Photolytic Aging of 4-Nitrophenol: Effects of Fresh and Aged Secondary Organic Aerosol on Atmospheric Lifetimes

Lydia Dolvin

Follow this and additional works at: https://scholarworks.wm.edu/honorstheses

Part of the Analytical Chemistry Commons, Atmospheric Sciences Commons, Climate Commons, and the Environmental Chemistry Commons

Recommended Citation

This Honors Thesis is brought to you for free and open access by the Theses, Dissertations, & Master Projects at W&M ScholarWorks. It has been accepted for inclusion in Undergraduate Honors Theses by an authorized administrator of W&M ScholarWorks. For more information, please contact scholarworks@wm.edu.
Photolytic Aging of 4-Nitrophenol: Effects of Fresh and Aged Secondary Organic Aerosol on Atmospheric Lifetimes

A thesis submitted in partial fulfillment of the requirement for the degree of Bachelor of Science in Chemistry from The College of William and Mary

by

Lydia Dolvin

Accepted for Honors

Dr. Rachel O’Brien, Advisor

Professor Mike Jabbur

Dr. Nathan Kidwell

Dr. Kristen Wustholz

Williamsburg, VA
May 6, 2020
Abstract

Organic aerosols in the atmosphere have a large impact on global climate and human health. Understanding the lifetimes and fates of these organics in the atmosphere is imperative for optimizing climate models and characterizing their contributions to net atmospheric warming. The warming and cooling properties of aerosols are related to their abilities to absorb or scatter light. Brown carbon is a type of organic aerosol that is of particular interest due to its ability to absorb light in the visible range. These absorption and scattering properties can change, however, if the aerosols are subjected to photolytic or chemical aging. These aging processes are limiting factors on an aerosol’s atmospheric lifetime.

In the atmosphere aerosols exist in the dry and aqueous phase. Aqueous aerosols may be found in cloud-water systems, where photolytic and chemical aging can still take place. The literature reports characterizations of different secondary organic aerosol (SOA) component lifetimes in these cloud-water systems, but often does not investigate these lifetimes in “dirty” systems where more than one type of SOA molecule exists. This overlooks the potential for interactions between aerosols of different compositions and ages. In this work, we investigate the photolytic lifetimes of 4-nitrophenol under atmospheric cloud-water conditions. We characterize these lifetimes both alone and in a mixed system with α-pinene SOA by analyzing the kinetics of 4-nitrophenol photolysis. The presence of SOA seems to have an important impact on the photolytic lifetimes of 4-nitrophenol, with fresh SOA accelerating the rate of photo-decay and aged SOA slowing it. We hypothesize that OH radicals produced as photo-products contribute to the photo-decay of this brown carbon when in a system with other organic SOA.
# Table of Contents

Abstract ................................................................................................................................................. i  
List of Figures ......................................................................................................................................... iii  
List of Tables ........................................................................................................................................... iii  
Acknowledgements .............................................................................................................................. iv  

**Chapter 1. Background and Motivations** ......................................................................................... 1  
1.1 Introduction ...................................................................................................................................... 1  
1.2 What are Aerosols? ......................................................................................................................... 1  
1.3 What is Brown Carbon? .................................................................................................................. 5  
1.4 OH Radical Processing ..................................................................................................................... 7  
1.5 Implications for Climate and Health ............................................................................................... 8  

**Chapter 2. Methodologies** ............................................................................................................... 9  
2.1 Aerosol Preparation .......................................................................................................................... 9  
2.2 Brown Carbon Preparation ............................................................................................................ 10  
2.3 Photolysis Experiment ................................................................................................................... 11  

**Chapter 3. Results** ......................................................................................................................... 14  
3.1 Absorption Cross-section of 4-Nitrophenol ...................................................................................... 14  
3.2 Data Analysis ................................................................................................................................. 16  
3.3 Photolysis of 4-Nitrophenol ............................................................................................................ 18  
3.4 Effect of Adding SOA to 4-Nitrophenol Photolysis ......................................................................... 23  
3.5 Photolysis of Fresh SOA at Varied Concentrations ....................................................................... 31  
3.6 Addition of Fe (II) and Fenton Chemistry ....................................................................................... 34  

**Conclusion** ....................................................................................................................................... 36  
**References** ....................................................................................................................................... 37  
**Appendix** ......................................................................................................................................... 41
List of Figures

Figure 1: Overview of atmospheric processes..............................................................3
Figure 2: α-pinene oxidation.........................................................................................4
Figure 3: Light availability in the atmosphere...............................................................6
Figure 4: Photolysis set-up........................................................................................12
Figure 5: Beer’s Law example......................................................................................15
Figure 6: Absorption cross-section of 4-nitrophenol..................................................16
Figure 7: Example of y-offset exponential fit..............................................................18
Figure 8: Photolysis spectra of 4-nitrophenol..............................................................20
Figure 9: Kinetic fit of 4-nitrophenol photolysis.........................................................22
Figure 10: Difference in photolysis spectra for 4-nitrophenol......................................23
Figure 11: Absorption spectra of 4-nitrophenol and SOA..........................................25
Figure 12a: Photolysis spectra for fresh SOA............................................................26
Figure 12b: Kinetic fit of fresh SOA photolysis...........................................................26
Figure 13a: Photolysis spectra for aged SOA.............................................................27
Figure 13b: Kinetic fit of aged SOA photolysis...........................................................27
Figure 14a: Photolysis spectra and difference of 4-nitrophenol..................................28
Figure 14b: Photolysis spectra and difference of 4-nitrophenol with fresh SOA.........28
Figure 14c: Photolysis spectra and difference of 4-nitrophenol with aged SOA..........28
Figure 15a: Kinetic fits of 4-nitrophenol with and without SOA...............................29
Figure 15b: Lifetime comparisons for 4-nitrophenol with and without SOA..............30
Figure 16: Kinetic fits of 4-nitrophenol with varied additions of fresh SOA...............31
Figure 17: Estimated OH radical exposure...............................................................33
Figure 18: Kinetics of 4-nitrophenol with Fe (II)........................................................35

List of Tables

Table 1: Time intervals example..................................................................................21
Table 2: Summary of atmospheric lifetimes...............................................................31
Acknowledgements

I wish to acknowledge all the generous sources of support that made this project possible. First, thank you to the William & Mary Charles Center for funding my work over the course of two summers through the Monroe Grant and the Williams & Mary Honors Fellowship program. Their financial support encourages the pursuit of independent research at the College and without it I would not be the chemist I am today. Thank you also to the Virginia Space Grant Consortium who believed in my project enough to contribute to my research and fund an invaluable trip to ACS San Diego so I could present the work. This too has been invaluable for my career and for their support I am very grateful. This research was performed using the lab facilities and equipment belonging to the Chemistry Department at William and Mary.

A huge thank you to Dr. Rachel O’Brien for being an incredible mentor to me during my time working as a researcher at the College. She has taught me more than anyone else in my college career and has always been a fantastic resource for guidance and support. I would also like to recognize Michael Ambrose, Tanner Braman, and William Perrine for being equal partners in doing the research that is highlighted in this thesis, as well as Corey Thrasher and Emma Walhout for their support in the lab generating SOA and analyzing data. Being a part of the O’Brien lab group has been a true joy, and I thank all of its members for being such a kind and thoughtful community.

