

# Calculating Equilibrium Phase Distribution during the Formation of Secondary Organic Aerosol Using COSMOtherm

Chen Wang,<sup>†</sup> Kai-Uwe Goss,<sup>‡,§</sup> Ying Duan Lei,<sup>†</sup> Jonathan P. D. Abbatt,<sup>†</sup> and Frank Wania<sup>\*,†</sup>

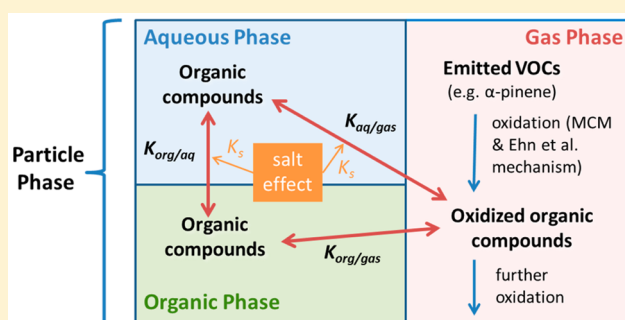
<sup>†</sup>Department of Physical and Environmental Sciences and Department of Chemistry, University of Toronto Scarborough, 1265 Military Trail, Toronto, ON, M1C 1A4, Canada

<sup>‡</sup>Department of Analytical Environmental Chemistry, Centre for Environmental Research UFZ Leipzig-Halle, Permoserstraße 15, Leipzig D-04318, Germany

<sup>§</sup>Institute of Chemistry, University of Halle-Wittenberg, Kurt-Mothes-Straße 2, Halle D-06120, Germany

## S Supporting Information

**ABSTRACT:** Challenges in the parametrization of compound distribution between the gas and particle phase contribute significantly to the uncertainty in the prediction of secondary organic aerosol (SOA) formation and are rooted in the complexity and variability of atmospheric condensed matter, which includes water, salts, and a multitude of organic oxidation products, often in two separated phases. Here, we explore the use of the commercial quantum-chemistry-based software COSMOtherm to predict equilibrium partitioning and Setchenow coefficients of a suite of oxidation products of  $\alpha$ -pinene ozonolysis in an aerosol that is assumed to separate into an organic-enriched phase and an electrolyte-enriched aqueous phase. The predicted coefficients are used to estimate the phase distribution of the organic compounds, water and ammonium sulfate, the resulting phase composition, and the SOA yield. Four scenarios that differ in terms of organic loading, liquid water content, and chemical aging are compared. The organic compounds partition preferentially to the organic phase rather than the aqueous phase for the studied aerosol scenarios, partially due to the salting-out effect. Extremely low volatile organic compounds are predicted to be the dominant species in the organic aerosols at low loadings and an important component at higher loadings. The highest concentration of oxidation products in the condensed phase is predicted for a scenario assuming the presence of non-phase-separated cloud droplets. Partitioning into an organic aerosol phase composed of the oxidation products is predicted to be similar to partitioning into a phase composed of a single organic surrogate molecule, suggesting that the calculation procedure can be simplified without major loss of accuracy. COSMOtherm is shown to produce results that are comparable to those obtained using group contribution methods. COSMOtherm is likely to have a much larger application domain than those group contribution methods because it is based on fundamental principles with little calibration.



## INTRODUCTION

Currently, different models are available to predict gas–particle partitioning during the formation of secondary organic aerosol (SOA).<sup>1</sup> The equilibrium partitioning theory first applied to atmospheric gas–particle partitioning by Pankow,<sup>2</sup> the empirical two-product model,<sup>3</sup> and the volatility basis set approach<sup>4,5</sup> are often used to model SOA yield in chamber experiments under dry conditions. Most implementations of these approaches presently used in atmospheric large-scale models ignore the presence of water and thus the potential for phase separation in the particles, i.e., the occurrence of an aqueous phase in addition to the organic aerosol phase. Ignoring the potential for organic compounds to partition to an aqueous aerosol phase and to react in that phase to form low-volatility products can be problematic when predicting aerosol mass under ambient atmospheric conditions or in chamber experiments with higher relative humidity (RH).<sup>6–8</sup> The thermodynamic molecular-based approach by Pun et al.<sup>9</sup> was

one of the first models describing SOA formation, which included partitioning into both organic and water phases based on the water affinity of the species. These methods do not always make use of specific information about chemical structure or composition of the particle phase. For example, in the volatility basis set method, organic compounds are grouped into different bins according to their volatility, which is usually predicted or measured by comparison with standard compounds with known vapor pressure.

The availability of information on the composition and structure of SOA compounds, either from chamber experiments or modeling studies, such as those based on the Master Chemical Mechanism (MCM),<sup>10</sup> have allowed for the develop-

Received: March 29, 2015

Revised: June 12, 2015

Accepted: June 16, 2015

Published: June 16, 2015

Table 1. Oxidation Products and Corresponding Yields for the Ozonolysis of  $\alpha$ -Pinene<sup>a</sup>

	name <sup>b</sup>	molar yield <sup>c</sup> (%)		name <sup>b</sup>	molar yield <sup>c</sup> (%)
Ehn 1	C20H30O18	0.0304 <sup>d</sup>	MCM 4	C811OH	0.0137
Ehn 2	C10H16O8	0.0304 <sup>d</sup>	MCM 5	C812OOH	0.0213
Ehn 3	C10H14O7	0.0304 <sup>d</sup>	MCM 6	C813OOH	0.0083
Ehn 4	C20H28O14	0.0304 <sup>e</sup>	MCM 7	C89CO2H	0.0600
Ehn 5	C13H18O10	0.0304 <sup>e</sup>	MCM 8	C921OOH	0.0244
Ehn 6	C10H14O7_aged	0.0304 <sup>e</sup>	MCM 9	C97OOH	0.1150
MCM 1	C107OOH	0.2385	MCM 10	HOPINONIC	0.0150
MCM 2	C108OOH	0.0731	MCM 11	PINIC	0.0333
MCM 3	C109OOH	0.0193	MCM 12	PINONIC	0.1401

<sup>a</sup>The 12 MCM compounds and corresponding stoichiometric yields were derived from MCM chamber simulations,<sup>18</sup> including only compounds that are likely to partition to a significant degree to the condensed phase. The 8% molar yield is evenly distributed to three Ehn et al. compounds in scenarios 1, 2 and 4 and to three different Ehn et al. compounds in scenario 3. <sup>b</sup>Names for MCM compounds were assigned by the MCM model.<sup>18</sup> For Ehn et al. compounds, the chemical formula is given, and “\_aged” is used to distinguish Ehn compound 3 and Ehn compound 6. <sup>c</sup>Stoichiometric molar yields (mole of compound formed per mole of  $\alpha$ -pinene reacted) rely on two assumptions: (i) conservation of total carbon mass from the parent hydrocarbon and (ii) products given in Table 1 of Shilling et al.<sup>18</sup> for 0.9 ppbv  $\alpha$ -pinene reacted to make up 92% of the yield, and Ehn et al. compounds make up the other 8% in equal proportions. In scenarios 1, 2, and 4, Ehn 1, 2, and 3 are assumed to be the dominant species, while in scenario 3, Ehn 4, 5, and 6 are dominant. <sup>d</sup>In scenarios 1, 2, and 4; 0 in scenario 3. <sup>e</sup>In scenario 4; otherwise 0.

