

# Atmospheric Particle Formation From The Ozonolysis Of Alkenes In The Presence Of SO<sub>2</sub>

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**Abstract.** Laboratory studies on new particle formation have been performed in a flow tube in the system O<sub>3</sub>/alkene/SO<sub>2</sub> using  $\alpha$ -pinene, *trans*-butene, and tetramethylethylene (TME) as model alkenes. Reactant concentrations were kept close to atmospheric conditions. In the absence of SO<sub>2</sub>, no particle formation was observed. The number of newly formed particles was found to be H<sub>2</sub>SO<sub>4</sub>-controlled. No distinct contribution of different organic products from the ozonolysis was discovered. For conditions where particle formation occurred, H<sub>2</sub>SO<sub>4</sub> concentrations of a few 10<sup>7</sup> molecule cm<sup>-3</sup> were calculated, similar to observations in the atmosphere.

*Key Words:* Heterogeneous nucleation; laboratory experiments

## Introduction

The formation mechanisms leading to new atmospheric aerosol particles are still subject of intensive research. The goal of the present study was to investigate the particle formation in the system H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O using in situ produced H<sub>2</sub>SO<sub>4</sub> from the reaction of SO<sub>2</sub> with OH radicals. OH radicals were formed from alkene ozonolysis. In contrast to earlier studies, the ozonolysis was conducted for reactant concentrations closer to realistic atmospheric conditions (mixing ratio for alkenes: mostly 2 ppb and for O<sub>3</sub>: 25 - 30 ppb). In additional experiments H<sub>2</sub>SO<sub>4</sub> was produced via ozone photolysis.

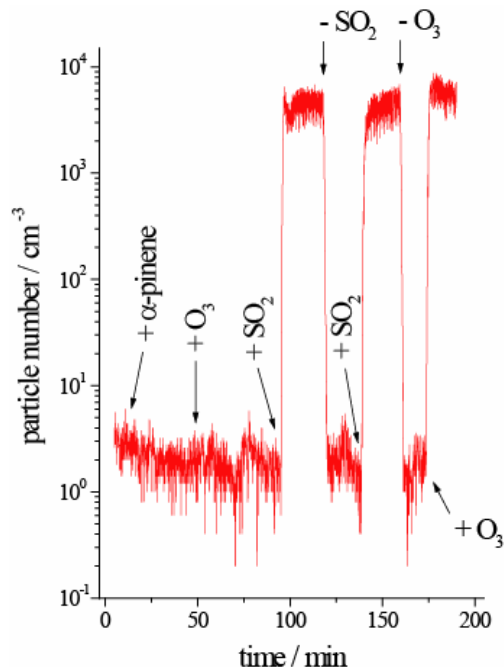
## Experimental Set-up

The experiments have been performed in the *I/T-LFT (Institute for Tropospheric Research – Laminar Flow Tube)*. The *I/T-LFT* consists of a 505 cm quartz tube (i.d. 8 cm) surrounded with a thermo-jacket. For the photolytic generation of OH radicals, the flow-tube is equipped with eight low pressure UV-lamps for quasi homogeneous and continuous illumination. At the outlet of the flow tube an ozone analyzer (Thermo Environmental Instruments 49C), a dew point sensor (General Eastern HygroM4), and an UCPC (TSI 3025) for integral particle measurements were attached. Particle size distributions ( $d_p > 3$  nm) were determined using a Differential Mobility Particle Sizer (DMPS). NH<sub>3</sub> concentrations of the carrier gas were determined before entering the flow tube using a wet annular denuder system described by <sup>1)</sup>. O<sub>3</sub> produced from a low pressure Hg lamp was introduced through an inlet into the *I/T-LFT* after dilution with the carrier gas. The alkenes and SO<sub>2</sub> premixed with the carrier gas were added through three symmetrically distributed ports around the inlet. Before adding the reactants, the

carrier gas passed a humidifier. Initial concentrations were (unit: molecule  $\text{cm}^{-3}$ ); alkenes:  $(1.5\text{--}18) \times 10^{10}$ ,  $\text{O}_3$ :  $(6.2\text{--}7.6) \times 10^{11}$ , and  $\text{SO}_2$ :  $(2\text{--}740) \times 10^{10}$ . Alkenes used in the experiments were  $\alpha$ -pinene, tetramethylethylene (TME) and *trans*-butene.

