Gas/Particulate Phase Products and Secondary Aerosol Yields from the Ozonolysis of (E)-β-Farnesene

Ivan Kourtchev, Iustinian Bejan, John R. Sodeau and John C. Wenger

Department of Chemistry and Environmental Research Institute
University College Cork, Ireland
Introduction

Sesquiterpenes are a class of terpenes that consist of three isoprene units and have the molecular formula $\text{C}_{15}\text{H}_{24}$

- Emitted by a large variety of plants (e.g., Scots pine, birch, oak.. )
- Very reactive towards $\text{O}_3$, $\text{OH}^\cdot$ and $\text{NO}_3^\cdot$
- Short lived compounds
- No agreement on the contribution of sesquiterpenes to the global budget of BVOCs
A number of laboratory studies have been performed on a series of sesquiterpenes with cyclic structures (e.g., β-caryophellene, α-humulene,..)

No information concerning the atmospheric reactivity of farnesene, an acyclic compound emitted from a wide range of plants (Duhl et al., 2008, *Biogeoosciences*) and detected in various branch enclosure studies (e.g., Goldstein et al., 2004 *Geophys. Res. Lett.*, Helmig et al., 2007 *ES&T*)

![Chemical Structures and Reaction Pathways](image)
Objectives

- To identify gas and particle phase products from farnesene/O<sub>3</sub> reactions;
- To determine aerosol yields under various conditions (e.g., RH, effect of scavenger & aerosol seed).
CRAC atmospheric simulation chamber

- FEP foil;
- Volume of 3.91 m$^3$;
- Four fans;
- In situ FTIR spectroscopy using a path length of 229.6 m;
- SMPS (TSI Model 3080; CPC 3010 & DMA 3081).
Gas/particle phase collection

- Five channel annular denuder
- Coated with XAD-4 resin
- Flow: 15 L/min
Methods

**PFBHA derivatization**

\[
\text{O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA)}
\]

\[
\text{PFBHA oxime}
\]

**BSTFA derivatization**

\[
\text{Bis(trimethylsilyl)trifluoroacetamide (BSTFA)}
\]

Agilent 6890 GC coupled to Agilent 5975 quadrupole MS

Varian 3800 GC coupled to Ion trap-MS Varian Saturn 2000
Carbonyl gas-phase species

All species except tentatively identified 4-methyl-8-methyldeca-4,9-dienal have been detected in ambient samples by various groups.
Mechanism for gas phase ozonolysis of (E)-β-farnesene

\[ k_{O_3} = 4.01 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Kourtchev et al., 2009, *Atmos. Environ.* 43, 3182-3190

\[ k_{DB1} \approx k_{DB2} \gg k_{B3} \approx k_{DB4} \]

EPI SuiteTM software (US EPA, 2007)
Particle-phase species

Also observed in the gas phase!!!

4-oxopentanoic acid

4-oxopentanal

5-hydroxy-4-oxopentanal

succinic acid

2-hydroxyacetic acid

All species have been detected in ambient samples by various groups.
Gas phase mechanism of 4-oxopentanoic acid

Pathway I

\[(E)-\beta\text{-farnesene}\]

\[\text{Acetone}\]

\[\text{(E)-4-methyl-8-methyleneocta-4,9-dienal}\]

\[\text{4-oxopentanal}\]

\[\text{4-methylenehex-5-enal}\]
Gas/particle partitioning coefficients

\[
K_p \text{exp} = \frac{C_{\text{particle}}}{C_{\text{gas}} \times [\text{aerosol}]}
\]

\(K_p = (1.68 \pm 1.22) \times 10^{-3} \text{ m}^3 \text{ µg}^{-1}\)

4-oxopentanal

\(K_p = (1.98 \pm 1.34) \times 10^{-2} \text{ m}^3 \text{ µg}^{-1}\)

4-oxopentanoic acid

\(K_p = 1.3 \times 10^{-4} \text{ m}^3 \text{ µg}^{-1}\) (Hellen et al., ES&T, 2008)

\(K_p = 1.77 \times 10^{-4} \text{ m}^3 \text{ µg}^{-1}\) (Healy et al., ACP, 2008)

2-methyl-4-oxo-2-pentenal

\(K_p = 2.53 \times 10^{-2} \text{ m}^3 \text{ µg}^{-1}\) (Kavouras et al, 2002)

Cis-pinic acid

Odum et al., 1996 (ES&T)

Healy et al., ACP, 2008

Hellen et al., ES&T, 2008

Kavouras et al, 2002
SOA formation from \((E)\)-\(\beta\)-farnesene/O\(_3\) reactions

**Initial concentration**
\[ C_{\text{(E)-farnesene}} = 80 \text{ ppb} - 1.1 \text{ ppm} \]
\[ C_{O_3} = 240 \text{ ppb} - 3.3 \text{ ppm} \]

**Conditions**
- Dry experiment (RH<0.1%)
- Dry experiment + scavenger (CO)
- RH=50% + scavenger (CO)
- RH=50% + scavenger (CO) + \((\text{NH}_4)_2\text{SO}_4\) seed
- RH 0-80% + scavenger (CO)
- Different scavengers (FTIR limitations)

Instantaneous particle formation!
Limitation of SMPS (resolution 3 min)!

Farnesene decay was monitored using in situ FTIR
Aerosol growth monitored with SMPS
(E)-β-Farnesene time-dependent growth curve

690 ppb (E)-β-farnesene + scavenger + (NH₄)₂SO₄ seed
Dry without scavenger
SOA yield ~43% at conc. 80 ppb to 1.1 ppm

\[ Y = M_0 \sum \left( \frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_0} \right) \]

One compound model

<table>
<thead>
<tr>
<th>RH(0.03%) + scav.</th>
<th>RH(50%) + scav.</th>
<th>RH(50%) + scav. + seed</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>( K )</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>0.19</td>
<td>0.0049</td>
<td>0.1687</td>
</tr>
</tbody>
</table>
Relative Humidity Influence on SOA Yield

[Graph showing the relationship between RH and yield for 150 ppb (E)-β-farnesene with CO and without seed.]
Conclusions

- \((E)-\beta\)-farnesene has a lifetime \(~1\) hour with respect to reaction with ozone - react close to its source and have an impact at local level;

- \((E)-\beta\)-farnesene/O\(_3\) is another possible source of the ubiquitous carbonyls (acetone, 4-oxopentanal and 6-methylhept-5-en-2-one) and acids (4-oxopentanoic acid and succinic acid);

- High Kp values for 4-oxopentanal and 4-oxopentanoic acids confirm their significance in SOA formation;

- SOA yields varied from 0.05-43% depending on the conditions (conc., RH, presence of OH scavenger);

- Presence of OH scavenger decreases aerosol yield indicating Criegee intermediates produce OH and that OH/(\(E\))-\(\beta\)-farnesene reactions produces SOA;

- RH decreases SOA yield dramatically at low conc. but has minimal effect at high conc. of \((E)-\beta\)-farnesene;

- The presence of neutral aerosol seed does not have a significant influence on the SOA yield
Future plans

Photooxidation of \((E)-\beta\)-farnesene (gas and particulate phase organic composition, SOA yields)

Thank you for your attention