Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Electronic Supplementary Information for

Is Secondary Organic Aerosol Yield Governed by Kinetic Factors Rather Than Equilibrium Partitioning?

Chen Wang[1], Frank Wania[1], and Kai-Uwe Goss[2,3*]

[1]Department of Physical and Environmental Sciences and Department of Chemistry, University of Toronto Scarborough, 1265 Military Trail, Toronto, ON, M1C 1A4, Canada

[2]Department of Analytical Environmental Chemistry, Centre for Environmental Research UFZ Leipzig-Halle, Permoserstraße 15, Leipzig, D-04318, Germany

[3]Institute of Chemistry, University of Halle-Wittenberg, Kurt-Mothes-Straße 2, Halle, D-06120, Germany

[*]Corresponding author: kai-uwe.goss@ufz.de, ++49 341 235 1411

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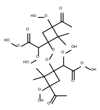
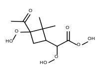
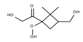
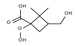
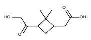
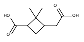
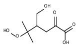
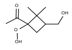
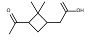
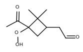
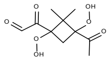
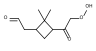
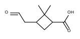
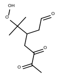
Description of the method

The method is based on and modified from (Wang et al., 2015). The calculation is for 60% relative humidity and 25°C. SOA is assumed to be formed from the equilibrium gas-particle partitioning of 15 organic products of the ozonolysis of α-pinene (Table S1) into a liquid-like particle without consideration of condensed phase viscosity or reaction.

Table S1 Oxidation products and corresponding yields for the ozonolysis of α-pinene. List of species and yield is the same as that in scenario 1 by (Wang et al., 2015), with C20H30O18 as an extremely low volatile organic compound (ELVOC) and the rest as semi-volatile organic compounds (SVOCs).

Name	Structure	molar yield	molar mass	Name	Structure	molar yield	molar mass
C20H30O18		0.0304	558	C10H16O8		0.0304	264
C921OOH		0.0244	204	C812OOH		0.0213	190
HOPINONIC		0.0150	200	PINIC		0.0333	186
C813OOH		0.0083	206	C97OOH		0.1150	188
PINONIC		0.1401	184	C811OH		0.0137	158
C107OOH		0.2385	200	C10H14O7		0.0304	246
C109OOH		0.0193	200	C89CO2H		0.0600	170
C108OOH		0.0731	216				

Note the compounds' name, structure and corresponding stoichiometric yields were derived from Master Chemical Mechanism chamber simulations (Shilling et al., 2009) with additional three compounds proposed by (Wang et al., 2015) based on the results in (Ehn et al., 2014).

The condensed phase is assumed to separate into an organic-enriched phase and an aqueous-electrolyte enriched phase. The density of organic and aqueous phase is assumed to be 1.2 and 1 g/mL, respectively. We assume the atmosphere initially contains an organic seed of 0.5 µg of C20H20O18 (the compound with the lowest vapor pressure among all of the products, Figure S1). A fixed aqueous phase volume is determined by the amount of ammonium sulfate. This is calculated at 60% RH and 2.64 µg/m^3 ammonium sulfate using AIOMFAC (Zuend et al., 2008; Zuend and Seinfeld, 2012). We account for the influence of inorganic salts on gas-particle partitioning (salting-out effect) and also the partitioning of water into the organic phase. Water in the organic phase is calculated from the gas-organic phase partitioning and the relative humidity. The quantum chemistry program COSMOtherm (Version C30_1401 with BP_TZVP_C30_1401 parametrization, COSMOlogic, GmbH & Co. KG, Leverkusen, Germany, 2014) (Klamt, 2005; Klamt and Eckert, 2000) was used to calculate partitioning coefficients among the three phases as well as the salting-out effects using methods described previously (Wang et al., 2015; Wang et al., 2014; Wania et al., 2014).