ment of models that explicitly account for the chemical composition of the gas-phase oxidation products.<sup>1,11</sup> These models can provide more details on the composition, phase separation, and yield of SOA. Currently existing models, such as the group contribution methods X-UNIFAC (UNIQUAC Functional-group Activity Coefficients)<sup>12,13</sup> and AIOMFAC (Aerosol Inorganic–Organic Mixtures Functional-groups Activity Coefficients), are used to calculate activity coefficients in the particle phase. When combined with measured or estimated saturation vapor pressure, this allows for the estimation of the partitioning of organic compounds between the gas and particle phase. While in practice, activity coefficients are often assumed to be 1 in order to simplify the calculation, the assumption of ideal mixing in the condensed phase is often not appropriate.<sup>14,17</sup>

The condensed phase is usually a mixture of hydrophilic and hydrophobic organic compounds, water, and inorganic species. Partitioning of organic compounds between the gas and particle phase is influenced by the presence of large quantities of inorganic salts in the aerosol, which is known as the salt effect. As one of the major salts in the environment, ammonium sulfate, in particular, has a significant influence on the solubility of organic compounds in the aqueous phase.<sup>18,19</sup> This effect usually increases the activity of organic compounds in solutions with high salt content, i.e., leads to “salting out”, and is thus responsible for phase separation.<sup>17,20–24</sup> Nonideal mixing in the presence of inorganic salts and under different RH has indeed been shown to result in the separation of particles into a phase largely composed of organic compounds and a phase dominated by water, inorganic salts and some water-soluble organics.<sup>14</sup> Other studies showed that ammonium sulfate resulted in both salting-out and salting-in effects for alcohols and organic acids, depending on the nature and number of functional groups as well as on the salt concentration.<sup>19</sup> Some substances, in particular small water-soluble organic compounds such as glyoxal, have been found to partition more to the aqueous phase in the presence of ammonium sulfate.<sup>25</sup> Such “salting in” is likely due to the influence of salts on the aldehyde’s hydration equilibrium and due to reactions of salts with those substances.<sup>25</sup>

Furthermore, gas–particle partitioning during SOA formation is a dynamic process, i.e., the composition of the condensed particle phase changes due to the condensation or

evaporation of organic compounds into or out of the particle phase, which in turn has an influence on the partition coefficients. The traditional modeling approaches often fail to capture this iterative aspect of the aerosol partitioning and formation processes.

In many regards, the MCM-AIOMFAC-EVAPORATION (EVAPORATION stands for Estimation of Vapor Pressure of ORganics, Accounting for Temperature, Intramolecular, and Nonadditivity effects)<sup>26</sup> model combination by Zuend and Seinfeld<sup>14</sup> represents the state-of-the-art for predicting gas–particle partitioning equilibrium during SOA formation. It accounts for nonideality and phase separation in the condensed phase, i.e., the activity coefficients of organic compounds in the particle are not assumed to be unity but are calculated by AIOMFAC based on the composition of the condensed phase(s) and temperature. According to the calculated activity coefficients, the particle is allowed to separate into two phases to minimize the free energy of the system. As group contribution approaches, both AIOMFAC and EVAPORATION depend on a calibration with empirical data.

Orders of magnitude differences in vapor pressures predicted with different methods have been reported previously.<sup>27–29</sup> The potentially large uncertainty of an approach that relies on the prediction of both activity coefficients and vapor pressures has been discussed previously.<sup>30,31</sup> Wania et al.<sup>30</sup> proposed several methods for directly predicting gas–particle phase partitioning of SOA compounds, which could substitute for approaches that require the prediction of both activity coefficient and vapor pressure. The agreement in the partition coefficients between the organic matter component and the gas phase of an aerosol predicted by different methods was better than the agreement typically achieved by different vapor pressure estimation methods. One method, the commercial quantum-chemistry-based method COSMO-RS (Conductor like Screening Model for Realistic Solvents),<sup>32,33</sup> is able to calculate partition coefficients for any compound in any mixture. Because it is not limited by a calibration of group interaction parameters, COSMO-RS has potentially a much wider application range than group contribution methods. This suggests that the COSMO-RS method, in particular, may be a valuable alternative to the vapor pressure-based approaches to modeling gas–particle partitioning of SOA compounds (including the salt effect).

In this study, we aim to demonstrate that it is feasible to predict the equilibrium phase partitioning, aerosol particle composition, and mass during SOA formation using an approach that relies on quantum-chemical calculations and not on empirical calibration data. Specifically, the COSMO-RS method is used to predict the phase distribution behavior of oxidation products formed during  $\alpha$ -pinene ozonolysis under atmospherically relevant conditions (temperature, RH, salt content, aerosol loadings, etc.). The results of the calculations are used to illustrate the influence of the salting-out effect in the aqueous aerosol phase, of particle phase separation, and of the dynamic changes in phase composition on gas–particle partitioning.

## MODELING APPROACH

**Case Study:  $\alpha$ -Pinene Ozonolysis System.** A mixture of oxidation products from  $\alpha$ -pinene ozonolysis, ammonium sulfate, and water was chosen as the system for investigating gas–particle partitioning and SOA formation. We selected 18 SOA compounds to represent the myriad of substances formed during the ozonolysis of  $\alpha$ -pinene (Table 1). Stoichiometric yields and chemical structures for 12 of those products were provided by the MCM (structures in Figure S2, Supporting Information).<sup>14,34</sup> Six additional structures and a plausible formation scheme were proposed according to the reaction mechanisms for the formation of extremely low volatile organic compounds (ELVOCs) in Ehn et al.<sup>35</sup> (details in Figure S1). Three of the six compounds are formed from aging reactions such as intra- and intermolecular peroxy hemiacetal reaction or reactions of  $\alpha$ -pinene oxidation products with C<sub>2</sub> or C<sub>3</sub> molecules. As Ehn et al.<sup>35</sup> estimated a molar yield of 8% for the ELVOCs, we assumed MCM products and Ehn et al. compounds to make up 92% and 8% of the total carbon mass. The 8% molar yield was evenly distributed among the Ehn et al. compounds in our simulation.

**Gas–Particle Phase Partitioning.** Several assumptions are made in this work. The particle is assumed to be liquid-like, without considering the potential occurrence of a glassy state. The crystallization of both ammonium sulfate and organic compounds is ignored, which is plausible at the RH (60%) applied in our calculation. Furthermore, we assume that the particle phase separates into an organic-enriched phase and an aqueous, electrolyte-enriched phase. This was previously shown to be the case for  $\alpha$ -pinene aerosol at a wide range of RH.<sup>14,36</sup> Finally, reactions in either the aqueous (e.g., acid-catalyzed chemistry) or organic phase (e.g., oligomerization) are not considered. The former includes dissociation of carboxylic acids and the hydration of aldehydes to diols, which could increase the preference of the oxidation products for the aqueous phase.

Partitioning of organic compound  $i$  between gas and organic phase, between gas and aqueous phase, and between organic and aqueous phase is described by equilibrium partition coefficients as follows:

$$K_{\text{org/gas},i} = 1/K_{\text{gas/org},i} = C_{\text{org},i}/C_{\text{gas},i} \quad (1)$$

$$K_{\text{aq/gas},i} = 1/K_{\text{gas/aq},i} = C_{\text{aq},i}/C_{\text{gas},i} \quad (2)$$

$$K_{\text{org/aq},i} = 1/K_{\text{aq/org},i} = C_{\text{org},i}/C_{\text{aq},i} \quad (3)$$

$C_{\text{org},i}$ ,  $C_{\text{gas},i}$ , and  $C_{\text{aq},i}$  ( $\mu\text{g}/\text{m}^3$ ,  $\mu\text{g}$  of compound  $i$  per  $\text{m}^3$  of each phase) are the equilibrium concentrations of compound  $i$  in the organic, gas, and aqueous phase, respectively. Partitioning between the aqueous phase and the gas or organic phase also

depends on the presence of salts in the aqueous phase, as described by the Setschenow equation<sup>37</sup>

$$\log(K_{1/\text{salt water},i}/K_{1/\text{water},i}) = K_{S,i}[\text{salt}] \quad (4)$$

where  $K_{S,i}$  ( $\text{M}^{-1}$ ) is the empirical Setschenow coefficient for organic compound  $i$  and  $[\text{salt}]$  ( $\text{mol}/\text{L}$ ) is the salt solution concentration.  $K_{1/\text{salt water}}$  and  $K_{1/\text{water}}$  are equilibrium partition coefficients of an organic solute  $i$  between a nonaqueous (gas or organic) phase and the aqueous phase.

