

HPALD2 is a Peroxyhemiacetal and a Source of SOA

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Abstract

Isoprene, a volatile organic compound (VOC) is emitted largely by vegetation at a rate of 512 Tg/yr. Based on theoretical calculations and mass spectrometric evidence, Z- δ -hydroperoxyalkenal structures (HPALD1 and HPALD2) have been assigned to $C_5H_8O_3$ gas-phase compounds accounting for up to 12% of the total first-generation isoprene oxidation products. The putative HPALDs are conjugated carbonyls expected to have a significant absorption cross section at ambient UV wavelengths (> 315 nm). Fast internal energy transfer from the excited alkenal to the O-OH bond is predicted to cause rapid bond dissociation degradation into volatile fragments, with little or no formation of SOA.

We undertook synthesis of HPALD2 to verify the structure assigned solely from mass spectrometry. By proton NMR, HPALD2 exists exclusively as the peroxyhemiacetal tautomer, with no carbonyl detected, even in D_2O . Tautomerization to the cyclic peroxyhemiacetal is strongly favored by the Z geometry of HPALD2. The peroxyhemiacetal structure of the isoprene photochemical oxidation product was confirmed by matching the IMS drift time of the synthetic standard with a major $C_5H_8O_3$ product from hydroxyl radical oxidation of isoprene.

Lacking the conjugated chromophore, the peroxyhemiacetal does not absorb at > 250 nm and will persist at ambient UV wavelengths. In chamber experiments, OH oxidation caused rapid nucleation in the absence of seed, and reactive uptake in the presence of both $(NH_4)_2SO_4$ and $(NH_4)HSO_4$ seed. Products at m/z $C_5H_8O_5$, $C_5H_{10}O_5$, $C_5H_{10}O_6$ were detected by on-line monitoring of the gas phase by an iodide-CIMS-high resolution time-of-flight mass spectrometer (HR-ToF-MS). Analysis of filter extracts by hydrophilic interaction liquid chromatography coupled to an electrospray ionization HR-ToF-MS detector operated in the negative mode showed major products with compositions $C_5H_{10}O_5$ in all experiments, and major sulfated products with compositions $C_5H_{10}O_6S$ and $C_3H_6O_6S$ in seeded experiments.