

## Effective absorption cross sections and photolysis rates of anthropogenic and biogenic secondary organic aerosols



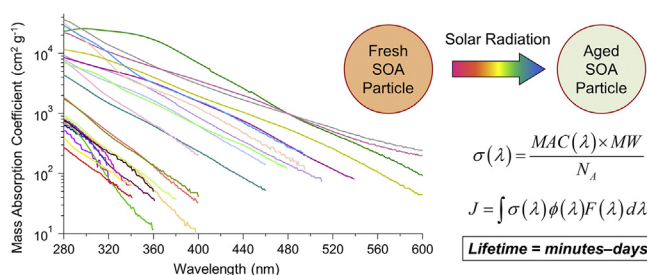
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### HIGHLIGHTS

- We measured mass absorption coefficients for a number of different types of SOA.
- We estimated the rates of condensed-phase photochemical processes in SOA.
- These processes can potentially be as fast as oxidation of SOA by gas-phase radicals.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Mass absorption coefficient (MAC) values were measured for secondary organic aerosol (SOA) samples produced by flow tube ozonolysis and smog chamber photooxidation of a wide range of volatile organic compounds (VOC), specifically:  $\alpha$ -pinene,  $\beta$ -pinene,  $\beta$ -myrcene, d-limonene, farnesene, guaiacol, imidazole, isoprene, linalool, ocimene, p-xylene, 1-methylpyrrole, and 2-methylpyrrole. Both low- $\text{NO}_x$  and high- $\text{NO}_x$  conditions were employed during the chamber photooxidation experiments. MAC values were converted into effective molecular absorption cross sections assuming an average molecular weight of 300 g/mol for SOA compounds. The upper limits for the effective photolysis rates of SOA compounds were calculated by assuming unity photolysis quantum yields and convoluting the absorption cross sections with a time-dependent solar spectral flux. A more realistic estimate for the photolysis rates relying on the quantum yield of acetone was also obtained. The results show that condensed-phase photolysis of SOA compounds can potentially occur with effective lifetimes ranging from minutes to days, suggesting that photolysis is an efficient and largely overlooked mechanism of SOA aging.

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## 1. Introduction

Primary organic aerosol (POA) directly emitted from anthropogenic and biogenic sources and secondary organic aerosol (SOA) produced by gas-phase or aqueous-phase oxidation of atmospheric

volatile organic compounds (VOC) have both health and climate relevance (Ervens et al., 2011; Finlayson-Pitts and Pitts, 2000; Solomon et al., 2007). Biogenic VOC that contribute the most to SOA production include isoprene,  $\alpha$ -pinene,  $\beta$ -pinene, myrcene, and limonene (Geron et al., 2000). In urban areas, major sources of VOC are from fossil fuel combustion as well as industrial emissions (World Health, 1989). Once in the atmosphere, organic aerosol (OA) is known to undergo both physical and chemical aging processes from reactions with sunlight and atmospheric oxidants (George

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et al., 2015). It is important to understand the nature of these changes in order to predict the health and climate impacts of atmospheric aerosols that travel long distances from the point of their initial formation.

Prevalent chemical mechanisms for OA aging involve multi-phase oxidation of OA constituents by atmospheric oxidants. The most dominant oxidant involved in the multiphase oxidation of OA, as well as aqueous-phase oxidation of water-soluble atmospheric organics, is the OH radical (Ervens et al., 2011; George et al., 2015). NO<sub>3</sub>, O<sub>3</sub>, and other oxidants also contribute to these aging processes. OA compounds can additionally be aged by condensed-phase photochemical reactions occurring in the bulk of the SOA material upon exposure to solar actinic radiation (George et al., 2015). Currently, experimental evidence to determine the relative importance of condensed-phase photochemistry occurring in OA relative to multi-phase oxidation processes is limited. Chamber studies have begun to examine this effect by studying the properties and composition of SOA before and after exposure to UV light. Presto et al. (2005) found that the formation of  $\alpha$ -pinene ozonolysis SOA in a smog chamber was suppressed by 20–40% when exposed to UV light. Kroll et al. (2006) observed that low-NO<sub>x</sub> isoprene SOA grew during the initial irradiation period, but that was followed by a decrease in particle size as the SOA mixture was further irradiated. However,  $\beta$ -pinene low-NO<sub>x</sub> SOA particles did not shrink upon irradiation, indicating that the photochemical effects of UV exposure are dependent on the chemical composition of the SOA. Surratt et al. (2006) detected a similar decrease in the particle size of low-NO<sub>x</sub> isoprene SOA upon irradiation. In these experiments, it was difficult to separate the effects of gas-phase and condensed-phase photochemistry. To bypass this limitation, Epstein et al. (2014) used a denuder to remove VOC from  $\alpha$ -pinene ozonolysis SOA before the irradiation. They observed that UV light slightly reduced both the particle mass concentration and the average particle size; the fraction of organic peroxides in the particles decreased upon irradiation. Epstein et al. (2014) and Wong et al. (2014) similarly observed a reduction in the particle size for  $\alpha$ -pinene ozonolysis SOA material that was collected on a filter and re-aerosolized back in a photolysis chamber; the effect was larger at elevated relative humidity (RH). In contrast, Kourtchev et al. (2015) observed no significant change to molecular level composition of SOA prepared by ozonolysis of a mixture of four biogenic VOC ( $\alpha$ -pinene,  $\beta$ -pinene,  $\Delta$ 3-carene and isoprene) and exposed to actinic UV radiation. In summary, chamber experiments suggest that photochemical processes in SOA particles are possible, but the results are inconsistent.