**COSMOtherm Calculations.** All partition coefficients  $K_{\text{org/gas},i}$ ,  $K_{\text{aq/gas},i}$ , and  $K_{\text{org/aq},i}$  as well as  $K_{S,i}$  are predicted using the commercial software COSMOtherm (Version C30\_1401 with BP\_TZVP\_C30\_1401 parametrization, COSMOlogic, GmbH & Co. KG, Leverkusen, Germany, 2014).<sup>32,33</sup> COSMOtherm is a program for the quantitative calculation of solvation mixture thermodynamics based on quantum chemistry using the COSMO-RS theory.<sup>33,38</sup> The electrostatic interaction of a solvent with a solute is approximated by a dielectric continuum solvation model. Molecules are regarded as embedded in a virtual conductor in order to derive interaction energies. Statistical thermodynamics is then applied to obtain partition coefficients and other properties. It has been shown to be able to predict partition and salting-out coefficients for compounds involved in SOA formation.<sup>18,30,39</sup> In this approach, COSMOconfX13 (version 3.0, COSMOlogic) templates, based on Turbomole version 6.5, have been used for full energy minimization and conformer generation for all the involved compounds.<sup>40,41</sup> Optimized structure files (called COSMO files) of organic compounds are fed into COSMOtherm to calculate partition coefficients between two phases with known composition at a desired temperature (here 298 K). For ionizing organic compounds, COSMOtherm predictions are made for the neutral form of the molecules. As the typically dominant inorganic salt in SOA, ammonium sulfate is the only salt included in our calculations. Setschenow constants in ammonium sulfate solutions were predicted with COSMOtherm and corrected with an empirical regression as described by Wang et al.<sup>18</sup>

**Modeling of Three-Phase Partitioning.** We defined four scenarios (Table S1) that differ in terms of the composition and concentration of oxidation products and liquid water content (LWC) to explore their influence on gas–particle partitioning. Scenario 1 represents the beginning of an SOA formation event when only small amounts of  $\alpha$ -pinene oxidation products have been formed. Scenario 2 represents the main growth phase of SOA when oxidation products are present at higher concentrations. Scenario 3 finally represents a somewhat aged SOA at high organic loadings. In scenario 4, high RH leads to the condensation of cloud droplets. Table 1 lists the relative composition (molar yield) of the oxidation products assumed to prevail during each of the scenarios. Common to the first three scenarios is the assumption that the model system is composed of a gas phase (volume is  $1 \text{ m}^3$ ), an organic-enriched liquid phase, and an aqueous electrolyte-enriched phase. Total water in the system is calculated from its saturation vapor pressure at 298 K and 60% RH. Most of the water in the system is in the gas phase, and we assume that LWC in the aqueous phase is determined by the amount of ammonium sulfate (calculated with AIOMFAC by assuming a supersaturated ammonium sulfate liquid solution<sup>14,15,17,42</sup>); i.e., it is not dependent on the organic loadings.<sup>43</sup> The water concentration in the organic phase is calculated from the partition coefficient of water between the gas and organic phase and its



concentration in the gas phase. Salt only exists in the aqueous phase (because preliminary calculation results showed that only a very limited amount of salt will partition into the organic phase). Thus, the aqueous phase is assumed to have a fixed salt concentration ( $2.64 \mu\text{g}/\text{m}^3$ ) and water content ( $1.6 \mu\text{g}/\text{m}^3$ ) at 60% RH throughout the first three scenarios. These values are based on a scenario with moderate SOA mass loading ( $5 \mu\text{g}/\text{m}^3$ ) and 60% RH described in ref 14. In scenario 4, only one condensed phase is assumed to be present ( $\text{LWC} = 0.3 \text{ g}/\text{m}^3$ ). The density of organic and aqueous phase in the aerosol scenarios (1–3) is assumed to be 1.2 and 1 g/mL, respectively. The density of the condensed phase in scenario 4 is assumed to be 1 g/mL.

The partitioning behavior of the oxidation products into the condensed phases depends on the composition of those phases. This composition in turn depends on the partitioning behavior of the oxidation products. Therefore, iterative calculations of phase partitioning and phase composition were performed until the composition of all phases was constant. Table S1 (Supporting Information) provides the starting conditions applied to these iterative calculations. We assumed that initially the organic phase is made up of the organic compound with the lowest vapor pressure (Table S2). A starting organic phase mass was selected according to the total organic loading for different scenarios. Different starting organic phase masses (0.1, 0.5, and  $0.945 \mu\text{g}/\text{m}^3$ ) were tested for scenario 1, and they always converged to the same final composition and total aerosol mass. Thus, for scenarios 2 and 3, only one starting point was selected.

The basic assumption is mass conservation in the system

$$M_{t,i} = M_{p,i} + M_{g,i} \quad (5)$$

$$M_{p,i} = M_{\text{org},i} + M_{\text{aq},i} \quad (6)$$

where  $M_{t,i}$  is the total mass of species  $i$  in the studied system and  $M_{g,i}$  and  $M_{p,i}$  are the total mass in the gas and particle phase, respectively.  $M_{\text{org},i}$  and  $M_{\text{aq},i}$  are the mass in the organic and aqueous phase of the particle, respectively.

$$M_{\text{org},i} = C_{\text{org},i} V_{\text{org}} \quad (7)$$

$$M_{g,i} = C_{\text{gas},i} V_{\text{gas}} \quad (8)$$

$$M_{\text{aq},i} = C_{\text{aq},i} V_{\text{aq}} \quad (9)$$

$V_{\text{org}}$ ,  $V_{\text{gas}}$ , and  $V_{\text{aq}}$  are volume of organic phase, gas phase and aqueous phase, respectively.

The detailed procedure during the calculations is as follows:

- (1) For each oxidation product  $i$ , COSMOtherm calculates the partition coefficients  $K_{\text{org}/\text{gas},i}$ ,  $K_{\text{aq}/\text{gas},i}$  (aqueous phase without salt), and  $K_{\text{org}/\text{aq},i}$  at 25 °C. The partition coefficient of water between the gas and the organic condensed phase ( $K_{\text{org}/\text{gas},i}$ ) at 25 °C is also calculated.
- (2) Partition coefficients between aqueous and gas phase are corrected for the salting-out effect using

$$\begin{aligned} \log K_{\text{aq}/\text{gas},i,\text{corr}} &= \log K_{\text{aq}/\text{gas},i} - K_{S,i,\text{corr}}[\text{salt}] \\ &= \log K_{\text{aq}/\text{gas},i} - (0.334K_{S,i,\text{COSMOtherm}} \\ &\quad + 0.0604)[\text{salt}] \end{aligned} \quad (10)$$

where  $K_{S,i,\text{corr}}$  is obtained from an empirical relationship between COSMOtherm-predicted and measured  $K_S$  by Wang et al.<sup>18</sup>

