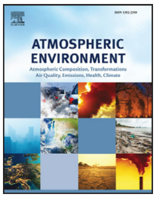
Atmospheric Environment 125 (2016) 243–251

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv



Experimental and theoretical studies on gas-phase reactions of NO_3 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 NO_3 radical with three methoxyphenols are obtained.
- Nitro-substituted derivatives are observed as major transformation products.
- Reaction mechanisms of methoxyphenols with NO_3 radicals are proposed.
- The rate constants of three methoxyphenols with NO_3 radicals are measured.

ARTICLE INFO

Article history:
Received 13 July 2015
Received in revised form 10 November 2015
Accepted 12 November 2015
Available online 1 December 2015

Keywords:
Methoxyphenol
NO_3 radical
Rate constant
Reaction mechanism

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 NO_3 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 NO_3 radicals were measured to be 3.2×10^{-12}, 2.4×10^{-13}, and 4.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, respectively. At a typical tropospheric concentration of NO_3 radicals (5×10^8 molecule cm^{-3}), atmospheric lifetimes for guaiacol, creosol, and syringol toward NO_3 radicals were 0.2, 2.3, and 1.4 h, respectively. These results indicate that the reaction with NO_3 radicals can be a major sink for methoxyphenols at night.

1. Introduction

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

---

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

* Corresponding author.

E-mail address: boyang@rcees.ac.cn (B. Yang).

http://dx.doi.org/10.1016/j.atmosenv.2015.11.028

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

Studies on the gas-phase atmospheric reactions of methoxyphenols are scarce, however. In one study, Lauraguais and Coeur-Tourneur et al. determined the rate constants and oxidation products of the gas-phase reaction between guaiacol, creosol, and syringol, and the OH radical (Coeur-Tourneur et al., 2010; Lauraguais et al., 2012, 2014b). The results revealed that the atmospheric lifetime of these compounds when reacting with OH radicals was about 2 h, and the primary products for the reaction of guaiacol and syringol with OH radicals were nitro derivatives. The gas-phase rate constants for the reaction of chlorine atoms with different methoxyphenols were also investigated, and the results showed that their atmospheric lifetimes were in a range of 12–21 h (Lauraguais et al., 2014a). In addition, the aqueous-phase photonitration, or radical-initiated reaction, between guaiacol and phenols forming SOAs have been reported (Kitanovski et al., 2014; Yu et al., 2014). The nitro-products were identified, and they are suspected constituents of atmospheric “brown” carbons. Other studies have been published on the heterogeneous ozonolysis of methoxyphenols adsorbed on silica particles (Net et al., 2010a, 2010b, 2011), aqueous-phase ozonolysis of methoxyphenols in solutions (Khudoshin et al., 2008; Ko et al., 2011), heterogeneous nitration of suspended methoxyphenol particles by reaction with NO_3 radicals (Liu et al., 2012), and heterogeneous oxidation kinetics of biomass-burning aerosol surrogates reacting with a series of atmospheric oxidants (Knopf et al., 2011). To the best of our knowledge, no study on the gas-phase reactions of methoxyphenols with NO_3 radicals has been reported, nor have their reaction mechanisms been delineated so far.

The NO_3 radical is one of the most important oxidants in the atmosphere, controlling the chemistry of the nighttime troposphere (Wayne et al., 1991). In the present work, the gas-phase reactions between guaiacol, creosol, and syringol, and NO_3 radicals were studied. Formation of the products and the decay of reactants were monitored on-line using a laboratory-built vacuum ultraviolet photoionization gas time-of-flight mass spectrometer (VUV-GTOFMS). This apparatus can produce the mass spectrum of organic gasses with less fragmentation, which has obvious advantages in the study of gas-phase organic reactions. The second-order rate constants for the reaction of methoxyphenols with NO_3 radicals at room temperature (298 ± 2 K) and 1 atm pressure were obtained using a relative rate method. With the aid of an off-line gas chromatography-mass spectrometer (GC-MS) and quantum chemistry methods, the predominating products were determined, and chemical reaction mechanisms were developed.

2. Experiment

2.1. Materials and equipment

The experimental setup was composed of an 180-L reaction chamber, an N_2O_5 vapor manipulator, and analytical instruments. The reaction chamber consists of a open head stainless steel drum (50 cm (diameter) × 60 cm (height)) and a Tedlar polyvinyl fluoride (PVF) film bag (50 cm (diameter) × 50 cm (length)). A small fan placed at the bottom of the chamber is used to mix reactants rapidly. The N_2O_5 vapor manipulator has been described elsewhere (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 ~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_2O_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 ($\overline{C_{NO3}t}$) was derived from the measured decay of the reference gases using the following equation:

$$\frac{\ln\left(C_{ref}/C_{ref0}\right)}{-k_{ref}} = \int_0^t C_{NO3}dt = \overline{C_{NO3}t} \tag{1}$$

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 radical 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.ch.cam.ac.uk/; Atkinson et al., 1984). The rate constant of methoxyphenol (k_m) is expressed in the following equation:

$$\ln(C_m/C_{mo}) = -k_m\overline{C_{NO3}t} \tag{2}$$

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

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