Gas-Phase Reactions of Methoxyphenols with NO$_3$ Radicals: Kinetics, Products, and Mechanisms

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1. INTRODUCTION

Biomass combustion is a significant source of air pollution in many parts of the world with contributions from both anthropogenic sources, such as biofuels, deforestation, etc., and natural sources, such as wildfires. Biomass combustion is estimated to contribute approximately 10−50% of the total organic fraction of aerosols, and it can be inferred that biomass combustion has a direct influence on both ambient air quality and climate change. Some earlier studies showed that wood-smoke exposure can lead to many adverse health effects, such as acute respiratory infections, tuberculosis, asthma, chronic obstructive pulmonary disease, lung cancer, cataracts, and blindness.

Natural wood consists of three basic polymers, cellulose, lignin, and hemicelluloses, and the lignin is estimated to account for 18−35% by mass. Methoxyphenols derived from the pyrolysis of lignin are thought to be ideal tracers for wood smoke, because they are major components in wood smoke and specific to biomass-combustion sources. Hawthorne et al. estimated the emission rates of methoxyphenol species from biomass combustion, ranging from 420 to 900 mg kg$^{-1}$ fuel. Even though some kinds of methoxyphenols have been proposed as aerosol markers for wood combustion and biomarkers to determine human-exposure levels, their reactivity in the atmosphere and their gas-phase chemical-reaction mechanisms have not been well characterized. Therefore, investigations of the physical and chemical behaviors of these compounds could provide crucial information in aerosol’s source apportionments.

4-Substituted guaiacols are important methoxyphenols and are quite abundant in ambient air. Eugenol and 4-ethylguaiacol are two typical 4-substituted guaiacols with an allyl group and an ethyl group as the side chain, respectively. Their structures, molecular weights (MWs), and vapor pressures (VPs) are listed in Table 1.

Table 1. Structures, MWs, and VPs of Eugenol and 4-Ethylguaiacol

| Name           | Structure | MW  | VP (Pa) |
|----------------|-----------|-----|---------|
| eugenol        | ![Eugenol Structure](image) | 164 | 3$^A$   |
| 4-ethylguaiacol| ![4-Ethylguaiacol Structure](image) | 152 | 2.3$^B$ |

$^A$Data from ref 66. $^B$Data calculated using Advanced Chemistry Development (ACD/Laboratories) software V11.02.
the investigation of the gas-phase reaction. In addition to the large, naturally occurring source, they are widely used in the food, medical, and chemical synthetic industries, meaning that humans routinely have close contract with these chemicals. After being emitted into the atmosphere, these compounds undergo a series of chemical reactions, leading to their removal from the troposphere or conversion into other compounds. Some experimental studies have investigated the rate coefficients of the gas-phase reactions of hydroxyl radicals with methoxyphenols and their contributions to SOA. Theoretical calculations have also been applied to the study of the conformations and electron diffraction of some methoxyphenols in their reactions with oxidants.

NO$_3$ radicals are important oxidants in the atmosphere at night, and their reactivities are comparable to those of OH radicals in the atmosphere during the day time. However, rare studies investigate the reaction between NO$_3$ radicals and methoxyphenol; therefore, it is vital to study the chemical reactions of NO$_3$ radicals with methoxyphenols to understand their transport and transformation behaviors in the atmosphere. In this study, the gas-phase reactions of NO$_3$ radicals with eugenol and 4-ethylguaiacol were investigated using a newly lab-built vacuum ultraviolet photoionization gas time-of-flight mass spectrometer (VUV-GTOFMS) and a gas chromatograph interfaced to a mass spectrometer (GC–MS). The VUV-GTOFMS was used to investigate the chemical reactions for the first time, which has advantages of soft ionization with less fragments and high sensitivity (with a detection limit to methoxyphenol is $\sim$0.2 ppbv). Theoretical analysis was applied to determine the products’ structures as well as the reaction mechanisms.

2. EXPERIMENTAL SECTION

2.1. Experimental Setup. Our experimental setup to analyze the gaseous reactions of methoxyphenols with NO$_3$ radicals consisted of a reaction chamber and analytical instruments, which is shown in Figure 1. In short, the experimental setup consisted of a reaction chamber, a VUV-GTOFMS, a NO$_3$ generator, and a device to capture products.

