretical Studies of Hydrogen Abstraction From Hydrofluoropropanes by Triplet Oxygen Atom

Dylan Bryant

Department of Chemistry,

The University of Tennessee at Chattanooga,

615 McCallie Ave,

Chattanooga Tennessee, 37403

1. Introduction

Hydrofluorocarbons (HFCs) are chemicals commonly used in products such as refrigerants, fire suppressants, and propellants in aerosol sprays. They replaced chlorofluorocarbons (CFCs), harmful chemicals responsible for breaking down the ozone layer. When compared to CFCs, HFCs have a lower ozone-depletion potential and therefore HFCs are being considered ozone-friendly gases. Unfortunately, HFCs are potentially greenhouse gases. Because of this, HFCs are still environmentally problematic and their long-term environmental impact is currently being investigated. One possible way to measure this impact is by measuring their atmospheric lifetimes. This would lead to a better understanding of how large an impact these molecules have the environment.

This degradation is made possible through different hydrogen abstraction in the troposphere. This occurs because the C-H bonds are susceptible to abstraction. Abstraction via hydroxyl radical is the most common pathway, but to fully characterize atmospheric lifetime abstraction via triplet oxygen must be considered. Understanding the triplet oxygen atom abstraction also gives useful insight into the degradation via hydroxyl radical.

The first part of this study uses computational methods to calculate various energy parameters for the hydrogen abstraction of hydrofluoropropanes (HFPs) through use of an oxygen atom. The typical reaction process is as follows:

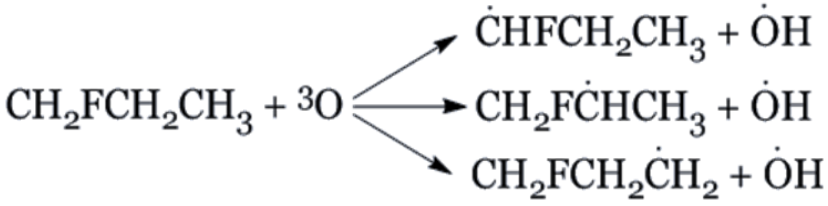


Figure 1. Mechanism for Hydrogen Abstraction using an Oxygen Atom from 1-Fluoropropane

Three different radicals can be formed due to possible abstraction of hydrogen from any one of the three carbons. This study examines all 28 hydrofluoropropanes: $CH_3CH_2CH_2F$ (R-**1**), CH_3CHFCH_3 (**R-2**), $CH_3CH_2CHF_2$ (**R-3**), CH_3CHFCH_2F (**R-4**), $CH_2FCH_2CH_2F$ (**R-5**), $CH_3CF_2CH_3$ (**R-6**), $CH_3CH_2CF_3$ (**R-7**), $CH_3CHFCHF_2$ (**R-8**), $CH_2FCH_2CHF_2$ (**R-9**), $CH_3CF_2CH_2F$ (**R-10**), $CH_2FCHFCH_2F$ (**R-11**), CH_3CHFCF_3 (**R-12**), $CH_2FCH_2CF_3$ (**R-13**), $CH_3CF_2CHF_2$ (**R-14**), $CHF_2CH_2CHF_2$ (**R-15**), $CH_2FCHFCHF_2$ (**R-16**), $CH_2FCF_2CH_2F$ (**R-17**), $CH_3CF_2CF_3$ (**R-18**), $CH_2FCHFCF_3$ (**R-19**), $CHF_2CH_2CF_3$ (**R-20**), $CH_2FCF_2CHF_2$ (**R-21**), $CHF_2CHFCHF_2$ (**R-22**), $CH_2FCF_2CF_3$ (**R-23**), CHF_2CHFCF_3 (**R-24**), $CF_3CH_2CF_3$ (**R-25**), $CHF_2CF_2CHF_2$ (**R-26**), $CHF_2CF_2CF_3$ (**R-27**), and CF_3CHFCF_3 (**R-28**). This study looks at the energetics of the hydrogen abstraction reactions, and the structures and the energetics of the saddle points for each hydrogen abstraction reaction.

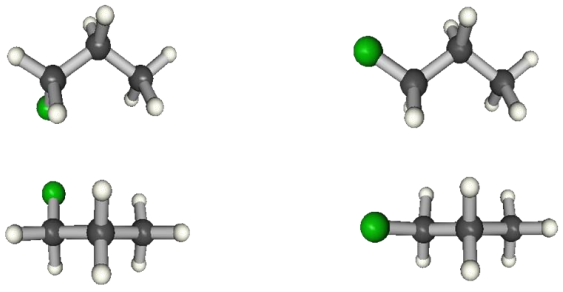


Figure 2. Hydrogen equivalence due to symmetry on 1-flouoroproane. Note that on the first structure 7 possible transitions states are possible while on 4 are possible on the second.

The 28 HFPS that were investigated generated a total of 269 saddle points. This large number is due to both the 1-3 products possible for each HFP and from the fact that abstraction of hydrogen on the same carbon is not always equivalent. The symmetry of the molecule plays a role in whether or not abstraction is equivalent. Figure 2 details this concept using one possible abstraction pathway for 1-fluoropropane.

All HFP reactant and radical geometries used in energy calculations were provided by previous research done by the Albu research group.

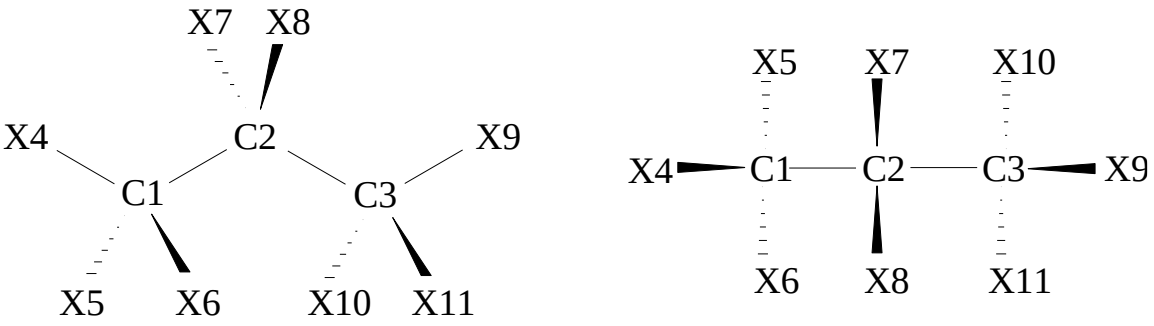
2. Computational Methodologies

All calculations in this study were carried out using the mPW1B95–44 hybrid density theory method with a 6-31+G(d,p) basis set. This particular theory was developed specifically for use in kinetic studies. This method makes use of the modified Perdew–Wang (mPW) gradient-corrected exchange functional and the B95 gradient-corrected correlation functional. The Hartree-Fock exchange contribution to the exchange energy is 44% in this method. All the reported results in this study were obtained using the mPW1B95–44/6-31+G(d,p) method.

Restricted wave functions were used for closed-shell systems and unrestricted wave functions for open-shell systems. The geometry optimizations were carried out using a normal convergence criteria and an ultrafine integration grid for numerical integrations. Vibrational frequency calculations were carried out to characterize the nature of each stationary point. All stationary points only have one imaginary frequency. All electronic structure calculations were performed using the Gaussian 09.

3. Results Discussion

Before discussing the results, is it useful to identify the notation scheme and parameters measured in the study. The following scheme will be referred to when identifying hydrofluoropropanes.



side view top view

X4, X5, X6, etc. refer to the location which fluorine or hydrogen can be located. This can also be used to for naming. For example F=4,7,8 should be understood as 1,2,2-trifluoropropane and H=5 refers to a hydrogen in position 5.

The reactions are labelled as, for example, **R-1A**, **R-1B**, and **R-1C** where **1A**, **1B** and **1C** are the fluoropropyl radicals that can be obtained from 1. Label **A** is used for the radical obtained by hydrogen abstraction from the lowest numbered C with H attached to it (i.e., carbon 1 or carbon 2 if carbon 1 does not have any H, or carbon 3 if carbons 1 and 2 does not have any hydrogens), **B** is used for the radical obtained by hydrogen abstraction from second lowest numbered C, and **C** is used for radical on carbon 3 only.

Each saddle point was characterized by the C···H, H···O, and C···O internuclear distances. The following energetic parameters were also used to characterize the saddle

points: ΔE is the classical (i.e., zero-point exclusive) energy of reaction, ΔH_0 is the zero-point-inclusive energy of reaction, $V^{\ddagger}$ is the classical (i.e., zero-point-exclusive) barrier height, $\Delta H_0^{\ddagger}$ is the zero-point-inclusive barrier height, $\Delta G_{298}^{\ddagger}$ is the zero-point-inclusive Gibbs, and $\omega^{\ddagger}$ is the imaginary frequency at the saddle point. All energies are reported relative to the respective values (zero-point inclusive or exclusive) of the reactants, which is considered the zero of energy.

When not explicitly stated, the saddle point with the lowest barrier height is assumed to be the most likely transition pathway for the given radical. The C···H, H···O, and C···O internuclear distances for the most likely transition pathway are listed for each radical.

4.1. Hydrogen Abstraction from $CH_2FCH_2CH_3$ by ^3O

$CH_2FCH_2CH_3$ reacts with triplet oxygen in the following three ways:

$CH_2FCH_2CH_3 + {}^3O \rightarrow CHFCH_2CH_3 + HO$ (**R-1A**)

$CH_2FCH_2CH_3 + {}^3O \rightarrow CH_2FCHCH_3 + HO$ (**R-1B**)

$CH_2FCH_2CH_3 + {}^3O \rightarrow CH_2FCH_2CH_2 + HO$ (**R-1C**)

For reaction **R-1A**, three saddle points (**1A-a, 1A-b, 1A-c**) were identified. All three saddle points has similar barrier heights around 9.62 kcal/mol. Normal mode analysis also revealed all three have similar imaginary frequencies around 1635*i* cm^{-1}. Although all reaction through each saddle point is possible due to small differences in the barrier height, the most likely transition pathway is **1A-a.** The C···H, H···O, and C···O internuclear distances are 1.278 A, 1.227 A, and 2.503 A, respectively, for **1A-a**.

