

http://pubs.acs.org/journal/aesccq

Products and Secondary Organic Aerosol Yields from the OH and NO₃ Radical-Initiated Oxidation of Resorcinol

Zachary Finewax,^{†,‡} Joost A. de Gouw,^{†,‡} and Paul J. Ziemann*^{,†,‡}

[†]Department of Chemistry and Biochemistry and [‡]Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, Colorado 80309, United States

Supporting Information

ABSTRACT: Resorcinol (1,3-benzenediol) has been observed in both laboratory and field studies reporting biomass burning emissions. As a result of its low vapor pressure, it has been suggested as a secondary organic aerosol (SOA) precursor, but its gas-phase oxidation has not been studied previously. Here, the reactions of resorcinol with OH radicals in the presence of NO_x and with NO_3 radicals in the presence of NO_2 were investigated to mimic oxidation under daytime and nighttime conditions. When resorcinol was added to the chamber in the presence of a high concentration of oxidant, the gas-phase chemistry of this highly reactive, low-volatility compound was investigated while minimizing its loss to the chamber walls. Gasand particle-phase products were identified using a combination



of thermal desorption particle beam mass spectrometry, chemical ionization—ion trap mass spectrometry, and proton transfer reaction—mass spectrometry. The major products identified were benzenetriol, nitrobenzenetriol, and hydroxymuconic semialdehyde in the particle phase and hydroxybenzoquinone and nitroresorcinol in the gas phase, and a reaction mechanism was developed to explain their formation. Hydroxybenzoquinone was determined to form through gas-phase oxidation of resorcinol and by heterogeneous oxidation of benzenetriol by nitric acid. Reactions with OH and NO₃ radicals produced SOA with yields of 0.86 and 0.09, respectively, but these values should be somewhat lower in the atmosphere where aerosol mass concentrations are lower and, thus, gas—particle partitioning is reduced.

KEYWORDS: volatile organic compounds, aromatic compounds, wildfire emissions, atmospheric oxidation, heterogeneous oxidation, oxidation mechanisms

INTRODUCTION

Emissions from biomass burning are an important source of organic gases and particles, which through a variety of mechanisms can influence visibility, human health, and climate.^{1,2} In some cases, biomass burning emissions can even affect air quality at locations thousands of kilometers away as a result of long-range transport.³ Gas-phase emissions from biomass burning can also undergo atmospheric reactions to produce compounds of low vapor pressure that partition onto pre-existing particles, causing an increase in particle mass. This secondary organic aerosol (SOA) is a major component of atmospheric particulate matter.⁴

There have been several laboratory studies measuring SOA formed from the oxidation of biomass burning emissions.^{5–8} Laboratory and field studies generally observe an increase in organic aerosol produced during photo-oxidation, 5,6,9,10 suggesting a significant contribution from oxidation of gasphase emissions. Speciated measurements of organic aerosol in fresh and aged smoke have determined that some compounds are emitted from biomass burning, whereas others are produced by the gas-phase oxidation of these emissions.⁷

certain compounds are formed when oxidizing a complex mixture, such as smoke. With the reaction of individual compounds under controlled laboratory conditions, one can determine which products observed in the field are produced from the oxidation of a given emission, allowing for incorporation of these products into explicit chemical reaction mechanisms.

Resorcinol (1,3-benzenediol) is emitted directly from biomass burning as a product of lignin pyrolysis¹¹ and has been observed in laboratory^{12–14} and field studies¹⁵ of biomass burning. In the aqueous phase, resorcinol oxidation produces considerable amounts of SOA.^{16,17} However, to our knowledge, there have been no measurements of the yields of molecular products or SOA formed from the gas-phase reactions of resorcinol with atmospheric oxidants. Because its

Special Issue: New Advances in Organic Aerosol Chemistry

Received:April 29, 2019Revised:June 12, 2019Accepted:June 13, 2019Published:June 13, 2019

ACS Publications © 2019 American Chemical Society

isomer, catechol (1,2-benzenediol), has been shown to produce significant amounts of SOA when reacted with OH^{18-20} and NO_3^{20} radicals, it is worthwhile to also study the ability of resorcinol to produce SOA from gas-phase reactions.

There are, unfortunately, inherent challenges in studying reactions of low-volatility organic compounds as a result of their tendency to be lost to the walls of the reactor. For example, in Teflon environmental chambers, compounds with sufficiently low vapor pressure can undergo rapid, equilibrium partitioning into the chamber walls in ~10 min, leading to errors in measured yields of products and SOA.²¹⁻²⁴ Field studies have indicated that the oxidation of low-volatility organic compounds is responsible for a large amount of the SOA found in the atmosphere,^{25,26} but the molecular origin of this SOA is unclear. It is therefore important to devise methods to study the oxidation of these compounds experimentally to help determine the sources of atmospheric SOA. In this study, it was possible to react resorcinol sufficiently quickly with OH radicals in the presence of NO_x and with NO_3 radicals in the presence of NO₂ to minimize the loss of resorcinol to the walls. We were thus able to obtain estimates of SOA yields, identify gas- and particle-phase reaction products, and propose mechanisms for these reactions under daytime and nighttime conditions.

EXPERIMENTAL SECTION

Chemicals. The following chemicals were used: ethyl acetate [high-performance liquid chromatography (HPLC) grade], methanol (HPLC grade, EMD Millipore), water (HPLC grade, Fisher Chemical), resorcinol (>99%, Sigma-Aldrich), 2-nitroresorcinol (98%, Sigma-Aldrich), O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA, >99%, Sigma-Aldrich), hydroquinone (>99%, Sigma-Aldrich), hydroxyquinol (99%, Sigma-Aldrich), dioctyl sebacate (>97%, Fluka), and nitric oxide (99%, Matheson Trigas). Methyl nitrite and N₂O₅ were prepared using the methods of Taylor et al.²⁷ and Atkinson et al.²⁸

Hydroxybenzoquinone was prepared²⁹ by adding a phosphate buffer at pH 8 to hydroquinone and allowing it to react with air for several minutes until a wine-red solution was formed. The solution was acidified with hydrochloric acid to pH 2 to prevent further oxidation, producing a pale-yellow solution, and its identity was confirmed by analyzing the solution using an Ocean Optics ultraviolet–visible (UV–vis) spectrophotometer.

Environmental Chamber Experiments. Reactions were carried out at room temperature and pressure (25 °C and 630 Torr) in an 8000 L FEP Teflon chamber that was filled with clean, dry air [hydrocarbons and $NO_x < 5$ ppb and relative humidity (RH) < 1%]. In each experiment, ~100 μ g m⁻³ of seed particles [dioctyl sebacate (DOS)] were added from an evaporation-condensation source to enhance condensation of organic vapors onto particles and, thus, reduce their loss to the chamber walls.^{21,23} For reactions initiated by OH radicals, 2 ppm of methyl nitrite (CH₃ONO) and 2 ppm of NO (to avert formation of O_3 and NO_3 radicals) were added to the chamber, the contents were mixed for 1 min with a Teflon-coated fan, and the blacklights were turned on at an intensity corresponding to NO₂ photolysis rates of 0.37 or 0.74 min⁻¹. A measured amount of resorcinol was then immediately added from a heated glass bulb by flushing with ultrahigh-purity (UHP) N₂. It typically took \sim 5 min to add all resorcinol,

which corresponded to a concentration of 400 ppb, and then the lights were turned off ~5 min later. Reactions initiated by NO₃ radicals were performed in the dark by adding 1 ppm of N₂O₅, which thermally decomposed to establish equilibrium with NO₃ + NO₂, and then immediately adding resorcinol, as described above.