- (3) The fractions of oxidation product  $i$  that partition to the aqueous and organic phase, respectively, are calculated according to

$$f_{\text{aq},i} = 1/(1 + K_{\text{gas}/\text{aq},i} V_{\text{gas}}/V_{\text{aq}} + K_{\text{org}/\text{aq},i} V_{\text{org}}/V_{\text{aq}}) \quad (11)$$

$$f_{\text{org},i} = 1/(1 + K_{\text{gas}/\text{org},i} V_{\text{gas}}/V_{\text{org}} + K_{\text{aq}/\text{org},i} V_{\text{aq}}/V_{\text{org}}) \quad (12)$$

Initially, the volumes of the aqueous ( $V_{\text{H}_2\text{O}}$ ) and organic phase ( $V_{\text{org,init}}$ ) are determined by the water volume in the aqueous phase (i.e., the LWC) and the assumed starting mass of the organic phase, respectively.  $V_{\text{org,init}}$  is 0 from the second iteration onward. New volumes of those phases are then calculated using

$$V_{\text{aq,new}} = V_{\text{H}_2\text{O}} + \sum_{i=1}^n M_{t,i} f_{\text{aq},i} \rho_i \quad (13)$$

$$V_{\text{org,new}} = V_{\text{org,init}} + \sum_{i=1}^n M_{t,i} f_{\text{org},i} \rho_i \quad (14)$$

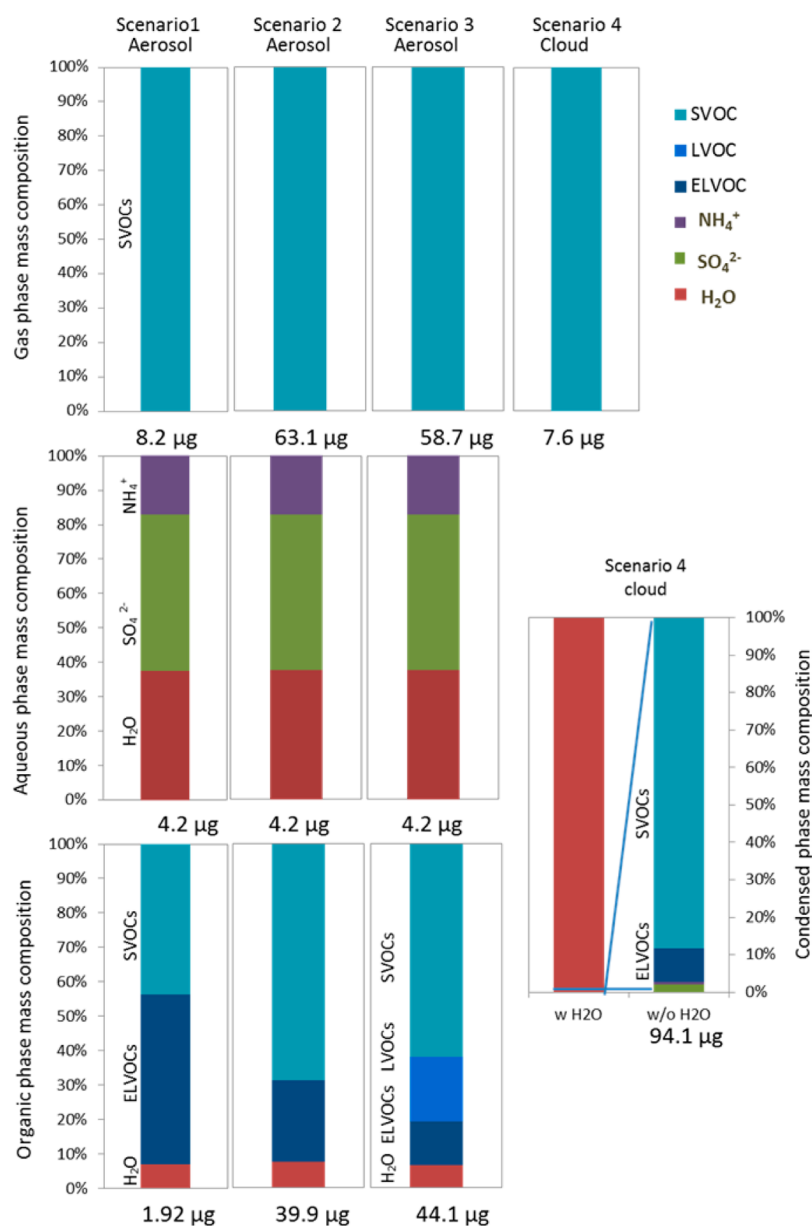
whereby the density of all products ( $\rho_i$ ) is assumed to be equal to 1.2 g/mL. The contribution of the organic compounds to the aqueous phase volume turned out to be negligibly small.

- (4) The amount of water that partitions to the organic phase is calculated from its  $K_{\text{org}/\text{gas}}$  and concentration in the gas phase by eq 1. The concentration of water in the gas phase is calculated based on ideal gas law at 25 °C and 60% RH for scenarios 1–3. A saturation vapor pressure for water at 25 °C of 3169 Pa was used.<sup>44</sup>
- (5) A new iteration starts with step 1 until the mass of each component in all three phases changes by less than 5%. Then, the final phase mass and composition are compared and discussed.

## RESULTS AND DISCUSSION

**Partition Coefficients.** The partition coefficients  $K_{\text{org}/\text{gas},i}$  and  $K_{\text{aq}/\text{gas},i}$  calculated for the different scenarios are compared in Figure S3. We categorize the compounds as follows: those with  $\log K_{\text{org}/\text{gas},i} < 13$  and  $\log K_{\text{aq}/\text{gas},i} < 13$  are semivolatile (SVOCs); compounds with  $\log K_{\text{org}/\text{gas},i} > 13$  or  $\log K_{\text{aq}/\text{gas},i} > 13$  are classified as low volatile (LVOCs); those with  $\log K_{\text{org}/\text{gas},i} > 16$  or  $\log K_{\text{aq}/\text{gas},i} > 16$  are considered extremely low volatile (ELVOCs) (refer to the Supporting Information for the categorization of organic compounds by saturation concentrations  $C^*$ ). In general, Ehn et al. compounds have higher  $K_{\text{org}/\text{gas},i}$ ; the two C20 compounds (C20H30O18 and C20H28O14) are ELVOCs, and C13H18O10 is an LVOC (details in Table S4). Other Ehn et al. compounds and all the MCM compounds belong to the SVOC category. C921OOH and C812OOH have the highest  $K_{\text{org}/\text{gas},i}$  among the MCM compounds. For all compounds, the partition coefficients  $K_{\text{org}/\text{gas},i}$  predicted for scenarios 1, 2, and 3 are very similar. This suggests that the organic phase mixtures tend to have similar solvation properties. For all organic compounds,  $K_{\text{aq}/\text{gas},i}$  in pure water is always lower (by an average of  $1.5 \pm 0.8$  orders of magnitude in scenario 1) than its corresponding  $K_{\text{org}/\text{gas},i}$ , indicating a higher preference for the condensed organic phase. The salting-out effect lowers  $K_{\text{aq}/\text{gas},i}$  an additional 2–3 orders of magnitude at conditions of 60% RH.