![Figure 1. Experimental setup in this study.](image)

The reaction chamber was composed of a thin-walled open-head stainless-steel drum with a volume of 180 L and a thin Tedlar polyvinyl fluoride (PVF) film bag. A magnetically driven fan was placed at the bottom of the chamber, with a speed of $\sim$1500 rpm, and it takes several seconds to get a homogeneously mixed reactant gas. The experiments were conducted at room temperature (298 ± 2 K) under atmospheric pressure, and the relative humidity in the reaction chamber was less than 10%, estimated from the residual filtered air in the chamber. Because the amounts of the methoxyphenol used in the experiment were little, 0.25 mL of pure liquid methoxyphenols and isoprene were diluted into 5 mL of dichloromethane solutions prior to use.

A lab-built VUV-GTOFMS was used to detect the real-time quantities of the reactants and products, and a newly published paper has introduced it in detail. Briefly, it consist of an RF-powered krypton lamp to produce VUV light radiation, with $5 \times 10^{14}$ photon s$^{-1}$ photon flux as well as $\sim$10 eV photon energy. After direct sampling, the gaseous compounds were initially photoionized via the VUV radiation after which the ions were detected with a reflection time-of-flight mass spectrometer. A GC–MS was also used to analyze the products. The GC–MS (Agilent 6890-5973) was composed of a gas chromatograph and a mass spectrometer. One microliter of the trapped sample was introduced into the GC–MS system via the pulsed splitless mode. The initial GC temperature was set to 40 °C for 2 min, followed by 20 °C min$^{-1}$ increased up to 150 °C, 10 °C min$^{-1}$ to 220 °C, and 5 °C min$^{-1}$ to 300 °C with each step held for 10 min. Helium (99%, Beijing Huayuan Gas Chemical Industry Co., Ltd.) was used as the carrier gas at a constant flow rate of 1 mL min$^{-1}$, and the interface temperature was maintained at 280 °C throughout the GC–MS assay. The reaction products were analyzed in the total-ion-chromatogram (TIC) mode of the GC–MS with some of them being identified by comparing their electron-ionization (EI) mass spectra with those from the Mass Spectral Library [National Institute of Standards and Technology (NIST), 2005]. The spectra not included in the Mass Spectral Library were determined by comparing their EI mass spectra with those of known samples or were inferred from theoretical studies.

2.2. Materials and Methods. 2.2.1. Kinetic Experiments. In two independent experiments, either 15 μL of prepared eugenol CH$_3$C$_6$H$_6$O solution or 12 μL of prepared 4-ethylguaiacol CH$_2$Cl$_2$ solutions were injected into the reaction chamber. After 200 s, 6 μL of isoprene CH$_3$C$_6$H$_6$O solution (as the reference compound used in the relative-rate technique) was injected as the methoxyphenol solutions were completely volatilized. By supposing that all the reactants were evaporated in the chamber, the final concentrations of the methoxyphenols and isoprene were calculated to be 500 ppbv ($\sim$1.2 × 10$^{13}$ molecules cm$^{-3}$). Subsequently, an N$_2$ stream with a volumetric flow rate of 0.5 L min$^{-1}$ was passed through a flask containing N$_2$O$_5$ powder, thus introducing gaseous N$_2$O$_5$ into the chamber continuously. Meanwhile, the signal intensity of the methoxyphenols and isoprene was recorded every 10 s with a fan worked throughout the reaction. NO$_3$ radicals were generated via the thermal decomposition of N$_2$O$_5$ which was synthesized via the dehydration of nitric acid. The detailed process of the N$_2$O$_5$ preparation has been described elsewhere, and the flask containing the N$_2$O$_5$ powder was maintained in a cold bath in which the temperature was set to $\sim$40 °C. It is necessary to add that because the stainless-steel drum was covered with a PVF film bag which was expandable, the pressure in the chamber kept stable. Besides, the change of the volume was negligible in 400 s because of the low rate of flow.

2.2.2. Product Identification. In a separate experiment to observe the reaction products, 50 μL of CH$_3$C$_6$H$_6$O solution containing methoxyphenol was injected into the reaction chamber to obtain a better signal-to-noise ratio for some minor products. When the signal intensity stabilized, N$_2$O$_5$ was...
introduced into the chamber via an N₂ stream at the same volumetric flow rate. The VUV-GTOF mass spectra were recorded at 10 s intervals. After the reaction lasted 10 min, all the air in the chamber was captured through liquid nitrogen in a flask. Thereafter, 5 mL of dichloromethane was used to extract the compounds until the liquid nitrogen evaporated completely. Finally, the dichloromethane solution was concentrated to 1 mL for GC–MS analysis.