Qualitative experiments with irradiation of bulk SOA samples were carried out by Walser et al. (2007) and Mang et al. (2008). Both studies showed that SOA particles formed from limonene ozonolysis absorbed radiation in the actinic region, most likely due to the carbonyl and peroxide functional groups present, and that the ensuing photochemistry generated a number of small VOC as detectable products. The carbonyl functional groups appeared to play a significant role in this aging, as evidenced by the production of measureable quantities of CO, CH<sub>4</sub>, acetaldehyde, acetone, and other VOC, many of which could be explained by standard Norrish type-I and Norrish type-II carbonyl photochemistry (Mang et al., 2008; Pan et al., 2009).

Condensed-phase photochemistry is not limited to the OA particles; it can also take place in cloud/fog droplets. The irradiation of aqueous extracts of limonene ozonolysis SOA resulted in a significant change in the molecular composition, in which oligomeric and carbonyl compounds were depleted (Bateman et al., 2011). The photolytic processing appeared to be more efficient when SOA was dissolved in an aqueous solution as compared to dry SOA particles. The direct aqueous photolysis of high-NO<sub>x</sub> isoprene SOA also

produced major changes in the molecular composition (Nguyen et al., 2012). On average, 30% of the SOA by mass was significantly modified, suggesting that the effects of direct aqueous photolysis should not be ignored. Aqueous solutions of light-absorbing OA compounds, such as SOA formed by photooxidation of naphthalene under high-NO<sub>x</sub> conditions, SOA formed by limonene ozonolysis and aged with ammonia vapor, and products of aqueous reaction of glyoxal and methylglyoxal with ammonium sulfate were shown to efficiently photobleach and undergo a large change in composition upon exposure to irradiation (Lee et al., 2014; Sareen et al., 2010; Zhao et al., 2015). Finally, a systematic study of photochemistry of different types of SOA by Romonosky et al. (2015) showed that aqueous photolysis may be an effective aging mechanism for SOA derived from biogenic, anthropogenic, and biomass burning VOC precursors.

The experiments done so far have been qualitative in nature; the diversity in structure and reactivity of VOC complicate the scientific understanding of the photochemistry of atmospheric aerosols. To better estimate the time scales of these photochemical processes under realistic atmospheric conditions, this study focuses on the quantitative measurements of absorption coefficients of SOA formed through the oxidation of biogenic and anthropogenic VOC using common atmospheric oxidants, specifically OH (in presence or absence of NO<sub>x</sub>) and O<sub>3</sub>. From these data, the rates of photolysis for a variety of SOA were calculated, resulting in a better understanding of the lifetimes of SOA in the atmosphere with respect to condensed-phase photochemistry.

## 2. Materials and methods

Both O<sub>3</sub>-initiated and OH-initiated oxidation conditions, with and without added NO<sub>x</sub>, were used to prepare model SOA from VOC as shown in Table 1 and Table 2. VOC were used at their stated commercial purity (Table S1). All experiments were performed under dry conditions (relative humidity < 2%) and in the absence of seed particles. The O<sub>3</sub>-initiated reactions were carried out in a 17 L flow tube reactor described by Bones et al. (2010). Liquid VOC was injected by a syringe pump at a rate of 25  $\mu$ L/h into a 5 SLM (standard liters per minute) flow of zero air. A 0.5 SLM flow of oxygen (Airgas; 99.994% purity) was sent through an ozone generator and a custom-made ozone photometric detector. The O<sub>3</sub>- and VOC-containing flows were mixed at the entrance of the flow cell. Typical mixing ratios in the flow cell ranged from 60 to 100 ppm (parts per million by volume) of O<sub>3</sub> and 10–30 ppm of VOC, respectively. Residence time in the flow tube was less than 5 min, but sufficient to oxidize most of the VOC and to form SOA. A 1-m charcoal denuder scrubbed the residual O<sub>3</sub> and gas-phase organic compounds from the flow exiting the reactor. Multiple SOA collection methods were used in the experiments. In some experiments, SOA was collected by impaction on foil substrates using a multi-orifice uniform-deposit impactor (MOUDI, MSP model 110-R) sampling at 30 SLM. In other experiments, SOA was collected on stage D of a Sioutas impactor (Sioutas, 2004) modified to accept either a CaF<sub>2</sub> window or foil substrates. The specified cut-off point of this impactor stage was 0.25  $\mu$ m at 9 SLM flow rate, but sampling was done at 15 SLM to drive the cut-off point to lower particle sizes. The foil substrates and CaF<sub>2</sub> windows were weighed before and after SOA collection to determine the mass of SOA collected. In several experiments, SOA was collected on polytetrafluoroethylene (PTFE) filters (Millipore fluoropore, 0.2  $\mu$ m pore size). Absorption coefficients from SOA collected on foil substrates, CaF<sub>2</sub> windows, and PTFE filters were comparable in magnitude. Depending on the yield of SOA, collection time for the flow tube was approximately 30 min to 2 h. The samples were either analyzed immediately or sealed and frozen for later analysis.

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