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

Bo Yang*, Haixu Zhang, Youfeng Wang, Peng Zhang, Jinian Shu, Wanqi Sun, Pengkun Ma

State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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 $3.2 \times 10^{-12}$, $2.4 \times 10^{-13}$, and $4.0 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, respectively. At a typical tropospheric concentration of NO₃ radicals ($5 \times 10^8$ 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 (Levieved 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 materials. 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; Standley and Simoneit, 1990; Simoneit et al., 1993), they have been...
considered as possible atmospheric wood smoke pollution tracers (Hawthorne et al., 1988, 1989; Simonet 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 phototiation, or radical-initiated reaction, between guaiacol and phenols forming SOAs have been reported (Kitanovski et al., 2014; Zhang et al., 2014). The analytical instrumentation included the lab-built VUV-GTOFMS, a Vaisala Humicap (HMM100) humifier, 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 $\sim 5 \times 10^{14}$ photon s$^{-1}$, and the photon energy was $\sim 10$ 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. N$_2$O$_5$ 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 NO$_3$ radicals cannot be directly monitored with our instruments, the rate coefficients of the gas-phase reaction between the methoxyphenols and NO$_3$ radicals were determined by a relative rate method. The NO$_3$ exposure (C$_{NO_3}$) was derived from the measured decay of the reference gases using the following equation:

$$\frac{\ln(C_{ref}/C_{ref0})}{-k_{ref}} = \int_{0}^{t} C_{NO_3} dt = C_{NO_3} t$$

(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 NO$_3$ 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 NO$_3$ radicals are $(5.1 \pm 1.6) \times 10^{-12}$ and $(7.0 \pm 2.0) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively (http://www.iupac-kinetic.chem.cam.ac.uk/; Atkinson et al., 1984). The rate constant of methoxyphenol ($k_m$) is expressed in the following equation:

$$\ln(C_m/C_{mo}) = -k_m C_{NO_3} t$$

(2)

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

In the kinetic experiments, $\sim 10$ 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 $\sim 500$ 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 1
Products Observed by VUV-GTofMS and GC-MS from the NO₃ radical Reaction with Methoxyphenols.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Oxidation product</th>
<th>MW</th>
<th>Structure</th>
<th>Retention time (min)</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guaiacol</td>
<td>Catechol</td>
<td>110</td>
<td><img src="image1" alt="Structure" /></td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1,2-Dimethoxybenzene</td>
<td>138</td>
<td><img src="image2" alt="Structure" /></td>
<td>21.9</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>Methoxybenzoquinone</td>
<td>138</td>
<td><img src="image3" alt="Structure" /></td>
<td>24.3</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>2-Methoxynitrobenzene</td>
<td>153</td>
<td><img src="image4" alt="Structure" /></td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>6-Nitroguaiacol</td>
<td>169</td>
<td><img src="image5" alt="Structure" /></td>
<td>28.0</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>4-Nitroguaiacol</td>
<td>169</td>
<td><img src="image6" alt="Structure" /></td>
<td>30.9</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>4,6-diNitroguaiacol</td>
<td>214</td>
<td><img src="image7" alt="Structure" /></td>
<td>37.5</td>
<td>0.04</td>
</tr>
<tr>
<td>Creosol</td>
<td>4-Methylcatechol</td>
<td>124</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>3,4-Dimethoxytoluene</td>
<td>152</td>
<td><img src="image8" alt="Structure" /></td>
<td>24.1</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>2-Nitro-5-methylanisole</td>
<td>167</td>
<td><img src="image9" alt="Structure" /></td>
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<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>6-Nitrocreosol</td>
<td>183</td>
<td><img src="image10" alt="Structure" /></td>
<td>30.3</td>
<td>1</td>
</tr>
<tr>
<td>Syringol</td>
<td>3-Methoxycatechol</td>
<td>140</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1,2,3-Trimethoxybenzene</td>
<td>168</td>
<td><img src="image11" alt="Structure" /></td>
<td>25.8</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>2,6-Dimethoxynitrobenzene</td>
<td>183</td>
<td><img src="image12" alt="Structure" /></td>
<td>30.2</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>2,6-Dimethoxyquinone</td>
<td>168</td>
<td><img src="image13" alt="Structure" /></td>
<td>31.7</td>
<td>0.49</td>
</tr>
</tbody>
</table>

