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Photochemical conversion of toluene in simulated atmospheric matrix and characterization of large molecular weight products by +APPI FT-ICR MS

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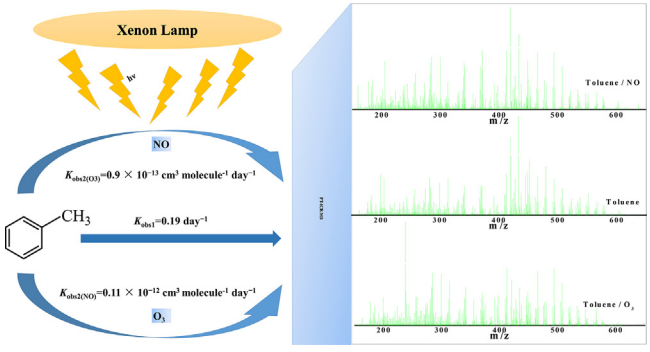
HIGHLIGHTS

- The kinetic rate constants of toluene photochemical conversion were obtained in three systems.
- The reaction sensitivity of ozone to temperature was lower than NO.
- The larger-weight molecule products containing up to O_6 heteroatoms were identified by FT-ICR MS.
- DBE values varied from 1 to 18 with carbon number ranging within 12–38.

GRAPHICAL ABSTRACT



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ABSTRACT

The lack of kinetic parameters of VOC photochemical conversion especially in the presence of NO and O_3, and product information, will result in the incomplete understanding for the occurrence of haze. In the present study, the photochemical conversion of toluene, one of most significant hydrocarbons of VOCs, in toluene, toluene/NO, toluene/O_3 and reaction systems was assessed for up to 4 days in a smog chamber at 278 K and 308 K. The results indicated that the addition of NO and O_3 promoted the conversion of toluene. The first-order kinetic rate constants of toluene assessed in the toluene reaction system at 278 K and 308 K were 0.12 and 0.19 day^{-1}, respectively. The second-order kinetic rate constants of toluene assessed in the toluene/NO were 0.1 × 10^{-13} cm^3 molecule^{-1} day^{-1} (at 278 K) and 0.9 × 10^{-13} cm^3 molecule^{-1} day^{-1} (at 308 K), and those in the toluene/O_3 reaction systems were 0.06 × 10^{-12} cm^3 molecule^{-1} day^{-1} (at 278 K) and 0.11 × 10^{-12} cm^3 molecule^{-1} day^{-1} (at 308 K). The small difference of second-order kinetic rate constants between 278 K and 308 K obtained for the toluene/O_3 system when compared with the toluene/NO system indicated the reduced reaction sensitivity of O_3 to the temperature. Several dozens of large molecule products containing up to O_6 heteroatoms were identified by positive ion atmospheric pressure photoionization (+APPI) coupled with Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), with double bond equivalents up to 18, and carbon numbers ranging within 12–38, respectively. The findings presented herein may provide a new train of thought for the photochemical reaction process of toluene and its conversion in ambient air.

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1. Introduction

Developed economic production, transportation, human production and activities have resulted in frequent and severe haze events in recent years (Zhang et al., 2014; Liu et al., 2013; Hu et al., 2015). The increasing emissions of volatile organic compounds (VOCs) at increasing concentrations have been recognized to be a key contributing factor to severe haze pollution (Liu et al., 2017a; Liu et al., 2016). A series of complex physicochemical transformation can occur between atmospheric VOCs and nitrogen oxides, resulting in the formation of ozone and secondary organic aerosols in urban and regional areas (Lyu et al., 2016; Geng et al., 2008). Thus, it is necessary to understand the fate of VOCs in the atmosphere especially in the presence of NO_x and O_3 for environmental assessment and to more comprehensively understand the occurrence of haze.

Toluene is considered as one of the most abundant aromatic hydrocarbons in ambient air and is mainly introduced into the tropospheric layer through fuel combustion, fuel evaporation, solvent use, and industrial processes (Elrod, 2011; Steinfeldm et al., 2016). As an important participant in photochemical processes of the lower troposphere, reactions between toluene and atmospheric oxidants, such as •OH, O_3, •NO_3, can form functional groups of carbonyl and nitro compounds, which can promote the formation of secondary organic aerosols through adsorption and absorption processes (Xu et al., 2015; Offenberg et al., 2007; Hu & Kamens, 2007). A series of chamber experiments focusing on the oxidation of toluene (Klotz et al., 1998; Hu et al., 2007) and associated analysis have identified the formation of γ-dicarbonyl intermediates via a ring-opening process and their influence on the simulated •OH and ozone concentrations (Hamilton et al., 2003). Cao & Jang (2010) explored a prediction model for the formation of secondary organic aerosol, including both partitioning and heterogeneous reactions, upon oxidation of toluene. The results indicated that the heterogeneous reactions of the second-generation products of toluene could considerably contribute to the total mass of secondary organic aerosol formed in the presence of inorganic seed aerosols. Sun et al. (2016) investigated the SOA formation potential and contribution factors of VOC combined with the fraction aerosol coefficient (FAC) during hazy episodes. It was found that the SOA formation potentials of alkanes, alkenes and aromatics were 0.3 ± 0.2 μg m^{-3}, 1.1 ± 1.0 μg m^{-3} and 6.5 ± 6.4 μg m^{-3}, respectively. Derwent et al. (1996) applied a photochemical trajectory model to describe the generation of ozone from the oxidation of 96 types of hydrocarbons in natural light and nitrogen oxides. The results showed that toluene, *n*-butane, (*o*-, *m*-, *p*-)xylene contributed to ~33% of photochemical ozone generation.

