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## Acid-catalyzed heterogeneous reaction of 3-methyl-2-buten-1-ol with hydrogen peroxide

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### ABSTRACT

Acid-catalyzed heterogeneous oxidation with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) has been suggested to be a potential pathway for secondary organic aerosol (SOA) formation from isoprene and its oxidation products. However, knowledge of the chemical mechanism and kinetics for this process is still incomplete. 3-Methyl-2-buten-1-ol (MBO321), an aliphatic alcohol structurally similar to isoprene, is emitted by pine forests and widely used in the manufacturing industries. Herein the uptake of MBO321 into  $\text{H}_2\text{SO}_4$ – $\text{H}_2\text{O}_2$  mixed solution was investigated using a flow-tube reactor coupled to a mass spectrometer. The reactive uptake coefficients ( $\gamma$ ) were acquired for the first time and were found to increase rapidly with increasing acid concentration. Corresponding aqueous-phase reactions were performed to further study the mechanism of this acid-catalyzed reaction. MBO321 could convert to 2-methyl-3-buten-2-ol (MBO232) and yield isoprene in acidic media. Organic hydroperoxides (ROOHs) were found to be generated through the acid-catalyzed route, which could undergo a rearrangement reaction and result in the formation of acetone and acetaldehyde. Organosulfates, which have been proposed to be SOA tracer compounds in the atmosphere, were also produced during the oxidation process. These results suggest that the heterogeneous acid-catalyzed reaction of MBO321 with  $\text{H}_2\text{O}_2$  may contribute to SOA mass under certain atmospheric conditions.

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### Introduction

Secondary organic aerosol (SOA), a significant and abundant component of atmospheric particulates, has received considerable attention because of its impacts on climate forcing, public health and regional visibility (Rosenfeld, 2006; Hallquist et al., 2009; Poschl, 2005). It is generally accepted that SOA is formed through the atmospheric oxidation of volatile organic compounds (VOCs) followed by gas-particle partitioning of the low-volatility products (Odum et al., 1996). Recent studies have

shown that chemical processes in the particle phase could also play an important role in SOA formation (Ervens et al., 2011; Shiraiwa et al., 2013). In particular, the acidic medium is considered to act as a catalyst in the heterogeneous reactions of VOCs such as aldehydes, epoxides and alkenes. For example, Jang et al. (2002) revealed that heterogeneous interactions of organic carbonyl compounds on acidic aerosols could result in a large increase in SOA mass. Liggio and Li (2008) found significant uptake of monoterpenes and sesquiterpenes onto acidic sulfate aerosols in smog chamber experiments. Surratt et al. (2010)

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showed that SOA mass yield increased dramatically under acidic conditions during low-NO<sub>x</sub> isoprene photooxidation, and this enhancement was attributed to acid-catalyzed particle-phase reactions. Chan et al. (2013) demonstrated oligomeric products formed through heterogeneous reactions of gaseous methyl vinyl ketone on acidic sulfate particles.

Ambient aerosols have been reported to be quite acidic in the troposphere. For instance, the pH of the particles in southern California was reported to be in the range of –2.4 to 0.2 (Li et al., 1997). Strongly acidic aerosols were observed in the northeastern United States (Ferek et al., 1983). Low levels of *in-situ* aerosol pH were also measured in megacities such as Beijing (average pH –0.52) and Shanghai (average pH –0.77) during summertime in 2004–2006 (Pathak et al., 2009). It is well recognized that hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) plays a central role in atmospheric oxidation (Jackson, 1999). Claeys et al. (2004) pointed out that acid-catalyzed oxidation with H<sub>2</sub>O<sub>2</sub> may be a new route to SOA from isoprene and its gas-phase products. Subsequently, smog chamber experiments confirmed that this process could contribute to SOA formation (Boge et al., 2006). Given the high solubility of H<sub>2</sub>O<sub>2</sub> in the aqueous phase, high gas-phase H<sub>2</sub>O<sub>2</sub> concentration and the presence of a certain mass fraction of water (H<sub>2</sub>O) in submicron aerosols (Hasson and Paulson, 2003; Hung and Wang, 2001; Arellanes et al., 2006), heterogeneous acid-catalyzed oxidation with H<sub>2</sub>O<sub>2</sub> could occur under certain circumstances.

