DOE *ASR* funded

Collaborative Aerosol Research: Laboratory Studies of the Chemical and Physical Properties of Atmospherically Relevant Secondary Organic Aerosols

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Introduction and Methods

The goal of our research is to utilize new and existing techniques to studying the formation, chemical composition, and phase states of atmospherically relevant SOA that are highlighted in the ASR Science and Program Plan. Our methods utilize state-of-the-art instrumentation to study and examine well-controlled laboratory generated carbonaceous particles through collaborative efforts with national and international colleagues.

(1) We developed a new method for controlling NO_x concentrations in the potential aerosol mass (PAM) reactor under high oxidant (i.e., O_3 and OH) concentrations to study anthropogenic-specific, NO_x-dependent SOA formation pathways.

(2) We are applying a new technique, broadband dielectric spectroscopy (BDS), to study the phase behavior, including the glass transition temperatures, of several relevant organic compounds.

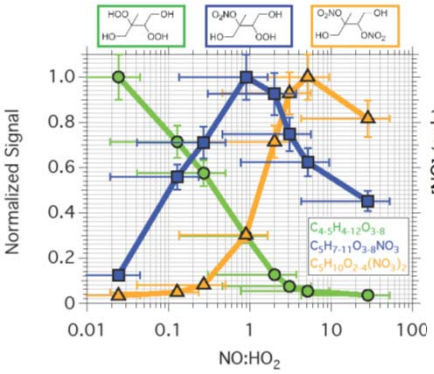
(3) We are studying the coagulation of charged particles in order understand the contribution of this process to optical properties of aerosols during experiment and field campaigns.

NO_x Dependent Reaction Pathways in PAM

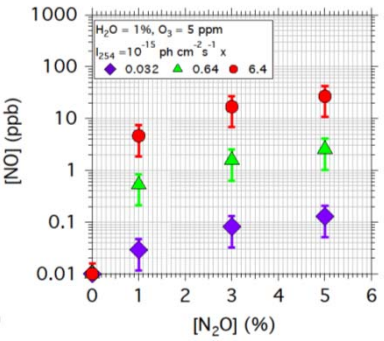
PAM was used for photo-oxidation of isoprene to form isoprene derived SOA. The NO:HO_2 concentrations are varied across 4 orders of magnitudes for this set of experiments.

$O_3 + h\nu_{254} \rightarrow O(^1D) + O_2$
$(H_2O + h\nu_{185} + O_2 \rightarrow OH + HO_2)$
$(N_2O + h\nu_{185} \rightarrow O(^1D) + N_2)$
$O(^1D) + H_2O \rightarrow 2OH$
$O(^1D) + N_2O \rightarrow 2NO$
$OH + O_3 \rightarrow HO_2 + O_2$
$NO + O_3 \rightarrow NO_2 + O_2$
$NO + HO_2 \rightarrow NO_2 + OH$

Reactions used to generate O_x, HO_x, and NO_x in oxidation flow reactors (red: if 185 nm radiation is present inside reactor in addition to 254 nm radiation).



Modeled steady-state [NO] as a function of [N_2O] input to the PAM oxidation flow reactor at I_{254} = 0.032×10^{15}, 0.64×10^{15} and 6.4×10^{15} ph cm^{-2} sec, [H_2O] = 1%, [O_3] = 5 ppm, mean residence time = 80 sec.



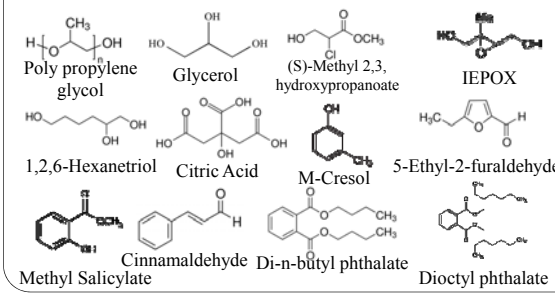
Normalized HR-ToF-NO_3-CIMS signals of isoprene oxidation products generated in the PAM oxidation flow reactor as a function of NO:HO_2. x axis represents the mixing ratio of N_2O and y axis represents the NO concentration.

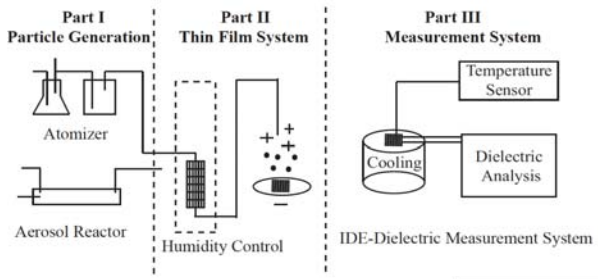
Glass Transition of Organic Compounds using Broadband Dielectric Spectroscopy

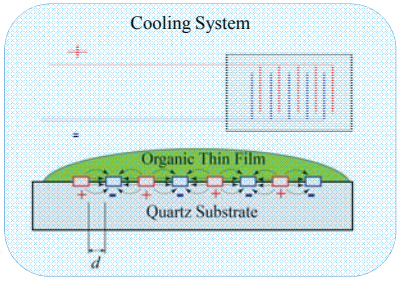
Pure, polar organic compounds that resembled the components of SOA were used, each candidate featuring alcohol and/or ketone groups attached to its parent chain.

