

Supporting Information: Boiling of catechol secondary organic aerosol when heated to mild temperatures (36-52 °C) due to carbon dioxide formation and high viscosity

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S1 Relevant chemical structures

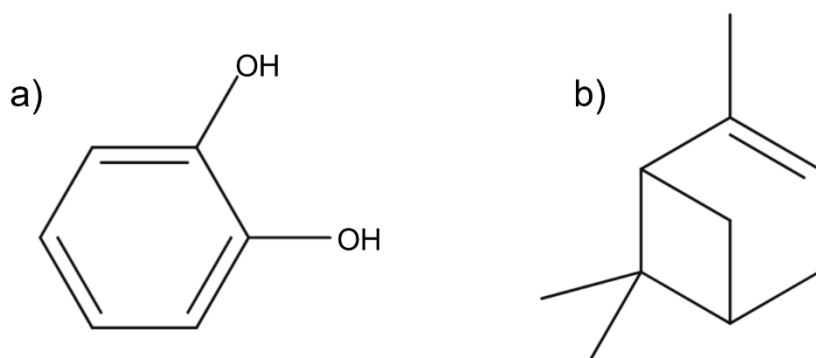


Figure S1. Chemical structures of (a) catechol and (b) α -pinene.

S2 Schematic of imaging experiments

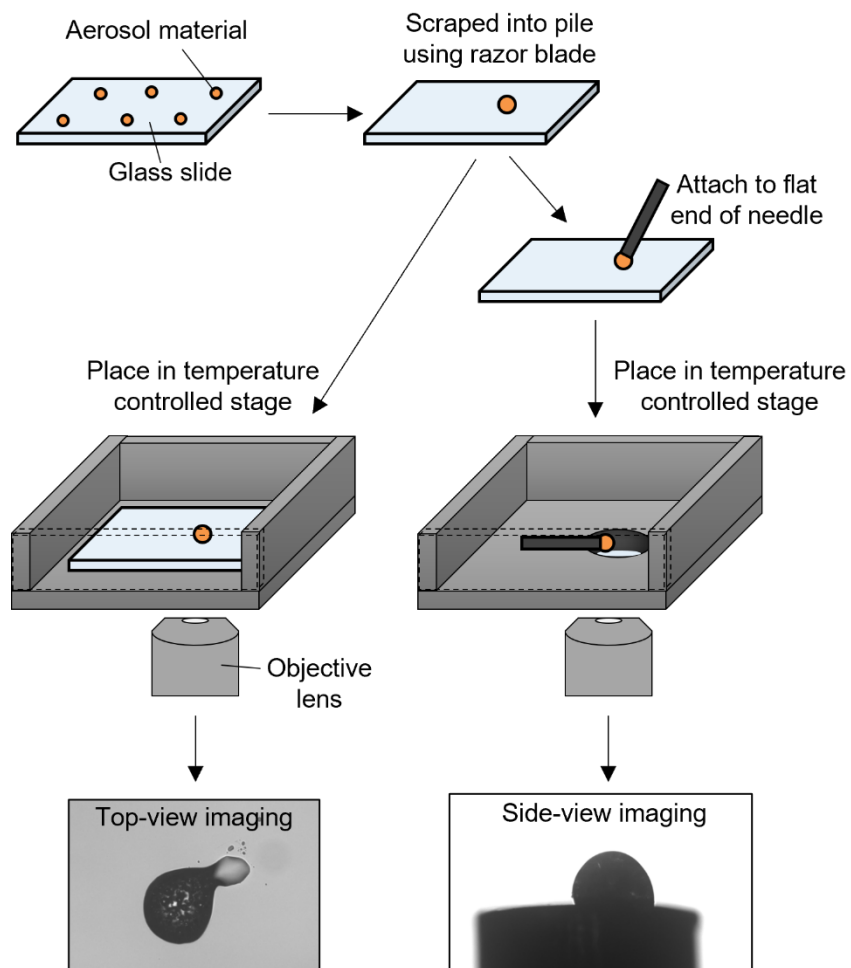


Figure S2. Schematic of the different types of sample preparation for particle imaging. Aerosol material was collected from the environmental chamber onto a glass slide using a multi-orifice single-stage impactor. The material was then scraped into a pile using a razor blade. For top-view imaging, the glass slide was directly placed into the temperature-controlled cell, which was mounted above a microscope. For side-view imaging, the material was attached to the flat end of a needle, which was then placed into the temperature-controlled cell.