Finally, I would like to thank my friends and family—thanks to my dearest friends Jenna Ollen and Bailey Hall for tolerating my complaints and inspiring me every day to get it done. Thank you to my faithful editor Luke Campopiano, who always makes sure my commas are in the right place. And thank you to my family for always supporting me in all of my endeavors, whether they be scientific or artistic or somewhere in between.
Chapter 1: Background and Motivations

1.1 Introduction/summary

Organic aerosols represent a significant fraction of atmospheric aerosols and have a large impact on both climate and human health. Their behaviors and compositions in the atmosphere are complex, owing to the diverse range of sources, phase-states, and atmospheric interactions that these particles may undergo during their lifetimes. Characterizing the lifetime of organic aerosols in the atmosphere enables us to quantify their contributions to net climate warming or cooling. While their impacts on the climate are represented in global climate modeling, these predictions are often out of step with our actual observations in the atmosphere. Laboratory research informs these models but much of the research on aerosols’ atmospheric lifetimes is done in isolation, characterizing only one variety of organic aerosol at a time. In the atmosphere, however, these systems mix and interact alongside each other. This means that there is a gap in the literature representing the behavior and lifetimes of organic aerosols in a “dirty” system, one more realistic to what is present in the atmosphere. Examining the photolytic lifetimes of organic aerosols and organic aerosol components in a system together reveals important shifts in chemical lifetimes that may better inform aerosol modeling and the way we think about lifetime in this complex system.

1.2 What Are Aerosols?

An aerosol is generally defined as a collection of liquid or solid particles suspended in air. This outlines a broad category of small particles that includes a huge variety of aerosol species. Aerosols can be anywhere from 10 µm to 1 nm in size and may be created by anthropogenic or biogenic sources. Their chemical compositions can vary widely, as can their phase states (liquid vs. solid particles) and their locations in the atmosphere. A single aerosol
may contain thousands of different organic species that can affect the behaviors of the particle. During their lifetimes in the atmosphere they may undergo chemical transformations and physical processes such as phase changes or chemical reactions, all of which contribute to the complexity of this large and diverse system. In order to understand the effects of aerosols in our atmosphere as a whole, it is necessary to hone in on the behaviors and impacts of specific aerosol types. This section will focus on organic aerosols (OA) and the fate of organics in the atmosphere. Organic molecules can be a large fraction (~50%) of the mass of fine mode (<1 um diameter) aerosol particles, meaning their behaviors are particularly relevant to the impact of aerosols as a whole.

An aerosol may have one of two roles in the atmosphere: light absorber or light scatterer. The proportion of light absorbing or light scattering aerosol species plays a role in determining whether aerosols are contributing to net warming or net cooling. Global temperature is largely determined by the balance of incoming and outgoing radiation, often referred to as the radiative forcing budget. The role of aerosols in this scheme is complicated. On one hand, “white” aerosols are efficient light scatterers that contribute to net cooling. In contrast, many species of aerosols that have absorptive components like black carbon (BC) and brown carbon (BrC) may be significant atmospheric absorbers. Organic aerosol’s absorption contributions are often underestimated and are still not well characterized. When do they absorb and when do they scatter light? How does their behavior evolve over time? What proportion of aerosols are primarily absorbers? These questions contribute to the large uncertainty when factoring the radiative contributions of aerosols into atmospheric models. Ultimately this uncertainty surrounding the radiative contributions of organic aerosols means that we cannot yet predict whether they contribute to net warming or cooling of our atmosphere.
The origins of organic aerosols are as diverse and varied as the aerosols themselves, but it is useful to understand a general cycle describing the origins and transformations that are common to organic material in the atmosphere (Figure 1). A significant portion of organic matter in the atmosphere is emitted by biogenic sources. Trees, plants, and other vegetation emit volatile organic compounds (VOC) in response to environmental stimuli that contribute an estimated 1000 Tg of organic matter to the atmosphere each year. Some species may emit primary organic aerosols directly, such as pollen or fungi spores, but the majority of plant species give off simple VOCs that are not yet aerosols. These are typically terpenes (isoprene being the most abundant) that have a low vapor pressure and are readily released into the atmosphere. The VOC that we study in this work is α-pinene, which is sourced from pine trees. Once emitted, a VOC may contribute to the chemistry of the atmosphere through oxidation and secondary organic aerosol formation.

Figure 1. A generalized overview of organic processes in the atmosphere.
A secondary organic aerosol (SOA) is defined as an aerosol particle that was not directly emitted but instead formed in the atmosphere, typically through oxidative processes. When VOC’s are emitted, they may interact with ozone, other chemical species, or light to undergo further chemistry (Figure 2). This lowers the vapor pressure and thus the volatility of these compounds, causing them to condense together to form particles. Through this process VOCs are large contributors to SOA formation. The resulting aerosols are a complex mixture of organic species that may be partitioning between phases or continuing to undergo physical and chemical transformation. Once formed, the organic molecules in secondary organic aerosol will continue to interact with other organic matter and with other reactive chemicals in the atmosphere. These processes are termed “aging” and they include reactions with hydroxyl radicals, nitrate radicals, ozone, as well as accretion or oligomerization reactions. In addition, SOA can be aged by sunlight and changes in the relative humidity (RH). The extent of these aging processes will depend on the time of day and atmospheric conditions.

There are two main pathways for SOA particles to be removed from the atmosphere: complete oxidation of the molecules in SOA to VOCs like CO₂, and physical (wet or dry)

![Diagram](image)

**Figure 2.** An example of SOA products formed via photo-oxidation of alpha pinene.
deposition. For wet deposition, aerosol particles that have dissolved in cloud water are deposited during rain or snow fall events. Wet deposition is thought to be the dominant removal process for particle-phase organics, but a large knowledge gap exists. There is much the scientific community still does not know about the lifetimes of aerosols in the atmosphere and the relative rates of their physical and chemical degradation processes.

1.3 What is Brown Carbon?

Emissions from vegetative matter are far from the only source of SOA. Another large contributor to both SOA and primary organic aerosol is biomass burning. The combustion of both natural fuels, such as wood or waste, and fossil fuels both produce primary and secondary organic aerosol emissions. The chemical makeup of these aerosols is distinct from those emitted directly from vegetation. Typically a mixture of black carbon and light absorbing organics called brown carbon are emitted. Black carbon acts as an absorber over a broad range of wavelengths (UV to IR) in the atmosphere and contributes to net warming. The emissions and behaviors of brown carbon are more complex, however. Brown carbon’s role as a light absorber in SOA generated by biomass burning was not recognized until recently and the extent of its contributions to net warming in the atmosphere are not fully known. The absorption wavelengths of brown carbons are often limited to the near-UV and the visible spectrum. These wavelengths overlap with the much wider absorbing range of black carbon, making it difficult to isolate and measure the absorption contributions of brown carbon directly. These uncertainties make over- and under-estimations of brown carbon’s contributions likely. The absorption behaviors and lifetimes of these brown carbon aerosols are directly relevant to the global contribution of aerosols to the planet’s radiative forcing budget, so it is important to reduce these uncertainties wherever possible.
The behavior of brown carbon in the atmosphere and its interactions with other aerosol components, namely those derived from VOCs, is the focus of this thesis. Brown carbon, like aerosol, is a broad term that includes a diverse set of organic compounds tied together by their common ability to absorb light in the visible region. Interaction with light in the visible range is especially relevant in the atmosphere because ozone blocks shorter wavelengths of light, allowing only the near UV and visible light into the stratosphere (Figure 3). Compounds commonly identified as brown carbon include nitro-aromatic compounds, humic-like substances, and other high weight organic compounds. Sources include primary pollutants like fossil fuel emissions and biomass burning. Brown carbon may be produced directly as primary aerosols or may form SOA after undergoing oxidation processes. Both primary and secondary brown carbon SOA are found to be absorptive. These compounds are potentially vulnerable to photochemical aging processes because of their ability to absorb light in the visible range.

