Computational Studies of Chemically Activated Ozonolysis Intermediates

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Purpose of this Work

• To characterize the energy surfaces of Criegee intermediates to better understand their intramolecular mechanistic pathways
• To predict the relative amounts of products based on relative activation and minima energies using statistical mechanics
• To model the concentration of OH radical in the troposphere due to reactions of ozone with alkenes (tetramethylethylene, methylpropene, and isoprene)
Where does the carbonyl oxide of interest come from?
The ozonolysis of 2,3-dimethyl-but-2-ene or 2-methylpropene
What makes up the System

• The system is made up of 11 atoms, which implies 27 variables and a 28-dimension energy surface. That is there are three variables for each atom and 6 are taken away by translation and rotation (3n-6), and energy is a function of these variables.

• The system is symmetric, so conformation of the carbonyl oxide has no effect.
Intramolecular reactions of the dimethyl carbonyl oxide

(All numbers are in units of Kcal/mole)

Numbers on the top are derived from the B3LYP method while the bottom are from the CBS-QB3 method.
Overview on the path of the vinylhydroperoxide

Homolysis

O

O

OH

Concerted

O

H

::O::H

Stepwise diradical

::O::H

O

H

::O::H

O

H

::O::H

O

H

::O::H

O

H

::O::H

O

H

::O::H

O

H

::O::H

O

H

::O::H

O

H

::O::H

O

H

::O::H

O

H

::O::H

O

H

::O::H

O

H

::O::H

O

H
Concerted Transition States and Homolysis

Out of Plane TS

\[
\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]

\[
\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]

\[
\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]

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\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]

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\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]

\[
\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]

In Plane TS

\[
\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]

\[
\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]

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\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]

\[
\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]

Homolysis

\[
\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]

\[
\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]

\[
\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]

\[
\begin{align*}
\text{OOH} & \quad \xrightarrow{0.0} \quad \text{OOH} \\
\text{0.0} & \quad \quad \text{0.0}
\end{align*}
\]
Stepwise Diradical Mechanism

1. Rotation about C-O bond
2. Formation of a diradical pair
3. In-plane swinging of hydroxy radical
4. Formation of 1-hydroxy-propan-2-one
Summary on the path of the vinylhydroperoxide

**Homolysis**
- B3LYP Max: 17.7
- CBS-QB3 Max: 20.6

**Concerted**
- B3LYP Max: 37.0
- CBS-QB3 Max: 27.1

**Stepwise diradical**
- B3LYP Max: 14.7
- CBS-QB3 Max: 22.6
Will hydroxy acetone react further?

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{C} & \quad \text{O} \\
0.0 & \quad 0.0
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{O} & \quad \text{H} \\
\cdot \text{OH} & \quad + \\
84.8 & \quad 89.8
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
23.8 & \quad 26.2
\end{align*}
\]

or

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{H} \\
19.0 & \quad 20.9
\end{align*}
\]
Reaction of vinoxy radical with molecular oxygen

\[
\text{O} + \text{O=O} \xrightarrow{1.1 \text{ \underline{2.4}}} \left[ \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \right] \frac{\pm}{-21.9 \text{ \underline{-27.4}}} \rightarrow \text{O=O}.
\]

"Heated"
Conformations of acetone peroxy radical
The six-membered ring gives lowest TS energy...

...So the primary hydroperoxy radical is formed
Conformational Analysis of acetone hydroperoxy radical

\[
\begin{align*}
\ce{O=O} & \quad \ce{1.1} \quad \ce{O=O} \\
& \quad \ce{0.4} \quad \ce{O=O}
\end{align*}
\]
What will the primary radical do?
Products

AE: 27.4
AE: 30.8

AE: 28.0
AE: 30.7

AE: 28.6
AE: 31.8

AE: 33.1
AE: 38.4

-39.5
-41.6

24.3 25.4

-6.2  -9.8

27.1  28.3
End Points
Why Study Isoprene?

- Isoprene is one of the most abundant natural alkenes released into the atmosphere.
- Due to isoprene’s abundance, an understanding of its reactivity with ozone is a major link to someday modeling OH radical concentration in the troposphere.
What makes up the System

• The system is made up of 12 atoms, which implies 30 variables and a 31-dimension energy surface. That is there are three variables for each atom and 6 are taken away by translation and rotation (3n-6), and energy is a function of these variables.

• The system is asymmetric, so different conformers of the carbonyl oxide will follow different paths
Intramolecular reactions of the carbonyl oxide formed from Isoprene
*From Dr. Kuwata's study of the parent system
Overview on the path of the vinylhydroperoxide

Homolysis

Concerted

Stepwise diradical

Different Stepwise diradical
Stepwise Diradical Mechanism

1. Rotation about C-O bond
2. Formation of a diradical pair
3. In-plane swinging of hydroxy radical
4. Formation of alcohol
Stepwise Diradical #2

[Chemical structures and reactions with energies and bond angles]
Overview on the path of the vinylhydroperoxide

\[
\begin{align*}
\text{Homolysis} & \quad \text{B3LYP Max: 17.9} \\
& \quad \text{CBS Max: 21.1} \\
\end{align*}
\]

\[
\begin{align*}
\text{Concerted} & \quad \text{B3LYP Max: 37.1} \\
& \quad \text{CBS Max: 27.6} \\
\end{align*}
\]

\[
\begin{align*}
\text{Stepwise diradical} & \quad \text{B3LYP Max: 15.3} \\
& \quad \text{CBS Max: At least 21.2} \\
\end{align*}
\]

\[
\begin{align*}
\text{Different Stepwise diradical} & \quad \text{B3LYP Max: 15.3} \\
& \quad \text{CBS Max: At least 21.2} \\
\end{align*}
\]
Other conformer of vinyl methyl substituted carbonyl oxide

\[
\begin{align*}
\text{ozone} & \rightarrow \text{cis-vinyl carbonyl oxide} \\
\text{isoprene} & \rightarrow \text{cis-vinyl carbonyl oxide}
\end{align*}
\]
Transition State Competition

\[
\begin{align*}
\text{O} & \quad \text{HO} \\
\text{??} & \quad \text{??} \\
-14.6 & \quad -26.0
\end{align*}
\]
Anti-methyl carbonyl oxide

Dioxilene formation

Breaking pi-bond and rotating

Dioxirane formation

1.5 hydrogen abstraction (carbene formation)

Cis-methyl carbonyl chemistry
Post-homolysis of dioxilene

Epoxide formation

1.2 hydrogen abstraction

Anti-tautomerization

Cis-Tautomerization

(notice the temperatures and coordinates indicated in the structures)
End Points
In the future . . .

- Use different methods to clear up the discrepancy between the B3LYP and CBS-QB3 method in the energy of diradical molecules,
- further characterize the energy surface of the isoprene-based carbonyl oxide,
- investigate the relative amounts of products based on the relative activation energies and minima using statistical mechanics,
- and study the possible reactions of the resulting molecules.
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