Experimental and theoretical studies on gas-phase reactions of NO₃ radicals with three methoxyphenols: Guaiacol, creosol, and syringol

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HIGHLIGHTS

- Reaction products of NO₃ radical with three methoxyphenols are obtained.
- Nitro-substituted derivatives are observed as major transformation products.
- Reaction mechanisms of methoxyphenols with NO₃ radicals are proposed.
- The rate constants of three methoxyphenols with NO₃ radicals are measured.

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ABSTRACT

Methoxyphenols, lignin pyrolysis products, are major biomass combustion components and are considered potential tracers for wood smoke emissions. Their atmospheric reactivity, however, has not been well characterized. Guaiacol, creosol, and syringol are three typical methoxyphenols generated in relatively high concentrations in fresh wood smoke. In this study, the gas-phase reactions of NO₃ radicals with these methoxyphenols were investigated using a laboratory-built vacuum ultraviolet photoionization gas time-of-flight mass spectrometer (VUV-GTOFMS) and off-line GC-MS. By combining experimental and theoretical methods, 4-nitroguaiacol, 6-nitroguaiacol, and 4,6-dinitroguaiacol were determined as the primary degradation products for guaiacol; similarly, 6-nitrocreosol and 3-nitrosyringol were identified for creosol and syringol, respectively. Using the relative rate method, rate constants at 298 K and 1 atm for the gas-phase reactions of guaiacol, creosol, and syringol with NO₃ radicals were measured to be 3.2×10^{-12} , 2.4×10^{-13} , and 4.0×10^{-13} cm³ molecule⁻¹ s⁻¹, respectively. At a typical tropospheric concentration of NO₃ radicals (5×10^8 molecule cm⁻³), atmospheric lifetimes for guaiacol, creosol, and syringol toward NO₃ radicals were 0.2, 2.3, and 1.4 h, respectively. These results indicate that the reaction with NO₃ radicals can be a major sink for methoxyphenols at night.

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1. Introduction

Biomass combustion is a major global source of gas- and particle-phase air pollutants, and thus has an important impact on human health (Lighty et al., 2000), regional and global air quality (Lelieveld et al., 2001), and climate (Langmann et al., 2009; Chen and Bond, 2010). Biomass combustion generates nearly 90% of the total global primary organic aerosol (POA) emissions (Bond et al., 2004) and also creates a vast quantity of gas-phase organic mate-

rials. Some of these gas-phase organics react in the atmosphere to form secondary organic aerosols (SOA) (Hennigan et al., 2011). Natural wood is a complex material consisting of two major chemical components, carbohydrates (40–50%) and lignin (18–35%) (Nolte et al., 2001; Schauer et al., 2001). Combustion of wood and other biomasses produces substantial amounts of methoxyphenols arising from the pyrolysis of lignin, which produces methoxyphenols at an emission rate of 900–4200 mg kg⁻¹ biomass (Hawthorne et al., 1989; Rogge et al., 1998; Schauer et al., 2001).

Most of the methoxyphenols produced from the pyrolysis of lignin are guaiacol and syringol derivatives (Hawthorne et al., 1989; Hays et al., 2002; Re-Poppi and Santiago-Silva, 2002; Simpson et al., 2005; Mazzoleni et al., 2007). Since methoxyphenols are unique to biomass combustion (Hawthorne et al., 1988, 1989; Stanley and Simoneit, 1990; Simoneit et al., 1993), they have been

Abbreviations: DFT, density functional theory; IRC, intrinsic reaction coordinate; POA, primary organic aerosol; SOA, secondary organic aerosol; VUV-GTOFMS, vacuum ultraviolet photoionization gas time-of-flight mass spectrometer.

