Phenolic carbonyls undergo rapid aqueous photodegradation to form low-volatility, light-absorbing products

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HIGHLIGHTS

- Biomass burning phenolic carbonyls readily partition to aqueous phases.
- Aqueous direct photodegradation is the dominant sink.
- Direct photodegradation results in the formation of low volatility products.
- Phenolic carbonyl oxidation products are a source of atmospheric brown carbon.

ARTICLE INFO

ABSTRACT

We investigated the aqueous photochemistry of six phenolic carbonyls - vanillin, acetovanillone, guaiacyl acetone, syringaldehyde, acetosyringone, and coniferyl aldehyde — that are emitted from wood combustion. The phenolic carbonyls absorb significant amounts of solar radiation and decay rapidly via direct photodegradation, with lifetimes (τ) of 13–140 min under Davis, CA winter solstice sunlight at midday (solar zenith angle = 62°). The one exception is guaiacyl acetone, where the carbonyl group is not directly connected to the aromatic ring: This species absorbs very little sunlight and undergoes direct photodegradation very slowly ($\tau > 10^3$ min). We also found that the triplet excited states ($^3C^*$) of the phenolic carbonyls rapidly oxidize syringol (a methoxyphenol without a carbonyl group), on timescales of 1–5 h for solutions containing 5 μM phenolic carbonyl. The direct photodegradation of the phenolic carbonyls, and the oxidation of syringol by $^3C^*$, both efficiently produce low volatility products, with SOA mass yields ranging from 80 to 140%. Contrary to most aliphatic carbonyls, under typical fog conditions we find that the primary sink for the aromatic phenolic carbonyls is direct photodegradation in the aqueous phase. In areas of significant wood combustion, phenolic carbonyls appear to be small but significant sources of aqueous SOA: over the course of a few hours, nearly all of the phenolic carbonyls will be converted to SOA via direct photodegradation, enhancing the POA mass from wood combustion by approximately 3–5%.

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1. Introduction

The importance of aqueous-phase chemistry is becoming increasingly clear in aerosol chemistry (Lim et al., 2005, 2010; Ervens et al., 2011; He et al., 2013). Traditional models typically underestimated secondary organic aerosol (SOA) mass loadings (Volkamer et al., 2006; Hallquist et al., 2009; Heald et al., 2011);

however, the addition of aqueous-phase processes can improve model predictions (Lim et al., 2010; He et al., 2013). We are particularly interested in the aqueous reactions of phenols and aromatic carbonyl compounds, which have relatively high Henry's Law constants and are released in large quantities from the combustion of lignin, the structural component of woody plants (Sander, 1999; Oros and Simoneit, 2001; Schauer et al., 2001). Within the class of aromatic carbonyls, "phenolic carbonyls" contain an -OH functional group on the aromatic ring, while the "non-phenolic carbonyls" do not. Phenols are rapidly oxidized in the aqueous phase by triplet excited states ($^3C^*$) of non-phenolic carbonyls and by hydroxyl radical (•OH) to form SOA (Canonica

et al., 2000; Sun et al., 2010; Li et al., 2014; Richards-Henderson et al., 2014; Smith et al., 2014, 2015). However, there is little information regarding the reactions of phenolic carbonyls, which are a significant fraction of wood combustion phenol products, accounting for 18% of hardwood and 22% of softwood phenol emissions (Schauer et al., 2001). Phenolic carbonyls are of intermediate volatility and possess high Henry's Law constants ($> 10^5$ M atm^{-1}) (EPI Suite V4.1). Under clear-sky conditions these compounds will be primarily in the gas phase, but they will readily partition into the aqueous phase under foggy or cloudy conditions.

The aqueous oxidation of small aliphatic carbonyl compounds has been previously studied (Faust et al., 1997; Guzmán et al., 2006; Epstein et al., 2013). Epstein et al. (2013) found that aqueous photolysis was a negligible sink for most small aliphatic carbonyls, which were primarily lost via gas-phase photolysis or hydroxyl radical (•OH) oxidation (gas or aqueous). In contrast with the aliphatic carbonyls, aqueous-phase photodegradation is likely to be a major sink for phenolic aromatic carbonyls because: (1) The compounds have high Henry's law constants (Sander, 1999); (2) conjugation of the aromatic ring and carbonyl functional group causes large light absorbance in the solar spectrum (Anastasio et al., 1997; Turro et al., 2010); and (3) the aromatic structure of the phenolic carbonyls hinders hydration of the carbonyl group, a process that decreases light absorption for aliphatic carbonyls (Hilal et al., 2005). The conjugated aromatic structure of phenolic carbonyls also suggests phenolic carbonyls in sunlight will form triplet excited states (Turro et al., 2010), which can oxidize aqueous phenols (Smith et al., 2014). Li et al. (2014) have shown that aqueous •OH oxidation and direct photodegradation of the phenolic carbonyl vanillin (Van) produces low-volatility mass, but they performed their experiments with 254 nm illumination, which is not present in tropospheric sunlight. Thus, while we expect that the photodegradation of phenolic carbonyls is important in atmospheric drops and particles, there is little experimental data quantifying the direct photodegradation kinetics and SOA yields.