Three saddle points (**1B-a, 1B-b, 1B-c)** were also found for **R-1B** reaction. **1B-a** has the highest barrier height at 10.08 kcal/mol and **1B-c** has the lowest at 9.85 kcal/mol. Normal mode analysis revealed all three have similar imaginary frequencies around 1630*i* cm^{-1}. For **1B-c** saddle point, C···H, H···O, and C···O internuclear distances are 1.283 A, 1.214 A, and 2.499 A, respectively.

Five saddle points (**1C-a** through **1C-e)** were identified for **R-1C** reaction. **1C-e** has the highest barrier height at 12.83 kcal/mol and **1C-b** has the lowest at 10.65 kcal/mol. Normal mode analysis revealed **1C-e** has the highest imaginary frequency of 1703*i* cm^{-1}, and **1C-b** has the lowest imaginary frequency at 1644*i* cm^{-1} respectively. For **1C-b** saddle point, C···H, H···O, and C···O internuclear distances are 1.298 A, 1.201 A, and 2.496 A, respectively. Among all three reactions, **R-1A** is the more likely radical product based on barrier height values.

4.2. Hydrogen Abstraction from CH_3CHFCH_3 by ^3O

CH_3CHFCH_3 reacts with triplet oxygen in the following two ways:

$CH_3CHFCH_3 + {}^3O \rightarrow CH_3CHFCH_2 + HO$ (**R-2A**)

$CH_3CHFCH_3 + {}^3O \rightarrow CH_3CFCH_3 + HO$ (**R-2B**)

Three saddle points, (**2A-a, 2A-b, 2A-c**) were identified for reaction **R-2A**. Saddle point **2A-a** has the lowest barrier height at 12.83 kcal/mol while **2A-b** and **2A-c** have similar barrier heights around 13.19 kcal/mol. The highest imaginary frequency of 1708*i* cm^{-1} corresponds to saddle point **2A-b** while **2A-c** has the lowest frequencies around 1697*i* cm^{-1}. C···H, H···O, and C···O internuclear distances are 1.315 A, 1.180 A, and 2.495 A, respectively, for **2A-a**.

Reaction **R-2B** was found to only have one saddle point (**2B-a**). The barrier height and imaginary frequency for **2B-b** are 7.68 kcal/m ol and 1490*i* cm^{-1} respectively. The zero point inclusive saddle point and Gibbs are 3.86 kcal/mol and 10.68 kcal/mol respectively. The ΔE and ΔV_o values are 1.11 kcal/mol and -2.97 kcal/mol. The C···H, H···O, and C···O internuclear distances are 1.258 A, 1.254 A, and 2.512 A respectively. Between the two reactions, **R-2B** is the most likely radical.

4.3. Hydrogen Abstraction from 4.4.3 $CHF_2CH_2CH_3$ by ^3O

The reaction of triplet oxygen with CHF_2CH2CH_3 in the following three ways:

$CHF_2CH_2CH_3 + {}^3O \rightarrow CF_2CH_2CH_3 + HO$ (**R-3A**)

$CHF_2CH_2CH_3 + {}^3O \rightarrow CHF_2CHCH_3 + HO$ (**R-3B**)

$CHF_2CH_2CH_3 + {}^3O \rightarrow CHF_2CH_2CH_2 + HO$ (**R-3C**)

For reaction **R-3A**, only two saddle points (**3A-a**, **3A-b**) were identified. Saddle point 3A-a has the lowest barrier height at 11.00 kcal/mol and 3A-b has the highest at 11.35 kcal/mol. **3A-a** also has the lowest imaginary frequency of 1720*i* cm^{-1} and **3A-b** has the highest imaginary frequency at 1732*i* cm^{-1}. The C···H, H···O, and C···O internuclear distances for **3A-a** are 1.290 A, 1.211 A, and 2.501 A respectively.

Three saddle points (**3B-a**, **3B-b**, **3B-c**) were identified for **R-3B**. The highest barrier height belongs to **3B-b** at 12.80 kcal/mol while both **3B-a** and **3B-c** have similar barrier heights around 12.04 kcal/mol. **3B-a** and **3B-c** have similar imaginary frequencies around 1710*i* cm^{-1} while **3B-b** is 1751*i* cm^{-1}. **3B-c** is the most likely due to a slightly lower barrier height. The internuclear distance for **3B-c**, C···H, H···O, and C···O, correspond to 1.300 A, 1.195 A, 2.493 A respectively.

Reaction **R-3C** has five saddle points (**3C-a** through **3C-e)**. Of the five saddle points, **3C-a** has the lowest barrier height at 12.16 kcal/mol and **3C-c** has the highest barrier height at 13.12 kcal/mol. **3C-a** also has the lowest imaginary frequency at 1685*i* cm^{-1} while **3C-b** has the highest at 1730*i* cm^{-1}. The C···H, H···O, and C···O, internuclear distances for **3C-a** are 1.306 A, 1.193 A, and 2.496 A respectively. Among the three reactions, **R3-A** is the most likely radical to form.

4.4. Hydrogen Abstraction from $CH_2FCHFCH_3$ by ^3O

The reaction of triplet oxygen with $CH_2FCHFCH_3$ in the following three ways:

$CH_2FCHFCH_3 + {}^3O \rightarrow CH_2FCHFCH_3 + HO$ (**R-4A)**

$CH_2FCHFCH_3 + {}^3O \rightarrow CH_2FCFCH_3 + HO$ (**R-4B**)

$CH_2FCHFCH_3 + {}^3O \rightarrow CH_3CHFCH_2 + HO$ (**R-4C**)

Reaction **R-4A** was found to have six saddle points (**4A-a** through **4A-f**). **4A-a** has the highest barrier height at 12.24 kcal/mol and **4A-d** has the lowest at 11.61 kcal/mol. **4A-b** has the highest imaginary frequency at 1772*i* cm^{-1} and **4A-d** has the lowest at 1736*i* cm^{-1}. For saddle point **4A-d**, the C···H, H···O, and C···O, internuclear distances are 1.306 A, 1.193 A, and 2.496 A respectively.

Three saddle points (**4B-a**, **4B-b**, **4B-c**) were found for reaction **R-4B**. The three saddle points were of similar energy, but **4B-b** has the lowest barrier height at 9.34 kcal/mol and **4B-a** has the highest at 10.39 kcal/mol. The imaginary frequencies followed a similar pattern with **4B-a** having the highest at 1675*i* cm^{-1} and **4B-b** having the lowest at 1615*i* cm^{-1}. The C···H, H···O, and C···O, internuclear distances for **4B-b** are 1.272 A, 1.234 A, and 2.506 A respectively.

Nine saddle points (**4C-a** through **4C-i**) were found for reaction **R-4C**. **4C-a** was found to be the lowest barrier height at 13.65 kcal/mol, and the highest corresponding to both **4C-f** and **4C-g** around 15.05 kcal/mol. **4C-i** has the lowest imaginary frequency of 1712*i* cm^{-1} and the highest imaginary frequency corresponds to 1781*i* cm^{-1}. For the saddle point **4C-a,** C···H, H···O, and C···O, internuclear distances are 1.327 A, 1.167 A, and 2.492 A respectively. Based on barrier height energies, **4B-b** is the most likely radical product.

4.5. Hydrogen Abstraction from 4.4.3 $CH_2FCH_2CH_2F$ by ^3O

The reaction of triplet oxygen with $CH_2FCH_2CH_2F$ yields two radicals:

$CH_2FCH_2CH_2F + {}^3O \rightarrow CHFCH_2CH_2F + HO$ (**R5-A**)

$CH_2FCH_2CH_2F + {}^3O \rightarrow CH_2FCHCH_2F + HO$ (**R5-B**)

Nine saddle points (**5A-a** through **5A-i**) were found for **R5-A**. **5A-c** was found to have the lowest barrier height at 10.75 kcal/mol and **5A-i** was found to have the highest at 12.95 kcal/mol. **5A-c** and **5A-i** were also found to have the lowest and highest zero-point-inclusive barrier height of 8.99 kcal/mol and 6.86 kcal/mol respectively. The C···H, H···O, and C···O, internuclear distances for **5C-a** are 1.276 A, 1.226 A, and 2.499 A respectively.

Six saddle points (**5B-a** through **5B-f**) were found for **R5-B**. Two saddle points, **5B-e B** and **5B-f** has similar barrier heights around 15.73 kcal/mol, which corresponds to the highest barrier height, while the lowest belonged to **5B-c** at 12.63 kcal/mol. **5B-c** also has the lowest zero-point-inclusive barrier height at 8.51 kcal/mol, and **5B-e B** and **5B-f** also has the highest zero-point-inclusive barrier height around 9.33 kcal/mol. The transition pathway is most likely to follow **5B-c**. For **5B-c**, The C···H, H···O, and C···O, internuclear distances are 1.309 A, 1.186 A, and 2.494 A respectively. From the above data, the most likely radical product is **R5-A**.

4.6. Hydrogen Abstraction from $CH_3CF_2CH_3$ by ^3O

The reaction of triplet oxygen with $CH_3CF_2CH_3$ yields one radical:

$CH_3CF_2CH_3 + {}^3O \rightarrow CH_2CF_2CH_3 + HO$ (**R6-A**)

Only two distinct saddle points (**6A-a** and **6A-b**) are possible for **R6-A**. **6A-a** has the lowest barrier height, zero-point-inclusive barrier height, zero-point-inclusive Gibbs and imaginary frequency at 15.13 kcal/mol, 10.96 kcal/mol, 17.40 kcal/mol, and 1721*i* cm^{-1} respectively. **6A-b** has the highest barrier height, zero-point-inclusive barrier height, zero-point-inclusive Gibbs, and imaginary frequency at 16.14 kcal/mol, 11.86 kcal/mol, 18.14 kcal/mol, and 1747*i* cm^{-1} respectively. For **6A-a**, The C···H, H···O, and C···O, internuclear distances are 1.334 A, 1.159 A, and 2.490 A respectively.