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considered as possible atmospheric wood smoke pollution tracers (Hawthorne et al., 1988, 1989; Simoneit et al., 1993). Guaiacol (2-methoxyphenol), creosol (4-methylguaiacol), and syringol (2,6-dimethoxyphenol) are the three methoxyphenols found at the highest concentrations in fresh wood smoke (Schauer et al., 2001). Their molecular structures and the labeled numbers on the aromatic ring are shown in Table 1. Due to the relatively high vapor pressures of guaiacol, creosol, and syringol at 25 °C (21, 8.1, and 0.45 Pa, respectively) (Sagebiel and Seiber, 1993), these compounds exist mainly in the gas-phase in the atmosphere (Schauer et al., 2001; Hays et al., 2002; Mazzoleni et al., 2007). These gaseous materials can be chemically modified by reaction with atmospheric oxidants. As a result, the atmospheric lifetimes of these compounds, and hence the ability to use them as wood smoke tracers, are largely dependent upon their gas-phase reactivities.

Studies on the gas-phase atmospheric reactions of methoxyphenols are scarce, however. In one study, Lauraguais and Coeur-Tourneur et al. determined the rate constants and oxidation products of the gas-phase reaction between guaiacol, creosol, and syringol, and the OH radical (Coeur-Tourneur et al., 2010; Lauraguais et al., 2012, 2014b). The results revealed that the atmospheric lifetime of these compounds when reacting with OH radicals was about 2 h, and the primary products for the reaction of guaiacol and syringol with OH radicals were nitro derivatives. The gas-phase rate constants for the reaction of chlorine atoms with different methoxyphenols were also investigated, and the results showed that their atmospheric lifetimes were in a range of 12–21 h (Lauraguais et al., 2014a). In addition, the aqueous-phase photolysis, or radical-initiated reaction, between guaiacol and phenols forming SOAs have been reported (Kitanovski et al., 2014; Yu et al., 2014). The nitro-products were identified, and they are suspected constituents of atmospheric “brown” carbons. Other studies have been published on the heterogeneous ozonolysis of methoxyphenols adsorbed on silica particles (Net et al., 2010a, 2010b, 2011), aqueous-phase ozonolysis of methoxyphenols in solutions (Khudoshin et al., 2008; Ko et al., 2011), heterogeneous nitration of suspended methoxyphenol particles by reaction with NO₃ radicals (Liu et al., 2012), and heterogeneous oxidation kinetics of biomass-burning aerosol surrogates reacting with a series of atmospheric oxidants (Knopf et al., 2011). To the best of our knowledge, no study on the gas-phase reactions of methoxyphenols with NO₃ radicals has been reported, nor have their reaction mechanisms been delineated so far.

The NO₃ radical is one of the most important oxidants in the atmosphere, controlling the chemistry of the nighttime troposphere (Wayne et al., 1991). In the present work, the gas-phase reactions between guaiacol, creosol, and syringol, and NO₃ radicals were studied. Formation of the products and the decay of reactants were monitored on-line using a laboratory-built vacuum ultraviolet photoionization gas time-of-flight mass spectrometer (VUV-GTOFMS). This apparatus can produce the mass spectrum of organic gasses with less fragmentation, which has obvious advantages in the study of gas-phase organic reactions. The second-order rate constants for the reaction of methoxyphenols with NO₃ radicals at room temperature (298 ± 2 K) and 1 atm pressure were obtained using a relative rate method. With the aid of an off-line gas chromatography-mass spectrometer (GC-MS) and quantum chemistry methods, the predominating products were determined, and chemical reaction mechanisms were developed.

2. Experiment

2.1. Materials and equipment

The experimental setup was composed of an 180-L reaction chamber, an N₂O₅ vapor manipulator, and analytical instruments.

