

## **Supplementary Material**

# **Ultrahigh-Resolution Mass Spectroscopic Analysis of Secondary Organic Aerosol Generated by Ozonolysis of Isoprene**

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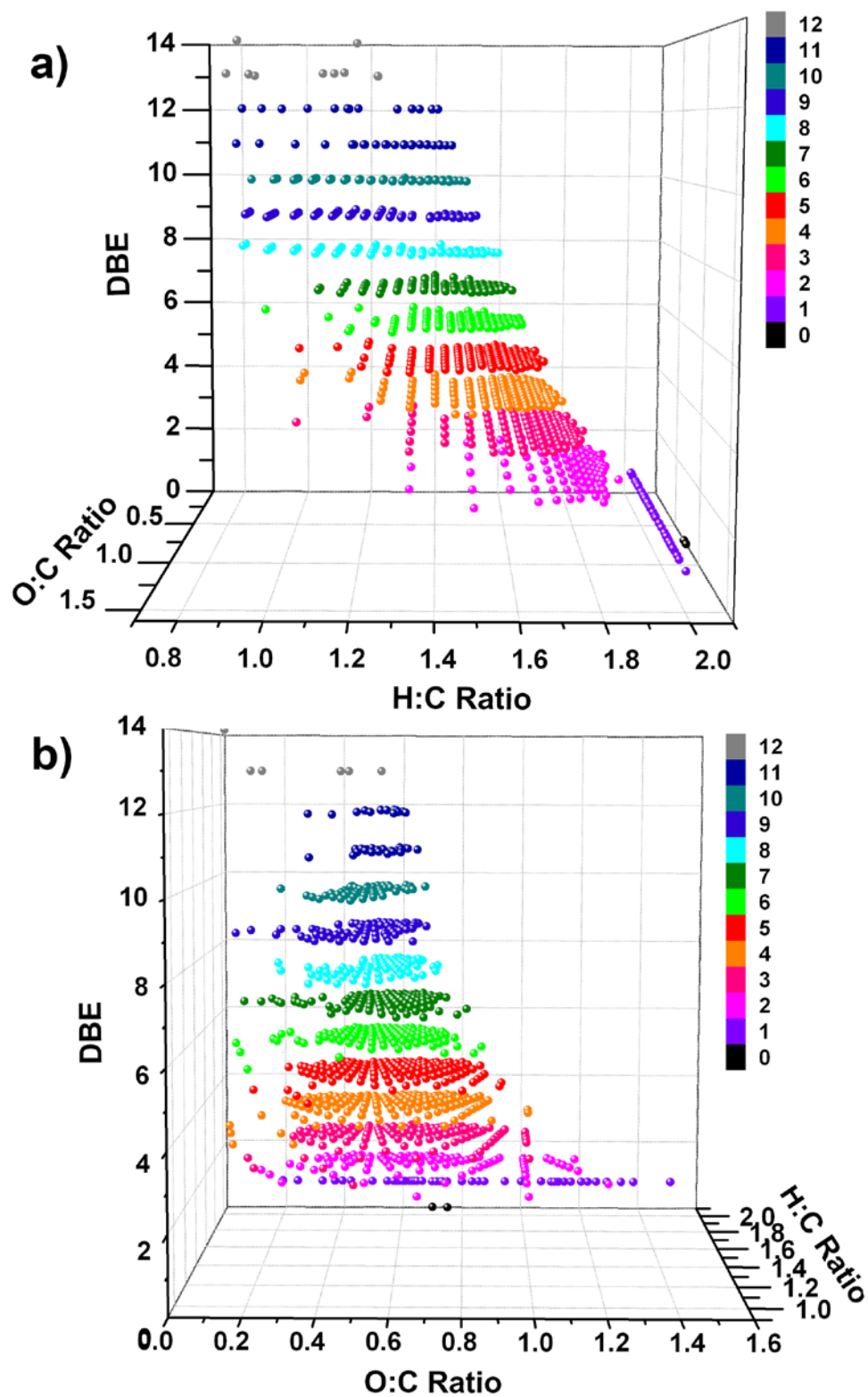
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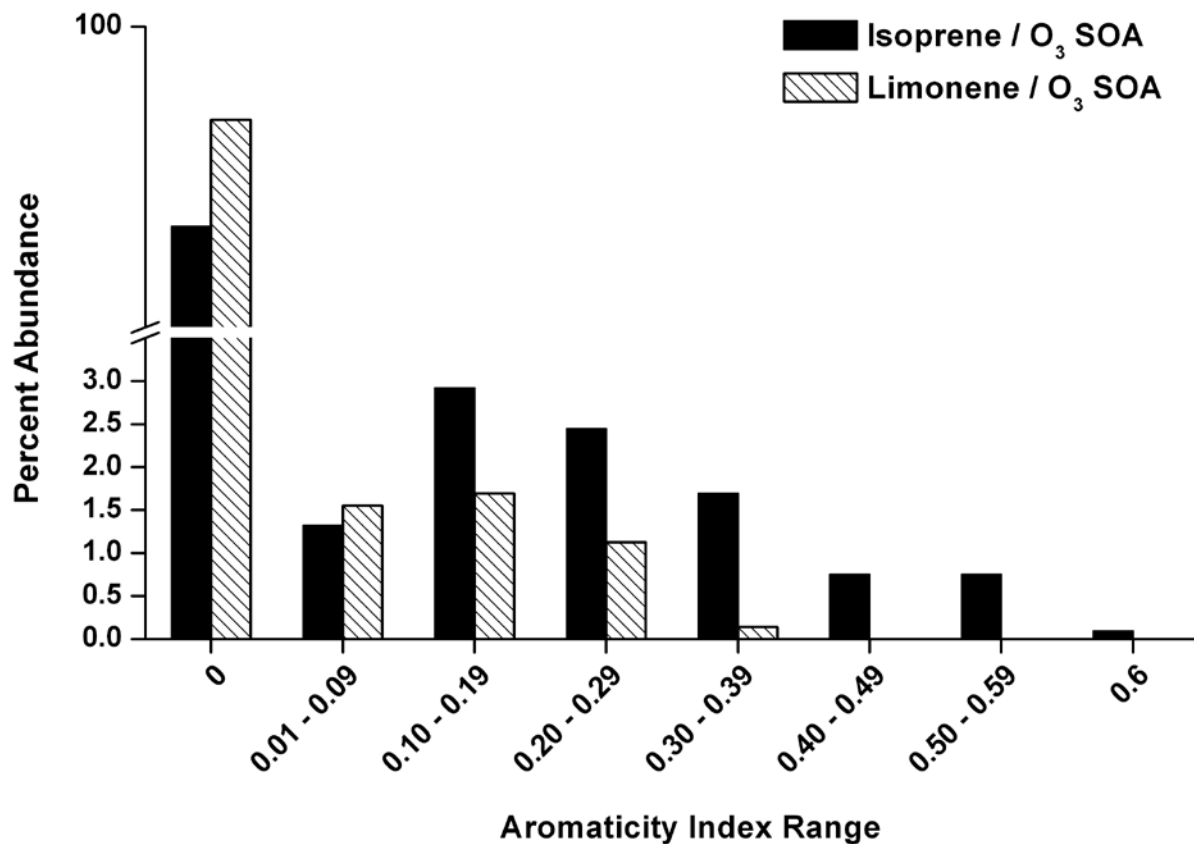
