Heterogeneous kinetics, products, and mechanisms of ferulic acid particles in the reaction with NO\(_3\) radicals

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HIGHLIGHTS

- Six degradation products of ferulic acid by NO\(_3\) radicals are identified.
- Reaction mechanisms of particulate ferulic acid with NO\(_3\) radicals were proposed.
- Effective rate constant was determined by a mixed-phase relative rate method.
- Uptake coefficient of NO\(_3\) radicals on ferulic acid particles was 0.17 ± 0.02.

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ABSTRACT

Methoxyphenols, as an important component of wood burning, are produced by lignin pyrolysis and considered to be the potential tracers for wood smoke emissions. In this work, the heterogeneous reaction between ferulic acid particles and NO\(_3\) radicals was investigated. Six products including oxalic acid, 4-vinylguaiacol, vanillin, 5-nitrovanillin, 5-nitroferulic acid, and caffeic acid were confirmed by gas chromatography-mass spectrometry (GC-MS). In addition, the reaction mechanisms were proposed and the main pathways were NO\(_3\) electrophilic addition to olefin and the meta-position to the hydroxyl group. The uptake coefficient of NO\(_3\) radicals on ferulic acid particles was 0.17 ± 0.02 and the effective rate constant under experimental conditions was \((1.71 ± 0.08) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). The results indicate that ferulic acid degradation by NO\(_3\) can be an important sink at night.

1. Introduction

Wood smoke emissions are as a major source of air pollution and can contribute more than 50% of the PM\(_{10}\) mass in the residential area (Bari et al., 2010). The increasing concentration of aerosols has subsequent adverse effects on ambient air quality, climate, and human health (Naehler et al., 2007). Generally, exposure to wood smoke is often correlated with respiratory diseases due to the inhalable size of the particles emitted by wood burning (Ezzati and Kammen, 2002; Naehler et al., 2007; Bolling et al., 2009).

Methoxyphenols produced by lignin pyrolysis are known as the potential tracers for wood smoke emissions, which widely exist in ambient atmospheric samples in high concentrations (Nolte et al., 2001; Alves et al., 2011). In recent years, the homogeneous reactivities of some methoxyphenols toward OH radicals (Coeur-Tourneur et al., 2010; Lauraguais et al., 2012, 2014a; Yee et al., 2013), NO\(_3\) radicals (Lauraguais et al., 2016; Yang et al., 2016; Zhang et al., 2016), chlorine atoms (Lauraguais et al., 2014b), and O\(_3\) (Ofner et al., 2011) have been investigated, and these studies mainly reported their reaction kinetics and the formation of secondary organic aerosols (SOA). Additionally, Net et al. (2010, 2011)
and O’Neill et al. (2014) have reported the heterogeneous ozonation of several methoxyphenols adsorbed on model particles. In our previous study, the kinetics, products, and mechanisms of heterogeneous reactions between three particulate methoxyphenols and NO$_3$ radicals have been reported (Liu et al., 2012a). All these show that the chemical behaviors of methoxyphenols have been attracting great attention. However, the heterogeneous reactivities of their suspended particles toward gaseous oxidants still need to be further explored.

Ferulic acid (Fig. 1), a type of methoxyphenols, is a representative unsaturated acid emitted from lignin pyrolysis (Nolte et al., 2001; Alves et al., 2011). However, its reactivity in the atmosphere has not been studied yet. It is well known that the chemical processing of organics would result in further influences on human health, climate, and air quality (Knopf et al., 2011). Therefore, from a health point of view, the knowledge on its chemical behaviors has significant impacts on assessing its toxicity and safety.

