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Atmospheric oxidation of volatile organic compounds can lead to the formation of secondary organic aerosol (SOA) through the gas/particle (G/P) partitioning of the oxidation products. Since water is ubiquitous in the atmosphere, the extent of the partitioning for any individual organic product depends not only on the amounts and properties of the partitioning organic compounds, but also on the amount of water present. Predicting the effects of water on the atmospheric G/P distributions of organic compounds is, therefore, central to understanding SOA formation. The goals of the current work are to gain understanding of how increases in RH affect (1) overall SOA yields, (2) water uptake by SOA, (3) the behaviors of individual oxidation products, and (4) the fundamental physical properties of the SOA phase that govern the G/P distribution of each of the oxidation products. Part 1 of this series considered SOA formation from five parent hydrocarbons in the absence of water. This paper predicts how adding RH to those systems uniformly increases both the amount of condensed organic mass and the amount of liquid water in the SOA phase. The presence of inorganic components is not considered. The effect of increasing RH is predicted to be stronger for SOA produced from cyclohexene as compared to SOA produced from four monoterpenes. This is likely a result of the greater general degree of oxidation (and hydrophilicity) of the cyclohexene products. Good agreement was obtained between predicted SOA yields and laboratory SOA yield data actually obtained in the presence of water. As RH increases, the compounds that play the largest roles in changing both the organic and water masses in the SOA phase are those with vapor pressures that are intermediate between those of essentially nonvolatile and highly volatile species. RH-driven changes in the compound-dependent G/P partitioning coefficient \(K_p\) result from changes in both the average molecular weight \(M_{\text{om}}\) of the absorbing organic/water phase, and the compound-dependent activity coefficient \(\gamma\) values. Adding water to the SOA phase by increasing the RH drives down \(M_{\text{om}}\) and thereby uniformly favors SOA condensation. The effect of RH on \(\gamma\) values is compound specific and depends on the hydrophilicity of the specific compound of interest; the more hydrophilic a compound, the more increasing RH will favor its condensation into the SOA phase. The results also indicate that it may be a useful first approximation to assume that \(\gamma = 1\) for many compounds making up SOA mixtures.

**Introduction**

Atmospheric oxidation of volatile organic compounds (VOCs) can lead to multiple products that have volatilities that are much lower than that of the VOC parent hydrocarbon (HC). Once condensable products have accumulated in the gas phase, the system can become saturated for that mix of products. Additional formation of such products will allow condensation of aerosol particulate matter (PM) to begin. In the atmosphere, primary organic products may be present, and condensable products may partition to those particles by absorption. PM formed in this manner is referred to as “secondary organic aerosol” (SOA). Oxidation of parent HCs with six or more carbon atoms can lead to SOA. (The vapor pressures of the oxidation products from parent HCs with fewer than six carbon atoms are generally too high to allow significant aerosol formation.) Once SOA production begins, the formation of increasing amounts of condensable products increases not only the mass concentration of SOA (\(M_o\, \mu g\, m^{-3}\)), but also the fractional extent of condensation for each of the products. As a result, the yield of SOA from the parent HC increases as \(M_o\) increases (1). Prior work has focused on the SOA yield \(Y\) defined according to

\[
Y = \frac{M_o}{\Delta HC}
\]

where \(\Delta HC\, (\mu g\, m^{-3})\) is the amount of parent HC that has reacted.

In any multicomponent SOA system, condensation of a given component occurs more easily than in a single component system because the impurity of the condensed phase effectively lowers the volatility of the compound. The use of gas/particle (G/P) partitioning theory to predict the amount of SOA that forms from a given parent organic compound therefore requires a compound-by-compound identification and quantification of all of the important condensable oxidation products. In part 1 of this series, Pankow et al. (2) demonstrate that good agreement can be obtained when this approach is used to predict the compound-specific laboratory SOA yield data of Yu et al. (3) and Kalberer et al. (4) for the ozone oxidation of five different parent HCs, namely \(\alpha\)-pinene, \(\beta\)-pinene, sabinene, \(\Delta^3\)-carene, and cyclohexene.