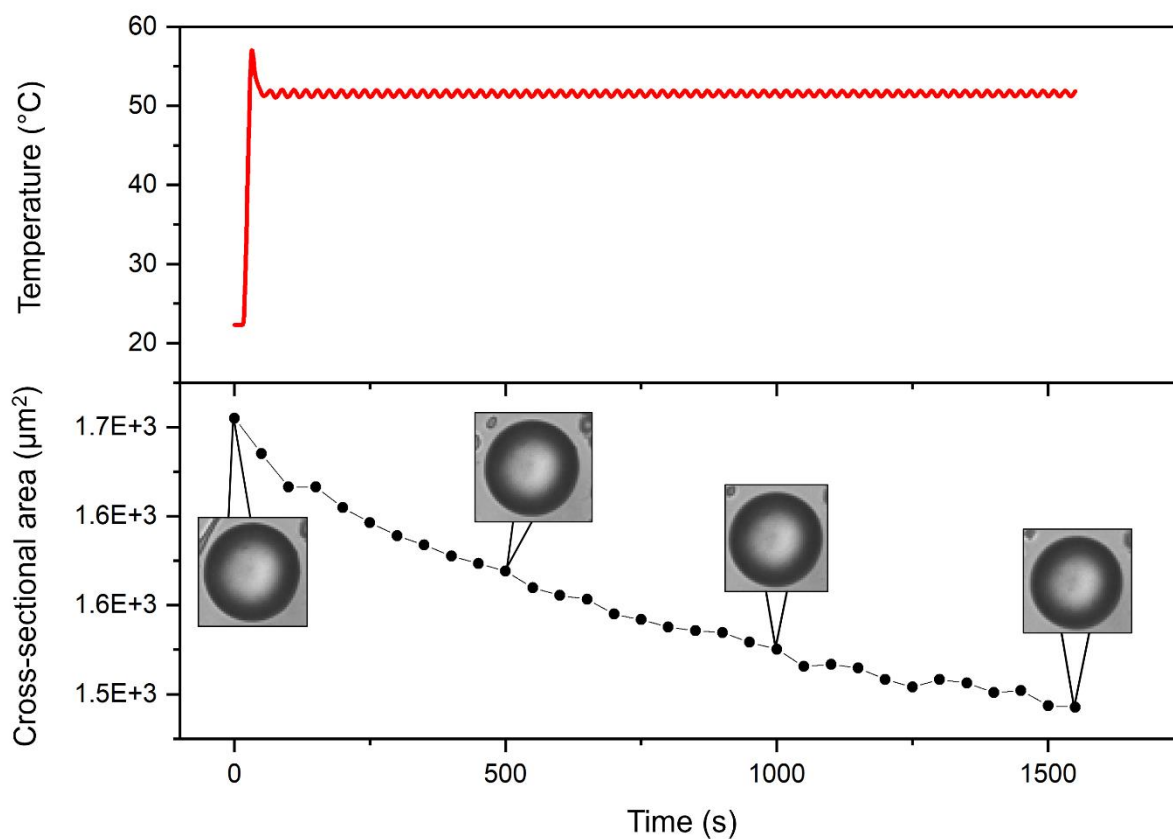


Figure S3. Imaging results from heating experiments with α -pinene SOA. The top panel shows the temperature profile during heating ($T = 52\text{ }^{\circ}\text{C}$). Corresponding cross-sectional areas of the α -pinene SOA particle (bottom panel) are shown. Top-view images of the particle on a hydrophobic glass slide are provided alongside the data. During heating, the cross-sectional area decreased by $\sim 10\%$. The particle shown here has a diameter of $\sim 50\text{ }\mu\text{m}$. Note, α -pinene SOA was too liquid-like (i.e., low viscosity) to scrape into a pile using a razor blade.

