

Formation processes of dimers measured in α -pinene secondary organic aerosol particles

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Formation of low-volatility compounds such as dimers detected in atmospheric aerosol particles will affect atmospheric organic aerosol level due to the influence from these dimers on volatility and viscosity of particles. In order to study formation mechanisms of dimers detected in forest particles,¹⁾ we used liquid chromatograph-mass spectrometry (LCMS) to analyze filter extracts of secondary organic aerosol (SOA) particles generated by chamber experiments on the oxidation of α -pinene. We determined the ratios of dimer to SOA mass for those with molecular weights (MWs) of 344, 358, and 368 as a function of experimental conditions including the oxidant of VOC, initial VOC concentration, the acidity of seed particles, and the temperature of chamber. We used 6 m³ NIES smog chamber and temperature-controllable 0.7 m³ Teflon bag chamber for generation of SOA particles. The dimer/SOA ratios measured for the reactions of O₃ with α -pinene were higher than those measured for the reactions of OH and NO₃ radicals with α -pinene. Formation of dimers barely occurred during reactions with OH and NO₃ radicals although the reactions of OH and NO₃ radicals with α -pinene forms carbonyl compounds, which could form dimers through acid catalyzed heterogeneous reactions, and organic peroxy radicals, which could form dimers through gas-phase association reactions. Furthermore, the concentrations of dimers with MWs of 344 and 358 in sample solutions showed linear correlations with the product from multiplication of the concentrations of corresponding monomers. Dimers with MW 358 could be successfully separated with a LC column from the chromatographic peaks of presumed monomers, pinic acid and terpenylic acid; suggesting that signals of dimers with MW 358 are not instrument artifacts and result from stable dimers existing in solution or particle phases. Dimers with MW 358 are likely to be formed through the reactions of Criegee intermediates; however, as formation process for dimer with MW 358 we cannot exclude hydrogen bonding formation²⁾ from monomers formed from the gas-phase reaction with O₃. This research has been supported by the Environmental Research and Technology Development Fund from Environmental Restoration and Conservation Agency (grant no.5-1801) and NIES Research Founding Type A.

Reference:

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