Secondary Organic Aerosol and Ozone Formation from Photo-oxidation of Select Low Vapor Pressure-Volatile Organic Compounds, hydrocarbon Solvents, and Generic Consumer Products in a Surrogate Atmospheric Environment

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Objectives

- Evaluate the evaporation rate, of specific Low Vapor Pressure-Volatile Organic Compounds (LVP-VOCs) in pure form and as part of mixtures as they are used in consumer products.
- Study ozone and SOA formation of select LVP-VOCs under low NOx conditions in a surrogate mixture.
- Apply experimental data from series LVP-VOCs oxidation experiments to the SAPRC-2011 mechanism to evaluate ozone formation.
- Compare ozone and SOA formation from consumer products with that from their LVP-VOCs components under the same conditions.
- Explore ozone and SOA formation of hydrocarbon solvents under low NOx conditions in a surrogate mixture.
Motivation
Ozone

VOC + NOx + sunlight → Ozone

Number of Basin-Days Exceeding 2015 Federal Ozone Health Standard Levels (>0.070 ppm) in SoCAB

Chart created from data on AQMD website

*Preliminary data, may change in validation process
Aerosol Formation

Gas Phase Oxidation Products

Volatile Organic Compounds (VOC)

- isoprene
- terpenes
- oxygenates...
- alkanes
- alkenes
- aromatics...

Evaporation
Condensation
Nucleation
Coagulation

Secondary Organic Aerosol (SOA)

Primary Organic Aerosol (POA)

Vegetation
Fuel/Industry
Open fires
Animal feedlots
Consumer products

VOC EMISSION

Paul J. Ziemann* and Roger Atkinson, 2012
Human Health

PM Enters through mouth and nose

$\text{PM}_{10}$ eliminated through coughing, sneezing, and swallowing

$\text{PM}_5$ travel deep into lungs, causing lung and heart problems

https://news.vanderbilt.edu/2012/09/21/her2-lung-cancer-therapy/
Reduced Visibility

Clean day

Not so clean day

Los Angeles

Gap between model prediction and ozone and fine PM formation.
Low Vapor Pressure-Volatile Organic Compounds (LVP-VOCs)

- High boiling point (BP)
- Low vapor pressure (<0.1mmHg)
- ≥12 carbon atoms

(Võ and Morris, 2012)

<table>
<thead>
<tr>
<th>Agency</th>
<th>BP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CARB, EPA, &amp; OTC</td>
<td>216</td>
</tr>
<tr>
<td>EU &amp; Canada</td>
<td>250</td>
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<td>Green Seal</td>
<td>280</td>
</tr>
</tbody>
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Low Vapor Pressure-Volatile Organic Compounds (LVP-VOCs)

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</tr>
</tbody>
</table>

Some LVP-VOC solvents being categorized as nonvolatile clearly volatilized at ambient conditions, nearly as rapidly as the traditional high volatility solvents they are meant to replace.
Low Vapor Pressure-Volatile Organic Compounds (LVP-VOCs)

- High boiling point (BP)
- Low vapor pressure (<0.1 mmHg)
- $\geq$ 12 carbon atoms

(Võ and Morris, 2012)

Nonvolatile

<table>
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</tr>
</tbody>
</table>

