Heterogeneous reaction of coniferyl alcohol adsorbed on silica particles with NO$_3$ radicals

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Changgeng Liu[*], Xiaoying Wen, Bin Wu

School of Resources and Environmental Engineering, Panzhihua University, Panzhihua 617000, China

ABSTRACT

4-[(1E)-3-Hydroxy-1-propenyl)]-2-methoxyphenol (coniferyl alcohol) is a potential marker compound for wood smoke emissions in the atmosphere. In this work, the heterogeneous reaction of coniferyl alcohol adsorbed on silica particles with NO$_3$ radicals was investigated. According to gas chromatography mass spectrometry (GC—MS) analysis, five products including glycolic acid, oxalic acid, 4-hydroxy-3-methoxy-benzaldehyde, 4-hydroxy-3-methoxy-benzoic acid, and 4-hydroxy-3-methoxy-5-nitrobenzaldehyde were confirmed. Based on the identified products, the reaction mechanisms were proposed and the favored sites for NO$_3$ electrophilic addition were olefinic C=C bond and the *meta*-position to the hydroxyl group in the benzene ring. The obtained results might shed light on the chemical behaviors of coniferyl alcohol at night.

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1. Introduction

Methoxyphenols produced by lignin pyrolysis are emitted into the atmosphere by biomass burning and known as the potential tracers for wood smoke emissions (Simoneit et al., 1993). Over the past few decades, great efforts have been made into detecting the concentration of methoxyphenols in ambient atmosphere (Hawthorne et al., 1989, 1992; Simoneit et al., 1993; Nolte et al., 2001; Simpson et al., 2005; Bari et al., 2009). Its atmospheric concentration could reach several μg m^{-3} (Hawthorne et al., 1992; Schauer and Cass, 2000; Simpson et al., 2005; Bari et al., 2009), and the highest concentration usually appears in a wood smoke-dominated time (Schauer and Cass, 2000; Simpson et al., 2005). This pollution could result in adverse effects on human health, air quality, and climate (Naeher et al., 2007). In recent years, the re-activities of methoxyphenols toward trace gaseous oxidants have been attracted great attention (Coeur-Tourneur et al., 2010; Net et al., 2010, 2011; Lauraguais et al., 2012, 2014a, 2014b, 2016; Liu et al., 2012; Yee et al., 2013; O'Neill et al., 2014; Yang et al., 2016; Zhang et al., 2016). These studies mainly reported their homogeneous reactions and the formation of secondary organic aerosols

(SOA), while their heterogeneous reactivities have been not well known. From a health point of view, understanding the chemical behaviors of methoxyphenols has great significance for their toxicity and safety assessments.

Coniferyl alcohol with a vapor pressure of ~1.2 × 10^{-3} (298 K) (http://www.chemspider.com/Chemical-Structure.1266063.html?rid=9d520dcc-7127-428f-98db-67e22a42b524, accessed 6 October 2016), is one of the three precursor lignin monomers and widely exists in ambient atmosphere (Nolte et al., 2001; Alves et al., 2011). Its emission rate was reported to be 18 μg g^{-1} of burnt wood (Nolte et al., 2001), while its chemical behaviors in the atmosphere have not been well known. Coniferyl alcohol in the process of at-mospheric transportation can react with trace gaseous species, such as NO$_3$ radicals. NO$_3$ radicals are the dominant oxidant in the nighttime with similar oxidative power as hydroxyl radicals (Karagulian and Rossi, 2005), and play an important role in the nighttime chemical processing of organics in the troposphere (Atkinson, 1991; Wayne et al., 1991). Coniferyl alcohol contains olefinic C=C bond and benzene ring, which are both the favored sites for the reactions with NO$_3$ radicals (Knopf et al., 2011; Liu et al., 2012; Lauraguais et al., 2016; Yang et al., 2016; Zhang et al., 2016). In this work, the heterogeneous reaction of coniferyl alcohol adsorbed on model particles with NO$_3$ radicals was investigated. The reaction products were identified by gas chromatography mass spectrome-try (GC-MS) analysis and the reaction mechanisms were proposed.

Mineral particles emitted into the atmosphere mostly derive

from arid and semi-arid regions, and play an important role in loading atmospheric particulate matters (Dentener et al., 1996; Ma et al., 2010). In addition, silica was regarded as one of the main constituents of authentic mineral dust (Usher et al., 2003; He et al., 2005). In previous studies, silica has been widely used as the model particles for heterogeneous reactions (Underwood et al., 2001; Perraudin et al., 2005, 2007; Miet et al., 2009, 2010; Ma et al., 2010; Net et al., 2010, 2011). Therefore, silica was selected as the representative surrogates of atmospheric mineral particles in this work.

