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

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Submitted to Atmospheric Environment on August 17, 2015.

Revised version submitted November 9, 2015

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 minutes 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 hours for solutions containing 5 μ M 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%.

Keywords: triplet excited state, phenol, biomass combustion, secondary organic aerosol, brown carbon

1. Introduction

The importance of aqueous-phase chemistry is becoming increasingly clear in aerosol chemistry (Lim et al., 2005; Lim et al., 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 ($\cdot OH$) to form SOA (Canonica et al., 2000; Sun et al., 2010; Li et al., 2014; Richards-Henderson et al., 2014; Smith et al., 2014; Smith et al., 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 ($> 10^5 \text{ M atm}^{-1}$) (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 ($\cdot\text{OH}$) 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 $\cdot\text{OH}$ 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 (Figure 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 $^3\text{C}^*$ and $\cdot\text{OH}$ as sinks for the phenolic carbonyls and their significance as sources of SOA in regions of wood combustion.

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

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88 **2. Methods**

89 *2.1 Samples and Illumination*

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

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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 $^3\text{C}^*$ 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 C₁₈ 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 ($j_{2\text{NB,exp}}$) 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.

2.4 Kinetic Analysis

The measured, apparent first-order rate constant for carbonyl loss ($j_{\text{ArOH,exp}}$) was determined as the negative of the slope of a plot of $\ln([\text{ArOH}]_t/[\text{ArOH}]_0)$ versus illumination time, where $[\text{ArOH}]$ is the concentration of carbonyl (at times t and zero). There was no significant loss of any compound in any dark control ($p > 0.05$). Similar methods were employed to calculate the apparent first-order rate constant of SYR loss (k'_{SYR}) in illuminated solution containing a phenolic carbonyl. Values of $j_{\text{ArOH,exp}}$ were normalized to sunlight conditions at midday on the winter solstice at Davis (solar zenith angle = 62° ; $j_{2\text{NB,win}} = 0.0070 \text{ s}^{-1}$) (Anastasio and McGregor, 2001) and were corrected for internal screening of simulated sunlight in the cuvette, to give the final value j_{ArOH} :

$$j_{\text{ArOH}} = \frac{\left(\frac{j_{\text{ArOH,exp}}}{j_{2\text{NB,exp}}}\right) \times j_{2\text{NB,win}}}{S_\lambda} \quad (1)$$

where S_λ is the light-absorption-weighted internal screening factor (section S2):

$$S_\lambda = \frac{\sum[(1 - 10^{-\epsilon_\lambda [C] l}) \times I'_\lambda]}{\sum[(2.303 \times \epsilon_\lambda [C] l) \times I'_\lambda]} \quad (2)$$

In this equation ϵ_λ is the molar absorptivity of a carbonyl at a given wavelength (Tables S1 – S12), $[C]$ is the carbonyl concentration, l is the path length of the illumination cell, and I'_λ is the photon flux of our illumination system at a given wavelength, determined as described in section S2 (Leifer, 1988; Zhang and Anastasio, 2003). Normalized first-order rate constants for SYR loss (k'_{SYR}) were determined in a similar manner. In some cases we examine carbonyl direct photodegradation rate constants that are corrected to winter solstice sunlight but not corrected for internal screening (i.e., using just the correction in the numerator of equation 1). We refer to these values as $j_{\text{ArOH,win}}$.

The pH behavior of the direct photooxidation kinetics of 5 μM vanillin was modeled using (Anastasio et al., 1997; Smith et al., 2014):

$$j_{\text{Van}} = j_{\text{HT}} + \frac{j_{\text{T}} - j_{\text{HT}}}{1 + \frac{[\text{H}^+]}{K_{\text{A}}}} \quad (3)$$

where j_{HT} and j_{T} are the first-order rate constants for loss of the protonated and neutral forms of the vanillin excited state, $[\text{H}^+]$ is the proton concentration, and K_{A} is the apparent acid-dissociation constant of the protonated triplet state. We determined K_{A} by fitting the experimental data to equation 3 with a three-parameter sigmoidal fit using SigmaPlot Version 11.