Ferulic acid contains benzene ring and olefinic C–C bond, which are both the favored sites for the reaction with NO$_3$ radicals (Knopf et al., 2011; Liu et al., 2012a; Lauraguais et al., 2016; Yang et al., 2016; Zhang et al., 2016). NO$_3$ radicals are the dominant oxidant in the nighttime with similar oxidative power as hydroxyl radicals (Karagulian and Rossi, 2005), and control the nighttime chemical processing of organics in the troposphere (Wayne et al., 1991). Its concentration in the troposphere could reach ~10$^{-10}$ molecules cm$^{-3}$ (Atkinson, 1991). For this reason, the aim of this work was to explore the heterogeneous kinetics and products of particulate ferulic acid degradation by NO$_3$ radicals. The reaction products were identified by gas chromatography mass spectrometry (GC-MS) and the reaction mechanisms were illustrated.

### 2. Experimental section

#### 2.1. Experimental setup

The scanning mobility particle sizer (SMPS) and the aerosol generator equipped with two tandem quartz tubes have been described in detail elsewhere (Liu et al., 2012a). Ferulic acid particles were generated through homogeneous nucleation. Azelaic acid was employed to produce nuclei due to its limited reactivity toward NO$_3$ radicals (Liu et al., 2012b). Azelaic acid in the first tube was vaporized and then nucleated in a nitrogen stream to produce nuclei through temperature gradient. A nitrogen stream with a flow rate of 0.8 L min$^{-1}$ flowed through the first tube, bringing the nuclei into the second tube, where azelaic acid nuclei were coated by ferulic acid vapor. The mean diameter and mass concentration of ferulic acid particles were ~330 nm and 438 ± 22 μg m$^{-3}$, respectively, measured by SMPS. The thickness of the coating was ~43 nm for ferulic acid, calculated according to the size distributions of particles before and after being coated by ferulic acid.

The reaction was performed in a chamber with a volume of ~180 L and its description was illustrated elsewhere (Liu et al., 2012a). The experiments were conducted under the ambient pressure at room temperature (~298 K). The relative humidity in the reaction chamber was approximately 5%, estimated from the residual filtered air in the chamber. When the concentration of ferulic acid particles reached the desired value, isoprene was injected into the reaction chamber. The concentration changes of gaseous isoprene and particulate ferulic acid in the chamber were monitored synchronously by an online atmospheric gas analysis mass spectrometer (QIC-20-HAL3F-RC, Hiden) and a real-time vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS), respectively. The initial concentration of isoprene in the chamber was ~1.0 x 10$^{14}$ molecules cm$^{-3}$, measured by detecting the mass peak at m/z 67 (C$_5$H$_7$I$^+$). Subsequently, a nitrogen stream with a flow rate of 0.8 L min$^{-1}$ passed through a flask containing N$_2$O$_5$ powders and brought gaseous N$_2$O$_5$ into the chamber, which produced NO$_3$ radicals by thermal decomposition at the room temperature (~298 K). The concentrations of NO$_3$ radicals in the experiment were ~3.6-8.3 x 10$^8$ molecules cm$^{-3}$, calculated based on the loss rates of isoprene. The wall losses of ferulic acid and isoprene in the absence of oxidants for 300 s were ~5%, monitored with VUV-ATOFMS and the atmospheric gas analysis mass spectrometer, respectively.

The decay of ferulic acid particles was monitored by a home-built VUV-ATOFMS. The detailed description of VUV-ATOFMS has been presented elsewhere (Shu et al., 2008). It consists of a source chamber, a differential chamber, and a detection chamber. A copper heater (~503 K) with a diameter of 8 mm placed in the detection chamber is used to vaporize the particles. The nascent organic vapor is photoionized by VUV light emitted from a VUV light lamp, of which the wavelength and a photon flux are ~123.6 nm and ~5 x 10$^{14}$ photons s$^{-1}$, respectively. The concentration of ferulic acid particles was linear to the signal intensity of the molecular ion mass peak measured by VUV-ATOFMS; thus the decay rate of signal intensity was equal to the decay rate of ferulic acid concentration (Shu et al., 2008).