Resorcinol was added while oxidants were already present in an attempt to react resorcinol in the gas phase before it could be lost to the chamber walls. Experiments in which resorcinol was allowed to achieve gas-wall partitioning equilibrium before OH radical formation was initiated resulted in no measurable production of SOA. This is consistent with the similarity of the estimated vapor pressure of resorcinol to that of 1,8-octanediol $(\sim 1 \times 10^{-3} \text{ Torr}^{30})$, a compound that completely partitioned into the Teflon film in previous experiments.²² This approach proved to be successful because the time scale for the reaction of resorcinol with OH or NO3 radicals is much shorter than the time scale for achieving gas-wall partitioning equilibrium in our chamber. Although the rate constant for the reaction of resorcinol with OH radicals is not known, the value calculated using a structure–activity relationship for aromatics³¹ is $5.7 \times$ 10^{-10} cm³ molecule⁻¹ s⁻¹, which is greater than the collision rate between resorcinol and OH radicals. Assuming instead that the rate constant is 1.04×10^{-10} cm³ molecule⁻¹ s⁻¹,³² the same as catechol (1,2-benzenediol), and using an OH radical concentration of 1×10^8 molecules cm⁻³ that is typical for the beginning of photo-oxidation,³³ the lifetime of resorcinol with respect to oxidation by OH radicals is ~100 s. Assuming that the rate constant for the reaction of resorcinol with NO_3 radicals is 9.8 $\times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, the same as with catechol, and using an NO3 radical concentration of 30 ppb (the maximum NO₃ radical concentration obtained from 1 ppm of N_2O_5 thermal decomposition equilibrium), the lifetime of resorcinol with respect to oxidation by NO3 radicals is ~ 0.2 s. Both reactions are significantly faster than the time scale for gas-wall partitioning in our chamber of ~600 s, thus allowing these reactions to occur before gas-wall partitioning becomes significant.

The decision to use 400 ppb of resorcinol in these experiments was also based on technical considerations, because this amount resulted in the formation of $\sim 1 \text{ mg m}^{-3}$ of SOA. Although this is much higher than typical atmospheric SOA concentrations, it is not yet clear how experiments should be conducted to best simulate atmospheric SOA formation. Use of a low concentration of precursor is likely to result in an underestimate of the SOA yield because of the loss of products by gas-wall partitioning, while the use of a high concentration is likely to overestimate the yield because of enhanced gasparticle partitioning and possibly multiphase reactions. 2^{1-24} Given this uncertainty, we chose to operate under conditions that optimized the amount of SOA formed and, thus, provided the most material for analysis. As shown below, by estimating product vapor pressures, we can attempt to predict the gasparticle partitioning of these compounds in the atmosphere.

Particle Analysis. Real-time mass spectra of the aerosol particles were measured throughout each experiment using thermal desorption particle beam mass spectrometry (TDPBMS).³⁴ In this instrument, particles are focused into a narrow beam as they pass through an aerodynamic lens and then enter a high-vacuum chamber, where they impact and vaporize on a copper rod that is heated to ~160 °C. The vapor is then impacted by 70 eV electrons, and the resulting ions are analyzed in a triple quadrupole mass spectrometer. Alter-

Scheme 1. Proposed Mechanism for Forming First-Generation Products from the Reaction of Resorcinol with OH Radicals in the Presence of $NO_x^{\ a}$



^{*a*}Products predominantly in the particle phase are red; products predominantly in the gas phase are green; and products found in both phases are blue. Note that the conversion of benzenetriol to hydroxybenzoquinone occurs in the particle phase, whereas all of the other reactions occur in the gas phase.

natively, the aerosol was collected after cooling the vaporizer to -40 °C and then desorbed by ramping the temperature at 2 °C min⁻¹ to 200 °C.³⁵ This temperature-programmed thermal desorption (TPTD) method separates compounds according to volatility, while the mass spectrometer is scanned. Aerosol volume concentrations were measured at 4.2 min intervals (average of up and down scan) using a scanning mobility particle sizer (SMPS)³⁶ and used to correct for particle wall loss during filter sampling.

After each reaction, replicate particle samples were collected for 100 min at a flow rate of $14 \pm 0.3 \text{ L} \text{min}^{-1}$ on preweighed Teflon filters (0.45 μ m pore size). Filters were reweighed to determine the sampled particle mass and then extracted separately (along with their perforated metal supports) in 4 mL of ethyl acetate. The extracts were dried in a stream of UHP N₂ and then weighed. In all experiments, the mass of the dried extracts and the mass collected on filters agreed within \pm 7%, indicating complete extraction. The dried extracts were redissolved in ethyl acetate to achieve 1–2 mg mL⁻¹ of sample and then stored at -25 °C until analyzed. All mass measurements were made using a Mettler Toledo XS3DU microbalance.

SOA extracts were fractionated and collected by reversedphase HPLC using a Shimadzu Prominence HPLC equipped with a Nexera X2 SPD-M30A UV–vis photodiode array (PDA) detector and Phenomenex Kinetex phenyl-hexyl column (250 mm × 4.6 mm × 5 μ m). The method used a flow rate of 0.2 mL min⁻¹, where mobile phase A was 10 mM phosphate buffer (95:5 water/methanol, pH ~ 2.6) and mobile phase B was methanol. The method was as follows: begin with 0% B and hold for 20 min, then increase B at 2% min⁻¹ to 50% B, hold for 25 min, then decrease to 0% B at 2% min⁻¹, and hold for 10 min.

Collected SOA fractions were dried in a stream of UHP N₂ and redissolved in 10 μ L of ethyl acetate prior to being analyzed using a Thermo Finnigan PolarisQ ion trap mass spectrometer with isobutane as the chemical ionization reagent gas (CI–ITMS).³⁷ Samples were inserted into the vacuum region using a direct-insertion probe and then vaporized into the ion source (maintained at 250 °C to reduce condensation of compounds on the walls) for mass analysis by increasing the probe temperature from 35 to 350 °C at a rate of 10 °C min⁻¹.

Gas-Phase Analysis. Quadrupole proton transfer reaction-mass spectrometry (PTR-MS) was used to monitor gasphase products in real time.³⁸ Briefly, sampled trace gases react with H_3O^+ ions by proton transfer, provided that the proton affinity of the analyte is greater than that of water. The reaction occurs inside the PTR-MS drift tube, which was set to a

Article



Figure 1. (A) Real-time TDPBMS mass spectra of SOA formed from the reaction of resorcinol with OH radicals in the presence of NO_x and mass spectra of (B) 1,2,3-benzenetriol, (C) 1,2,4-benzenetriol, and (D) 1,3,5-benzenetriol standards. Peaks as a result of DOS seed particles were removed from mass spectrum A.

pressure of 2.4 mbar and a voltage of 720 V for an E/N \approx 120 Td. The inlet system in this instrument prevents the efficient detection of low-volatility compounds as a result of long measurement delay times.³⁹

Gas-phase products were also collected on either PFBHAcoated (for carbonyl compounds) or uncoated annular denuders for 10 min at 10 L min⁻¹ immediately following the completion of a reaction. Denuders were extracted 3 times with 25 mL of dichloromethane, dried in a stream of UHP N₂, and reconstituted in 1 mL of ethyl acetate for CI–ITMS analysis, as described above. In addition, a Thermo 42 NO– NO₂–NO_x chemiluminescence analyzer was used to monitor the concentrations of NO and NO_x.

