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Supplement of

A model framework to retrieve thermodynamic and kinetic properties of organic aerosol from composition-resolved thermal desorption measurements

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Consideration of a refractive core in Eqs. (15) and (16)

Eqs. (15) and (16) are used to calculate the particle diameter D_P and organic fraction remaining Φ as a function of time t . For the secondary organic aerosol (SOA) formation experiments used in our study, size-selected effloresced ammonium sulfate seed particles (diameter $D_{P,c} = 50$ nm) were used. For simplicity, we assumed this seed material to form a refractive (non-
 5 evaporating) core in each SOA particle (typical diameter D_P of 200 nm). This core is taken into account through modifications of Eq. (15),

$$D_P(t) = \sqrt[3]{\frac{6}{\pi} \left(\frac{m_i}{\rho} (N_i(t) + N_{i,g}(t)) + \frac{\bar{m}}{\rho} (N_R(t) + N_{R,g}(t)) + \frac{m_c}{\rho_c} N_c \right)} \quad (S1)$$

and Eq. (16),

$$\Phi(t) = \frac{D_P(t)^3 - D_{P,c}^3}{D_{P,0}^3 - D_{P,c}^3} \quad (S2)$$

15 The density of the core material ρ_c and its molecular mass m_c are usually assumed to be different from the organic material. In this study, we used the bulk density of ammonium sulfate $\rho_c = 1770$ kg m⁻³ and for the organic fraction $\rho = 1200$ kg m⁻³, for a lack of better knowledge. The number of molecules in the core N_c results from knowing m_c , ρ_c and $D_{P,c}$. Note that the core material is, by default, neither modeled to evaporate nor to interact with the organic material.

Evaporation of a single compound, including oligomerization: 8 differential equations to be solved

15 As described in section 3, the core of the model consists of solving a set of differential equations. For the simple case of simulating evaporation of a single compound, but including the oligomerization terms, these are the following 8 differential equations.

$$\frac{dN_i}{dt} = -\frac{1}{\sqrt{2\pi \cdot k_B \cdot m_i \cdot T}} \cdot SA \cdot \alpha \cdot \Gamma \cdot P_i^* \cdot \chi_i + k_d^i \cdot N_{i,g} - k_g^i \cdot N_i \cdot \Phi \quad (S3)$$

$$\frac{dN_{i,g}}{dt} = k_g^i \cdot N_i - k_d^i \cdot N_{i,g} \quad (S4)$$

$$20 \quad \frac{dk_d^i}{dt} = k_d^i \cdot \frac{dT}{dt} \cdot \frac{E_{i,d}}{RT^2} \quad (S5)$$

$$\frac{dk_g^i}{dt} = k_g^i \cdot \frac{dT}{dt} \cdot \frac{E_{i,g}}{RT^2} \quad (S6)$$

$$\frac{dT}{dt} = R_T \quad (S7)$$

$$\frac{dC_i^*}{dt} = C_i^* \cdot \frac{dT}{dt} \cdot \frac{\Delta H}{RT^2} \quad (S8)$$

$$\frac{dN_{i,w}}{dt} = -\frac{dN_i}{dt} - \frac{dN_g}{dt} - k_{i,w,off} \cdot N_{i,w} \quad (S9)$$

$$25 \quad \frac{dk_{i,w,off}}{dt} = \frac{1}{\tau_{C_w}} \cdot \frac{dC_i^*}{dt} \quad (S10)$$

Description of variables (alphabetically; see main text for more details):

- C_i^* ... saturation concentration for composition i [$\mu\text{g m}^{-3}$]
- E_d ... activation energy for dissociation reaction [kJ mol^{-1}]
- 5 E_g ... activation energy for gluing reaction [kJ mol^{-1}]
- k_B ... Boltzmann constant ($1.38 \times 10^{23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1} = 1.38 \times 10^{23} \text{ J K}^{-1}$)
- k_d^i ... dissociation rate constant for composition i [s^{-1}]
- k_g^i ... “gluing” rate constant for composition i [s^{-1}]
- $k_{i,w,off}$... rate constant for evaporation off the wall/filter surfaces [s^{-1}]
- 10 m_i ... molecular mass of composition i [kg]
- N_i ... number of molecules of composition i in the particle in “free” form
- $N_{i,g}$... number of molecules of composition i in the particle in low-volatility (“glued”) form
- $N_{i,w}$... number of molecules of composition i on wall/filter surfaces
- P_i^* ... saturation vapor pressure for composition i [Pa] (calculated from C_i^*)
- 15 R ... universal gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$)
- R_T ... desorption temperature ramp rate, typically 0.14 K s^{-1} until $T = 200 \text{ }^\circ\text{C}$, then zero
- SA ... particle surface area [m^2]
- T ... desorption temperature [K]
- t ... time [s]
- 20 α ... evaporation coefficient ($0 < \alpha \leq 1$)
- Γ ... gas-phase diffusion limitation factor ($0 < \Gamma < 1$)
- ΔH ... enthalpy of vaporization or sublimation [kJ mol^{-1}]
- τC_w ... wall interaction parameter, here $8.77 \text{ mg m}^{-3} \text{ s}$
- Φ ... organic fraction remaining in the particle ($0 < \Phi \leq 1$)
- 25 χ_i ... Raoult term (mass fraction of N_i , $0 < \chi_i \leq 1$)

The equations are evaluated in MATLAB’s *ode15s* solver in the order (S7), (S8), (S6), (S5), (S4), (S3), (S10), (S9). The signal measured by the mass spectrometer is assumed to be proportional to the rate of the desorption of compound i from the wall/filter surfaces: $k_{i,w,off} N_{i,w}$.