![Figure 3](image.png)

**Figure 3.** A summary of light wavelengths available to the atmosphere. Shaded areas indicate light wavelengths that are filtered or blocked through absorption by water, ozone, or other atmospheric compounds.

One of these photochemical processes is photobleaching, or photo-decay. This is a decrease in the absorption properties of a compound as a result of photolysis, or exposure to light. When a molecule absorbs at a particular wavelength there is the possibility that the input of energy will cause a molecular bond to dissociate. Once the compound is chemically altered it
may no longer be able to absorb light at that wavelength or energy of light. Studies show that photobleaching does occur in atmospheric brown carbons, although the rates vary greatly between different molecular weight brown carbons. Photo-enhancement, a related process involving the formation of products that increase absorption properties, has also been observed in brown carbon produced by biomass burning.13 Nitrophenols and other nitro-aromatics in particular have been identified as common brown carbon species and used as characteristic “tracers” for biomass burning.14,15

1.4 OH Radical Processing

Free radicals contribute to the processing of SOA in the atmosphere alongside photolytic processes. OH radicals are common atmospheric oxidants in the daytime, while nitrate radicals are more common at night. These highly reactive species can contribute to the oxidation of aerosols in the atmosphere via heterogeneous oxidation.16 In this case, the oxidative effects are limited to the surface of the particle. Radicals may also be produced in the particles as a result of other aging processes. While photochemical aging is a primary step, photolysis can also produce radical byproducts that initiate secondary aging and oxidation within the aerosol. These secondary processes are of particular importance when aerosol particles are dissolved in cloud water where the aqueous phase state makes it much easier for radicals to mix throughout the droplet. The production of radicals as secondary products during photolysis is one possible explanation for the rapid oxidation that has been observed in cloud droplets. In the laboratory, the photolysis of SOA formed from α-pinene has been shown to produce OH radicals when photolyzed in aqueous solution.17 This type of SOA is used in the laboratory studies described in this manuscript.
1.5 Implications for Climate and Health

Brown carbon aerosols have a definite impact on the earth’s climate but the magnitude of that impact is still not well represented in climate modeling. Because of the complexity in their sources, composition, and behaviors, their effects are difficult to quantify with a high degree of certainty. When absorption due to brown carbon is included its chemical lifetime is often neglected. Applying an aging scheme to models increases the accuracy of the predicted behaviors of brown carbon aerosols. Laboratory work is primarily done on isolated systems, but it’s important to consider the interactions between brown carbon and other aerosol species that may affect chemical lifetimes. Studying aerosols in mixed systems will help to better characterize the transformations and changing behaviors that may occur under atmospheric conditions, ultimately providing insights that will improve our overall predictions of atmospheric processes.

In addition to climate concerns, brown carbon also presents a danger to human health. Many brown carbon molecules are known toxins or carcinogens and contribute to public health concerns over poor air quality and links to cardiovascular disease. Even at relatively low levels, anthropogenic aerosol pollution is correlated with increased risk of respiratory hospitalizations and mortality. Although these concerns are not directly related to photolytic lifetimes of brown carbon, further research on these chemical and physical lifetimes helps contribute to an understanding of their prevalence and thus impacts. Studying these behaviors can improve our understanding of the regional effects and the range of these aerosols’ impacts beyond their immediate sources.
Chapter 2: Methodologies

2.1 Aerosol Preparation

Secondary organic aerosol (SOA) was generated using $\alpha$-pinene from Sigma Aldrich. A 10 L glass jar equipped with Swagelok ports was used as the chamber to prepare the SOA. Ozone was created at ~1 ppm by flowing clean air through a Penray lamp (Model 600, Jelight Co. Inc.) at ~1.8 L min$^{-1}$ into the glass jar. $\alpha$-pinene was added at a rate of 20 µL hr$^{-1}$ using a syringe pump, a borosilicate capillary, and a Swagelok tee. Samples were then collected onto a preweighed 47 mm PTFE membrane filter with 2 µm pores (skcinc.com) at a flow rate of ~1.5 L min$^{-1}$. After 8-10 hours of collection, approximately 6-8 mg of material was collected. The loaded filters were then stored in petri dishes and frozen until they were removed for either photolysis or sample preparation.

Filters that were marked for photolysis were thawed for 10 minutes and then irradiated in a photolysis box using a mercury xenon arc lamp (Newport model 66902, lamp power 50-500 W). The photolysis box was custom built from airtight polycarbonate and was fitted with a hinged plastic door that has an o-ring seal. Zero air (Environics Series 7000) flowed continuously through the box using Swagelok ports at 1 L min$^{-1}$. The center of the door was removed and replaced with 0.001 inch PTFE film that was attached using with Kapton tape. SOA loaded filters were placed at the back of the box in petri dishes suspended by magnets. The entire box setup was placed ~9 cm from the lamp and the filters were left to be photolyzed for 4 days.

SOA was extracted from both fresh and aged (photolyzed) filters using acetonitrile. Each filter was cut into small fragments and placed into a clean, baked glass vial along with 2 mL of acetonitrile. After 20 minutes of agitation, the filter pieces were removed and the remaining
solution was dried down and concentrated for 30 minutes under a pure nitrogen airflow. The water soluble portions of the concentrated SOA were then re-hydrated with the addition of 200 µL ultrapure Milli-Q water (per filter) with constant swirling. This aqueous SOA solution was then ready for use in other experiments or characterizations.20

2.2 Brown Carbon Preparation

4-Nitrophenol is the brown carbon compound we have chosen to use as a model in our experiments. It was selected as a compound that can represent a subset of brown carbon molecules found in the atmosphere. It was also chosen for its relatively rapid aqueous photolysis rate and due to the fact that there are numerous experiments published in the literature that can be used for comparison. Nitrophenols are estimated to contribute to 1% of organic matter emitted from biomass burning sources, which amounts to 15 mg/kg of dry wood burned. Nitrophenols and other cyclic nitrogen substituted compounds are also noted as important tracers for both biomass burning and urban emissions. These compounds have also been observed as products of both biomass burning and anthropogenic emissions like those found in the Los Angeles Basin.12,21

Certain cleaning protocols were enforced in all of the experiments detailed here. All glass vials that were used were baked at 400 °C for 6 or more hours in order to eliminate any traces of organic material that could contaminate our samples. We used teflon lined caps in order to avoid leaching organic material into samples. All water used in solutions was ultrapure Milli-Q water sourced from a Milli-Q Direct® water purification system. Our 4-Nitrophenol stocks were kept away from light and were frozen or refrigerated when not in use.

Before preparing the 4-nitrophenol stock, we removed the Sigma-Aldrich 4-nitrophenol from the freezer where it was stored and allowed the container to reach room temperature before
opening. This kept condensation from forming on the material when the container was first opened. To make the stocks, 0.02 g of the solid 4-nitrophenol were weighed out using a high precision mass balance and were added to a clean baked glass vial. We then diluted it by adding Milli-Q water with a disposable glass pipette to a total mass of ~10 g (excluding the mass of the vial itself). We measured by mass instead of volume because it reduced the need for glassware baking and reduced the potential for contamination of the stock. Next, we capped the vial and agitated the crystals in the solution until they fully dissolved (~30 minutes of shaking).

The initial stock solution was still too concentrated for atmospheric relevance and our measurement techniques. A dilution was performed by pipetting 10.0 g of acidified Milli-Q water (HCl added to achieve a pH of 3.5). The pH of this acidified Milli-Q water stock was regularly monitored using a HQ11d portable pH meter with PHC201 pH electrodes. We then added 10 µL of the 4-nitrophenol stock to achieve a final substock concentration of 0.02 g/L or 14 µM. Other concentrations could be achieved by modifying the amount of substock added. After the substock was prepared, we checked the final pH to ensure it was within 3.5 to 3.7. In some instances, we omitted the pH modifications involved in this protocol if we were interested in measuring properties at different pHs. Generally, the pH of ~3.5-3.7 reflects the usual acidity of cloud water droplets found in the atmosphere. This also ensured that 4-nitrophenol remained in its protonated state for consistency across experiments.