SOA $\rightarrow$ $\rightarrow$ O$_3$
<table>
<thead>
<tr>
<th>Compound Name</th>
<th>CAS #</th>
<th>Chemical Formula</th>
<th>Molecular Structure</th>
<th>Boiling Point (°C)</th>
<th>Vapor Pressure (mm Hg)</th>
<th>$\bar{\sigma}c_0$</th>
<th>$\log_{10}(C^*)$ (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene Glycol</td>
<td>57-55-6</td>
<td>C₃H₈O₂</td>
<td><img src="image" alt="Propylene Glycol" /></td>
<td>188</td>
<td>0.08</td>
<td>-1.3</td>
<td>5.72</td>
</tr>
<tr>
<td>Diethylene Glycol</td>
<td>111-46-6</td>
<td>C₄H₁₀O₃</td>
<td><img src="image" alt="Diethylene Glycol" /></td>
<td>245</td>
<td>0.002</td>
<td>-1.0</td>
<td>4.51</td>
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<tr>
<td>Diethylene Glycol Ethyl Ether (DEGEE)</td>
<td>111-90-0</td>
<td>C₆H₁₄O₃</td>
<td><img src="image" alt="Diethylene Glycol Ethyl Ether" /></td>
<td>202</td>
<td>&lt;0.1</td>
<td>-1.3</td>
<td>5.96</td>
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<tr>
<td>Diethylene Glycol Monobutyl Ether (DEGBE)</td>
<td>112-34-5</td>
<td>C₆H₁₈O₃</td>
<td><img src="image" alt="Diethylene Glycol Monobutyl Ether" /></td>
<td>230</td>
<td>0.02</td>
<td>-1.5</td>
<td>5.28</td>
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<tr>
<td>Benzyl Alcohol</td>
<td>100-51-6</td>
<td>C₇H₈O</td>
<td><img src="image" alt="Benzyl Alcohol" /></td>
<td>205</td>
<td>0.094 @ 25 °C</td>
<td>-0.9</td>
<td>5.74</td>
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<tr>
<td>Dipropylene Glycol Methyl Ether Acetate (DPGMEA)</td>
<td>88917-22-0</td>
<td>C₉H₁₈O₄</td>
<td><img src="image" alt="Dipropylene Glycol Methyl Ether Acetate" /></td>
<td>209</td>
<td>0.08</td>
<td>-1.1</td>
<td>5.91</td>
</tr>
<tr>
<td>Dimethyl Glutarate (DBE-5)</td>
<td>1119-40-0</td>
<td>C₇H₁₂O₄</td>
<td><img src="image" alt="Dimethyl Glutarate" /></td>
<td>215</td>
<td>0.097</td>
<td>-0.6</td>
<td>4.33</td>
</tr>
<tr>
<td>n-Tridecane (n-C₁₃)</td>
<td>629-50-5</td>
<td>C₁₃H₂₈</td>
<td><img src="image" alt="n-Tridecane (n-C₁₃)" /></td>
<td>234</td>
<td>0.08 @25 °C</td>
<td>-2.2</td>
<td>5.74</td>
</tr>
<tr>
<td>n-Heptadecane (n-C₁₇)</td>
<td>629-78-7</td>
<td>C₁₇H₃₆</td>
<td><img src="image" alt="n-Heptadecane (n-C₁₇)" /></td>
<td>302</td>
<td>&lt;0.001</td>
<td>-2.1</td>
<td>4.61</td>
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<tr>
<td>Texanol</td>
<td>25265-77-4</td>
<td>C₁₂H₂₄O₃</td>
<td><img src="image" alt="Texanol" /></td>
<td>244</td>
<td>0.01</td>
<td>-1.5</td>
<td>4.64</td>
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<tr>
<td>Glyceryl Triacetate</td>
<td>102-76-1</td>
<td>C₉H₁₄O₆</td>
<td><img src="image" alt="Glyceryl Triacetate" /></td>
<td>260</td>
<td>0.0025 @ 25 °C</td>
<td>-0.2</td>
<td>4.50</td>
</tr>
<tr>
<td>Methyl Palmitate</td>
<td>112-39-0</td>
<td>C₁₇H₃₄O₂</td>
<td><img src="image" alt="Methyl Palmitate" /></td>
<td>417</td>
<td>0.038 @ 25 °C</td>
<td>-1.8</td>
<td>2.90</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>102-71-6</td>
<td>C₆H₁₅NO₃</td>
<td><img src="image" alt="Triethanolamine" /></td>
<td>335</td>
<td>8.38e-6@ 25 °C</td>
<td>-1.5</td>
<td>1.80</td>
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<tr>
<td>Glycerol</td>
<td>56-81-5</td>
<td>C₃H₈O₃</td>
<td><img src="image" alt="Glycerol" /></td>
<td>290</td>
<td>0.003@50 °C</td>
<td>-0.7</td>
<td>1.83</td>
</tr>
<tr>
<td>Product Name</td>
<td>Formulations (weight percent)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laundry detergent</td>
<td>51% water; 15% propylene glycol; 5% coconut fatty acid; 25% Pareth 25-9; 4% triethanolamine.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>General-Purpose Spray Cleaner</td>
<td>90.2% water; 5% diethylene glycol monobutyl ether; 0.5% tetrasodium EDTA; 1% ethylene glycol butyl ether; 3% cocamidopropylamine oxide (34% active); 0.3% triethanolamine.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caulk Remover</td>
<td>30% dimethyl glutarate, 10% dimethyl succinate, 5% dimethyl adipate, 1% ethanolamine, 1% ethylene glycol, 53% water.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paint Stripper Gel</td>
<td>40% N-methylpyrrolidone, 30% dimethyl glutarate, 20% dimethyl adipate, 5% PEG-15 cocamine, 5% d-limonene.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hand Lotion</td>
<td>86.67% water; 4% propylene glycol; 2% glycerol; 0.25% Carbopol Ultrez 20 Polymer; 0.28% Chlorphenesin Powder; 0.25% Methylparaben; 0.2% Xanthan Gum; 0.5% Sorbitan Laurate; 0.25% Behenyl Alcohol; 1% Petrolatum; 4% Squalane; 0.25% Dimethicone; 0.35% Arginine.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Hydrocarbon Solvents Studied