2. Materials and methods

2.1. Chemicals

Coniferyl alcohol (Aldrich, 98%), the silica powder AEROSIL R812 (Evonik Degussa, $\geq$99.8%), dichloromethane (J. T. Baker Co., chromatographic grade), bis(trimethylsilyl)-trifluoroacetamide (BSTFA) [Sigma-Aldrich, containing 10% trimethylchlorosilane (TMCS)], fuming nitric acid (Sinopharm Chemical Reagent Co., Ltd., 95%), P_2O_5 (Sinopharm Chemical Reagent Co., Ltd., 98%), Nitrogen (Chengdu Xinyuan Chemical Industry Co., Ltd., 99.99%) were used in this work.

2.2. Particle preparation

The preparation of the reactant particles has been described in detail elsewhere (Yang et al., 2012). Therefore, there is only a brief description represented. In this work, silica particles coated with coniferyl alcohol were produced by liquid-solid adsorption. A mixture including 20 mg of coniferyl alcohol, 150 mL of dichloromethane, and 1.5 g of silica powder was placed in a 250 mL rotary-evaporator bulb. The bulb was wrapped with an aluminium foil and sonicated for 30 min. Subsequently, the mixture was rotary evaporated at 40 °C and 850 $\pm$ 50 mbar for 60 min. The obtained particles were further dried by flowing N_2 gas for 15 min (Net et al., 2011). The recovery of coniferyl alcohol was (96 $\pm$ 5)%, which was measured by extraction from the coated silica particles. The prepared particles were stored in the dark at room temperature.

Assuming that the molecules of coniferyl alcohol had a spherical geometry, 20 mg of coniferyl alcohol in a single layer had a surface of ~127 m^2 (Net et al., 2011). The average diameter of silica powder AEROSIL R812 used in the experiments was 7 nm and the corresponding specific surface was 260 $\pm$ 30 m^2 g^{-1} 1.5 g of silica particles used in the experiments had a total specific surface of 390 m^2. Therefore, assuming a uniform particle surface coverage, the amount of coniferyl alcohol adsorbed on silica particles was less than a monolayer. The coverage percentage of silica particle surface coated with coniferyl alcohol was ~33%.

2.3. Experimental procedure

NO_3 radicals were produced by thermal decomposition of N_2O_5 powders, which were synthesized according to the experimental method reported by Yang et al. (2011). The heterogeneous reaction between ~300 mg of coated silica particles and NO_3 radicals was performed in a ~250 mL rotary Pyrex bulb under dark conditions at room temperature (~298 K) and ambient pressure. N_2 with a flow rate of 0.25 L min^{-1} passed through the N_2O_5 flask to bring NO_3 radicals into the bulb. The bulb was rotated at a rate of ~80 rpm to ensure that the particle surfaces could be contacted with NO_3 radicals sufficiently. The residence time of the vapor in the bulb was ~60 s. The concentration of NO_3 radicals was ~10^{12}–10^{13} molecules cm^{-3} in the experiments estimated using the reported equilibrium constants (Tuazon et al., 1984).

2.4. GC-MS analysis

After reaction, the solid particles were solvent-extracted in 30 mL of dichloromethane for 30 min by sonication. In order to separate the organics dissolved in dichloromethane from silica particles, the suspended particles in the solution were centrifuged (Model TGL-10C, Shanghai Anting Scientific Instrument Factory, China). Subsequently, the extracted solutions were filtrated with filters (PTFE 25-4, 25 mm × 0.45 mm, Whatman) (Yang et al., 2012). In the end, the clear solutions were analyzed immediately by GC-MS for quantification and product identification.