2.3 Photolysis Experiment

Photolysis was carried out on a number of different chemical mixtures in the aqueous phase. In this section, we will describe the general protocol that was applied regardless of the solution being photolyzed. All aqueous photolysis was carried out in ~3 mL quartz cuvettes that were sealed shut with vacuum grease and teflon tape. This was done to minimize evaporation.
Over the course of photolysis the masses of the cuvettes were recorded and, if necessary, a linear correction was applied to compensate for any changes in sample mass and concentration. The solution to be photolyzed was placed in a cuvette and positioned 14 inches in front of a mercury xenon arc lamp (Newport model 66902 lamp power 50–500 W) (Figure 4). The lamp emits photons across a similar wavelength range to the solar spectrum. This lamp is also fit with an IR filter cooled with circulating water and a 299 nm long pass filter to remove short wave UV light. This simulates the solar light energy that is accessible to the lower atmosphere (the 299 nm filter simulates removal of light by the ozone layer). The emission spectrum and flux of the lamp were measured with a calibrated UV/vis detector (Ocean Optics, USB4000). The cuvettes were left in front of the lamp and removed at specific time intervals for absorption spectrum measurements in a PerkinElmer LAMBDA 35 UV/vis spectrometer.

A UV/vis spectrometer measures the ability of a compound to absorb light at specific wavelengths. Briefly, light is diffracted by a monochromator into discrete wavelengths of light from 200 nm to 600 nm, in the case of our measurements. This light is then directed by

![Figure 4](image.png)

**Figure 4.** The set up for the photolysis experiments. Pictured are two quartz cuvettes which hold aqueous samples. Behind the cuvettes is the photolysis box used for photolyzing filters as described in Chapter 2.1.
mirrors through two sample cells, one containing water (the “blank”) and the other containing the compound of interest in solution. Certain wavelengths of light are absorbed more by the compound, while others have more transmission. The light that is transmitted is measured by a photodiode detector. Equation 1 defines transmittance (T) as the intensity of light transmitted through the sample (I) as a proportion of the total intensity of the initial incident light (I₀). This can then be converted to absorbance (A) by taking the negative logarithmic of transmittance (Equation 2).

\[
\text{Equation 1.} \quad T = \frac{I}{I_0}
\]

\[
\text{Equation 2.} \quad A = -\log \left( \frac{I}{I_0} \right)
\]

Absorbance is a unitless quantity that represents the proportion of light absorbed by the analyte. Measuring absorbance at multiple wavelengths results in an absorption spectrum. Since compounds have characteristic absorption spectra, measuring changes in absorbance can give information on the proportion of molecules that have undergone chemical changes as a result of the photolysis. All data processing and kinetics analysis were then performed in Excel and in Igor Pro.
Chapter 3: Results

3.1 Absorption Cross-section of 4-Nitrophenol

The absorption cross section of 4-nitrophenol in bulk aqueous solution ($\sigma(\lambda)$) is important for two reasons. First, it gives information about the ability of the molecule to absorb light at specific wavelengths. This information can be compared to different types of brown carbon molecules providing estimates of the extent of light absorption in the atmosphere. Second, obtaining the absorption cross section ($\sigma$) at a particular wavelength allows us to estimate kinetics at different solar fluxes.\(^{24}\) To estimate kinetics and to compare between different laboratory experiments, the first order photolysis rate constant, $J$, is used. In Equation 2, $\sigma(\lambda)$ refers to the absorption cross section as a function of wavelength, $F(\lambda)$ is the light flux as a function of wavelength, and $\phi$ is the quantum yield for the photolysis of a specific chemical A.

\textbf{Equation 2.} \quad J = \int \sigma(\lambda) F(\lambda) \, d\lambda \, \phi

Integrating across these terms gives the first-order decay for those conditions (light flux and wavelength range). Since this is first order, the rate constant $J$ is the reciprocal of the lifetime. Thus, $1/J$ is a chemical’s characteristic lifetime, the time it takes for the concentration to decay by 37%.$^{25}$ This type of analysis allows us to use our laboratory data to estimate chemical lifetimes for 4-nitrophenol at different solar fluxes which are approximating different atmospheric conditions.

For this project, we calculated the absorption cross section for 4-NPH by diluting a sample to create a calibration curve. An absorption cross-section is essentially a Beer’s law plot for every wavelength absorbed by a molecule. Beer’s law states that the absorbance (A) of a compound is directly dependent upon the path length through which the incident light must
travel through ($\ell$), the concentration of the compound ($c$), and the absorption coefficient ($\varepsilon$) specific to the compound (Equation 3).

**Equation 3.** $A = \varepsilon \ell c$

Plotting concentration ($c$) versus absorbance ($A$) with a path length of 1 cm gives a plot where the slope of the linear fit gives the absorption coefficient ($\varepsilon$) for a particular wavelength (Figure 5). With some unit conversions, the absorption coefficient can be stated in terms of $\sigma$ with units of cm$^2$ molecule$^{-1}$ and is calculated as a function of wavelength.

Our 4-nitrophenol absorption cross section was obtained using the PerkinElmer LAMBDA 35 UV/vis spectrometer. Absorption spectra were taken at decreasing 4-nitrophenol concentrations (~ 100 µL added per step) and the absorption at each concentration was plotted for each individual wavelength. These plots were then checked for linearity at high

![Graph](image)

**Figure 5.** An example of a calibration curve with Beer’s Law applied. The absorbance at 310 nm (y-axis) is plotted as a function of concentration (x-axis). If we match the equation of the linear fit with Beer’s Law, $A = \varepsilon \ell c$, we can derive the absorptivity constant $\varepsilon$. 
concentrations where calibration curves may become non-linear, and any non-linear points were excluded. A linear fit was applied and slopes obtained for each wavelength. These slopes were then transformed to $\sigma$ in cm$^2$ molecule$^{-1}$ and used to create an absorption cross-section plot (Figure 6). This gives us $\sigma(\lambda)$ required to calculate $J$ at different solar fluxes.

Figure 6. The absorption cross-section of 4-nitrophenol. This is generated by plotting absorptivity constants for each wavelength and yields $\sigma(\lambda)$, an important term for determining the atmospheric lifetime of a compound.

3.2 Data Analysis

All data analysis and graphing was performed in Excel and Igor Pro. Most of the data analysis in this work takes the form of assigning an atmospheric lifetime ($\tau$). The atmospheric lifetime is defined as the time it takes for $\sim$37% of the system of interest to decay. This is done by fitting the decay of the 4-nitrophenol peak (averaged over 310-319 nm) with a y-axis offset exponential. The generic form of this fit can be seen in Equation 4, where $y$ is the absorbance of the 4-nitrophenol peak, $y_0$ is the lowest point of the decay at which the change in absorbance appears to be 0, and $t$ is the time in minutes.
Equation 4. \( y = y_0 + Ae^{-t/\tau} \)

Fitting the observed first-order decays to this equation provides the constants \( A \) (unitless) and \( \tau \) (time, in minutes or hours). In plotting the data, we sometimes use a linear transformation of the exponential because it allows an easier comparison between lifetimes. Taking the natural log of the exponential fit and rearranging the terms yields Equation 5, where \( k \) is the inverse of \( \tau \) (\( k = \frac{1}{\tau} \)) in min\(^{-1}\).