<table>
<thead>
<tr>
<th>Compound</th>
<th>Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopar M</td>
<td>Low-aromatic mixture of alkanes, $C_{11}-C_{16}$ iso-alkanes, and cycloalkanes.</td>
</tr>
<tr>
<td>Conosol C200</td>
<td>Low-aromatic mixture of cycloparaffinic and isoparaffinic hydrocarbons ($C_5-C_{20}$).</td>
</tr>
<tr>
<td>Conosol-200*</td>
<td>A custom mixture of Conosol-70* and Conosol-400* blended to create Conosol-200* with appropriate viscosity and used prior to obtaining Conosol-200 (labelled in report as C-200**) from a major vendor.</td>
</tr>
<tr>
<td>Aromatics 200</td>
<td>Predominantly aromatic compounds.</td>
</tr>
</tbody>
</table>
Volatility Study of Select LVP-VOCs

Evaporation Chamber

Schematic for LVP-VOC volatilization measurement.
(Exchange air per hour=3.5)
Volatility and the extent of oxidation. Volatility ranges are identified with colored bands. ELVOC refers to extremely low volatility organic compounds (gray shading); LVOC refers to low volatility organic compounds (light red shading); SVOC refers to semi-volatile organic compounds (light green shading); IVOC refers to intermediate volatility organic compounds (light blue shading); VOC refers to volatile organic compounds (no shading); (Donahue VBS 2012).
Select LVP-VOCs can enter earth’s atmosphere and contribute to SOA and ozone formation at ambient conditions.
Volatility and the extent of oxidation. Volatility ranges are identified with colored bands. ELVOC refers to extremely low volatility organic compounds (gray shading); LVOC refers to low volatility organic compounds (light red shading); SVOC refers to semi-volatile organic compounds (light green shading); IVOC refers to intermediate volatility organic compounds (light blue shading); VOC refers to volatile organic compounds (no shading); (Donahue VBS 2012).

All of the chemical compounds studied fall into IVOC range.

Volatility and the extent of oxidation. Volatility ranges are identified with colored bands. ELVOC refers to extremely low volatility organic compounds (gray shading); LVOC refers to low volatility organic compounds (light red shading); SVOC refers to semi-volatile organic compounds (light green shading); IVOC refers to intermediate volatility organic compounds (light blue shading); VOC refers to volatile organic compounds (no shading); (Donahue VBS 2012).
Evanportion rate (calculated from weight loss results).