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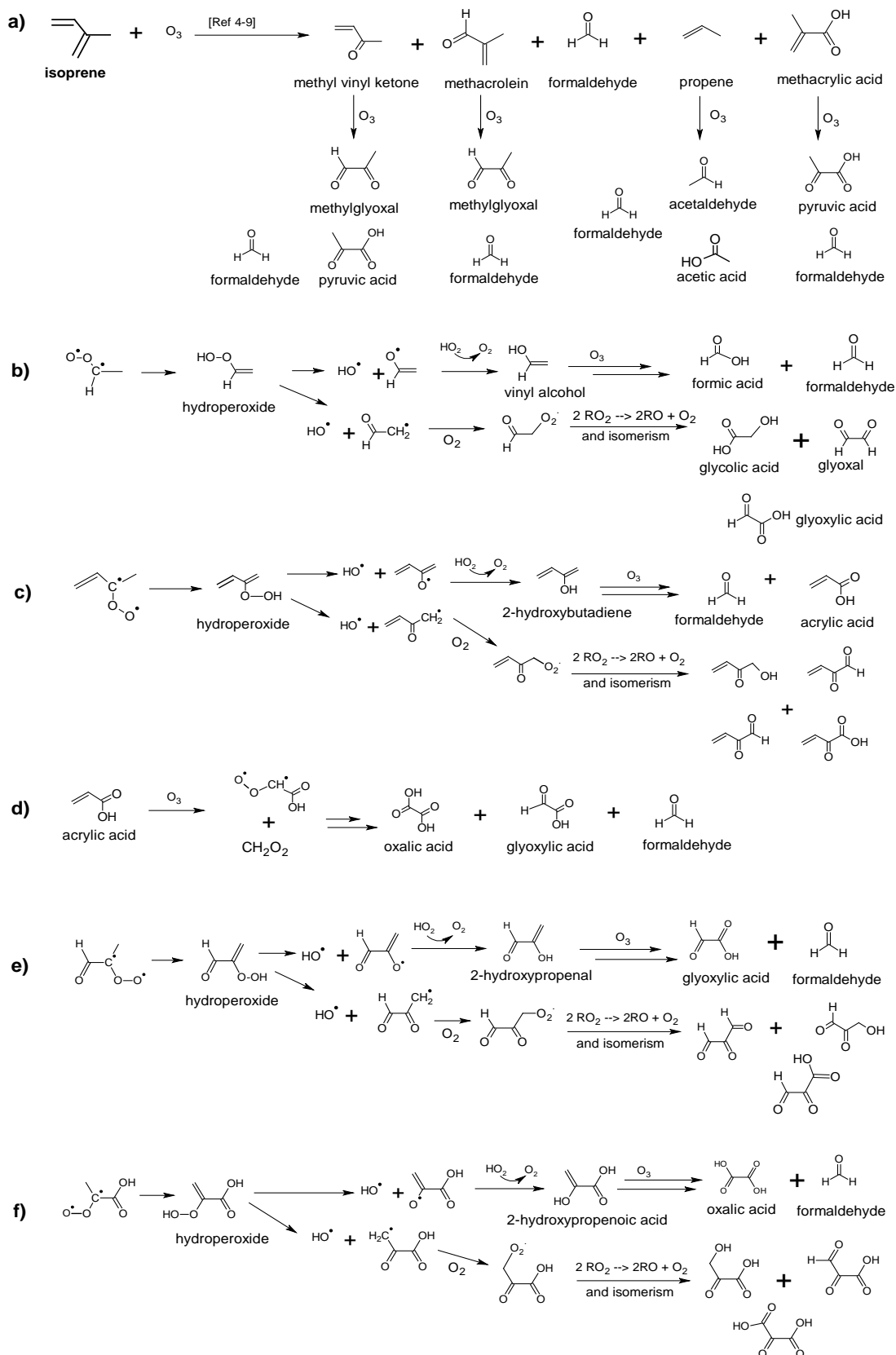
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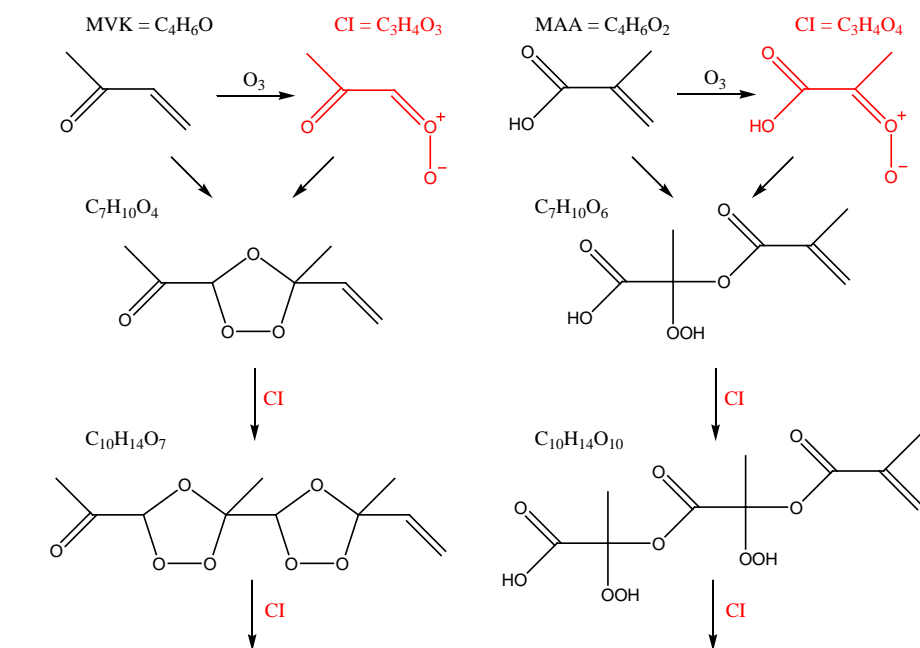
**Figure S1:** 3D version of Van Krevelen diagram in H:C, O:C, DBE dimensions from positive ion mode data. H:C ratio (a) and O:C ratio (b) both decrease with increasing DBE.