Equation 5. \( \ln \left( \frac{y-y_0}{A} \right) = -kt \)

Although it may seem obvious, many published analyses of atmospheric lifetimes similar to those discussed in this work do not employ an exponential fit with \( y \) offset. Instead, scientists take the natural log and assume that the absorbance decays to 0. This assumption is sometimes erroneous. Whether due to an analytical difference (as is the case for our system) or due to the system itself (for example, if there is a portion of material that cannot be photo-bleached), these systems do not always decay to 0. Figure 7 shows the difference in calculated \( \tau \) when we use an offset exponential fit and then a standard exponential fit on the same set of data. The offset fit seen in pink gives a lifetime of \( \tau = 3.1 \pm 0.3 \) hours while the standard exponential gives a lifetime of \( \tau = 4.1 \pm 0.2 \) hours. This is a fairly large discrepancy between lifetimes given by each fit, even with the relatively small \( y \)-offset we see for this system. Figure 7 demonstrates the importance of factoring this \( y \)-offset into the kinetic fit and measuring decay over time scales long enough to observe the end point of the decay. This feature is part of the reason we carried out the photolysis experiments for 20+ hours (described below).
18

The first step in understanding the interactions between 4-nitrophenol and SOA in our model system is to study the behavior of 4-nitrophenol alone. Other studies have characterized the atmospheric lifetime of nitrophenols using absorption spectroscopy methods similar to the ones used here.22,26,27 Vione et. al.27 studied the photodegradation and chemical removal processes that may act upon 4-nitrophenol in the atmosphere and measured photolytic lifetimes of 4-nitrophenol across a range of pH values. Zhao et. al.22 conducted similar photolytic lifetime experiments on brown carbon, but at shorter time scales. Qualitatively, the absorption spectra

Figure 7. An example of the difference between a y-offset exponential and exponential fit, applied to the same data set (4-Nitrophenol photolyzed alone). A linear fit was applied to each, excluding the points where the fit becomes nonlinear (beyond t = 7 hours).

3.3 Photolysis of 4-Nitrophenol

The first step in understanding the interactions between 4-nitrophenol and SOA in our model system is to study the behavior of 4-nitrophenol alone. Other studies have characterized the atmospheric lifetime of nitrophenols using absorption spectroscopy methods similar to the ones used here.22,26,27 Vione et. al.27 studied the photodegradation and chemical removal processes that may act upon 4-nitrophenol in the atmosphere and measured photolytic lifetimes of 4-nitrophenol across a range of pH values. Zhao et. al.22 conducted similar photolytic lifetime experiments on brown carbon, but at shorter time scales. Qualitatively, the absorption spectra
and photolytic decays that these researchers reported align with our measurements of 4-nitrophenol’s behavior.

Using the protocol detailed in the methodologies (Chapter 2.2) we created a dilute aqueous solution (0.02 g/L or 14 µM) of 4-nitrophenol to which HCl was added in order to achieve an atmospherically relevant pH of 3.5. An aliquot of this solution was placed in a small quartz cuvette where it would remain for both photolysis and UV/Vis absorption measurements.

Throughout the experiment the cuvette was removed from the lamp light and the 4-nitrophenol solution’s absorption was measured with the UV/Vis at varying intervals. Since it is a first order decay the absorbance of 4-nitrophenol appears to change more rapidly at the start of photolysis. To account for this, absorption spectra were taken every 15 minutes for the first few hours of photolysis and then were spread out to every few hours at later time intervals. An example measurement schedule is detailed in Table 1.

The result is a record of the absorption spectra of 4-nitrophenol over a 22 hour photolysis period (Fig. 8). The darkest line represents the absorption spectra at a photolysis time of t = 0 hours, while the most yellow line shows the absorption at a photolysis time of t = 22 hours. Our main peak of interest is found at ~320 nm. This is the strongest peak corresponding to 4-nitrophenol’s absorption in the visible range and it is the feature we chose to track its photo-decay. As the photolysis continues, this peak shrinks. This is a result of the light energy causing dissociation of 4-nitrophenol. By measuring the intensity of this peak over time we can measure the change in 4-nitrophenol’s absorption over time and obtain a kinetics curve.

It is important to note that this is not a perfect measure of 4-nitrophenol’s concentration or absorbing qualities over time. There is always the possibility that contaminants are present in the solution or 4-nitrophenol’s photolysis goes on to form additional photo-products that absorb over
the wavelengths of light where we are measuring. If this were the case, our kinetics would not be perfectly representative of 4-nitrophenol’s lifetime. We do not have strong reasons to believe that this happening, however, so we feel comfortable in using absorption data as a measure of 4-nitrophenol’s photodegradation in these sets of experiments. Our 4-nitrophenol spectra shown in Figure 8 exhibits the same features as those reported in Zhao et. al. in their investigation into the photochemical processing of atmospheric nitrophenols. They also report significant decay in 4-nitrophenol’s absorption at ~315 nm and observe the same initial increase in absorption seen at ~250 nm. Their photolysis measurements were conducted over 150 minutes of photolysis, which is a much shorter time scale than our 22 hours. This accounts for their inability to observe the eventual decay of that initial increase at ~250 nm. They do not specify the details of their kinetic analysis, but refer to 4-nitrophenol’s degradation as a “pseudo first-order decay.”

**Figure 8.** Absorption spectra of 4-nitrophenol measured over the course of 22 hour photolysis. The darkest line represents an absorption spectrum taken at photolysis time = 0 hours, while the lightest yellow line represents the absorption at the end of the photolysis period.
<table>
<thead>
<tr>
<th>Total time under lamp (hours)</th>
<th>Spectra File Name</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample A</td>
</tr>
<tr>
<td>0</td>
<td>EX001</td>
</tr>
<tr>
<td>0.25</td>
<td>EX004</td>
</tr>
<tr>
<td>0.5</td>
<td>EX007</td>
</tr>
<tr>
<td>0.75</td>
<td>EX010</td>
</tr>
<tr>
<td>1</td>
<td>EX013</td>
</tr>
<tr>
<td>1.25</td>
<td>EX016</td>
</tr>
<tr>
<td>1.5</td>
<td>EX019</td>
</tr>
<tr>
<td>1.75</td>
<td>EX022</td>
</tr>
<tr>
<td>2</td>
<td>EX025</td>
</tr>
<tr>
<td>2.5</td>
<td>EX028</td>
</tr>
<tr>
<td>3</td>
<td>EX031</td>
</tr>
<tr>
<td>3.5</td>
<td>EX034</td>
</tr>
<tr>
<td>4</td>
<td>EX037</td>
</tr>
<tr>
<td>4.5</td>
<td>EX040</td>
</tr>
<tr>
<td>5</td>
<td>EX043</td>
</tr>
<tr>
<td>5.5</td>
<td>EX046</td>
</tr>
<tr>
<td>6</td>
<td>EX049</td>
</tr>
<tr>
<td>6.5</td>
<td>EX052</td>
</tr>
<tr>
<td>7</td>
<td>EX055</td>
</tr>
<tr>
<td>7.5</td>
<td>EX058</td>
</tr>
<tr>
<td>8.5</td>
<td>EX061</td>
</tr>
<tr>
<td>9.5</td>
<td>EX064</td>
</tr>
<tr>
<td>10.5</td>
<td>EX067</td>
</tr>
<tr>
<td>11.5</td>
<td>EX070</td>
</tr>
<tr>
<td>12.5</td>
<td>EX073</td>
</tr>
<tr>
<td>13.5</td>
<td>EX076</td>
</tr>
<tr>
<td>14.5</td>
<td>EX079</td>
</tr>
<tr>
<td>15.15</td>
<td>EX082</td>
</tr>
<tr>
<td>19.15</td>
<td>EX085</td>
</tr>
<tr>
<td>19.65</td>
<td>EX088</td>
</tr>
<tr>
<td>20.15</td>
<td>EX091</td>
</tr>
<tr>
<td>20.65</td>
<td>EX094</td>
</tr>
<tr>
<td>21.15</td>
<td>EX097</td>
</tr>
</tbody>
</table>