2.3. Computational Methods. All the calculations were performed with the Gaussian 09 program. The B3LYP level of theory with the 6-31G(d,p) basis set was applied to optimize the geometries. Vibrational frequencies were calculated to compute the zero-point vibrational energy and characterize the stationary points (local minima or transition states) with the same level of theory. The intrinsic reaction-coordinate calculations were also conducted to ensure that the transition-state structures connected the desired intermediates (local minima).

3. RESULTS AND DISCUSSION

3.1. Gas-Phase Kinetics. In this study, the rate coefficients of the gas-phase reaction of methoxyphenols with NO₃ were investigated using a relative-rate method. Briefly, the relative-rate technique is based on the competition between two reactants for reaction with one reactive species. For two organics, M and R, reacting with NO₃ radicals their respective reactions and the rate equations of can be written as follows:

\[
\begin{align*}
M + NO_3 & \rightarrow \text{products} \\
R + NO_3 & \rightarrow \text{products} \\
\frac{-d[M]}{dt} & = \kappa_M \times [M] \times NO_3 \\
\frac{-d[R]}{dt} & = \kappa_R \times [R] \times NO_3
\end{align*}
\]

(1) (2) (3) (4)

Then eq 5 can be derived from (3) and (4)

\[
\frac{d[M]}{d[R]} = \frac{\kappa_M}{\kappa_R} \times \frac{[M]}{[R]}
\]

After taking the logarithm, the calculation formula is written as follows:

\[
\ln(C_{M0}/C_M) = \frac{\kappa_M}{\kappa_R} \ln(C_{R0}/C_R)
\]

(6)

In this experiment, C₀ and Cᵣ are the initial and real-time concentrations of isoprene, respectively; κᵣ represents the reaction-rate coefficient of gas-phase isoprene with NO₃ radicals; Cₐ₀ and Cₐ are the initial and real-time concentrations of the methoxyphenols; and κₐ is the reaction-rate coefficient of the gas-phase methoxyphenol with NO₃ radicals. On the basis of the degradation rate of isoprene, the average concentrations of the NO₃ radicals during the reactions with eugenol and 4-ethylguaiacol were estimated to be ~5 × 10⁻¹⁰ molecules cm⁻³.

Before the kinetic characteristics of the two investigated methoxyphenols were investigated, the relative-rate method in this experiment system was initially tested. Figure S1 shows the plots of ln(Cₐ₀/Cₐ) versus ln(Cₐ₀/Cₐ) for 1,4-cyclohexadiene versus isoprene under the same experiment condition and analysis method. The coefficient for 1,4-cyclohexadiene and NO₃ was obtained to be (5.8 ± 0.9) × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ in consideration of uncertainties from experiment as well as the errors from literature value for isoprene. Compared with the published data 6.6 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹, the experiment and analysis method is proved to be reliable.

Figure 2 shows the plots of ln(Cₐ₀/Cₐ) versus ln(Cₐ₀/Cₐ) for the two methoxyphenols, and the error bars represent the standard deviations of three duplicate tests. The two plots shown in Figure 2 were well fitted by using a linear regression (R² = 0.9879 and 0.9967, respectively). The obtained slopes corresponded to the rate-coefficient ratio κ_M/κ_R from which κ_M could be calculated because κ_R was known. In the last ten years, many studies have obtained rate coefficients for the reaction of isoprene with NO₃ ranging from 5.9 × 10⁻¹³ to 7.3 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ for eugenol and 4-ethylguaiacol, the rate coefficients were (1.6 ± 0.4) × 10⁻¹³ and (1.1 ± 0.2) × 10⁻¹² cm³ molecule⁻¹ s⁻¹, respectively.

Accordingly, the rate coefficient of NO₃ with 4-ethylguaiacol was about an order of magnitude greater than that with eugenol, possibly resulting from the different functional groups. According to the theoretical calculations, the energy barriers of the NO₃-addition processes were 3.06 and 1.90 kcal mol⁻¹ for eugenol and 4-ethylguaiacol, respectively. Besides, the rate coefficients of NO₃ with phenol and cresol isomers were reported by previous studies. In consequence, the functional groups influenced the barrier heights of the NO₃-addition processes, thus leading to significant differences in the reaction rates even though they possess similar structures.

