

# Heterogeneous Ice Nucleation During Ozonolysis of Organic Thin Films on Aqueous Solution Droplets

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## Background Information

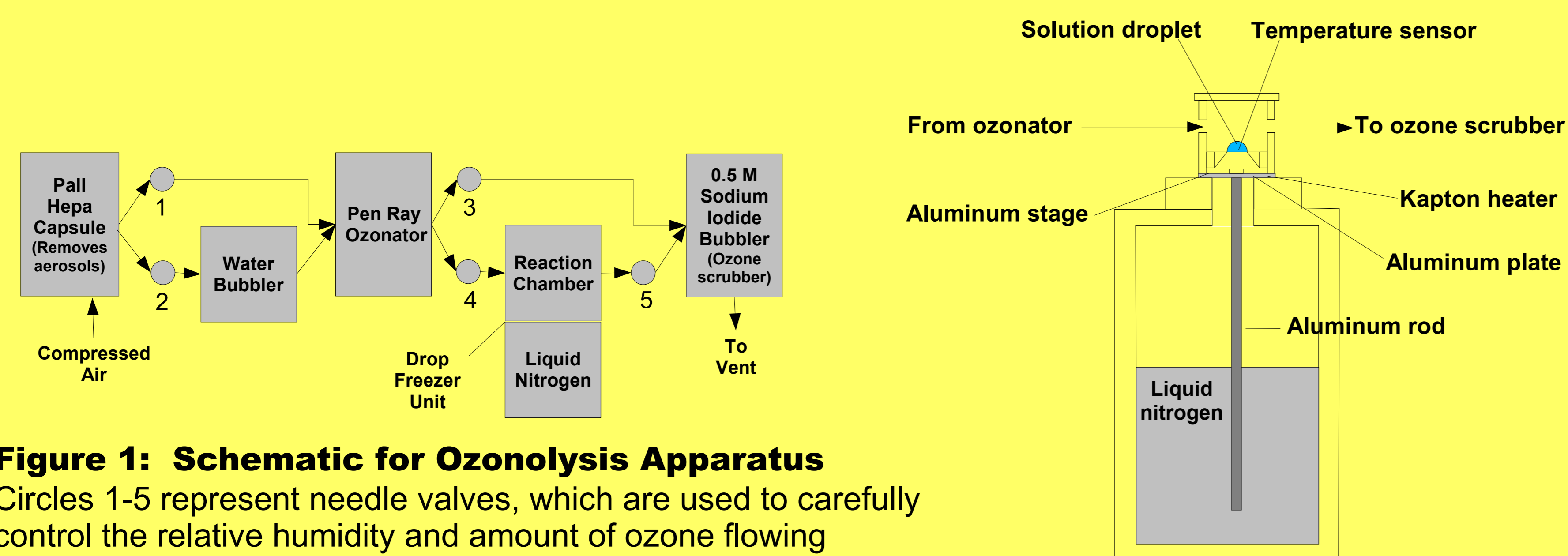
The mechanism by which ice is created affects cloud properties and processes. Although homogeneous ice nucleation is reasonably well understood both experimentally and theoretically, heterogeneous ice nucleation is not [1]. Since deep convection in the tropics lofts organic materials high into the atmosphere, it is important to achieve an understanding of heterogeneous nucleation and how it affects cirrus cloud formation.

Sources of atmospheric organic compounds include combustion, biomass burning, emissions from vegetation, and sea spray which contains organic material from the ocean's surface [2,3]. Fatty acids such as stearic acid and oleic acid are common organic constituents. The reaction of oleic acid with atmospheric ozone has recently become a model for understanding how atmospheric oxidation processes affect organic particles. Over the past six years, more than twenty publications have described reactive uptake coefficients, primary products, secondary reactions, mechanisms, and other aspects of this oxidation [3,4,5].