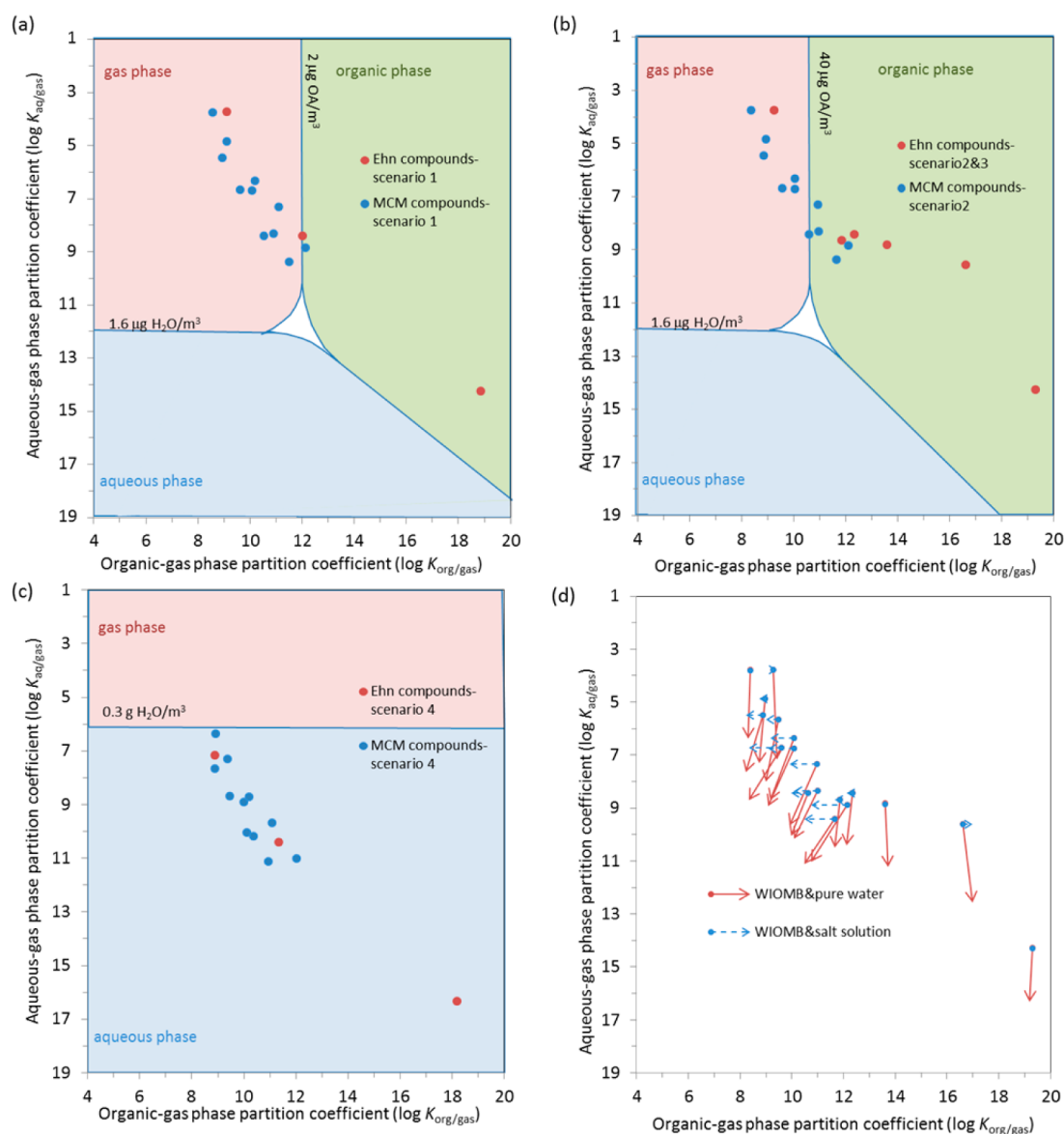
**Figure 2.** Gas, aqueous, and organic phase composition calculated for different scenarios. The columns reveal the mass fractions of each component in the gas (top panels, water vapor not included), aqueous (middle panels), and organic phase (bottom panels). In scenario 4, only one condensed phase exists, and the two columns represent the phase composition including water (w H<sub>2</sub>O) and without water (w/o H<sub>2</sub>O). The total mass of all species in a phase is shown at the bottom of each column. Detailed information on the composition is shown in Table S4 and Figure S4.

and ELVOCs still contributed about two-thirds of the SOA mass at higher loadings ( $\sim 10 \mu\text{g}/\text{m}^3$ ).<sup>35</sup> In agreement with these observations, in our simulation, the proposed compounds based on Ehn et al.'s mechanism (even though not all are ELVOCs according to our definition) constitute about 66% and 36% (with ELVOCs contributing 49% and 24%) of the total aerosol mass at low loading ( $1.92 \mu\text{g}/\text{m}^3$ ) and high loading ( $39.9 \mu\text{g}/\text{m}^3$ ), respectively. This supports the notion that ELVOCs are the main SOA source at low loadings in the chamber experiment.

Scenario 3 has a slightly higher organic phase mass than scenario 2 because aging will generally increase the preference for the condensed phase. The Ehn et al. compounds make up 41% of the condensed phase in scenario 3 in comparison with 36% in scenario 2. Aging reactions such as intramolecular peroxy hemiacetal reaction or reactions with C<sub>2</sub> or C<sub>3</sub>

molecules (Figure. S1) can yield products of low volatility, potentially increasing particle mass.

The mass fraction of water in the organic phase is nearly unaffected by the SOA loading (7.0% scenario 1 vs 7.5% scenario 2). The water content in the organic phase in terms of mole fraction is relatively high: 52% and 57% for high and low organic loadings, respectively. AIOMFAC similarly calculated a mole fraction of water in the organic phase of around  $\sim 50\%$  at 60% RH for different loadings.<sup>14</sup> As written by Zuend and Seinfeld,<sup>14</sup> "This is enough water to significantly influence the overall viscosity in the organic phase and prevent a glass transition." However, the mass fraction of water is low because of its low molar mass compared to the organic compounds. Because partitioning is related to the mass composition of the organic phase, the presence of water will not change the



**Figure 3.** Oxidation products of  $\alpha$ -pinene in the chemical partitioning space, with pink, blue, and green indicating the combinations of equilibrium partition properties that lead to dominant distribution into the gas, aqueous, and organic phases, respectively. Three panels represent scenarios 1 (a), 2 and 3 (b), and 4 (c). Panel (d) displays the influence of salting-out and organic phase composition on phase partitioning. The origin of each arrow corresponds to the partition coefficients calculated in scenarios 2 and 3. The end of the red arrows is the location obtained when WIOMB, and pure water is used as a surrogate for the organic phase and the aqueous phase, respectively. The end of the blue arrows represents partition coefficients into WIOMB and salt solutions with the same concentration of ammonium sulfate as in aerosol scenarios, but without organic compounds.

solvation properties of the organic phase as much as might be surmised from the high mole fraction.

**SOA Yield.** The SOA mass yields, calculated as the ratio between the total organic compound mass in the condensed phase and the mass of precursor VOC reacted, was 24% ( $1.8 \mu\text{g}/\text{m}^3$ ), 48% ( $36.3 \mu\text{g}/\text{m}^3$ ), and 55% ( $41.3 \mu\text{g}/\text{m}^3$ ) for scenarios 1, 2, and 3, respectively. An SOA yield that increases with increasing SOA loadings agrees with chamber studies.<sup>34,46,47</sup> However, our SOA yields are higher than those reported for chamber experiments: Ehn et al.<sup>35</sup> reported a SOA mass yield of 10.3% at a SOA loading of  $8.8 \mu\text{g}/\text{m}^3$  and Shilling et al.<sup>46</sup> reported a yield of 27% at  $40 \mu\text{g}/\text{m}^3$ . Among possible reasons for these discrepancies are differences between the structures and stoichiometric yields of  $\alpha$ -pinene oxidation products in the experiments and proposed here. Also, our calculations account only for partitioning, while other loss

processes such as wall loss, deposition, or further reactions may have occurred in the experiments. In particular, at low loadings, wall loss becomes important. The uncertainty during model calculation, e.g., in the predicted partition coefficients, is another source of error. Previous studies show that the root-mean-square error (rmse) for COSMOtherm-predicted partitioning coefficients is generally lower than 1 log unit when compared with measured values or values predicted with other methods.<sup>30,48–50</sup> Scenario 4 gave the highest concentration of oxidation products in the condensed cloudwater phase ( $91.4 \mu\text{g}/\text{m}^3$ ) and, therefore, the highest mass yield (121%) among all scenarios.