When the partitioning mechanism involves absorptive uptake, as into an SOA phase, the G/P partition coefficient \(K_p\) for each compound is given by (5, 6)

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\[ K_p = \frac{c_p(n g/\mu g)}{c_g(n g/m^3)} = \frac{F/TSP}{A} = \frac{760RT f_{om}}{10^6 MW_{om} \zeta p_0^o} \]  

where \( c_p(n g/\mu g) \) is the concentration in the particle phase; \( c_g(n g/m^3) \) is the concentration in the gas phase; \( F(n g/m^3) \) is the total suspended PM concentration; \( R(m^3/atm mol^{-1} K^{-1}) \) is the ideal gas constant; \( T(K) \) is the temperature; \( f_{om} \) is the weight fraction of the TSP that comprises the absorbing organic material (om) phase; \( MW_{om}(g/mol) \) is the number average molecular weight of the absorbing om phase; \( \zeta \) is the activity coefficient; and \( p_0^o \) (Torr) is the saturation vapor pressure of the compound as a liquid (sub-cooled if the compound is a solid at ambient temperature). Each \( \zeta \) is a function of the composition of the aerosol mixture and the temperature; each \( p_0^o \) is a strong function of the temperature.

Since water is ubiquitous in the atmosphere, ambient particles very frequently include some liquid water, and in the case of particles containing SOA, the water will affect \( f_{om}, MW_{om}, \) the amount of PM, and the values of all of the \( \zeta \). Thus, the extent of partitioning of any individual organic compound into a liquid aerosol phase therefore can depend not only on the amounts and properties of the organic compounds in the phase, but also on the amount of water present. Consequently, predicting the effects of water on the atmospheric G/P distributions of organic compounds is central to understanding atmospheric SOA formation. Indeed, as the relative humidity (RH) changes, an organic aerosol will take up or lose water in such a manner as to maintain the activity of water in the condensed phase equal to that represented by the RH. As RH increases, some of the partitioning organic compounds will be drawn more extensively into the aerosol phase; portions of some of the more hydrophobic compounds may be driven out of the aerosol phase and back into the gas phase.

Just as the partitioning of organic compounds to organic aerosols is affected by the amount of water present, so too will the partitioning of water to such aerosols be affected by the amounts and properties of the organic compounds in the aerosols. In samples taken in rural airsheds, Saxena et al. (7) concluded that the amount of water present was larger than could be accounted for based on equilibrium with the inorganic components of the aerosol alone. As a result, Saxena and Hildemann (8) examined available aerosol composition data and concluded that the organic compounds that will be most affected by water in atmospheric aerosols are compounds that possess multiple oxygen-containing groups (i.e., multiple alcohols, ketones, aldehydes, and acids, and combinations thereof). The potential roles of organic compounds such as citric, malic, and succinic acids have been considered by predicting water uptake by these individual compounds (9).

While the majority of laboratory investigations of SOA formation have been carried out in the absence of significant water, Edney et al. (10) have measured the effect of varying amounts of water on the amount of SOA formed from the oxidation of toluene in the presence of ammonium sulfate seed aerosol, and Cocker et al. (11, 12) report on the effect of RH on SOA formed from the oxidation of α-pinene, m-xylene, and 1,3,5-trimethylbenzene with and without seed aerosol. In their experiments, Edney et al. (10) concluded that varying RH did not affect the amount of SOA that formed from the oxidation of toluene. Cocker et al. (11, 12) found that varying the RH affected the total mass of SOA condensed with each of the three parent HCs that they studied, though for the two aromatic HCs an effect of RH was only observed after the SOA had aged somewhat, presumably undergoing further oxidation with concomitant changes in the amounts and properties of the condensed compounds. We conclude that a compound-specific view of the SOA formation process that considers the complexity of multiple-condensing compounds is needed to adequately understand the coupled behavior of water and partitioning organic compounds in SOA systems.