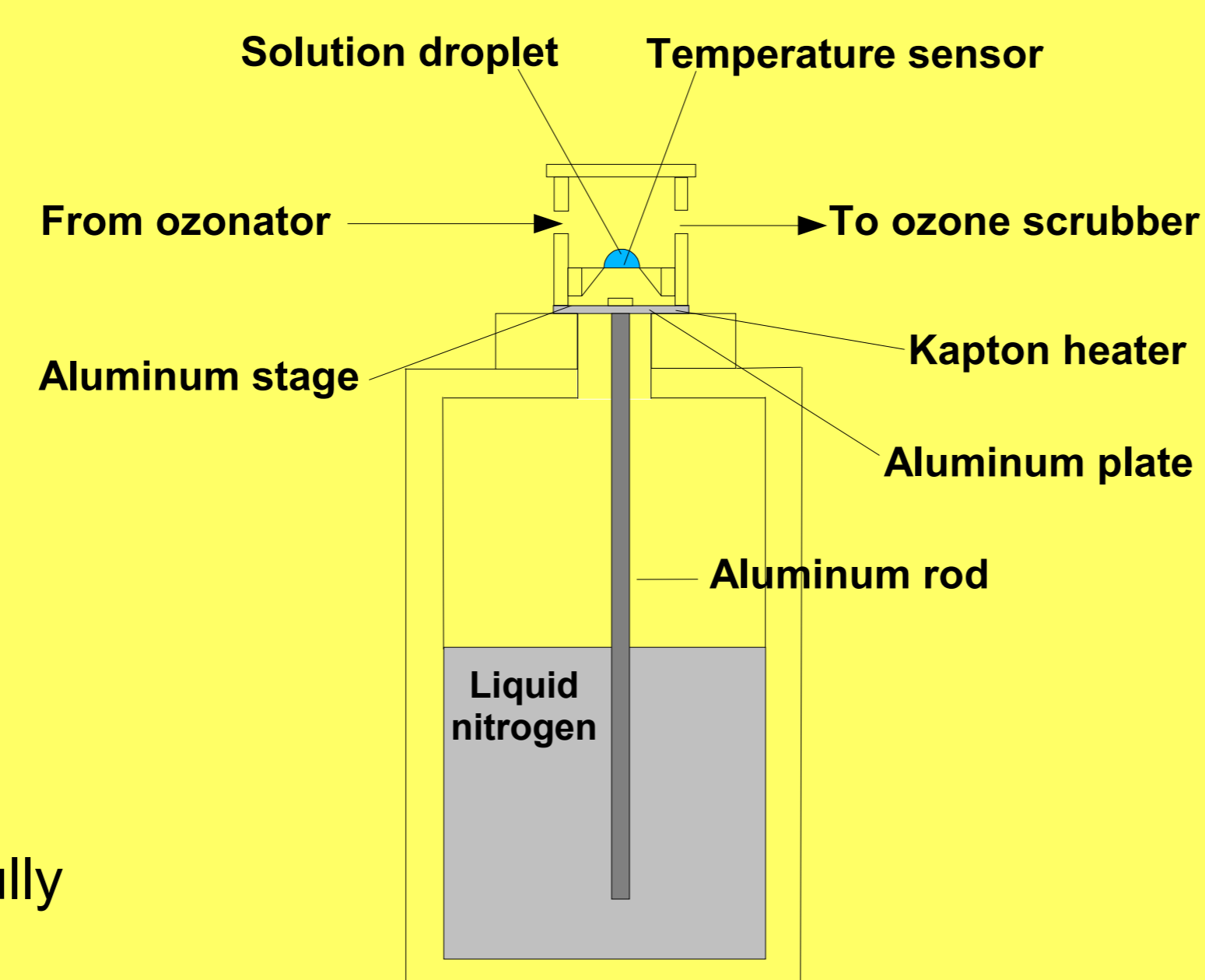
## Experimental Methods

With this background information in mind, we built an ozonolysis apparatus (Figure 1) in tandem with a solution drop freezer (Figure 2) to study the freezing point of 10-microliter, aqueous 0.25 M sodium chloride solution droplets coated with thin layers of 18-carbon fatty acids or alcohols (Table 1). We determined the freezing points before and after ozonolysis for solution droplets coated with stearic acid, oleic acid, cis-13-octadecenoic acid, oleyl alcohol, and 1-octadecanol. During the experiments, temperature cycling was controlled by a computer-driven Lakeshore Model 331 temperature controller connected to both a Kapton flexible heater and a temperature sensor. Every 45 minutes, the droplet temperature cycled from 5°C to less than -30°C. Freezing point temperatures were collected for 7-8 hours before and after the coated droplet was exposed to ozone. More than a 100-fold stoichiometric excess of ozone was used over 6-8 hours.

Needle valves 1-5 in Figure 1 were used to adjust the relative humidity to 9.0 %, the ozone concentration to 0.5 ppm, and the flow rate through the reaction chamber to approximately 0.1 L/min. A relative humidity of 9.0 % corresponds to 2.9 mb, which is the saturation vapor pressure over water at -10°C. These experimental conditions along with the use of solution droplets allowed us to minimize any change in droplet size during our experiments.