The reaction chamber consists of a open head stainless steel drum (50 cm (diameter) × 60 cm (height)) and a Tedlar polyvinyl fluoride (PVF) film bag (50 cm (diameter) × 50 cm (length)). A small fan placed at the bottom of the chamber is used to mix reactants rapidly. The N₂O₅ vapor manipulator has been described elsewhere (Zhang et al., 2014). The analytical instrumentation included the lab-built VUV-GTOFMS, a Vaisala Humicap (HMM100) humidifier, and a GC-MS (Agilent 6890). Gas-phase organic materials injected into the chamber were sampled directly with the VUV-GTOFMS through a copper tube, which was heated to ~373 K to reduce condensation loss of the gas-phase organic samples. In the VUV-GTOFMS, organic vapors were photoionized with a VUV light radiated from an RF-powered krypton lamp. The photon flux was ~5 × 10¹⁴ photon s⁻¹, and the photon energy was ~10 eV. Each time-of-flight mass spectrum takes 10 s for acquisition and 1 s for data file storage. The detection limit of the VUV-GTOFMS is 0.2 ppbv (parts per billion by volume) to guaiacol. The relative humidity in the reaction chamber measured by a Vaisala Humicap was 10 ± 3% at 298 ± 2 K and 1 atm. N₂O₅ was synthesized by dehydrating concentrated nitric acid (Yang et al., 2011) and kept in a liquid nitrogen cold trap before use.

2.2. Methods

Before each experiment, the reaction chamber was filled with filtered air. The filtered air was passed through activated carbon and silica gel to control the relative humidity of the chamber, and to remove airborne particles ensuring the mass concentration less than 0.5 μg m⁻³. Since the concentration of NO₃ radicals cannot be directly monitored with our instruments, the rate coefficients of the gas-phase reaction between the methoxyphenols and NO₃ radicals were determined by a relative rate method. The NO₃ exposure ($\overline{C_{NO_3}t}$) was derived from the measured decay of the reference gases using the following equation:

$$\frac{\ln(C_{ref}/C_{ref0})}{-k_{ref}} = \int_0^t C_{NO_3} dt = \overline{C_{NO_3}t} \quad (1)$$

where C_{ref} and C_{ref0} are the time-dependent and initial concentrations of the reference gas, and k_{ref} is the reaction rate constant for the reaction of gas-phase reference gas and NO₃ radicals. After several preliminary screening experiments, 2-methyl-2-butene was selected as the reference compound for guaiacol due to the rapid decay rate of guaiacol in the reaction experiment, whereas isoprene was chosen for creosol and syringol. The reported rate constants of 2-methyl-2-butene and isoprene with NO₃ radical are (5.1 ± 1.6) × 10⁻¹² and (7.0 ± 2.0) × 10⁻¹³ cm³ molecule⁻¹ s⁻¹, respectively (<http://www.iupac-kinetic.ch.cam.ac.uk/>; Atkinson et al., 1984). The rate constant of methoxyphenol (k_m) is expressed in the following equation:

$$\ln(C_m/C_{m0}) = -k_m \overline{C_{NO_3}t} \quad (2)$$

where C_m and C_{m0} are the time-dependent and initial concentrations of methoxyphenols.

In the kinetic experiments, ~10 μL of a dichloromethane solution containing methoxyphenol or reference compound (0.4 mol L⁻¹) was injected into the reaction chamber separately. Assuming it volatilized completely, the concentration of the individual methoxyphenol and reference compound was calculated to be ~500 ppbv using its known total mass and the known volume of the reaction chamber. The signal intensities of methoxyphenol and the reference compound were monitored simultaneously

Table 1Products Observed by VUV-GTOFMS and GC-MS from the NO₃ radical Reaction with Methoxyphenols.

Reactant	Oxidation product	MW	Structure	Retention time (min)	η
Guaiacol (MW 124)	Catechol	110		–	–
	1,2-Dimethoxybenzene	138		21.9	<0.01
	Methoxybenzoquinone	138		24.3	0.02
	2-Methoxynitrobenzene	153		–	–
	6-Nitroguaiacol ^b	169		28.0	0.49
	4-Nitroguaiacol ^{a,b}	169		30.9	1
	4,6-diNitroguaiacol ^c	214		37.5	0.04
Creosol (MW 138)	4-Methylcatechol	124		–	–
	3,4-Dimethoxytoluene	152		24.1	<0.01
	2-Nitro-5-methylanisole	167		26.5	<0.01
	6-Nitrocreosol ^b	183		30.3	1
Syringol (MW 154)	3-Methoxycatechol	140		–	–
	1,2,3-Trimethoxybenzene ^d	168		25.8	<0.01
	2,6-Dimethoxynitrobenzene	183		30.2	0.04
	2,6-Dimethoxyquinone ^c	168		31.7	0.49