4.7. Hydrogen Abstraction from $CF_3CH_2CH_3$ by ^3O

The reaction of triplet oxygen with $CH_2FCH_2CH_2F$ yields two radicals:

$CF_3CH_2CH_3 + {}^3O \rightarrow CF_3CHCH_3 + HO$ (**R7-A**)

$CF_3CH_2CH_3 + {}^3O \rightarrow CF_3CH_2CH_2 + HO$ (**R7-B**)

Only one saddle point (**7A-a**) was found for **R7-A**. The barrier height, delta H, zero-point-inclusive Gibbs, and imaginary frequency are 14.02 kcal/mol, 9.72 kcal/mol, 16.48 kcal/mol, and 1777*i* cm^{-1} respectively. The overall ΔE and ΔV_o values are 7.00kcal/mol and 1.36 kcal/mol respectively. The C···H, H···O, and C···O, internuclear distances are 1.314 A, 1.178 A, and 2.490 A respectively.

Two saddle point (**7B-a** and **7B-b**) were found for **R7-B**. **7B-b** has the lowest barrier height of 9.24 kcal/mol, and **7B-a** has the highest at 13.51 kcal/mol. The **7B-b** C···H, H···O, and C···O, internuclear distances are 1.334 A, 1.177 A, and 2.490 A respectively. Based on barrier height values, **R7-B** is the most radical product.

4.8. Hydrogen Abstraction from CHF_2CHFCH_3 by ^3O

The reaction of triplet oxygen with CHF_2CHFCH_3 yields three radicals:

$CHF_2CHFCH_3 + {}^3O \rightarrow CHFCH_2CH_2F + HO$ (**R8-A**)

$CHF_2CHFCH_3 + {}^3O \rightarrow CH_2FCH_2CH_2F + HO$ (**R8-B**)

$CHF_2CHFCH_3 + {}^3O \rightarrow CH_2FCHCHF + HO$ (**R8-C**)

Three saddle points (**8A-a**, **8A-b**, and **8A-c**) were found for **R8-A**. The barrier heights for **8A-a**, **8A-b**, and **8A-c** are 13.51 kcal/mol, 13.55 kcal/mol, and 13.19 kcal/mol respectively. The **8A-a**, **8A-b**, and **8A-c** imaginary frequencies are 1772*i* cm^{-1} 1734*i* cm^{-1}, and 1717*i* cm^{-1}. The C···H, H···O, and C···O, internuclear distances for **8A-a** are 1.311 A, 1.184 A, and 2.493 A respectively.

For **R8-B**, three saddle points (**8B-a**, **8B-b**, and **8B-c**) were found. The barrier heights for **8B-a**, **8B-b**, and **8B-c** are 12.38 kcal/mol, 11.24 kcal/mol, and 12.70 kcal/mol respectively. The **8B-a**, **8B-b**, and **8B-c** zero-point-inclusive barrier height are 8.25 kcal/mol, 7.18 kcal/mol, and 8.67 kcal/mol respectively. **8B-b** is the most likely transition pathway. For **8B-b,** The C···H, H···O, and C···O, internuclear distances are 1.288 A, 1.211 A, and 2.497 A respectively.

For **R8-C**, nine saddle points (**8C-a** through **8C-i**) were found. The highest barrier height corresponded to **8C-i** at 17.48 kcal/mol, and the lowest barrier height corresponded to **8C-c** at 13.96 kcal/mol. **8C-c** also has the lowest **c** zero-point-inclusive barrier height at 9.75 kcal/mol while **8C-h** has the highest at 13.71 kcal/mol. The C···H, H···O, and C···O, internuclear distances for **8C-c** are 1.324 A, 1.172 A, and 2.491 A respectively. From the above data, **R8-B** is the most likely radical to form.

4.9. Hydrogen Abstraction from $CH_2FCH_2CHF_2$ by ^3O

The reaction of triplet oxygen with $CH_2FCH_2CHF_2$ yields three radicals:

$CH_2FCH_2CHF_2 + {}^3O \rightarrow CHFCH_2CHF_2 + HO$ (**R9-A**)

$CH_2FCH_2CHF_2 + {}^3O \rightarrow CH_2FCHCHF_2 + HO$ (**R9-B**)

$CH_2FCH_2CHF_2 + {}^3O \rightarrow CH_2FCH_2CF_2 + HO$ (**R9-C**)

R9-A was found to have five saddle points (**9A-a** through **9A-e)**. **9A-e** has the highest barrier height of 13.86 kcal/mol, and **9A-a** has the lowest barrier height at 13.06 kcal/mol. **9A-a** also hard the largest imaginary frequency at 1827*i* cm^{-1}, and **9A-c** having the lowest at 1729*i* cm^{-1}. The C···H, H···O, and C···O, internuclear distances for **9A-a** are 1.307 A, 1.187 A, and 2.492 A respectively.

Nine saddle points (**9B-a** through **9B-i**) were found for **R9-B**. **9B-b** has the lowest barrier height, zero-point-inclusive barrier height, and zero-point at 14.77 kcal/mol, 10.37 kcal/mol, and 17.08 kcal/mol respectively. **9B-f** has the highest barrier height, zero-point-inclusive barrier height, and zero-point-inclusive Gibbs 17.65 kcal/mol, 13.19 kcal/mol, and 19.85 kcal/mol respectively. The C···H, H···O, and C···O, internuclear distances for **9B-b** are 1.325 A, 1.167 A, and 2.492 A respectively.

Nine saddle points (**9C-a** through **9C-i**) were found for **R9-C**. The lowest barrier height is found from **9C-b** at 11.80 kcal/mol, while the highest barrier height is found from **9C-h** at 14.44 kcal/mol. The largest imaginary frequency is found from **9C-g** at 1787*i* cm^{-1}. The smallest imaginary frequency is found from **9C-f** at 1670*i* cm^{-1}. For **9C-b**, The C···H, H···O, and C···O, internuclear distances are 1.291 A, 1.204 A, and 2.494 A respectively. **R9-A** is the most likely radical based on the above barrier heights.

4.10. Hydrogen Abstraction from $CH_2FCH_2CHF_2$ by ^3O

The reaction of triplet oxygen with $CH_2FCH_2CHF_2$ yields two radicals:

$CH_2FCF_2CH_3 + {}^3O \rightarrow CHFCF_2CH_3 + HO$ (**R10-A**)

$CH_2FCF_2CH_3 + {}^3O \rightarrow CH_2FCF_2CH_2 + HO$ (**R10-B**)

Three saddle points (**10A-a**, **10A-b**, **10A-c**) were found for **R10-A**. The barrier heights for **10A-a**, **10A-b**, and **10A-c** 14.75 kcal/mol, 13.46 kcal/mol, and 14.89 kcal/mol respectively. The imaginary frequencies for **10A-a**, **10A-b**, and **10A-c** were found to be 1831*i* cm^{-1}, 1804*i* cm^{-1}, and 1792*i* cm^{-1} respectively. **10A-b** is the most likely transition pathway. For **10A-b**, The C···H, H···O, and C···O, internuclear distances are 1.309 A, 1.187 A, and 2.493 A respectively.

Five saddle points (**10B-a** through **10B-e**) exists for **R10-B**. The lowest barrier height corresponds to **10B-a** at 15.55 kcal/mol, and the highest barrier height corresponds to **10B-e** at 18.96 kcal/mol. Normal mode analysis revealed **10B-a** has the smallest imaginary frequency at 1720*i* cm^{-1}, and that **10B-b** has the highest at 1771*i* cm^{-1}. The C···H, H···O, and C···O, internuclear distances for **10B-a**, the most likely transition pathway, were found to be 1.338 A, 1.155 A, and 2.489 A respectively. From the above data, **R10-A** is the most likely radical product.

4.11. Hydrogen Abstraction from $CH_2FCHFCH_2F$ by ^3O

The reaction of triplet oxygen with $CH_2FCHFCH_2F$ yields two radicals:

$CH_2FCHFCH_2F + {}^3O \rightarrow CHFCHFCH_2F + HO$ (**R11-A**)

$CH_2FCHFCH_2F + {}^3O \rightarrow CH_2FCFCH_2F + HO$ (**R11-B**)

Eighteen saddle points (**11A-a** through **11A-r**) were found for **R11-A**. The barrier heights found range from 12.37 kcal/mol to 15.66 kcal/mol with the lowest corresponding to **11A-d** and the highest to **11A-o**. The lowest zero-point-inclusive Gibb also corresponded to **11A-d at 15.05 kcal/mol** while the highest zero-point-inclusive Gibbs was found for **11A-q** at 18.70 kcal/mol. The most likely transition pathway correspond to **11A-d**. For **11A-d**, The C···H, H···O, and C···O, internuclear distances are 1.302 A, 1.196 A, and 2.493 A respectively.

Six Saddle points (**11B-a** through **11-f**) were found for **R11-B**. The barrier heights found were 12.67 kcal/mol, 11.54 kcal/mol, 13.29 kcal/mol, 14.49 kcal/mol, 14.30 kcal/mol, and 15.24 kcal/mol for **11B-a** through **11-f** respectively. The smallest imaginary frequency corresponded to **11B-e** at 1700*i* cm^{-1}, and the largest corresponded to **11Bd** at 1795*i* cm^{-1}. The C···H, H···O, and C···O, internuclear distances for **11B-b** are 1.293 A, 1.207 A, and 2.499 A respectively. Based on barrier heights, **R11-B** is the most likely radical.

4.12. Hydrogen Abstraction from CF_3CHFCH_3 by ^3O

The reaction of triplet oxygen with CF_3CHFCH_3 yields two radicals:

$CF_3CHFCH_3 + {}^3O \rightarrow CF_3CFCH_3 + HO$ (**R12-A**)

$CF_3CHFCH_3 + {}^3O \rightarrow CF_3CHFCH_2 + HO$ (**R12-B**)

One saddle point (**12A-a**) was found for **R12-A**. The barrier height, zero-point-inclusive barrier height, zero-point-inclusive Gibbs, and imaginary frequency for **12A-a** are 13.05 kcal/mol, 8.86 kcal/mol 15.66 kcal/mol, and 1813*i* cm^{-1} respectively. The C···H, H···O, and C···O, internuclear distances are 1.301 A, 1.195 A, and 2.495 A respectively.

