Direct measurements of vinoxy radicals and formaldehyde from ozonolysis of *trans*- and *cis*-2-butene

New insights into OH radical formation and secondary chemistry

**Mixtli Campos-Pineda** and **Jingsong Zhang**
Department of Chemistry
University of California, Riverside

ACM
UC Davis
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Importance of Ozonolysis Reactions of Alkenes

• Significant oxidation pathway of alkenes in troposphere
• Secondary organic aerosol (SOA) production
• Production of OH radical (10-90% yield): strong oxidizer
• Production of Criegee intermediate (CI): strong oxidizer; CI reactions with NO₂, SO₂, H₂O etc.

Challenges

• OH production mechanism is not completely established
• Limited information about the yields, kinetics, and mechanisms of CI in ozonolysis reactions of alkenes.
Mechanism of Ozonolysis Reactions of Alkenes

Highly exothermic ~ 60 kcal/mole

Potential Energy

POZ primary ozonide

stabilized CI (sCI) bimolecular reactions /thermal dissociation

Oxidation

Organic acid, ester, etc.

Secondary organic aerosol (SOA)

Atmospheric SO₂ (H₂O)₂ oxidation Aerosol Nucleation

Taatjes, et.al. PCCP 2013
2-butene ozonolysis

anti-Cl and syn-Cl branching

\[ 
\begin{align*}
1 - \alpha & + \alpha \\
1 - \beta & + \beta \\
\end{align*}
\]

\[ 
\begin{align*}
Y_{OH} t2b & \approx 0.64 \\
Y_{OH} c2b & \approx 0.33
\end{align*}
\]

Atkinson, Paulson, Donahue, Anderson, Kroll, Marston, Cremer, Lester, and many others.

\[ 
\begin{align*}
CH_4 + CO_2 \\
CH_3OH + CO \\
CH_2CO + H_2O \\
OH + CH_3CO
\end{align*}
\]
2-butene ozonolysis:

- Nascent yield of sCI close to 0.

- At low pressure, most CI produced as “hot” CI and undergoes decomposition/isomerization.

- Only a small amount of sCI is depleted by thermal decomposition and bimolecular reactions.

Hatakeyama et al, JPC. 88 (1984) 4736
2-butene ozonolysis

anti-Cl and syn-Cl branching

Y_{OH} \ t2b \sim 0.64
Y_{OH} \ c2b \sim 0.33

• Vinoxy radical is a unique indicator of syn-Cl
• Measurements elucidate OH production pathway and syn-Cl branching ratio
Secondary reaction of vinoxy with $O_2$

\[ O_2 + CH_2CHO + (M) \rightarrow OOCH_2CHO \rightarrow HCHO + CO + OH \]
\[ \rightarrow (CHO)_2 + OH \]

OH yield from vinoxy:
~ 100%-50% in low pressure 0-100 Torr
~ 20%-0% at ambient pressure \( \rightarrow \) vinoxy yield < OH yield (0.64)


\((CHO)_2\) yield 0.10-0.15 (10-320 Torr) Zhu et al. (1995)
Upper limit of HCHO yield 0.90-0.85 \( \rightarrow \) constraint for vinoxy
2-butene ozonolysis

anti-Cl and syn-Cl branching

\[ O_3 + \text{2-butene} \rightarrow 1- \alpha + \alpha \]
\[ 1- \beta + \beta \]

\[ \alpha < Y_{OH} \text{ t2b} \quad Y_{OH} \text{ t2b} \approx 0.64 \]
\[ \beta < Y_{OH} \text{ c2b} \quad Y_{OH} \text{ c2b} \approx 0.33 \]

\[ \text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{CH}_2\text{CO} + \text{HO}_2 \quad (1) \]
\[ \rightarrow (\text{CHO})_2 + \text{HO} \quad (2) \]
\[ \rightarrow \text{HCHO} + \text{CO} + \text{HO} \quad (3) \]
\[ \text{CH}_2\text{CHO} + \text{O}_2 (+\text{M}) \rightarrow \text{CH}_2\text{O}_2\text{CHO}(+\text{M}) \quad (4) \]

- Measurements of HCHO offer constraints to improve the kinetic model.

- Vinoxy radical is a unique indicator of syn-Cl
- Measurements elucidate OH production pathway and syn-Cl branching ratio
Experimental Setup

- Ozonolysis of alkenes is carried out using a flow reactor:

- Reaction products are measured using cavity ring-down spectroscopy (CRDS).

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Measurement of ·CH$_2$CHO and HCHO

\[
\left( \frac{1}{\tau(\lambda)} - \frac{1}{\tau_0(\lambda)} \right) = \frac{dc}{L} \left( \sigma_{\text{vinoxy}}(\lambda)N_{\text{vinoxy}} + \sigma_{\text{form}}(\lambda)N_{\text{form}} + f(\lambda) \right)
\]

Cantrell et al. JPC, 94 (1990) 3902
Results

Vinoxy radical yield

Steady-state vinoxy “yield” ratio of c2b/t2b $\sim 0.55 \Rightarrow \frac{[\text{syn-Cl}]_{c2b}}{[\text{syn-Cl}]_{t2b}} = 0.6$

Consistent with $Y_{OH}$ ratio c2b/t2b: 0.33/0.64 = 0.52 (Atkinson et al.)