Since an SOA phase can contain water, if \( M_o(\mu g/m^3) \) is the organic-only portion of SOA concentration, then we define \( M_i(\mu g/m^3) \) as the total SOA concentration with

\[ M_i = M_o + M_w \]  

where \( M_w(\mu g/m^3) \) is the water-only portion of the aerosol concentration. When SOA forms in the presence of water, we therefore provide the following definitions of yield:

\[ Y_o = \frac{M_o}{\Delta HC} \]  
\[ Y_w = \frac{M_w}{\Delta HC} \]  
\[ Y_t = \frac{M_i}{\Delta HC} = Y_o + Y_w \]

This study will focus on the same five systems studied by Yu et al. (3) and Kalberer et al. (4) that were considered earlier (2). Our continued interest in those studies stems from the fact that much of the SOA mass formed in those systems was identified. In the present study, we predict SOA formation in those systems as a function of hypothetically added RH. In this context, we note that Yu et al. (3) and Kalberer et al. (4) both utilized an aerosol of ammonium sulfate as a seed upon which SOA was allowed to condense. The predictions of SOA formation made here as a function of RH therefore apply solely to the organic portions of the Yu et al. (3) and Kalberer et al. (4) SOA, with no ammonium sulfate seed present.

The specific goals of the current work are to gain an understanding of how increases in RH affect (1) overall SOA yields, (2) water uptake by SOA, (3) the behaviors of individual oxidation products relative to one another, and (4) the fundamental physical properties of the SOA phase that in turn drive either the uptake or outgassing of each of the oxidation products. The oxidation products that have been identified in the five systems exhibit many of the molecular characteristics common to SOA systems. Thus, the results obtained here are expected to be a useful guide to how SOA systems will respond in general to changes in RH. A direct comparison of these calculated water uptake results with actual laboratory SOA formation data would require systematic laboratory measurements of RH-dependent SOA yields in the absence of inorganic seed aerosol. Such SOA particle formation will occur by homogeneous nucleation, with the resulting aerosols being mixtures of organic compounds and water only. However, systematic SOA formation experiments with detailed G/P molecular speciation have not been carried out in the absence of seed aerosol for the five systems of interest here. Overall SOA yields as a function of \( M_o \) have, nevertheless, been recently measured at selected RH values in the α-pinene-ozone system by Cocker et al. (11, 12), and those results will be discussed further below.

We begin with a brief review of the product distributions measured in the five dry systems considered earlier (2). We next give an overview of the model used to calculate multi-
Summary of Gas/SOA Distributions in Five RH = 0% Systems

General, RH = 0%. In Pankow et al. (2), we considered the formation of SOA at RH = 0% from five different parent HCs. For each of several of those parent HCs, we modeled the results from multiple different experimental runs. In this paper, we select one representative experiment for each of the parent HCs for detailed consideration. The structures and mean carbon oxidation states for the products formed are given in Table 1. The measured SOA yield results from refs 3 and 4 are summarized in Table 2 for the five experiments along with the corresponding predicted model results from ref 2.

“Product X” for each case in Tables 1 and 2 represents the sum of all products that either (1) could not be fully chemically identified or (2) could not be fully represented using the existing UNIFAC structural groups. (All of the compounds in the second category were minor constituents of the SOA phase.) Because all of the components of an SOA phase will affect the total SOA mass, the values of each of the components were used in our previous work (2) it was necessary to select a specific compound type for product X for the SOA formed from each of the parent HCs. This was done based on the partial information that was available on the compositions of the compounds assigned to compound X (2). We also note that (1) since a single exact structure for compound X could not be assigned for any of the five cases, it was not possible to assign a single vapor pressure and (2) the goal in ref 2 was to focus on the G/P partitioning of the identified products, and to match the predicted overall partitioning to the total measured concentration of SOA. Therefore, in those calculations, the amount of product X in the SOA phase could be fixed at the measured amount by giving it a very low value of $p_L^0$; any additional amount in the gas phase did not matter.