Our goal in this work is to examine the aqueous chemistry and SOA potential of six phenolic carbonyls released from biomass combustion (Fig. 1): Van, acetovanillone (AVan), guaiacyl acetone (GA), syringaldehyde (SyrAld), acetosyringone (ASyr), and coniferyl aldehyde (ConifAld). We first measure light absorption by these compounds, then determine the rate constants and quantum yields of direct photodegradation under simulated sunlight, assess their potential to oxidize an aqueous-phase phenol (syringol (SYR)), measure their SOA mass yields, and quantify light absorption by the SOA. Finally, we assess the relative importance of direct photodegradation and oxidation by $^3C^*$ and •OH as sinks for the phenolic

carbonyls and their significance as sources of SOA in regions of wood combustion.

2. Methods

2.1. Samples and illumination

Air-saturated samples containing a phenolic carbonyl were continuously stirred at 20 °C and illuminated in airtight, far-UV quartz cells (1- or 5-cm pathlength; Spectrocell) using simulated sunlight from a 1000 W Xe arc lamp with downstream optical filters (Galbavy et al., 2010; Smith et al., 2014, 2015). Samples were saturated with air to match the concentrations of oxygen present in atmospheric drops. An example of our lamp photon flux is shown in Supplemental Fig. S1. Dark control samples were wrapped in aluminum foil and kept at 20 °C in the same illumination chamber but out of the light. Aqueous carbonyls were studied at concentrations from 1 to 100 μM, a range estimated for drops in areas impacted by biomass burning (Anastasio et al., 1997; Schauer and Cass, 2000; Schauer et al., 2001); as described below, we primarily use data from experiments with lower carbonyl concentrations (≤ 20 μM) to avoid conditions of very high light absorption. We illuminated samples until approximately 50% of the initial amount of phenolic carbonyl remained for both the direct photodegradation and syringol oxidation experiments. In another type of experiment we examined the ability of phenolic carbonyl triplets to oxidize syringol (2,6-dimethoxyphenol), a phenol that does not absorb light. In these experiments we prepared solutions containing 5 μM of phenolic carbonyl, varying concentrations of syringol (10−100 μM) at pH 5 and illuminated the samples until approximately half of the phenolic carbonyl remained.

Details of chemicals used are in Supplemental Section S1. Throughout this work we use the terms "phenol" and "ArOH" to refer generically to any phenolic species (including phenolic carbonyls), the term "carbonyl" to refer to a generic phenolic carbonyl, and $^3C^*$ to refer to a generic chromophore triplet excited state.

2.2. Chemical analysis

Periodically during illumination, small aliquots of solution were removed from the illuminated and dark cells to measure the concentrations of carbonyls (and, in some cases, syringol) using HPLC. The HPLC consisted of: Shimadzu LC-10AT pump, ThermoScientific BetaBasic-18 C_{18} column (3 mm × 250 mm), Shimadzu-10AT UV-Vis detector (using detection wavelengths of 269, 310, 275, 306, 297, 336 nm, and 275 nm for syringol (SYR), vanillin (Van), acetovanillone (AVan), syringaldehyde (SyrAld), acetosyringone (ASyr), coniferyl aldehyde (ConifAld), and guaiacyl acetone (GA) respectively), degassed eluent of 20:80 acetonitrile:water, and a flow rate of 0.70 mL min^{-1}. The concentration of hydrogen peroxide in our stock solution was determined on each day it was used by measuring absorbance at 240 nm using a Shimadzu UV-2501PC spectrophotometer (Smith et al., 2015). We measured the photon flux on each experiment day by determining the photolysis rate constant ($j_{2NB,exp}$) of aqueous 10 μM 2-nitrobenzaldehyde (2NB) in the same cell used for the phenol illumination (Galbavy et al., 2010). Solution pH was measured using an Orion model 420A pH meter. Molar absorptivities of each carbonyl were determined by measuring the absorbance of five independent carbonyl concentrations in a Shimadzu UVPC-2501PC spectrophotometer, then taking the linear regression slope of a plot of absorbance versus concentration at each wavelength.
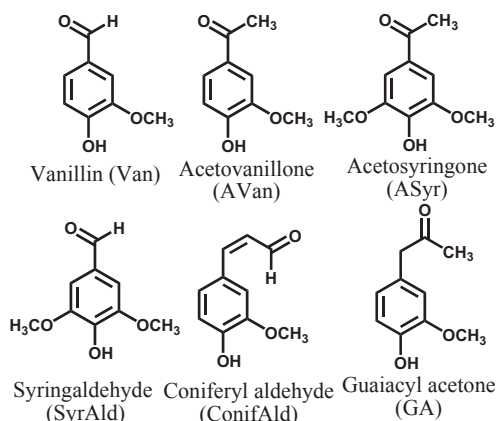

Fig. 1. Structures and abbreviations of the phenolic carbonyls used in this study.