

Supporting information:

Secondary organic aerosol formation from isoprene photooxidation

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Blank runs. Irradiation of the chambers in the absence of isoprene is always found to lead to negligible aerosol growth. Prior to the start of the experiment (introduction of reagents), the chambers are relatively particle-free, with number densities of <100 particles/cm³, corresponding to volume densities below $0.2 \mu\text{m}^3/\text{cm}^3$. Irradiation of ~ 3 ppm H₂O₂ leads to no increase in particle number or volume, as measured by the DMA. In the presence of ammonium sulfate seed, which provides surface area for the condensation of semivolatile compounds, very small growth cannot be measured by the DMA, due to loss of particles to the chamber walls and signal-to-noise considerations. However, in this case the AMS detects only a very minimal increase in organic mass ($<0.1 \mu\text{g}/\text{m}^3$), also suggesting negligible aerosol growth in the absence of isoprene. Similar results are obtained when NO_x is added to the system. Irradiation of a mixture of ~ 3 ppm H₂O₂ and 300 ppb NO leads to no measurable increase in either volume or organic mass, both in the absence and the presence of inorganic seed. Hence we are confident that aerosol growth we measure, using both the DMA and the AMS, is a result of gas-particle partitioning of isoprene oxidation products.

It was found that irradiation of H₂O₂/NO mixtures, even in the absence of particles, leads to a persistent NO_x signal in our NO_x monitor (of 5-20 ppb), which was traced to the particle filter between the chamber and the instrument. This persistent interference is not observed when NO_x/hydrocarbon or HONO/NO_x/hydrocarbon mixtures are irradiated, so is likely related to the presence of H₂O₂. In between experiments the contaminated particle filter is cleaned by sending high quantities of air through it for several hours. Thus the interference is not significant at the beginning of experiments, but may affect measurements of total NO_x somewhat as the experiment progresses. No such interference was seen in the measurements of NO or O₃.

Potential role of impurities. As the yields we measure are low, on the order of 1-6%, the possibility that minor impurities in the isoprene used (Aldrich, 99.8%) may contribute to the observed aerosol growth must be considered. GC-MS analysis of the isoprene indicates that the primary impurity is a terpene (isoprene dimer, C₁₀H₁₆), and proton transfer reaction-mass spectrometry (PTR-MS) measurements of the gas-phase compounds in the chamber after isoprene injection also show a 0.2% terpene impurity, consistent with the assay from the chemical supplier. No other compounds were detected by either GC-MS or PTR-MS. The gas-phase oxidation of terpenes is well-known to form SOA, so this impurity may contribute to the SOA observed in our isoprene photooxidation experiments. However, a 0.2% impurity (0.4% by mass) can at most account for a 0.4% SOA yield, even assuming an SOA yield of 100% from this

compound; this is almost certainly an overestimate. The yields we measure in this study from isoprene photooxidation are significantly higher than this upper limit. Further, mass spectra of the SOA in the current experiments are fundamentally different from those of SOA from terpene photooxidation [see Figure S1]. Thus the terpene impurity in the isoprene is unlikely to contribute substantially to the aerosol production in our chamber, and at the very most can account only for a small fraction of the SOA growth observed.