All had the same starting volume.

Semi-empirical Prediction Equation

\[
\text{Evaporation rate} = 0.00284 \times \text{Molecular weight} \times \text{Vapor Pressure}
\]

\[R^2 = 0.98053\]
The relation of initial liquid LVP-VOC and final gas concentration in equilibrium zone

\[ P_\alpha \cdot \Phi_\alpha = x_\alpha \cdot \gamma_\alpha \cdot P_\alpha^{sat} \]

\( \Phi_\alpha \): Gas phase activity, 1 for high dilution system;
\( x_\alpha \): Mole fraction of \( \alpha \) component in mixture, 1 for pure compound;
\( \gamma_\alpha \): Aqueous phase activity, 1 for pure compound;
\( P_\alpha^{sat} \): Saturation pressure of component \( \alpha \) in air.
\( P_\alpha \): Partial pressure of component \( \alpha \) in air.
How about mixtures?
Evaporation of a LVP-VOC from a Consumer Product

Selected Ion Flow Tube Mass Spectrometry

Air in

200 ul mixture

Air out
A linear increase is observed with increasing volume of LVP-VOC placed into the evaporation chamber.
The relation of initial liquid LVP-VOC and final gas concentration

\[ P_\alpha \cdot \Phi_\alpha = x_\alpha \cdot \gamma_\alpha \cdot P_{\alpha}^{sat} \]

\( P_\alpha \): Partial pressure of component \( \alpha \) in air.
\( P_{\alpha}^{sat} \): Saturation pressure of component \( \alpha \) in air.
\( \Phi_\alpha \): Gas phase activity, 1 for high dilution system;
\( x_\alpha \): Mole fraction of \( \alpha \) component in mixture, 1 for pure compound;
\( \gamma_\alpha \): Aqueous phase activity, 1 for pure compound.

The relation of initial liquid LVP-VOC and final gas concentration in equilibrium zone.
Evaporation Results of Pure LVP-VOC

Mass transfer limited.

Evaporation results of three pure LVP-VOCs.
Why Viscosity is not important?

Stokes-Einstein relationship

\[ D = \frac{k_B T}{6\pi \eta \ast d} \quad \tau = \frac{L^2}{D} \]

\( k_B \): Boltzmann constant, \( 1.38 \times 10^{-23} \text{ m}^2 \text{kg} \text{s}^{-2} \text{K}^{-1} \);
\( T \): Temperature of the evaporation system, 298K;
\( \eta \): Viscosity of liquid LVP-VOC;
\( d \): Diffusive length.
\( \tau \): Characteristic time of mass transfer
\( L \): Relevant length in vertical direction.
\( D \): Molecular diffusivity.

The co-relation of viscosity, diffusivity, mixing time and evaporation particle scale. Spherical particles with microscopic length dimensions (1 nm to 10 mm).

Koop et al., 2011

<table>
<thead>
<tr>
<th>Diffusivity (cm²/s)</th>
<th>Water</th>
<th>Honey</th>
<th>Propylene Glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (Pa*s)</td>
<td>8.9e⁻⁴</td>
<td>6.3</td>
<td>4.2e⁻²</td>
</tr>
</tbody>
</table>
Evaporation Results of Pure LVP-VOC and its Mixture

Volume of LVP equals volume of LVP in the consumer product.

Volume of LVP equals volume of consumer product.