#### 2.2. GC-MS analysis

In order to assign the TOF mass spectra of reaction products, GC-MS analysis was performed to identify the products formed in the reaction of surface-bound ferulic acid with NO$_3$ radicals. The detailed descriptions of sample preparation and GC-MS analysis have been presented elsewhere (Liu et al., 2012a). GC-MS analysis was conducted before and after derivatization with BSTFA. Each derivatization solution was prepared by incubating the mixture of ~2 mL extracted solution and ~200 μL BSTFA for ~24 h at room temperature. The reaction products were analyzed by GC-MS in the total ion chromatogram (TIC) mode and identified by comparing their electron ionization (EI) mass spectra with those from a Mass Spectral Library [the National Institute of Standards and Technology (NIST) 2005]. Compared with the available mass spectra in the NIST 2005 library, the product with the match rate over 90% could be identified. The mass range from 30 to 500 amu was used in the process of data acquisition.

#### 2.3. Chemicals

Ferulic acid (Acros, 99%), bis(trimethylsilyl)trifluoroacetamide (BSTFA) [Sigma-Aldrich, containing 10% trimethylchlorosilane (TMCS)], dichloromethane (J. T. Baker Co., chromatographic grade) were used in the experiments. Azelaic acid (99%), fuming nitric acid (95%), P$_2$O$_5$ (98%), absolute ethyl alcohol (99.7%) were from Sinopharm Chemical Reagent Co., Ltd. Nitrogen (99.99%) and nitrogen dioxide (15.9%) were from Beijing Huayuan Gas Chemical Industry Co., Ltd.

### 3. Results and discussion

In this work, the maximum average concentrations of N$_2$O$_5$ and NO$_2$ were ~5.5 x 10$^{12}$ and ~3.1 x 10$^{13}$ molecules cm$^{-3}$, respectively,
estimated by thermal decomposition rate of N$_2$O$_5$ at 298 K (Ide et al., 2008) and the loss rates of isoprene. Knopf et al. (2011) indicated that the uptake coefficient of N$_2$O$_5$ on methoxyphenols was ~3 orders of magnitude smaller than that of NO$_3$ radicals, thus the degradation of ferulic acid by N$_2$O$_5$ was not taken into account. In a single experiment, no obvious decay and product were observed by VUV-ATOFMS when particulate ferulic acid was exposed to NO$_2$ with a concentration of $-5.5 \times 10^{12}$ molecules cm$^{-3}$ for 600 s. Since the maximum acquisition time for kinetic data in the experiments was less than 300 s, the degradation of ferulic acid by NO$_2$ was also ignored in this work.

3.1. Reaction products

The products detected and identified by GC-MS are listed in Table 1. As shown in Fig. 2A, the mass peak at m/z 194 was resulted from the molecular ion of ferulic acid. The time-of-flight (TOF) mass spectrum of the products obtained by exposing ferulic acid particles to NO$_3$ radicals for 150 s is shown in Fig. 2B. Its mass peaks at m/z 197 and 239 were tentatively assigned to be the molecular ions of 5-nitrovanillin and 5-nitroferulic acid, respectively, based on GC-MS analysis. Additionally, other four products including oxalic acid (after derivatization), 4-vinylguaiacol, vanillin, and caffeic acid (after derivatization) were confirmed by GC-MS, and their retention times were 5.1, 5.7, 7.7, and 12.7 min (Table 1), respectively. Their corresponding mass spectra from GC-MS analysis are shown in Fig. 3. In this work, some products were not detected by VUV-ATOFMS while identified by GC-MS; the reason might be the different detection limits of the two instruments (Gao et al., 2008). Besides, it was speculated that the impact of VUV photoionization process on the products could be ignored due to few fragments observed in the TOF mass spectra of products during experimental process.

Ng et al. (2008) reported that an organic acid compound (C$_5$H$_7$N$_2$O, m/z 239) was detected as one of the SOA products for the reaction of gaseous isoprene with NO$_3$ radicals, which has a same molecular weight as that of 5-nitroferulic acid. In order to investigate the potential contributions of SOA products to the mass spectra acquired in this work, the reaction between gaseous isoprene and NO$_2$ radicals was conducted alone and in-situ observed by VUV-ATOFMS for 300 s. The concentration of isoprene was the same as that used for the kinetic experiments. The results showed that no obvious mass peaks were detected by VUV-ATOFMS, which might be resulted from the low sensitivity of VUV-ATOFMS.