For **R12-B**, three saddle points (**12B-a**, **12B-b**, and **12B-c**) were found. The barrier heights for **12B-a**, **12B-b**, and **12B-c** were found to be 15.44 kcal/mol, 16.12 kcal/mol, and 16.34 kcal/mol respectively. The imaginary frequencies were 1746*i* cm^{-1}, 1751*i* cm^{-1}, and 1777*i* cm^{-1}. **12B-a** is the most likely transition pathway. The C···H, H···O, and C···O, internuclear distances for **12B-a** are 1.330 A, 1.160 A, and 2.487 A respectively. Overall, **R12-A** is the most likely radical product.

4.13. Hydrogen Abstraction from $CF_3CH_2CH_2F$ by ^3O

The reaction of triplet oxygen with $CF_3CH_2CH_2F$ yields two radicals:

$CF_3CH_2CH_2F + {}^3O \rightarrow CF_3CHCH_2F + HO$ (**R13-A**)

$CF_3CH_2CH_2F + {}^3O \rightarrow CF_3CH_2CHF + HO$ (**R13-B**)

Three saddle points (**13A-a**, **13A-b**, and **13A-c**) exists for **R13-A**. The barrier heights for **13A-a**, **13A-b**, and **13A-c** are 17.15 kcal/mol, 16.35 kcal/mol, and 17.06 kcal/mol respectively. The zero-point-inclusive Gibbs for **13A-a**, **13A-b**, and **13A-c** are 19.69 kcal/mol, 19.27 kcal/mol, and 19.61 kcal/mol respectively. The most likely transition pathway corresponds to **13A-b**. For **13A-b**, the C···H, H···O, and C···O, internuclear distances are 1.087 A, 3.208 A, and 3.222 A respectively.

Three saddle points (**13B-a**, **13B-b**, and **13B-c**) were found for **R13-B**. The barrier heights for **13B-a**, **13B-b**, and **13B-c** are 12.27 kcal/mol, 13.23 kcal/mol, and 12.47 kcal/mol respectively. The imaginary frequencies for **13A-a**, **13A-b**, and **13A-c** are 1749*i* cm^{-1}, 1794*i* cm^{-1}, and 1789*i* cm^{-1} respectively. The most likely transition pathway corresponds to **13B-a**. For **13B-a**, the C···H, H···O, and C···O, internuclear distances are 1.290 A, 1.207 A, and 2.494 A respectively. Overall, the most likely radical product is **R13-B**.

4.14. Hydrogen Abstraction from $CHF_2CF_2CH_3$ by ^3O

The reaction of triplet oxygen with $CHF_2CF_2CH_3$ yields two radicals:

$CHF_2CF_2CH_3 + {}^3O \rightarrow CF_2CF_2CH_3 + HO$ (**R14-A**)

$CHF_2CF_2CH_3 + {}^3O \rightarrow CHF_2CF_2CH_2 + HO$ (**R14-B**)

For **R14-A**, only two saddle points (**14A-a** and **14A-b**) were found. The barrier height, zero-point-inclusive barrier height, zero-point-inclusive Gibbs, and imaginary frequency for **14A-a** is 15.50 kcal/mol, 11.27 kcal/mol, 18.11 kcal/mol, and 1850*i* cm^{-1} respectively. For **14A-b**, the zero-point-inclusive barrier height, zero-point-inclusive Gibbs, and imaginary frequency is 15.67 kcal/mol, 11.56 kcal/mol, 18.38 kcal/mol, and 1829*i* cm^{-1} respectively. The most likely transition pathway corresponds to **14A-a**. For **14A-a**, the C···H, H···O, and C···O, internuclear distances are 1.328 A, 1.167 A, and 2.491 A respectively.

Five saddle points (**14B-a** through **14B-e**) were found for **R14-B**. The lowest barrier height found corresponds to **14B-a** at 17.59 kcal/mol, and the highest corresponds to **14B-e** at 19.86 kcal/mol. Normal mode analysis revealed **14B-c** has the smallest imaginary frequency at 1736*i* cm^{-1}, and that **14B-e** has the largest at 1761*i* cm^{-1}. The C···H, H···O, and C···O, internuclear distances for **14B-a** are 1.350 A, 1.145 A, and 2.495 A respectively. From the above information radical product **R14-A** is most likely radical to form.

4.15. Hydrogen Abstraction from $CHF_2CH_2CH_2F$ by ^3O

The reaction of triplet oxygen with $CHF_2CH_2CH_2F$ yields two radicals:

$CHF_2CH_2CH_2F + {}^3O \rightarrow CF_2CH_2CH_2F + HO$ (**R15-A**)

$CHF_2CH_2CH_2F + {}^3O \rightarrow CHF_2CHCH_2F + HO$ (**R15-B**)

Five saddle points (**15A-a** through **15A-e**) were found for **R15-A**. **15A-a** has the lowest barrier height at 13.78 kcal/mol, and **15A-e** has the highest at 15.80 kcal/mol. Zero-point-inclusive Gibbs follows the same trend with **15A-a** having the smallest at 16.07 kcal/mol, and **15A-e** having the largest at 18.59 kcal/mol. The C···H, H···O, and C···O, internuclear distances for **15A-a** are 1.312 A, 1.182 A, and 2.492 A respectively.

Six saddle points (**15B-a** through **15B-f**) were found for **R15-B**. The lowest barrier height corresponds to **15B-b** at 17.40 kcal/mol, and the highest corresponds to **15B-f** at 21.00 kcal/mol. Normal mode analysis revealed **15B-f** has the lowest imaginary frequency at 1758*i* cm^{-1}, and **15B-d** has the highest at 1782*i* cm^{-1}. For **15B-b**, the C···H, H···O, and C···O, internuclear distances are 1.350 A, 1.146 A, and 2.492 A respectively. From the above data, **R15-A** is the most likely radical product.

4.16. Hydrogen Abstraction from CHF_2CHFCH_2F by ^3O

The reaction of triplet oxygen with CHF_2CHFCH_2F yields three radicals:

$CHF_2CHFCH_2F + {}^3O \rightarrow CF_2CHFCH_2F + HO$ (**R16-A**)

$CHF_2CHFCH_2F + {}^3O \rightarrow CHF_2CFCH_2F + HO$ (**R16-B**)

$CHF_2CHFCH_2F + {}^3O \rightarrow CHF_2CHFCHF + HO$ (**R16-C**)

Nine saddle points (**16A-a** through **16A-i**) were found for **R16-A**. Of the computed classical barrier heights, **16A-b** was found to have the lowest at 15.11 kcal/mol, and **16A-f** was found to have the highest at 16.11 kcal/mol. The ΔH_o for all possible saddle points for **R16-A** was 2.704 kcal/mol. The C···H, H···O, and C···O, internuclear distances for **16A-b** are 1.319 A, 1.175 A, and 2.491 A respectively.

Nine saddle points (**16B-a** through **16B-i**) were also found for **R16-B**. The lowest barrier height was found for **16B-a** at 13.92 kcal/mol, and the highest was found for **16B-h** at 17.66 kcal/mol. For the imaginary frequencies, **16B-f** was found to have the small imaginary frequency at 1790*i* cm^{-1}, and **16B-h** has the largest at 1843*i* cm^{-1}. The C···H, H···O, and C···O, internuclear distances for **16B-a** are 1.321 A, 1.187 A, and 2.493 A respectively.

Eighteen saddle points (**16C-a** through **16C-r**) were found for **R16-C**. The lowest barrier height found corresponds to **16C-a** at 13.98 kcal/mol, and the highest corresponds to **16C-r** at 17.62 kcal/mol. The ΔH_o for the reaction was 0.458 kcal/mol and the ΔE was 4.745 kcal/mol. For **16C-a**, the C···H, H···O, and C···O, internuclear distances are 1.310 A, 1.182 A, and 2.490 A respectively. **R6-B** is the most likely radical product.

4.17. Hydrogen Abstraction from $CH_2FCF_2CH_2F$ by ^3O

The reaction of triplet oxygen with yields $CH_2FCF_2CH_2F$ one radical:

$CH_2FCF_2CH_2F + {}^3O \rightarrow CHFCF_2CH_2F + HO$ (**R17-A**)

Nine saddle points (**17A-a** through **17A-i**) were found for **R17-A**. **17A-b** was found to have the lowest barrier height at 15.33 kcal/mol, and **17A-i** was found to have the highest at 18.43 kcal/mol. **17A-b** also has the lowest calculated zero-point-inclusive barrier height and zero-point-inclusive Gibbs barrier at 11.10 kcal/mol and 17.48 kcal/mol respectively. The ΔH_o for the reaction was 2.32 kcal/mol, and the ΔE was 6.61 kcal/mol. The C···H, H···O, and C···O, internuclear distances for **17A-b**, the most likely transition pathway, are 1.322 A, 1.171 A, and 2.492 A respectively.

4.18. Hydrogen Abstraction from $CF_3CF_2CH_3$ by 3O

The reaction of triplet oxygen with $CF_3CF_2CH_3$ yields one radical:

$CF_3CF_2CH_3 + {}^3O \rightarrow CF_2CHFCH_2F + HO$ (**R18-A**)

Only two saddle points (**18A-a** and **18A-b**) were found for **R18-A**. Barrier heights for **18A-a** and **18A-b** were 18.00 kcal/mol and 18.34 kcal/mol respectively. The ΔH_o for the reaction was 6.17 kcal/mol, and the ΔE was 610.82 kcal/mol. Normal mode analysis for **18A-a** and **18A-b** revealed imaginary frequencies of 1735*i* cm^{-1} and 1750*i* cm^{-1} respectively. For **18A-a** and **18A-b** the zero-point-inclusive barrier height were 13.57 kcal/mol and 14.00 kcal/mol respectively. The zero-point-inclusive Gibss for **18A-a** and **18A-b** were 20.24 kcal/mol and 20.81 kcal/mol respectively. The most like likely transition pathway is **18A-a**. For **18A-a**, the C···H, H···O, and C···O, internuclear distances are 1.353 A, 1.139 A, and 2.491 A respectively.