We also predicted O:C and H:C ratios in the SOA. The O:C ratio at lower loading was 0.75, higher than the ratios of 0.57 and 0.54 calculated at high loadings in scenarios 2 and 3. The higher fraction of ELVOCs at low loading is responsible for the



higher O:C ratio. At higher loadings, increased contribution from SVOCs to the SOA leads to the lower O:C ratio. The calculated H:C ratios are quite close in the different scenarios with an average of  $1.59 \pm 0.03$ . The predicted O:C and H:C values are consistent with the ratios of  $0.7 \pm 0.1$  and  $1.5 \pm 0.1$  measured by Ehn et al.<sup>35</sup> In agreement with our simulations, they also noted a slight decrease in the O:C ratio over time (extended data Figure in ref 35) due to more SVOCs being able to condense at higher SOA loading.

**Chemical Partitioning Space.** The two-dimensional partitioning space defined by the equilibrium partition coefficients  $K_{aq/gas}$  and  $K_{org/gas}$  introduced recently<sup>39</sup> is used here to further illustrate the phase distribution behavior of the  $\alpha$ -pinene oxidation products considered in our simulations. In panels a–c of Figure 3, the lines between the differently colored fields indicate partitioning property combinations that lead to equal distribution between two phases for the specified LWC and organic aerosol loadings (OA) in the four scenarios: (a)  $1.6 \mu\text{g}/\text{m}^3$  LWC and  $2 \mu\text{g}/\text{m}^3$  OA in scenario 1, (b)  $1.6 \mu\text{g}/\text{m}^3$  LWC and  $40 \mu\text{g}/\text{m}^3$  OA in scenario 2 and 3, and (c)  $0.3 \text{ g}/\text{m}^3$  LWC and  $0 \mu\text{g}/\text{m}^3$  OA in scenario 4. MCM compounds and Ehn et al. compounds were placed into the chemical space according to their partition coefficients using blue and red markers, respectively. The chemical space plots illustrate our findings above: at low organic loadings ( $\sim 2 \mu\text{g}/\text{m}^3$ ), the organic phase is the dominant phase for ELVOCs and some SVOCs; more compounds partition to the organic phase at a higher organic loading ( $40 \mu\text{g}/\text{m}^3$ ); the aqueous phase is not a dominant phase at LWC relevant to aerosol ( $1.6 \mu\text{g}/\text{m}^3$ ), whereas most compounds partition into the aqueous phase at higher LWC ( $0.3 \text{ g}/\text{m}^3$ ) in the cloud scenario.

**Potential for Simplified Approaches to Gas–Particle Partitioning Estimation.** We also used COSMOtherm to estimate  $K_{org/gas,i}$  and  $K_{aq/gas,i}$  using water-insoluble organic matter structure B (WIOMB, Figure S5, Supporting Information) proposed by Kalberer et al.<sup>51</sup> as a surrogate for the organic phase<sup>30</sup> and pure water as well as an ammonium sulfate solution (with the same concentration as in the simulated aerosol scenarios but without organic compounds) as the aqueous phase. In Figure 3d, we illustrate the influence of using a simplified phase composition on the partitioning of compounds. The displacement in the partitioning space (i.e., the length of the arrows) is caused by the difference in the partition coefficients that occurs when WIOMB and pure water are used to represent the organic and aqueous phase instead of the actual aerosol phases in scenarios 2 and 3. The vertical displacement indicates the discrepancy in  $K_{aq/gas,i}$  values, showing the influence of the salting-out effect (and, to a much smaller extent, of the presence of other organic compounds in the aqueous phase) on  $K_{aq/gas,i}$ . The horizontal displacement indicates the discrepancy in  $K_{org/gas,i}$  values when using WIOMB as the organic phase instead of the actual organic phase mixture.

In general, the vertical distance is larger than the horizontal distance for the red arrows. The small horizontal distance reflects that for all compounds in scenarios 1–3; the  $K_{org/gas,i}$  calculated using WIOMB is very similar to the  $K_{org/gas,i}$  calculated for the actual organic aerosol phase (Figure S3). The large vertical displacements emphasize the importance of the salting-out effect on  $K_{aq/gas,i}$ . However, the negligible vertical displacement for blue arrows indicates the similarity of  $K_{aq/gas,i}$  in aqueous aerosol phases that either contain or do not contain other organic compounds.

This suggests that in many cases complex iterative calculations to determine the solvation properties of the actual mixture of oxidation products in the organic aerosol phase may not be necessary. Instead, as previously suggested for the oxidation products of *n*-alkanes,<sup>30</sup> the solvation properties of a complex organic aerosol phase may be well represented by a surrogate, like WIOMB. Similarly, it appears justified to often ignore the influence of the small amount of organic compounds in the aqueous phase on the solvation properties of that phase. However, the presence of a large quantity of inorganic salts cannot be ignored because the salting-out effect is the main reason for the low organic content in the aqueous phase and the reason for phase separation in the aerosol.<sup>20</sup>

Even though the aqueous phase is not an important phase for partitioning of  $\alpha$ -pinene oxidation products in the aerosol scenarios considered here, this does not necessarily mean we could ignore the presence of an electrolyte-rich aqueous aerosol phase. Our findings apply to the specified conditions (organic, inorganic species and loadings) and may not be easily extrapolated to other simulation conditions and other SOA systems (different precursors). Also, reactions in the aqueous phase could potentially lead to a higher effective uptake of organics in the aqueous phase. In light of our work and that by Zuend and Seinfeld<sup>14</sup> and Mouchel-Vallon et al.,<sup>45</sup> significant fractions of the  $\alpha$ -pinene ozonolysis products may be found in the aqueous phase at higher RH and especially when clouds form. Some of the dissolved organic compounds may be processed in the condensed aerosol phase or cloud droplets, modifying both the mass and composition of the condensed phase.

**Merits of the Presented Approach.** As a quantum-chemistry based model, COSMOtherm provides the capability of simulating solvation mixture thermodynamics for any organic–inorganic SOA mixture. However, one challenge for modeling the gas–particle partitioning of a SOA system is the requirement to identify the specific compounds present in the modeled system. Because of the variety and complexity of actual aerosol, most of the components, especially the organic fractions, are unresolved in both laboratory and field. Most compound-specific modeling approaches, including ours, therefore depend on molecular structures and reaction yields predicted by chemistry reaction mechanisms such as MCM.