### Table 1

| Number | Name                | Structure | RT (min) | MW (g mol$^{-1}$) | Formula       | Standard confirmed |
|--------|---------------------|-----------|----------|-------------------|---------------|-------------------|
| I      | Oxalic acid$^*$     |           | 5.1      | 90                | C$_2$H$_2$O$_4$ | ¥                  |
| II     | 4-Vinylguaiacol     |           | 5.7      | 150               | C$_9$H$_{10}$O$_2$ | ¥                  |
| III    | Vanillin            |           | 7.7      | 152               | C$_9$H$_8$O$_3$ | ¥                  |
| IV     | 5-Nitrovanillin      |           | 9.9      | 197               | C$_8$H$_7$NO$_5$ | ¥                  |
| V      | 5-Nitroferulic acid |           | 11.9     | 239               | C$_7$H$_6$NO$_6$ | –                  |
| VI     | Caffeic acid$^*$    |           | 12.7     | 180               | C$_9$H$_8$O$_4$ | ¥                  |

RT is the retention time, and MW is the molecular weight of compounds. Asterisks denote the products only identified by GC-MS analysis after derivatization by BSTFA.
ATOFMS toward the particles with small diameters (<70 nm) (Yang et al., 2010). The similar phenomena have been observed by VUV-ATOFMS in the homogeneous ozonization reactions of pirimiphos-methyl and phenanthrene (Yang et al., 2010; Zhang et al., 2010). Additionally, Ng et al. (2008) indicated that C5H7N2O/C09 was a minor SOA product due to its very small chromatographic peak area, and SOA began to form after ~10 min of reaction time. Considering that the maximum acquisition time for kinetic data in the experiments was less than 300 s, it was deemed that the interferences on the acquired mass spectra caused by the reaction of gaseous isoprene with NO3 radicals could be ignored in this work.

Fig. 3. EI mass spectra of TMCS derivative oxalic acid (A), 4-vinylguaiacol (B), vanillin (C), 5-nitrovanillin (D), 5-nitroferulic acid (E), and TMCS derivative caffeic acid (F) obtained in the experiments.
In the earlier studies, vanillin and 4-vinylguaiacol were identified as the products of ferulic acid through pyrolysis and microbial degradation (Fiddler et al., 1967; Lima et al., 2008; Mishra et al., 2014). Oxalic acid, vanillin, and 5-nitrovanillin were reported as the products of coniferyl aldehyde with NO$_3$ radicals (Liu et al., 2012a). Additionally, oxalic acid and vanillin were also the ozonization products of coniferyl alcohol and coniferyl aldehyde (Net et al., 2010, 2011). Oxalic acid as the smallest dicarboxylic acid widely existed on atmospheric particles (Chebbi and Carlier, 1996). Vanillin and 4-vinylguaiacol emitted by wood smoke were always found in both particle and gas phases in ambient atmosphere (Fiddler et al., 1966; Noite et al., 2001).

3.2. Reaction mechanisms

Based on the products identified, the mechanisms for the heterogeneous reaction of ferulic acid particles with NO$_3$ radicals were proposed. The reaction mechanisms containing two main pathways are illustrated in Fig. 4.

Zhang et al. (2016) have reported that NO$_3$ addition to the meta-position of the carbon connecting the hydroxyl group is the favored site with the lowest energy barrier for eugenol, which has a similar chemical structure as that of ferulic acid. The site is activated toward NO$_3$ electrophilic addition by the hydroxyl, methoxyl, and olefinic groups, which could donate electron density to the benzene ring through resonance or inductive effects (Lauraguais et al., 2016). Additionally, the reactions of NO$_3$ addition to the benzene ring of methoxyphenols were reported to be exothermic (Lauraguais et al., 2016; Zhang et al., 2016). Therefore, the nitratocyclohexadienyl-type radical (intermediate I) should be formed by NO$_3$ meta-addition to the hydroxyl substituent (Atkinson et al., 1990; Atkinson, 1991). Subsequently, the NO$_2$ ortho-addition to the hydroxyl group produced intermediate II (Zhang et al., 2016), which was followed by the collapse of intermediate species and the loss of nitric acid to produce 5-nitroferulic acid. This process is well known as nitro-substituted reaction (Atkinson et al., 1990; Atkinson, 1991).

