Supplementary Material

Formation of Brown Carbon via Reactions of Ammonia with Secondary Organic Aerosols from Biogenic and Anthropogenic Precursors

Katelyn M. Updyke, Tran B. Nguyen Sergey A. Nizkorodov*

Department of Chemistry, University of California, Irvine, California 92697, USA

* Corresponding author: nizkorod@uci.edu, 949-824-1262

The following supporting information is available for this article: the structures and suppliers of all precursors used for the generation of SOA samples (Table S1); tests for the solubility of SOA samples in water and methanol (Fig. S1 and Fig. S2); tests for the completeness of SOA extraction from the filter (Fig. S3); sensitivity of the degree of browning to the substrate used for SOA collection (Fig. S4); proof that browning chemistry is not a result of impurities present in the SOA precursor (Fig. S5); time dependence for the browning process (Fig. S6).

Table S1. The structures of all precursors used for the generation of SOA samples that were subjected to chemical aging, abbreviations by which they are referred to in the main text, and their commercial sources and purities.

Compound	Abbreviation	Manufacturer / purity	Structure
α-Cedrene	CED	Sigma Aldrich, ≥99%	
Farnesene	FAR	Sigma Aldrich, 99.9% (mixture of isomers)	
α-Humulene	HUM	Sigma Aldrich, 98.8%	
Isoprene	ISO	Sigma Aldrich, 99%	
d-Limonene	LIM	Sigma Aldrich, 97%	
Naphthalene	NAP	Fisher, 98%	
α-Pinene	PIN	Sigma Aldrich, 98%	
Tetradecane	TET	Sigma Aldrich, 99%	
1,3,5-Trimethylbenzene	TMB	Sigma Aldrich, 99.3%	
Pine Needle	PNO	Sigma Aldrich,	α-pinene (30%)
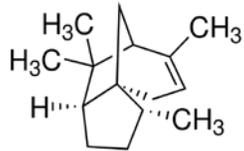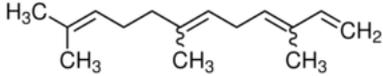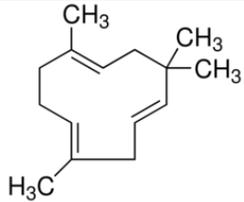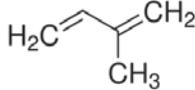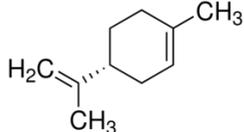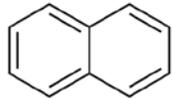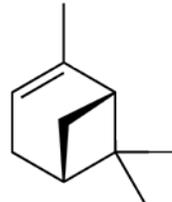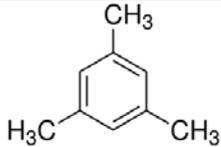
Oil[1]		100%	 δ-3-carene (4-12%) camphene (5-7%) *≤10%: limonene, β-pinene, santene, camphor, isoborneol, α-terpineol*
			≤5%: trace amounts of terpenes and sesquiterpenes.
Cedar Leaf Oil[2]	CLO	Sigma Aldrich, 100%	 α-thujone (50%)
			 Beyerene (5-15%) *≤10%: fenchone, β-thujone, simuene, sabinene*
			≤5%: trace amounts of terpenes and sesquiterpenes.
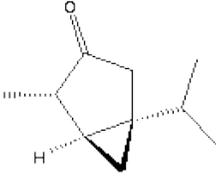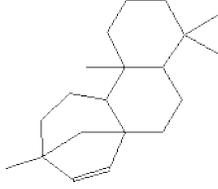
[1] TheGoodScentsCompany.com: http://www.thegoodscentscompany.com/gca/gc1019031.html

[2] TheGoodScentsCompany.com: http://www.thegoodscentscompany.com/gca/gc1002891.html