## $\text{H}_2\text{SO}_4$ from alkene ozonolysis

Figure 1 shows integral UCPC particle number measurements from the ozonolysis of  $\alpha$ -pinene in the presence of  $\text{SO}_2$  depending on the presence of the three different reactants in the carrier gas. In the absence of  $\text{SO}_2$ , from the ozonolysis of  $\alpha$ -pinene no particle formation was visible under the conditions used ( $\alpha$ -pinene:  $5.0 \times 10^{10}$  molecule  $\text{cm}^{-3}$  and  $\text{O}_3$ :  $6.4 \times 10^{11}$  molecule  $\text{cm}^{-3}$ ). This finding is in line with earlier observations from the IfT-LFT where particle formation only occurred for an  $\alpha$ -pinene conversion above  $3 \times 10^{11}$  molecule  $\text{cm}^{-3}$  <sup>2</sup>). From a modelling study, for the conditions used here, an  $\alpha$ -pinene conversion of  $1.9 \times 10^9$  molecule  $\text{cm}^{-3}$  was calculated, see below. After adding  $\text{SO}_2$  ( $\text{SO}_2$ :  $7.4 \times 10^{11}$  molecule  $\text{cm}^{-3}$ ), formation of new particles took place. These particles most likely consisted of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ . Possible pathways leading to  $\text{H}_2\text{SO}_4$  are  $\text{OH} + \text{SO}_2$  and Criegee Intermediate +  $\text{SO}_2$ .  $\text{OH}$  radicals and the Criegee Intermediates represent reactive products of the alkene ozonolysis. Switching off either the  $\text{SO}_2$  or the  $\text{O}_3$  flow (in order to terminate the formation of  $\text{OH}$  and the Criegee Intermediates) the particle number went down to the background level, cf. Figure 1. This finding supports that  $\text{H}_2\text{SO}_4$  (as the oxidation product of  $\text{SO}_2$ ) is accountable for the measured particle formation. Similar behavior was also observed using *trans*-butene or tetramethylethylene (TME) instead of  $\alpha$ -pinene.



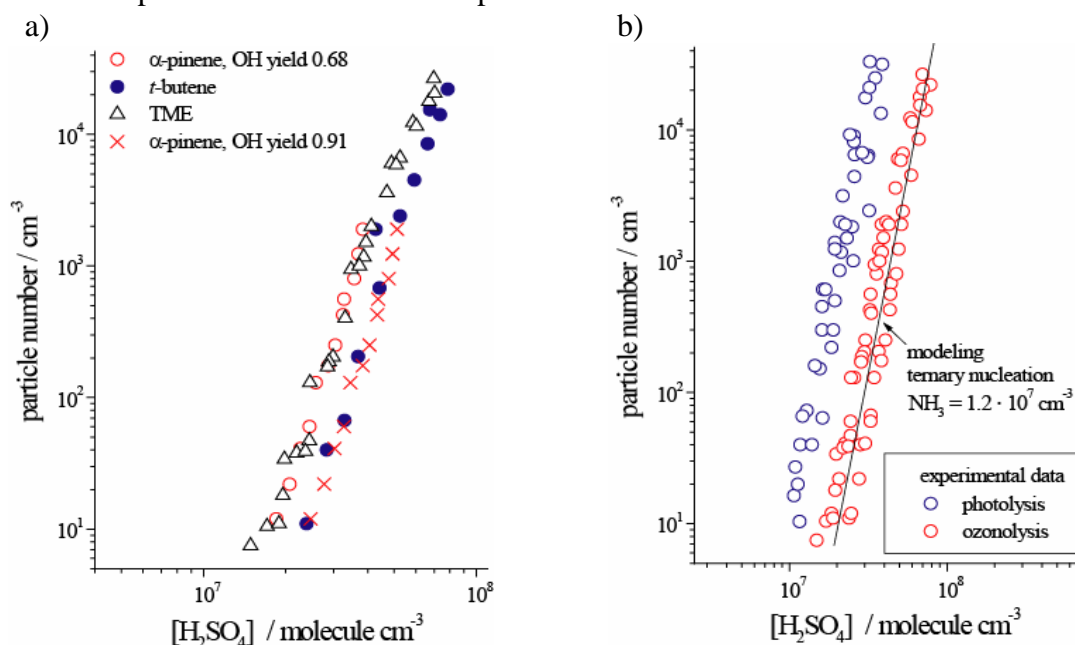
**Figure 1:** Integral UCPC particle number measurements from the ozonolysis of  $\alpha$ -pinene in the presence of  $\text{SO}_2$  for different gas compositions (r.h. = 74%, if present  $\alpha$ -pinene:  $5.0 \times 10^{10}$ ,  $\text{O}_3$ :  $6.4 \times 10^{11}$ ,  $\text{SO}_2$ :  $7.4 \times 10^{11}$  molecule  $\text{cm}^{-3}$ ).