A previous study has shown that the reaction of phenol takes place with NO₃ radicals and not with N₂O₃ or with NO₂. In a series of supplemental experiments, the rate coefficient of NO₂ + methoxyphenols was <6.7 × 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹. Therefore, the reactivity of NO₂ was ignored. Additionally, wall loss was also ignored in the data processing, because the signal intensity was stably maintained for more than 80 s, whereas the kinetic experiments were accomplished within 60 s.

3.2. Reaction Products. The TOF mass spectra of the eugenol and 4-ethylguaiacol before their reactions are shown in Figures S2 (A) and S2 (B), respectively, of the Supporting Information. There were only molecular-ion peaks of the two methoxyphenols in the given segments. According to Figure S3,
the signal intensity of some product decreased dramatically after 200 s; therefore, parts A and B of Figure 3 show the TOF mass spectra of the eugenol and 4-ethylguaiacol exposed to NO₃ for 200 and 400 s, respectively, to show the products as much as possible. The products labeled in the spectra were determined according to the following reaction-mechanism analysis, and Table 2 lists every product detected in the experiments. Because the products observed only by GC−MS cannot be excluded from GC sampling, this kind of products is labeled as speculated in mechanism analysis. Details about identification of primary and secondary products are stated in the Supporting Information.

In Figure 3A, the mass peak at m/z = 164 corresponded to the molecular-ion peak of the reactant eugenol, and the mass peaks at m/z = 166, 192, 209, and 220 represented the molecular-ion peaks of the products (4-hydroxy-3-methoxyphenyl)acetaldehyde, 5-allyl-2-hydroxy-3-methoxybenzaldehyde, 4-allyl-2-methoxy-6-nitrophenol, and 5-allyl-2-hydroxy-3-methoxy-1,4-benzenedialdehyde, respectively. Indeed, 5-allyl-3-nitrocatechol (MW: 195) was observed via GC−MS analysis only.

In Figure 3B, the mass peak at m/z = 152 was derived from the molecular ion of the reactant 4-ethylguaiacol. The mass peaks at m/z = 150, 166, 181, 195, and 213 corresponded to the molecular ions of the products 2-methoxy-4-vinylphenol, 4-

![Figure 3](https://example.com/figure3.png)

**Figure 3.** TOF mass spectra of methoxyphenols and the products of their reaction with NO₃ radicals: eugenol (A) and 4-ethylguaiacol (B).

| Name                                           | MW  | Structure       |
|------------------------------------------------|-----|-----------------|
| (4-hydroxy-3-methoxyphenyl) acetaldehyde³      | 166 | ![Structure](https://example.com/structure1.png) |
| 5-allyl-2-hydroxy-3-methoxybenzaldehyde³       | 192 | ![Structure](https://example.com/structure2.png) |
| 5-allyl-3-nitrocatechol³                        | 195 | ![Structure](https://example.com/structure3.png) |
| 4-allyl-2-methoxy-6-nitrophenol³,B,C           | 209 | ![Structure](https://example.com/structure4.png) |
| 5-allyl-2-hydroxy-3-methoxy-1,4-benzenedialdehyde³ | 220 | ![Structure](https://example.com/structure5.png) |
| 4-ethylcatechol³                               | 138 | ![Structure](https://example.com/structure6.png) |
| 2-methoxy-4-vinylphenol³                      | 150 | ![Structure](https://example.com/structure7.png) |
| 4-hydroxy-3-methoxyacetophenone³              | 166 | ![Structure](https://example.com/structure8.png) |
| 6-nitro-3,4-dihydroxystyrene³,B,C³            | 181 | ![Structure](https://example.com/structure9.png) |
| 4-ethyl-5-nitro-1,2-dihydroxybenzene³          | 183 | ![Structure](https://example.com/structure10.png) |
| 2-methoxy-5-nitro-4-vinylphenol³,B,C           | 195 | ![Structure](https://example.com/structure11.png) |
| 4-ethyl-2-methoxy-5-nitrophenol³,B,C           | 197 | ![Structure](https://example.com/structure12.png) |
| 4-hydroxy-2-nitro-5-methoxybenzaldehyde³,B,C³ | 197 | ![Structure](https://example.com/structure13.png) |
| 1-guaiacyl-ethan-1-nitrate³,B,C                | 213 | ![Structure](https://example.com/structure14.png) |

³Observed via VUV−GTOFMS. ⁴Observed via GC−MS. ⁵Inferred from theoretical calculations. ⁶Secondary product.
hydroxy-3-methoxyacetophenone, 6-nitro-3,4-dihydroxystir-
ene, 2-methoxy-5-nitro-4-vinylphenol, and 1-guaiacylethyl-1
nitrate, respectively. The mass peak at \( m/z = 197 \) corresponded
to the molecular ions of two products, 4-ethyl-2-methoxy-5-
nitrophenol and 4-hydroxy-2-nitro-5-methoxybenzaldehyde
(>99% in amount), according to the separate peaks in the
GC−MS spectrogram. Besides, the products 4-ethylcatechol
and 4-ethyl-5-nitro-1,2-dihydroxybenzene with MWs of 138
and 183 were observed via GC−MS only.