Trends varies. For some consumer products, LVP ingredients cross-linked to other materials.
UCR CE-CERT Chamber Facility

- 90 m³ each
- Insulated enclosure (purified air flushed)
- Temperature control (5-45ºC)
- Humidity Control

Surrogate

1ppm H₂O₂ as needed + 25 ppb NOₓ + 1.1ppmC

LVP-VOCs/Mixture
Gas-phase Analysis

GC-FID – Hydrocarbon decay
SIFT-MS – Gas phase concentration
(Selected Ion Flow Tube – Mass Spectrometer)
Gas Analyzer – $O_3$, NO, NO$_x$

Particle-phase Analysis

HR-ToF-AMS – bulk chemical composition
(High Resolution Time-of-Flight Mass Spectrometer)
SMPS – volume concentration and size distribution
(Scanning Mobility Particle Sizer)
APM-SMPS – density
(Aerosol Particle Mass Analyzer – SMPS)
VTDMA – volatility
(Volatility Tandem Differential Mobility Analyzer)
HTDMA – hygroscopicity
(Hygroscopicity Tandem Differential Mobility Analyzer)
A simplified ROG surrogate was used for this work to mimic total urban atmospheric reactivity. Seven representative compounds used were n-butane, n-Octane, ethylene, propylene, trans-2-butene, toluene, and m-xylene.
Volume Fraction Remaining (VFR) = \( (\frac{D_f}{D_i})^3 \)
Aerosol Particle Mass Analyzer – SMPS

www.kanomax.com

(Malloy et al., 2009)
High-Resolution-Time-of-Flight Aerosol Mass Spectrometer

V-mode: higher sensitivity
W-mode: higher mass resolution
Particle size range: 35 nm ~ 1.5 µm

(DeCarlo, et al. 2006)
All LVP-VOCs maintained a constant concentration within measurement error.
Ozone Formation from Select Individual LVP-VOCs
O₃ formation was suppressed?
Larger changes in radical concentrations, NO$_x$ loadings, etc. than expected to occur within the more complex ambient atmosphere with its more significant reservoir.
Ozone formation from individual LVP-VOCs with surrogate, NO$_x$, and H$_2$O$_2$
Ozone formation comparison between runs with or without H₂O₂
The summary of $O_3$ prediction results during experiment (elapsed time in hour) for LVP-VOCs by the SAPRC-11 model.

<table>
<thead>
<tr>
<th></th>
<th>EPA2027A</th>
<th>EPA1891A</th>
<th>EPA2030A</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBE-$5+H_2O_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DGBE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DGBE+$H_2O_2$</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

- **Test Experiment**
- **Base Experiment**
- **Test Calc**
- **Base Calc**

<table>
<thead>
<tr>
<th>Incremental Reactivity $\Delta (O_3-NO)$ (molar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.3</td>
</tr>
<tr>
<td>-0.2</td>
</tr>
<tr>
<td>-0.1</td>
</tr>
<tr>
<td>0.0</td>
</tr>
<tr>
<td>0.1</td>
</tr>
<tr>
<td>0.2</td>
</tr>
<tr>
<td>0.3</td>
</tr>
</tbody>
</table>

The summary of $O_3$ prediction results during experiment (elapsed time in hour) for LVP-VOCs by the SAPRC-11 model.
Ozone Formation from Select Consumer Products
Ozone formation trends for each consumer product injected into surrogate mixture.
Ozone formation from consumer products in surrogate mixture with enhanced $\text{H}_2\text{O}_2$. 

Ozone Concentration (ppb) vs. Irradiation Time (min) 

- **Lotion (4% Propylene Glycol)** 
- **Laundry detergent (15% Propylene Glycol)** 
- **Surrogate + $\text{H}_2\text{O}_2$**

Ozone formation from consumer products in surrogate mixture with enhanced $\text{H}_2\text{O}_2$. 