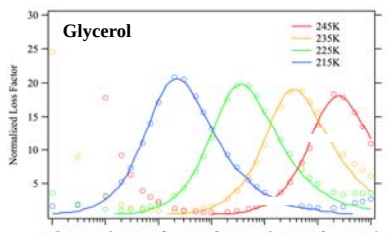
Table 1: Summary of the Compounds the Studied

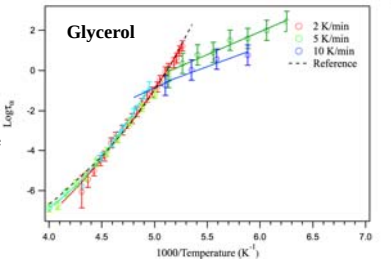
Compound	Chemical Formula	T_g (K)
Poly propylene glycol	$(C_3H_8O_2)_n$	227
Glycerol	$C_3H_8O_3$	194
(S)-Methyl 2,3, hydroxypropanoate	$C_4H_8O_4$	201
IEPOX	$C_5H_{10}O_3$	162
1,2,6-Hexanetriol	$C_6H_{14}O_3$	205
Citric Acid	$C_6H_8O_7$	322
M-Cresol	C_7H_8O	218
5-Ethyl-2-furaldehyde	$C_7H_8O_2$	170
Methyl Salicylate	$C_8H_8O_3$	202
Cinnamaldehyde	C_9H_8O	190
Di-n-butyl phthalate	$C_{16}H_{22}O_4$	193
Dioctyl Phthalate	$C_{24}H_{38}O_4$	210

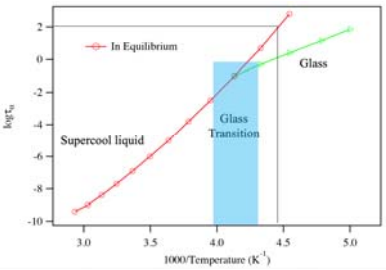


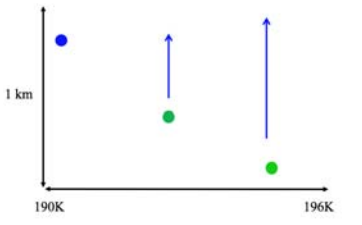






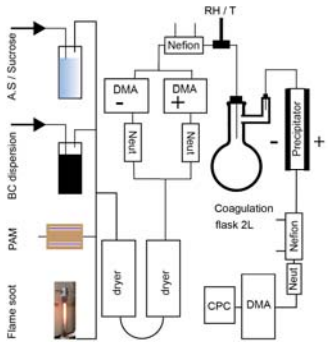




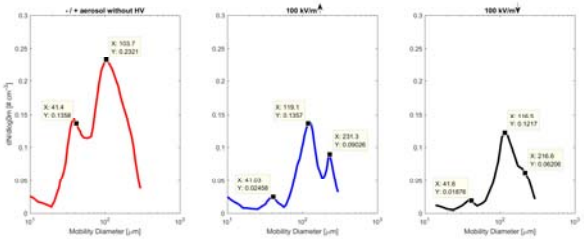


Cooling rates also influence the glass transition temperatures due to the kinetic nature of the glass forming process. Glycerol is cooled at three different cooling rates and only two cooling rates show observable glass transition in the temperature region studied. 2K/min shows no glass formation when T >190 K. 5 K/min and 10 K/min cooling rate yield T*g*=194 K and 198 K, respectively. The differences between the three temperatures correspond to a vertical height of 1 km when aerosols are undrafted into the free troposphere.

Aerosol Coagulation



Experimental setup of the electrostatic enhanced coagulation technique



The plot above shows the experimental results of opposite charge coagulation and uncoagulated charge removal using an electrostatic precipitator. The left graph shows the aerosol number-diameter distribution passing through a non-charged precipitator. The middle plot and the right plot show the aerosol distributions after passing through a upward and downward facing electrical field, respectively. The zero-charge coagulated particles were retained in experiment 2 and 3.

Conclusions and Acknowledgement

- A new method for controlling NO_x and HO_x concentrations in the PAM was used to simulate the photo-oxidation of isoprene under anthropogenic conditions. The oxidation products are analyzed by I-CIMS so as to infer the chemical pathways of SOA formation under anthropogenic conditions.
- The cooling rate dependent glass transition temperatures were measured by the broadband dielectric spectroscopy. The results provide more insight into the phase properties of organic particulate matter, and how that affect the reactivity and climate effects of aerosols.
- A novel charged induced coagulation method was through electrostatic precipitation. This method will be used to generated coagulated bare soot and organic coated soot particles in order to study the effects of aerosol coagulation in optical property measurement. .

This work is supported by DOE award DE-SC0011935, NSF awards AGS-1536939, AGS-1537446, CHE-1507673, CHE-1506768 and the Boston College Undergraduate Research Fund.