Figure S1. Test for the solubility of SOA samples in water and methanol. Two identical samples of CED/O$_3$ SOA were synthesized and collected on separate Teflon membranes. Each sample was sonicated in water or methanol and analyzed using UV/Vis spectroscopy. *MAC* was calculated using Eq. (2) as if the entire sample was dissolved. The difference in the resulting MAC values shows that SOA is more soluble in methanol and much less soluble in water. Similar observations of poor water solubility were made for SOA produced from aromatic precursors, tetradecane, essential oils, and sesquiterpenes. In contrast, SOA samples prepared from monoterpenes and isoprene were more soluble in water (see next figure).
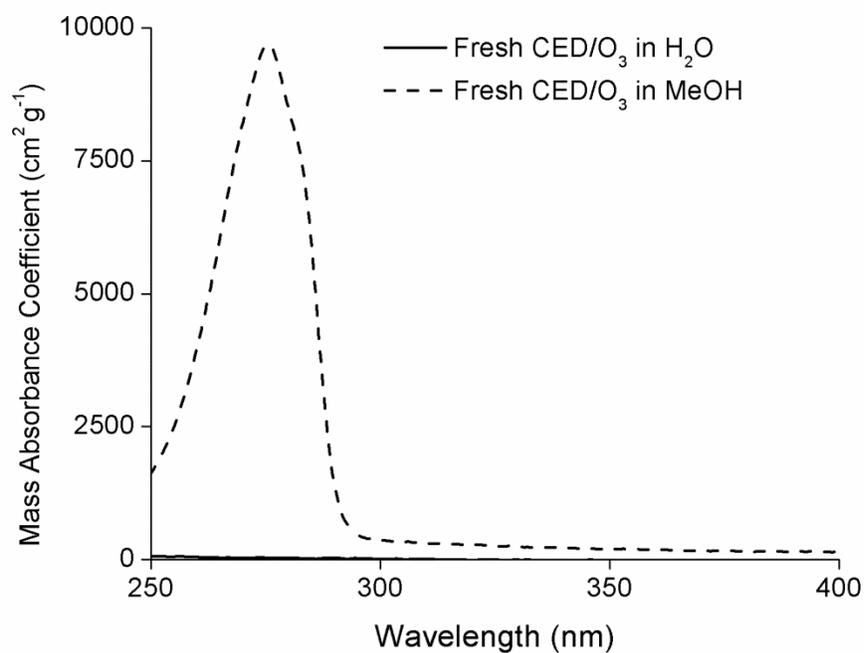
Figure S2. Test for the solubility of SOA samples in water and methanol. Similar to Figure S1, but for fresh LIM/O_3 SOA. Unlike the CED/O_3 SOA case, the LIM/O_3 SOA is soluble in both methanol and water. The subtle differences between the spectra can be ascribed to partial esterification and hemiacetal formation from SOA compounds occurring in methanol, and partial hydrolysis of SOA compounds occurring in water.
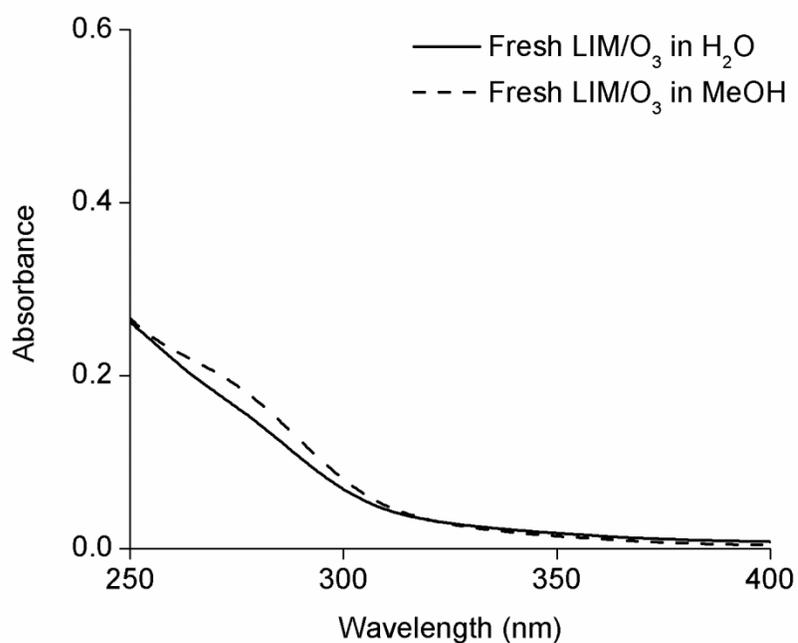