SOA Yields. Mass-based SOA yields were determined as the mass of SOA formed/mass of resorcinol reacted ($M_{SOA}/\Delta Res$), where M_{SOA} ($\mu g m^{-3}$) is the mass of particles collected on a filter/sampled air volume and ΔRes ($\mu g m^{-3}$) is the mass of resorcinol that reacted. M_{SOA} was corrected for particle wall loss during filter sampling and for the DOS seed component using aerosol volume concentrations measured with the SMPS.⁴⁰ Aerosol volume concentrations reached a maximum within 10 min of stopping OH radical formation by turning off the blacklights and within 15 min of adding resorcinol in the NO₃ radical reactions. The delay in reaching maximum volume concentrations is likely due to additional time required for the chamber to become well-mixed, in addition to the 4 min time resolution of SMPS data points. The fan was not turned on during resorcinol addition to the chamber, to reduce the rate of vapor wall loss as a result of increased turbulence.²³ Because resorcinol could not be measured via gas collection onto Tenax adsorbent followed by gas chromatography with a flame ionization detector (GC-FID) analysis, the reaction of resorcinol was assumed to be complete, so that ΔRes is the mass of added resorcinol/chamber volume. This assumption should be reasonable, because (as discussed above) the lifetime for resorcinol with respect to reaction with OH radicals was ~100 s, the lights were on for ~10 min (including the ~5 min required to add resorcinol to the chamber), and the time scale for achieving gas-wall partitioning equilibrium was ~600 s. This is also true for the reactions with NO₃ radicals, because the lifetime for resorcinol in that reaction was ~ 0.2 s and excess N₂O₅ was present in the chamber.

RESULTS AND DISCUSSION

Proposed Reaction Mechanisms. The proposed mechanism for the formation of first-generation products from the reactions of resorcinol with OH and NO_3 radicals in the presence of NO_x is shown in Scheme 1. The mechanism was

developed using results of previous studies of the oxidation of aromatic compounds $^{41-43}$ and the products identified here, which are discussed below. The OH radical reaction can proceed via three pathways: 1,2- or 1,4-ring addition to form an OH-aromatic adduct or abstraction of a phenolic H atom to form an *m*-hydroxyphenoxy or *m*-semiguinone radical. For each of these, the radical that is formed (resonance structures are shown in the scheme) can add O_2 to form an organoperoxy radical (RO_2^{\bullet}) or NO₂ to form a nitroaromatic product that terminates the reaction. The cyclic α -hydroxyperoxy radical formed from O₂ addition to an OH-aromatic adduct will either decompose to a benzenetriol and HO₂, isomerize to a bicyclic alkyl radical, or react with NO to form a cyclic α hydroxyalkoxy radical and NO2. The bicyclic alkyl radical will either decompose to form ring-opened products, such as glyoxal, glucic acid, and maleic anhydride (which were observed in PTR-MS, as discussed below), or add O₂ to form a bicyclic organoperoxy radical. This RO₂[•] radical will react with NO under the conditions of these experiments or with other RO_2^{\bullet} radicals or HO_2 under low NO_x conditions, likely forming a variety of ring-retaining and ring-opened products by pathways similar to those identified for simpler aromatic compounds.⁴⁴ Because no clear evidence for these was observed here, they are not shown in Scheme 1. According to structure-activity calculations, 45,46 the cyclic α -hydroxyalkoxy radical will decompose at a first-order rate of $\sim 10^{12}$ s⁻¹ (many orders of magnitude faster than isomerization) to a ring-opened α -hydroxyalkyl radical, which then reacts with O₂ to form hydroxymuconic semialdehyde and HO₂. We note that, for NO concentrations less than ~100 ppb (much lower than the >1 ppm of NO concentrations used here), the reaction of the cyclic α -hydroxyperoxy radical with NO will no longer compete with decomposition and isomerization,⁴² and thus, hydroxymuconic semialdehyde would not be expected to form under atmospheric conditions. The msemiquinone peroxy radical formed by the addition of O_2 to the *m*-semiquinone radical can react with NO to form NO₂ and a *m*-semiquinone alkoxy radical, which then reacts with O₂ to form hydroxybenzoquinone and HO₂, whereas the addition of NO₂ to the *m*-semiquinone radical leads to 4-nitroresorcinol.

The NO₃ radical reaction of resorcinol in the presence of NO₂ only proceeds through phenolic H atom abstraction, similar to the pathway shown in Scheme 1 for the OH radical reaction. This has been observed in reactions of NO₃ radicals with phenol⁴¹ and catechol.²⁰ For resorcinol, the reaction produces two compounds, nitroresorcinol and hydroxybenzoquinone, which are formed by the same mechanisms as in the OH radical reaction, except that the *m*-semiquinone peroxy radical is converted to the *m*-semiquinone alkoxy radical by reaction with a RO₂[•] or NO₃ radical [forming an alkoxy radical (RO[•]) and NO₂, respectively] instead of by reaction with NO.

As shown, the inclusion of only first-generation products in this scheme is appropriate. Only one second-generation product (dihydroxybenzoquinone) of a gas-phase reaction was identified from gas and particle analyses, and on the basis of PTR–MS signals, its concentration was <5% of that of hydroxybenzoquinone from which it was formed. Although nitroresorcinol was available in the gas phase for further reaction, because nitroaromatic compounds react ~30 times more slowly than their unsubstituted aromatic analogues, ^{47,48} it is unlikely that a significant amount reacted during the 10 min reaction. As for the other first-generation products, because of

their low vapor pressures they were almost entirely in the particle phase, where the rate of reaction with either OH or NO_3 radicals is greatly reduced.

OH Radical Reactions. Particle-Phase Products. The reaction of resorcinol with OH radicals in the presence of NO_x produced SOA with a yield of 0.86. The real-time particle mass spectra, shown in Figure 1A, display significant peaks at m/z171, 142, 126, 108, 97, 80, and 52. The peaks at m/z 126, 108, 97, 80, and 52 are assigned to the 1,2,3-benzenetriol and 1,2,4benzenetriol isomers [molecular weight (MW) of 126], both of which have significant peaks at these masses in the standard mass spectra shown in panels B and C of Figure 2.49 The presence of benzenetriols in the particles is consistent with predictions based on their (non-isomer-specific) saturation concentration (C*) of 50 μ g m⁻³ (calculated using SIMPOL.1³⁰), a mass concentration of particles of $\sim 1 \text{ mg}$ m⁻³, and gas-particle partitioning theory.⁵⁰ This product assignment is supported by the TPTD profiles presented in Figure 2A, which show a peak at 51 °C in the m/z 126 profile and peaks at 49 °C in the m/z 108 and 80 profiles. We note that bumps in the profiles at locations other than the maximum are artifacts of the smoothing procedure. The 2 °C difference in desorption temperatures is small but significant and consistent with the presence of two isomers with slightly different vapor pressures. Because hydrogen bonding between ortho hydroxyl groups on an aromatic ring increases compound vapor pressure,¹⁴ 1,2,3-benzenetriol is expected to be more volatile than 1,2,4-benzenetriol and, thus, desorb first. It is unlikely that 1,3,5-benzenetriol is also present, because the standard mass spectrum shown in Figure 1D indicates that significant peaks should also be present at m/z 111 and 85 but are not (Figure 1A). A proposed mechanism of formation of 1,2,3-benzenetriol and 1,2,4-benzenetriol as a result of 1,2- or 1,4-addition of the OH radical is shown in Scheme 1. The formation of 1,3,5-benzenetriol by 1,5-addition does not occur because electron-donating groups direct electrophilic aromatic substitution to ortho and para positions and the 1,5-addition is meta to both OH groups. This is reflected in the much smaller calculated rate coefficients for OH addition meta to electrondonating groups.³⁰ On the basis of the SOA mass yield of 0.86 and the dominance of benzenetriol in the particle mass spectrum, if we assume that the SOA contained only this compound, then (by multiplying by a resorcinol/benzenetriol MW ratio of 0.87), the upper limit for the molar yield of benzenetriol is 0.75. Although this value overestimates the yield, it provides a useful indication of the importance of benzenetriol as a product of this reaction.