2.5 Secondary Organic Aerosol Measurement

SOA mass yields were determined using methods similar to our previous work (Smith et al., 2014; Smith et al., 2015). For direct photodegradation experiments, solutions contained 100 μM carbonyl, while experiments examining syringol oxidation by the carbonyl triplet state contained 5 μM carbonyl and 100 μM SYR. All SOA mass yield experiments were performed at pH 5. Solutions were illuminated until the carbonyl concentration decreased by approximately 50%. 10 mL of solution were then placed in a baked, pre-weighed aluminum cup, which was blown down to dryness with specialty-grade nitrogen gas (99.997%; Praxair) (Smith et al., 2014). This blow-down typically took 5 – 8 hours. The cups were then weighed again (CAHN 29 electrobalance; precision of $\pm 1 \mu\text{g}$) and the SOA mass yield was calculated by:

$$Y_{\text{SOA}} = \frac{(\text{Mass of illuminated sample} - \text{Mass of dark sample})}{\text{Mass of phenol reacted}} \quad (4)$$

2.6 Mass Absorption Coefficient (MAC)

UV-Vis absorption measurements of phenolic carbonyls and their products were performed on illuminated solutions containing 10 μ M initial carbonyl at pH 5. MAC values for these mixtures were calculated using Equation 5 (Chen and Bond, 2010; Nguyen et al., 2012):

$$\text{MAC (cm}^2\text{g}^{-1}\text{)} = \frac{2.303 \times A}{l \times ([\text{Carbonyl}]_t + (Y_{\text{SOA}} \times \Delta[\text{Carbonyl}]))} \quad (5)$$

where A is the base-10 absorbance of the solution, l is the cell pathlength (5 cm), $[\text{Carbonyl}]_t$ is the amount of carbonyl remaining at time t (mg cm^{-3}), Y_{SOA} is the SOA mass yield ($\text{mg}_{\text{SOA}} \text{mg}_{\text{ArOH reacted}}^{-1}$), and $\Delta[\text{Carbonyl}]$ is amount of carbonyl reacted (mg cm^{-3}). As described in Section S4, we also determined MAC values for the products formed from direct photodegradation of the phenolic carbonyls.

3. Results and Discussion

3.1 Sunlight Absorption by Phenolic Carbonyls

We begin by investigating light absorption by phenolic carbonyls in the wavelengths of tropospheric sunlight ($\lambda \geq 290$ nm). The conjugated π -electron structures of phenolic carbonyls (Figure 1) allow these compounds to absorb significant amounts of solar radiation relative to phenol ($\text{C}_6\text{H}_5\text{OH}$), guaiacol (2-methoxyphenol) and syringol (2,6-dimethoxyphenol) (Figure 2). ConifAld has the highest molar absorptivity (ϵ_λ) values and absorbs to the longest wavelengths ($\lambda \geq 400$ nm) due to its conjugated carbonyl-alkene-aromatic ring functionality (Figures 1 and 2). The peak absorptivity values above 300 nm range from near $21000 \text{ M}^{-1} \text{ cm}^{-1}$ for ConifAld to $600 \text{ M}^{-1} \text{ cm}^{-1}$ for GA, (Table 1). In comparison, above 300 nm HOOH absorptivities are $< 1 \text{ M}^{-1} \text{ cm}^{-1}$ (Chu and Anastasio, 2005) and glyoxal absorptivities are $< 15 \text{ M}^{-1} \text{ cm}^{-1}$ (Malik and Joens, 2000). We do not observe a pH dependence in ϵ_λ values for any of the phenolic carbonyls between pH 2

and 5, consistent with the fact that ground-state phenolic carbonyls have pK_{HB+} values for the carbonyl group below pH 0 (Yates and Stewart, 1959) and pK_A values for the phenol of approximately 9 and higher (Tratnyek and Holgne, 1991). Molar absorptivities are compiled in Tables S1-S11 and Figure S2 for the phenolic carbonyls and six other phenols (phenol, guaiacol, syringol, catechol, resorcinol and hydroquinone).

Figure 2: Measured base-10 aqueous molar absorptivities (ϵ_λ) for the phenolic carbonyls and phenol (PhOH, C₆H₅OH), guaiacol (GUA, 2-methoxyphenol), and syringol (SYR, 2,6-dimethoxyphenol) (colored lines). The black line is the midday Davis winter solstice actinic flux (zenith angle = 62°) from the NCAR TUV Model (NCAR, 2014). ϵ_λ values are tabulated in the Supplemental Section, Tables S1 – S12.

To understand the potential for photochemistry with the phenolic carbonyls, we first calculated their rates of light absorption ($R_{\text{light,abs}}$) for aqueous drops containing 1 μM of carbonyl under Davis, midday, winter-solstice sunlight (Section S2). As shown in Table 1, rates of light absorption are typically $\sim (2\text{--}6) \times 10^{-7}$ mol-photons $\text{L}^{-1} \text{s}^{-1}$ but the value for GA is approximately 40 times lower than this while the value for ConifAld is 7 times higher. These values are orders of magnitude larger than rates of sunlight absorption for other aqueous chromophores – such as

100 μM HOOH (2×10^{-10} mol-photons $\text{L}^{-1}\text{s}^{-1}$) (Chu and Anastasio, 2005) or 10 μM benzaldehyde (6×10^{-9} mol-photons $\text{L}^{-1}\text{s}^{-1}$) (Anastasio et al., 1997).