**Table 1.** A sample table showing the standard time intervals over which spectra were measured during the course of a photolysis experiment.
The kinetics of the photodegradation of a 4-nitrophenol population can be seen in Figure 9. The kinetics are modeled by plotting the average absorbance across 310-319 nm over 22 hours of photolysis. This tracks the decay of 4-nitrophenol’s main absorption peak. The decay is fit with an exponential and gives a laboratory “atmospheric” lifetime of $\tau = 3.33 \pm 0.06$ hours for our photolysis of 4-nitrophenol. It is notable that the system does not decay to an absorption of 0. This is likely due to the way the instrument blanks are run between samples (a cuvette filled with MilliQ in the holder for the blank and no cuvette in the sample path). This also affects the fit used to model the kinetics and was discussed above in the Data Analysis section (Chapter 3.2).

We can also attempt to compare these results to other published work. Based on the figures reported by Zhao et. al.\textsuperscript{22} we believe that their atmospheric lifetime values were determined using a slightly different kinetic fit than the one we employ here, for reasons discussed in Chapter 3.2. We are also unable to directly compare our kinetic values to theirs because they do not report an actinometric flux in their publication. Any difference between our

![Figure 9](image_url)

**Figure 9.** The kinetics of the photo-decay of 4-nitrophenol’s absorption peak over 310-319 nm. Absorption was plotted as a function of time and a y-offset exponential fit was applied.
respective light sources will result in a different reported lifetime. For these reasons quantitative comparisons to this work are difficult to make.

As stated above, we do not know the products of this photochemistry, only that the 4-nitrophenol molecule loses its ability to be an absorber in the visible light range. In this spectrum we also see the growth of a new absorber at ~250 nm. This may be better seen in Figure 10. Here, the spectra are plotted as the difference over time from the initial spectrum at \( t = 0 \). Although we do not know exactly what the source of this new absorption peak is, it may be the result of a new product formation. This feature may be a subject of future studies in the O’Brien group that will attempt to characterize the chemical contents of these mixtures during photolysis.

### 3.4 Effect of Adding SOA to 4-Nitrophenol Photolysis

After gaining an understanding of the photolysis of brown carbon alone, we were ready to test a more complicated system. In the aqueous cloud water environment that we are
approximating, it is very likely for different components to be present and mixing. Brown carbon molecules and other SOA material may be able to interact in cloud water in the atmosphere and it is important to understand the behaviors of these components together as well as in isolation. There are a number of possibilities for these compounds to affect the other and themselves, including, but not limited to, secondary photochemistry (the creation of OH radicals as a result of photolysis in the samples). For these studies we focus on the effect that α-pinene SOA has when it is mixed with 4-nitrophenol in our aqueous system. We focus on changes to 4-nitrophenol because its photodegradation is easily measured using the previously detailed experimental methods. This doesn’t mean that there aren’t implications for α-pinene SOA in a mixed system as well, but that is a topic for future studies. In the atmosphere, it is also important to consider the age and thus, the photoactivity level of the SOA. Both newly formed (“fresh SOA”) and photo-bleached SOA (photolytically aged) particles may be present in the atmosphere. For these reasons we tested the effect of both fresh (un-photolyzed) and aged (photolyzed) α-pinene SOA on 4-nitrophenol’s photolytic lifetime.

The details of the SOA production can be found in Chapter 2.1. Because of the methods used to generate, collect, and extract the α-pinene SOA, it is difficult to know the exact concentration of SOA in the final aqueous solution. We used offline aerosol mass spectrometry (offline-AMS) to measure the approximate concentration of α-pinene SOA in the samples. 25 μL of SOA was added to achieve a final sample concentration of ~1200 μL.20,28
Since we measure 4-nitrophenol’s photo-decay by the size of the absorption peak averaged over 310-319 nm, it is important to verify that the addition of SOA will not interfere with these measurements. Both fresh and aged SOA are not strong absorbers in the visible range, so they should contribute a negligible amount to 4-Nitrophenol’s absorption peak of interest. In Figure 11, the absorption spectra of both fresh and aged SOA are shown in comparison to that of 4-nitrophenol. From these initial spectra we can see there is very little overlap between the absorption of fresh or aged SOA and 4-nitrophenol. In order to make sure there were no conflicting absorbance measurements we tested the absorption spectra and kinetics of the fresh and aged SOA by themselves. Fresh SOA and aged SOA were each put into solution in separate cuvettes and photolyzed according to the same methods used for 4-nitrophenol (described in Chapter 2.3). The resulting absorption spectra and kinetics of fresh α-pinene SOA can be seen in Figures 12a and 12b. There is a small change in absorbance below 300 nm, but very little movement in the 310-319 nm range where 4-nitrophenol is measured. The kinetics graphed in

Figure 11. A side-by-side comparison of the absorption spectra of 4-nitrophenol, fresh α- pinene SOA, and aged α- pinene SOA.
Fig. 10b are measurements showing the change in absorbance averaged over 310-319 nm over 22 hours. We can see very little change in absorbance over the 22 hours. Some photo-decay does occur, but it is limited to decay from an absorbance of 0.05 to one of 0.04 (arbitrary units). Compared to the photo-decay observed in the 4-nitrophenol peak (0.26 to 0.03 a.u.) this is a very small change that occurs over a long period of time. From this, we can conclude that fresh α-pinene SOA does not absorb or decay strongly enough in the visible region to obscure or hide features in 4-nitrophenol’s chromophore peak. Taken together, this means that when the absorption of SOA and 4-nitrophenol are measured together in a mixed system, 4-nitrophenol’s photodegradation is visible, easily measured, and not affected by absorbance due to the addition of fresh SOA.

The aged SOA shows a similarly small amount of change in its absorbance over Fig. 12a. Absorption spectra of aqueous fresh α-pinene SOA measured over the course of 22 hour photolysis. The darkest line represents an absorption spectrum taken at photolysis time = 0 hours, while the lightest yellow line represents the absorption at the end of the photolysis period.

Fig. 12b. The kinetics of the photo-decay of fresh α-pinene SOA’s absorption peak over 310-319 nm. Average absorption was plotted as a function of time and a y-offset exponential fit was applied.
time. (Figure 13a). There is very little decay associated with the 22 hour photolysis, and what little decay that is absorbed is also between absorbances of 0.05 and 0.04 a.u. The kinetics plot shows a very rapid initial photo-decay in the first hour followed by little to no activity in the remaining 22 hours (Figure 13b). This initial photo-decay may be from the aged SOA material itself or from some contaminant or artifact leftover from its processing and extraction. In either case the magnitude of this small decay is not great enough to cause issues when interpreting the absorbance of 4-nitrophenol in the same range. This result is not unexpected, since the aged SOA has already been photolyzed for several days on a filter before its extraction. We can be reasonably confident that any changes in absorption we see in this range are dominated by changes in 4-nitrophenol’s absorption properties and not the absorption of the SOA.

After establishing the independence of the 4-nitrophenol

**Figure 13a.** Absorption spectra of aqueous aged α-pinene SOA measured over the course of 22 hour photolysis. The darkest line represents an absorption spectrum taken at photolysis time = 0 hours, while the lightest yellow line represents the absorption at the end of the photolysis period.

