Heterogeneous Nucleation of Ice Catalyzed by High Molecular Weight Organic Compounds, Before and After Ozonolysis, Using Octadecene as a Model

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Abstract

High altitude clouds may be affected by the products of biomass burning, which can be lofted into the upper troposphere through deep convection. To further complicate the picture, once in the atmosphere, organic compounds may be transformed through oxidation, possibly changing their characteristics as freezing catalysts. Using 1- and 9-octadecene as a model for unsaturated, non-polar high molecular weight organic compounds, we will show that exposure to ozone does not change the characteristic temperature at which a coating of octadecene catalyzes heterogeneous ice nucleation. In addition, the phase of the octadecene (liquid or crystalline) when ozonolysis takes place does not affect the characteristic freezing temperature.

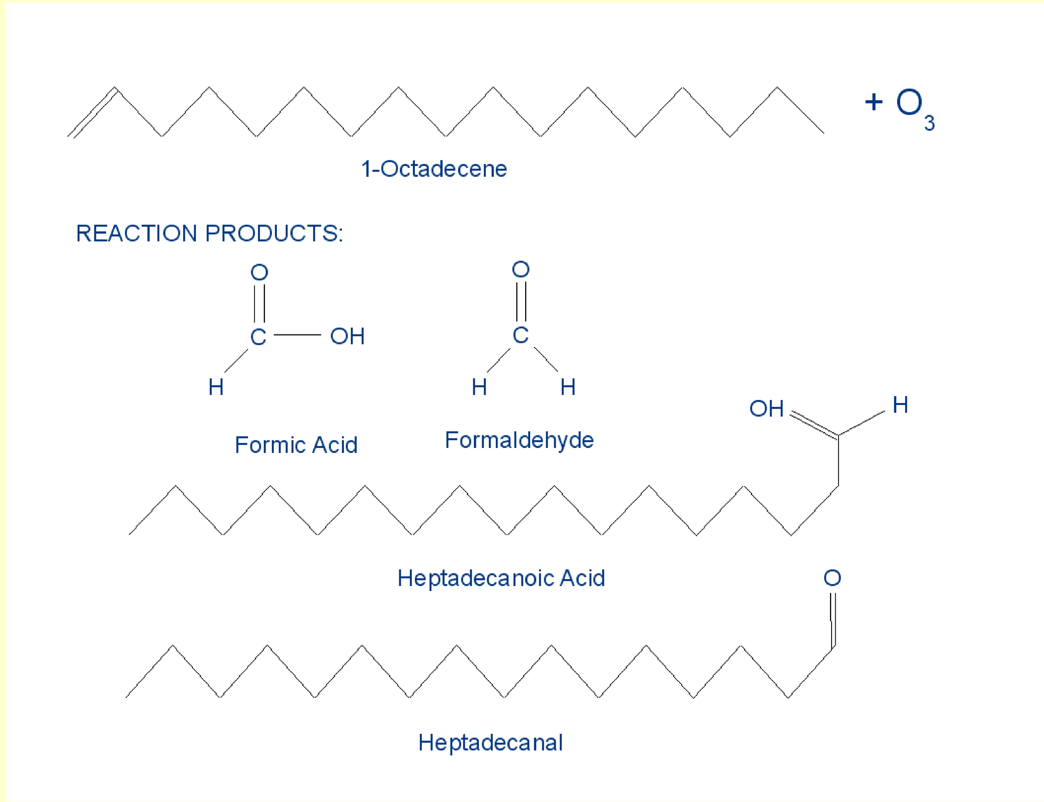
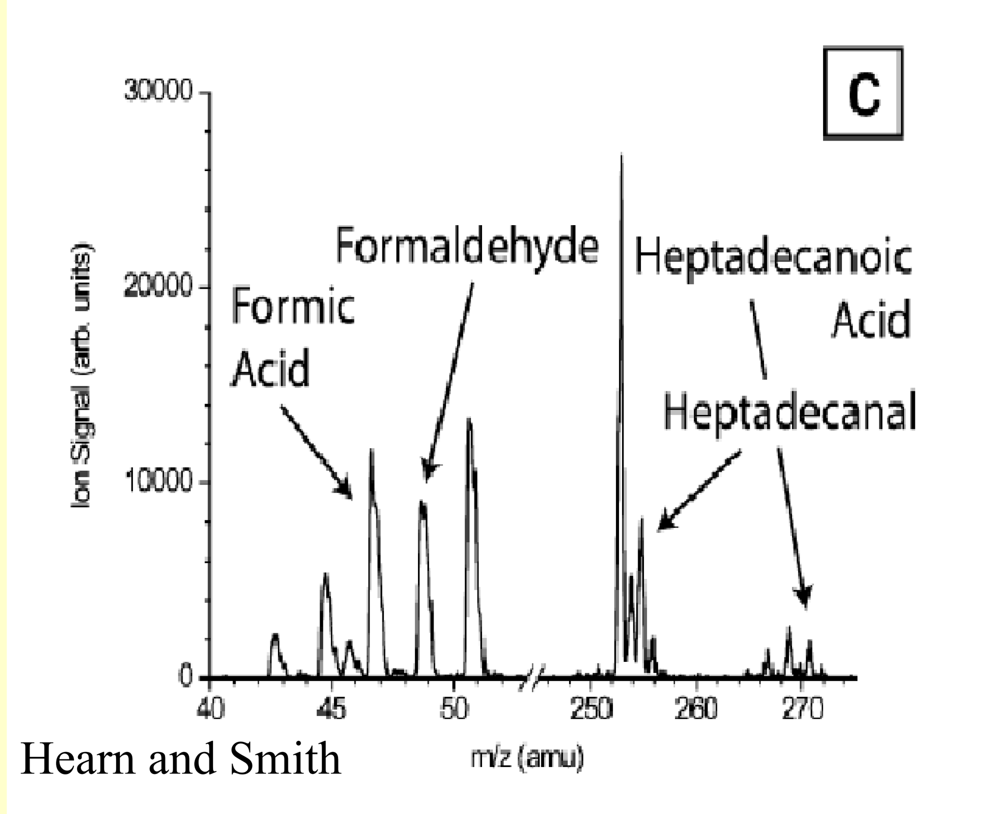