S3 PTR-MS flow cell background and correlation of C_3H_7O and $C_3H_9O_2^+$

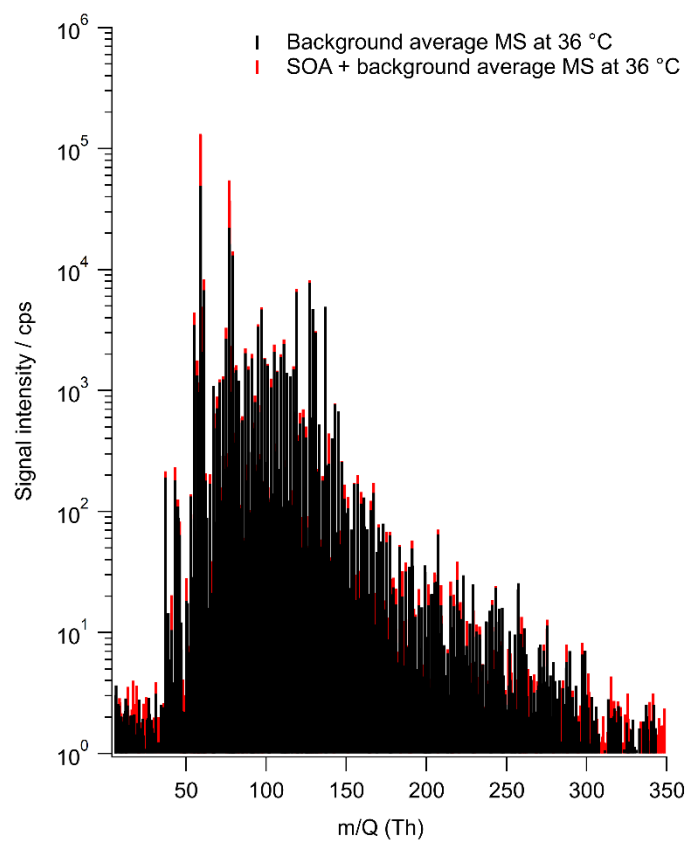


Figure S4. PTR-MS results for SOA samples heated to 36 °C. For clarity, only peaks up to m/Q 350 are shown, as peaks outside of the range were very small in comparison.

