

## Investigation on the SOA formation mechanism in isoprene ozonolysis by chemical ionization mass spectrometry

Satoshi Inomata<sup>1\*</sup>, HIROKAWA, Jun<sup>2</sup>, Yosuke Sakamoto<sup>2</sup>, Hiroshi Tanimoto<sup>1</sup>, Kei Sato<sup>1</sup>, OKUMURA, Motonori<sup>3</sup>, TOHNO, Susumu<sup>3</sup>

<sup>1</sup>National Institute for Environmental Studies, <sup>2</sup>Faculty of Environmental Earth Science, Hokkaido University, <sup>3</sup>Graduate School of Energy Science, Kyoto University

Isoprene is the most abundant volatile organic compound (VOC) emitted from the earth and is producing a large amount of SOA by oxidation processes in the atmosphere. There are three oxidation processes for isoprene. The OH reaction is a major oxidation process in daytime. SOA yield and mechanism have been extensively investigated in many research groups so far. The NO<sub>3</sub> reaction occurs in night time. SOA yield of the O<sub>3</sub> reaction is known to be small compared with those of other reactions. The O<sub>3</sub> reaction occurs in both daytime and nighttime. Since the ozone reaction could couple with other oxidation processes, we think that it is important to understand the mechanism of SOA formation in the O<sub>3</sub> reaction. For the purpose, we detected semi-volatile organic compounds produced in the oxidation processes in both gaseous and aerosol phases by chemical ionization mass spectrometry that allows for sensitive measurement of VOC without any pretreatment.

The reaction was investigated using 6 m<sup>3</sup> smog chamber. The initial concentrations of isoprene and ozone were fixed as 2 ppmv and 4 ppmv, respectively. In this reaction, OH radical is regenerated, so we did the experiments with OH radical scavenger. Cyclohexane and CO were used as an OH radical scavenger. The experiment was carried out under dry conditions and without sees particles. Gaseous reactants and products were monitored by FT-IR and proton transfer reaction-mass spectrometer (PTR-MS). SOA size distribution and concentration were monitored by Fast Mobility Particle Sizer (FMPS) within 10 minutes from the start of the reaction and Scanning Mobility Particle Sizer (SMPS) for the whole reaction time. After 2 hours, formed SOA was collected on three filters and was analyzed by PTR-MS, GC/MS and LC/MS. In addition to the smog chamber experiments, similar experiments were carried out using 1 m<sup>3</sup> Teflon bag in order to compare PTR-MS data with negative ion-chemical ionization mass spectrometer (NI-CIMS) data.

Same ion signals were observed in both gaseous and aerosol phases by NI-CIMS and were assigned to oligomeric hydroperoxides involving Criegee intermediate (molecular weight 46) as a chain unit. PTR-MS detected the oligomeric hydroperoxides as [M-OH]<sup>+</sup> ion. Since these compounds were observed in both gaseous and aerosol phases, it is concluded that they are key species for the SOA formation of isoprene ozonolysis. In SOA, hemiacetals involving formaldehyde (MW30) and/or MACR (MW70) were observed by PTR-MS. So, we found that the SOA formed in the isoprene ozonolysis consists of oligomeric hydroperoxides involving Criegee intermediate as a chain unit and hemiacetals involving formaldehyde and/or MACR.

Gas-aerosol partitioning of each VOC was estimated from ion signals in both gaseous and aerosol phases by PTR-MS. Gas-phase concentrations at each mass number were determined from mass spectrum observed after the reaction. Aerosol-phase concentrations were estimated from total ion signals summed during the heating of the filter. We assume that VOC is evaporated during the analysis time of 2 hours. From the ratio of aerosol-phase concentration to gas-phase concentration, we estimated saturation vapor pressures of compounds in the mass range between 100 and 200 to be approximately 10<sup>-4</sup> Torr. On the other hand, from the fitting of SOA yield curve by four-product volatility basis model, model suggested that species 10<sup>-4</sup> Torr of saturation vapor pressure are dominant in SOA. These are consistent with the compounds observed in the mass range between 100 and 200 and we assigned those as oligomeric hydroperoxides and hemiacetals.

Keywords: isoprene, ozonolysis, chemical ionization mass spectrometry, proton transfer reaction mass spectrometer, secondary organic aerosol, Criegee intermediate