**Figure 13b.** The kinetics of the photo-decay of aged α-pinene SOA’s absorption peak over 310-319 nm. Average absorption was plotted as a function of time and a y-offset exponential fit was applied.
absorption spectrum we were ready to approach the photolysis of a mixed system. We measured the absorption and photolytic lifetimes of 4-nitrophenol with fresh and aged α-pinene SOA using the same procedures detailed in Chapter 2.3. We then recorded the spectra at the same regular time intervals over 22 hours and determined a photolytic lifetime. Figures 14a, 14b, and 14c show the absorption spectra over time for 4-nitrophenol alone, 4-nitrophenol with fresh SOA, and 4-nitrophenol with aged SOA, respectively. The absorption differences over time are in-set into each plot. The most obvious differences between these plots are seen below 300 nm in the near-UV range. In the spectra for fresh SOA there is slightly more absorption at 280 nm than there is in either of the others. This corresponds to the absorption of carbonyls that are common in fresh SOA. In the spectra containing aged SOA there is a visible growth of

---

**Figure 14.** Absorption spectra of 4-nitrophenol in system alone (a), with fresh α-pinene SOA (b) and with aged α-pinene SOA (c) over 22 hours of photolysis. The change in absorption for each wavelength over the photolysis period is inset into the upper right corner. The growth and decay in spectrum (a) and (c) appear to be similar while (b) shows more growth below 250 nm.
absorbance at 250 nm. This is likely due to the formation of other products that may be similar to those seen in the 4-nitrophenol alone spectra, although we don’t know what those specific products may be.

Figure 15a gives the photolytic lifetimes ($\tau$) of 4-nitrophenol in each mixture measured by the average absorbance over 310-319 nm. These values are also summarized in Table 2, while Figure 15b compares the photolytic lifetimes directly. The lifetimes were obtained by fitting the kinetics curve with an exponential offset fit as described in Chapter 3.2. 4-Nitrophenol in a system with fresh SOA appears to degrade the fastest, followed by 4-nitrophenol alone, and then 4-nitrophenol mixed with aged SOA with the slowest lifetime. From our laboratory lifetimes we can estimate an atmospheric lifetime. For these calculations we used an atmospheric solar flux provided by Hodzic et. al.29 Quantum yields were derived using an iterative approach with Equation 2, in which the absorption cross-section ($\sigma(\lambda)$) and lamp flux ($F(\lambda)$) are known and the quantum yield ($\phi$) is estimated and revised until the characteristic lifetime ($\tau$) matches those observed in the laboratory studies. We report a quantum yield in the same order of magnitude as Vione et. al.27 who report $\phi = 3.3 \times 10^{-4}$ for photo-decay of 4-nitrophenol.

Figure 15a. Comparison between the kinetics of the photo-decay of 4-nitrophenol alone and in system with fresh or aged $\alpha$-pinene SOA. All absorbances were averaged over 310-319 nm. Average absorption was plotted as a function of time and a y-offset exponential fit was applied to each.
We used slightly different wavelengths to track the absorption, which may account for the slight differences in quantum yield.

At first glance, these results seem counterintuitive—why would the addition of fresh SOA accelerate 4-nitrophenol’s photo-decay while aged SOA slows it down? We believe the explanation lies in the production of OH radicals.

Both nitrophenols and α-pinene SOA have been shown to produce OH radicals when photolyzed in the aqueous phase, and we have some evidence to support that 4-nitrophenol is indeed producing OH radicals during our photolysis experiment (see Chapter 3.6 below). 4-nitrophenol by itself is likely producing OH radicals that contribute to its rate of photo-decay. This secondary chemistry is then amplified when fresh SOA is added to the system. As the fresh SOA is photolyzed it produces OH radicals along with 4-nitrophenol, which accelerates the photo-decay even further. However, the aged SOA has already been thoroughly photolyzed. Whatever photochemistry it is capable of has likely already occurred. When it is put into the system with 4-nitrophenol it is a much smaller contributor to secondary photochemistry. We suspect that aged SOA also acts as an OH radical sink for those radicals produced by 4-nitrophenol. OH radicals are very strong oxidizers and are not discriminate in the compounds that they oxidize. Thus when 4-nitrophenol produces a certain amount of OH radicals their effects are then split between

![Figure 15b](image-url) A direct comparison between the photolytic lifetimes (τ) measured for 4-nitrophenol alone and 4-nitrophenol with fresh, aged α-pinene SOA.
oxidizing 4-nitrophenol and the aged SOA. This results in a slower photo-decay for 4-nitrophenol than is observed when it is isolated.

<table>
<thead>
<tr>
<th>sample</th>
<th>Lab lifetime, $\tau$ (hrs)</th>
<th>Ambient lifetime, $\tau$ (hrs)</th>
<th>Quantum yield $\times 10^{-4}$ (molecule per photon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-NPh</td>
<td>3.32</td>
<td>~10</td>
<td>1.5</td>
</tr>
<tr>
<td>4-NPh + Fresh SOA</td>
<td>3.06</td>
<td>~9</td>
<td>1.7</td>
</tr>
<tr>
<td>4-NPh + Aged SOA</td>
<td>4.25</td>
<td>~13</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Table 2.** A summary of the laboratory lifetimes, atmospheric lifetimes, and quantum yields for 4-nitrophenol alone and in system with fresh and aged SOA. The lifetime ($\tau$) represents the amount of time it takes for ~37% of the sample to decay.

### 3.5 Photolysis of Fresh SOA at Varied Concentrations

After observing the effects of fresh SOA on the degradation of 4-nitrophenol, we decided to test the effect of varying the concentrations of fresh SOA in solution with 4-nitrophenol. The results of this experiment are preliminary but may inform the subject of future studies in the O’Brien group. Three cuvettes were prepared containing ~14 µM 4-nitrophenol and 30 µL, 40 µL, or 50 µL of $\alpha$-pinene SOA stock were added to one cuvette each. This resulted in SOA

*Figure 16.** Comparison between the kinetics of the photo-decay of 4-nitrophenol with varying amounts of added fresh $\alpha$-pinene SOA. All absorbances were averaged over 310-319 nm. Average absorption was plotted as a function of time and a y-offset exponential fit was applied to each.
concentrations of approximately 1400 μM, 1900 μM, and 2400 μM, respectively. These cuvettes were then photolyzed and measured using the previously described protocols. Y-offset exponential fits were applied and lifetimes found for each fresh SOA concentration. The kinetic fits in Figure 16 show a fairly dramatic decrease in photolytic lifetime with increasing fresh SOA in solution. This analysis is essentially treating 4-NPh as a tracer for the production of OH radicals by fresh α-pinene SOA. If this result is repeatable, it indicates that the kinetics of SOA photo-degradation may depend strongly on the concentration of the SOA in the solution. Given that cloud water can have a wide range of organic concentrations, this may be important to consider for atmospheric photolysis. To our knowledge, this effect has not been previously reported in the literature.

