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Photodegradation of secondary organic aerosol generated from limonene oxidation by ozone studied with chemical ionization mass spectrometry

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Abstract. Photodegradation of secondary organic aerosol (SOA) prepared by ozone-initiated oxidation of D-limonene is studied with an action spectroscopy approach, which relies on detection of volatile photoproducts with chemical ionization mass-spectrometry as a function of the UV irradiation wavelength. Efficient photodegradation is observed for a broad range of ozone (0.1 – 300 ppm) and D-limonene (0.02 – 3 ppm) concentrations used in the preparation of SOA. The observed photoproducts are dominated by oxygenated C1-C3 compounds such as methanol, formic acid, acetaldehyde, acetic acid, and acetone. The irradiation wavelength dependence of the combined yield of the photoproducts closely tracks the absorption spectrum of the SOA material suggesting that photodegradation is not limited to the UV wavelengths. Kinetic simulations suggest that RO_2+HO_2/RO_2 reactions represent the dominant route to photochemically active carbonyl and peroxide species in the limonene SOA prepared in these experiments. Similar photodegradation processes are likely to occur in realistic SOA produced by OH- or O_3-initiated oxidation of biogenic volatile organic compounds in clean air.

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