The peak at m/z 171 is assigned to the M⁺ ions of nitrobenzenetriol isomers (MW of 171). The TPTD profile of this ion (Figure 2B), which peaks at 84 °C, is consistent with this assignment because nitrobenzenetriol ($C^* = 0.5 \ \mu g \ m^{-3}$) is less volatile than benzenetriol ($C^* = 50 \ \mu g \ m^{-3}$). One of the isomers was successfully isolated by HPLC and analyzed by CI–ITMS, leading to its assignment as 5-nitro-1,2,3-benzenetriol. The mass spectrum and peak assignments are shown in Figure S1 of the Supporting Information. The peaks at m/z 141 and 125 in Figure 1A are attributed to $[M - NO]^+$ and $[M - NO_2]^+$ ions, where loss of NO occurs by rearrangement to produce a C–O bond that is stabilized by resonance with the aromatic ring.⁵¹

The peak at m/z 142 in Figure 1A is assigned to the M⁺ ions of hydroxymuconic semialdehyde and benzenetetraol (MW of 142). On the basis of their C^{*} values of 80 and 0.3 μ g m⁻³,



Figure 2. TPTD profiles of SOA formed from the reaction of resorcinol with OH radicals in the presence of NO_x corresponding to (A) benzenetriol isomers, (B) nitrobenzenetriol isomers, (C) hydroxymuconic semialdehyde and benzenetetraol isomers, and (D) total ion signal. The dashed lines in panel D correspond to C* values of 100, 10, and 1 μ g m⁻³. Profiles were smoothed to better resolve desorption temperatures, and the signal from DOS seed particles was removed.

they should desorb in the same range as benzenetriol and nitrobenzenetriol, as observed, and exist predominantly in the particle phase. We speculate that hydroxymuconic semialdehyde was the greater contributor to this peak because it is a first-generation product, whereas benzenetetraol is a second-generation product formed from benzenetriol by a similar reaction to the reaction that formed benzenetriol (Scheme 1).

The peak at m/z 155 in Figure 1A is assigned to the M⁺ ions of the nitroresorcinol isomers (MW of 155). The low intensity of this signal is somewhat surprising, because 4-nitrocatechol was the dominant component of SOA formed in the OH radical reaction of catechol and existed entirely in the particle phase.²⁰ Because resorcinol and catechol are structural isomers, one might expect that similar products are produced with roughly similar yields and vapor pressures. This suggests that the OH radical reaction of resorcinol occurs by a different reaction mechanism than catechol and/or that the major nitroresorcinol isomers are much more volatile than 4nitrocatechol, as discussed below.

The thermal desorption profile of the total ion signal (TIS) of the SOA is shown in Figure 2D. Because the TIS is proportional to aerosol mass,⁵² this profile is effectively a volatility distribution of the SOA. The C^* scale at the top of the figure is based on a previously measured relationship between the desorption temperature and compound vapor pressure determined using a homologous series of linear alkanes with relatively well-known vapor pressures.²⁰ For reference, the C* values estimated from the peaks in the benzenetriol and nitrobenzenetriol profiles are 5 and 0.1 μ g m⁻³, which are about an order of magnitude lower than values of 50 and 0.5 μ g m⁻³ calculated using SIMPOL.1.³⁰ Considering the uncertainties in the calibration and the SIMPOL.1 calculations and the effects of the SOA matrix on desorption, the agreement suggests that the profile provides a reasonably quantitative representation of the volatility distribution. The long tail above ~100 °C is attributed mostly to material that desorbed at lower temperatures and then condensed onto cooler surfaces, only to desorb again as the vaporizer temperature increased. The dashed lines in the figure correspond to C* values of 100, 10, and 1 μ g m⁻³, indicating that, under a wide range of atmospheric conditions, a significant amount of aerosol should be formed from this reaction. For example, because only $\sim 25\%$ of the area under the curve is associated with material with C^* of >10 μ g m⁻³, an organic aerosol mass concentration typical of a polluted area,⁴ the SOA yield at such a location may not be much less than the value of 0.86 measured here. We also note that, from the area under the curve attributed to benzenetriol, the molar yield of this compound is probably closer to ~ 0.3 than 0.75, the maximum yield estimated above by assuming all of the SOA consisted of this compound.

Gas-Phase Products. Ions corresponding to gas-phase products formed from the reaction of resorcinol with OH radicals in the presence of NO_x were detected by PTR–MS at m/z 59, 89, 99, 125, 138, 141, and 156, as shown in Figure 3. The peak at m/z 62 is the $[M + H]^+$ ion from methyl nitrite (MW of 61), the OH radical source. The small peaks at m/z 156 and 138 can be assigned to the $[M + H]^+$ and $[M + H - H_2O]^+$ ions of nitroresorcinol isomers (MW of 155). Whereas the $[M + H]^+$ ion is indicative of any nitroresorcinol isomer, loss of H₂O is only observed in proton transfer reactions of nitroaromatics when a nitro group is *ortho* to a hydroxyl group,⁵³ although the elevated collision energy in PTR–MS typically makes the loss of H₂O more efficient. Nitroresorcinols are formed by abstraction of a phenolic H atom followed by



Figure 3. PTR–MS mass spectrum of gas-phase products formed from the reaction of resorcinol with OH radicals in the presence of NO_x . Chamber background peaks have been removed, and the m/z 62 peak corresponds to protonated methyl nitrite, the OH radical source.

reaction with NO₂ and rearrangement to restore aromaticity,⁴¹ as described above. The *o*-semiquinone radical formed by H atom abstraction produces favorable sites for NO₂ addition either *ortho* or *para* to the hydroxyl substituents, leading to the

formation of either 2-nitroresorcinol or 4-nitroresorcinol. A comparison of the HPLC retention time of a 2-nitroresorcinol standard to those of the products formed from reactions of resorcinol with OH radicals in the presence of NO_x and sampled with a denuder indicated that no 2-nitroresorcinol was present. It is therefore likely that the only nitroresorcinol produced from these reactions is 4-nitroresorcinol.

It is also interesting that 4-nitroresorcinol ($C^* = 1 \times 10^4 \,\mu g m^{-3}$) appears to be present in the gas phase and in particles in these reactions, because 4-nitrocatechol ($C^* = 10 \,\mu g m^{-3}$) was essentially only in the particle phase at the chamber concentrations observed in our previous experiments.²⁰ For 4-nitroresorcinol, hydroxyl and nitro groups are *ortho*-substituted, which can result in significant hydrogen bonding between the two groups through formation of a six-membered ring. This intramolecular interaction can significantly increase the vapor pressure of 4-nitroresorcinol compared to its isomer, 4-nitrocatechol. Similarly, Hatch et al.¹⁴ measured the gas–particle partitioning of benzenediol isomers from wood combustion and estimated that the vapor pressure of catechol (1,2-benzenediol) was a factor of 18 higher than hydroquinone (1,4-benzenediol), likely as a result of the hydrogen bonding



Figure 4. (A) PTR–MS time profiles of selected ions of gas-phase products formed from the reaction of resorcinol with OH radicals in the presence of NO_{x^r} (B) PTR–MS and TDPBMS time profiles of selected ions of gas- and particle-phase products formed from the reaction of resorcinol with OH radicals in the presence of NO_{x^r} with 1 ppm of NH_3 added 70 min after photo-oxidation was immediately stopped by turning off the lights. The profiles have been smoothed using the boxcar method.