The decays in Figure 16 show a poor fit at early times. To determine the source of this we used the photo-decay of the 4-nitrophenol peak to estimate the effective OH radical production generated by the fresh SOA ([OH]). Figure 17 shows the estimated OH radical production that can be “seen” by 4-nitrophenol for each addition of fresh SOA. This is a measure of the OH radicals that accelerate the photo-decay of 4-nitrophenol calculated using Equation 6. Equation 6 does not provide a full account of OH radical production in this system. Since it relies on the change in absorbance (y) of the 4-nitrophenol peak, it can only quantify the 4-nitrophenol’s OH exposure. In other words, only the OH radicals that contribute to 4-nitrophenol’s photo-decay can be estimated using this measure.

\[ \text{Equation 6. } \text{OH exposure} = \frac{\Delta \ln \left( \frac{y_0}{y} \right)}{k_{OH}} \]

To estimate the OH radical exposure we found the difference between the decay in the 4-nitrophenol + SOA system and the 4-nitrophenol alone system at a particular time in the photolysis. This was divided by the rate constant for OH formation \( k_{OH} \), where \( k_{OH} = 6.2 \times 10^9 \).
M⁻¹ s⁻¹ to give the OH exposure in M s. We could then plot these OH exposures as a function of time (s) and apply a linear fit to each. The slope of the fit gave the approximate concentration of OH exposure over the course of photolysis. In Figure 17, only the initial data points are shown as this analysis does not work when the tracer, 4-nitrophenol, runs out.

In Figure 17, the OH exposure starts close to 0 at the start of photolysis. There is a delayed effect seen at early time points for all three SOA concentrations. This is best seen on the 30 µL line. For this smallest addition of fresh SOA it takes ~45 minutes for OH production to be measured in significant amounts. This is partially a result of our measurement limitations. Since we cannot measure OH radicals directly with our methods, we rely on 4-nitrophenol as a tracer molecule to indirectly measure the OH radical concentration through its effects on the 4-nitrophenol photo-decay. OH exposure was measured by comparing the accelerated 4-nitrophenol decay when in solution with fresh SOA to the measured decay of 4-nitrophenol alone. The values associated with each data set give the estimated total OH exposure over 120 minutes of photolysis.

Figure 17. The estimated OH exposure reflected in 4-nitrophenol’s photo-decay. OH exposure was measured by comparing the accelerated 4-nitrophenol decay when in solution with fresh SOA to the measured decay of 4-nitrophenol alone. The values associated with each data set give the estimated total OH exposure over 120 minutes of photolysis.
nitrophenol’s characteristic peak at \(~315\) nm. There is certainly OH radical material being produced in the 45 minutes that aren’t represented by these methods. We suspect that the OH produced before \(t = 45\) minutes are split between 4-nitrophenol, the SOA, and some contaminant in the sample, so that the effect of the OH radicals is not seen until the contaminant has been oxidized. This contaminant may be solvent leftover from the SOA extraction process or some other unknown. In the future we will attempt to eliminate or reduce the effects of this contaminant.

### 3.6 Addition of Fe(II) and Fenton Chemistry

Another preliminary experiment was conducted testing the effects of Fe (II) on aerosol systems. While these studies still require further development before they produce valuable conclusions in their own right, we include one of them in this thesis because it supports the idea that 4-NPh produces OH radicals when photolyzed. Fe (II) has been studied in the atmosphere as having a role in chemical oxidation via a process known as Fenton chemistry. In the presence of \(H_2O_2\) and sunlight, Fe (II) is harnessed to start an OH radical photochemical production cycle that may account for a significant proportion of daytime OH radical production.31

After conducting a preliminary test involving Fe (II) in our cuvettes, the cuvettes were washed using the standard cleaning protocol (MilliQ water and acetonitrile, detailed in Chapter 2.2). This protocol was not enough, however, to eliminate trace amounts of Fe (II) from the cuvette. As a result our next experiment, a routine photolysis of 4-nitrophenol, was contaminated with a small amount of Fe (II). We realized this when the photodegradation of 4-nitrophenol occurred at a rate much faster than usual (Figure 18). With a \(\tau = 1.21\) the atmospheric lifetime was nearly halved. After thorough cleaning of the cuvettes with HNO₃ the accelerated photodegradation did not occur again.
The photo-Fenton cycle with Fe (II) requires an initial input of H₂O₂ or some other OH radical source to begin the catalytic cycle. Thus, this accidental experiment confirmed the suspected production of OH radicals from the photolysis of nitrophenols in our system, a phenomenon that has been reported elsewhere in the literature. This adds support to our hypothesis that both 4-nitrophenol and fresh SOA are contributing to secondary photochemistry through the production of OH radicals. In the future we plan to continue investigating Fe(II) and its effects in these complex mixtures found in atmospheric systems.

Figure 18. The kinetics of the photo-decay of 4-nitrophenol in system with Fe(II). The absorbance plotted is the average absorbance over 310-319 nm. Average absorption was plotted as a function of time and a y-offset exponential fit was applied to obtain a lifetime (τ).
Conclusion

It is clear that the photolytic lifetimes of these brown carbon species may be significantly affected when considered in an aqueous cloud-water system with other organic aerosols. These effects are still dependent on a number of factors like phase state, aerosol age, solar flux, and relative concentrations, all of which contribute to the complexity of the lives of organics in the atmosphere. Fresh SOA is capable of producing OH radicals when photolyzed, and this OH radical production can then go on to accelerate the photo-decay of other organic species around it. On the other hand, photolytically aged SOA may dampen the effects of these OH radicals by acting as a sink: being oxidized without contributing to their production. This is important to consider, as a large fraction of SOA that ends up dissolved in cloud water may already be photobleached before it reaches the cloud. Thus, future laboratory experiments should consider the photo-activity of the mixed systems.

For fresh SOA, the concentration may also be a factor, enhancing or diminishing the radical production. Other atmospherically relevant species like Fe(II) may contribute as well. Future research will continue to characterize the impacts that mixed systems may produce, including, but not limited to, continuing studies confirming the SOA concentration effects we have seen in our preliminary experiments and working more with Fe(II) to explore Fenton chemistry.
References

(1) Aerosol - an overview | ScienceDirect Topics


(21) Sareen, N.; Carlton, A. G.; Surratt, J. D.; Gold, A.; Lee, B.; Lopez-Hilfiker, F. D.; Mohr,


(33) Feltracco, M.; Barbaro, E.; Contini, D.; Zangrando, R.; Toscano, G.; Battistel, D.; Barbante, C.; Gambaro, A. Photo-Oxidation Products of α-Pinene in Coarse, Fine and

Appendix

Figure 14. The absorption cross-section of 4-nitrophenol across a range of pH values. pH was adjusted by adding HCl or NaOH into aqueous solution. All photolysis experiments were conducted at pH ~3.6, where there is a characteristic absorption peak at 400 nm and no absorption at 400 nm. At more basic pH the dominant absorption peak is at 500 nm.

Figure 19. Absorption spectra of 4-nitrophenol with 30 µL fresh SOA measured over the course of 17 hour photolysis. The darkest line represents an absorption spectrum taken at photolysis time = 0 hours, while the lightest yellow line represents the absorption at the end of the photolysis period. These spectra correspond with the kinetics discussed in Figure 15.
**Figure 20.** Absorption spectra of 4-nitrophenol with 40 µL fresh SOA measured over the course of 17 hour photolysis. The darkest line represents an absorption spectrum taken at photolysis time = 0 hours, while the lightest yellow line represents the absorption at the end of the photolysis period. These spectra correspond with the kinetics discussed in Figure 15.

**Figure 21.** Absorption spectra of 4-nitrophenol with 30 µL fresh SOA measured over the course of 17 hour photolysis. The darkest line represents an absorption spectrum taken at photolysis time = 0 hours, while the lightest yellow line represents the absorption at the end of the photolysis period. These spectra correspond with the kinetics discussed in Figure 15.
Figure 22. Absorption spectra of 4-nitrophenol with small amount of Fe (II) measured over the course of 22 hour photolysis. The darkest line represents an absorption spectrum taken at photolysis time = 0 hours, while the lightest yellow line represents the absorption at the end of the photolysis period. These spectra correspond with the kinetics discussed in Figure 17.