**Figure S2:** Histogram of the distribution of aromaticity index values in the isoprene/O<sub>3</sub> SOA measured in this work and in the limonene/O<sub>3</sub> SOA measured in Ref. (1). The percent abundance gives the percent of the assigned peaks in the positive ion mass spectrum that corresponds to molecules with AI values in the specified range. The vast majority of the peaks had AI = 0 necessitating a break in the vertical axis.



**Figure S3: Selected processes occurring during ozonolysis of isoprene in a NO<sub>x</sub> free environment.** (a) First- and second-generation isoprene ozonolysis products based on Refs. (2-6). (b,c,e,f) Carbonyl oxides with CH bond alpha to COO bonds have low barriers to form hydroperoxides. These hydroperoxides decompose to give OH and alkyl and alkoxy radicals. (d) Acrylic acid and other unsaturated products may undergo further oxidation by ozone to a limited extent.



**Figure S4:** Examples of possible Criegee intermediate driven oligomerization routes in the isoprene/O<sub>3</sub> SOA formation. Left panel: repeated addition of Criegee intermediate (CI) of methyl vinyl ketone (MVK) to MVK, resulting in polymeric 1,2,4-trioxolane. Right panel: repeated addition of CI of methacrylic acid (MAA) to MAA resulting in polymeric hydroperoxides. The compounds generated as a result of such Criegee intermediate chemistry condense in SOA, and continue chemisorbing small carbonyls and carboxylic acids. Results of this study suggest that formaldehyde (CH<sub>2</sub>O) is amongst the most important volatile molecules that can be chemisorbed by SOA.

#### References used in the figure captions

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