Photochemical Production of Light-Absorbing Syringol Secondary Organic Aerosol (SOA) in Droplets using an Atmospheric Simulation Chamber

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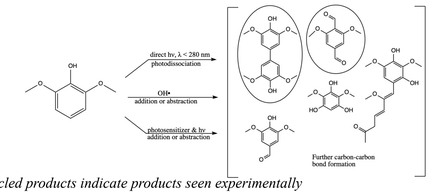
Does syringol behave the same in a cloud chamber as in bulk studies?

Previous studies have shown that SOA material produced with an OH source and with a photosensitizer shares chemical and optical features.[1]

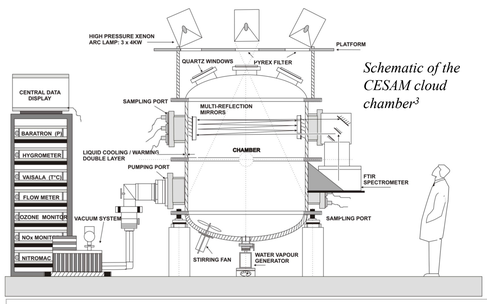
Dark syringol reactions have produced a dimer that absorbs at 470 nm.[2]

H abstraction and OH addition pathways may produce different O/C ratios in products with different polarities and different optical properties, which each influence the atmospheric implications of these SOA products.



Circled products indicate products seen experimentally

UPEC Cloud Chamber

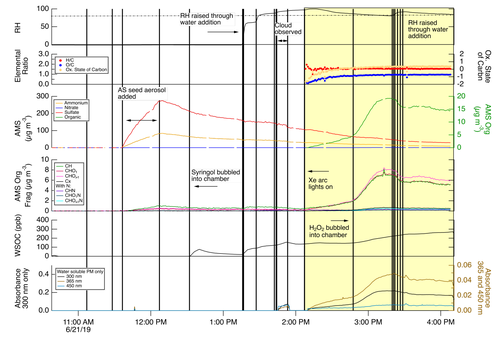


Schematic of the CESAM cloud chamber[3]

Aerosol Mass Spectrometer (ToF-AMS and LToF-AMS)
Cavity Attenuated Phase Shift Spectrometer (CAPS)
Scanning Mobility Particle Sizer (SMPS)
Soluble OC and absorbance: PILS - Waveguide Spectrometer - Total Organic Carbon Analyzer
VOCs: Proton Transfer Reaction Mass Spectrometer (PTRMS)
Filter collection

Syringol forms light-absorbing SOA on deliquesced, irradiated aerosol, with and without an OH radical source

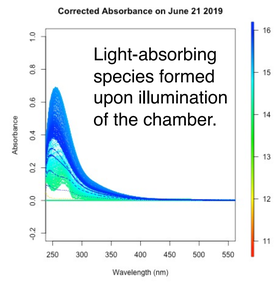
Brown SOA formed upon illumination of the chamber with deliquesced AS aerosol.



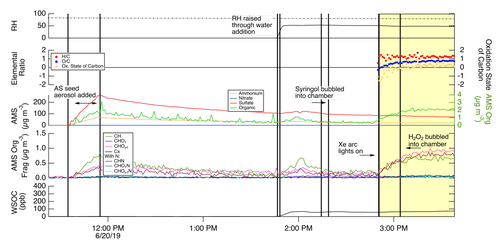
SOA formation was faster, *but not chemically distinct*, with ·OH.

A *slight* preference for $CHO_{>1}$ develops with ·OH photooxidation.

A short-lived product with absorption around 289 nm was observed ONLY during the cloud. This was repeatable.



SOA did not form without deliquesced aerosol.



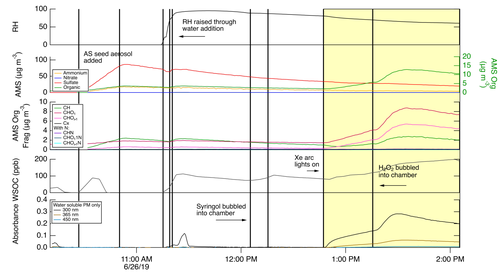
When the humidity remained below the deliquescence RH, SOA formation was limited to 2 $\mu g\ m^{-3}$.

Under dry conditions, the addition of an OH radical source had little effect.

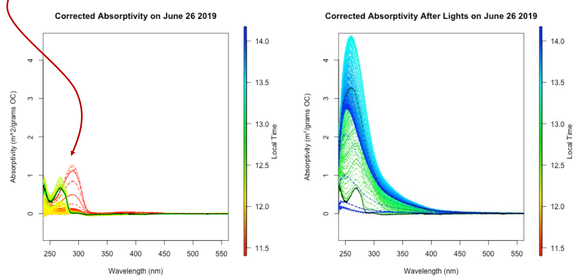
No measurable absorbance was detected during this experiment.

We observed the dark reaction product syringol dimer, which disappeared upon illumination.

Cloud product seen previously appears upon humidification; photobrowning is repeated



The short-lived cloud product appeared again, this time before additional syringol was added to the chamber.



Photobrowning without ·OH

What mechanism is responsible for light-induced brown carbon formation in our experiments?

With HOOH, we observed similar O/C ratios, and broad visible absorbance, to previous studies.

Without HOOH, we also observed browning. Why?

Possible explanations:

(a) **Direct absorption** of the Xe arc lamp radiation ~270 nm by syringol (little relevance to atmospheric processes but possible in the chamber)[4]

(b) Trace impurities or rapid, trace **syringaldehyde** formation, with syringaldehyde behaving as a photosensitizer[5]

(c) **Red-shifted absorption of syringol, and greater quantum yield**, at the air-water interface of deliquesced aerosol (a guaiacol redshift at the air-ice interface is attributed to the aromatic ring, not the substituents, which are common to syringol)[6]

Conclusions

Unexpected photobrowning in our experiments may imply an additional mechanism for this biomass-burning derived compound to influence BB SOA chemical and optical properties.

Further analysis of our mass spectra and end-of-day filters may provide insight into this mechanism.

In general, our observations support the previous bulk studies of syringol in terms of reactivity and brown carbon production.

Literature cited

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Further information

Contact me at lhawkins@g.hmc.edu if you have a question or comment.

Information on the CESAM facility is available here.