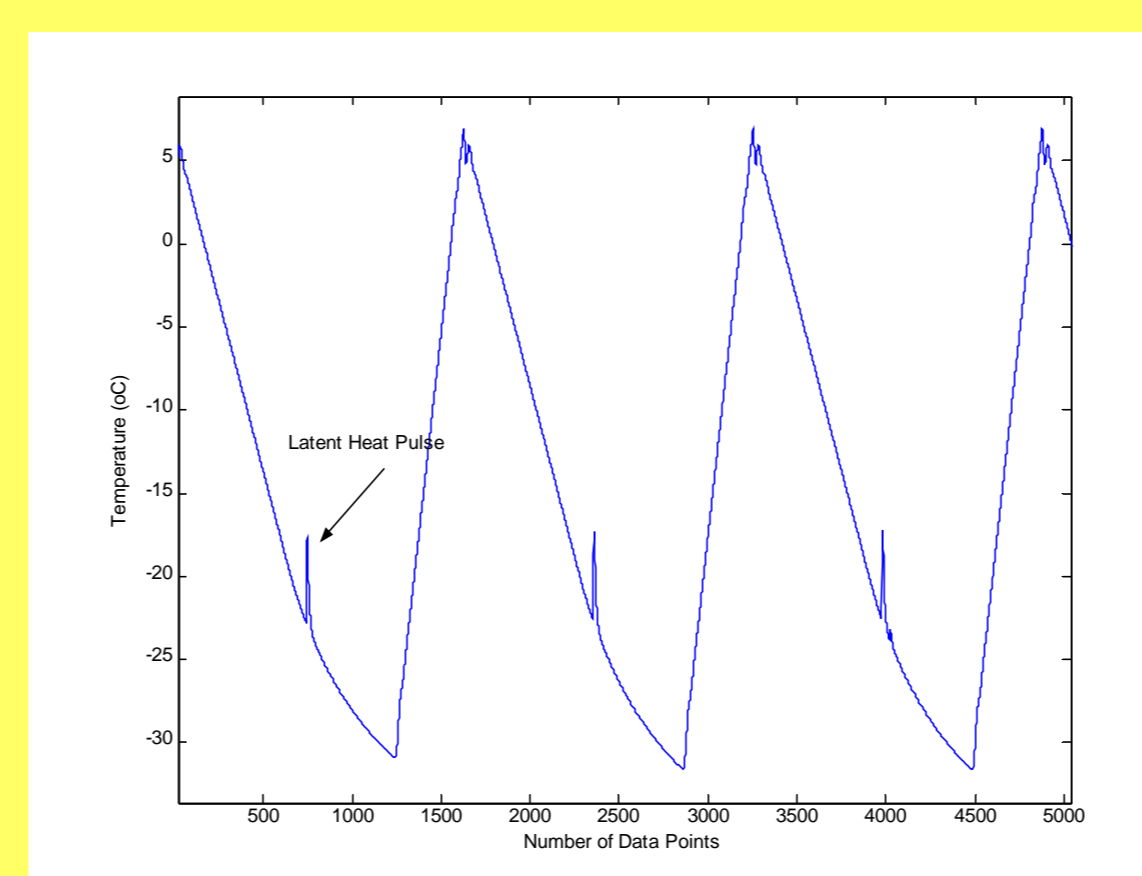
**Figure 1: Schematic for Ozonolysis Apparatus**  
Circles 1-5 represent needle valves, which are used to carefully control the relative humidity and amount of ozone flowing through the reaction chamber.