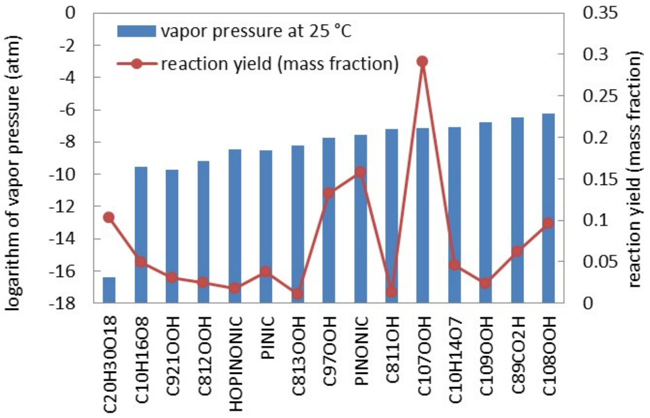


Figure S1 Vapor pressure (COSMOtherm prediction at 25 °C) and reaction yield (normalized in mass fractions) for each organic product

The mass of organic compounds in the aqueous phase is much lower than in the organic phase, which increases in the first 60 iterations and starts to decrease slightly from that on. Overall, the aqueous phase composition is relatively stable and the major organic components are C812OOH, PINIC and C813OOH (Figure S2).

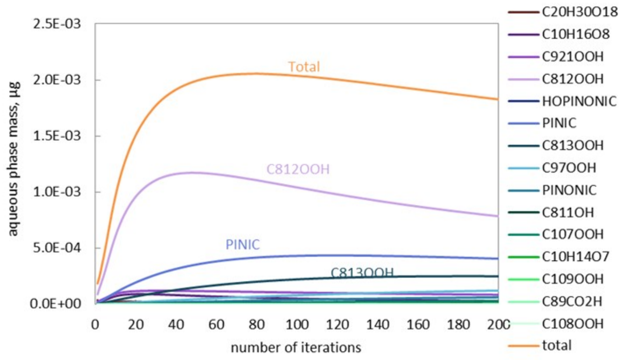


Figure S2 Aqueous phase mass and composition change (water and salt not included)

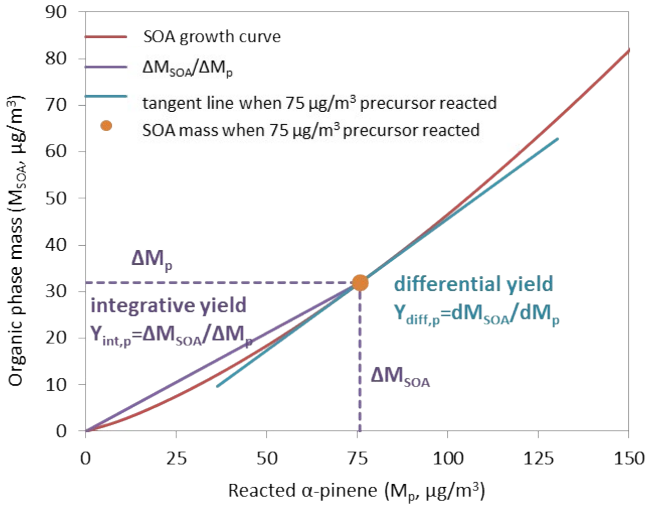


Figure S3 Total SOA organic phase mass as a function of reacted amount of α-pinene