The VUV-GTOFMS could detect most of the products, but
the benzenediol-type compounds could not be observed,
possibly because of their low concentrations in the chamber.
Some products were not observed with the off-line GC−MS
because of their instability, such as the intermediate product 1-
guaiacylethyl-1 nitrate.

### 3.3. Reaction Pathways

On the basis of the identified products and the sequence of their appearance in the mass spectra obtained with the VUV-GTOFMS, reaction pathways
and mechanisms of the two methoxyphenols with NO3 radicals were proposed.

Figure 4 illustrates the reaction mechanism of eugenol with NO3 radicals. Pathway I involved the reaction of an NO3 radical with the C=C bonds in the side chain and the formation of corresponding aldehydes [(4-hydroxy-3-methoxyphenyl)-acetalddehyde and formaldehyde] and either an NO or NO2 radical, which is a common reaction in the atmosphere.49,50 Pathway II was a nitro-substituted reaction that began with NO3 radicals adding to the aromatic ring and produced a nitratocyclohexadienyl-type radical (intermediate I).51 In this step, NO3 could then add to the C3, C5, or C6 atoms on the aromatic ring, according to the theoretical calculations. The possible addition pathways and related thermodynamic data are listed in Figure S5 of the Supporting Information. On the basis of these data, a pathway deriving from the NO3 addition at the C5 position had the lowest energy barrier (3.06 kcal mol−1), indicating the most energy-favorable addition pathway. In the next step, NO2 added to the C6 position to form intermediate II, which was calculated to be barrierless, followed by elimination of an HNO3 molecule, generating the product 4-allyl-2-methoxyl-6-nitrophenol. Figure 5 shows the energy profile of the entire nitration process. The transformation of methoxy into hydroxyl has been observed in the heterogeneous reaction between methoxyphenols and NO3 radicals or ozone, though a detailed reaction mechanism has not yet been clarified.15,52 Accordingly, 5-allyl-3-nitrocatechol was speculatively formed. The reaction mechanism of pathway III remains unknown at this time. Given the VUV-GTOFMS results, the products [M + 28] and [M + 56] were postulated to be 5-allyl-2-hydroxy-3-methoxybenzaldehyde and 5-allyl-2-hydroxy-3-methoxy-1,4-benzenedialdehyde.

The reaction pathway of 4-ethylguaiacol with NO3 radicals is illustrated in Figure 6. In pathway I, the NO3 radical first abstracted an H atom from the ethyl group, contributing to an intermediate radical I, and this kind of hydrogen abstraction has been reported recently.53 In this step, NO3 could then add to the C3, C5, or C6 atoms on the aromatic ring, according to the theoretical calculations. Furthermore, the intermediate radical I was transformed into 4-hydroxy-3-methoxyacetophenone through a series of reactions given in the scheme and proposed in ref 54. A previous study suggested that a double bond could be formed through the
elimination of nitric acid from the intermediate secondary nitrate.52 Similarly, in this reaction, intermediate I can also reaction with NO₃ to form 1-guaiacyl-ethyl-1 nitrate. 2-Methoxy-4-vinylphenol was then formed through the elimination of nitric acid. In addition, the nitro-product 2-methoxy-5-nitro-4-vinylphenol was produced through the secondary nitro-substituted reaction, and then 6-nitro-3,4-dihydroxysterene was speculatively produced in the same manner as that of 5-allyl-3-nitrocatechol in pathway II of the eugenol reaction. Indeed, 4-hydroxy-2-nitro-5-methoxybenzaldehyde was identified via GC-MS and was likely transformed from 2-methoxy-5-nitro-4-vinylphenol, similar to the results of previous studies.50,54 Pathway II was a nitro-substituted reaction described above. Initially, NO₃ radicals added to the aromatic ring in ten possible ways, as shown in Figure S6 of the Supporting Information. One of the pathways involving the NO₃ addition at the C6 atom had the lowest energy barrier (1.90 kcal mol⁻¹). Then, NO₂ added to the C5 atom, which was also calculated to be barrierless, followed by the elimination of HNO₃ to yield the nitro-substituted product 4-ethyl-2-methoxy-5-nitrophenol, which could also contribute to the formation of 2-methoxy-5-nitro-4-vinylphenol. The energy profile of this process is shown in Figure 7. In pathway III, 4-ethylcatechol was initially produced. Next, 4-ethyl-5-nitro-1,2-dihydroxybenzene was formed through the secondary nitro-substituted reaction of 4-ethylcatechol. Similar to the production of 5-allyl-3-nitrocatechol in pathway II of the eugenol reaction, 4-ethyl-5-nitro-1,2-dihydroxybenzene might also be transferred from 4-ethyl-2-methoxy-5-nitrophenol.