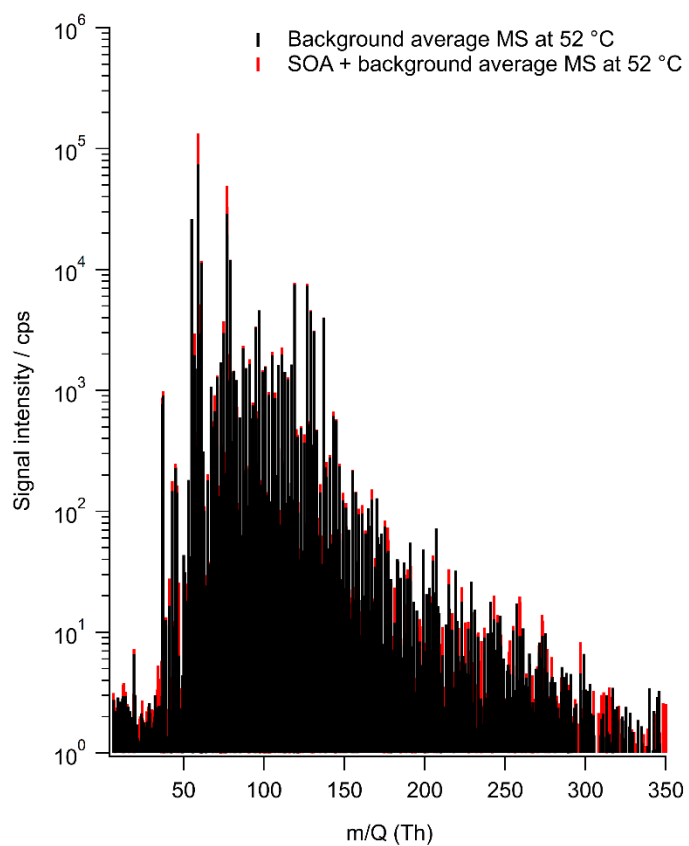


Figure S5. PTR-MS results for SOA samples heated to 52 °C. For clarity, only peaks up to m/Q 350 are shown, as peaks outside of the range were very small in comparison.

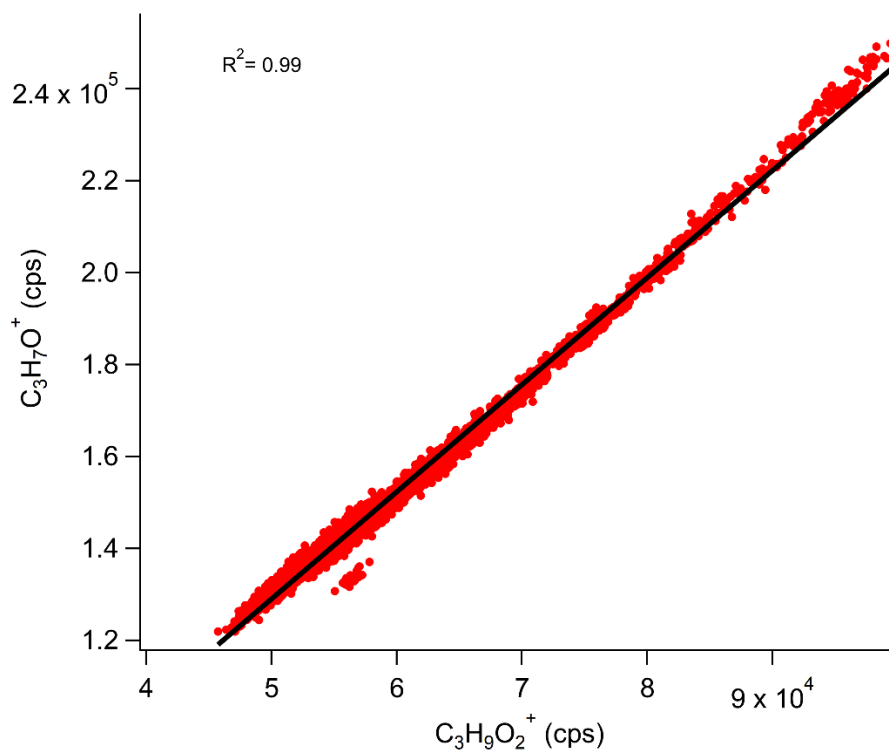


Figure S6. Scatter plot of $C_3H_7O^+$, likely acetone, and $C_3H_9O_2^+$, likely acetone-water cluster. The correlation plot has an R^2 of 0.99 suggesting that the two signals are strongly correlated in source.