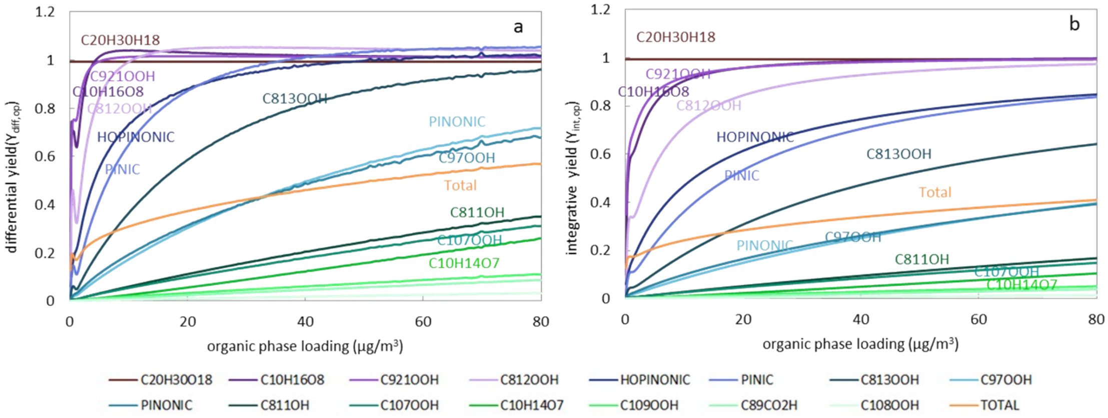


Figure S4 The differential yield and integrative yield versus organic phase loading

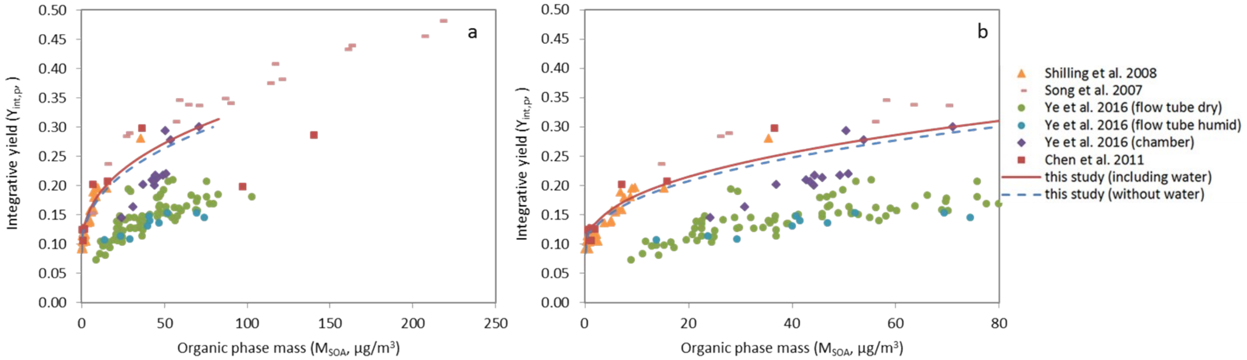


Figure S5 Comparison of SOA integrative yield between this study and laboratory studies. Panel a shows organic phase mass: 0-250 μg/m³. Panel b shows organic phase mass: 0-80 μg/m³

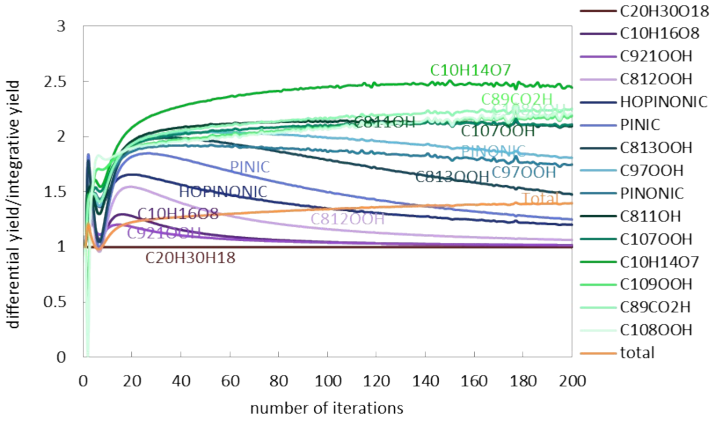


Figure S6 The ratio between differential yield and integrative yield

Partitioning coefficient of one organic compound between organic and gas phase ($K_{org/gas}$ in unit of m^3 gas per m^3 organic phase) is defined as the ratio of equilibrium organic phase concentration and the equilibrium gas phase concentration. $K_{org/gas}$s are relatively stable during the iterations (change of $\log K_{org/gas}$ is mostly less than one order of magnitude), with only some fluctuation during the first few iterations. This is different from the dramatic change of the phase composition.

