Manuscript Title: Particle phase acidity and oligomer formation in secondary organic aerosols

Authors: Song Gao, Nga L. Ng, Melita Keywood, Varuntida Varutbangkul, Roya Bahreini, Athanasios Nenes, Jiwen He, Kee Y. Yoo, J. L. Beauchamp, Robert P. Hodyss Richard C. Flagan & John H. Seinfeld* (*corresponding author)

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Figure S1. The extracted ion chromatograms of 185, 171, 199 and 183 ions detected by the LC-MS in the SOA from the same α-pinenene ozonolysis experiment as shown in Figures 2(a) and 3(a). A Nova-Pak C_{18} column (300 x 3.9 mm, Waters) was used in the
LC. 185 and 183 are identified as cis-pinic acid and cis-pinonic acid, respectively, by comparing with standard compounds. 171 and 199 are tentatively identified as norpinic acid and hydroxy pinonic acid, respectively, although isomers are likely present. The molecular structures of these four compounds are drawn alongside the corresponding ion chromatograms (only one isomer is drawn for the 199 ion).
Figure S2. Ion trap mass spectrum (negative mode) of the extract of SOA from the same α-pinene ozonolysis experiment as shown in Figures 2(a) and 3(a). In all SOA samples from α-pinene ozonolysis, 185, 171 and 199 are detected as the most abundant low-MW species (after deprotonation), by both the EI-MS and LC-MS (see text). The identified (185) and tentatively identified (171, 199)
structures are shown next to their corresponding ions. The 863.1 ion is from the instrument background. All other background ion intensities are lower than 1% of the maximum intensity (m/z = 185.0, designated as 100%). Consistent with the tandem mass spectra (MS/MS), the small oligomers with m/z of 329, 343, 357, 371, and 385 (after deprotonation) correspond to the possible combination of two norpinalic acids (MW = 156), norpinalic acid and norpinonic acid (170), two norpinonic acids, norpinonic acid and pinonic acid (MW = 184), pinonaldehyde (MW = 168) and hydroxy pinonic acid (MW = 200), respectively, through gem-diol reaction (see reference 13 for structures of these monomers). Combination of other monomers resulting from α-pinene ozonolysis is very likely, through the reactions proposed in the text.
**Figure S3.** Ion trap mass spectrum (+ ion mode) of the extract of a typical blank filter serving as the background MS. In the m/z range of 150 to 1600, most ion intensities are below 400000. The several exceptions, such as 268.9, 413.3, 514.8, 596.7, and 803.2 ions, are not among the most abundant ions in the IT-MS of SOA samples from α-pinene ozonolysis (e.g., see Figures 2, 4, and 5) or cycloalkene ozonolysis. Most likely, they come from either solvent or instrument background.
Figure S4. Ion trap mass spectra (+ ion mode) of the extracts of SOA from another pair of α-pinene (96
ppb) ozonolysis experiments: (a) on MgSO₄-only seed. (b) on MgSO₄-H₂SO₄ seed. Other experimental conditions are identical.
**Figure S5.** The likely structures of 313, 171 and 185 fragment ions in Figure 3(a). It is worth noting that our Figure 3(a) is similar to Figure 9 in Hoffmann et al., *J. Geophys. Res.*, 103, 25,569 – 25,578 (1998), where they used atmospheric pressure chemical ionization (APCI)-MS to analyze SOA samples from α-pinene ozonolysis. Besides the well-known inherent artifact with APCI technique of forming adducts and clusters during analysis, a fundamental difference is Hoffmann et al. interpreted the 357 ion as a molecular cluster formed through intermolecular forces (i.e., H-bonding) between acids, whereas we propose the 357 ion as a true dimer formed through covalent bonds via gem-diol reaction. Covalent bonding is much stronger than H-bonding, therefore making the formation and presence of the dimers in SOA, depicted in our Figure 3(a), more feasible.
Figure S6. Ion trap mass spectrum (-ion mode) of the extract of SOA from the ozonolysis of 184 ppb cycloheptene on dry (NH₄)₂SO₄ seed. The background ion intensities are lower than 5% of the maximum intensity (m/z = 373.1, designated as 100%).