In this work, GC-MS analysis was conducted before and after derivatization with BSTFA containing 10% TMCS, because the reaction products might contain hydroxyl or carboxyl group (Net et al., 2010, 2011; Liu et al., 2012). These groups could not be detected by direct analysis, owing to the strong interaction with the stationary phase in the chromatographic column or the small amount of products formed in the reaction (Net et al., 2010). An Agilent 6890 GC-MS equipped with a 30 m × 0.25 mm × 0.25 μm HP-5 capillary column and an HP-5973 quadrupole mass filter with a 70 eV electron impact (EI) ionizer was applied to detect the products. The solution sample with a volume of 1 μL was injected by the pulsed splitless mode. GC temperature was set at 80 °C for 1 min, followed by an increase rate of 15 °C min^{-1} to 220 °C, finally to 300 °C at a rate of 25 °C min^{-1} and kept for 15 min (Net et al., 2010). The total ion chromatogram (TIC) mode was used to analyze the products, which were identified through comparing their EI mass spectra with those from a Mass Spectral Library [the National Institute of Standards and Technology (NIST) 2005]. 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.
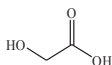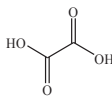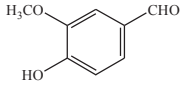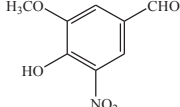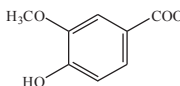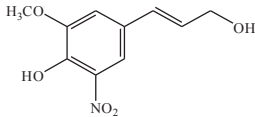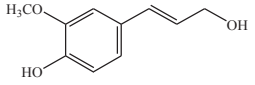
3. Results and discussion

3.1. Reaction products

In previous studies, uptake coefficients of N_2O_5, HNO_3, and NO_2 on biomass burning aerosols and polycyclic aromatic hydrocarbon surfaces were reported to be ~3–5 orders of magnitude smaller than those of NO_3 radicals, though the concentration of NO_3 radicals was ~3–4 orders of magnitude smaller than those of N_2O_5, HNO_3, and NO_2 (Gross and Bertram, 2008; Knopf et al., 2011). Thus, the degradation of coniferyl alcohol by N_2O_5, HNO_3, and NO_2 was not taken into account in this work.

The products identified by GC-MS analysis are shown in Table 1, and their corresponding mass spectra are illustrated in Fig. 1. As shown in Table 1, glycolic acid (after derivatization), oxalic acid (after derivatization), 4-hydroxy-3-methoxy-benzaldehyde (vanillin), 4-hydroxy-3-methoxy-benzoic acid (vanillic acid, after derivatization), and 4-hydroxy-3-methoxy-5-nitrobenzaldehyde (5-nitrovanillin) were identified as the products of coniferyl alcohol with NO_3 radicals. Their retention times were 4.54, 5.09, 7.75, 10.53, and 9.91 min, respectively. Additionally, one nitro-substituted product was observed but not identified successfully due to the lack of standard mass spectrum in the NIST library. Recently, with the help of theoretical calculations and GC-MS analysis, Zhang et al. (2016) have reported that 4-allyl-2-methoxyl-6-nitrophenol is the predominant nitro-derivative from the reaction of NO_3 radicals with 4-allyl-2-methoxyphenol, which has a similar chemical structure as that of coniferyl alcohol. In addition, 4-hydroxy-3-methoxy-5-nitrobenzaldehyde was identified as the product in this work. Consequently, we speculated that the nitro-substituted site was the *ortho*-position to the hydroxyl group (−OH) in the benzene ring. Then the nitro-substituted

Table 1
Products identified in the heterogeneous reaction of coniferyl alcohol with NO_3 radicals.

Name	Structure	Formula	MW	RT	η	Identified
Glycolic acid[*]		$C_2H_4O_3$	76	4.54	42.19	✓
Oxalic acid[*]		$C_2H_2O_4$	90	5.09	6.76	✓
4-Hydroxy-3-methoxy-benzaldehyde (Vanillin)		$C_8H_8O_3$	152	7.75	34.62	✓
4-Hydroxy-3-methoxy-5-nitrobenzaldehyde (5-Nitrovanillin)		$C_8H_7NO_5$	197	9.91	7.38	✓
4-Hydroxy-3-methoxy-benzoic acid [*] (Vanillic acid)		$C_8H_8O_4$	168	10.53	8.55	✓
4-[(1E)-3-Hydroxy-1-propenyl)]-2-methoxy-6-nitrophenol (5-Nitroconiferyl alcohol)		$C_{10}H_{11}NO_5$	225	11.68	100	–
4-[(1E)-3-Hydroxy-1-propenyl)]-2-methoxyphenol (Coniferyl alcohol)		$C_{10}H_{12}O_3$	180	10.82	–	✓