Here, the gas–particle partitioning framework was applied to the  $\alpha$ -pinene/ammonium sulfate SOA system to serve as an example. The generally good agreement between this work and chamber experiments as well as with other modeling studies for this system demonstrates the method's applicability. In comparison with other approaches, which mainly rely on vapor pressure-based group contribution methods, our approach requires no direct calibration, with the exception of the empirical correction for COSMOtherm-predicted salting-out coefficients. A quantum-chemistry based approach is not constrained by applicability domain limits in the same way that group contribution methods are. A drawback is the considerable time (hours to days depending on the molecular size) and computing resources required for the quantum-chemical calculations. Clearly, both empirical and quantum-chemistry-based approaches have their merits and can complement each other. Applying and evaluating the presented framework to other SOA systems should be the subject of future work. It is also desirable to improve COSMOtherm's prediction of the salting-out effect to eliminate the need for any correction based on empirical data. Furthermore, acid



dissociation and hydration of aldehydes should be included in the future.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Additional information on the reaction scheme, parameters for different scenarios, information for the organic compounds, partitioning coefficients, and compositions of different phases, and surrogate structure for SOA. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01584.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Tel: +1-416-287-7225. E-mail: frank.wania@utoronto.ca.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We are grateful to Ran Zhao, Nadine Borduas, and Joel Thornton for assistance in generating plausible molecular structures and reaction yields of  $\alpha$ -pinene oxidation products. Funding from the Natural Sciences and Engineering Research Council of Canada, a Special Opportunity Graduate Travel Fellowship of the Department of Chemistry at the University of Toronto, and the German Academic Exchange Service is acknowledged.

## ■ REFERENCES

- (1) Chan, M. N.; Chan, A. W. H.; Chhabra, P. S.; Surratt, J. D.; Seinfeld, J. H. Modeling of secondary organic aerosol yields from laboratory chamber data. *Atmos. Chem. Phys.* **2009**, *9* (15), 5669–5680.
- (2) Pankow, J. F. An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol. *Atmos. Environ.* **1994**, *28*, 189–193.
- (3) Odum, J. R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R. C.; Seinfeld, J. H. Gas/particle partitioning and secondary organic aerosol yields. *Environ. Sci. Technol.* **1996**, *30*, 2580–2585.
- (4) Donahue, N. M.; Robinson, A. L.; Stanier, C. O.; Pandis, S. N. Coupled partitioning, dilution, and chemical aging of semivolatile organics. *Environ. Sci. Technol.* **2006**, *40* (8), 2635–2643.
- (5) Donahue, N. M.; Epstein, S. A.; Pandis, S. N.; Robinson, A. L. A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics. *Atmos. Chem. Phys.* **2011**, *11* (7), 3303–3318.
- (6) Carlton, A. G.; Turpin, B. J. Particle partitioning potential of organic compounds is highest in the Eastern US and driven by anthropogenic water. *Atmos. Chem. Phys.* **2013**, *13* (20), 10203–10214.
- (7) Chang, W. L.; Griffin, R. J.; Dabdub, D. Partitioning phase preference for secondary organic aerosol in an urban atmosphere. *Proc. Nat. Acad. Sci. U.S.A.* **2010**, *107* (15), 6705–6710.
- (8) Parikh, H. M.; Carlton, A. G.; Vizuete, W.; Kamens, R. M. Modeling secondary organic aerosol using a dynamic partitioning approach incorporating particle aqueous-phase chemistry. *Atmos. Environ.* **2011**, *45* (5), 1126–1137.
- (9) Pun, B. K.; Griffin, R. J.; Seigneur, C.; Seinfeld, J. H. Secondary organic aerosol - 2. Thermodynamic model for gas/particle partitioning of molecular constituents. *J. Geophys. Res. - Atmos.* **2002**, *107*, D17.
- (10) Saunders, S. M.; Jenkin, M. E.; Derwent, R. G.; Pilling, M. J. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds. *Atmos. Chem. Phys.* **2003**, *3*, 161–180.
- (11) Donahue, N. M.; Robinson, A. L.; Trump, E. R.; Riipinen, I.; Kroll, J. H. Volatility and aging of atmospheric organic aerosol. *Atmos. Aerosol Chem.* **2014**, *339*, 97–143.
- (12) Asher, W. E.; Pankow, J. F. Vapor pressure prediction for alkenoic and aromatic organic compounds by a UNIFAC-based group contribution method. *Atmos. Environ.* **2006**, *40* (19), 3588–3600.
- (13) Erdakos, G. B.; Chang, E. I.; Pankow, J. F.; Seinfeld, J. H. Prediction of activity coefficients in liquid aerosol particles containing organic compounds, dissolved inorganic salts, and water - Part 3: Organic compounds, water, and ionic constituents by consideration of short-, mid-, and long-range effects using X-UNIFAC.3. *Atmos. Environ.* **2006**, *40* (33), 6437–6452.
- (14) Zuend, A.; Seinfeld, J. H. Modeling the gas–particle partitioning of secondary organic aerosol: The importance of liquid–liquid phase separation. *Atmos. Chem. Phys.* **2012**, *12* (9), 3857–3882.
- (15) Zuend, A.; Marcolli, C.; Luo, B. P.; Peter, T. A thermodynamic model of mixed organic-inorganic aerosols to predict activity coefficients. *Atmos. Chem. Phys.* **2008**, *8* (16), 4559–4593.
- (16) Zuend, A.; Marcolli, C.; Booth, A. M.; Lienhard, D. M.; Soonsin, V.; Krieger, U. K.; Topping, D. O.; McFiggans, G.; Peter, T.; Seinfeld, J. H. New and extended parameterization of the thermodynamic model AIOMFAC: Calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups. *Atmos. Chem. Phys.* **2011**, *11* (17), 9155–9206.
- (17) Zuend, A.; Marcolli, C.; Peter, T.; Seinfeld, J. H. Computation of liquid-liquid equilibria and phase stabilities: implications for RH-dependent gas/particle partitioning of organic-inorganic aerosols. *Atmos. Chem. Phys.* **2010**, *10* (16), 7795–7820.
- (18) Wang, C.; Lei, Y. D.; Endo, S.; Wania, F. Modeling the salting-out effect in ammonium sulfate solutions. *Environ. Sci. Technol.* **2014**, *48* (22), 13238–13245.
- (19) Marcolli, C.; Krieger, U. K. Phase changes during hygroscopic cycles of mixed organic/inorganic model systems of tropospheric aerosols. *J. Phys. Chem. A* **2006**, *110* (5), 1881–1893.
- (20) You, Y.; Smith, M. L.; Song, M. J.; Martin, S. T.; Bertram, A. K. Liquid-liquid phase separation in atmospherically relevant particles consisting of organic species and inorganic salts. *Int. Rev. Phys. Chem.* **2014**, *33* (1), 43–77.
- (21) Song, M.; Marcolli, C.; Krieger, U. K.; Zuend, A.; Peter, T. Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles. *Atmos. Chem. Phys.* **2012**, *12* (5), 2691–2712.
- (22) Song, M.; Marcolli, C.; Krieger, U. K.; Zuend, A.; Peter, T. Liquid-liquid phase separation in aerosol particles: Dependence on O:C, organic functionalities, and compositional complexity. *Geophys. Res. Lett.* **2012**, *39*.
- (23) You, Y.; Renbaum-Wolff, L.; Bertram, A. K. Liquid–liquid phase separation in particles containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium nitrate or sodium chloride. *Atmos. Chem. Phys.* **2013**, *13* (23), 11723–11734.
- (24) Bertram, A. K.; Martin, S. T.; Hanna, S. J.; Smith, M. L.; Bodsworth, A.; Chen, Q.; Kuwata, M.; Liu, A.; You, Y.; Zorn, S. R. Predicting the relative humidities of liquid-liquid phase separation, efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and water using the organic-to-sulfate mass ratio of the particle and the oxygen-to-carbon elemental ratio of the organic component. *Atmos. Chem. Phys.* **2011**, *11* (21), 10995–11006.
- (25) Kampf, C. J.; Waxman, E. M.; Slowik, J. G.; Dommen, J.; Pfaffenberger, L.; Praplan, A. P.; Prevot, A. S. H.; Baltensperger, U.; Hoffmann, T.; Volkamer, R. Effective Henry's law partitioning and the salting constant of glyoxal in aerosols containing sulfate. *Environ. Sci. Technol.* **2013**, *47* (9), 4236–4244.
- (26) Compernelle, S.; Ceulemans, K.; Muller, J. F. EVAPORATION: a new vapour pressure estimation method for organic molecules including non-additivity and intramolecular interactions. *Atmos. Chem. Phys.* **2011**, *11* (18), 9431–9450.
- (27) Topping, D.; Barley, M.; McFiggans, G. Including phase separation in a unified model to calculate partitioning of vapours to

mixed inorganic-organic aerosol particles. *Faraday Disc.* **2013**, *165*, 273–288.