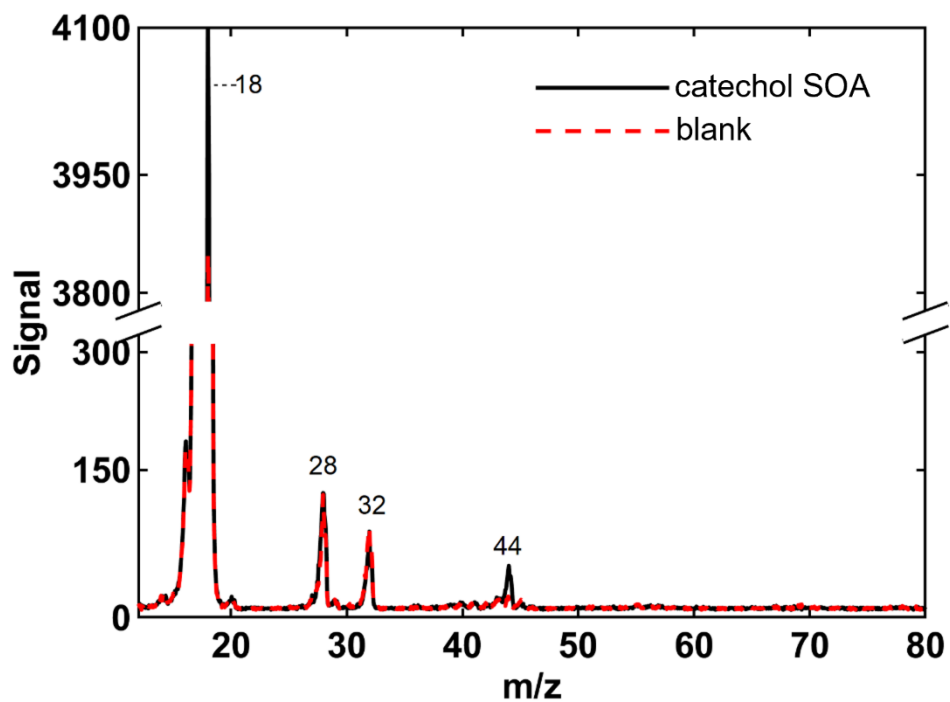


Figure S7. EI mass spectra collected from the heating of catechol SOA (solid black) and blank (dashed red) samples. The peaks at m/z 18, 28, 32, and 44 are assigned to water, nitrogen, oxygen, and carbon dioxide, respectively. The range m/z 80-250 is omitted because no peaks were identified.

The most intense peaks from the UHPLC-HESI-HRMS experiments are summarized in Table S1. Two relatively large peaks in the unheated samples were at m/z 171.0663 (corresponding to neutral formula $C_8H_{12}O_4$) and 185.0820 (corresponding to neutral formula $C_9H_{14}O_4$). These peaks were assigned to terpenylic acid and pinic acid, respectively, which are α -pinene ozonolysis oxidation products and likely due to cross-contamination from α -pinene SOA generated in the same environmental chamber prior to generating catechol SOA. These peaks increased in relative intensity when the sample was heated to 52 °C, and we interpret this as a result of higher thermal stability of the α -pinene SOA compounds compared to the catechol SOA compounds (Fig. S8).