RT is the retention time (min), MW is the molecular weight of compound (g mol^{-1}), and η is the relative abundances of the products from the results of GC–MS analysis (%), calculated by integrating their peak areas. Asterisks denote the products only identified by GC–MS analysis after derivatization by BSTFA.

product was tentatively assigned to be 4-[(1E)-3-hydroxy-1-propenyl)]-2-methoxy-6-nitrophenol (5-nitroconiferyl alcohol), and its retention time was 11.68 min. As shown in Fig. 1F, its molecular ion peak locates at m/z 225, which is 45 amu smaller than that of coniferyl alcohol (m/z 180). The mass spacing of 45 amu between them suggests a hydrogen atom loss (−1 amu) and an addition of a NO_2 group (+46 amu) during the reaction. The similar substituted phenomena have been reported in the reactions of methoxyphenols with NO_3 radicals (Liu et al., 2012; Yang et al., 2016; Zhang et al., 2016).

Compared with the ozonization products of coniferyl alcohol, glycolic acid, oxalic acid, 4-hydroxy-3-methoxy-benzaldehyde, 4-hydroxy-3-methoxy-benzoic acid were observed in this work, while 3,4-dihydroxybenzoic acid was not detected (Net et al., 2011). The former four products were also identified as the products of (2E)-3-(4-hydroxy-3-methoxyphenyl)acrylaldehyde (coniferyl aldehyde) in the reactions with O_3 and NO_3 radicals (Net et al., 2010; Liu et al., 2012). Oxalic acid is well known as the smallest dicarboxylic acid on the condense particles in the atmosphere (Chebbi and Carlier, 1996). 4-Hydroxy-3-methoxy-benzaldehyde and 4-hydroxy-3-methoxy-benzoic acid widely exist in the ambient atmosphere in both particle and gas phases (Hawthorne et al., 1989, 1992; Simoneit et al., 1993; Nolte et al., 2001; Simpson et al., 2005). In recent years, some nitro-substituted aromatics were pointed out as the important composition of SOA from biomass burning, and might be taken as the potential tracers (Kitanovski et al., 2012; Lauraguais et al., 2014b). However, the quick photolysis of ortho-nitrophenol derivates was reported (Bejan et al., 2006, 2007). Thus, whether nitro-substituted products

should be used as the tracers for wood smoke emissions needs to be further discussed.

3.2. Reaction mechanisms

Based on the identified products, the mechanisms of the heterogeneous reaction between particulate coniferyl alcohol and NO_3 radicals were proposed. The reaction mechanisms containing two pathways are illustrated in Scheme 1.

