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The Chemistry of Isoprene Hydroxy Hydroperoxides (ISOPOOH)

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Organic hydroperoxides are important oxidation products of volatile organic compounds, especially under low-NO_x conditions. Despite their large global importance, the low-NO_x pathways are not well understood. High-NO_x oxidation pathways that typically produce carbonyls have been studied extensively. The formation of organic hydroperoxides makes the study of low-NO_x pathways challenging, as this class of compounds is not commercially available and the synthetic methods used to prepare them are still underdeveloped. This poses challenges for both quantification of these low-NO_x products as well as characterization of instruments with them. Isoprene hydroxyhydroperoxides (ISOPOOH) are the main first-generation products of the low-NO_x isoprene oxidation pathway; it is estimated that globally over 50% of isoprene peroxy radicals form ISOPOOH. We present a study of the kinetics of the formation of several ISOPOOH isomers as well as their atmospheric sinks. We also present instrument characterization studies that demonstrate that ISOPOOH is an interference in both GC and PTR-MS measurements. In these instruments ISOPOOH isomers are observed as the corresponding products (carbonyls) of the high-NO_x pathway. We discuss the interference mechanism as well as the implications of this interference on studies of OH reactivity, O:C ratios, OH recycling and secondary organic aerosol formation.