Figure S3. Test for the completeness of SOA extraction from the filter. Fresh LIM/O_3 SOA was collected on a Teflon membrane and then immediately sonicated in ~5 mL methanol for extraction. After the first extraction, the solution was analyzed using UV/Vis spectroscopy and the spectrum is shown in black color. Subsequently, the same Teflon filter was sonicated again in ~5 mL of methanol for a second extraction to remove any remaining sample on the filter. The resulting UV/Vis spectrum had an order of magnitude smaller peak absorbance suggesting that the first extraction of the methanol-soluble material was >90% complete.
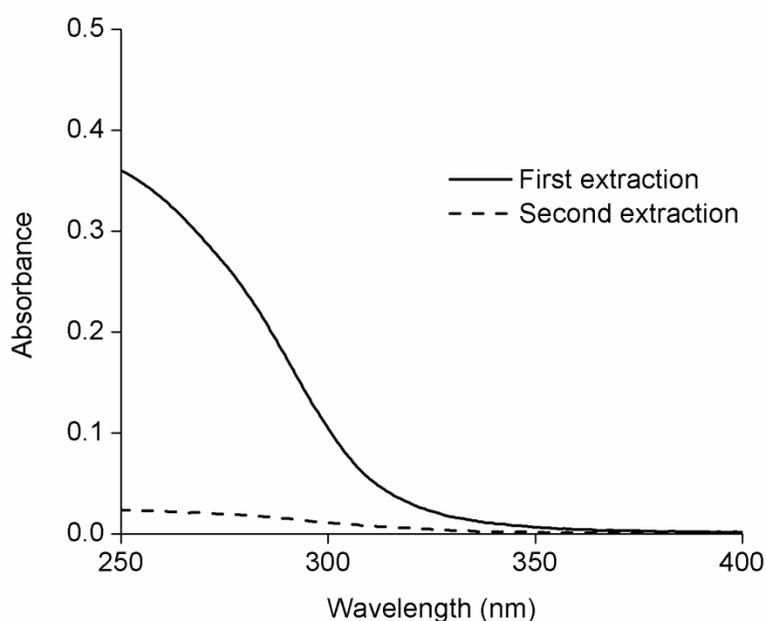
Figure S4. Lack of sensitivity of the degree of browning to the substrate used for SOA collection. LIM/O$_3$ SOA was collected on PTFE membrane and aluminum foil by impaction, and aged using gas phase ammonia in the dark for 24 hours. The UV/Vis spectra of the extracted aged SOA have comparable shape and peak values of ΔMAC, so the browning reaction is clearly not mediated by the substrate. The small differences between the spectra may have something to do with the amount of water capable of sticking to the Teflon (less hygroscopic) and foil (more hygroscopic). Presence of water has significant effect on browning because the chromophores are formed from the SOA compounds and ammonia in condensation-type processes (see *Nguyen et al.* (2012)).
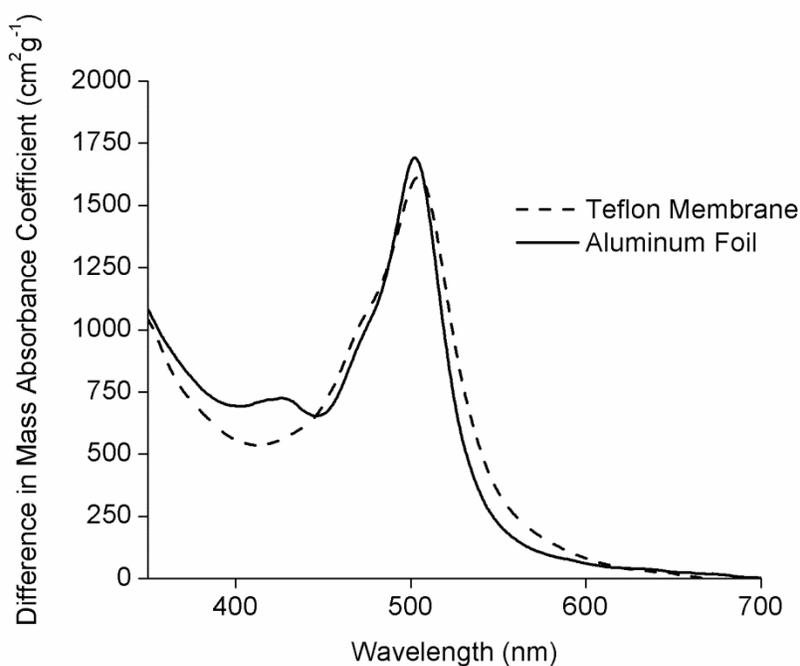