(continued on next page)
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. \( NO_2 \) and \( NO_3 \) 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 (\( \Gamma_{NO_3} \)), 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 \((0–5.0) \times 10^{10} \text{ molecules cm}^{-3}\) according to the loss rates of reference compounds. The initial concentra-
tion of \( N_2O_5 \) and the maximum concentration of NO\(_2\) in the kinetic experiments are calculated to be \((1.0–1.4) \times 10^{13}\) and \(\sim 1.2 \times 10^{13}\) molecules cm\(^{-3}\), respectively. The calculation method is shown in the SI. The direct reactions of \( N_2O_3 \) and NO\(_3\) with the methoxyphenols were not detected for the following reasons. The major reaction mechanism of \( N_2O_5/NO_3/NO_2 \) with methoxyphenol is the same as those of PAHs and phenol (Jessen et al., 2011). And \( N_2O_3 \) has been ruled out as a reactive species for PAHs toward \( N_2O_3/NO_3/NO_2 \) mixture (Ghigo et al., 2006). In addition, the reaction rate constant of \( N_2O_3 \) with guaiacol was calculated to be \(1.2 \times 10^{-23}\) 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 \(2.4 \times 10^{13}\) 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 mass products of the three methoxyphenols. The mass peaks from these oxidation products can be divided into four categories: (1) \([M+45]^+\) or \([M+90]^+\), (2) \([M-14]^+\), (3) \([M+14]^+\), and (4) \([M+29]^+\). 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 \([M+45]^+\) 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, \([M+90]^+\) 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 observed 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 \([M-14]^+\) were derived from the transformation of the methoxy (-OCH\(_3\)) group into the hydroxyl (-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 \([M+14]^+\) resulted from either transformation of the hydroxyl (-OH) group into the methoxy (-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 \([M+29]^+\) 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 nitroguaiaicol, 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-nitroguaiaicol (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

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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 NO₃ radical to form nitрогuaiacols deriving from H abstraction of the hydroxyl group and addition-elimination reactions initiated at C1 position. The unit of embedded potential barriers $\Delta E$ and reaction enthalpies $\Delta H$ is kcal/mol.

The second mechanism starts with the electrophilic addition of the NO₃ radical onto the aromatic ring. For guaiacol, there are three C positions possessing the electronegativity that can be added by the NO₃ 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 NO₃ radical onto C1 has the smallest energy barrier. The scheme of reactions initiated by addition of the NO₃ 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 NO₃ 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 NO₂ addition on either C6 or C4 to form intermediates 1-IM2-6 or 1-IM2-4. Then, the NO₃ 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 NO₃ 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 NO₃ 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 NO₂ addition on either C6 or C4 to form intermediates 1-IM2-6 or 1-IM2-4. Then, the NO₃ 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.

For creosol, only C5 showing electronegativity that can be added by the NO₃ radical, and for syringol, two positions C1 and C4 can be initially attacked by the NO₃ 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 NO₃ radical with guaiacol, creosol, and syringol are shown in Fig. 5. Table S1 shows the relative energies ($\Delta E$ in kcal/mol), relative enthalpies ($\Delta H$ in kcal/mol), and Gibbs free energies ($\Delta G$ in kcal/mol) of the stationary points on the ground-state potential energy surface for all the NO₃-initiated addition-elimination reactions.
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 $5 \times 10^{18}$ 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 ($3.8 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) (Atkinson et al., 1992). The high reaction rate of guaiacol may 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 ($3.4 \times 10^{-17}$, $2.0 \times 10^{-15}$, and $9.0 \times 10^{-17}$ 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
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 NO$_3$ radicals are slow, with atmospheric residence times estimated to be 13 days and at least 2 days due to the reactivity with OH and NO$_3$ 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 (Justinian 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-dinitroguaiacil (4,6-DNG) were identified as nitro products from the reaction of guaiacol with NO$_3$ 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 PM$_{10}$ aerosols and aqueous-phase photoinitiation 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 El 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.

**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.

**References**