Pathway I was initiated by the NO_3 electrophilic addition on one of the two double-bonded carbons, which was regarded as the more favorable way rather than an H-abstraction (Wayne et al., 1991; Finlayson-Pitts and Pitts, 2000). This was followed by an addition of O_2 to produce two nitrooxyperoxy radicals (intermediates I[a] and I[b]) (Atkinson, 1991; Canosa-Mas et al., 1999; Klotz et al., 2004; Picquet-Varrault et al., 2010). NO_3 radicals should predominantly attack 3-hydroxyl-1-propenyl group (−CH═CHCH$_2$OH) in β-position (Berndt and Böge, 1997). Thus, the formation of intermediate I[b] should be the primary channel. The observed products suggested that the nitrooxyperoxy radicals could produce the corresponding alkoxy radicals (intermediates II[a] and II[b]) through the reactions with NO_3 radicals, which can then undergo C–C bond scission to generate 4-hydroxy-3-methoxy-benzaldehyde, NO_2, and glycolaldehyde (Canosa-Mas et al., 1999; Klotz et al., 2004; Picquet-Varrault et al., 2010). The previous studies indicated that the reaction of NO_3 radicals with conjugated C═C double bond would lead to a chain scission and it was a favored way to degrade unsaturated organics (Atkinson, 1991; Canosa-Mas et al., 1999; Klotz et al., 2004; Picquet-Varrault et al.,
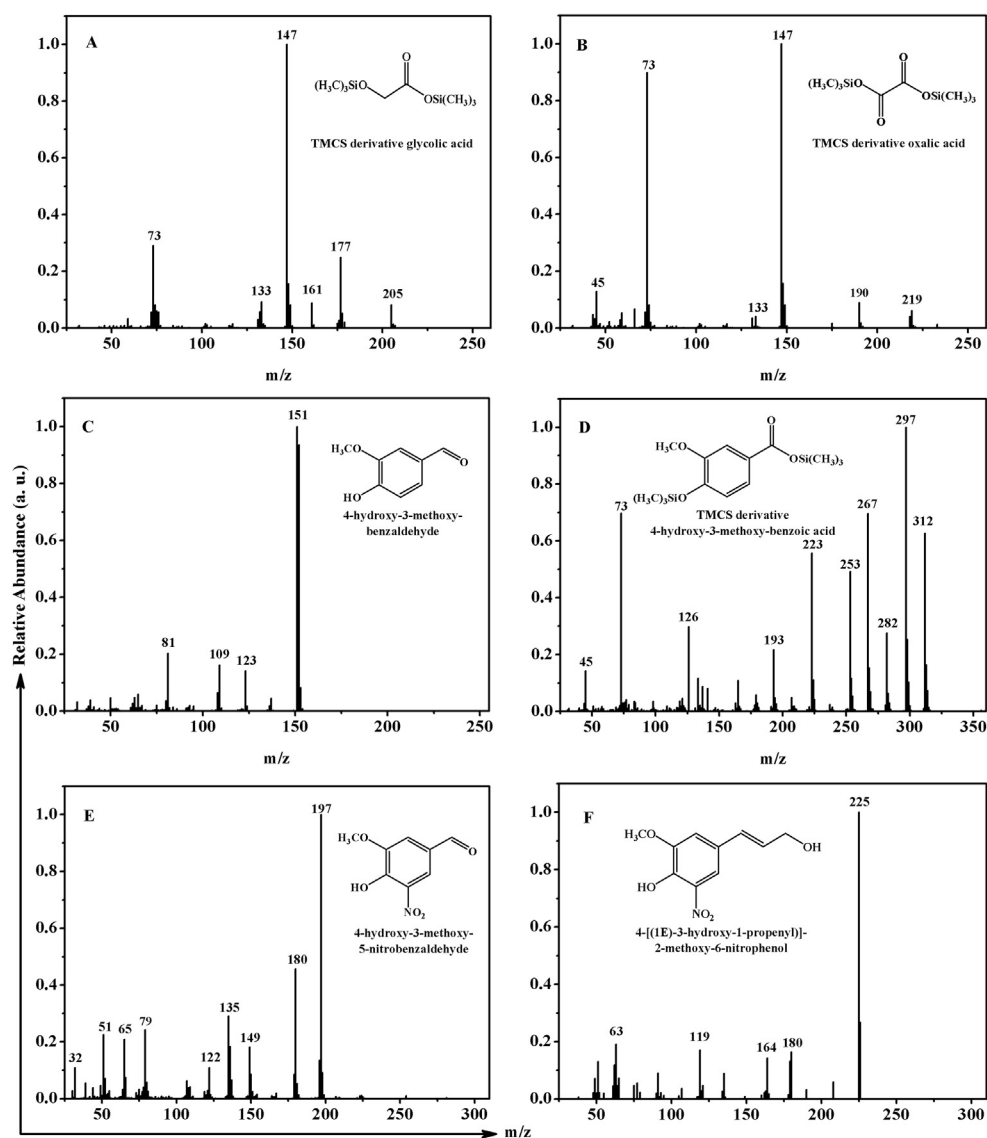
Fig. 1. EI mass spectra of TMCS derivative glycolic acid (A), TMCS derivative oxalic acid (B), 4-hydroxy-3-methoxy-benzaldehyde (C), TMCS derivative 4-hydroxy-3-methoxy-benzoic acid (D), 4-hydroxy-3-methoxy-5-nitrobenzaldehyde (E), and 4-[(1E)-3-hydroxy-1-propenyl)]-2-methoxy-6-nitrophenol (F).
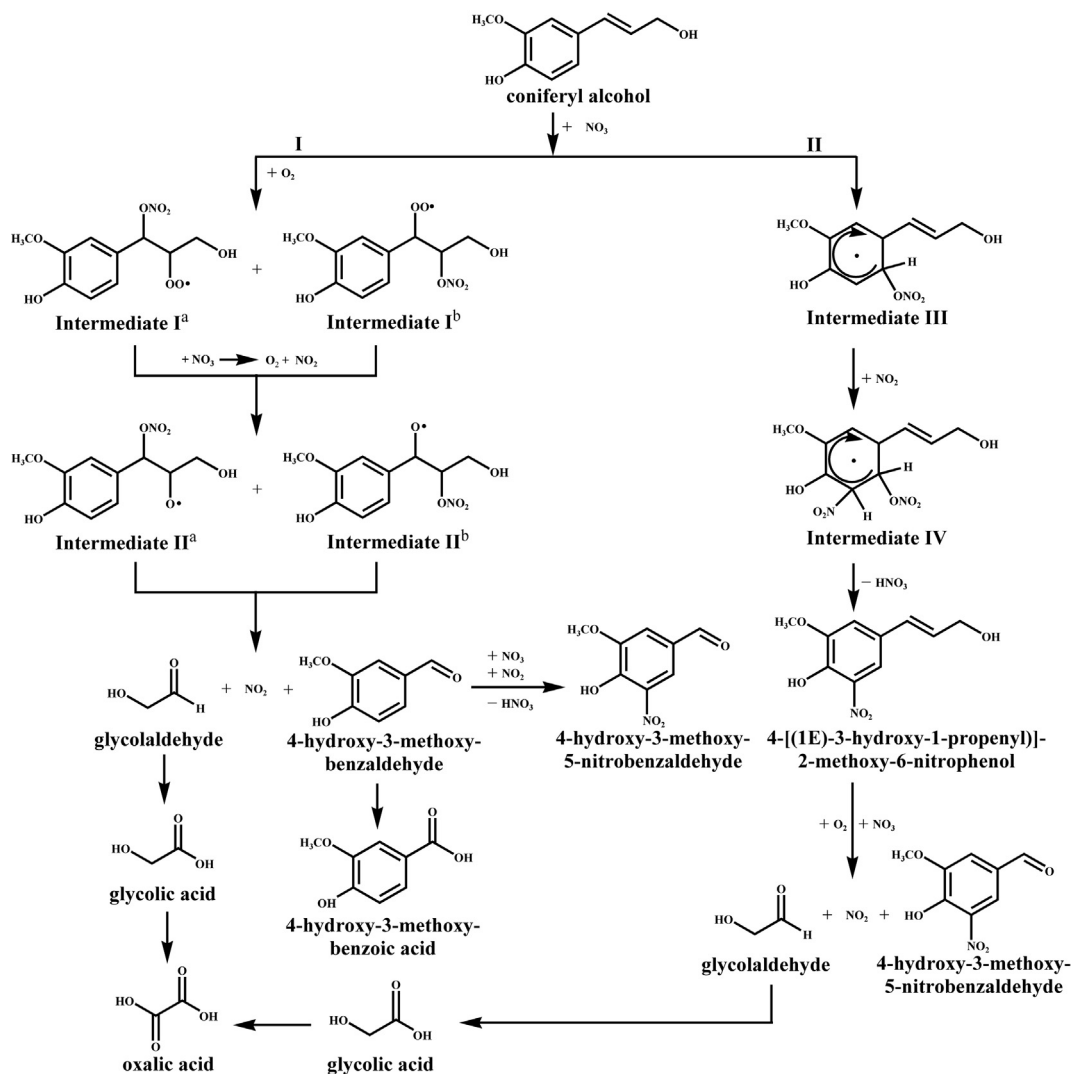
2010). On the contrary, H-abstraction from methoxyl or olefinic substituent was a marginal or negligible way for reactions with NO_3 radicals (Lauraguais et al., 2016). In this work, glycolaldehyde was speculated to be finally converted into glycolic acid by an addition of OH radical to the carbonyl group, which was reported previously by Net et al. (2011). Certainly, it is well known that OH radicals could be produced through the reactions of NO_3 radicals with unsaturated organic compounds (Canosa-Mas et al., 1999; Salisbury et al., 2001). With the similar mechanism, 4-hydroxy-3-methoxy-benzaldehyde and glycolic acid were further converted into 4-hydroxy-3-methoxy-benzoic acid and oxalic acid, respectively (Net et al., 2011; Liu et al., 2012).