Figure 5. (A) Real-time TDPBMS mass spectrum of SOA and (B) PTR–MS mass spectrum gas-phase products formed from the reaction of resorcinol with NO₃ radicals in the presence of NO₂. Contributions from DOS particles and chamber background peaks have been removed.

between the *ortho* hydroxyl groups. Although 4-nitrocatechol contains two *ortho*-substituted hydroxyl groups, the hydrogen bonding between nitro and hydroxyl groups is likely greater as a result of the formation of a six-membered ring when hydrogen bonded to the nitro group.

2-Hydroxy-1,4-benzoquinone (MW of 124, hereafter referred to as hydroxybenzoquinone) was observed as the dominant product in the gas phase, as indicated by the peak at m/z 125 from the $[M + H]^+$ ion (Figure 3). The m/z 125 peak has previously been attributed to this compound in laboratory experiments of biomass burning.⁵⁴ It was also observed in the CI-ITMS mass spectrum of the PFBHA-coated denuder sample and confirmed by the PFBHA-derivatized hydroxybenzoquinone standard shown in Figure S2 of the Supporting Information, with the peak at m/z 515 being a result of the [M + H]⁺ ion of a doubly derivatized dicarbonyl (MW of 124) with MW of 514. The presence of hydroxybenzoquinone in the gas phase is consistent with its C* value of $2 \times 10^4 \,\mu \text{g m}^{-3}$. As seen in Figure 4A, the concentration of hydroxybenzoquinone increased during photo-oxidation and continued to slowly increase after the lights were turned off. The vapor pressure of this compound can lead to substantial tubing delays in PTR-MS³⁹ and may contribute to some of the observed increase. However, because hydroxybenzoquinone and nitroresorcinol have similar vapor pressures, the observed increase in the hydroxybenzoquinone signal cannot be solely due to partitioning between the tubing and gas phase. The increase also cannot be due to continued OH radical reactions of resorcinol, because the OH radical concentration becomes negligible as soon as the blacklights are turned off. Instead, we postulate that this compound is formed by the heterogeneous oxidation of benzenetriol by HNO₃ (Scheme 1), which is formed in the chamber from the $OH + NO_2$ reaction. This same oxidation reaction has been shown to occur in biological systems.⁵⁵ To test this hypothesis, in one experiment, 1 ppm of NH₃ was added to the chamber 70 min after turning off the blacklights. NH₃ reacted rapidly with HNO₃ to form solid NH₄NO₃ (because the RH was <1%), which was detected as an increase in the m/z 46 (NO₂⁺) signal measured by TDPBMS and an increase in aerosol volume measured by SMPS. As shown in Figure 4B, removal of HNO₃ caused the gas-phase concentration of hydroxybenzoquinone to stop increasing, supporting the hypothesis that it was formed by the heterogeneous oxidation of benzenetriol by HNO_3 . The addition of NH_3 did not appear to affect gas-particle partitioning, formation, or loss of products other than NH_4NO_3 , because no significant changes were observed in any peaks in the TDPBMS mass spectrum other than m/z 46.

The peak at m/z 141 in Figure 3 is assigned to the $[M + H]^+$ ion of dihydroxybenzoquinone. This is a second-generation product, likely formed in the gas phase from hydroxybenzoquinone through a similar mechanism to the one that formed hydroxybenzoquinone (Scheme 1) and also heterogeneously by the oxidation of benzenetetraol by HNO₃ (where HNO₃ is reduced to NO₂⁻). Because of the high water solubility of HNO₃, this reaction may be more important at higher RH. Peaks at m/z 59, 89, and 99 are assigned to $[M + H]^+$ ions of the ring-opened products glyoxal (OHCCHO, with MW of 58), glucic acid [OHCCH(OH)CHO, with MW of 98], and maleic anhydride $[C_2H_2(CO)_2O$, with MW of 98], respectively, which have been identified in other studies of the oxidation of aromatic compounds from decomposition of the bicyclic radical.^{41,42}

NO₃ Radical Reactions. *Particle-Phase Products.* The reaction of resorcinol with NO₃ radicals produced SOA with a yield of 0.09, far less than the yield of 0.86 for the reaction with OH radicals. This can be explained by the differences in the reaction mechanisms (Scheme 1) and, thus, the products formed from each reaction. While reactions with OH radicals primarily involved addition to the aromatic ring to form a variety of low-volatility products, reactions with NO₃ radicals occurred solely by abstraction of a phenolic H atom to produce much more volatile nitroresorcinol and hydroxybenzoquinone products.

The only product observed in particles was nitroresorcinol (MW of 155), which was identified by peaks at m/z 69, 80, 97, 125, and 155 in the TDPBMS mass spectrum shown in Figure 5A. The peak at m/z 155 corresponds to the M⁺ ion, and the peaks at m/z 125, 97, 80, and 69 correspond to $[M - NO]^+$, $[M - NO - CO]^+$ ions. It is interesting to note the absence of an m/z 109 peak in this mass spectrum, which would correspond to the $[M - NO_2]^+$ ion. The National Institute of Standards and Technology (NIST) database contains a mass spectrum of 2-nitroresorcinol that contains m/z 109 but not m/z 125,⁴⁹ indicating that 2-nitroresorcinol is not produced in this reaction.

Gas-Phase Products. Nitroresorcinol was also observed in the gas phase, along with hydroxybenzoquinone (MW of 124). The peaks at m/z 156 and 138 in the PTR–MS mass spectrum shown in Figure 5B can be assigned to the $[M + H]^+$ and [M + $H - H_2O$ ⁺ ions of nitroresorcinol isomers, and as discussed above for the OH radical reaction, because the [M + H - H_2O]⁺ ion is only formed when the OH and NO₂ groups are ortho-substituted, the only possible isomer produced is 4nitroresorcinol. Hydroxybenzoquinone was identified by the peak at m/z 125, the same peak used to assign this compound as a product of the OH radical reaction (Figure 3). Unlike in that reaction, however, in the NO3 radical reaction none of hydroxybenzoquinone is formed heterogeneously, because the required benzenetriol precursor is only formed by OH radical addition to the aromatic ring. Nitric acid (MW of 63) is also observed as the $[M + H]^+$ ion at m/z 64, consistent with phenolic H atom abstraction by NO₃ radicals.

CONCLUSIONS AND ATMOSPHERIC IMPLICATIONS

The results of the experiments described here provide an improved understanding of the influence of isomer structure on the mechanisms and products of reactions of aromatic diols with atmospheric oxidants and subsequent SOA formation. It is useful in this regard to compare the results of this study to those obtained previously for similar reactions of catechol,²⁰ which is emitted from wildfires in significantly larger quantities than resorcinol and is also (unlike resorcinol) produced by OH radical-initiated reactions of phenol.^{42,56} Although these compounds both react with NO₃ radicals solely by abstraction of a phenolic H atom, in reactions with OH radicals, this pathway is more important for catechol than for resorcinol, which instead reacts more via OH radical addition to the aromatic ring.

Whereas the dominant product of OH and NO3 radicalinitiated reactions of catechol in the presence of NO_x was 4nitrocatechol (molar yields of 0.31 and 0.91, respectively),²⁰ reactions of resorcinol with OH radicals produced mostly benzenetriol, nitrobenzenetriol, and hydroxybenzoquinone, while reactions with NO3 radicals produced nitroresorcinol and hydroxybenzoquinone. In addition, hydroxybenzoquinone was apparently formed via heterogeneous oxidation of benzenetriol by HNO₃ in the OH radical reaction. This compound has been observed in small quantities as both a primary and secondary emission in laboratory biomass burning experiments,^{7,54} and although resorcinol is only observed in small quantities in such experiments,^{10,13} it is possible that resorcinol oxidation is responsible for hydroxybenzoquinone observed in wildfire plumes. Because catechol is typically present in far greater quantities than resorcinol in biomass burning emissions,^{11,14,15} atmospheric concentrations of 4nitrocatechol are much higher than those of the 4-nitroresorcinol isomer.