3.2 Kinetics for Carbonyl Direct Photodegradation

As illustrated in Figure S3, upon exposure to simulated sunlight, aqueous carbonyls undergo rapid first-order direct photodegradation. There is no significant loss of any compound in the dark ($p > 0.05$). Since the apparent first-order rate constants for loss of phenols via reactions with non-phenolic aromatic carbonyl triplet excited states depends on phenol concentrations (Smith et al., 2014), we also examined the concentration dependence of phenolic carbonyl photodegradation. As shown in Figure S4, measured values of j_{ArOH} decrease with increasing carbonyl concentration. However, this apparent decrease is because the higher concentration of carbonyl leads to more light absorption in the solution, which decreases the volume-averaged photon flux. This effect can be quantified with the internal light screening factor S (Equation 2), where a value of 1 indicates no internal screening and smaller values indicate greater screening. Values of S decrease with increasing carbonyl concentration in the same manner as j_{ArOH} (Figure S4A), except in the highest absorbing solutions where the screening factor no longer tracks light transmittance through the solution (Figure S4B). Correcting $j_{\text{ArOH,win}}$ values for S (to give rate constant j_{ArOH} ; Equation 1) shows that the photodegradation rate constant is independent of concentration for all species at pH 5 (Figure S5) but at pH 2, j_{ArOH} for ConifAld and AVan increases with concentration, for reasons that we do not understand.

We next investigated j_{ArOH} as a function of pH, with a focus on vanillin because of its large emissions from both hard and softwood burning (Schauer et al., 2001). As shown in Figure 3A, j_{Van} depends on pH, with rate constants at pH 3 (and below) nearly two times higher than values at pH 5 (and above). This pH dependence suggests that the excimer of Van (i.e., the charge-

transfer complex formed between an excited state Van molecule and a separate ground state Van molecule (Birks, 1973; Turro et al., 2010)), is sensitive to solution acid/base chemistry. The phenolic carbonyls in this study are most likely sterically hindered from undergoing intramolecular excited state reactions, and will most likely form intermolecular excimers that result in the eventual destruction of the carbonyl (Birks, 1973; Turro et al., 2010). Fitting the Van loss data in Figure 3A with Equation 3, we find the $pK_{(HT^+)}$ of the protonated vanillin triplet excited state is 4.0 ± 0.2 , similar to the value for the protonated triplet excited state of DMB (3.3 ± 0.1) (Smith et al., 2014). For vanillin the ratio of direct photodegradation at high pH to low pH (i.e., j_T/j_{HT}) is 1.8 (Table 1), which is the opposite of the trend found by Benitez et al. (1997) and Li et al. (2014) between pH 2 and pH 7. In these previous experiments samples were illuminated with wavelengths between 185 and 385 nm (Benitez et al., 1997) and at 254 nm (Li et al., 2014). However, the bulk of these wavelengths are below 300 nm and are not present in tropospheric sunlight; as shown in Figure S2, they correspond to different absorption bands in Vanillin rather than the 308-nm band that is relevant to the troposphere and is accessed by our simulated sunlight (Figure S2). As discussed later, the relative reactivities of the protonated and neutral forms of the vanillin triplet also depend on the vanillin concentration.

Figure 3: Panel A shows how the direct photodegradation rate constant for 5 μ M vanillin (j_{Van}), and the corresponding quantum yield (section S3), depend on solution acidity. The dashed blue line is the fit of the data to equation 3. The white circle and square are results from two pH 5 control experiments: high ionic strength (5 mM sodium sulfate) and with 100 μ M ammonium chloride, respectively. Error bars represent ± 1 SE, propagated from errors in j_{light} and j_{2NB} (Equation 2). Panel B contains direct photodegradation rate constants (j_{ArOH}) from 1 μ M carbonyl experiments at pH 2 (left bar in each pair) and 5 (right bar) after correction for internal light screening and normalization to Davis winter solstice actinic flux. Error bars represent the propagated error of averages ($\pm 1\sigma$; $n=2$) for each compound. The rate constant for guaiacyl acetone (GA) loss at pH 5 is not statistically significant from zero.

There is some evidence to suggest that ionic strength and certain inorganic species (e.g., chloride) may interfere with some direct photodegradation reactions (Birks, 1973; Jammoul et al., 2009; Turro et al., 2010). To investigate the effect of ionic strength, we created a Van solution at pH 4.8 with the ionic strength of a pH 2 solution ($I = 0.015 \text{ M}$) using NaSO_4 (white circle, Figure 3A). To investigate the effect of chloride, we added $100 \mu\text{M}$ NH_4Cl to a pH 5 solution (white square, Figure 3A). In both cases the controls are not statistically different from

the original result at pH 5, indicating that neither ionic strength nor chloride has a significant effect on the direct photodegradation of vanillin.

