

Supporting Information

Chemical Analysis of Complex Organic Mixtures Using Reactive Nanospray Desorption Electrospray Ionization Mass Spectrometry

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Secondary organic aerosol from ozone initiated oxidation of limonene (LSOA) was produced in an inflatable Teflon reaction chamber following procedures described in our previous studies.¹⁻² Samples of LSOA were deposited onto Teflon (polytetrafluoroethylene, PTFE) ring supported membranes of 47 mm diameter (Whatman, Inc.) using a rotating Micro-Orifice Uniform Deposit Impactor (MOUDI), model 110R (MSP, Inc). Collected LSOA material was distributed evenly over a 27 mm diameter impaction area, located in the center of a 47 mm diameter substrate. As in our previous studies,³ we analyzed samples from the 8th stage of MOUDI that collects particles of aerodynamic sizes in a range of 0.18-0.32 μm .

Chemical aging of the substrate-deposited LSOA samples was performed following an experimental procedure described elsewhere.³ Briefly, the sample was placed onto a plastic plate and allowed to float in a covered Petri dish containing 0.1 M aqueous solution of NH_4NO_3 (Aldrich Inc, 99.99% purity) for 12 hours. In this experiment, the sample is exposed to a gas-phase mixture of NH_3 , HNO_3 and H_2O with equilibrium partial pressures of less than 1.2×10^{-7} atm for $\text{NH}_{3(\text{g})}$ and 1.6×10^{-13} atm for $\text{HNO}_{3(\text{g})}$, and ca. 85% RH estimated using the AIM-II model⁴. Previous studies^{3, 5} showed that chemical aging of LSOA by reactions with ammonia results in visible browning of the initially white LSOA sample following the formation of light-absorbing nitrogen-containing products. Formation of these species has been attributed to the reactions of ammonia with aldehyde and ketone groups in the LSOA molecules, converting them into terminal imines (R-C=NH_2), open-chain imino groups ($\text{R}_1\text{-C=NH-R}_2$), and other nitrogen-containing compounds.³

Data processing was performed as described in our previous studies. Specifically, mass spectral features with a minimum signal-to-noise ratio of 5 were extracted from the averaged mass spectra of the background and the sample using Decon 2LS software developed at PNNL (<http://ncrr.pnl.gov/software/>). The background peaks were removed by aligning the LSOA and background spectra and eliminating most of the features observed in the background spectrum except for the peaks occurring with a minimum of 2.5 times greater intensity in the signal than in the background. The signal peaks were subsequently grouped using the first- and second-order mass defect analysis⁶ described elsewhere. Formula assignments were performed using MIDAS Molecular Formula Calculator (<http://magnet.fsu.edu/~midas/>).

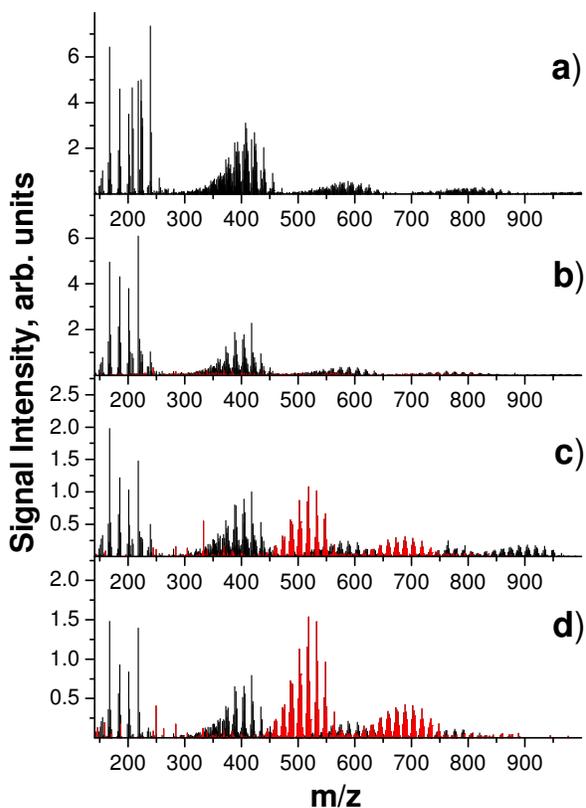


Figure S1. High-resolution nano-DESI spectra of the aged LSOA material analyzed using a) 1 μM , b) 5 μM , c) 50 μM , and d) 100 μM solution of GT in acetonitrile. Peaks corresponding to the products of reaction between LSOA and GT are highlighted in red

Table S1. Monomeric LSOA constituents and the corresponding reaction products observed using reactive nano-DESI analysis of LSOA with 50 μ M GT solution.

m/z	Relative Abundance, %	[M+GT] ⁺ (131.1059)	[M+GT- H ₂ O] ⁺ (113.0953)	DBE	Neutral Formula (M)
[M+H]⁺					
141.0911	3.0		254.1864	3	C ₈ H ₁₂ O ₂
149.0962	7.8			5	C ₁₀ H ₁₂ O
151.0755	6.2			5	C ₉ H ₁₀ O ₂
151.1118	6.6	282.2177		4	C ₁₀ H ₁₄ O
153.0911	25.2	284.1969		4	C ₉ H ₁₂ O ₂
155.0703	1.7	286.1762		4	C ₈ H ₁₀ O ₃
155.1067	24.5			3	C ₉ H ₁₄ O ₂
157.086	2.7		270.1813	3	C ₈ H ₁₂ O ₃
165.091	35.1			5	C ₁₀ H ₁₂ O ₂
167.1066	100.0	298.2125		4	C ₁₀ H ₁₄ O ₂
169.0859	18.4	300.1918		4	C ₉ H ₁₂ O ₃
169.1223	9.0		282.2176	3	C ₁₀ H ₁₆ O ₂
171.1016	6.6	302.2074	284.1969	3	C ₉ H ₁₄ O ₃
183.1015	40.5	314.2074		4	C ₁₀ H ₁₄ O ₃
185.0808	2.7	316.1867		4	C ₉ H ₁₂ O ₄
185.1172	42.6	316.223	298.2125	3	C ₁₀ H ₁₆ O ₃
187.0965	6.3		300.1918	3	C ₉ H ₁₄ O ₄
189.1121	1.3		302.2074	2	C ₉ H ₁₆ O ₄
199.0965	4.6	330.2023	312.1918	4	C ₁₀ H ₁₄ O ₄
201.1121	34.8		314.2074	3	C ₁₀ H ₁₆ O ₄
217.1071	1.1		330.2024	3	C ₁₀ H ₁₆ O ₅
[M+Na]⁺					
		[M+GT] ⁺ (109.1239)	[M+GT- H ₂ O] ⁺ (91.1134)		
207.0991	16.6	316.223	298.2125	3	C ₁₀ H ₁₆ O ₃
209.0574	2.5			8	C ₁₂ H ₁₀ O ₂
209.0784	4.0		300.1918	3	C ₉ H ₁₄ O ₄
223.0731	30.3			8	C ₁₃ H ₁₂ O ₂
223.094	48.6		314.2074	3	C ₁₀ H ₁₆ O ₄
225.0523	11.4			8	C ₁₂ H ₁₀ O ₃
225.1097	1.5		316.223	2	C ₁₀ H ₁₈ O ₄
227.068	1.7			7	C ₁₂ H ₁₂ O ₃
239.068	90.5			8	C ₁₃ H ₁₂ O ₃
239.089	2.2		330.2023	3	C ₁₀ H ₁₆ O ₅

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