It also is interesting to compare the differences in the measured yields of SOA formed from the OH and NO₃ radical reactions of catechol and resorcinol. Differences are expected to be primarily a result of differences in the product vapor pressures, because no clear evidence was observed in TPTD profiles for low-volatility oligomers formed by multiphase reactions. Products with C* values less than the aerosol mass concentration in the chamber (~1 mg m⁻³) should be predominantly in particles, thus contributing to SOA formation in these experiments, whereas those with higher C* values should be predominantly in the gas phase. SOA yields should be somewhat lower in the atmosphere, where aerosol mass concentrations are lower and, thus, gas-particle partitioning is reduced. Although not all of the SOA products were identified and only the molar yield of benzenetriol could be estimated (~ 0.3), comparing C* values of the observed products to the aerosol mass concentration helps to explain the trends in the SOA yields.

In the OH radical reaction, the SOA yields were 1.34 for catechol²⁰ and 0.86 for resorcinol, a difference of a factor of ~1.5. SOA produced in the catechol reaction contained 4-nitrocatechol ($C^* = 80 \ \mu g \ m^{-3}$), the sole product of the H atom abstraction pathway, in addition to nitrobenzenetriol ($C^* = 0.5 \ \mu g \ m^{-3}$) and unidentified ring-opened products formed from OH radical addition pathways. SOA produced in the resorcinol reaction contained benzenetriol ($C^* = 50 \ \mu g \ m^{-3}$) and hydroxymuconic semialdehyde ($C^* = 80 \ \mu g \ m^{-3}$) formed

from OH addition pathways, while the hydroxybenzoquinone ($C^* = 2 \times 10^4 \ \mu g \ m^{-3}$) and nitroresorcinol ($C^* = 1 \times 10^4 \ \mu g \ m^{-3}$) products of H atom abstraction pathways formed very little or no SOA.

In contrast, in the NO₃ radical reactions, the SOA yields were 1.50 for catechol²⁰ and 0.09 for resorcinol, a difference of a factor of ~15. SOA produced from the catechol reaction consisted only of 4-nitrocatechol ($C^* = 80 \ \mu g \ m^{-3}$), which is formed by the H atom abstraction pathway and is the sole reaction product.¹⁹ Similarly, SOA produced in the resorcinol reaction consisted only of 4-nitroresorcinol ($C^* = 1 \times 10^4 \,\mu g$ m^{-3}), although it was not the sole reaction product. Hydroxybenzoquinone ($C^* = 2 \times 10^4 \ \mu g \ m^{-3}$) was also formed but was only observed in the gas phase, along with 4nitroresorcinol. For the NO3 radical reactions, the lower SOA yield from resorcinol can thus be attributed to two factors: the formation of hydroxybenzoquinone, which is very volatile and not formed in the catechol reaction, and the high vapor pressure of nitroresorcinol compared to nitrocatechol. The difference in the vapor pressures of these isomers is due to the location of the nitro group, which is ortho to a hydroxyl group in 4-nitroresorcinol but meta and para relative to the hydroxyl groups in 4-nitrocatechol. The ortho configuration increases intramolecular hydrogen bonding, thus increasing the vapor pressure and reducing the extent of gas-particle partitioning of 4-nitroresorcinol compared to 4-nitrocatechol. The differences in SOA yields between these two benzenediol isomers highlight the importance of understanding mechanisms of VOC oxidation reactions and the need for chemical speciation in field studies to accurately quantify and constrain SOA formation in the atmosphere.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsearthspace-chem.9b00112.

Mass spectra of 5-nitro-1,2,3-benzenetriol (Figure S1) and PFBHA-derivatized hydroxybenzoquinone (Figure S2) (PDF)

AUTHOR INFORMATION

Corresponding Author

*Telephone: 303-492-9654. Fax: 303-492-1149. E-mail: paul. ziemann@colorado.edu.

ORCID 🔍

Joost A. de Gouw: 0000-0002-0385-1826 Paul J. Ziemann: 0000-0001-7419-0044

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based on work supported by the National Science Foundation (NSF) under Grants AGS-1740610 and AGS-1420007.

REFERENCES

(1) de Gouw, J.; Jimenez, J. L. Organic Aerosols in the Earth's Atmosphere. *Environ. Sci. Technol.* **2009**, *43*, 7614–7618.

(2) Akagi, S. K.; Yokelson, R. J.; Wiedinmyer, C.; Alvarado, M. J.; Reid, J. S.; Karl, T.; Crounse, J. D.; Wennberg, P. O. Emission Factors for Open and Domestic Biomass Burning for Use in Atmospheric Models. *Atmos. Chem. Phys.* 2011, 11, 4039-4072.

(3) Val Martin, M.; Logan, J. A.; Kahn, R. A.; Leung, F.-Y.; Nelson, D. L.; Diner, D. J. Smoke Injection Heights from Fires in North America: Analysis of 5 Years of Satellite Observations. *Atmos. Chem. Phys.* **2010**, *10*, 1491–1510.

(4) Zhang, Q.; Jimenez, J. L.; Canagaratna, M. R.; Allan, J. D.; Coe, H.; Ulbrich, I.; Alfarra, M. R.; Takami, A.; Middlebrook, A. M.; Sun, Y. L.; Dzepina, K.; Dunlea, E.; Docherty, K.; DeCarlo, P. F.; Salcedo, D.; Onasch, T.; Jayne, J. T.; Miyoshi, T.; Shimono, A.; Hatakeyama, S.; Takegawa, N.; Kondo, Y.; Schneider, J.; Drewnick, F.; Borrmann, S.; Weimer, S.; Demerjian, K.; Williams, P.; Bower, K.; Bahreini, R.; Cottrell, L.; Griffin, R. J.; Rautiainen, J.; Sun, J. Y.; Zhang, Y. M.; Worsnop, D. R. Ubiquity and Dominance of Oxygenated Species in Organic Aerosols in Anthropogenically-Influenced Northern Hemisphere Midlatitudes. *Geophys. Res. Lett.* **2007**, *34*, L13801.

(5) Ortega, A. M.; Day, D. A.; Cubison, M. J.; Brune, W. H.; Bon, D.; de Gouw, J. A.; Jimenez, J. L. Secondary Organic Aerosol Formation and Primary Organic Aerosol Oxidation from Biomass-Burning Smoke in a Flow Reactor during FLAME-3. *Atmos. Chem. Phys.* **2013**, *13*, 11551–11571.

(6) Bruns, E. A.; Krapf, M.; Orasche, J.; Huang, Y.; Zimmermann, R.; Drinovec, L.; Močnik, G.; El-Haddad, I.; Slowik, J. G.; Dommen, J.; Baltensperger, U.; Prévot, A. S. H. Characterization of Primary and Secondary Wood Combustion Products Generated under Different Burner Loads. *Atmos. Chem. Phys.* **2015**, *15*, 2825–2841.

(7) Tiitta, P.; Leskinen, A.; Hao, L.; Yli-Pirilä, P.; Kortelainen, M.; Grigonyte, J.; Tissari, J.; Lamberg, H.; Hartikainen, A.; Kuuspalo, K.; Kortelainen, A.-M.; Virtanen, A.; Lehtinen, K. E. J.; Komppula, M.; Pieber, S.; Prévot, A. S. H.; Onasch, T. B.; Worsnop, D. R.; Czech, H.; Zimmermann, R.; Jokiniemi, J.; Sippula, O. Transformation of Logwood Combustion Emissions in a Smog Chamber: Formation of Secondary Organic Aerosol and Changes in the Primary Organic Aerosol upon Daytime and Nighttime Aging. *Atmos. Chem. Phys.* **2016**, *16*, 13251–13269.