As described above, we modeled the data in Figure 3A as a function of the mole fraction of the protonated and neutral forms of the carbonyl excimer (α_{HT} and α_T , respectively, where $\alpha_{HT} = 1 + [H^+]/K_A$ and $\alpha_{HT} = 1 - \alpha_T$). The total rate of carbonyl loss at a given pH can be expressed as the sum of the loss rates for the protonated and neutral triplets (Smith et al., 2014):

$$j_{Van} = \alpha_{HT}j_{HT} + \alpha_Tj_T \quad (6)$$

Given the acid dependence of j_{Van} , we also characterized the pH dependence of direct photodegradation of the other phenolic carbonyls by measuring rate constants at pH 2 (protonated excited state) and 5 (neutral excited state), which we label j_{HT} and j_T , respectively. As shown in Figure 3B, rate constants at pH 5 range from $8.2 \times 10^{-4} \text{ min}^{-1}$ for guaiacyl acetone to 0.080 min^{-1} for coniferaldehyde, corresponding to lifetimes of 1200 to 13 min, respectively. On average, j_{ArOH} for a given carbonyl is 1.6 ± 0.2 times faster at pH 5 than at pH 2, with a range of ratios of 1.5 to 2.5 (Figure 3). This modest decrease in direct photodegradation might be because the addition of protons can interfere with the formation of excimers in highly polar solvents (Gould et al., 1994). In contrast to the pH dependence for direct photodegradation of the phenolic carbonyls, phenol oxidation by the triplet excited state of 3,4-dimethoxybenzaldehyde (DMB) shows the opposite behavior, with faster reactions at low pH (Smith et al., 2014). Our interpretation of the latter results is that the protonated DMB triplet state is more reactive than the neutral form (Anastasio et al., 1997).

As shown in Table 1, carbonyl reactivity generally follows the trend in $R_{\text{light,abs}}$, with ConifAld possessing the fastest reactivity, followed by SyrAld and ASyr, then Van and AVan, and finally GA. The reactivity within the aldehyde/ketone pairs of SyrAld/ASyr and Van/AVan at either pH 2 or 5 is essentially equal, a result of greater light absorption by the aldehyde form but higher quantum efficiencies for loss for the ketone form (Table 1). GA showed the slowest loss, 7 times slower than Van at pH 2, and no statistically significant loss ($p > 0.05$) at pH 5.

3.3 Quantum Yields of Carbonyl Direct Photodegradation

We calculated the apparent quantum yield for direct photodegradation of each carbonyl during simulated sunlight illumination (Φ_{sun}) using the calculated rates of light absorption and measured rate constants for carbonyl loss (Section S2; Table 1). Φ_{sun} values for Van (at 5 μM) are larger at pH > 4 , following a typical proton dissociation curve with an apparent pK_A of 4.0 (Section 3.2; Figure 3A). However, this effect appears to be concentration dependent, as Φ_{sun} values for 30 μM Van at pH 2 and 5 are not statistically different (Figure S6). As shown in Table 1, Φ_{sun} values for the six phenolic carbonyls at pH 5 are in the range of $(0.90 - 7.0) \times 10^{-3}$ with the exception of GA, where the quantum yield for loss is not statistically different from zero. At pH 2, quantum yields are approximately 2 to 3 times lower than the corresponding pH 5 values except for GA. Our values of Φ_{sun} at pH 5 are 2 - 3 times lower than quantum yields determined with 313 nm illumination in pH 3.7 solutions (Anastasio, 1994). There are no reports of ConifAld quantum yields in aqueous solution, but the value for illuminated ($\lambda > 300 \text{ nm}$) ConifAld adsorbed on silica particles in the presence of ozone is 0.014×10^{-3} , which is approximately 60 times lower than our solution value (Net et al., 2010). Our pH 5 value of Φ_{sun} for Van is 150 times lower than a recent value reported with 254 nm illumination, $\Phi_{254\text{nm}} = 0.28$ (Li et al., 2014). 254 nm is near a minimum in the Van absorption spectrum (Figure S2) and is

primarily part of the absorption band centered at 279 nm, whereas simulated sunlight in our study involves the absorption band at 308 nm (Figure S2). Thus photons in the 279-nm absorption band appear to destroy Van more efficiently. A contribution from this band might also be the reason that the $\Phi_{313\text{nm}}$ values are higher than our Φ_{sun} values (Table 1), although it is also possible that the quantum yield decreases with increasing wavelength throughout the 308-nm band. This wavelength dependence of Φ indicates that using the apparent quantum yield with simulated sunlight (Φ_{sun} in Table 1) is a better choice than single wavelength values for tropospheric chemistry applications.