For each of the examples in Table 2, the three most abundant product types account for 70–92% of the total measured SOA mass. In the four monoterpene systems, 55–78% of the SOA mass was found to be composed of oxo-acid and diacid products. The cyclohexene system was the only system found to produce a hydroxy-diacid, and in Table 2 cyclohexene case, the diacids and hydroxy-diacids accounted for 83% of the total measured SOA mass formed.

For the higher vapor pressure compounds, Yu et al. (3) and Kalberer et al. (4) generally reported larger measured amounts in the SOA phase than were predicted by the model results of Pankow et al. (2). As we have discussed (2), this may have been the result of positive artifacts from the denuder sampling method used to make the SOA phase measurements. The possibility that this artifact affected the data is not problematic for this current work because those more volatile compounds did not contribute significantly to the measured total SOA concentration, and the major goal here is to predict the extent to which, and the reasons why, adding RH can affect the overall amount of SOA formed from the five parent HCs of interest.

α-Pinene, RH = 0%. For the α-pinene-ozone case in Table 2a, four of the five product types account for 93% of the total measured SOA mass: three oxo-acids (37%); two diacids (23%); one hydroxy-acid (18%); and one hydroxy-oxo-aldehyde (16%). For this system, the model predicts significantly more oxo-acid products in the SOA phase relative to the hydroxy-oxo-aldehydes. As in the other monoterpene systems, the measured total (G+P) amount of oxo-acids exceeds that of the hydroxy-acids. Although the oxo-acids exhibit higher $p_L^0$ values than do the hydroxy-acids, the amounts of the oxo-acids produced from the parent α-pinene are larger.

β-Pinene, RH = 0%. For the β-pinene-ozone system case in Table 2a, three of the four product types account for 91% of the total measured SOA mass: three oxo-acids (44%); two diacids (31%); and one hydroxy-oxo product (17%). Although the $p_L^0$ value of the hydroxy-oxo product is relatively large, its UNIFAC predicted vapor pressure is too high to allow a significant amount to condense into the aerosol.

Sabinene, RH = 0%. For the sabinene-ozone system in Table 2a, four of the six product types account for 95% of the total measured SOA mass: two hydroxy-acids (40%); three diacids (29%); one hydroxy-oxo product (15%); and one oxo product (12%). The measured composition of the SOA phase is somewhat different from the predicted composition. For example, the diacids are predicted to be 61% of the SOA mass, and the hydroxy-oxo and oxo products, because of their large $p_L^0$ values, are predicted to together account for only about 0.2% of the SOA mass.

Δ3-Carene, RH = 0%. For the Δ3-carene-ozone system in Table 2a, four of the seven product types account for 92% of the total SOA mass: three oxo-acids (61%); two diacids (17%); one hydroxy-acid (8%); and one oxo-aldehyde (6%). Because of their large $p_L^0$ values, the model predicted that the oxo-acid products would actually comprise less than 1% of the total SOA mass.

Cyclohexene, RH = 0%. For the cyclohexene-ozone system in Table 2b, four of the six product types account for 95% of the total SOA mass: two hydroxy-diacids (66%); five diacids (17%); three oxo-acids (9%); and one hydroxy-aldehyde product (4%).

Organic-Water Gas/Particle SOA Equilibrium Model

The underlying mathematical formalism and computational procedure that can be used to calculate the amounts of the individual compounds in the SOA phase were originally described by Pankow (6) and discussed again in Pankow et al. (2). Briefly, the method solves the matrix equation representation of a multicomponent G/P distribution, where each partitioning compound satisfies its own version of eq 2.