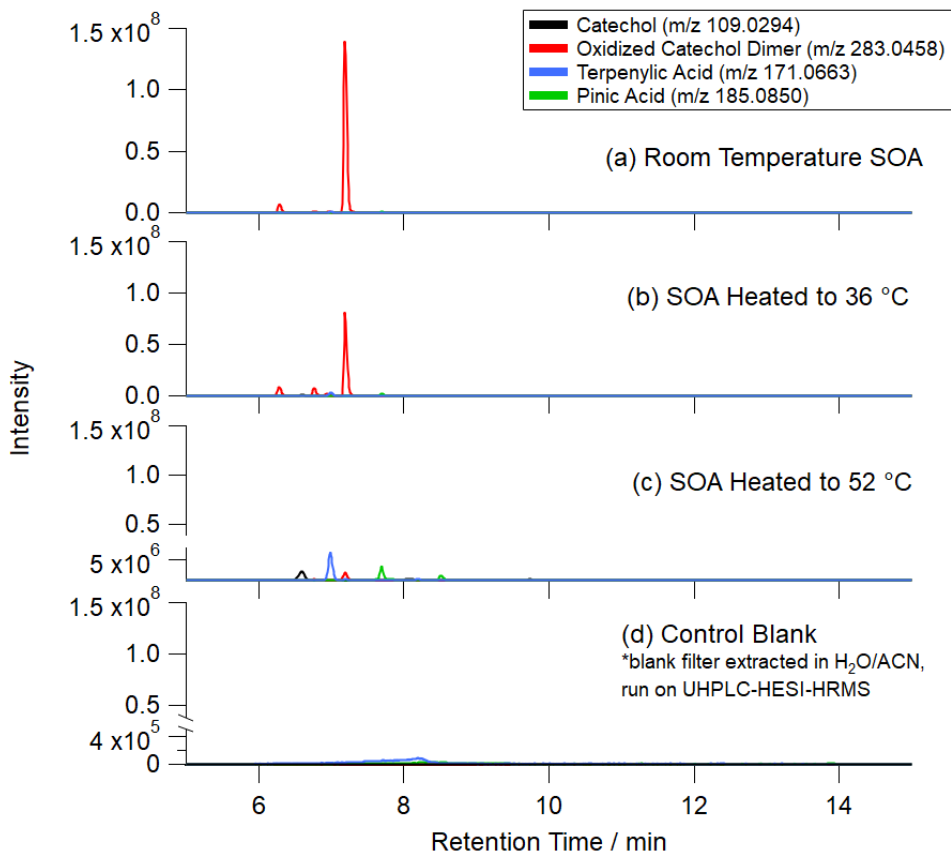


Figure S8. UHPLC-HESI-HRMS extracted ion chromatograms corresponding to catechol (black trace), oxidized catechol dimer (red trace), terpenylic acid (blue trace), and pinic acid (green trace) for room temperature SOA (a), SOA heated to 36 °C (b), SOA heated to 52 °C (c), and a control blank (d). The control blank represents a blank filter that was extracted in H₂O/ACN (1:1 v/v) and run on UHPLC-HESI-HRMS during the same sequence as the SOA samples. Terpenylic acid and pinic acid (monoterpene oxidation products) contamination peaks were not present in the control blank, but are present in the catechol ozonolysis SOA samples due to carryover from previous chamber experiments. The split axis in panel (c) demonstrates the decline of the oxidized catechol dimer peak and the enhancement of the contamination peaks. Note the split axis in panel (d) was used to further illustrate the lack of presence of these contamination species in the control blank.

For the samples heated to 52 °C, the mass spectra also showed many $C_{15}H_{24}O_x$ compounds, which can be assigned to sesquiterpene oxidation products. These compounds could theoretically be forming from catechol SOA degradation reactions, but more likely the collected SOA was also contaminated with sesquiterpene products. Sesquiterpene SOA was also generated in the same environmental chamber prior to generating catechol SOA.

Table S1. Summary of the most intense peaks from the mass spectra in Figure 1. Peaks that are repeated amongst catechol SOA at different temperatures are presented in bold font.