Pathway II was initiated by the addition of a NO$_3$ radical on the C=C double bond, subsequently added by an oxygen molecule to produce two nitrooxyperoxy radicals (intermediates III$^a$ and III$^b$) (Atkinson, 1991; Canosa-Mas et al., 1999; Klotz et al., 2004). NO$_3$
radicals should predominantly attack acrylic acid group (-CH=CHCOOH) in β-position (Berndt and Böge, 1997). Thus, the formation of intermediate III\(^b\) should be the primary channel. Through the reactions with NO\(_3\) radicals, the intermediates III\(^a\) and III\(^b\) could produce the corresponding oxyl radicals (intermediates IV\(^a\) and IV\(^b\)), which can then undergo C-C bond scission to generate glyoxylic acid, NO\(_2\), and vanillin (Canosa-Mas et al., 1999; Klotz et al., 2004). The reaction of NO\(_3\) radicals with conjugated C=C double bond was a favored way to degrade unsaturated organics and would lead to a chain scission (Atkinson, 1991; Canosa-Mas et al., 1999). On the contrary, H-abstraction from methoxyl substituent was a marginal or negligible way for reaction with NO\(_3\) radicals (Lauraguais et al., 2016). In this work, glyoxylic acid was speculated to be finally converted into oxalic acid by an addition of hydroxyl radical to the carbonyl group, which was reported previously by Net et al. (2010). Vanillin could produce 5-nitrovanillin through nitro-substituted reaction (pathway I) (Liu et al., 2012a). Through pathway II, 5-nitroferulic acid could further produce oxalic acid and 5-nitrovanillin.

The formations of 4-vinylguaiacol and caffeic acid were minor channels compared to pathways I and II, which were not included in the Fig. 4.4-Vinylguaiacol might be produced by H-abstract and a carbon dioxide loss from carboxyl group (Das et al., 2002; Salgado et al., 2008). Caffeic acid was speculated to be resulted from the hydroxylation by hydroxyl radicals. The similar process about 3,4-dihydroxybenzoic acid formed through the ozonization of methoxophenols has been reported (Net et al., 2010, 2011). Certainly, it is well known that hydroxyl radicals could be produced by the reactions of unsaturated organic compounds with NO\(_3\) radicals (Canosa-Mas et al., 1999; Salisbury et al., 2001).

### 3.3. Heterogeneous kinetics

In this work, the heterogeneous kinetics was studied with a mixed-phase relative rate method. The average concentration of NO\(_3\) radicals in the chamber was \(-5.1 \times 10^{10}\) molecules cm\(^{-3}\), calculated according to the loss rates of isoprene (Smith et al., 2009). The recommended rate constant of isoprene with NO\(_3\) radicals is \(7.0 \times 10^{-13}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (http://www.iupac-kinetic.ch.cam.ac.uk/).

The uptake coefficient can be presented as the following equation (Liu et al., 2012b):

\[
\ln(C_F/C_{F0}) = -\text{k}_{\text{eff}}C_{NO_3}t
\]  

Here \(C_{F0}\) and \(C_F\) are the normalized initial and real-time concentrations of ferulic acid, and \(\text{k}_{\text{eff}}\) is the effective rate constant (cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)).