The photochemical ozone creation potential along an idealized trajectory has been extensively examined, and most studies on product identification have been focused on low molecular weight compounds (Derwent et al., 1996; Zhang et al., 2016). However, the influence of ozone and nitric oxides on the degradation of VOCs is not yet to be determined. Additionally, investigations on the formation of larger molecular weight compounds during the oxidation of toluene and the effect of NO and O_3 on the gas-phase rate kinetics of toluene have received little attention. Therefore, conducting relevant work in these areas is important.

This work aimed at dealing with the photochemical degradation of toluene, one of the most significant kind of VOCs, with the discussion about the rate kinetics in the oxidation process and the generation of larger molecular weight products. Specifically, the photoconversion of toluene was assessed in three reaction systems (1) toluene; (2) toluene/NO; and (3) toluene/O_3. The gas-phase rate kinetics were evaluated and the generated products were characterized by positive ion atmospheric pressure photoionization mode (+APPI) coupled with Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS).

2. Materials and methods

2.1. Reagents

Methanol (HPLC grade, ≥99.0%) was supplied by J.T. Baker (Center Valley, PA, Avantor Performance Materials, Inc., USA). The 1000 ppm toluene standard gas (toluene mixed with 99.999% high purity nitrogen) and 1000 ppm nitric oxide standard gas (nitric oxide mixed with 99.999% high purity nitrogen) were supplied by Beijing Haike Yuanchang practical utility gas company. Resultant air and nitrogen gas with a purity of 99.999% serve as clean air matrix; both gases were supplied by the aforementioned company.

2.2. Sample preparation

The photodegradation of toluene with purified air as a matrix was conducted in a smog chamber at a precisely controlled temperature (278 ± 2 K, 308 ± 2 K) and atmospheric pressure. The indoor smog chamber was dominated with a Teflon film with a film thickness of 0.075 mm. The whole reactor are set inside an opaque box. The inner parts of the reactor are made of Teflon to avoid the inner wall effect. The main reactor unit was bag-like with a quantitative inlet volume of 8 L. A xenon lamp with a radiation spectrum distribution in the range of 200–900 nm and radiation strength of 0.049 mW/cm^2 was used. Three types of systems were assessed: (1) toluene; (2) toluene/NO; and (3) and toluene/O_3. The initial concentrations of toluene, O_3, and NO in the reaction systems were respectively 500, 200, and 250 ppb. The reaction systems were flushed several times with the matrix (purified air) before the reaction to eliminate interference. The analysis of toluene was carried out by putting the thermal desorption tube directly in the thermal desorption device. The samplings were collected quantitatively using 50 mL three-way connecting pump to the small pipe of stainless steel. All the adsorption tubes were aged in their first use and blanked before sampling. After sampling, the adsorption tubes were sealed at both ends with a Teflon sleeve and a metal nut, then wrapped with clean aluminum foil and placed in a clean and sealed storage container at 4 °C prior to subsequent handling. The container was equipped with an activated carbon package and silica gel to prevent contamination. The ozone generator (Thermo 49i-PS, Waltham, MA, USA) was used to produce the required ozone concentration in the toluene/O_3 reaction system. O_3 and NO concentrations were measured using an ozone analyzer (Thermo 49i, Waltham, MA, USA) and a nitrogen oxide analyzer (Thermo 42i, Waltham, MA, USA), respectively, at an analysis rate of 1.4 L/min.

2.3. TD-GC/MS analysis

The concentration of toluene was analyzed using a TD-GC/MS instrument (Agilent 7890a-7000a, Marker International, Santa Clara, CA, USA) equipped with an Agilent DB-624 capillary column (60 m × 0.32 mm × 1.80 μm; Santa Clara, CA, USA). The thermal desorption sample method was used to analyze the target pollutant. The thermal desorption device was purged with high-purity nitrogen gas, and desorption (2-step process) proceeded as follows. In the first desorption step, the absorbent tube, containing the samples, was heated to 280 °C for 10 min, after which the samples were transferred via carrier gas to the cold hydrazine for sample collection. The parameters were cooled to 0 °C for 10 min. After completion of the first desorption step, cold hydrazine parameters were rapidly heated to 300 °C for 3 min, and the resulting samples were transferred via carrier gas to a gas chromatograph for analysis.

2.4. FT-ICR MS analysis

Through the Teflon hose connection to the reactor, absorption bottle which contained 25 mL of methanol solvent and sampling pump with