It is necessary to add that the H-abstraction of the hydroxy group was likely performed initially in the reaction of the phenols with NO₃ radicals, leading to the formation of phenoxy radicals.45,55 However, according to theoretical calculation (Figure S7), it was not an energy-optimal pathway to form nitrination products, because the structural rearrangement is associated with a large barrier after NO₂ addition.47 A study has shown that phenoxy radicals could react with HO₂, thus regenerating the phenols.56 Some other studies have also shown the possibility of phenoxy radicals forming methoxybenzoquinone.57 In this study, the calculated barrier heights for structural rearrangement after NO₂ addition to phenoxy radicals were 50.35 and 50.25 kcal mol⁻¹, corresponding to eugenol and 4-ethylguaiacol, respectively. Therefore, it would be more favorable to add both NO₃ and NO₂ before the elimination of HNO₃ (the addition-elimination-reaction channel).47

4. CONCLUSIONS AND IMPLICATIONS

In this study, reaction-rate coefficients, degradation products, and chemical mechanisms of the gas-phase reactions of eugenol and 4-ethylguaiacol with NO₃ radicals were investigated by combining experimental and theoretical methods. The calculated, nighttime, atmospheric lifetimes of eugenol and 4-ethylguaiacol toward NO₃ radicals were ~3.5 and 0.5 h, respectively, under a typical tropospheric concentration of 5 × 10⁸ molecules cm⁻³ of the NO₃ radical.50 Therefore, these two kinds of methoxyphenols had high reactivities with NO₃ during the night, revealing an important sink for these types of compounds and indicating that they are not suitable tracers like some other methoxyphenols.22 Because of their high reactivities, the fraction of these organic compounds in the atmosphere changes over time, and this factor should be considered in source apportionment and air-pollution model studies.

It has been pointed out that some atmospheric nitro-aromatic compounds were identified in urban aerosols, have been shown to be important constituents of secondary biomass-burning aerosols (BBAs), and thus have been proposed as suitable tracer compounds.59-63 In this study, seven nitro-substituted products were produced in the reaction of the two methoxyphenols with NO₃ radicals, and they were major degradation products, on the basis of the relative signal intensities observed with VUV-GTOFMS. It was reported that reactivities of 2-nitrophenol toward OH and NO₃ radicals were slow,60 and the atmospheric lifetimes were estimated to be 13 days and at least 2 days due to the reaction with OH and NO₃ radicals, respectively, whereas its photolysis rates was rapid.64,65 Therefore, whether nitro derivatives observed in this study can be wood combustion tracers still needs to be further studied. In addition, alkyl groups with more than two C atoms formed double bonds, such as in the reaction of 4-ethylguaiacol with NO₃ radicals. Some studies have shown that alkenes have high
reactivities in the atmosphere both experimentally and theoretically. Therefore, the formation of double bonds should lead to some secondary reactions with NO₃ radicals or other atmospheric oxidants, thus making the reaction process even more complex. Above all, the obtained kinetics, products, and mechanisms of the methoxyphenols with NO₃ radicals in this study should be useful in understanding the atmospheric evolutions of methoxyphenols.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b10406.

Manufacturers and purity of the chemicals used in this study. Plots of experimental data for 1,4-cyclohexadiene. The TOF mass spectra of methoxyphenols before reactions. Identification of secondary products. Signal intensities of reaction products. Six and ten possible addition–elimination reaction channels of nitro-substituted reaction for eugenol and 4-ethylguaiacol, as well as the corresponding energy height. Scheme of the H abstraction and the corresponding energy barrier. (PDF)

**AUTHOR INFORMATION**

Notes

The authors declare no competing financial interest.

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