(continued on next page)

Table 1 (continued)

Reactant	Oxidation product	MW	Structure	Retention time (min)	η
	3-Nitrosyringol ^b	199		38.0	1

“–” represents the product not detected by the GC-MS.

η The relative signal intensities of the products obtained by GC-MS.

^a Confirmed by analysis of the commercial standard.

^b Confirmed by DFT theoretical calculation.

^c Compared with the available mass spectra in the NIST 2005 library (match rate >95%).

^d Compared with the available mass spectra in the NIST 2005 library (match rate >80%).

using the VUV-GTOFMS until they stabilized. Subsequently, N_2O_5 was eluted by passing a stream of N_2 (0.5 L min^{-1}) over the N_2O_5 crystals held in a cooling bath (233 K), and then introduced into the chamber. NO_3 and NO_2 were generated by the thermal decomposition of N_2O_5 under a chamber temperature of 298 K. At the same time, the decay of methoxyphenol and the reference compound was measured online using the VUV-GTOFMS to obtain kinetic data. The duration of the kinetic experiments is within 5 min. The reliability of the experimental method and setup was evaluated using 1,4-cyclohexadiene of which the rate coefficient was established in the literature. The reaction rate constant of 1,4-cyclohexadiene obtained from triplicate measurements with isoprene as reference compound was $(6.2 \pm 1.9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which covers the published value, $6.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Wayne et al., 1991).

In the experiments for determining the reaction products, only methoxyphenol was injected into the reaction chamber at a relatively high concentration ($\sim 2.0 \text{ ppmv}$). N_2O_5 was introduced into the chamber under the same conditions as used in the kinetic experiments. Formation of the oxidation products was analyzed online using the VUV-GTOFMS. The reaction lasted 3–6 min. After the reaction, both gas- and particle-phase substances in the reaction chamber were collected by liquid nitrogen washing. The collection apparatus was described in a previous study (Zhang et al., 2014). The reaction products were then dissolved in $\sim 5 \text{ mL}$ dichloromethane, extracted by sonication and analyzed immediately by GC-MS. Analytical procedures for use of the GC-MS and a list of chemicals used in this study are provided in the Supporting Information (SI).

2.3. Computational method

All calculations were performed using the Gaussian 09 program (Frisch et al., 2009). Geometry optimization and frequency analysis of the reactants, intermediates, transition states, and products were conducted using density functional theory (DFT) at the B3LYP/6-31 + G(d,p) level. For each transition state, the intrinsic reaction coordinate (IRC) calculation was performed to verify that the transition state connected the correct intermediate structures. Flexible potential energy surface scanning was conducted to confirm that H-abstraction from hydroxyl groups was a barrierless pathway.

3. Results and discussions

3.1. Rate constants

The wall losses of gaseous methoxyphenols and the reference compounds were ignored because no changes were detected in their concentrations within 5 min in the absence of NO_3 radicals.

By plotting $\ln(C_m/C_{m0})$ versus NO_3 exposure ($\overline{C_{\text{NO}_3}}t$), the rate constants (k_m) are obtained from the slopes of the lines, as shown in Fig. 1. The gas-phase rate constants for the reactions of guaiacol, creosol, and syringol with NO_3 radicals are $(3.2 \pm 1.4) \times 10^{-12}$, $(2.4 \pm 1.7) \times 10^{-13}$, and $(4.0 \pm 4.7) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Uncertainties were calculated using the standard deviations of the rate constants derived from triplicate measurements and the accumulative uncertainties from the rate constants of reference compounds.

