

AMS and LC/MS analyses of SOA from the photooxidation of aromatic hydrocarbons: chemical structure and aging rate

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Oxygenated organic aerosol (OOA) observed in remote areas is believed to be aged secondary organic aerosol (SOA); however, the reaction processes relevant to SOA aging remain unclear. Recently, we measured mass spectra of SOA formed from the photooxidation of aromatic hydrocarbons using an Aerodyne aerosol mass spectrometer (AMS), and suggested that SOA aging delayed with increasing the number of alkyl groups involved in a precursor aromatic molecule. In this study, we selected benzene and 1,3,5-trimethylbenzene (TMB) as the SOA precursor to analyze SOA formed from the photooxidation chamber experiments in the presence of NO_x using a high-resolution time-of-flight AMS (H-ToF-AMS) and a liquid chromatograph/time-of-flight mass spectrometer (LC/TOF-MS). A van Krevelen diagram was studied using the O:C and H:C ratios obtained by H-ToF-AMS for SOA. The results showed that organics present in SOA are rich in carboxylic acids or hydroxy carbonyls, and the O:C ratio of SOA formed by the reaction of 1,3,5-TMB is lower than benzene. Analytical results of LC/TOF-MS showed that particulate products formed by the reaction of 1,3,5-TMB are rich in ketocarboxylic acids. These results indicated that SOA aging proceed mainly by formation of carboxylic acids, and the rate of SOA aging in laboratory chambers is limited by the oxidation of ketone groups. Aging of SOA formed by laboratory chamber experiments is delayed compared with ambient OOA; this is because, the experimental duration is insufficient, or conventional laboratory chamber experiments cannot simulate the ketocarboxylic acid oxidation known to proceed in the aqueous phase. Further, it was newly suggested that the ratio of particulate nitrophenols formed by the reaction of 1,3,5-TMB to total SOA mass is lower than benzene.

Keywords: aromatic hydrocarbons, secondary organic aerosol, aerosol aging, photochemical smog chamber, liquid chromatography-mass spectrometry, aerosol mass spectrometry