Accurate Identification of Dimers from α-Pinene Oxidation Using High-Resolution Collision-Induced Dissociation Mass Spectrometry

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Highly oxidized dimers from α-pinene oxidation are essential to the atmospheric chemistry field because they are efficient precursors of secondary organic aerosols. Here we apply high-resolution collision-induced dissociation (CID) mass spectrometry with an atmospheric pressure ionization (API) source to accurately identify the origin of dimers from α-pinene + O_3/OH/NO_x reactions. The CID spectra and specific fragmentation patterns suggest that (i) a large fraction of dimer ions detected in full-scan mass spectra can be hydrogen-bonded clusters, which are instrument artifacts; these clusters form owing to the adiabatic expansion between the API source inside a mass spectrometer, and (ii) the residual small fraction includes covalently-bonded dimers, such as hydroperoxide-type dimers, that are formed from reactions between a stabilized Criegee Intermediate (sCI) and oxidized monomers. This work highlights the importance of accurate identification and quantification of dimers for mechanistic and kinetic studies of α-pinene-derived dimer formation using ion intensities detected by mass spectrometry.

Keywords: α-Pinene, Oxidation, Dimer, High-resolution collision-induced dissociation mass spectrometry, Hydrogen-bonded artifact cluster