4.19. Hydrogen Abstraction from CF_3CHFCH_2F by 3O

The reaction of triplet oxygen with CF_3CHFCH_2F yields two radicals:

$CF_3CHFCH_2F + {}^3O \rightarrow CF_3CFCH_2F + HO$ (**R19-A**)

$CF_3CHFCH_2F + {}^3O \rightarrow CF_3CHFCHF + HO$ (**R19-B**)

Three saddle points (**19A-a**, **19A-b**, and **19A-c**) were found for **R19-A**. The barrier heights for **19A-a** and **19A-b** were both around 15.57 kcal/mol while **19A-c** has a barrier height of 16.86 kcal/mol. The ΔH_o for the reaction was 0.426 kcal/mol. Normal mode analysis revealed imaginary frequencies of 1869*i* cm^{-1}, 1861*i* cm^{-1}, and 1858*i* cm^{-1} respectively. The most likely transition pathway for **R19-A** is **19A-b**. For **19A-b**, the C···H, H···O, and C···O, internuclear distances are 1.311 A, 1.187 A, and 2.494 A respectively.

Six saddle points (**19B-a** through **19B-f**) were found for **R19-B**. The lowest barrier height was found for **19B-e** at 14.53 kcal/mol, and the highest barrier height was found for **19B-b** at 15.21 kcal/mol. **19B-a** has the smallest imaginary frequency of 1821*i* cm^{-1}, and **19B-b** has the largest at 1868*i* cm^{-1}. The ΔH_o for the reaction was -0.00992 kcal/mol. For **19B-e**, the C···H, H···O, and C···O, internuclear distances are 1.315 A, 1.181 A, and 2.492 A respectively. Based on the barrier heights, **R19-B** is the most likely radical product.

4.20. Hydrogen Abstraction from $CF_3CH_2CHF_2$ by ^3O

The reaction of triplet oxygen with $CF_3CH_2CHF_2$ yields two radicals:

$CF_3CH_2CHF_2 + {}^3O \rightarrow CF_3CHCHF_2 + HO$ (**R20-A**)

$CF_3CH_2CHF_2 + {}^3O \rightarrow CF_3CH_2CF_2 + HO$ (**R20-B**)

Three saddle points (**20A-a**, **20A-b**, and **20A-c**) were found for **R20A-a**. Computed barrier heights for **20A-a**, **20A-b**, and **20A-c** were 19.21 kcal/mol, 18.51 kcal/mol, and 20.14 kcal/mol. The zero-point-inclusive barrier heights for **20A-a**, **20A-b**, and **20A-c** were 21.20 kcal/mol 20.78 kcal/mol, and 22.61 kcal/mol respectively. The overall change in energy for the reaction was 9.56 kcal/mol. Based on barrier heights, **20A-b** is the most likely transition pathway. The C···H, H···O, and C···O, internuclear distances for **20A-b** are 1.357 A, 1.138 A, and 2.492 A respectively.

Only two saddle points (**20B-a** and **20B-b**) were found for **R20-B**. **20B-a** and **20B-b** has barrier heights of 13.95 kcal/mol and 14.36 kcal/mol respectively. The zero-point-inclusive Gibbs for **20B-a** and **20B-b** were found to be 16.91 kcal/mol and 17.36 kcal/mol respectively. Imaginary frequencies for **20B-a** and **20B-b** were 1847*i* cm^{-1} and 1799*i* cm^{-1} respectively. The most likely transition pathway corresponds to **20B-b**. The C···H, H···O, and C···O, internuclear distances for **20B-b** are 1.357 A, 1.200 A, and 2.496 A respectively. Based on the barrier heights, **R20-B** is the most likely radical formed.

4.21. Hydrogen Abstraction from $CHF_2CF_2CH_2F$ by ^3O

The reaction of triplet oxygen with $CHF_2CF_2CH_2F$ yields two radicals:

$CHF_2CF_2CH_2F + {}^3O \rightarrow CF_2CF_2CH_2F + HO$ (**R21-A**)

$CHF_2CF_2CH_2F + {}^3O \rightarrow CHF_2CF_2CHF + HO$ (**R21-B**)

For **R21-A**, five saddle points (**21A-a** through **21A-e**) were found. **21A-a** was found to have the lowest barrier height at 15.94 kcal/mol, and **21A-e** was found to have the highest at 16.96 kcal/mol. The ΔH_o and ΔE for the reaction were 3.17 kcal/mol and 6.79 kcal/mol respectively. Normal mode analysis revealed the largest and smallest imaginary frequencies of 1898*i* cm^{-1} and 1835*i* cm^{-1} for **21A-a** and **21A-d** respectively. For **21A-a**, the C···H, H···O, and C···O, internuclear distances are 1.329 A, 1.164 A, and 2.491 A respectively.

Nine saddle points (**21B-a** through **21B-i**) were found for **R21-B**. The lowest barrier height of 15.81 kcal/mol was found for **21B-d**, and the highest barrier height of 18.35 kcal/mol was found for **21B-i**. **21B-f** was found to have the lowest zero-point-inclusive barrier height at 10.49 kcal/mol, and **21B-c** was found to have the highest at 19.96 kcal/mol. The overall change in energy for the reaction was 6.24 kcal/mol. For **21B-d**, the C···H, H···O, and C···O, internuclear distances are 1.319 A, 1.176 A, and 2.494 A respectively. Among the two reactions, **R21-B** is the most likely radical product.

4.22. Hydrogen Abstraction from $CHF_2CHFCHF_2$ by ^3O

The reaction of triplet oxygen with $CHF_2CHFCHF_2$ yields two radicals:

$CHF_2CHFCHF_2 + {}^3O \rightarrow CF_2CHFCHF_2 + HO$ (**R22-A**)

$CHF_2CHFCHF_2 + {}^3O \rightarrow CHF_2CFCHF_2 + HO$ (**R22-B**)

Nine saddle points (**22A-a** through **22A-i**) was found for **R22-A**. The lowest barrier height, **22A-a**, has a value of 14.60 kcal/mol, and the highest barrier height, **22A-e**, has a barrier height of 16.30 kcal/mol. The largest imaginary frequency belonged to **22A-h** at 1876*i* cm^{-1}, and the smallest frequency belonged to **22A-g** at 1811*i* cm^{-1}. The ΔH_o for the reaction was 1.55 kcal/mol. For **22A-a**, the C···H, H···O, and C···O, internuclear distances are 1.317 A, 1.176 A, and 2.490 A respectively.

Six saddle points (**22B-a** through **22B-f**) were found for **R22-B**. Barrier heights for the lowest and highest saddle points, **22B-a** and **22B-d**, were 15.60 kcal/mol and 18.11 kcal/mol respectively. The largest zero-point-inclusive Gibbs corresponds to **22B-e** at 20.62 kcal/mol, and the smallest corresponds to **22B-a** at 18.40 kcal/mol. The overall change in energy for the reaction was 5.20 kcal/mol. For **22B-a**, the C···H, H···O, and C···O, internuclear distances are 1.327 A, 1.169 A, and 2.494 A respectively. Based on barrier heights, **R22-A** is the most likely radical.

4.23. Hydrogen Abstraction from $CF_3CF_2CH_2F$ by ^3O

The reaction of triplet oxygen with $CF_3CF_2CH_2F$ yields one radical:

$CF_3CF_2CH_2F + {}^3O \rightarrow CF_3CF_2C_2F + HO$ (**R23-A**)

Three saddle points (**23A-a**, **23A-b**, and **23A-c**) were found for **R22-A**. Computed barrier heights for **23A-a**, **23A-b**, and **23A-c** were 15.86 kcal/mol, 16.18 kcal/mol and 16.48 kcal/mol respectively. The ΔE and ΔH_o for the reaction was 5.85 kcal/mol and 1.59 kcal/mol respectively. The C···H, H···O, and C···O, internuclear distances for **23A-a**, the most likely transition pathway, are 1.324 A, 1.170 A, and 2.493 A respectively.

4.24. Hydrogen Abstraction from $CF_3CHFCHF_2$ by ^3O

The reaction of triplet oxygen with $CF_3CHFCHF_2$ yields two radicals:

$CF_3CHFCHF_2 + {}^3O \rightarrow CF_3CFCHF_2 + HO$ (**R24-A**)

$CF_3CHFCHF_2 + {}^3O \rightarrow CF_3CHFCF_2 + HO$ (**R24-A**)

Three saddle points (**24A-a**, **24A-b**, and **24A-c**) were found for **R24-A**. Computer barrier heights for **24A-a**, **24A-b**, and **24A-c** were 17.31 kcal/mol, 17.32 kcal/mol, and 18.39 kcal/mol respectively. Normal mode analysis of **24A-a**, **24A-b**, and **24A-c** revealed imaginary frequencies of 1868*i* cm^{-1}, 1882*i* cm^{-1}, and 1887*i* cm^{-1} respectively. The most likely transition pathway corresponds to **24A-a**. For **24A-a**, The C···H, H···O, and C···O, internuclear distances are 1.342 A, 1.155 A, and 2.494 A respectively.

Three saddle points (**24B-a**, **24B-b**, and **24B-c**) were found for **R24-B**. Barrier heights for **24B-a**, **24B-b**, and **24B-c** were 15.91 kcal/mol, 15.90 kcal/mol, and 15.84 kcal/mol respectively. The ΔH of the reaction was 2.22 kcal/mol. **24B-b** is the most likely transition pathway. . For **24B-b**, the C···H, H···O, and C···O, internuclear distances are 1.329 A, 1.165 A, and 2.493 A respectively. **R24-B** is the most likely radical product.