With the help of theoretical calculations, Zhang et al. (2016) have reported that the NO_3 *meta*-addition to the OH site is the most energy-favorable addition pathway with the lowest energy barrier for 4-allyl-2-methoxyphenol, which has a similar chemical structure as that of coniferyl alcohol. 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 reaction of NO_3 addition to the benzene ring of methoxyphenols was reported to be exothermic (Lauraguais et al., 2016; Zhang et al., 2016). Hence, pathway II in this work should be begun with NO_3 *meta*-addition to the OH site, resulting in a nitratocyclohexadienyl-type radical (intermediate III) (Atkinson et al., 1990; Atkinson, 1991; Zhang et al., 2016). Subsequently, the NO_2 *ortho*-addition to the OH site produced intermediate IV (Yang et al., 2016; Zhang et al., 2016). The similar intermediate formed in the nitro-substituted reaction of 4-allyl-2-methoxyphenol with NO_3 radicals has been calculated to be barrierless (Zhang et al., 2016). The intermediate IV was followed by the elimination of a HNO_3 molecule, and produced 4-[(1E)-3-hydroxy-1-propenyl)]-2-methoxy-6-nitrophenol (Liu et al., 2012; Yang et al., 2016; Zhang et al., 2016), which could further generate glycolic acid and 4-hydroxy-3-methoxy-5-nitrobenzaldehyde through pathway I.