3.4 Oxidation of Syringol by Phenolic Carbonyls

We next investigate the oxidation of a non-carbonyl phenol (syringol; SYR) by the triplet excited state of a phenolic carbonyl. SYR is oxidized rapidly by the triplet states of non-phenolic aromatic carbonyls (Smith et al., 2014), but it is unclear if a similar reaction occurs with phenolic carbonyls. As shown in Figure S3b, this reaction does occur, with SYR following rapid first-order decay in illuminated solution containing 5 μM of a phenolic carbonyl. There is no significant direct photodegradation or dark loss of SYR under our experimental conditions (Smith et al., 2014). Overall, for solutions containing 5 μM phenolic carbonyl, measured lifetimes of SYR are similar with all five carbonyls (at all SYR concentrations) at pH 5, with an average value of 3.2 ± 1.0 hours ($n = 30$) (Figure S3). This lifetime is similar to that for oxidation of SYR by the triplet state of 5 μM DMB (average $\tau = 1.9$ hours) and oxidation via $\cdot\text{OH}$ (at 10^{-15} M, $\tau = 1.6$ hours) at pH 5. However, the rapid direct photodegradation of phenolic carbonyls ($\tau < 2.2$ hours) will suppress their concentrations in atmospheric drops, suggesting they are a minor sink for other phenols. More information on the oxidation of phenols by the triplet excited state of phenolic carbonyls is in supplemental section S4.

3.5 Secondary Organic Aerosol Mass Yields

To complement previous studies, which show that the aqueous oxidation of phenols by $\bullet\text{OH}$ and excited triplet states of non-phenolic aromatic carbonyls efficiently produces low-volatility products (Gelencsér and Varga, 2005; Sun et al., 2010; Li et al., 2014; Smith et al., 2014), here we examine SOA mass yields (Y_{SOA}) from the direct photodegradation of the phenolic carbonyls. Solutions containing 100 μM phenolic carbonyl were illuminated with simulated sunlight, blown dry with N_2 , and then the mass of SOA was measured.

As shown in Figure S8, direct photodegradation experiments produce large amounts of low-volatility mass relative to the dark controls. However, the dark controls often contain significant amounts of mass following blowdown, primarily from the phenolic carbonyl reactant that was not evaporated during blowdown (Figure S8). Another reason for high masses in some of the dark solutions is that evaporation appears to have produced SOA mass, especially for SyrAld and ConifAld (Figure S8). This evaporation-induced production of low-volatility organics has been seen previously for limonene under acidic conditions (Nguyen et al., 2012), and also in our previous work with benzene-diols (Smith et al., 2015). For the current phenolic carbonyls, the evaporation-induced reaction might be an acid-catalyzed aldol condensation to form oligomers (Nguyen et al., 2012). Although our solutions are initially pH 5, as they evaporate the acidity will increase due to concentrating the H_2SO_4 .

To correct for these two dark mechanisms, we first subtract the mass of unreacted phenolic carbonyl in the illuminated and dark sample blowdown masses, then subtract the remaining dark mass from the illuminated sample mass (to correct for evaporation-induced products and other material such as sulfate) (Equation 4). The resulting average ($\pm 1 \sigma$) values of Y_{SOA} for direct photodegradation are 81 (± 8)% for Van, 82 (± 7)% for AVan, 68 (± 5)% for SyrAld, 82 (± 8)%

for ASyr, and 120 ($\pm$ 21)% for ConifAld (Figure 4). These values are generally lower than those measured for SOA from oxidation of phenols and benzene-diols by $\cdot\text{OH}$ and $^3\text{C}^*$ (Smith et al., 2014; Smith et al., 2015). ConifAld is an exception, with a yield similar to that for SOA from phenols oxidized by the DMB triplet state, possibly due to the presence of the reactive alkene functional group (Figure 1). Previous studies of phenol oxidation by $\cdot\text{OH}$ and $^3\text{C}^*$ observed high amounts of oligomer formation (Yu et al., 2014), and our high Y_{SOA} values here suggest similar reaction mechanisms for the phenolic carbonyls. This is broadly consistent with the work of Li et al. (2014), who found that the direct photodegradation of Van at 254 nm produced a wide variety of oxidized Van monomers, ring-opening products, and oligomers.