The governing matrix equation relates the individual mass concentrations of the compounds in the aerosol phase, $F_i$, to the total concentrations, $T_i$, and has the form

$$
\begin{pmatrix}
\frac{F_{i,guess}}{T_i} \\
\frac{F_{i}}{T_i} \\
\end{pmatrix}
= \begin{pmatrix}
\left( \frac{p_L^0}{p_P} \right)^6 & 0 \\
0 & \left( \frac{p_L^0}{p_P} \right)^6 \\
\end{pmatrix}
\begin{pmatrix}
\frac{p_L^0}{p_P} & 0 \\
0 & \frac{p_L^0}{p_P} \\
\end{pmatrix}
\begin{pmatrix}
\frac{m_{i,guess}}{M_i} \\
\frac{m_i}{M_i} \\
\end{pmatrix}
$$

(7)

where each $K_{p,aim} = K_{f,aim}$. For a given guess value $M_{i,guess}$ and measured vector $T$, Pankow et al. (2) discuss (1) how eq 7 can be solved iteratively to yield a corresponding vector $F$ and (2) the fact that the resulting vector $F$ does not necessarily satisfy the relationship

$$
\sum_i F_i = 1000 M_{i,guess}
$$

(8)

Thus, finding the desired (i.e. equilibrium) vector of SOA concentrations $F$ can be achieved iteratively by choosing...
<table>
<thead>
<tr>
<th>Compound</th>
<th>( \overline{C} )</th>
<th>Structure</th>
<th>Parent HC</th>
<th>Compound</th>
<th>( \overline{C} )</th>
<th>Structure</th>
<th>Parent HC</th>
</tr>
</thead>
<tbody>
<tr>
<td>norpinic acid</td>
<td>-0.5</td>
<td></td>
<td>( \alpha, \beta )</td>
<td>norsabinic acid</td>
<td>-0.5</td>
<td></td>
<td>s</td>
</tr>
<tr>
<td>pinic acid</td>
<td>-0.7</td>
<td></td>
<td>( \alpha, \beta, s, \Delta )</td>
<td>sabinic acid</td>
<td>-0.7</td>
<td></td>
<td>s</td>
</tr>
<tr>
<td>hydroxy pinonic acid</td>
<td>-0.8</td>
<td></td>
<td>( \alpha, \beta )</td>
<td>( S_0 ) (1-(2-isopropyl)-2-formyl-cyclopropyl-methanoic acid)</td>
<td>-0.8</td>
<td></td>
<td>s</td>
</tr>
<tr>
<td>norpinonic acid and isomers</td>
<td>-0.9</td>
<td></td>
<td>( \alpha, \beta )</td>
<td>( S_{10} ) (1-(2-isopropyl)-3-(1-oxo-2-hydroxy-ethyl)-cyclopropyl-ethanoic acid)</td>
<td>-0.8</td>
<td></td>
<td>s</td>
</tr>
<tr>
<td>pinonic acid</td>
<td>-1.0</td>
<td></td>
<td>( \alpha, \beta )</td>
<td>norsabinonic acid and isomers</td>
<td>-0.9</td>
<td></td>
<td>s</td>
</tr>
<tr>
<td>X (in the ( \alpha )-pinene and ( \beta )-pinene systems)</td>
<td>-1.0</td>
<td></td>
<td>( \alpha, \beta )</td>
<td>X (in the sabinene system)</td>
<td>-0.9</td>
<td></td>
<td>s</td>
</tr>
<tr>
<td>hydroxy pinonaldehydes</td>
<td>-1.0</td>
<td></td>
<td>( \alpha )</td>
<td>hydroxy sabina ketones</td>
<td>-1.1</td>
<td></td>
<td>s</td>
</tr>
<tr>
<td>norpinonaldehyde</td>
<td>-1.1</td>
<td></td>
<td>( \alpha )</td>
<td>sabina ketone</td>
<td>-1.3</td>
<td></td>
<td>s</td>
</tr>
<tr>
<td>pinonaldehyde</td>
<td>-1.2</td>
<td></td>
<td>( \alpha )</td>
<td>( C_4 ) (2-hydroxy-4-oxo-butanoic acid)</td>
<td>0.5</td>
<td></td>
<td>( \Delta )</td>
</tr>
<tr>
<td>hydroxy norpinonic acid</td>
<td>-0.7</td>
<td></td>
<td>( \beta )</td>
<td>3-caric acid</td>
<td>-0.7</td>
<td></td>
<td>( \Delta )</td>
</tr>
<tr>
<td>hydroxy pina ketone</td>
<td>-1.1</td>
<td></td>
<td>( \beta )</td>
<td>hydroxy-3-caronic acid</td>
<td>-0.8</td>
<td></td>
<td>( \Delta )</td>
</tr>
<tr>
<td>nor-3-caronic acid and isomers</td>
<td>-0.9</td>
<td></td>
<td>( \Delta )</td>
<td>2-hydroxy-adipic acid</td>
<td>0.0</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>3-caronic acid</td>
<td>-1.0</td>
<td></td>
<td>( \Delta )</td>
<td>glutaric acid</td>
<td>0.0</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>X (in the ( \Delta^3 )-carene system)</td>
<td>-1.0</td>
<td></td>
<td>( \Delta )</td>
<td>4-oxo-butanoic acid</td>
<td>0.0</td>
<td></td>
<td>c</td>
</tr>
</tbody>
</table>
successive $M_{tl,guess}$ values, obtaining successive $\mathbf{F}$ solutions, and thereby minimizing the variable $e$:

$$
e = \sum_{i=1}^{n} F_i - 1000 M_{tl,guess}$$  \hspace{1cm} (9)

to within some small tolerance of zero.

Pankow et al. (2) solved eq 7 for given measured total concentrations $T_i$ (ng m$^{-3}$) of different series of partitioning organic compounds. The same procedure was used here for each of the five cases by considering water to be a component like all the others. To step through a range of final equilibrium RH values, the total amount of water $T_w$ was stepped through a range of values, and eq 7 was solved for each, thereby yielding all of the equilibrium gas and particle concentrations as a function of RH at the temperature of interest. These calculations utilized the same $p_L$ values, product X designations and amounts, and UNIFAC-based method for predicting composition-dependent SOA-phase organic $\xi$ values as employed earlier (2). Because few thermodynamic data are available for water in organic liquids systems at the low-RH end of the composition range, UNIFAC was also used to compute the composition-dependent $\xi$ values for water. Finally, as before (2), we assumed a one-phase SOA system, in this case with $f_{om} = 1$ so that

$$
f_{omTSP} = TSP = M_t$$  \hspace{1cm} (10)

As noted above, in prior work (2), we considered product X to be nonvolatile so that the model would exactly reproduce the amount of X found in the SOA phase. The fact that some of the compounds making up each X might have been capable of G/P exchange was not a problem. In the presence of water, locking the G/P distribution of product X has the potential to be problematic because the nature of each SOA phase can vary depending on the value of RH, and product X, like all other compounds, will change the position of its G/P equilibrium. The greater the degree that product X contributes to the SOA phase of interest, the greater the underestimation of the RH effect as computed here. In the discussions below, we focus primarily on two experiments (one $\alpha$-pinene-O$_3$ and one cyclohexene-O$_3$) in which the amounts of product X invoked were either zero or less than 7%, and so the product X ºlockº is not problematic. In the $\Delta^3$-carene experiment summarized in Table 2a, however, product X comprised