(28) Valorso, R.; Aumont, B.; Camredon, M.; Raventos-Duran, T.; Mouchel-Vallon, C.; Ng, N. L.; Seinfeld, J. H.; Lee-Taylor, J.; Madronich, S. Explicit modelling of SOA formation from alpha-pinene photooxidation: sensitivity to vapour pressure estimation. *Atmos. Chem. Phys.* **2011**, *11* (14), 6895–6910.

(29) Barley, M. H.; McFiggans, G. The critical assessment of vapour pressure estimation methods for use in modelling the formation of atmospheric organic aerosol. *Atmos. Chem. Phys.* **2010**, *10* (2), 749–767.

(30) Wania, F.; Lei, Y. D.; Wang, C.; Abbatt, J. P. D.; Goss, K. U. Novel methods for predicting gas–particle partitioning during the formation of secondary organic aerosol. *Atmos. Chem. Phys.* **2014**, *14* (23), 13189–13204.

(31) McFiggans, G.; Topping, D. O.; Barley, M. H. The sensitivity of secondary organic aerosol component partitioning to the predictions of component properties - Part 1: A systematic evaluation of some available estimation techniques. *Atmos. Chem. Phys.* **2010**, *10* (21), 10255–10272.

(32) Klamt, A.; Eckert, F. COSMO-RS: a novel and efficient method for the a priori prediction of thermophysical data of liquids. *Fluid Phase Equilib.* **2000**, *172* (1), 43–72.

(33) Klamt, A. *From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*; Elsevier: Amsterdam, 2005.

(34) Shilling, J. E.; Chen, Q.; King, S. M.; Rosenoern, T.; Kroll, J. H.; Worsnop, D. R.; DeCarlo, P. F.; Aiken, A. C.; Sueper, D.; Jimenez, J. L.; Martin, S. T. Loading-dependent elemental composition of alpha-pinene SOA particles. *Atmos. Chem. Phys.* **2009**, *9* (3), 771–782.

(35) Ehn, M.; Thornton, J. A.; Kleist, E.; Sipila, M.; Junninen, H.; Pullinen, I.; Springer, M.; Rubach, F.; Tillmann, R.; Lee, B.; Lopez-Hilfiker, F.; Andres, S.; Acir, I. H.; Rissanen, M.; Jokinen, T.; Schobesberger, S.; Kangasluoma, J.; Kontkanen, J.; Nieminen, T.; Kurten, T.; Nielsen, L. B.; Jorgensen, S.; Kjaergaard, H. G.; Canagaratna, M.; Dal Maso, M.; Berndt, T.; Petaja, T.; Wahner, A.; Kerminen, V. M.; Kulmala, M.; Worsnop, D. R.; Wildt, J.; Mentel, T. F. A large source of low-volatility secondary organic aerosol. *Nature* **2014**, *506* (7489), 476–479.

(36) You, Y.; Renbaum-Wolff, L.; Carreras-Sospedra, M.; Hanna, S. J.; Hiranuma, N.; Kamal, S.; Smith, M. L.; Zhang, X.; Weber, R. J.; Shilling, J. E.; Dabdub, D.; Martin, S. T.; Bertram, A. K. Images reveal that atmospheric particles can undergo liquid-liquid phase separations. *Proc. Nat. Acad. Sci. U.S.A.* **2012**, *109* (33), 13188–13193.

(37) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2nd ed.; John Wiley & Sons: Hoboken, 2003.

(38) Eckert, F.; Klamt, A. Fast solvent screening via quantum chemistry: COSMO-RS approach. *AIChE J.* **2002**, *48*, 369.

(39) Wania, F.; Lei, Y. D.; Wang, C.; Abbatt, J. P. D.; Goss, K. U. Using the chemical equilibrium partitioning space to explore factors influencing the phase distribution of compounds involved in secondary organic aerosol formation. *Atmos. Chem. Phys.* **2015**, *15* (6), 3395–3412.

(40) Vainio, M. J.; Johnson, M. S. Generating conformer ensembles using a multiobjective genetic algorithm. *J. Chem. Inf. Model.* **2007**, *47* (6), 2462–2474.

(41) TURBOMOLE V6.5 2013, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007; TURBOMOLE GmbH, since 2007 available from <http://www.turbomole.com> (accessed on 20. 11. 2014).

(42) AIOMFAC-web, Available from <http://www.aiomfac.caltech.edu> (accessed on 15. 2. 2015).

(43) Petters, M. D.; Kreidenweis, S. M. A single parameter representation of hygroscopic growth and cloud condensation nucleus activity. *Atmos. Chem. Phys.* **2007**, *7* (8), 1961–1971.

(44) Stimson, H. F. Some precise measurements of the vapor pressure of water in the range from 25 to 100 °C. *Int. J. Res. Natl. Bur. Stand.* **1969**, *73A*, 493–496.

(45) Mouchel-Vallon, C.; Bräuer, P.; Camredon, M.; Valorso, R.; Madronich, S.; Herrmann, H.; Aumont, B. Explicit modeling of volatile organic compounds partitioning in the atmospheric aqueous phase. *Atmos. Chem. Phys.* **2013**, *13* (2), 1023–1037.

(46) Shilling, J. E.; Chen, Q.; King, S. M.; Rosenoern, T.; Kroll, J. H.; Worsnop, D. R.; McKinney, K. A.; Martin, S. T. Particle mass yield in secondary organic aerosol formed by the dark ozonolysis of  $\alpha$ -pinene. *Atmos. Chem. Phys.* **2008**, *8* (7), 2073–2088.

(47) Pfaffenberger, L.; Barmet, P.; Slowik, J. G.; Praplan, A. P.; Dommen, J.; Prévôt, A. S. H.; Baltensperger, U. The link between organic aerosol mass loading and degree of oxygenation: an  $\alpha$ -pinene photooxidation study. *Atmos. Chem. Phys.* **2013**, *13* (13), 6493–6506.

(48) Stenzel, A.; Endo, M.; Goss, K. U. Measurements and predictions of hexadecane/air partition coefficients for 387 environmentally relevant compounds. *J. Chromatogr. A* **2012**, *1220*, 132–142.

(49) Geisler, A.; Oemisch, L.; Endo, S.; Goss, K.-U. Predicting storage–lipid water partitioning of organic solutes from molecular structure. *Environ. Sci. Technol.* **2015**, *49* (9), 5538–5545.

(50) Stenzel, A.; Goss, K. U.; Endo, S. Prediction of partition coefficients for complex environmental contaminants: Validation of COSMOtherm, ABSOLV, and SPARC. *Environ. Toxicol. Chem.* **2014**, *33* (7), 1537–1543.

(51) Kalberer, M.; Paulsen, D.; Sax, M.; Steinbacher, M.; Dommen, J.; Prevot, A. S. H.; Fisseha, R.; Weingartner, E.; Frankevich, V.; Zenobi, R.; Baltensperger, U. Identification of polymers as major components of atmospheric organic aerosols. *Science* **2004**, *303* (5664), 1659–1662.