4.25. Hydrogen Abstraction from $CF_3CH_2CF_3$ by ^3O

The reaction of triplet oxygen with $CF_3CH_2CF_3$ yields one radical:

$CF_3CH_2CF_3 + {}^3O \rightarrow CF_3CH_2CF_3 + HO$ (**R25-A**)

Only one saddle point (**25A-a**) was found for **25A-a**. The barrier height, zero-point-inclusive barrier height, and zero-point-inclusive Gibbs of the reaction were 20.47 kcal/mol, 15.71 kcal/mol, and 21.36 kcal/mol respectively. The overall ΔE and ΔH_o of the reaction were found to be 11.19 kcal/mol and 6.77 kcal/mol respectively. The C···H, H···O, and C···O, internuclear distances are 1.376 A, 1.124 A, and 2.500 A respectively.

4.26. Hydrogen Abstraction from $CHF_2CF_2CHF_2$ by ^3O

The reaction of triplet oxygen with $CHF_2CF_2CHF_2$ yields one radical:

$CHF_2CF_2CHF_2 + {}^3O \rightarrow CF_2CF_2CHF_2 + HO$ (**R26-A**)

Four saddle points (**26A-a** through **26A-e**) were found for **R26-A**. The lowest barrier height was found for **26A-d** at 16.18 kcal/mol, and the highest barrier height was found for **26A-e** at 18.07 kcal/mol. The ΔH_o of the reaction was 2.82 kcal/mol. Normal mode analysis revealed **26A-e** has the lowest imaginary frequency of 1855*i* cm^{-1}, and **26A-c** has the highest at 1892*i* cm^{-1}. For **26A-d**, The C···H, H···O, and C···O, internuclear distances are 1.321 A, 1.174 A, and 2.493 A respectively.

4.27. Hydrogen Abstraction from $CF_3CF_2CHF_2$ by ^3O

The reaction of triplet oxygen with $CF_3CF_2CHF_2$ yields one radical:

$CF_3CF_2CHF_2 + {}^3O \rightarrow CF_3CF_2CF_2 + HO$ (**R27-A**)

Only two saddle points (**27A-a** and **27A-b**) were found for **R27-A**. The barrier height, zero-point-inclusive barrier height, and zero-point-inclusive Gibbs for **27A-a** were 16.08 kcal/mol, 11.90 kcal/mol, and 18.70 kcal/mol respectively. The barrier highest, zero-point-inclusive barrier height, and zero-point-inclusive Gibbs for **27A-b** were 16.51 kcal/mol, 12.20 kcal/mol, and 19.02 kcal/mol respectively. The ΔE and ΔH_o for the reaction was 6.17 kcal/mol and 2.40 kcal/mol respectively. The C···H, H···O, and C···O, internuclear distances are 1.329 A, 1.165 A, and 2.493 A respectively.

4.28. Hydrogen Abstraction from CF_3CHFCF_3 by ^3O

The reaction of triplet oxygen with CF_3CHFCF_3 yields one radical:

$CF_3CHFCF_3 + {}^3O \rightarrow CF_3CFCF_3 + HO$ (**R28-A**)

Only one saddle point (**28A-a**) was found for **R28-A**. The barrier height, zero-point-inclusive barrier height, and ΔG for **28A-a** was 17.97 kcal/mol, 13.49 kcal/mol, and 19.78 kcal/mol respectively. The ΔE and ΔH_o for the reaction was 6.29 kcal/mol and 2.53 kcal/mol respectively. The C···H, H···O, and C···O, internuclear distances are 1.346 A, 1.151 A, and 2.497 A respectively.

4.29. Hydrogen Abstraction from $CH_3CH_2CH_3$ by ^3O

For completeness of study, the hydrogen abstraction of propane was also analyzed. The reaction of triplet oxygen with $CH_3CH_2CH_3$ yields two radicals:

$$CH_3CH_2CH_3 + OH \rightarrow CH_3CH_2CH_2 + H_2O \quad \textbf{(R29-A)}$$

$$CH_3CH_2CH_3 + OH \rightarrow CH_3CHCH_3 + H_2O \quad \textbf{(R29-B)}$$

Two saddle points (**29A-a** and **29A-b**) were found for **R29-A**. . The barrier height, zero-point-inclusive barrier height, and ΔG for **29A-a** was 10.18 kcal/mol, 6.23 kcal/mol, and 12.37 kcal/mol respectively. The barrier height, zero-point-inclusive barrier height, and zero-point-inclusive Gibbs for **29A-b** was 10.68 kcal/mol, 6.79 kcal/mol, and 12.96 kcal/mol respectively. The ΔE and ΔH_o for the reaction was 6.51 kcal/mol and 1.66 kcal/mol respectively. The most likely transition pathway corresponds to **29A-a**. The C···H, H···O, and C···O, internuclear distances for **29A-a** are 1.293 A, 1.207 A, and 2.499 A respectively.

Only one saddle point (**29B-a**) was found for **R29-B**. . The barrier height, zero-point-inclusive barrier height, and zero-point-inclusive Gibbs for **29B-a** were 7.52 kcal/mol, 3.61 kcal/mol, and 9.86 kcal/mol respectively. The ΔE and ΔH_o for the reaction was 2.72 kcal/mol and -2.24 kcal/mol respectively. The imaginary frequency was found to be 1647*i* cm^{-1}. The C···H, H···O, and C···O, internuclear distances for are 1.264 A, 1.243 A, and 2.507 A respectively. The most likely radical product corresponds to **29B-a**.

5.1. Discussion-Geometry Correlations

Figures 3 through 10 show some interesting correlations between geometrical and energetic parameters for the 269 saddle points. In each graph, the blue dots represent saddle points for the hydrogen abstraction from positions 4 or 9, the green dot represents saddle points for the hydrogen abstraction from positions 5, 6, 10, or 11, and the red dots represents saddle points for the hydrogen abstraction from positions 7 or 8.

Figures 3 and 4 compare the classical barrier height with respect to the O···H distance and C···H distance respectively. Barrier height values fell between 7.5 kcal/mol and 20.0 kcal/mol while values for C···H and O···H distance were found in the range of 1.225 A and 1.375 A and 1.12 A and 1.26 A respectively. From the graphs it appears as barrier height increases C···H distances increase and O···H distance decrease.

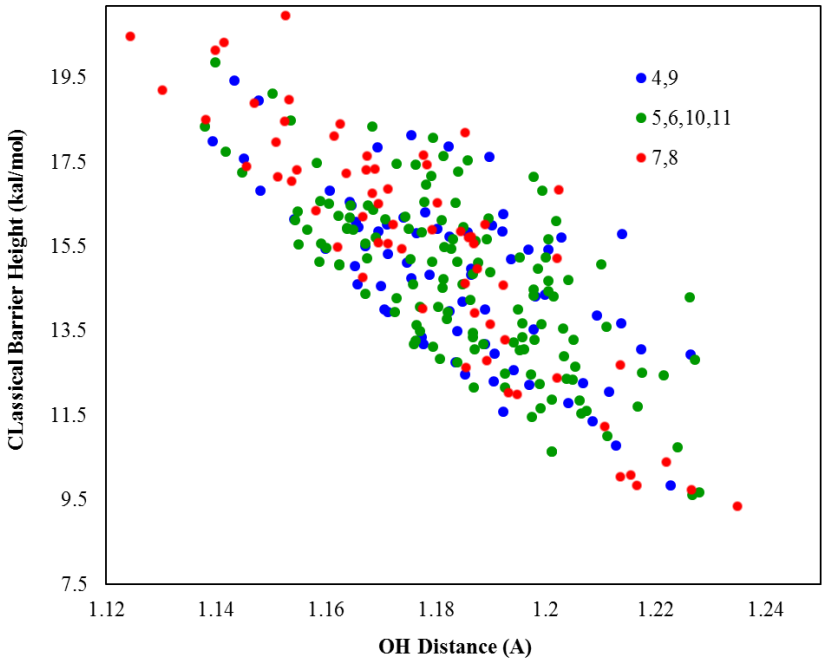


Figure 3: Classical barrier height distribution versus the O–H distance for all saddle points of hydrogen abstraction reactions by ^{3}O

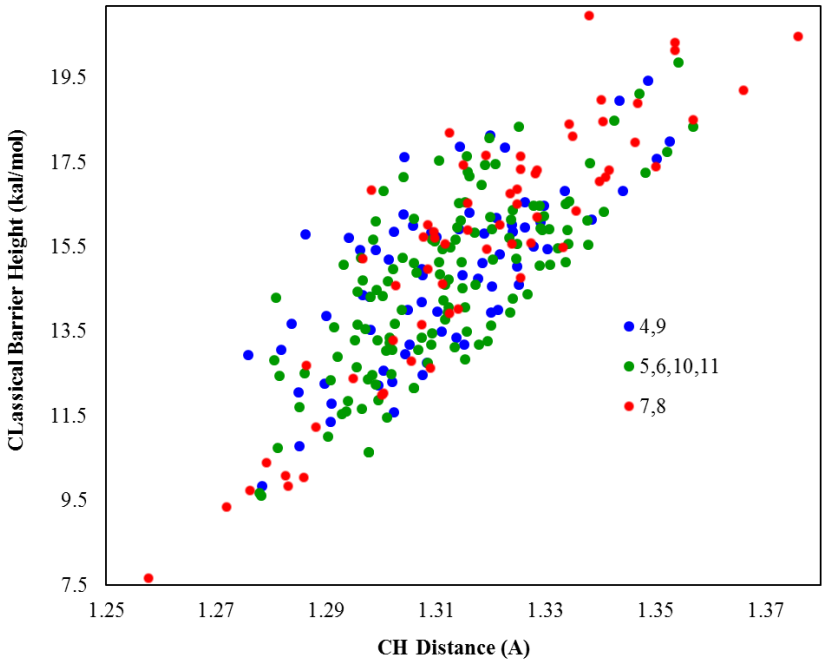


Figure 4: Classical barrier height distribution versus the C–H distance for all saddle points of hydrogen abstraction reactions by ^{3}O