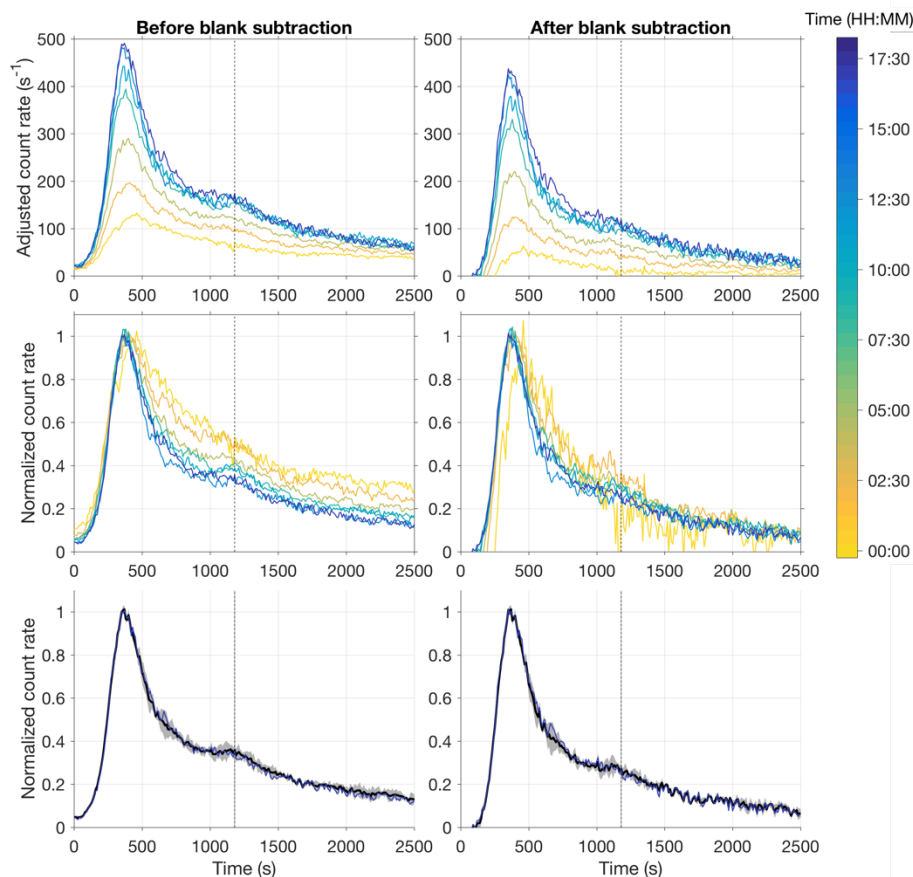
- 30 The model is able to explicitly model more than one compound i simultaneously, in which case Eqs. (S3) to (S6) and (S8) to (S10) are solved for each compound. I.e., the number of differential equations to be solved for n compounds is $1+7n$. Note that for reproducing the thermogram of a single evaporating compound i as it evaporates from SOA, Φ is typically calculated as per Eq. (15), i.e. we summarize all organic compounds other than compound i and also simulate the evaporation of that bulk. In that case, $n = 2$.

The model currently holds the option of including a 2nd low-volatility state, either formed from “glued” or from “free” molecules, but decomposing into the same compound i . With either of these options, the number of differential equations increases to $1+9n$.

Eq. (11), here Eq. (S3), derives from Eq. (10a) and includes a simplification regarding the oligomerization (“gluing”) reaction, as described in the main text. Without that simplification, K_g^{ij} (size $n \times n$, symmetric) replaces k_g^i (size n), and the number of differential equations is $1+6.5n+0.5n^2$ or $1+8.5n+0.5n^2$.

Reproducibility and stability of thermograms during SOA experiments

For our main test case, the thermogram for composition $C_8H_{12}O_5$ (Figs. 9-11) during α -pinene dark ozonolysis, we present here the time evolution of this thermogram as measured leading up to the condition of steady state in the chamber (Fig. S1).
10 In particular after blank measurements are subtracted (right-hand panels), the thermogram shape become stable with time even as concentrations are still noticeably increasing (center right). The thermograms are remarkably reproducible, in particular also for the blank-corrected thermograms, which are subject to the additional variation between the blank measurements. As illustrated by the bottom panels, an average normalized thermograms from the final three measurements (i.e., closest to steady-state conditions) are practically indistinguishable from the final measurement, which is the
15 thermogram used in the thorough analysis in section 5.1 (Figs. 9-11).



5 **Figure S1:** The seven thermograms for composition $C_8H_{12}O_5$ leading up to the thermogram used in this work (section 5.1, Figs. 9-11), which is included in the darkest blue and representing steady-state conditions for dark α -pinene ozonolysis ($[O_3] = 84$ ppbv, $[\alpha\text{-pinene reacted}] = 6.7$ ppbv). The color scheme represents time at which the sample was taken from the chamber. Desorption starts at 0 s. The vertical dashed lines at ca. 1200 s mark the time when a desorption temperature of 200 °C has been reached and is subsequently maintained. (Data are shown only until 2500 s since the start of desorption to show more clearly the time during the temperature ramp (25 to 200 °C), which contains most information.) The top left-hand panel shows count rates adjusted for reagent ion concentration and volume of sampled chamber air; the top right-hand panel is additionally corrected for background signal as determined by blank measurements. In the center panels, the data are normalized to 1 for comparing thermogram shapes. The bottom panels reproduce the final thermogram (dark blue line) and also shows the mean of the final three thermograms (black bold line) plus standard deviation (gray shades).

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