The ranges of NO_3 concentrations used in the kinetic experiment were estimated to be $(0\text{--}5.0) \times 10^{10} \text{ molecules cm}^{-3}$ according to the loss rates of reference compounds. The initial concentra-

Fig. 1. Plots of $\ln(C_m/C_{m0})$ vs NO_3 exposure for guaiacol (A), creosol (B), and syringol (C).

tion of N_2O_5 and the maximum concentration of NO_2 in the kinetic experiments are calculated to be $(1.0\text{--}1.4) \times 10^{13}$ and $\sim 1.2 \times 10^{13}$ molecules cm^{-3} , respectively. The calculation method is shown in the SI. The direct reactions of N_2O_5 and NO_2 with the methoxyphenols were ignored for the following reasons. The major reaction mechanism of $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ with methoxyphenol is the same as those of PAHs and phenol (Jessen et al., 2011). And N_2O_5 has been ruled out as a reactive species for PAHs toward $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ mixture (Chigo et al., 2006). In addition, the reaction rate constant of N_2O_5 with guaiacol was calculated to be 1.2×10^{-23} cm^3 molecule $^{-1}$ s $^{-1}$ at 298 K using theoretical method (shown in SI). In a separate experiment, no decay of gas-phase methoxyphenol was observed with VUV-GTOFMS under 2.4×10^{13} molecules cm^{-3} of NO_2 .

3.2. Oxidation products

Fig. 2 shows the time-of-flight (TOF) mass spectra of the oxidation products from guaiacol, creosol, and syringol exposed to NO_3 radicals for 3 min, 5 min, and 6 min respectively. The mass peaks at m/z 30, 32, and 46 are derived from the molecular ions of NO , O_2 , and NO_2 . The signal intensity of all mass peaks in the spectra was normalized to that of O_2 . The O_2 molecular ion was generated via photoelectron bombardment. In addition to the mass peaks for guaiacol (m/z 124), creosol (m/z 138), and syringol (m/z 154), the VUV-GTOFMS detected some other mass peaks in the spectra, which were attributed to the oxidation products of the three methoxyphenols. The mass peaks from these oxidation products can be divided into four categories: (1) $[\text{M} + 45]^+$ or $[\text{M} + 90]^+$, (2) $[\text{M} - 14]^+$, (3) $[\text{M} + 14]^+$, and (4) $[\text{M} + 29]^+$. Combined with GC-MS

analysis and theoretical calculations, assignments were made for the products corresponding to these peaks. Their chemical structures are shown in the Table 1. As marked in the Table 1, the products are confirmed by analysis of the commercial standard (a), DFT theoretical calculation (b), or mass spectral library match (c and d). Some of the products observed by VUV-GTOFMS were not detected by GC-MS, probably because of the different detection limits for the two instruments. In addition, some higher MW products may be present in particle-phase, which cannot be observed by VUV-GTOFMS. Thus, the relative signal intensities of products are calculated based on the data of GC-MS.

Category 1 products ($[\text{M} + 45]^+$) were determined to be nitro-substitution products resulting from one nitro group added (NO_2 , mol wt 46), and one hydrogen atom removed (H, mol wt 1) from the substitution position. Consequently, $[\text{M} + 90]^+$ represents a dinitro product. Based on the relative signal intensities shown in Table 1, the nitro derivatives are main products from the gas-phase reaction of methoxyphenols with NO_3 radicals. These products were identified either by theoretical or experimental methods, or both. It should be noted that the relative yields of reaction products obtained by experiments may be different from those under atmospheric conditions. For example, more products derived from O_2 addition (such as quinones) might be produced under an extremely low NO_2 concentration. However, since nitro derivatives were also reported as major reaction products for guaiacol and OH radical reaction (Lauraguais et al., 2014b), these derivatives might be important products for methoxyphenols in the atmosphere. Category 2 products ($[\text{M} - 14]^+$) were derived from the transformation of the methoxy ($-\text{OCH}_3$) group into the hydroxyl ($-\text{OH}$) group. This transformation has been observed by photolysis and NO_3 -initiated oxidation of vanillic acid (Net et al., 2011; Liu et al., 2012). Category 3 products ($[\text{M} + 14]^+$) resulted from either transformation of the hydroxyl ($-\text{OH}$) group into the methoxy ($-\text{OCH}_3$) group or the formation of quinone at C1 and C4 position. These products were determined using GC-MS analytical procedure and comparison of the EI characteristic peaks of the homologous products (as shown in Figs. S1 and S2 in Supporting Information). It should be noted that the formation of quinone was not observed from the reaction of creosol because the C4 position of creosol is occupied by a methyl group. Category 4 products ($[\text{M} + 29]^+$) were tentatively identified as nitro-substitution products at the C1 position, which occurred with the addition of a nitro group (NO_2 , mol wt 46) and subtraction of a hydroxyl group (OH, mol wt 17).

