Identifying a Missing Link: Confirmation of the Structure and Origin of 4-hydroperoxy-3-methylbut-2-enal (4-HPALD) with an Authentic Standard

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Abstract

Isoprene (C_5H_8) is the largest non-methane volatile organic compound emitted into the atmosphere. Isoprene reacts rapidly with ambient hydroxyl radicals (OH) and subsequent addition of O_2 results in the formation alkyl peroxy (RO_2) radicals. The fate of the initially formed RO_2 radicals has been the focus of continuing theoretical and experimental research. Under pristine conditions where bimolecular reactions of RO_2 are limited, the thermodynamically favored RO_2 undergoes an intramolecular H-shift followed by reaction with O_2 and elimination of HO_2 to yield 4-hydroperoxy aldehyde (4-HPALD, $C_5H_8O_3$), predicted to account for up to 13% of first-generation isoprene photochemical oxidation products. Mass spectrometric evidence has been reported for 4-HPALD, but lack of an authentic standard has precluded definitive confirmation of both the structure of 4-HPALD and its origin as a first-generation product of OH oxidation of isoprene.

We report the synthesis and characterization of 4-HPALD and establish that it is a major product of isoprene oxidation. Synthetic 4-HPALD is isolated as the peroxyhemiacetal. As expected for the 4-hydroperoxy aldehyde, ^{1}H NMR spectra show no evidence for equilibration with the carbonyl form, even in protic solvents, and gas-phase chemical analysis by CIMS also shows only a single form. OH oxidation of isoprene in an oxidation flow reactor coupled to an ion mobility source with an HR-CIMS detector unequivocally demonstrates 4-HPALD (and likely also 1-HPALD) as isoprene oxidation products. Although HPALDs have been discounted as significant contributors to SOA, oxidation of 4-HPALD in a potential aerosol mass (PAM) reactor in the presence of ozone and OH indicates 4-HPALD rapidly undergoes autooxidation reactions forming low-volatility particulate products. We have confirmed highly oxygenated compounds with compositions $C_5H_8O_6$ and $C_5H_{10}O_6$ likely from OH oxidation, and $C_5H_{10}O_7$ and $C_5H_{10}O_8$ compounds likely products of ozonolysis. The PAM oxidation experiment further

demonstrates that the highly oxygenated, low-volatility products efficiently nucleate particles.

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