Figure 4: Average SOA mass yields. The left portion of the plot shows yields for direct photodegradation of Van (n=4), AVan (n=1), SyrAld (n=3), ASyr (n=1) and ConifAld (n=3). Errors of individual experiments represent the propagated error from equation 4 for phenol loss and analytical mass uncertainty. The right portion of the plot shows SOA yields from SYR oxidation by the triplet excited state ($^3\text{C}^*$) of Van (n=5) and SyrAld (n=3). SYR SOA mass was corrected by subtracting the SOA mass formed by direct photodegradation of the phenolic carbonyl. These corrections were < 15% for SyrAld and <11% for Van.

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371 We next investigated SOA mass yields from the oxidation of syringol by the triplet excited state
 372 of Van or SyrAld. Solutions containing 5 μM of a phenolic carbonyl and 100 μM SYR were
 373 illuminated until approximately 50% of the phenolic carbonyl remained. The calculated SOA
 374 mass from the direct photodegradation of the phenolic carbonyl was subtracted from the
 375 resulting low-volatility mass in the mixture. The oxidation of SYR by phenolic carbonyls
 376 efficiently produce low volatility mass, but the resulting product masses are lower than for direct
 377 photodegradation due to slower SYR oxidation rates (Figure S7a and Figure S8). The resulting
 378 values of Y_{SOA} for SYR oxidation by Van and SyrAld are 111 (± 7) % and 78 (± 15) % (Figure
 379 4). These yields are similar to the SOA yields from oxidation of SYR by $\cdot\text{OH}$ or the triplet state
 380 of 3,4-dimethoxybenzaldehyde (98 and 114%, respectively) (Smith et al., 2014; Smith et al.,
 381 2015).

382 **3.6 Light Absorption by Phenolic Carbonyl SOA**

383 Brown carbon particles, which absorb significant amounts of sunlight, have both primary and
 384 secondary sources in the atmosphere (Chen and Bond, 2010; Updyke et al., 2012). Since

biomass burning is a large source of brown carbon globally (Chen and Bond, 2010), we examine in this section how illumination of aqueous phenolic carbonyls affects their light absorption. UV-Vis analyses of the phenolic carbonyl solutions show an overall loss of light absorption during illumination, as illustrated in Figure 5A for vanillin and shown for the other compounds in Figure S9. At the same time, however, there is an increase in absorption at longer wavelengths, where the original carbonyl did not absorb light (Figure 5; Figure S9). Thus photodegradation transforms highly-absorbing phenolic carbonyls into other forms of brown carbon that absorb less efficiently, though with additional absorbance at longer wavelengths. Our results are similar to a recent investigation of nitrophenol direct photodegradation at 254 nm, where total absorbance rapidly declined, but some long-wavelength absorbance appeared (Zhao et al., 2015).

As shown in Figure 5B, the mass absorption coefficients (MAC) for Van, ConifAld, SyrAld, and ASyr have peak values above 290 nm that are near 1.4×10^5 , 2.9×10^5 , 1.6×10^5 , and 1.2×10^5 $\text{cm}^2 \text{g}^{-1}$, respectively. In comparison, the SOA produced after illuminating for one carbonyl half-life has peak MAC values that are approximately 2 to 5 times lower (Figure 5B). The increase in light absorption at long wavelengths is consistent with oligomeric products, which have large, conjugated π -electron systems (Chang and Thompson, 2010). To put this into perspective, the MAC values for phenolic carbonyl SOA from Van, ConifAld, SyrAld, and ASyr are approximately 2, 2, 6, and 4 times larger, respectively, than fresh biomass-burning particles (Chen and Bond, 2010) (Figure 5; Figure S9). Along the same vein, MAC values for phenolic carbonyl SOA are typically much higher than those for SOA from limonene, isoprene, and other gas-phase precursors, even after treatment with ammonia (Nguyen et al., 2012; Updyke et al., 2012).

Figure 5: Mass absorption coefficient (MAC) values for phenolic carbonyls and their aqueous SOA products. Panel A shows the change in overall MAC for the mixture of reactant and products during direct photodegradation of 10 μM Vanillin at different illumination times. Panel B shows the MAC values for each phenolic carbonyl (solid lines) and for the aqueous SOA products at an illumination time of the phenolic carbonyl half-life (dashed line). ASyr values are noisier because they were measured at 1 μM . Detailed MAC calculations are in Section S4.

