Investigation of Aqueous Phase Photo-oxidation of Nitroaromatic Compounds In Brown Carbon Aerosol using Aerosol-TOF-CIMS

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Introduction

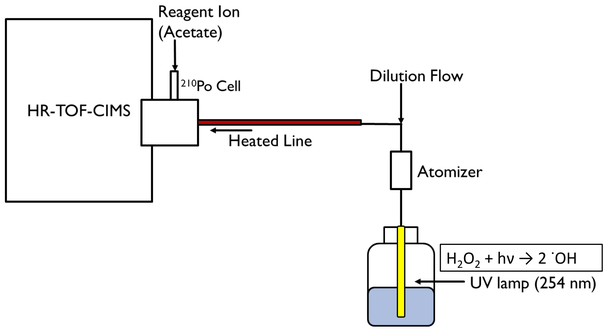
- Light absorbing organic aerosol (brown carbon) can impact climate through absorption of solar radiation[1]
- Little is known about the chemical composition of chromophores in brown carbon and their atmospheric transformations
- Nitrophenols have been identified as a brown carbon species associated with biomass burning aerosol[2]
- Aqueous phase photo-oxidation can change light absorption properties of brown carbon aerosol[3]

Objectives:

1. Determine the rate constant for reaction of nitrocatechol with OH
2. Identify reaction products and their relationship to light absorptivity

Methods

Aerosol-TOF-CIMS



- Reaction solution contains 30µM nitrocatechol and 1mM H_2O_2 as the OH precursor
- Kinetics experiment: includes 30µM levoglucosan as reference compound
- Photo-oxidation initiated by UV lamp (254 nm)
- Reaction solution is atomized, then sent through a heated line (150°C) to volatilize compounds for detection by Aerodyne TOF-CIMS
- Reagent ion: acetate ($CH_3C(O)O^-$)
- Absorption measurements by liquid waveguide capillary UV-Vis spectrometer

Kinetics

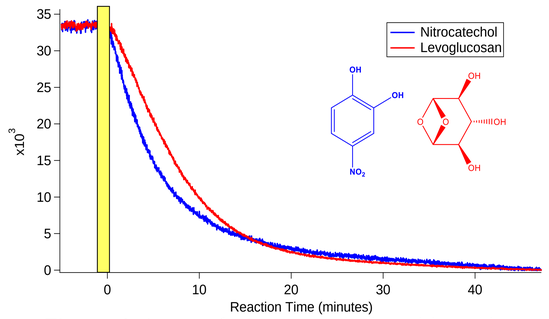


Figure 1. Loss of nitrocatechol and levoglucosan by reaction with OH.

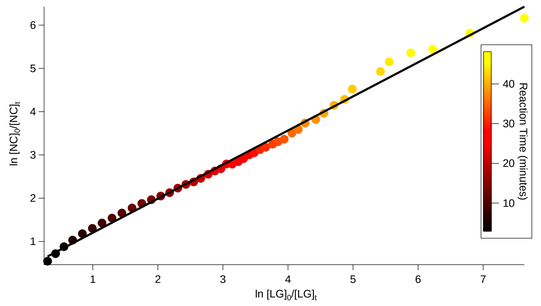


Figure 2. Relative kinetics for nitrocatechol with levoglucosan as reference.

Relative Rate Kinetics:

$$ln\left(\frac{[NC]_0}{[NC]_t}\right) = \frac{k_{NC}^{II}}{k_{LG}^{II}} \times \ln\left(\frac{[LG]_0}{[LG]_t}\right)$$

$$k_{NC}^{II} = 1.24 \times 10^9\ M^{-1}s^{-1}$$

$$[OH]_{aq} = 1 \times 10^{-13} M$$

$$\tau_{1/2} = 2.2\ hours$$

Reaction Products

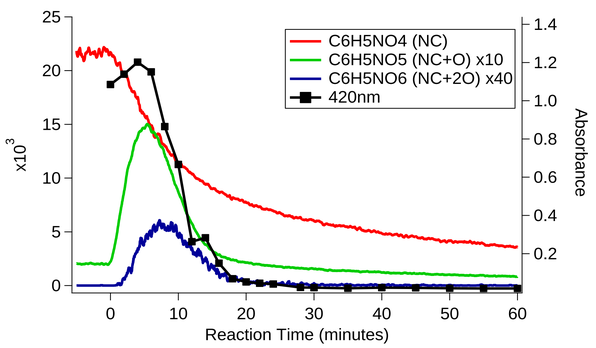


Figure 5. Photo-oxidation of nitrocatechol and formation of functionalized products.

