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A kinetic mechanism for predicting secondary organic aerosol formation from toluene oxidation in the presence of NO_x and natural sunlight

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Abstract

A kinetic mechanism to predict secondary organic aerosol (SOA) formation from the photo-oxidation of toluene was developed. Aerosol phase chemistry that includes nucleation, gas–particle partitioning and particle-phase reactions as well as the gas-phase chemistry of toluene and its degradation products were represented. The mechanism was evaluated against experimental data obtained from the University of North Carolina (UNC) 270 m^3 dual outdoor aerosol smog chamber facility. The model adequately simulates the decay of toluene, the nitric oxide (NO) to nitrogen dioxide (NO_2) conversion and ozone formation. It also provides a reasonable prediction of SOA production under different conditions that range from 15 to 300 $\mu g\,m^{-3}$. Speciation of simulated aerosol material shows that up to 70% of the aerosol mass comes from oligomers and polymers depending on initial reactant concentrations. The dominant particle-phase species predicted by the mechanism are glyoxal oligomers, ketene oligomers from the photolysis of the toluene OH reaction product 2-methyl-2,4-hexadienedial, organic nitrates, methyl nitro-phenol analogues, C7 organic peroxides, acylperoxy nitrates and for the low-concentration experiments, unsaturated hydroxy nitro acids.

Keywords: Toluene; Kinetic mechanism; Aerosol modeling; Secondary organic aerosol (SOA)

1. Introduction

Aromatic hydrocarbons are an important class of volatile organic compounds (VOCs) present in the atmosphere, and their yearly global emission concentrations are estimated to range from 18.7 to 25 $Tg\,yr^{-1}$ (Piccot et al., 1997; Ehhalt, 1999). Toluene is the most abundant of the aromatic hydrocarbons, and it has an average atmospheric concentration ranging from 50 pptV in rural air to 10 ppbV or higher in urban air. Most atmospheric aromatics emissions come from anthropogenic sources such as transportation, solvent use and fuel combustion (Calvert et al., 2002). The major removal pathway of aromatic hydrocarbons from the atmosphere is through reaction with the hydroxyl radical (OH) (Calvert et al., 2002). Single ring aromatic hydrocarbons, because of their high anthropogenic emission and atmospheric rates, are significant contributors to ozone and secondary

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organic aerosol (SOA) formation in urban areas (Makar et al., 2003). A model calculation predicts that up to 40% of photochemically produced ozone over northern Europe can be attributed to emissions of aromatics (Derwent et al., 1996). Highly oxygenated compounds, such as hydroxyaldehydes, polyketones and hydroxyketoacids formed during the photo-oxidation of toluene have been identified in many chamber studies (Edney et al., 2001; Jang and Kamens, 2001b; Kleindienst et al., 2004). These products have relatively low vapor pressures that can either self-nucleate to form ultra fine particles or rapidly partition onto existing particles and reach a gas–particle equilibrium (Holes et al., 1995; Odum et al., 1997; Jang and Kamens, 2001b; Hurley et al., 2001). However, recent product studies on the identification of toluene SOA by Hamilton et al. (2005) suggest that these C3–C7 oxygenated products contribute no more than 10% of the toluene SOA mass.

In addition to gas–particle partitioning, heterogeneous reactions are proposed to take place in the particle phase. This aids in the reactive uptake of volatile aldehyde compounds and the formation of large molecules within the aerosol. Oligomers formed by particle-phase reactions have been observed in the α-pinene system in the presence of acidified inorganic particles (Jang et al., 2002; Tolocka et al., 2004; Gao et al., 2004), in the 1,3,5-trimethylbenzene system in the absence of any seed particles (Kalberer et al., 2004), and in the glyoxal system with both non-acid and acidic seeds aerosols (Liggio et al., 2005a, b).

A number of models have been proposed and developed to predict the SOA formation from aromatic hydrocarbons by using gas–particle partitioning theory. However, these models (1) do not describe or represent particle-phase reactions (Odum et al., 1997; Pun et al., 2002; Dechapanya et al., 2003a, b; Stroud et al., 2004; Griffin et al., 2005); (2) or do not explicitly represent the potential products that lead to SOA formation (Odum et al., 1997; Pun et al., 2002; Dechapanya et al., 2003a, b); (3) or have not been evaluated against smog-chamber data (Pun et al., 2002; Dechapanya et al., 2003a, b); (4) or have questionable ability to simultaneously predict observed SOA, O_3 and NO_x behavior (Johnson et al., 2004, 2005). In this work, a predictive kinetic chemical mechanism for the photo-oxidation of toluene is presented and applied to predict the SOA and ozone formation observed in University of North Carolina (UNC) dual outdoor aerosol smog chambers. This model is based on atmospheric processes that bring about SOA formation. Particle-phase reactions of some major carbonyl products and gas–particle partitioning processes have been integrated with fundamental gas-phase chemistry. In a companion paper by Hu and Kamens (2007), the model is also evaluated with experimental data sets obtained in different chamber facilities.

2. Experimental section

Experiments were carried out in the UNC 270 m^3 dual outdoor aerosol smog chamber facility located in Pittsboro, NC. Chamber descriptions are described elsewhere (Lee et al., 2004). Each chamber half is designated as either north or south. Prior to each experiment, the chambers were continuously flushed with clean rural air for 12–16 h and then purged overnight with dry clean air from a clean air generator. Before the injection of hydrocarbons and oxides of nitrogen (NO_x), an inert gas, sulfur hexafluoride (SF6) was added to the chamber and its concentration was chromatographically measured (Leungsakul et al., 2005b). The loss rate of SF6 over the course of each experiment was used as the dilution rate and applied to all species in the model. Toluene was introduced into the chamber by vaporizing a measured amount of pure liquid toluene (98%, Aldrich, Milwaukee, WI) in a U-tube that was gently heated by a hot air heat gun, and flushed by a dry nitrogen stream. After obtaining the desired toluene concentration, nitric oxide (NO), nitrogen dioxide (NO_2) and, in one case, propylene, were injected into the chamber from high-pressure cylinders. The internal chamber mixing fans were operated during each injection and then shut off 2 min after the injection. This provided uniform chamber concentrations before the start of an experiment. Gas-phase toluene was measured by gas chromatography (GC, Shimadzu Model 14A, column: 30 m, 0.25 mm i.d., J&W DB-1, 0.25 m film thickness) with a flame ionization detector (FID). A liquid nitrogen cryo-trap was used to pre-concentrate gas-phase toluene. Propylene was measured by gas chromatography using a packed column (2 m × 3.2 mm stainless steel with 60–80 mesh, porapak Q at 86 °C) and an FID for detection. Injected hydrocarbons were sampled every 10 min. Calibrations were performed before each experiment by comparing these with a US National Institute of Standards and Technology traceable