3.3. Atmospheric implications

As shown in Fig. 2, the decay rate of coniferyl alcohol was determined to be 2.9×10^{-3} s^{-1}, calculated using the exponential

Scheme 1. Proposed pathways of the heterogeneous reaction between NO_3 radicals and coniferyl alcohol adsorbed on silica particles.
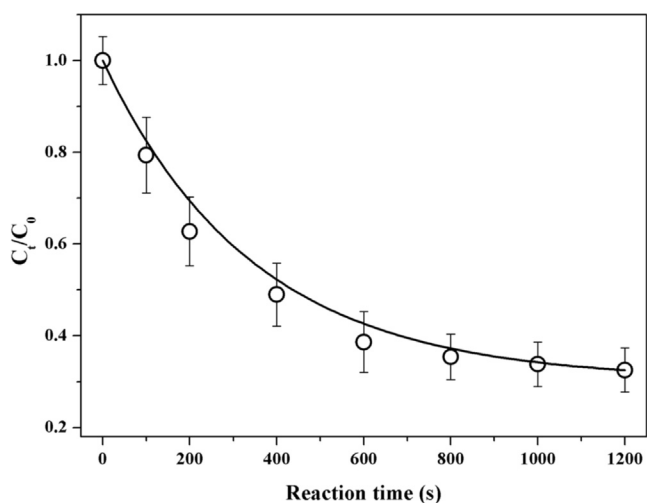

Fig. 2. Decays of normalized concentration of coniferyl alcohol adsorbed on silica particles versus time, corresponding to the heterogeneous reaction with NO_3 radicals and exponential fitting.

decay via non-linear least square fitting. It indicates that the degradation of coniferyl alcohol by NO_3 radicals is effectively. The reported decay rates of methoxyphenols with O_3 were on the order of ~10^{-5}–10^{-6} s^{-1} (Net et al., 2010; O'Neill et al., 2014), which was ~2–3 orders of magnitude slower than that obtained in this work. Thus, NO_3 radicals might have a more significant effect on the degradation of methoxyphenols than O_3 does.

Through nitro-substituted reaction, the particles hygroscopicity and its activity of cloud condensation nuclei (CCN) would be affected negatively by nitro-products (Suda et al., 2014). Meanwhile, more volatile products were produced through chain scission or intermediate decomposition. Therefore, the chemical processes of methoxyphenols with NO_3 radicals could lead to subsequent effects on air quality and climate. Recent studies showed that methoxyphenols in the reactions with trace gaseous oxidants might have a significant contribution to SOA (Hennigan et al., 2011; Lauraguais et al., 2012, 2014b; Yee et al., 2013). SOA contain an important amount of organic acids, such as glycolic acid, oxalic acid and 4-hydroxy-3-methoxy-benzoic acid identified in this work, which have been reported to serve as nucleating species for aerosol growth (Christoffersen et al., 1998). The results also indicate that the heterogeneous reaction of coniferyl alcohol with

NO$_3$ radicals may be another source of organic acids in the atmosphere.

4. Conclusions

In this work, the heterogeneous reactivity of coniferyl alcohol toward NO$_3$ radicals was investigated. Five products including glycolic acid, oxalic acid, 4-hydroxy-3-methoxy-benzaldehyde, 4-hydroxy-3-methoxy-benzoic acid, and 4-hydroxy-3-methoxy-5-nitrobenzaldehyde were identified and confirmed by their standard mass spectra. Additionally, the reaction mechanisms were proposed to explain the formation of products. The experimental results might help further understand the chemical behaviors of coniferyl alcohol in nighttime atmosphere.

Acknowledgements

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