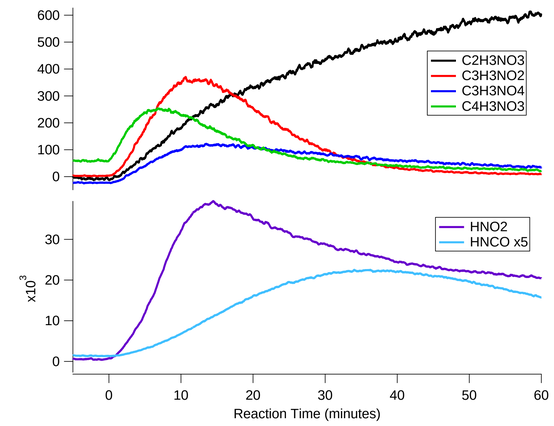


Figure 6. Formation of fragmented products.

- Photo-oxidation of nitrocatechol leads to functionalization by addition of oxygen
- NC+O and NC+2O are detected as products almost immediately after reaction begins
- Absorption maximum at 420 nm occurs at the same time as the maximum concentration of the functionalized products

- Further photo-oxidation leads to fragmentation to form smaller nitrogen-containing molecules
- Fragmented products do not contribute to absorption
- Most products that form are subsequently oxidized, however $C_2H_3NO_3$ seems to be resistant to photo-oxidation
- HNO_2 (HONO) and HNCO are also significant products that are formed throughout the reaction

UV/Vis Absorbance

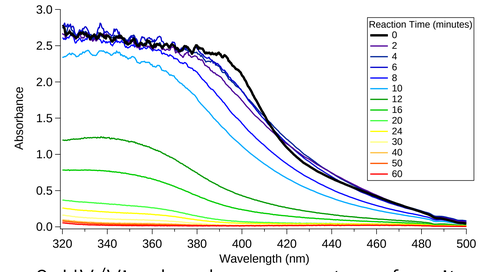


Figure 3. UV/Vis absorbance spectrum for nitrocatechol solution as a function of OH reaction time.

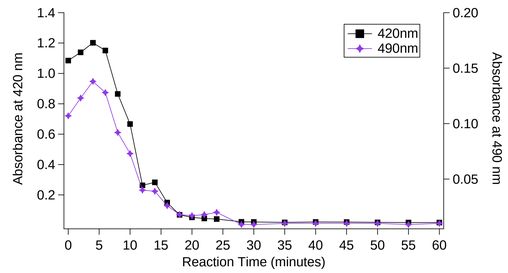
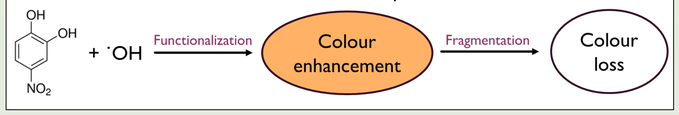


Figure 4. UV/Vis absorbance at 420 nm and 490 nm for nitrocatechol solution as a function of OH reaction time.

Conclusions

1. Nitrocatechol reacts rapidly with OH in the aqueous phase.
2. UV/Vis absorption of nitrocatechol decreases to approximately zero over 60 minutes of reaction time.
3. Absorption in region around 420 and 490 nm increases in the first 6 minutes, coinciding with formation of oxygen-functionalized products.
4. Subsequent formation of fragmented products do not contribute to absorption.



References

[1] Y. Feng, V. Ramanathan, V. R. Kotamarthi, Brown carbon: A significant atmospheric absorber of solar radiation. Atmos. Chem. Phys. 13, 8607–8621 (2013).
[2] Y. Iinuma, O. Böge, H. Herrmann, Methyl-nitrocatechols: Atmospheric tracer compounds for biomass burning secondary organic aerosols. Environ. Sci. Technol. 44, 8453–8459 (2010).
[3] R. Zhao et al., Photochemical processing of aqueous atmospheric brown carbon. Atmos. Chem. Phys. 15, 6087–6100 (2015).