Figure 2 (left). Schematic diagrams of 1-octadecene and the reaction product resulting from ozonolysis.

Figure 3(right). Proton-transfer mass spectra of vaporized particles after 1-octadecene reaction with ozone



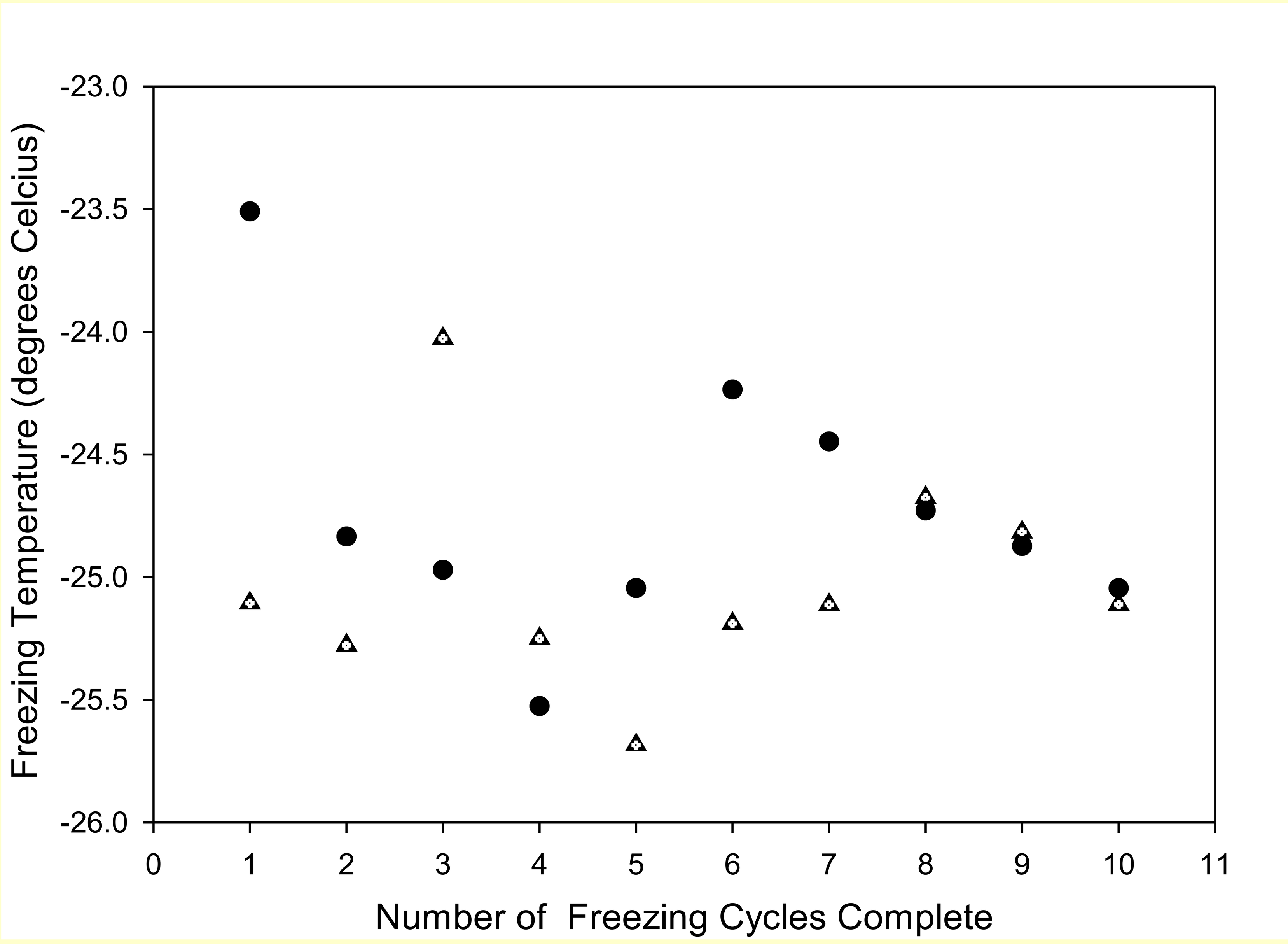