3.7 Atmospheric Oxidation of Phenolic Carbonyls and Formation of SOA

In this section we first assess the relative importance of direct photodegradation and oxidation by hydroxyl radical as sinks for phenolic carbonyls in a cloudy/foggy atmosphere. For aqueous rate

constants between the phenolic carbonyls and $\cdot\text{OH}$ we used literature values for Van ($6.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; Mahal et al., 2001; Gontor et al., 2012) and AVan ($8.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; Benitez et al., 2005) and assumed diffusion-controlled rate constants for the others (aqueous = $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$; gas-phase = $1 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Li et al., 2014)). To ease comparisons, we use the same conditions and approach as Epstein et al. (2013), including a gas-phase $\cdot\text{OH}$ concentration of $1 \times 10^6 \text{ molecules cm}^{-3}$ and the lower aqueous $\cdot\text{OH}$ concentration of $7.5 \times 10^{-15} \text{ M}$, although this is at the upper end of measured values (Arakaki et al., 2013) (Section S6). Aqueous direct photodegradation rate constants were calculated using the data in Table 1. We assume the indoor drop photon flux is 1.5 times higher than in the gas-phase (Mayer and Madronich, 2004). There is little to no information for Φ values for gas-phase aromatic compounds. Thus for our calculations we assume the Φ ratio of phenolic carbonyls in the gas and aqueous phase ($\Phi_{\text{gas}} / \Phi_{\text{aq}}$) is equal to 7, estimated from the ratio of sunlight values for gas-phase benzaldehyde ($\Phi_{\text{gas}} = 0.05$) and aqueous-phase acetophenone ($\Phi_{\text{aq}} = 0.007$) (Carter, 1990; Anastasio, 1994) (Section S6).

Epstein et al. (2013) found that gas-phase photolysis and $\cdot\text{OH}$ oxidation were the dominant fates for nearly all of the aliphatic carbonyls they considered, while aqueous reactions (photodegradation and $\cdot\text{OH}$ oxidation) were negligible. In contrast, we find that aqueous photodegradation is a major or dominant loss pathway for five of the six phenolic aromatic carbonyls (Figure S10), accounting for 36 to 94% of loss for Van, AVan, SyrAld, ASyr, and ConifAld. Aqueous photodegradation dominates for these compounds because they have much higher Henry's law constants (3.6×10^5 to $6.9 \times 10^8 \text{ M atm}^{-1}$; Table S16) and much faster rate constants for photodegradation (0.7×10^{-2} to $8.0 \times 10^{-2} \text{ min}^{-1}$; Table 1) compared to the aliphatic carbonyls (Epstein et al., 2013). There are two phenolic carbonyls - guaicyl acetone and syringyl

acetone - where aqueous photodegradation is a negligible sink (approximately 1% of total loss). While these compounds have high Henry's law constants, their carbonyl functional groups are not conjugated to the aromatic ring (leading to small amounts of sunlight absorption) so that aqueous $\cdot\text{OH}$ is the major sink (Table S16). Aqueous reactions with triplet excited states are likely a similarly important sink (Smith et al., 2014), but this pathway is not considered in this simple treatment.

We next estimate SOA production from the aqueous direct photodegradation of phenolic carbonyls in a foggy/cloudy area with significant biomass combustion (and a liquid water content of $1.0 \times 10^{-7} L_{\text{aq}} L_{\text{gas}}^{-1}$). We determine the total (gas and particle) phenolic carbonyl concentrations using emission factors from soft and hardwood burning (Schauer et al., 2001) and reported primary organic aerosol (POA) concentrations from wood combustion during a stagnation event in Bakersfield, CA (Schauer and Cass, 2000) (Section S7). Assuming Henry's Law equilibrium, and complete reaction of each aqueous carbonyl (since the aqueous lifetimes are short; Table S17), the amount of SOA formed from direct photodegradation of aqueous phenolic carbonyls increases the wood combustion POA mass by 2.7% under hardwood burning and 5.2% for softwood burning. For the wintertime Bakersfield event this corresponds to an aqueous SOA mass from phenolic carbonyls of approximately $0.4 \mu\text{g m}^{-3}$, which is a small enhancement (4%) on the $9.4 \mu\text{g m}^{-3}$ of POA from wood combustion (Section S7). Thus aqueous photodegradation of phenolic carbonyls provides a rapid, but modest, increase in OA from wood combustion. However, the phenolic carbonyl contribution to aqueous SOA would approximately double if the slower, $\cdot\text{OH}$ - and $^3\text{C}^*$ -mediated reactions of guaiacyl acetone and syringyl acetone were included, based on analogous reactions with other phenols that do not absorb appreciable sunlight (Smith et al., 2014).