3.3. Reaction mechanisms

To elucidate the chemical mechanism of the gas-phase reaction between a methoxyphenol and an NO_3 radical, and to assist in the determination of the oxidation products that have not yet been identified (i.e., nitrocreosol and nitrosyringol), theoretical studies on the formation of nitro products were performed. Taking guaiacol for example, there are two possible pathways to form a nitroguaiacol, namely the H abstraction and addition-elimination mechanisms, as shown in the Fig. 3.

The first mechanism involves H abstraction from the OH group by the NO_3 radical producing the intermediate IM1abs and HNO_3 . This reaction is followed by the addition of NO_2 on the C6 position forming IM2abs. Then IM2abs transforms into 6-nitroguaiacol (6-NG) through the transition state, TS1abs. However, this reaction is hard to accomplish under normal temperature and pressure conditions since the transformation of IM2abs into 6-NG in the H-abstraction mechanism, requires overcoming an energy barrier of 50.1 kcal mol $^{-1}$. The phenoxy radical (IM1abs) may react with HO_2 to regenerate guaiacol, as has been reported for the reactions of

Fig. 2. TOF mass spectra of the oxidation products from the reactions of guaiacol (A), creosol (B), and syringol (C) with NO_3 radicals.

Fig. 3. Schemes for the reaction of guaiacol with NO_3 radical to form nitroguaiacols deriving from H abstraction of the hydroxyl group and addition-elimination reactions initiated at C1 position. The unit of embedded potential barriers ΔE and reaction enthalpies ΔH is kcal/mol.

phenols and the NO_3 radical (Atkinson et al., 1992), or the formation of methoxybenzoquinone via a series of common atmospheric chemical reactions (Kautzman et al., 2010).

The second mechanism starts with the electrophilic addition of the NO_3 radical onto the aromatic ring. For guaiacol, there are three C positions possessing the electronegativity that can be added by the NO_3 radical, i.e., at C1, C4, and C5. Comparing the three, C1 has the highest electronegativity. It was also found that the addition of the NO_3 radical onto C1 has the smallest energy barrier. The scheme of reactions initiated by addition of the NO_3 radical onto the C4 and C5 positions, and the related energy barriers, is shown in Fig. S3. Therefore, the most energy favorable pathway shown in Fig. 3 is the NO_3 addition onto the C1 position to form the intermediate 1-IM via the reaction complex 1-RC, and the transition state 1-TS1, followed by NO_2 addition on either C6 or C4 to form intermediates 1-IM2-6 or 1-IM2-4. Then, the NO_3 group abstracts an H atom on C6 or C4 through transition states 1-TS2-6 and 1-TS2-4 to generate the 6-NG and 4-nitroguaiacol (4-NG) products, respectively. The profile of potential energy surfaces for the above series of reactions is shown in Fig. 4.