UCR
Ozone Formation from Select Hydrocarbon Solvents
Ozone formation for solvent mixtures. Two Conosol C200 mixtures were investigated for ozone formation (local vendor (*) and large vendor (**)). Aromatic-200 is not shown due to interferences of the Aromatic 200 with the UV absorption of the ozone analyzer.
Ozone formation from surrogate with hydrocarbon solvent mixtures and H$_2$O$_2$ added.
SOA Formation from Select Individual LVP-VOCs
Half of the select LVP-VOCs did not form noticeable SOA.
SOA Formation from Select LVP-VOCs + Surrogate + NOx

DBE-5 and Propylene Glycol did not form noticeable SOA even at elevated OH radical concentrations.
SOA formation was the highest for conditions that favored greater consumption of the LVP-VOC.
Aerosol Yield

\[ Y = \frac{\Delta M_o}{\Delta HC} \]

\[ Y = \sum_i Y_i = M_o \sum_i \frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_o} \]

\( \alpha_i \): mass-based stoichiometric coefficient

\( K_{om,i} \): gas-particle partitioning coefficient

\( M_o \): mass of aerosol formed

At small \( M_o \)

\[ Y \approx M_o \sum_i \alpha_i K_{om,i} \]

More organic aerosol present, more aerosol will form

\((\text{Odum, et al. 1996; Odum, et al. 1997 a,b;})\)
<table>
<thead>
<tr>
<th>Run #</th>
<th>Compound</th>
<th>$\Delta$HC (µg/m$^3$)</th>
<th>$\Delta$M (µg/m$^3$)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA1883</td>
<td>Diethylene Glycol</td>
<td>140.00</td>
<td>3.40</td>
<td>0.02</td>
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<tr>
<td>EPA1886</td>
<td>DEGEE</td>
<td>338.18</td>
<td>23.00</td>
<td>0.07</td>
</tr>
<tr>
<td>EPA1887</td>
<td>Diethylene Glycol</td>
<td>309.95</td>
<td>2.58</td>
<td>0.01</td>
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<tr>
<td>EPA1888</td>
<td>Propylene Glycol</td>
<td>84.93</td>
<td>0.16</td>
<td>0.00</td>
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<td>EPA1891</td>
<td>DEGBE</td>
<td>293.13</td>
<td>47.80</td>
<td>0.16</td>
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<tr>
<td>EPA1892</td>
<td>n-Tridecane</td>
<td>183.76</td>
<td>14.69</td>
<td>0.08</td>
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<tr>
<td>EPA1910</td>
<td>n-Heptadecane</td>
<td>199.86</td>
<td>103.60</td>
<td>0.52</td>
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<tr>
<td>EPA1911</td>
<td>DBE-5</td>
<td>158.00</td>
<td>9.73</td>
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<td>EPA1987</td>
<td>Benzyl Alcohol</td>
<td>186.91</td>
<td>43.20</td>
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<td>EPA2023</td>
<td>DPGMEA</td>
<td>255.06</td>
<td>6.00</td>
<td>0.02</td>
</tr>
<tr>
<td>EPA2024</td>
<td>Texanol</td>
<td>151.29</td>
<td>1.10</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Typical Aerosol Yield for Aromatics

Yield curves for C₆-C₉ aromatics.
Comparison of SOA formation with and without H$_2$O$_2$ for select LVP-VOCs in the presence of NO$_x$ and surrogate.

More aerosols formed after injecting H$_2$O$_2$ for LVP-VOCs that formed measurable SOA.
Comparison of SOA formation with and without H$_2$O$_2$ for select LVP-VOCs.
SOA Formation from Select Consumer Products
SOA formation from LVP-VOCs containing consumer products with surrogate and NO\textsubscript{x}. 

**Diagram Description:**
- **General purpose spray cleaner (5% DEGBE)**
- **Laundry detergent (15% Propylene Glycol)**
- **Lotion (4% Propylene Glycol)**
- **Caulk remover/no water (30% DBE-5)**
- **Caulk remover (30% DBE-5)**
- **Paint stripper (30% DBE-5)**
- **Surrogate**

**Graph Details:**
- **Y-axis:** Corrected SOA mass concentration (\(\mu g/m^3\))
- **X-axis:** Irradiation Time (min)
- **Legend:**
  - Red square: General purpose spray cleaner (5% DEGBE)
  - Orange circle: Laundry detergent (15% Propylene Glycol)
  - Yellow triangle: Lotion (4% Propylene Glycol)
  - Pink triangle: Caulk remover/no water (30% DBE-5)
  - Purple triangle: Caulk remover (30% DBE-5)
  - Blue triangle: Paint stripper (30% DBE-5)
  - Black triangle: Surrogate