| Compound | $\bar{C}$ | Structure | Parent HC$^b$ | Compound | $\bar{C}$ | Structure | Parent HC$^b$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>hydroxy caronaldehydes</td>
<td>-1.0</td>
<td><img src="image1" alt="Structure" /></td>
<td>$\Delta$</td>
<td>adipic acid</td>
<td>-0.3</td>
<td><img src="image2" alt="Structure" /></td>
<td>c</td>
</tr>
<tr>
<td>caronaldehyde</td>
<td>-1.2</td>
<td><img src="image3" alt="Structure" /></td>
<td>$\Delta$</td>
<td>5-oxo-pentanoic acid</td>
<td>-0.4</td>
<td><img src="image4" alt="Structure" /></td>
<td>c</td>
</tr>
<tr>
<td>C$_8$ (2,6-dimethyl-4-heptanone)</td>
<td>-1.8</td>
<td><img src="image5" alt="Structure" /></td>
<td>$\Delta$</td>
<td>1,4-butanedia</td>
<td>-0.5</td>
<td><img src="image6" alt="Structure" /></td>
<td>c</td>
</tr>
<tr>
<td>oxalic acid</td>
<td>3.0</td>
<td><img src="image7" alt="Structure" /></td>
<td>c</td>
<td>6-oxo-hexanoic acid</td>
<td>-0.7</td>
<td><img src="image8" alt="Structure" /></td>
<td>c</td>
</tr>
<tr>
<td>malonic acid</td>
<td>1.3</td>
<td><img src="image9" alt="Structure" /></td>
<td>c</td>
<td>2-hydroxy-pentanoic acid</td>
<td>-0.8</td>
<td><img src="image10" alt="Structure" /></td>
<td>c</td>
</tr>
<tr>
<td>succinic acid</td>
<td>0.5</td>
<td><img src="image11" alt="Structure" /></td>
<td>c</td>
<td>glutaraldehyde</td>
<td>-0.8</td>
<td><img src="image12" alt="Structure" /></td>
<td>c</td>
</tr>
<tr>
<td>X (in the cyclohexene system)</td>
<td>0.5</td>
<td><img src="image13" alt="Structure" /></td>
<td>c</td>
<td>adipaldehyde</td>
<td>-1.0</td>
<td><img src="image14" alt="Structure" /></td>
<td>c</td>
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<tr>
<td>2-hydroxy-glutaric acid</td>
<td>0.4</td>
<td><img src="image15" alt="Structure" /></td>
<td>c</td>
<td>4-hydroxy-butyraldehyde</td>
<td>-1.0</td>
<td><img src="image16" alt="Structure" /></td>
<td>c</td>
</tr>
</tbody>
</table>

$^a$ For each organic product, the mean carbon oxidation state $\bar{C}$ was computed as the average oxidation state for all the carbon atoms in the molecule. Each $\bar{C}$ was computed as usual by assigning each pair of electrons in each covalent bond to the more electronegative element. In the compounds of interest here, this convention leads to oxidation states for hydrogen and oxygen of H(+1.0) and O(-2.0), respectively. For a neutral organic molecule, the result is $\bar{C} = \frac{\sum n_i \times (+1.0) + n_o \times (-2.0)}{n_C}$, where $n_h$, $n_o$, and $n_c$ are the numbers of hydrogens, oxygens, and carbons in the molecule. $^b$ $\alpha$ = $\alpha$-pinene, $\beta$ = $\beta$-pinene, s = sabinene, $\Delta$ = $\Delta^3$-carene, c = cyclohexene.
### TABLE 2

(a) Product Distributions for the Four Monoterpane SOA Systems at 306–307 K and RH = 0%;
Measured Distributions Based on Yu et al. (3); Predicted Distributions Based on Pankow et al. (2)