Vinoxy tracks syn-Cl and $Y_{OH}$, confirming syn-Cl as the dominant source of OH
Ozonolysis mechanism:

<table>
<thead>
<tr>
<th># k</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.30E-16</td>
<td>C4H8+O3===&gt;CH3CHO + 0.1CH3CHOO + 0.9H3CCHOO</td>
</tr>
<tr>
<td>7.00E+05</td>
<td>H3CCHOO==&gt;C2H4O2</td>
</tr>
<tr>
<td>3.00E+05</td>
<td>H3CCHOO==&gt;CH2CHO + OH</td>
</tr>
<tr>
<td>6.60E+04</td>
<td>C2H4O2==&gt;CH2CO + H2O</td>
</tr>
<tr>
<td>1.16E+05</td>
<td>C2H4O2==&gt;CH3OH + CO</td>
</tr>
<tr>
<td>1.83E+05</td>
<td>C2H4O2==&gt;CH4 + CO2</td>
</tr>
<tr>
<td>2.50E+05</td>
<td>C2H4O2==&gt;CH3CO + OH</td>
</tr>
<tr>
<td>2.05E+05</td>
<td>C2H4O2==&gt;CH3 + CO2 + H</td>
</tr>
<tr>
<td>1.80E+05</td>
<td>C2H4O2==&gt;HCHO + CH2O</td>
</tr>
<tr>
<td>6.40E-11</td>
<td>OH + C4H8 ==&gt; C4H8OH</td>
</tr>
<tr>
<td>9.13E-13</td>
<td>O3 + C4H8OH ==&gt; CH3CHOH + CH3CHO + O2</td>
</tr>
<tr>
<td>1.00E-13</td>
<td>O2 + C4H8OH ==&gt; OOC4H8OH</td>
</tr>
</tbody>
</table>
# Ozonolysis mechanism:

<table>
<thead>
<tr>
<th># k</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>VINOXY + O2</td>
<td></td>
</tr>
<tr>
<td>1.65E-14</td>
<td>CH2CHO + O2 ==&gt; CHOCHO + OH</td>
</tr>
<tr>
<td>5.50E-15</td>
<td>CH2CHO + O2 ==&gt; HCHO + CO + OH</td>
</tr>
<tr>
<td>4.40E-14</td>
<td>CH2CHO + O2 ==&gt; CH2CO + HO2</td>
</tr>
<tr>
<td>4.40E-14</td>
<td>CH2CHO + O2 ==&gt; OOCH2CHO</td>
</tr>
</tbody>
</table>

VINOXY UNIMOLECULAR REACTIONS

<table>
<thead>
<tr>
<th># k</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00E+01</td>
<td>CH2CHO ==&gt; OHCH2C</td>
</tr>
<tr>
<td>6.60E+03</td>
<td>CH2CHO ==&gt; 0.18HCHO + 0.18 + 0.82CH2CHO</td>
</tr>
</tbody>
</table>

STABILIZED CI REACTIONS

<table>
<thead>
<tr>
<th># k</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00E+01</td>
<td>CH3CHOO ==&gt; HHCCOOHH</td>
</tr>
<tr>
<td>160</td>
<td>CH3CHOO ==&gt; CH2CHO + OH</td>
</tr>
<tr>
<td>1.10E-12</td>
<td>CH3CHO + CH3CHOO ==&gt; C4H8O3</td>
</tr>
<tr>
<td>2.60E-14</td>
<td>CH3CHO + CH3CHOO ==&gt; CH3COOH + CH3CHO</td>
</tr>
<tr>
<td>3.60E-15</td>
<td>CH3CHO + CH3CHOO ==&gt; H2O + HCHO + HCHO + H2C2</td>
</tr>
<tr>
<td>1.70E-16</td>
<td>CH3CHOO + O3 ==&gt; CH3CHO + O2 + O2</td>
</tr>
<tr>
<td>4.00E-18</td>
<td>CH3CHOO + H2O ==&gt; C2H6O3</td>
</tr>
<tr>
<td>1.00E-15</td>
<td>CH3CHOO + C4H8 ==&gt; CH3CHOOC4H8</td>
</tr>
<tr>
<td>1.00E-12</td>
<td>CH3CHOO + HCHO ==&gt; C3H6O3</td>
</tr>
<tr>
<td>1.00E-11</td>
<td>CH3CHOO + CH2CHO ==&gt; CH3CHOOCH2CHO</td>
</tr>
</tbody>
</table>

+ HOx, Ox, …
Vinoxy radical from mechanism

- Kinetic model adequately reproduces vinoxy radical in c2b and t2b ozonolysis.

- Vinoxy yield (syn-Cl) yield:
  - $\alpha \sim 0.5$ in t2b
  - $\beta \sim 0.3$ in c2b

- Consistent with OH yield:
  - $Y_{OH} \sim 1.25\alpha \sim 0.64$ in t2b
  - $Y_{OH} \sim 1.25\beta \sim 0.33$ in c2b
Results

HCHO yield

- Yield of HCHO \( \sim 0.11 \)
- Compare with Tuazon et al.: \( y_{\text{HCHO}} = 0.166 \)
- \( y_{\text{HCHO}} \) ratio of \( \text{c2b/t2b} \sim 1 \)
- Larger than the vinoxy yield ratio (\( \sim 0.6 \))
  \( \rightarrow \) Additional source of HCHO from anti-Cl
HCHO from mechanism

Experiment
Simulation
N (molecule/cc)
Ozone (molecule/cc)

trans-2-butene

cis-2-butene
Summary of new mechanistic findings

➢ HCHO yield ratio is ~1: \( a \approx z \approx 0.15 \)

➢ Model indicates OH comes mostly from syn-Cl


\[ \text{HCHO yield ratio is} \approx 1: \ a \approx z \approx 0.15 \]
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