Figure S5. Proof that browning chemistry is not a result of impurities present in the SOA precursor. In this test, d-Limonene (Sigma Aldrich, 97%) was oxidized with ozone using the flow tube reactor and the resulting SOA was collected on PTFE filter and aged with gas phase ammonia in the dark. d-Limonene was then purified slowly by vacuum distillation, and its purity was confirmed by NMR. Purified limonene was oxidized with ozone in the flow tube reactor and the SOA was collected and aged for 5 days on a PTFE filter in the same way. The SOA was extracted in water and analyzed with UV/Vis spectroscopy. The similarity between the absorption spectra strongly suggests that browning reactions are driven by oxidation products of d-limonene, and not by its oxidized impurities. The differences in the spectra are representatives of the typical level of reproducibility in these aging experiments.
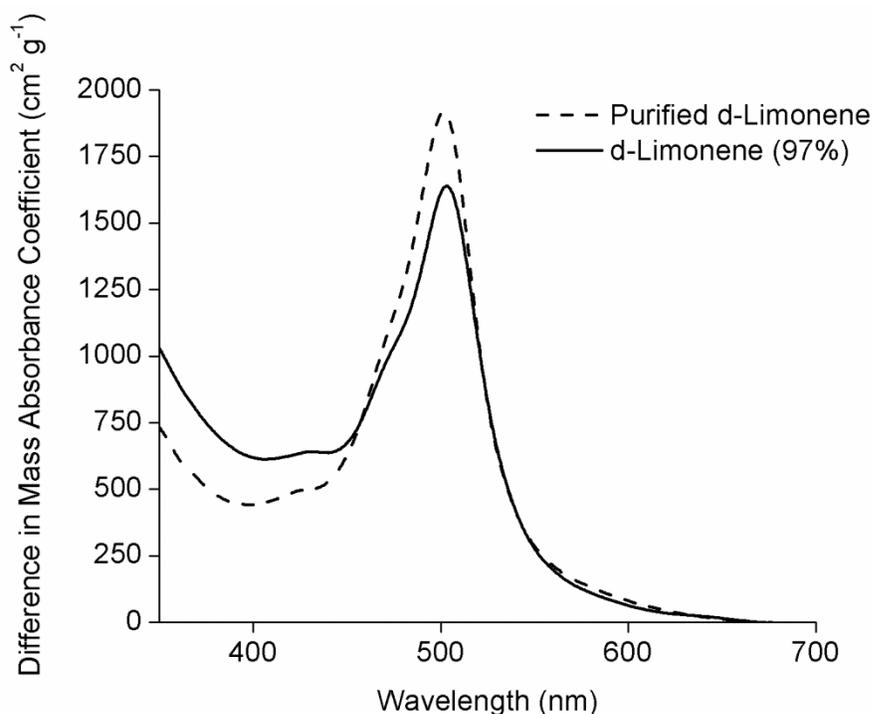
Figure S6. Time dependence for the browning process. Multiple LIM/O_3 SOA samples were generated under identical conditions, collected on Teflon filter membranes, and subjected to the same method of chemical aging with gaseous ammonia for varying amounts of time. Each sample was extracted in methanol, and analyzed using UV/Vis spectroscopy. This plot shows the peak values of *MAC* at 500 nm. The results show that browning saturates after 5 days of aging. The sigmoidal time dependence is consistent with a two-step formation mechanism for the 500 nm chromophores described by *Nguyen et al.* (2012).