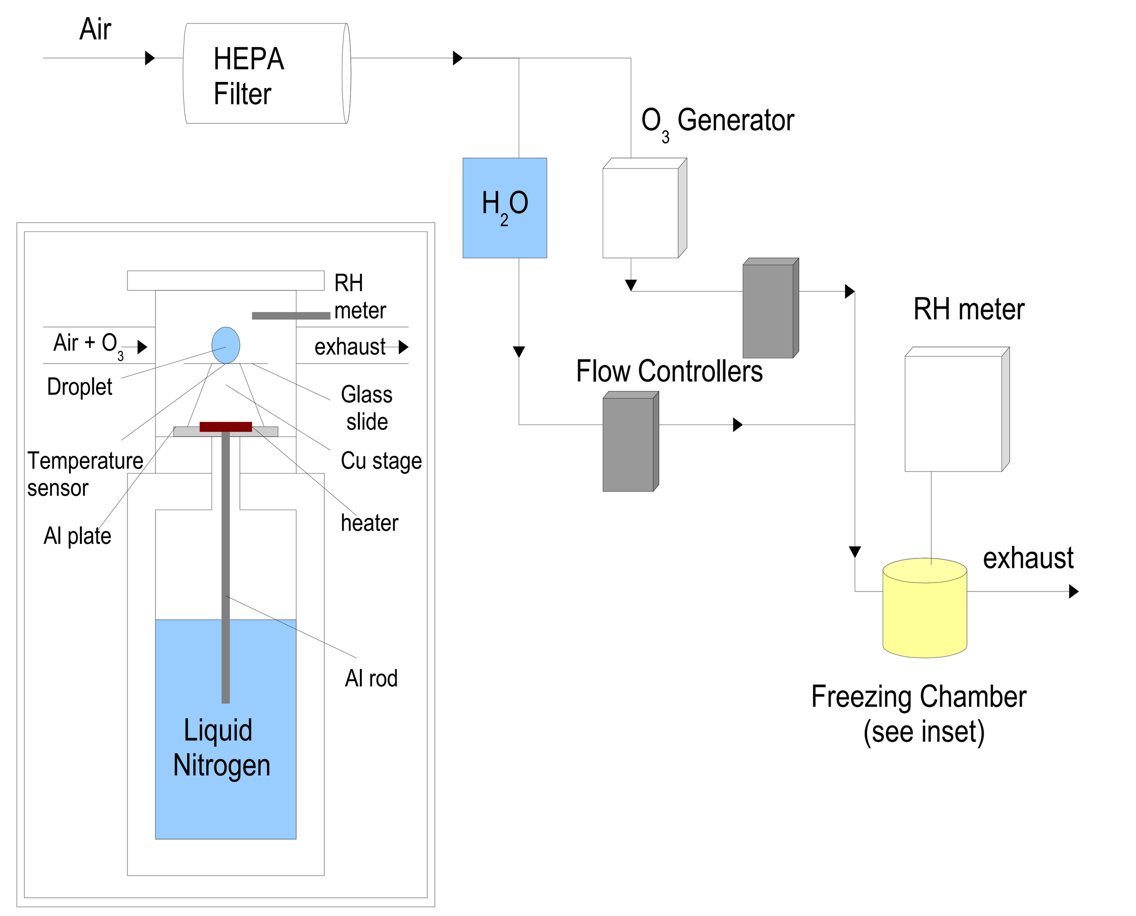
Figure 1. Typical data from a test of the freezing point of water catalyzed by 1-octadecene before and after exposure to ozone. The solid circles are T_{freeze} before exposure to ozone and the triangles are T_{freeze} after. ($T_{ozone} = T_{max} = 20$ ºC)

