

Changes of aerosol properties during the ozonolysis of unsaturated carboxylic acids in the absence and presence of oxygen

¹C. Keunecke, ²M. Beck, ²T. Hoffmann, ¹T. Zeuch

¹Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Göttingen, 37077, Germany

²Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, Mainz, 55128, Germany

Keywords: SOA, Ozone, Alkene oxidation, Organic acids

Presenting author email: tzeuch1@gwdg.de

In the past decades large efforts have been made in laboratory studies to elucidate the secondary organic aerosol (SOA) formation mechanism. Critical issues have been studied such as reaction product formation and the influence of relative humidity, temperature, presence of additional organic matter and seed aerosol. However, the mechanism of organic nucleation is still not fully understood. Consequently significant uncertainty remains in closing the gap between laboratory experiments, theoretical predictions, nucleation rates and particle growth rates observed in field studies. In a recent study we could show that (besides volatility considerations of detected reaction products) SOA formation during alkene ozonolysis experiments depends also on kinetic parameters and is strongly linked to intermediate species like peroxy radicals (Wolf *et al.*, 2009, 2011).

In order to allow for a controlled reaction chamber filling and minimized aerosol wall losses during laboratory SOA experiments (e.g. a large reaction volume to surface ratio), we apply a 64 L stationary reaction cell with ozone / alkene premixing chambers, FTIR spectroscopy for gas phase species analysis and a SMPS system for measuring particle size distributions in the submicron size range. With this type of reactor design we achieve a well controlled mixing within two seconds which defines a precise starting point of the chemical reaction and allows a controlled variation of process parameters including reaction pressure (Wolf *et al.* 2011). The particles produced in these experiments were sampled on a filter. For the product analysis we employed liquid chromatography/mass spectrometry (LC/ESI-MS). With this combined approach the influence of reaction conditions like absence and presence of oxygen or pressure on gas phase chemistry and aerosol composition is elucidated.

Fig. 1 shows that the presence of various amounts of oxygen in the reactive mixture strongly influences the observed particle number concentrations during the ozonolysis of methacrylic and butenoic acid. For O_2 partial pressures below 1 mbar a significant increase of particle numbers is observed for both carboxylic acids. The mass spectrometric analysis of the aerosol composition for the experiment with butenoic acid revealed that the highest mass fraction ($m/z > 230$) was not present in experiments in the absence of O_2 where higher (!) aerosol yields were observed in terms of particle number concentration and mass. An increased

yield of a product with m/z 205 was found in the nitrogen atmosphere experiment.

The influence of oxygen in ozonolysis experiments is related to secondary oxidation steps. In the vinylhydroperoxide pathway the Criegee intermediate (CI) decomposes forming OH radicals and an alkyl radical R, which reacts with O_2 to RO_2 , a peroxy radical. In the case of the two acids under study the addition O_2 to the larger CI leads to highly oxidized intermediates. On average they tend to decompose into products with increased volatility compared to the experiment in nitrogen. However, the influence of peroxy chemistry on the build-up of compounds with low volatility is reflected in the presence of the highest mass fraction ($m/z > 230$) in the synthetic air experiments with butenoic acid.

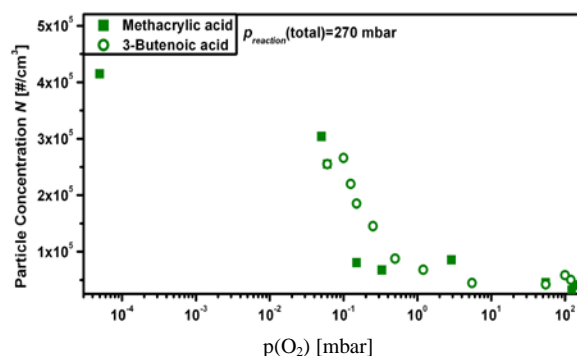


Figure 2. This figure illustrates the dependence of the total particle concentration on the amount of oxygen in the reactive mixture. Constant quantities of reactants were converted: $p_{0, \text{acid}}=5$ Pa, $p_{0, \text{ozone}}=0.1$ Pa for 3-Butenoic acid, $p_{0, \text{ozone}}=0.2$ Pa for Methacrylic acid.

J. L. Wolf, M. A. Suhm, and T. Zeuch, *Ang. Chem. Int. Ed.*, **48** (2009), 2231.

J. L. Wolf, S. Richters, J. Pecher, and T. Zeuch, *Phys. Chem. Chem. Phys.*, **13** (2011) 10952.