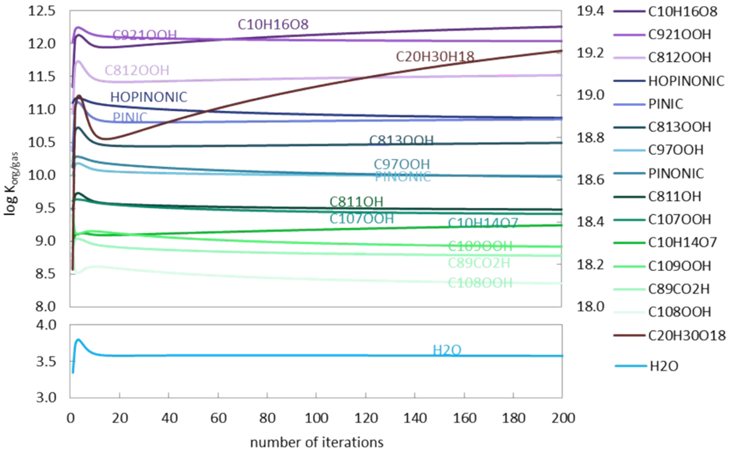


Figure S7 Logarithm of organic-gas phase partitioning coefficient ($\log K_{org/gas}$) at different iterations. $\log K_{org/gas}$ for C20H20O18 is shown on the second Y-axis.

Calculation of activity coefficients in organic phase

The gas-particle (or organic matter) partitioning coefficients defined by Pankow (1994) is:

$$K_{org,i}' = R \cdot T / (10^6 \cdot \gamma_i \cdot p_{L,i}^* \cdot M_{org}) \qquad (1)$$

where R is gas constant ($m^3\,Pa\,K^{-1}\,mol^{-1}$), T is temperature (K), M_{org} is the average molecular weight of the absorbing organics (g/mol), $p_{L,i}^*$ is the saturation vapour pressure of i in its pure liquid state (Pa) and γ_i is the activity coefficient of species i in the organic phase. $K_{org,i}'$ is in unit of m^3 (air) /μg (absorbing organics). $K_{org,i}'$ can be converted to $K_{org/gas}$ (in unit of m^3 (air) / m^3 (absorbing organics)) by assuming a density of the absorbing organic of 1.2 g/cm^3.

With eq (1), we can calculate the activity coefficient γ_i of each compound in the organic phase by assuming M_{org} is 200 g/mol, or using the actual organic phase average molar weight (Figure S8).

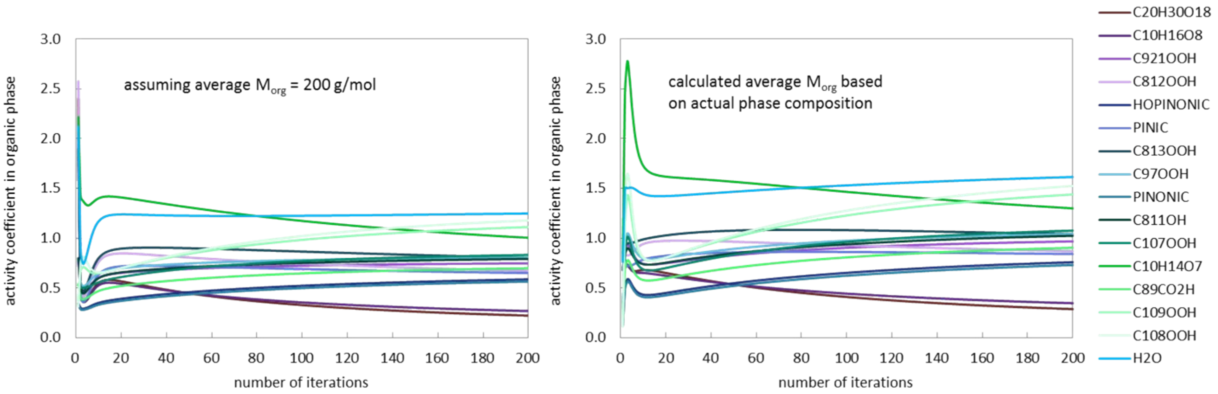


Figure S8 Activity coefficients for each component in the organic phase.