In summary, the nitroguaiacol isomers formed through the most favorable pathway predicted in theoretical calculations were consistent with those observed in our experiments. In our experiments, there were two nitroguaiacol isomers observed by GC-MS. By comparing the retention time of a 5-nitroguaiacol (5-NG) commercial standard with those observed by GC-MS, 5-NG was excluded as a possible oxidation product. This result also ruled out the reaction pathways initiated by the C4 and C5 positions as well as the formation of 3-NG as a product. Considering that there are only four nitroguaiacol isomers possible (3-, 4-, 5-, and 6-NG), the observed nitroguaiacol isomers must be 4-NG and 6-NG, which agreed with the prediction of theoretical study.

Hence, theoretical calculations were used to help determine the nitrocreosol and nitrosyringol isomers produced, for which there were no standards available nor were they available in the NIST library. The profile of potential energy surfaces for the reactions of creosol and syringol with NO_3 radicals is shown in Figs. S4 and S5.

Fig. 4. Profile of the potential energy surface for the reaction of guaiacol with NO_3 radical to form nitroguaiacols deriving from H abstraction of the hydroxyl group and addition-elimination reactions initiated at C1 position.

For creosol, only C5 showing electronegativity that can be added by the NO_3 radical, and for syringol, two positions C1 and C4 can be initially attacked by the NO_3 radical. Based on the reaction barriers, the most favorable reaction products for creosol and syringol are 6-Nitrocreosol (6-NC) and 3-Nitrosyringol (3-NS), respectively. Since there is only one nitro-product observed on chromatograms of creosol and syringol individually, the nitration products of creosol and syringol are tentatively identified as 6-NC and 3-NS. Combined experimental and theoretical results, the proposed reaction mechanism for the gas-phase reaction of the NO_3 radical with guaiacol, creosol, and syringol are shown in Fig. 5. Table S1 shows the relative energies (ΔE in kcal/mol), relative enthalpies (ΔH in kcal/mol), and Gibbs free energies (ΔG in kcal/mol) of the stationary points on the ground-state potential energy surface for all the NO_3 -initiated addition-elimination reactions.

Fig. 5. Proposed reaction mechanisms for the reaction of guaiacol (A), creosol (B), and syringol (C) with NO_3 radicals.

4. Conclusion and implications

The reactivity of gaseous methoxyphenols (guaiacol, creosol, and syringol) with two important atmospheric oxidants (NO_3 and OH radicals), as well as the atmospheric lifetimes for these compounds are compared in Table 2. Under a typical tropospheric concentration of 5×10^8 molecules cm^{-3} for the NO_3 radical (Shu and Atkinson, 1995), the atmospheric lifetimes for guaiacol, creosol, and syringol reacting with the NO_3 radical are 0.2, 2.3, and 1.4 h, respectively, which are comparable with those with the OH radical. These lifetimes indicate that the OH radical is an important oxidation agent concerning methoxyphenols' degradation during the daytime, whereas the NO_3 radical is the dominant oxidant at night. Guaiacol exhibited an amazing reactivity with the NO_3 radical, with a lifetime ten times shorter than that with the OH radical. The rate of reaction between guaiacol and the NO_3 radical

is also about ten times faster than the other two methoxyphenols, and is similar to that of phenol (3.8×10^{-12} cm^3 molecule $^{-1}$ s $^{-1}$) (Atkinson et al., 1992). The high reaction rate of guaiacol may be because the initial reaction between guaiacol and NO_3 radicals proceeds at the C1 position adjacent to the hydroxyl group (like the reaction of phenol with NO_3 radicals), whereas the reactions with creosol and syringol occur at other C atoms on the aromatic ring. Nevertheless, the reaction rates of creosol and syringol are still much faster than those of toluene, benzaldehyde, and methoxybenzene (3.4×10^{-17} , 2.0×10^{-15} , and 9.0×10^{-17} cm^3 molecule $^{-1}$ s $^{-1}$, respectively) (Atkinson et al., 1987). Therefore, based on this study and the studies reported in the literature (Atkinson et al., 1987), the general reactivity order involving NO_3 radicals is phenols > methoxyphenols > methoxybenzenes.