(8) Bertrand, A.; Stefenelli, G.; Jen, C. N.; Pieber, S. M.; Bruns, E. A.; Ni, H.; Temime-Roussel, B.; Slowik, J. G.; Goldstein, A. H.; El Haddad, I.; Baltensperger, U.; Prévot, A. S. H.; Wortham, H.; Marchand, N. Evolution of the Chemical Fingerprint of Biomass Burning Organic Aerosol during Aging. *Atmos. Chem. Phys.* **2018**, *18*, 7607–7624.

(9) Hecobian, A.; Liu, Z.; Hennigan, C. J.; Huey, L. G.; Jimenez, J. L.; Cubison, M. J.; Vay, S.; Diskin, G. S.; Sachse, G. W.; Wisthaler, A.; Mikoviny, T.; Weinheimer, A. J.; Liao, J.; Knapp, D. J.; Wennberg, P. O.; Kürten, A.; Crounse, J. D.; St. Clair, J.; Wang, Y.; Weber, R. J. Comparison of Chemical Characteristics of 495 Biomass Burning Plumes Intercepted by the NASA DC-8 Aircraft during the ARCTAS/ CARB-2008 Field Campaign. *Atmos. Chem. Phys.* **2011**, *11*, 13325–13337.

(10) Bruns, E. A.; El Haddad, I.; Slowik, J. G.; Kilic, D.; Klein, F.; Baltensperger, U.; Prévôt, A. S. H. Identification of Significant Precursor Gases of Secondary Organic Aerosols from Residential Wood Combustion. *Sci. Rep.* **2016**, *6*, 27881.

(11) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. Measurement of Emissions from Air Pollution Sources. 3. C1-C29 Organic Compounds from Fireplace Combustion of Wood. *Environ. Sci. Technol.* **2001**, *35*, 1716–1728.

(12) Wang, Z.; Bi, X.; Sheng, G.; Fu, J. Characterization of Organic Compounds and Molecular Tracers from Biomass Burning Smoke in South China I: Broad-Leaf Trees and Shrubs. *Atmos. Environ.* **2009**, 43, 3096–3102.

(13) Veres, P.; Roberts, J. M.; Burling, I. R.; Warneke, C.; de Gouw, J.; Yokelson, R. J. Measurements of Gas-Phase Inorganic and Organic Acids from Biomass Fires by Negative-Ion Proton-Transfer Chemical-Ionization Mass Spectrometry. *J. Geophys. Res.: Atmos.* **2010**, *115*, D23302.

(14) Hatch, L. E.; Rivas-Ubach, A.; Jen, C. N.; Lipton, M.; Goldstein, A. H.; Barsanti, K. C. Measurements of I/SVOCs in Biomass-Burning Smoke Using Solid-Phase Extraction Disks and Two-Dimensional Gas Chromatography. Atmos. Chem. Phys. 2018, 18, 17801–17817.

(15) Alves, C. A.; Vicente, A.; Monteiro, C.; Gonçalves, C.; Evtyugina, M.; Pio, C. Emission of Trace Gases and Organic Components in Smoke Particles from a Wildfire in a Mixed-Evergreen Forest in Portugal. *Sci. Total Environ.* **2011**, *409*, 1466–1475.

(16) Smith, J. D.; Kinney, H.; Anastasio, C. Aqueous Benzene-Diols React with an Organic Triplet Excited State and Hydroxyl Radical to Form Secondary Organic Aerosol. *Phys. Chem. Chem. Phys.* **2015**, *17*, 10227–10237.

(17) Schnitzler, E. G.; Abbatt, J. P. D. Heterogeneous OH Oxidation of Secondary Brown Carbon Aerosol. *Atmos. Chem. Phys.* **2018**, *18*, 14539–14553.

(18) Nakao, S.; Clark, C.; Tang, P.; Sato, K.; Cocker, D. Secondary Organic Aerosol Formation from Phenolic Compounds in the Absence of NO_x . *Atmos. Chem. Phys.* **2011**, *11*, 10649–10660.

(19) Borrás, E.; Tortajada-Genaro, L. A. Secondary Organic Aerosol Formation from the Photo-Oxidation of Benzene. *Atmos. Environ.* **2012**, 47, 154–163.

(20) Finewax, Z.; de Gouw, J. A.; Ziemann, P. J. Identification and Quantification of 4-Nitrocatechol Formed from OH and NO_3 Radical-Initiated Reactions of Catechol in Air in the Presence of NO_x : Implications for Secondary Organic Aerosol Formation from Biomass Burning. *Environ. Sci. Technol.* **2018**, *52*, 1981–1989.

(21) Matsunaga, A.; Ziemann, P. J. Gas-Wall Partitioning of Organic Compounds in a Teflon Film Chamber and Potential Effects on Reaction Product and Aerosol Yield Measurements. *Aerosol Sci. Technol.* **2010**, *44*, 881–892.

(22) Yeh, G. K.; Ziemann, P. J. Gas-Wall Partitioning of Oxygenated Organic Compounds: Measurements, Structure-Activity Relationships, and Correlation with Gas Chromatographic Retention Factor. *Aerosol Sci. Technol.* **2015**, *49*, 727–738.

(23) Krechmer, J. E.; Pagonis, D.; Ziemann, P. J.; Jimenez, J. L. Quantification of Gas-Wall Partitioning in Teflon Environmental Chambers Using Rapid Bursts of Low-Volatility Oxidized Species Generated in Situ. *Environ. Sci. Technol.* **2016**, *50*, 5757–5765.

(24) Huang, Y.; Zhao, R.; Charan, S. M.; Kenseth, C. M.; Zhang, X.; Seinfeld, J. H. Unified Theory of Vapor-Wall Mass Transport in Teflon-Walled Environmental Chambers. *Environ. Sci. Technol.* **2018**, *52*, 2134–2142.

(25) Palm, B. B.; Campuzano-Jost, P.; Ortega, A. M.; Day, D. A.; Kaser, L.; Jud, W.; Karl, T.; Hansel, A.; Hunter, J. F.; Cross, E. S.; Kroll, J. H.; Peng, Z.; Brune, W. H.; Jimenez, J. L. In Situ Secondary Organic Aerosol Formation from Ambient Pine Forest Air Using an Oxidation Flow Reactor. *Atmos. Chem. Phys.* **2016**, *16*, 2943–2970.

(26) Hunter, J. F.; Day, D. A.; Palm, B. B.; Yatavelli, R. L. N.; Chan, A. W. H.; Kaser, L.; Cappellin, L.; Hayes, P. L.; Cross, E. S.; Carrasquillo, A. J.; Campuzano-Jost, P.; Stark, H.; Zhao, Y.; Hohaus, T.; Smith, J. N.; Hansel, A.; Karl, T.; Goldstein, A. H.; Guenther, A.; Worsnop, D. R.; Thornton, J. A.; Heald, C. L.; Jimenez, J. L.; Kroll, J. H. Comprehensive Characterization of Atmospheric Organic Carbon at a Forested Site. *Nat. Geosci.* **2017**, *10*, 748–753.

(27) Taylor, W. D.; Allston, T. D.; Moscato, M. J.; Fazekas, G. B.; Kozlowski, R.; Takacs, G. A. Atmospheric Photodissociation Lifetimes for Nitromethane, Methyl Nitrite, and Methyl Nitrate. *Int. J. Chem. Kinet.* **1980**, *12*, 231–240.