Fig. 5 shows the plot of \(\ln(C_F/C_{F0})\) versus \(C_{NO_3}t\) for ferulic acid radicals. The wall losses (~5%) of ferulic acid particles and isoprene were ignored. Error bars were the standard deviation of duplicate experiments. The value of \(\text{k}_{\text{eff}}\) was calculated to be \((1.71 \pm 0.08) \times 10^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) using the linear least-squares fitting \((R^2 > 0.98)\). It was several times lower than those

### Table 2

Comparison of kinetic data for heterogeneous reactions of particulate methoxophenols with O\(_3\) and NO\(_3\) radicals.

| Compounds       | Structure | Formula         | MW (g mol\(^{-1}\)) | \(k_{\text{eff}}\) (cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) | \(\gamma\) |
|-----------------|-----------|-----------------|---------------------|------------------------------------------------|----------|
|                 |           |                 |                     | \(k_{\text{eff}}\) with O\(_3\) radicals | NO\(_3\) radicals |         |
| Coniferyl       | ![Image](https://example.com/coniferyl.png) | C\(_{10}\)H\(_{10}\)O\(_3\) | 178 | \(7.2 \times 10^{-19}\) | \(3.5 \times 10^{-12}\) \(\text{b}\) | 0.28\(\text{c}\) |
| Syringaldehyde  | ![Image](https://example.com/syringaldehyde.png) | C\(_{8}\)H\(_{12}\)O\(_4\) | 182 | – | \(5.7 \times 10^{-12}\) \(\text{b}\) | 0.33\(\text{b}\) |
| Vanillic acid   | ![Image](https://example.com/vanillic.png) | C\(_{6}\)H\(_{4}\)O\(_4\) | 168 | – | \(5.2 \times 10^{-12}\) \(\text{b}\) | 0.31\(\text{b}\) |
| Ferulic acid    | ![Image](https://example.com/ferulic.png) | C\(_{10}\)H\(_{10}\)O\(_4\) | 194 | – | \(1.71 \times 10^{-12}\) \(\text{c}\) | 0.17\(\text{c}\) |

MW, \(k_{\text{eff}}\), and \(\gamma\) are the molecular weight of compounds, effective rate constant, and uptake coefficient, respectively.

\(\text{a}\) Data derived from Net et al. (2010).

\(\text{b}\) Data derived from Liu et al. (2012a).

\(\text{c}\) This work.
Thus, NO$_3$ radicals might have a more significant effect on ferulic acid degradation than ozone does at nighttime.

3.4. Atmospheric implications

Recent studies showed that methoxyphenols in the reactions with trace gaseous oxidants might have a significant contribution to SOA formation (Lauraguais et al., 2012, 2014b; Yee et al., 2013). SOA contain an important amount of organic acids, such as oxalic acid and caffeic acid identified in this work, which could serve as nucleating species for aerosol growth (Christoffersen et al., 1998). Based on the reported particle size distribution of wood smoke (Christoffersen et al., 1998), the uptake coefficient of NO$_3$ radicals with polycyclic aromatic hydrocarbons (PAHs) was much faster than that of ozone by 2–6 orders of magnitude (Shiraiwa et al., 2009; Liu et al., 2012b). Thus, NO$_3$ radicals might have a more significant effect on ferulic acid degradation than ozone does at nighttime.

processes of methoxyphenols with NO$_3$ radicals could lead to subsequent effects on air quality and climate.

4. Conclusion

In this work, the heterogeneous reaction of ferulic acid particles with NO$_3$ radicals was investigated. Assisted with GC-MS analysis, oxalic acid, 4-vinylguaiacol, vanillin, 5-nitrovanillin, 5-nitroferulic acid, and caffeic acid were observed and confirmed as the products. The uptake coefficient of NO$_3$ radicals on ferulic acid particles was $0.17 \pm 0.02$, calculated according to the average NO$_3$ concentration and the consumption ratio of ferulic acid. The effective rate constant was $(1.71 \pm 0.08) \times 10^{-12} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$, calculated using a mixed-phase relative rate method. Additionally, the reaction mechanisms were proposed to explain the formation of products. The experimental results might help further understand the chemical behaviors of ferulic acid in nighttime atmosphere.

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