

# Heterogeneous SOA yield from ozonolysis of monoterpenes in the presence of inorganic acid

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Received 26 May 2006; received in revised form 22 September 2006; accepted 8 October 2006

## Abstract

The secondary organic aerosol (SOA) yield of a series of monoterpenes was investigated to determine the relative amounts of organic mass, which can be attributed to mass produced by heterogeneous acid-catalyzed reactions. Five monoterpenes ( $\alpha$ -pinene, terpinolene, *d*-limonene,  $\Delta^2$ -carene,  $\beta$ -pinene) were studied using a 2 m<sup>3</sup> indoor Teflon chamber and SOA was created in the presence of both acidic and neutral inorganic seed aerosol. The relative humidity was varied to create differing acidic seed environments. The heterogeneous aerosol production was influenced by the seed mass concentration, the acidity of the inorganic seed aerosol, and also molecular structure of the monoterpene ozonolysis products. This study also can be incorporated with our previously presented model of the kinetic expression for SOA mass production from heterogeneous acid-catalyzed reactions.

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*Keywords:* Monoterpenes; SOA; Heterogeneous reactions; Acid catalyst; Ozonolysis

## 1. Introduction

Terpenes are ever-present atmospheric organic compounds of biogenic origin (Rasmussen, 1972), which are susceptible to oxidation by OH radicals, as well as ozone in the atmosphere because of the unsaturated carbon–carbon double bonds present in these compounds (Atkinson and Arey, 2003; Calogirou et al., 1999; Hakola et al., 1994). Due to the large amounts of biogenics emitted into the atmosphere (Müller, 1992; Guenther et al., 1995), the secondary organic aerosol (SOA) burden on the

total organic aerosol mass may be significant (Andreae and Crutzen, 1997).

The formation of SOA has often been attributed to the partitioning of oxidation products of a VOC to existing aerosols (Colville and Griffin, 2004a; Griffin et al., 1999; Kamens et al., 1999; Odum et al., 1996; Jang and Kamens, 1999; Pankow, 1987, 1994), and to a lesser extent, from the new particle formation via nucleation of oxidation products (Kavouras and Stephanou, 2002). Recently aerosol growth through particle-phase heterogeneous reactions has been proposed (Gao et al., 2004; Jang et al., 2004, 2006; Jang and Kamens, 2001; Kalberer et al., 2004; Tolocka et al., 2004) as another pathway for the formation of SOA. Atmospheric acidic particle surfaces can accelerate heterogeneous

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reactions of secondary organic products created from the gas-phase oxidation reactions of reactive volatile organic carbons (VOCs). Atmospheric particles have been measured to have pH values as low as 0.25 (Pathak et al., 2004), which falls within the range of particle acidity used to study acid-catalyzed heterogeneous reactions. Thus it is extremely important to understand the contributions of heterogeneous acid-catalyzed reactions on SOA flux, as the occurrence of these reactions in the atmosphere is accelerated due to the acidity of atmospheric particles.

This study aims to further our understanding of the aerosol yield increases by heterogeneous acid-catalyzed reactions through determining how this increase varies with the initial terpene structure. Terpenes which produce products that are more reactive for heterogeneous reactions in aerosol should have higher increases in SOA when in the presence of acidic seed as compared to neutral seed; acid acts a catalyst increasing oligomer formation (Jang et al., 2002; Czoschke et al., 2003; Czoschke and Jang, 2006; Iinuma et al., 2004).

The major goals of this study were threefold: (1) investigate the relationship between the molecular structures of a series of monoterpenes that took place in ozonolysis reactions and the subsequent SOA yield due to heterogeneous acid-catalyzed reactions; (2) determine the influences of preexisting seed aerosols on SOA yields; and (3) quantify the SOA yield increase for various monoterpenes at a range of different humidities and acidities of seed aerosols.

## 2. Experimental section

The SOA yield study was carried out in an indoor 2.16 m<sup>3</sup> chamber constructed of Teflon. All experiments were conducted in the dark to prevent photochemical reactions of VOCs. The chamber was filled with clean air from two clean air generators: a Whatman FT-IR purge gas generator (model 75–52) and an Aadco 737 pure air generator. The percent relative humidity (%RH) was controlled by bubbling clean air through distilled water and was measured by a Hanna instruments thermo hygrometer HI 9160C, which was also used to measure temperature. Seed aerosol was generated using a TSI constant output Atomizer model 3076. The acidic seed solution was composed of a 2:3 volume ratio of H<sub>2</sub>SO<sub>4</sub>–NH<sub>4</sub>HSO<sub>4</sub> of 0.01 M aqueous solutions. The neutral seed solution was

composed of a 1:1 volume ratio of 0.01 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution to H<sub>2</sub>O. The particle concentration and population was monitored by a TSI scanning mobility particle sizer (SMPS) (Model 3080) in series with a TSI condensation nuclei counter (CNC) (Model, 3025A). The scanning time of aerosol through the internal plumbing column of the SMPS was 3 min with a sheath flow rate of 2 L min<sup>-1</sup>. The SMPS measured particle size data over a size range of 20–835 nm.

Ozone was added to the chamber by passing clean air past a Jelight UV lamp model 600, before entering the chamber. Ozone levels were measured using a Thermo Electron Instruments UV photometric O<sub>3</sub> analyzer model 49. The terpenes used in this investigation are shown in Fig. 1A and B, they were purchased from Sigma Aldrich with a purity of >98%. The terpenes were injected into the chamber by volatilization using a gentle stream of clean air through a heated manifold. The accuracy of the terpene injection and the unreacted terpene were determined by a FID-GC. Table 1 tabulates the experimental conditions used for the experimental data presented here.

## 3. Results and discussion

### 3.1. Aerosol yields

The most common way to determine the SOA yield has been defined by Odum et al. (1996) as,  $Y = \Delta M / \Delta HC$  measuring the change in aerosol mass  $\Delta M$  ( $\mu\text{g m}^{-3}$ ) and dividing by the amount of hydrocarbons reacted  $\Delta HC$  ( $\mu\text{g m}^{-3}$ ). In our study, the SOA yields for the neutral particles are consistent with yields from previous studies (Grosjean et al., 1993; Hakola et al., 1994; Keywood et al., 2004) where reactions were conducted under excess ozone conditions. In this study, the highest yield in the neutral system was limonene followed in order by terpinolene,  $\Delta^2$ -carene,  $\alpha$ -pinene, and  $\beta$ -pinene (Table 1). This order was consistent at both 20%RH and 40%RH showing that the partitioning processes were similar at the various %RH in systems, where heterogeneous reactions are not acid-catalyzed. The neutral seeded experiments are used as a standard to measure effects of particle acidity on SOA formation in acidic seeded experiments.

In order to investigate the aerosol mass contribution from acid-catalyzed heterogeneous reactions, we define the heterogeneous acid-catalyzed aerosol

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