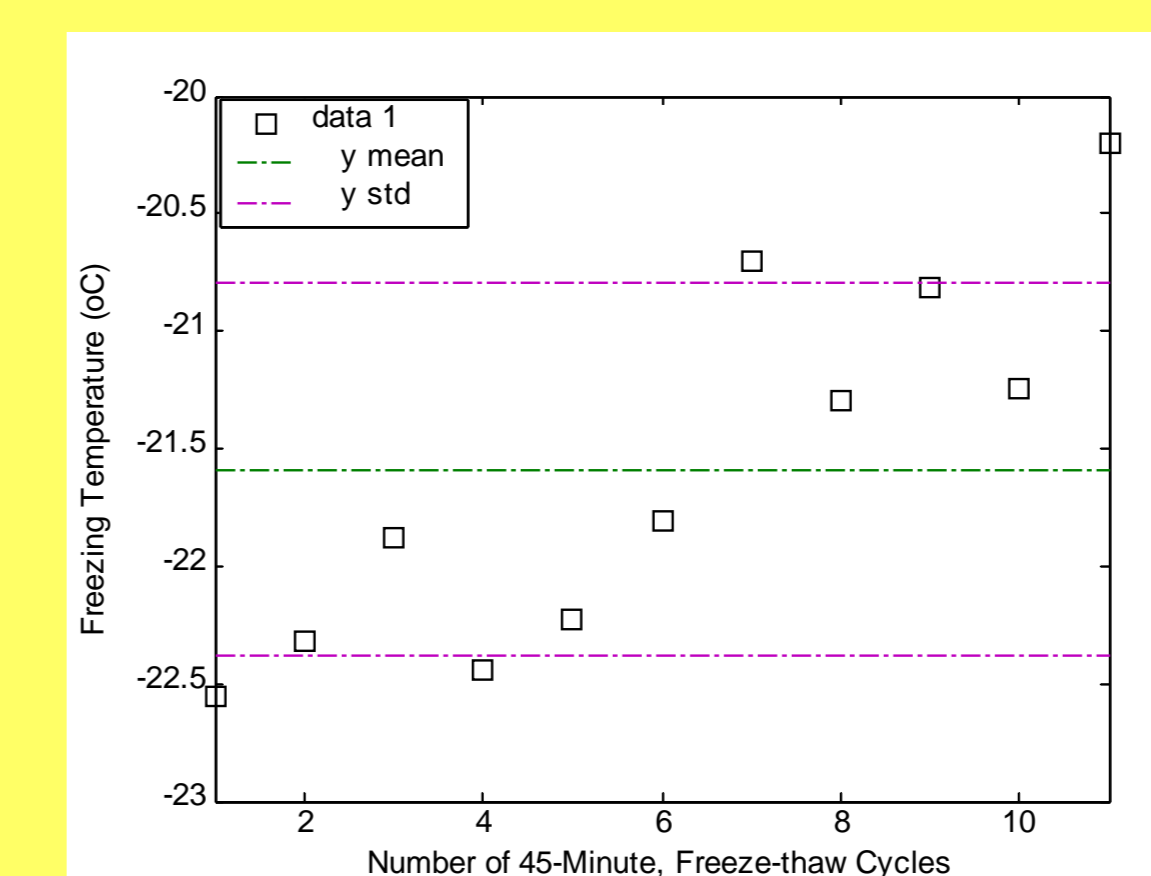
**Figure 2: Drop Freezer Unit**

## Results

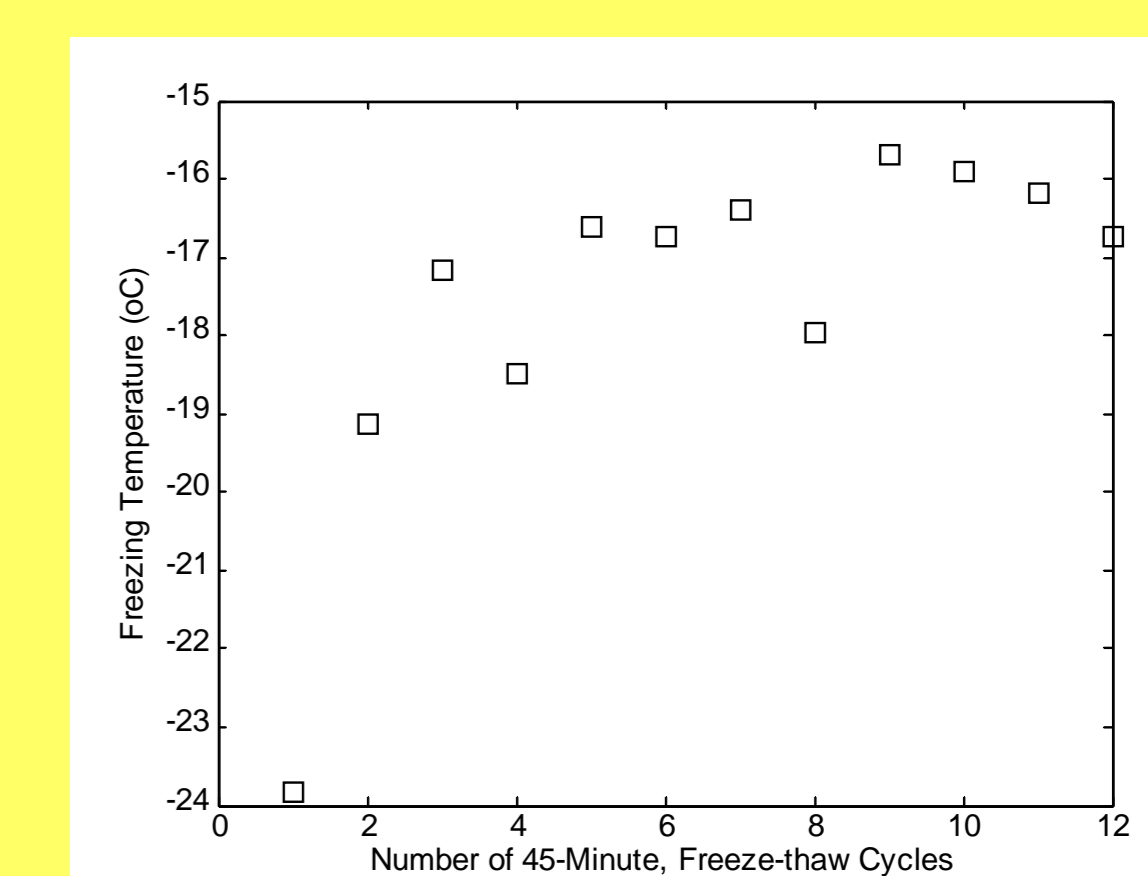
Initial results were monitored in Lab View but statistical analysis was performed in MATLAB. Figure 3 shows typical temperature cycling with a latent heat pulse observed whenever the solution droplet freezes. Temperature ramp rates typically decreased at 1.5°C/min and increased at 3.5°C/min. Figure 4 shows individual freezing temperatures corresponding to each latent heat pulse for an oleic acid thin film after ozonolysis on an aqueous 0.25 M sodium chloride solution droplet. From similar such data, the mean freezing temperatures and standard deviations shown in Table 1 were obtained. The results in Table 1 show little change in mean freezing temperature before and after ozonolysis for all of the organic compounds studied except oleyl alcohol. Figure 5 shows a sharp increase in freezing temperature when an aqueous 0.25 M sodium chloride solution droplet with an oleyl alcohol thin film is first ozonized.



**Figure 3. Latent Heat Pulses After Ozonolysis for an Oleic Acid Thin Film on a 0.25 M NaCl(aq) Droplet**



**Figure 4. Mean Freezing Temp. After Ozonolysis for an Oleic Acid Thin Film on a 0.25 M NaCl(aq) Solution Droplet**



**Figure 5. Freezing Temp. During Ozonolysis of an Oleyl Alcohol Thin Film on a 0.25 M NaCl(aq) Droplet**

**Table 1. Mean Freezing Temperature for Aqueous 0.25 M NaCl Solution Droplets with an Organic Thin Film**

Thin Film	Structural Formula	Freezing Temperature Before Ozonolysis (°C)	Freezing Temperature After Ozonolysis (°C)