(28) Atkinson, R.; Plum, C. N.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N. Rate Constants for the Gas-Phase Reactions of Nitrate Radicals with a Series of Organics in Air at 298 \pm 1 K. *J. Phys. Chem.* **1984**, *88*, 1210–1215.

(29) Machado, F.; Boule, P. Phototransformation of Resorcinol Induced by Excitation of Nitrite and Nitrate Ions. II: Nitrate Ions. *Toxicol. Environ. Chem.* **1994**, *42*, 165–173.

(30) Pankow, J. F.; Asher, W. E. SIMPOL.1: A Simple Group Contribution Method for Predicting Vapor Pressures and Enthalpies of Vaporization of Multifunctional Organic Compounds. *Atmos. Chem. Phys.* **2008**, *8*, 2773–2796.

(31) Atkinson, R. Atmospheric Lifetimes of Dibenzo-p-Dioxins and Dibenzofurans. *Sci. Total Environ.* **1991**, *104*, 17–33.

(32) Olariu, R. I.; Barnes, I.; Becker, K. H.; Klotz, B. Rate Coefficients for the Dihydroxybenzenes and Radicals with Selected Gas-Phase Reaction of OH Benzoquinones. *Int. J. Chem. Kinet.* **2000**, 32, 696–702.

(33) Lim, Y. B.; Ziemann, P. J. Kinetics of the Heterogeneous Conversion of 1,4-Hydroxycarbonyls to Cyclic Hemiacetals and Dihydrofurans on Organic Aerosol Particles. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8029–8039.

(34) Tobias, H. J.; Kooiman, P. M.; Docherty, K. S.; Ziemann, P. J. Real-Time Chemical Analysis of Organic Aerosols Using a Thermal Desorption Particle Beam Mass Spectrometer. *Aerosol Sci. Technol.* **2000**, 33, 170–190.

(35) Tobias, H. J.; Ziemann, P. J. Compound Identification in Organic Aerosols Using Temperature-Programmed Thermal Desorption Particle Beam Mass Spectrometry. *Anal. Chem.* **1999**, *71*, 3428– 3435.

(36) Docherty, K. S.; Ziemann, P. J. Effects of Stabilized Criegee Intermediate and OH Radical Scavengers on Aerosol Formation from Reactions of β -Pinene with O3. *Aerosol Sci. Technol.* **2003**, *37*, 877–891.

(37) Ranney, A. P.; Ziemann, P. J. Identification and Quantification of Oxidized Organic Aerosol Compounds Using Derivatization, Liquid Chromatography, and Chemical Ionization Mass Spectrometry. *Aerosol Sci. Technol.* **2017**, *51*, 342–353.

(38) de Gouw, J.; Warneke, C. Measurements of Volatile Organic Compounds in the Earth's Atmosphere Using Proton-Transfer-Reaction Mass Spectrometry. *Mass Spectrom. Rev.* **2007**, *26*, 223–257. (39) Pagonis, D.; Krechmer, J. E.; De Gouw, J.; Jimenez, J. L.; Ziemann, P. J. Effects of Gas-Wall Partitioning in Teflon Tubing and Instrumentation on Time-Resolved Measurements of Gas-Phase Organic Compounds. *Atmos. Meas. Tech.* **2017**, *10*, 4687–4696.

(40) Yeh, G. K.; Claflin, M. S.; Ziemann, P. J. Products and Mechanism of the Reaction of 1-Pentadecene with NO3 Radicals and the Effect of a -ONO2 Group on Alkoxy Radical Decomposition. *J. Phys. Chem. A* **2015**, *119*, 10684–10696.

(41) Atkinson, R.; Aschmann, S. M.; Arey, J. Reactions of OH and NO3 Radicals with Phenol, Cresols, and 2-Nitrophenol at 296 ± 2 K. *Environ. Sci. Technol.* **1992**, *26*, 1397–1403.

(42) Volkamer, R.; Klotz, B.; Barnes, I.; Imamura, T.; Wirtz, K.; Washida, N.; Becker, K. H.; Platt, U. OH-Initiated Oxidation of Benzene: Part I. Phenol Formation under Atmospheric Conditions. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1598–1610.

(43) Klotz, B.; Volkamer, R.; Hurley, M. D.; Andersen, M. P. S.; Nielsen, O. J.; Barnes, I.; Imamura, T.; Wirtz, K.; Becker, K. H.; Platt, U.; Wallington, T. J.; Washida, N. OH-Initiated Oxidation of Benzene Part II. Influence of Elevated NO x Concentrations. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4399–4411.

(44) Ziemann, P. J.; Atkinson, R. Kinetics, Products, and Mechanisms of Secondary Organic Aerosol Formation. *Chem. Soc. Rev.* 2012, *41*, 6582–6605.

(45) Vereecken, L.; Peeters, J. Decomposition of Substituted Alkoxy Radicals—Part I: A Generalized Structure-Activity Relationship for Reaction Barrier Heights. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9062– 9074.

(46) Vereecken, L.; Peeters, J. A Structure-Activity Relationship for the Rate Coefficient of H-Migration in Substituted Alkoxy Radicals. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12608–12620.

(47) Atkinson, R.; Aschmann, S. M. Rate Constants for the Gas-Phase Reactions of the OH Radical with the Cresols and Dimethylphenols at 296 ± 2 K. *Int. J. Chem. Kinet.* **1990**, *22*, 59–67. (48) Bejan, I.; Barnes, I.; Olariu, R. I.; Zhou, S.; Wiesen, P.; Benter, T. Investigations on the Gas-Phase Photolysis and OH Radical Kinetics of Methyl-2-Nitrophenols. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5686–5692.

(49) https://webbook.nist.gov/ (accessed April 10, 2019).

(50) Donahue, N. M.; Robinson, A. L.; Stanier, C. O.; Pandis, S. N. Coupled Partitioning, Dilution, and Chemical Aging of Semivolatile Organics. *Environ. Sci. Technol.* **2006**, *40*, 2635–2643.

ACS Earth and Space Chemistry

(51) McLafferty, F. W.; Tureek, F. Interpretation of Mass Spectra, 4th ed.; University Science Books: Herndon, VA, 1993.

(52) Crable, G. F.; Coggeshall, N. D. Application of Total Ionization Principles to Mass Spectrometric Analysis. *Anal. Chem.* **1958**, *30*, 310–313.

(53) Harrison, A. G.; Kallury, R. K. M. R. Chemical Ionization Mass-Spectra of Mononitroarenes. *Org. Mass Spectrom.* **1980**, *15*, 284–288.

(54) Koss, A. R.; Sekimoto, K.; Gilman, J. B.; Selimovic, V.; Coggon, M. M.; Zarzana, K. J.; Yuan, B.; Lerner, B. M.; Brown, S. S.; Jimenez, J. L.; Krechmer, J.; Roberts, J. M.; Warneke, C.; Yokelson, R. J.; de Gouw, J. Non-Methane Organic Gas Emissions from Biomass Burning: Identification, Quantification, and Emission Factors from PTR-ToF during the FIREX 2016 Laboratory Experiment. *Atmos. Chem. Phys.* **2018**, *18*, 3299–3319.

(55) Philipp, B.; Schink, B. Evidence of Two Oxidative Reaction Steps Initiating Anaerobic Degradation of Resorcinol (1,3-Dihydroxybenzene) by the Denitrifying Bacterium *Azoarcus anaerobius*. *J. Bacteriol.* **1998**, *180*, 3644–3649.

(56) Olariu, R. I.; Klotz, B.; Barnes, I.; Becker, K. H.; Mocanu, R. FT-IR Study of the Ring-Retaining Products from the Reaction of OH Radicals with Phenol, *o-*, *m-*, and *p-*Cresol. *Atmos. Environ.* **2002**, *36*, 3685–3697.