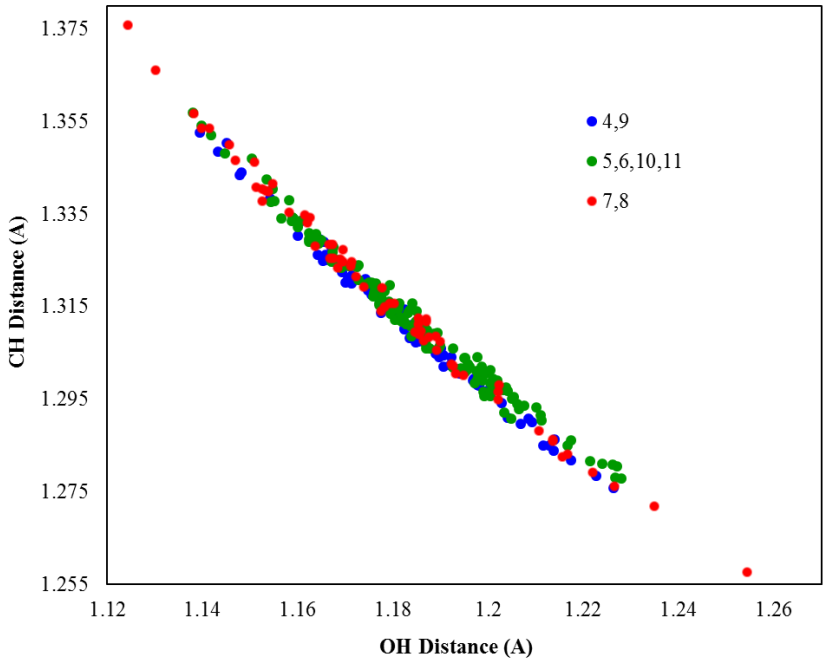


Figure 5: The C–H distance versus the O–H distance for all saddle points of hydrogen abstraction reactions by ^3O

Figure 5 compares the C···H distances versus the O···H distances for the saddle points. In general, hydrogen abstractions from positions 4 or 9 occurs at shorter C···H distances, implying a more reactant like saddle point. Abstraction from positions 5, 6, 10, or 11 appear to have a mix of early and late saddle points, but overall have more product like saddle points than the other two sites. Abstraction from positions 7 or 8 generally fall in the middle with the exceptions occurring at the beginnings and end of the graph. It appears abstractions from position 7 or 8 have the potential to occur extremely early or extremely late. Figures 6 and 7 compare the C···O distances with the C···H distances and O···H distances respectively. The C···O distances ranged from 2.48 A to 2.52 A. It was found that large C···O distances typically correspond to short C···H distances, and large O···H distances.

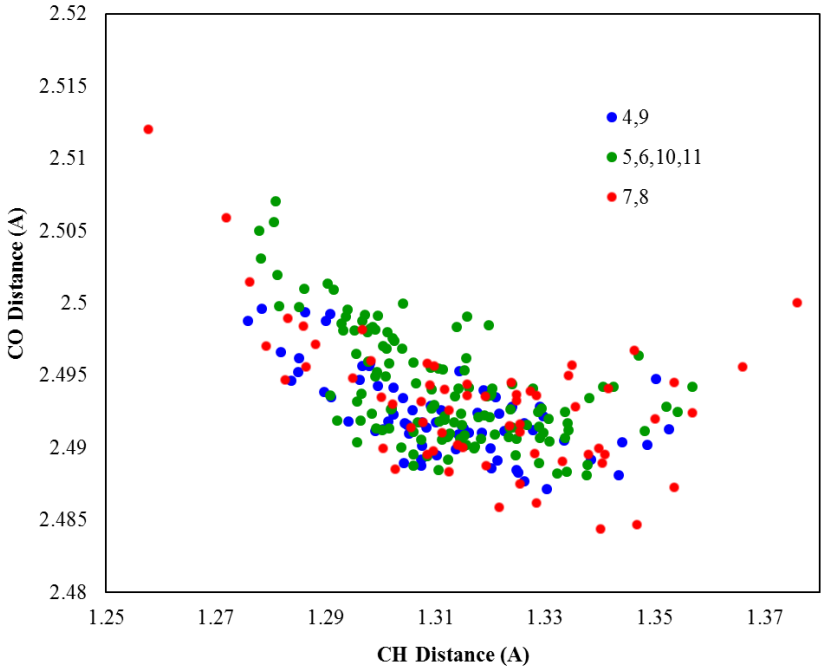


Figure 6: The C–O distance versus the C–H distance for all saddle points of hydrogen abstraction reactions by ^3O

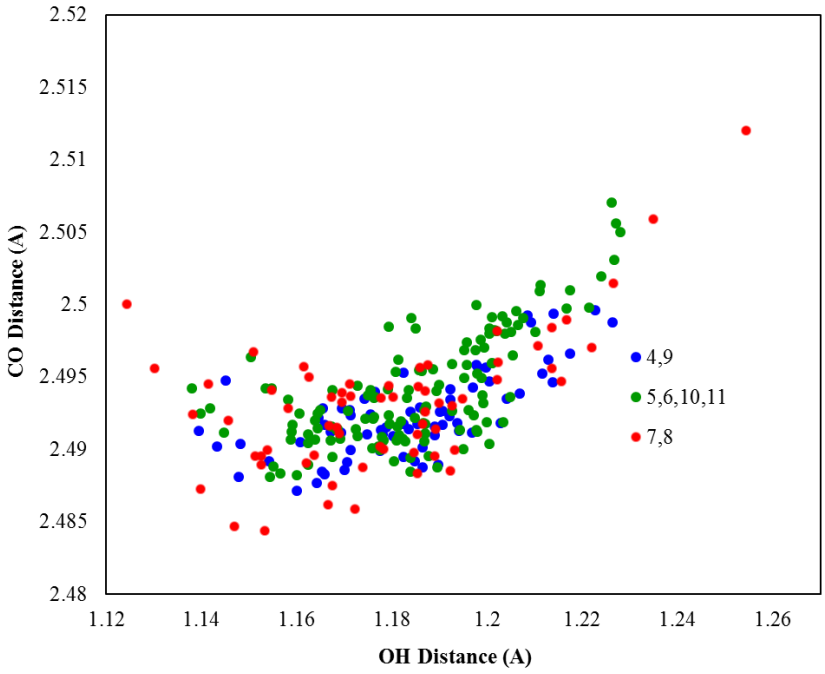


Figure 7: The C–O distance versus the O–H distance for all saddle points of hydrogen abstraction reactions by ^3O

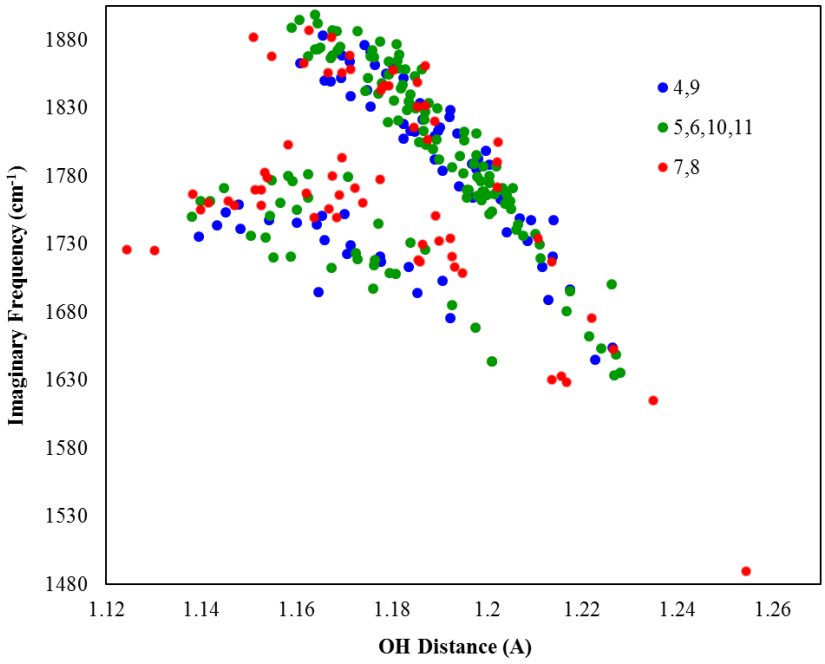


Figure 8: Imaginary frequency distribution versus the O–H distance for all saddle points of hydrogen abstraction reactions by ^{3}O

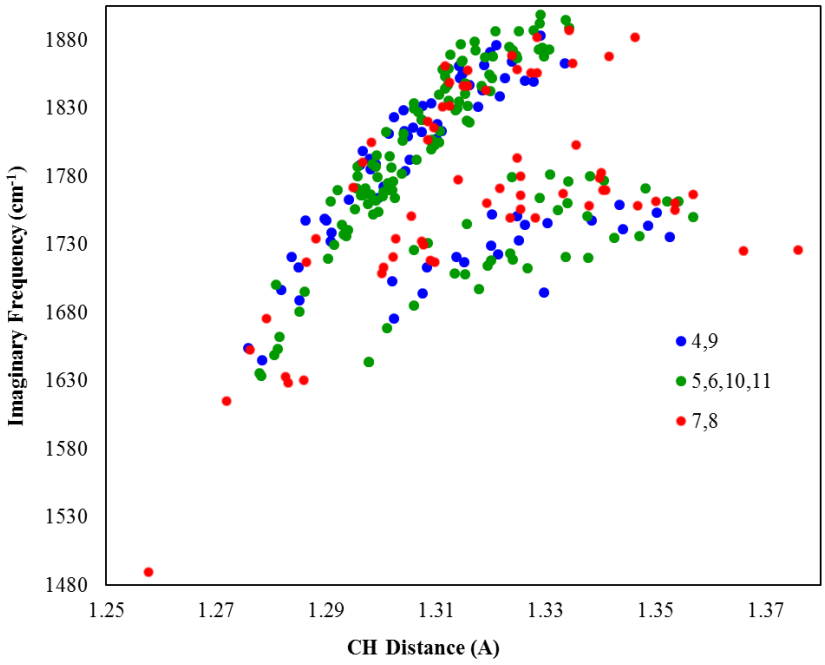


Figure 9: Imaginary frequency distribution versus the C–H distance for all saddle points of hydrogen abstraction reactions by ^{3}O