**SOA formation from LVP-VOCs containing consumer products with surrogate and NO\textsubscript{x}.**
SOA formation from LVP-VOCs containing consumer products with surrogate, NO\textsubscript{x}, and H\textsubscript{2}O\textsubscript{2}
Comparison of SOA formation from single LVP-VOCs with that from mixtures in the presence of surrogate and NOx. Colored individual LVP matched with corresponding consumer products. Consumer products formed more SOA than LVP-VOCs alone.
The presence of other chemicals in the consumer product influences the reactivity and aerosol formation routes.

Comparison of SOA formation from single LVP-VOCs with that from mixtures in the presence of surrogate and NO\(_x\). Colored individual LVP matched with corresponding consumer products.
SOA Formation from Select Hydrocarbon Solvents
SOA Formation (Hydrocarbon Solvents + Surrogate + NO\textsubscript{x})

![Graph showing PM volume corrected concentration vs. Irradiation Time (min)]
SOA Formation (Hydrocarbon Solvents + Surrogate + NO\textsubscript{x} + H\textsubscript{2}O\textsubscript{2})
Relationship of SOA to chemical structures glycol ether case study
Molecular Structure of Ethers Investigated

- Diethylene glycol ethyl ether (DEGEE)
- Diethylene glycol methyl ether (DEGME)
- Diethylene glycol butyl ether (DEGBE)
- Ethylene glycol diethyl ether (EGDEE)
- Di(propylene glycol) butyl ether (DPEGBE)
- Diethylene glycol dimethyl ether (DEGDME)
- 1-(2-Methoxyethoxy)-2-methyl-2-propanol (12M2MP)
- 1, 2-Dimethoxyethane
- 1,3-Diethoxy-2-propanol (13D2P)
- 3,3-Diethoxy-1-propanol (33D1P)
SOA yield from glycol ethers and related ethers in absence of NOx. (Colored by the amount of ether (precursor) reacted to aid in visual comparison of which ethers on a per ether reacted basis is producing the greatest relative amount of SOA)

- SOA formation from the photo-oxidation of selected ethers is associated with the presence and location of –OH.
- Dominating SOA precursor: Ethers with -(OCH2CH2)2 – OH structure.
- The SOA fractional yields of ether depend on the amount of ether precursor reacted.
Summary

• The UCR CE-CERT environmental chambers were suitable to meet the goals of the study of ozone and SOA formation from LVP-VOCs.
• Most LVP-VOCs studied evaporated (>95%) in less than 6 months.
• SAPRC-11 as evaluated for the LVP-VOCs studied and was found to predict well the gas-phase chemistry and ozone formation from the compounds.
• The hypothesis that LVP-VOCs begin with lower vapor pressure than VOCs and therefore will form more secondary aerosol was proven to be generally not true for the compounds studied. Half LVP-VOCs did not form SOA. However, several selected LVP-VOCs formed appreciable SOA.
• Chemical structure was found to be a significant driver of SOA formation (e.g., glycol ether case study).
• Lab created generic consumer products had a weak influence on ozone formation from the surrogate mixture but strongly affected SOA formation, which can not be explained solely by the results of the pure LVP-VOC experiments.
• Hydrocarbon solvents formed appreciable SOA.
Future Work

- SOA and ozone formation from photo-oxidation of other classes of LVP-VOCs.
- Evaporation study about mass transfer kinetic limitations.
- Predict the influence of hydroperoxy levels on SOA generation as a function of HO₂/NO.
- A detailed study on their SOA formation as a function of chain length and branching is necessary to provide experimental parameters needed to predict overall ambient impacts of alkanes on SOA formation. (e.g., relationship seen for glycol ethers)
- Vapor and particle wall loss.


Funding sources

Thank you!