The calculated activity coefficients are smaller than 1 for most of the compounds, expect for H_2O and C10H14O7. This means SOA mass would be underestimated by assuming activity coefficient of one for these compounds in SOA. There is a decrease of activity coefficient for C20H30O18, C10H16O8, C10H14O7, C812OOH, C813OOH and PINIC with more iterations, indicating that the phase composition becomes more favorable.

O:C and H:C ratios of the organic phase are calculated for SOA at different loadings and iterations (Figure S9). O:C is higher at lower loadings while H:C is the opposite. O:C decreases from 0.90 at the beginning (C20H30O18) to 0.56 at loading of 80 μg/m^3 (see phase composition in Figure 2b).

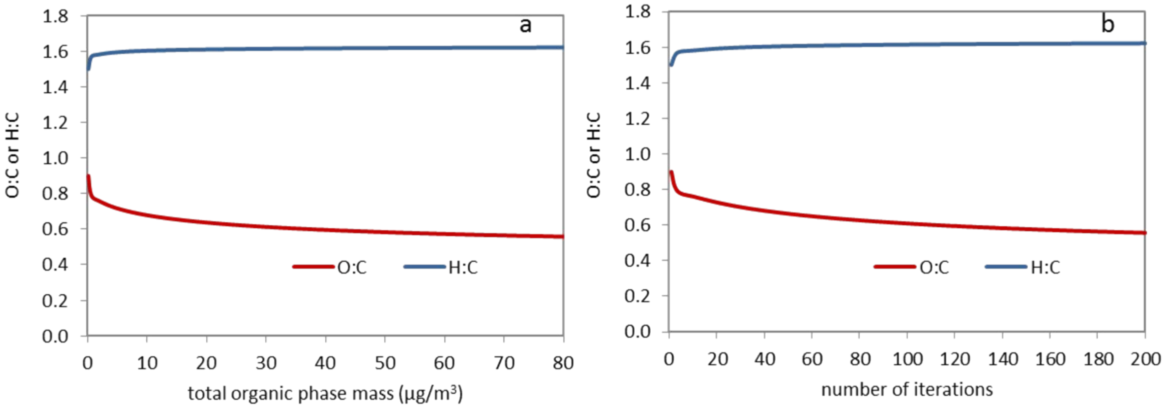


Figure S9 O:C and H:C ratios in aerosol organic phase

Contribution of water in the organic phase

Other than the organic compounds, water is another important component in the organic phase, contributing an average of 4-5% of the mass in the organic phase (Figure 2b). Water uptake in reality is more complicated (Jathar et al., 2016; Pajunoja et al., 2015). In this study, equilibrium partitioning of water between gas and organic phase is the only pathway for water uptake by organics. In the first few iterations, water mass fraction in the organic phase is relatively higher due to higher organic-gas partitioning coefficients (Figure S7). The decrease of water fraction agrees with the trend of decreasing O:C ratio (Figure S9) at the beginning. This is reasonable because a higher O:C ratio suggests a higher polarity and larger ability to take up water.

Comparison with Wang et al. (2015)

The composition and mass in this study at the 100th iteration are compared for the scenario in (Wang et al., 2015) when 100 μg of α-pinene oxidation products partition to form SOA. The mass and composition in both organic phase and aqueous phase are very similar in the two scenarios when the total amount of added oxidation products is the same. Most organic compounds are in the organic phase, in agreement with previous studies for α-pinene ozonolysis products (Mouchel-Vallon et al., 2013; Wang et al., 2015; Zuend and Seinfeld, 2012). The small fraction in aqueous phase is due to the low water solubility of these oxidation products and salting out effect of ammonium sulfate in the aqueous phase, as well as the small liquid water content. In the organic phase, compounds with higher partitioning coefficients and usually lower vapor pressure (See Figure S1 and S7 in supporting information) are the dominant components. Water contributes around 5% of the mass in the organic phase. Organic compounds contribute only little to the aqueous phase, whose composition is also similar in the two scenarios. Major organic component in the aqueous phases are C812OOH, PINIC, and C813OOH.

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