Catechol + O ₃ SOA	Major observed <i>m/z</i>	Major calculated <i>m/z</i>	Chemical formula of neutral species	Percent Normalized Intensity (%)	Possible assignments
Room Temperature	109.0294	109.0295	C₆H₆O₂	6	Catechol
	135.0451	135.0452	C ₈ H ₈ O ₂	4	
	141.0193	141.0193	C ₆ H ₆ O ₄	9	
	151.0764	151.0765	C ₉ H ₁₂ O ₂	10	
	171.0663	171.0663	C₈H₁₂O₄	15	Terpenylic acid*
	177.0556	177.0557	C ₁₀ H ₁₀ O ₃	14	
	185.0820	185.0819	C₉H₁₄O₄	10	Pinic acid*
	195.0663	195.0663	C ₁₀ H ₁₂ O ₄	8	
	221.0454	221.0455	C ₁₁ H ₁₀ O ₅	26	
	239.0561	239.0561	C ₁₁ H ₁₂ O ₆	10	
	283.0458	283.0459	C₁₂H₁₂O₈	100	Oxidized catechol dimer
	305.0278	-	-	5	
	382.9711	-	-	5	
Heated 36 °C	109.0294	109.0295	C₆H₆O₂	5	Catechol
	141.0193	141.0193	C ₆ H ₆ O ₄	13	
	151.0764	151.0765	C ₉ H ₁₂ O ₂	10	
	171.0663	171.0663	C₈H₁₂O₄	13	Terpenylic acid*
	177.0557	177.0557	C ₁₀ H ₁₀ O ₃	18	
	179.0351	179.0350	C ₉ H ₈ O ₄	5	
	185.0820	185.0819	C₉H₁₄O₄	13	Pinic acid*
	195.0662	195.0663	C ₁₀ H ₁₂ O ₄	8	
	221.0454	221.0455	C ₁₁ H ₁₀ O ₅	31	
	239.0561	239.0561	C ₁₁ H ₁₂ O ₆	10	
	283.0457	283.0459	C₁₂H₁₂O₈	100	Oxidized catechol dimer
	299.0408	299.0409	C ₁₂ H ₁₂ O ₉	14	
	305.0275	-	-	7	
	319.0826	319.0823	C ₁₆ H ₁₆ O ₇	6	
	355.1035	355.1035	C ₁₆ H ₂₀ O ₉	4	
Heated 52 °C	109.0294	109.0295	C₆H₆O₂	19	Catechol
	171.0663	171.0663	C₈H₁₂O₄	51	Terpenylic acid*
	185.0820	185.0819	C₉H₁₄O₄	38	Pinic acid*
	251.1653	251.1653	C ₁₅ H ₂₄ O ₃	57	—*
	253.1447	253.1445	C ₁₄ H ₂₂ O ₄	47	
	267.1603	267.1602	C ₁₅ H ₂₄ O ₄	42	—*
	283.1551	283.1551	C ₁₅ H ₂₄ O ₅	16	
	293.1759	293.1758	C ₁₇ H ₂₆ O ₄	100	
	297.1531	-	-	38	
	299.1499	299.1500	C ₁₅ H ₂₄ O ₆	40	—*

* Possible sesquiterpene contamination.

S6 Supplemental Video Descriptions

Video S1. Imaging of catechol SOA during a temperature ramp experiment (corresponding to Fig. 1 in the main text). The particle was attached to a needle to capture side-view images. The initial area-equivalent diameter of the particle (at $t = 0$) was $132\ \mu\text{m}$, which grew to a maximum of $259\ \mu\text{m}$ at $1725\ \text{s}$. Note that the temperature values in the video haven't been corrected for the offset of the temperature-controlled cell, so the actual temperatures are $\sim 0\text{--}5\ ^\circ\text{C}$ higher than shown here. The correct temperatures are shown in Fig. 1.

Video S2. Imaging of catechol SOA during heating to $36\ ^\circ\text{C}$ (corresponding to Fig. 2 in the main text). The particle was attached to a needle to capture side-view images. The initial area-equivalent diameter of the particle (at $t = 0$) was $\sim 150\ \mu\text{m}$. Note that the temperature values in the video haven't been corrected for the offset of the temperature-controlled cell, so the actual temperatures are $\sim 1\ ^\circ\text{C}$ higher than shown here. The correct temperatures are shown in Fig. 2.

Video S3. Imaging of catechol SOA during heating to $52\ ^\circ\text{C}$ (corresponding to Fig. 3 in the main text). The particle was placed on a hydrophobic glass slide to capture top-view images. The initial area-equivalent diameter of the particle (at $t = 0$) was $\sim 150\ \mu\text{m}$. Note that the temperatures in the video haven't been corrected for the offset of the temperature-controlled cell, so the actual temperatures are $\sim 2\ ^\circ\text{C}$ higher than shown here. The correct temperatures are shown in Fig. 3.

References

Zhao, Z., Yang, X., Lee, J., Tolentino, R., Mayorga, R., Zhang, W. and Zhang, H.: Diverse Reactions in Highly Functionalized Organic Aerosols during Thermal Desorption, *ACS Earth Sp. Chem.*, 4(2), 283–296, doi:10.1021/acsearthspacechem.9b00312, 2020.