4. Conclusions

Phenolic carbonyls are a large class of intermediate volatility, very soluble, and highly reactive organic compounds released during biomass combustion. These compounds undergo rapid aqueous direct photodegradation, with lifetimes of 20 to 90 min (at pH 5), to efficiently form low-volatility products. In contrast to aliphatic carbonyls, aqueous photoreaction is a major or dominant sink for phenolic carbonyls in a foggy or cloudy atmosphere, accounting for approximately 30-95 % of the overall rate of loss. The triplet excited state of phenolic carbonyls can oxidize syringol in solution, but this is likely a minor sink for this and other non-carbonyl phenols. The direct photodegradation of phenolic carbonyls efficiently produces SOA, with mass yields typically near 80%. The SOA produced from phenolic carbonyl direct photodegradation absorbs 2-6 times more solar radiation than freshly emitted biomass burning particles. Our results indicate that aqueous SOA formation from the direct photodegradation of phenolic carbonyls can increase the primary organic aerosol mass from wood combustion by 3 - 5% during a fog or cloud event. The fast rates of aqueous photodegradation and high emission rates from biomass burning suggest phenolic carbonyls can be a modest, and previously unappreciated, source of aqueous light-absorbing SOA in air masses impacted by biomass burning.

Acknowledgements: Funding for this research was provided by the National Science Foundation (Grant Number AGS-1036675), the University of California Toxic Substances Research and Teaching Program (TSR&TP) through the Atmospheric Aerosols and Health Lead Campus Program, and the California Agricultural Experiment Station (Project CA-D-LAW-6403-RR).

489 Table 1: Kinetic information for carbonyl direct photodegradation
 490

	λ_{max} (nm) ^a	$\epsilon_{\lambda_{\text{max}}}$ (10^3 M ⁻¹ cm ⁻¹)	$R_{\text{light,abs}} \times 10^7$ (mol-photons L ⁻¹ s ⁻¹) ^b	$j_{\text{HT}} \times 10^2$ (min ⁻¹) ^c	$j_{\text{T}} \times 10^2$ (min ⁻¹) ^c	$\phi_{\text{sun}} \times 10^3$ ^f		$\phi_{313\text{nm}} \times 10^3$ ^g
						pH 2	pH 5	
Vanillin (Van)	309	9.16	2.9 ± 0.4	0.8 ± 0.2	1.4 ± 0.1	0.87 ± 0.13	1.9 ± 0.3	5.4 ± 0.6
Acetovanillone (AVan)	305	7.86	1.7 ± 0.4	0.7 ± 0.1 ^d	1.5 ± 0.1	2.1 ± 0.4	3.9 ± 0.8	8.3 ± 2.0
Syringaldehyde (SyrAld)	306	12.2	6.0 ± 1.2	2.8 ± 0.3	4.5 ± 0.3	2.6 ± 0.1	4.6 ± 0.2	13 ± 2
Acetosyringone (ASyr)	300	10.6	2.3 ± 0.5	3.1 ± 0.7	4.7 ± 0.4	2.3 ± 0.1	7.0 ± 0.6	20 ± 3
Coniferyl Aldehyde (ConifAld)	337	21.7	31 ± 6.2	3.2 ± 0.4 ^d	8.0 ± 0.5	0.41 ± 0.03	0.92 ± 0.03	-
Guaiacyl Acetone (GA)	300	0.550	0.09 ± 0.01	0.008 ± 0.002 ^e	0.004 ± 0.02 ^e	0.11 ± 0.07 ^e	0.12 ± 0.75 ^e	-

491 ^a Peak wavelength based on absorptivity at values $\lambda \geq 300$ nm.

492 ^b Calculated rate of light absorption using molar absorptivities listed in Tables S2-S12 in drops
 493 containing 1 μM carbonyl under midday Davis, CA winter solstice sunlight. Values are adjusted
 494 to account for an in-drop photon flux enhancement of 1.5 relative to the gas phase (Mayer and
 495 Madronich, 2004). Actinic flux values (I_{λ}) obtained from TUV actinic flux model (section S6)
 496 (NCAR, 2014). Errors represent 1 σ , determined from replicate molar absorptivity
 497 measurements.

498 ^c Each value is an average of results for experiments containing 1-20 μM carbonyl (Figure S5),
 499 except as noted below, normalized to Davis, CA winter solstice sunlight, and corrected for
 500 internal light screening. Errors represent $\pm$ one standard error.

501 ^d Value taken from 1 μM carbonyl experiment; see Section 3.1 and Figure S4 for the measured
 502 dependence on carbonyl concentration, which is likely due to very high internal screening.

503 ^e Guaiacyl acetone values were determined from 10 μM experiments due to very slow amounts
 504 of loss.

505 ^f Data from experiments with 1 μM carbonyl, where the internal light screening is minimized.
 506 Values measured at higher carbonyl concentrations are generally similar (Figure S5), but less
 507 certain because of the greater light screening. Errors are $\pm$ one standard error propagated from
 508 values of $R_{\text{light,abs}}$ and j_{HT} (or j_{T}), respectively (Section S3).

509 ^g Data from Anastasio (1994) measured with 313 nm irradiation using 10 μM carbonyl at pH 3.7.
 510 Errors are $\pm$ one standard error.

511
 512

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