Compound	*T_{freeze} (before O_3)*	*T_{freeze} (after O_3)*	*Notes*
1-octadecene $CH_2=CH(CH_2)_{15}CH_3$ 2.5nmol deposited onto drop (multilayer film) -10 °C exposure to O_3, T_{max} = 12 °C	-23.8 ± 2	-24.5 ± 2.3	Octadecene melting point: T_{melt} = 17 °C $T_{ozone} < T_{melt}$ $T_{max} < T_{melt}$
1-octadecene 500 nmol deposited onto drop -10 °C exposure to O_3, T_{max} = 12 °C	-22.4 ± 2.1	-21.2 ± 2.4	$T_{ozone} < T_{melt}$ $T_{max} < T_{melt}$
1-octadecene 2.5 nmol deposited onto drop 20 °C exposure to O_3, T_{max} = 12 °C	-22.2 ± 2.5	-21.5 ± 2.3	$T_{ozone} > T_{melt}$ $T_{max} < T_{melt}$
1-octadecene 2.5 nmol deposited onto drop 20 °C exposure to O_3, T_{max} = 20 °C	-23 ± 1.6	-23 ± 1.3	$T_{ozone} > T_{melt}$ $T_{max} > T_{melt}$
9-octadecene $CH_3(CH_2)_7CH=CH(CH_2)_7CH_3$ 2.5 nmol deposited onto drop -10 °C exposure to O_3, T_{max} = 20 °C	-23.3 ± 1.3	-24 ±1	$T_{ozone} < T_{melt}$ $T_{max} > T_{melt}$
9-octadecene 2.5 nmol deposited onto drop 20 °C exposure to O_3, T_{max} = 20 °C	-25 ± .5	-25 ± .5	$T_{ozone} > T_{melt}$ $T_{max} > T_{melt}$

•**Experimental Details**

•Procedure

- Freeze pure water droplet (5 µl) 3-4 times to verify $T_{freeze} < -24$ ºC
- Deposit organic film on droplet (via chloroform spreading solution)
- Freeze droplet-film at least 10 times
- Expose droplet (unfrozen) to ozone for 0.25 to 5 hours.
- Freeze droplet at least 10 times



RH at the droplet is ~ 100% to ensure it neither grows nor shrinks during the experiment.

Concentration of O_3 is ~ 0.5 ppm

$-dT/dt = 2$ K/min
$+dT/dt = 4$ K/min

Freezing of the droplet is detected from the presence of the latent heat pulse.

Why is there no change in T_{freeze} after exposing octadecene to O_3?

1. Temperature during ozonolysis < T_{melt} and T_{max} during subsequent freezing cycles < T_{melt},
The octadecene is frozen during ozonolysis – only top layer reacts. Reacted products never in contact with water.
2. Temperature during ozonolysis < T_{melt} and T_{max} during subsequent freezing cycles > T_{melt}
The organic film is frozen during ozonolysis – only top layer reacts. Reacted products (i.e. compounds with polar head groups) must re-orient toward water and/or diffuse through organic film to water interface.
3. Temperature during ozonolysis > T_{melt} and T_{max} during subsequent freezing cycles < T_{melt}
The octadecene is liquid during ozonolysis – While the diffusion time for the ozone into the film is sufficient*, during subsequent freezing cycles the film is frozen and therefore the reaction products cannot reorient into a configuration conducive to ice nucleation
4. Temperature during ozonolysis > T_{melt} and T_{max} during subsequent freezing cycles > T_{melt}
The octadecene is liquid during ozonolysis and the reaction products are able to reorient during the freezing process – reaction products do not lend themselves to better ice nucleation than octadecene alone. Acids have been shown to be poor ice nucleators. Therefore, while the reaction products interact with the drop, they do not necessarily improve nucleation.

*Reorientation time and diffusion time are small compared to time spent at $T > T_{melt}$.

References:
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