Stearic Acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	-23.4 ± 0.4	-24.1 ± 0.3
Oleic Acid	cis-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH=CH(CH <sub>2</sub> ) <sub>7</sub> COOH	-21.9 ± 0.4	-21.6 ± 0.8
cis-13-Octadecenoic Acid	cis-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH=CH(CH <sub>2</sub> ) <sub>11</sub> COOH	-21.5 ± 2.5	-22.2 ± 1.5
Oleyl Alcohol	cis-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH=CH(CH <sub>2</sub> ) <sub>7</sub> CH <sub>2</sub> OH	-21.9 ± 1.1	-16.7 ± 1.0
1-Octadecanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CH <sub>2</sub> OH	-16.2 ± 1.2	-19.4 ± 1.0
None	None	-25.0 ± 0.9	-25.0 ± 0.9

## Discussion

Table 1 shows little change in mean freezing temperature before and after ozonolysis for most of the organic thin films studied. The lack of a significant temperature change for oleic acid may be good news for atmospheric modelers since the well-studied reaction of oleic acid with ozone is known to give a complex mixture of products [4,5]. The increase in freezing temperature after ozonolysis of the oleyl alcohol thin film may be due to better -OH head group orientation at the alcohol-water interface after removal of the carbon-carbon double bond. Head group orientation is known to influence heterogeneous ice nucleation by long-chain aliphatic alcohol thin films [6].

## References

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