A52D-07 A Cyclic Peroxyhemiacetal is a Previously Unrecognized Source of Isoprene-Derived Secondary Organic Aerosol

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- *152 B (Convention Center)*

Abstract

The photochemical oxidation of isoprene has been studied intensely since the initial recognition that isoprene was recognized as a major contributor to secondary organic aerosol. Efforts to account for unexpectedly high levels of OH in isoprene rich environments led to the proposal that OH_x ($HO + HO_2$) was recycled by the decomposition of isoprene-derived hydroperoxy radicals via intramolecular H transfers to yield HO_2 and isomeric 4-hydroperoxy-2-methyl- and 4-hydroperoxy-3-methylbut-2-enals (C_5-hydroperoxyalkenyls; (HPALDs). Evidence from chamber oxidation of isoprene by hydroxyl radical monitored directly by CF_3O^- CIMS provided the first support for structures consistent with HPALD composition at unit mass resolution and subsequently, at the level of isomer resolution by coupling the chamber GC/CF_3O^- CIMS. However, definitive structural confirmation requires comparison with an authentic standard and accurate mass measurement. Based on the identification of the cyclic peroxyhemiacetal 3-hydroxy-1,2-dioxane as a predominant oxidation product of bis-*n*-butylperoxide, we synthesized the peroxyhemiacetal 5-methyl-3,6-dihydro-1,2-dioxin-3-ol as the preferred form of the isoprene oxidation product. Since the cyclic peroxyhemiacetal does not absorb in the ambient UV-vis range and is not photolabile it is a potential source of SOA by further OH oxidation. We have verified the cyclic peroxyhemiacetal structure of a major first-generation isoprene oxidation by matching IMS drift times with the synthetic standard and have proposed structures for marker compounds in extracts of chamber SOA. The availability of authentic standards enabled us to monitor the evolution of peroxyhemiacetal formation relative to the first-generation ISOPOOH and second-generation *trans*-β-IEPOX photoproducts and to demonstrate a steady state concentration of peroxyhemiacetal isomers relative to *trans*-β-IEPOX under steady state chamber conditions (~3h).

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