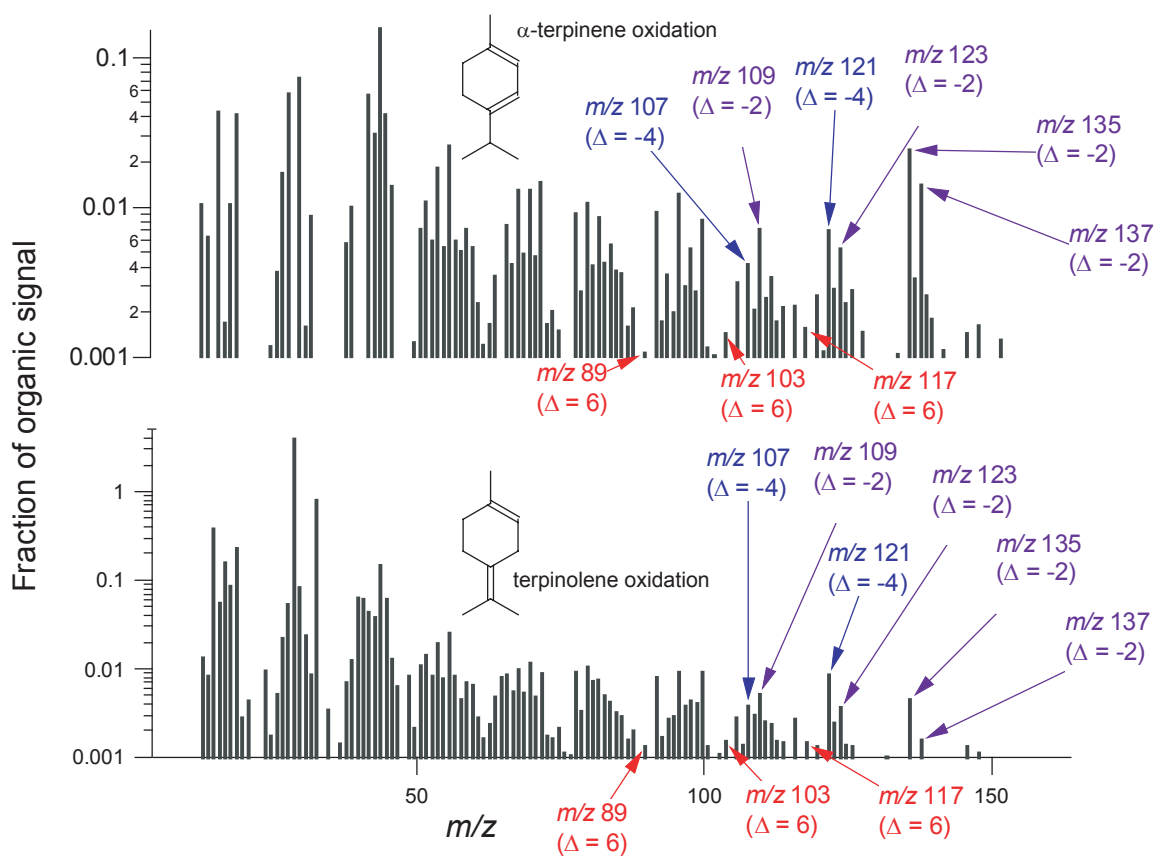


Figure S1. AMS spectra for the photooxidation of two representative terpenes, α -terpinene (upper panel) and terpinolene (lower panel), under high- NO_x conditions. Both are substantially different from the SOA formed from isoprene under similar conditions (Figure 6 of text), with major peaks of $m/z > 50$ (in blue) substantially different from isoprene SOA (in red). See Ref. 29 for description of the delta-series analysis.

Low concentration runs. By contrast, the chemical composition of SOA formed in isoprene oxidation is found to be invariant over a range of isoprene concentrations. Shown in Figure S2 is a comparison between AMS spectra of high isoprene (450 ppb) and low isoprene (8 ppb) oxidation experiments. Both exhibit the same major peaks, strongly suggesting that the even the very low SOA loadings observed are from the oxidation of isoprene and not some impurity in the chamber.

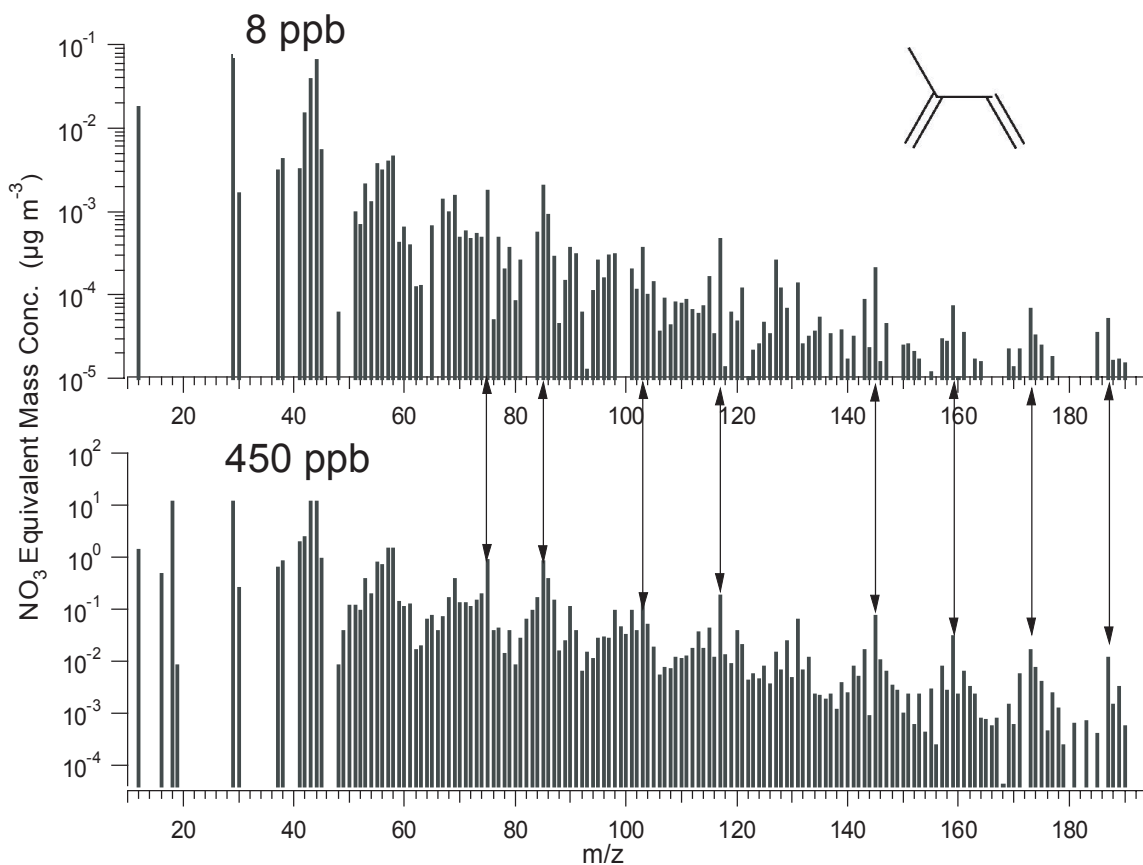


Figure S2. AMS spectra for the photooxidation of isoprene at two concentrations: 8 ppb (upper panel) and 450 ppb (lower panel), under high-NO_x conditions. Both are very similar qualitatively, with the same major peaks extending out to high mass, indicating observed SOA growth at very low isoprene concentrations is indeed from isoprene oxidation and not an impurity.

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