The high reactivities of methoxyphenols with NO_3 and OH radicals mean that gas-phase methoxyphenols are too reactive to be

Table 2

Rate coefficients for the reaction of NO₃ and OH radicals with the three methoxyphenols and the associated atmospheric lifetimes.

Compounds	NO ₃ radicals		OH radicals	
	$k_{\text{NO}_3}^a$	$\tau_{\text{NO}_3}^b$	k_{OH}^c	τ_{OH}^d
Guaiacol	32 ± 14^e	0.2^e	7.5 ± 0.4^f	2.0^f
Creosol	2.4 ± 1.7^e	2.3^e	9.5 ± 0.6^f	1.8^f
Syringol	4.0 ± 4.7^e	1.4^e	9.7 ± 1.1^g	1.8^g

^a Units of 10^{-13} cm³ molecule⁻¹ s⁻¹.

^b Lifetime in hours. $\tau_{\text{NO}_3} = 1/k_{\text{NO}_3}[\text{NO}_3]$, where 12 h nighttime average $[\text{NO}_3] = 5 \times 10^8$ molecules cm⁻³ (Shu and Atkinson, 1995).

^c Units of 10^{-11} cm³ molecule⁻¹ s⁻¹.

^d Lifetime in hours. $\tau_{\text{OH}} = 1/k_{\text{OH}}[\text{OH}]$, where 12 h daily average $[\text{OH}] = 1.6 \times 10^6$ molecules cm⁻³ (Prinn et al., 1995).

^e This work, with conditions at 298 ± 2 K and 1 atm.

^f Data derived from Coeur-Tourneur et al. with conditions at 294 ± 2 K and 1 atm (Coeur-Tourneur et al., 2010).

^g Data derived from Lauraguais et al. with conditions at 294 ± 2 K and 1 atm (Lauraguais et al., 2012).

used as tracers for wood smoke emissions during either the day or night. If released into the atmosphere, the methoxyphenols would rapidly transform forming nitro-derivatives released nearby the pollution sources. It is reported that reactivities of 2-nitrophenol towards OH and NO₃ radicals are slow, with atmospheric residence times are estimated to be 13 days and at least 2 days due to the reaction with OH and NO₃ radicals, respectively (Harrison et al., 2005). However, the photolysis rates of ortho-nitrophenol derivatives are rapid, with atmospheric lifetimes on the order of an hour (Iustinian et al., 2006, 2007). Therefore, whether nitro derivatives observed in this study can be wood combustion tracers still needs to be further studied.

From our experimental and theoretical study, 4-NG, 6-NG, and 4,6-dinitroguaiacol (4,6-DNG) were identified as nitro products from the reaction of guaiacol with NO₃ radicals. The nitro isomers have differences with those produced by reaction with OH radicals, which also include 3-NG and 5-NG, (Lauraguais et al., 2014b) but show some consistencies with those observed in winter PM₁₀ aerosols and aqueous-phase photolysis of guaiacol (Kitanovski et al., 2014). Since 6-NG is not available commercially, laboratory experiments and field measurements in previous studies could not confirm the presence of 6-NG in their samples (Kitanovski et al., 2012, 2014; Lauraguais et al., 2014b). The present study provides an evidence for the gas-phase formation of 6-NG. The information concerning its retention time and EI mass spectrum (shown in Fig. S6) may be helpful in its analysis in the future. In addition, the integrated and effective atmospheric chemical reaction rate constants of methoxyphenols may serve as a “photochemical clock” to estimate the age of an air mass from biomass combustion (Rudolph and Johnen, 1990; Rudolph and Czuba, 2000; Tseng et al., 2009). It should be noted that the partitioning of the products between gas- and particle-phase would be taken into account when using this method. Since the presence of nitro groups may increase the toxicity in humans and animals (Kitanovski et al., 2014), more attention should be given to the atmospheric detection and toxicological impact of these nitro-derivatives.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2015.11.028>.

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