Emissions of 3-methyl-2-buten-1-ol (MBO321) have been observed from several species of pine and different types of vegetation (Konig et al., 1995; Zhao et al., 2006). It is also widely used as a fragrance ingredient in the manufacturing industries such as in shampoos, cosmetics, fine fragrances and household cleaners. Its worldwide use was reported to be in the range of 1–10 tons/year (McGinty et al., 2010). 2-Methyl-3-buten-2-ol (MBO232), an important biogenic hydrocarbon emitted in large quantities by pine forests, has been suggested to play a role in SOA formation (Liu et al., 2011; Jaoui et al., 2012). With a structure similar to MBO232, MBO321 may also produce SOA under certain conditions. Previous studies have investigated the gas-phase reactions of MBO321 with several oxidants such as O<sub>3</sub>, Cl and NO<sub>3</sub> (Grosjean and Grosjean, 1999; Noda et al., 2002; Rodriguez et al., 2008). To the best of our knowledge, information on the acid-catalyzed heterogeneous reaction of MBO321 and H<sub>2</sub>O<sub>2</sub> is still lacking, which is one of the important aspects in evaluating the atmospheric implications of this process. Hence, in the present work, the uptake of MBO321 into aqueous solutions of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and H<sub>2</sub>O<sub>2</sub> was studied. Corresponding aqueous-phase reactions were conducted to

further survey the mechanism. The reactive uptake coefficients ( $\gamma$ ) were acquired for the first time and reaction pathways were proposed on the basis of product information. Organic hydroperoxides (ROOHs) and organosulfates were found to be produced through this acid-catalyzed process, indicating that this route may make a potential contribution to SOA formation.

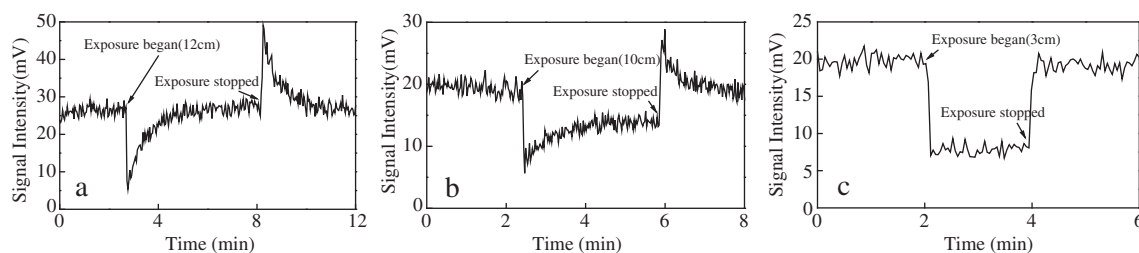
## 1. Experimental section

### 1.1. Uptake experiments

The uptake measurements were carried out using a rotated wetted-wall reactor coupled to a single-photon ionization time of flight mass spectrometer (SPI-TOFMS, home-built, Beijing, China), similarly to our previous work (Liu et al., 2011). Briefly, a rotating cylinder (length  $L = 30$  cm, inner radius  $R = 1.25$  cm, rotating rate  $r = 10$ – $15$  r/min) was put into the flow-tube, holding a small volume of solution (about 3.5 mL) to form a liquid film (about 0.15 mm thickness) evenly on the inner wall. A glass stirring bar was placed on the bottom of the inner cylinder to make sure the solution could be spread and mixed sufficiently. Reactant gas was introduced into the flow reactor at a small flow rate (10% of the carrier gas) through a moveable injector centered in the rotating cylinder. A mixture of helium (He) and water vapor in equilibrium with the solution was used as carrier gas to avoid changes in solution composition during the time frame of the experiment. The experiments were performed in the acidity range of 40 to 60 wt.% H<sub>2</sub>SO<sub>4</sub> at room temperature (298 K). 1 wt.% H<sub>2</sub>O<sub>2</sub> was used in the uptake experiments. Hung and Wang (2001) reported that the average value of the H<sub>2</sub>O<sub>2</sub> concentration in the aerosol phase was 21 ng/m<sup>3</sup>. Considering the typical aerosol mass loading at that site is on the order of 2 to 140  $\mu\text{g}/\text{m}^3$  and water generally accounts for less than half of the aerosol mass loading, the H<sub>2</sub>O<sub>2</sub> concentration is a little lower than that used in this study. The flow reactor was operated under approximate laminar flow conditions (Reynolds number smaller than 2000). Typically, the MBO321 concentration in the reactor was in the order of  $1.12 \times 10^{14}$  to  $4.23 \times 10^{14}$  mol/cm<sup>3</sup>. Details of SPI-TOFMS and the chemicals used in the experiments are described in the Supporting Information.

### 1.2. Gas-phase product identification

To further study the gas-phase products, off-line FTIR spectrometer experiments were carried out. The gas-phase products



**Fig. 1** – Typical uptake profiles of 3-methyl-2-buten-1-ol. (a) reversible uptake into 30 wt.% H<sub>2</sub>SO<sub>4</sub> solution; (b) partially irreversible uptake into 40 wt.% H<sub>2</sub>SO<sub>4</sub> solution; (c) irreversible uptake into 60 wt.% H<sub>2</sub>SO<sub>4</sub> solution. H<sub>2</sub>SO<sub>4</sub>: sulfuric acid.

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