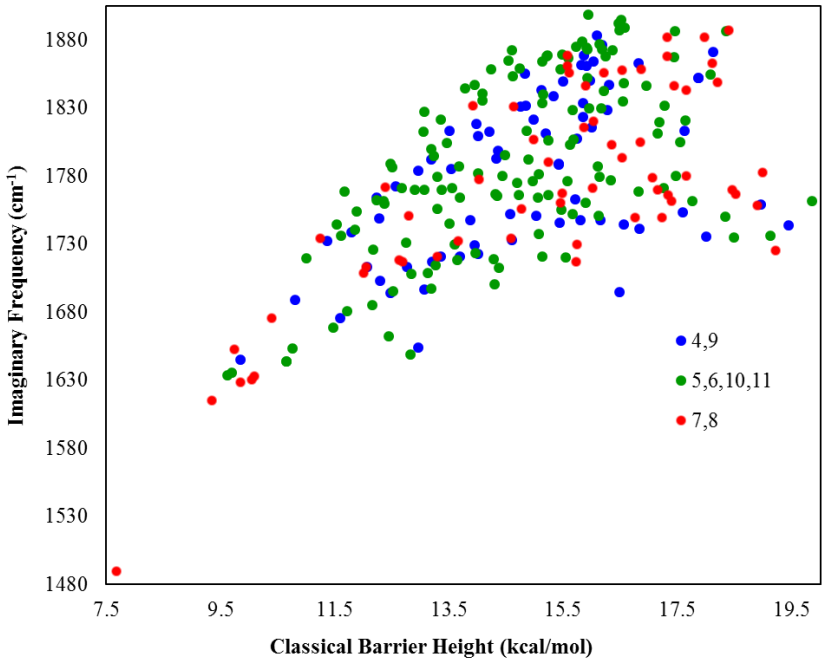


Figure 10: Imaginary frequency variation with the classical barrier height of all saddle points of the hydrogen abstraction reaction by ^{3}O

Figures 9 through 10 compare the imaginary frequency with the C···H distances, O···H distances, and classical barrier height. Imaginary frequency values ranged from 1489*i* cm^{-1} to 1898*i* cm^{-1}. A high imaginary frequency indicates a large negative force constant at the saddle point which corresponds to a narrow barrier. Conversely, a low imaginary frequency indicates a lower negative force constant which corresponds to a wider barrier. In general, small C···H distances and large O···H distances correspond to small imaginary frequencies, and large C···H distances and small O···H distances correspond to large imaginary frequencies. From this, it can be said that as the number of fluorine increase (going from small C···H distances and large O···H distances to large C···H distances and small O···H distances) the barrier gets smaller. Also in general, as the classical barrier height energy increases, the imaginary frequencies diecrease.

5.2. Discussion-Nearest Neighbor Effect

Tables 1 through 4 detail the effects of the substituents of the neighboring carbons. The effects of neighboring carbons were only investigated for the lowest energy saddle points. All distances are in angstroms and all energies in kcal/mol.

Several trends were found by the nearest neighbor effect. In general, as the number of fluorine increases on the HFP, the barrier height increases. The saddle point also becomes more product like as detailed by the increase in the C···H distance and the decrease in O···H distance. More specifically, a greater barrier height increase occurs when the nearest neighbor gains fluorine than when the next nearest neighbor gains fluorine. There also appears to be a relationship between the distribution of fluorine and the barrier height. On a molecule that has an uneven distribution of fluorine, abstraction from a carbon with more fluorine tend to be high than a hydrogen abstraction from a carbon on the same molecule with fewer fluorine.

Table 1 Saddle point characteristics for hydrogen abstraction reactions by triplet oxygen from a CH_3 group of fluoropropanes

Nearest neighbor	Next-nearest neighbor	$V^{\ddagger}$	Lowest-energy saddle point	$r^{\ddagger}_{C\cdots H}$	$r^{\ddagger}_{H\cdots O}$
$-CH_2-$	$-CH_3$	10.18	**29A-a**	1.293	1.207
$-CH_2-$	$-CH_2F$	10.65	**1C-b**	1.298	1.201
$-CH_2-$	$-CHF_2$	12.15	**3C-a**	1.306	1.193
$-CH_2-$	$-CF_3$	13.35	**7B-a**	1.314	1.177
–CHF–	$-CH_3$	12.83	**2A-a**	1.315	1.181
–CHF–	$-CH_2F$	13.26	**4C-h**	1.319	1.176
–CHF–	$-CHF_2$	13.96	**8C-c**	1.324	1.172
–CHF–	$-CF_3$	15.44	**12B-a**	1.330	1.160
$-CF_2-$	$-CH_3$	15.13	**6A-a**	1.334	1.159
$-CF_2-$	$-CH_2F$	15.54	**10B-a**	1.338	1.155
$-CF_2-$	$-CHF_2$	17.59	**14B-a**	1.350	1.145
$-CF_2-$	$-CF_3$	18.00	**18A-a**	1.353	1.139

Table 2 Saddle point characteristics for hydrogen abstraction reactions by triplet oxygen from a CH_2F group of fluoropropanes

Nearest neighbor	Next-nearest neighbor	Lowest-energy saddle point	$V^{\ddagger}$	$r^{\ddagger}_{C\cdots H}$	$r^{\ddagger}_{H\cdots O}$
–CH_2–	–CH_3	**1A-a**	9.62	1.278	1.227
–CH_2–	–CH_2F	**5A-c**	10.76	1.281	1.224
–CH_2–	–CHF_2	**9C-b**	11.80	1.291	1.204
–CH_2–	–CF_3	**13A-b**	16.35	1.335	1.158
–CHF–	–CH_3	**4A-d**	11.62	1.294	1.207
–CHF–	–CH_2F	**11B-a**	13.07	1.302	1.196
–CHF–	–CHF_2	**16C-a**	13.40	1.310	1.182
–CHF–	–CF_3	**19B-e**	14.53	1.315	1.181
–CF_2–	–CH_3	**10A-b**	13.46	1.309	1.187
–CF_2–	–CH_2F	**17A-b**	15.33	1.322	1.171
–CF_2–	–CHF_2	**21B-d**	15.81	1.319	1.176
–CF_2–	–CF_3	**23A-a**	15.86	1.324	1.170

Table 3 Saddle point characteristics for hydrogen abstraction reactions by triplet oxygen from a CHF_2 group of fluoropropanes

Nearest neighbor	Next-nearest neighbor	Lowest-energy saddle point	$V^{\ddagger}$	$r^{\ddagger}_{C\cdots H}$	$r^{\ddagger}_{H\cdots O}$
–CH_2–	–CH_3	**3A-a**	11.01	1.290	1.211
–CH_2–	–CH_2F	**9A-a**	13.06	1.307	1.187
–CH_2–	–CHF_2	**15A-a**	13.78	1.311	1.182
–CH_2–	–CF_3	**20B-a**	13.95	1.312	1.182
–CHF–	–CH_3	**8A-c**	13.19	1.309	1.189
–CHF–	–CH_2F	**16A-b**	15.11	1.319	1.175
–CHF–	–CHF_2	**22A-a**	14.60	1.317	1.176
–CHF–	–CF_3	**24B-c**	15.84	1.317	1.177
–CF_2–	–CH_3	**14A-a**	15.50	1.328	1.167
–CF_2–	–CH_2F	**21A-a**	15.94	1.1.329	1.164
–CF_2–	–CHF_2	**26A-d**	16.18	1.321	1.174
–CF_2–	–CF_3	**27A-a**	16.08	1.329	1.165

Table 4 Saddle point characteristics for hydrogen abstraction reactions by triplet oxygen from a CH_2 group of fluoropropanes

Neighbors		Lowest-energy saddle point	$V^{\ddagger}$	$r^{\ddagger}_{C\cdots H}$	$r^{\ddagger}_{H\cdots O}$
H_3C–	–CH_3	**29B-a**	7.52	1.264	1.244
H_3C–	–CH_2F	**1B-c**	9.85	1.283	1.217
H_3C–	–CHF_2	**3B-c**	12.01	1.300	1.195
FH_2C–	–CH_2F	**5B-c**	12.63	1.309	1.186
H_3C–	–CF_3	**7A-a**	14.03	1.314	1.177
FH_2C–	–CHF_2	**9B-b**	14.77	1.325	1.167
FH_2C–	–CF_3	**13B-a**	12.27	1.290	1.207
F_2HC–	–CHF_2	**15B-b**	17.40	1.350	1.146
F_2HC–	–CF_3	**20A-b**	18.51	1.357	1.138
F_3C–	–CF_3	**25A-a**	20.47	1.376	1.124

Table 5 Saddle point characteristics for hydrogen abstraction reactions by triplet oxygen from a CHF group of fluoropropanes

Neighbors		Lowest-energy saddle point	$V^{\ddagger}$	$r^{\ddagger}_{C\cdots H}$	$r^{\ddagger}_{H\cdots O}$
H_3C–	–CH_3	**2B-a**	7.68	1.258	1.254
H_3C–	–CH_2F	**4B-b**	9.34	1.272	1.235
H_3C–	–CHF_2	**8B-b**	11.24	1.288	1.211
FH_2C–	–CH_2F	**11B-b**	11.539	1.293	1.207
H_3C–	–CF_3	**12A-a**	13.05	1.300	1.195
FH_2C–	–CHF_2	**16B-a**	13.92	1.312	1.189
FH_2C–	–CF_3	**19A-b**	15.57	1.312	1.187
F_2HC–	–CHF_2	**22B-a**	15.60	1.327	1.169
F_2HC–	–CF_3	**24A-a**	17.31	1.342	1.155
F_3C–	–CF_3	**28A-a**	17.97	1.346	1.151

Conclusions

This paper completed a computational study of all 269 saddle points for the hydrogen abstraction reactions the 28 hydrofluoropropanes by triplet oxygen. mPW1B95–44/6-31+G(d,p) level of theory was used to carry out this research. The saddle points were characterized based on several energy parameters, and the most likely transition state and radical product were identified. Finally, some general conclusions were made by compare geometric parameters and by looking at the nearest neighbor effects.