## Modelling of H<sub>2</sub>SO<sub>4</sub> formation

In a modelling study, the amount of H<sub>2</sub>SO<sub>4</sub> formed in the flow tube was calculated considering the following simplified reaction pathways for the ozonolysis:



“Int.” stands for the Criegee Intermediates formed in pathway (1) and for other intermediates (except for OH) oxidizing SO<sub>2</sub>. The corresponding rate coefficients as well as the OH radical yields “y” were taken from the literature or estimated. Figures 2a) and b) show the dependence of newly formed particles on the H<sub>2</sub>SO<sub>4</sub> concentration calculated. In Figure 2a), all points lie almost at the same curve independent of the alkene used in the experiments. This suggests H<sub>2</sub>SO<sub>4</sub> as the dominating species in the nucleation process. For the α-pinene system the calculations were performed using OH yields of 0.91<sup>3)</sup> and 0.68<sup>2)</sup> in pathway (1). The value of 0.91 is the highest yield reported in the literature<sup>3)</sup>. The comparison of the calculated H<sub>2</sub>SO<sub>4</sub> concentrations for an OH yield of 0.68 and 0.91 shows that the differences emerging in Figure 2a) can be explained by uncertainties of the OH yields or other input parameters such as the rate coefficients or by uncertainties arising from the model itself. As a result of these experiments, there was no clear indication for a participation of the different alkene oxidation products in the nucleation process.



**Figure 2:** Observed particle number from ozonolysis experiments depending on the calculated H<sub>2</sub>SO<sub>4</sub> concentration (a) and experimental data from the ozonolysis and the photolysis, r.h. = 28 % (b). In the modeling, ternary nucleation was assumed (Korhonen et al., 1999) with a constant NH<sub>3</sub> concentration of 1.2 x 10<sup>7</sup> molecule cm<sup>-3</sup>.

In field measurements performed at different continental sites with simultaneous particle and gaseous H<sub>2</sub>SO<sub>4</sub> detection, formation of new particles occurred for peak H<sub>2</sub>SO<sub>4</sub> concentrations of (1 – 5) × 10<sup>7</sup> molecule cm<sup>-3</sup> with formation rates of about one particle cm<sup>-3</sup> s<sup>-1</sup> <sup>4,5)</sup>. The results from the present study indicate particle formation starting at approximately 2 × 10<sup>7</sup> molecule cm<sup>-3</sup> of H<sub>2</sub>SO<sub>4</sub>, cf. Figure 2a). As in the *I/T-LFT* experiment the H<sub>2</sub>SO<sub>4</sub> concentration grew up continuously in the course of the reaction, particle formation should mainly occur at the end of the flow tube at the highest H<sub>2</sub>SO<sub>4</sub> level. Therefore, a nucleation time of only a few seconds can be assumed. This results in an estimate for the nucleation rate of a few particles cm<sup>-3</sup> s<sup>-1</sup> (N = 10 particles cm<sup>-3</sup> for [H<sub>2</sub>SO<sub>4</sub>] approximately 2 × 10<sup>7</sup> molecule cm<sup>-3</sup>, cf. Figure 2a) to be in line with the values derived from the field measurements <sup>4,5)</sup>. On the other hand, from laboratory studies nucleation rates of about one particle cm<sup>-3</sup> s<sup>-1</sup> were reported for H<sub>2</sub>SO<sub>4</sub> concentrations of 10<sup>10</sup> molecule cm<sup>-3</sup> and more <sup>6,7)</sup>. Obviously, for a nearly identical nucleation rate there is a gap of approximately three orders of magnitude in the H<sub>2</sub>SO<sub>4</sub> concentration between the laboratory studies in the literature and the field measurements including the laboratory study presented here. One possible explanation is that the nucleation process in the present study as well as in the field measurements was controlled by the ternary nucleation H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O-NH<sub>3</sub>.<sup>8)</sup> For the carrier gas used in the *I/T-LFT* experiments, by means of denuder measurements, the NH<sub>3</sub> concentration was found to be below the detection limit of 9 pptv. Therefore, to assess the possible contribution of NH<sub>3</sub> to the observed particle formation, calculations were performed using a box model considering the reaction system described by pathways (1) – (6) and particle formation due to ternary nucleation of a H<sub>2</sub>SO<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O vapor system. For the nucleation rate, a parameterization proposed by <sup>9)</sup> was used. Successive model runs have been performed with altered initial concentrations of SO<sub>2</sub>, alkene, and O<sub>3</sub> for a temperature of 295 K and a relative humidity of 28 %. The NH<sub>3</sub> concentration was considered as a free parameter. Best agreement was found for an assumed NH<sub>3</sub> concentration of 1.2 × 10<sup>7</sup> molecule cm<sup>-3</sup> (mixing ratio: 0.5 pptv), cf. Figure 2b). In order to confirm our experimental findings from the ozonolysis we performed experiments with OH formation via ozone photolysis and subsequent reaction of O(<sup>1</sup>D) with water vapor. As seen in Figure 2b), the agreement between both data sets (photolysis and ozonolysis) is excellent.

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