<table>
<thead>
<tr>
<th>Product</th>
<th>( P_{(Torr)} )</th>
<th>( \alpha_{pred} )</th>
<th>% of ( M_0 )</th>
<th>( \phi \times 100% )</th>
<th>( X ) (mole fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-pinene experiment 06/17/98a, 306 K (measured ( \Delta H = 244 \mu g m^{-3} )); ( M_0 ) measured = 38.8 ( \mu g m^{-3} ); ( M_0 ) predicted = 40.2 ( \mu g m^{-3} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydroxy-o xo-acid (OH-CO-COOH)</td>
<td>2.03 ( \times 10^{-6} )</td>
<td>0.0397</td>
<td>17.7</td>
<td>16.5</td>
<td>56.8</td>
</tr>
<tr>
<td>hydroxy pinonic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \beta )-pinene experiment 06/11/98b, 307 K (measured ( \Delta H = 421 \mu g m^{-3} )); ( M_0 ) measured = 18.9 ( \mu g m^{-3} ); ( M_0 ) predicted = 40.4 ( \mu g m^{-3} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydroxy-o xo-acid (OH-CO-COOH)</td>
<td>2.03 ( \times 10^{-6} )</td>
<td>0.0554</td>
<td>5.6</td>
<td>3.8</td>
<td>39.5</td>
</tr>
<tr>
<td>hydroxy pinonic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \gamma )-sabinene experiment 06/15/98a, 306 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydroxy pininic acid</td>
<td>2.10 ( \times 10^{-6} )</td>
<td>0.0661</td>
<td>22.2</td>
<td>28.1</td>
<td>50.9</td>
</tr>
<tr>
<td>norpinic acid</td>
<td>7.50 ( \times 10^{-6} )</td>
<td>0.0012</td>
<td>0.3</td>
<td>0.3</td>
<td>55.6</td>
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<tr>
<td>o xo-acid (CO-COOH)</td>
<td>8.17 ( \times 10^{-6} )</td>
<td>0.1129</td>
<td>19.4</td>
<td>24.1</td>
<td>22.2</td>
</tr>
<tr>
<td>X</td>
<td>1.00 ( \times 10^{-12} )</td>
<td>0.0167</td>
<td>6.8</td>
<td>7.3</td>
<td>100.0</td>
</tr>
<tr>
<td>pinonic acid</td>
<td>2.22 ( \times 10^{-6} )</td>
<td>0.0568</td>
<td>10.3</td>
<td>22.8</td>
<td>16.5</td>
</tr>
<tr>
<td>norpinonic acid and isomers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydroxy-o xo-aldehyde (OH-CO-CHO)</td>
<td>2.29 ( \times 10^{-4} )</td>
<td>0.0762</td>
<td>15.9</td>
<td>0.9</td>
<td>17.9</td>
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<tr>
<td>hydroxy pinonaldehydes</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>pinonaldehyde</td>
<td>4.63 ( \times 10^{-2} )</td>
<td>0.1458</td>
<td>6.3</td>
<td>0.007</td>
<td>4.7</td>
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<tr>
<td>norpinonaldehyde</td>
<td>1.74 ( \times 10^{-1} )</td>
<td>0.0208</td>
<td>1.1</td>
<td>0.0003</td>
<td>7.7</td>
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<tr>
<td>sabinene experiment 06/15/98a, 306 K (measured ( \Delta H = 501 \mu g m^{-3} )); ( M_0 ) measured = 17.6 ( \mu g m^{-3} ); ( M_0 ) predicted = 11.7 ( \mu g m^{-3} )</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>hydroxy-o xo-acid (OH-CO-COOH)</td>
<td>2.03 ( \times 10^{-6} )</td>
<td>0.0021</td>
<td>0.8</td>
<td>3.6</td>
<td>14.3</td>
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<tr>
<td>isopropyl)-3-(1-iso- propyl)-3-(1-oxo-2-hydroxy-ethyl)-cyclopropyl- ethanoic acid</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>diacid (COOH-COOH)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta^3 )-carene experiment 06/15/98b, 306 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydroxy-o xo-acid (OH-CO-COOH)</td>
<td>2.03 ( \times 10^{-6} )</td>
<td>0.0162</td>
<td>7.7</td>
<td>12.0</td>
<td>59.5</td>
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<tr>
<td>hydroxy pininic acid</td>
<td></td>
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</tr>
<tr>
<td>( \Delta^3 )-carene experiment 06/15/98b, 306 K (measured ( \Delta H = 485 \mu g m^{-3} )); ( M_0 ) measured = 63.3 ( \mu g m^{-3} ); ( M_0 ) predicted = 44.9 ( \mu g m^{-3} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydroxy-o xo-acid (OH-CO-COOH)</td>
<td>4.77 ( \times 10^{-3} )</td>
<td>0.0061</td>
<td>4.1</td>
<td>0.0002</td>
<td>55.7</td>
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<tr>
<td>3-caric acid</td>
<td>5.38 ( \times 10^{-2} )</td>
<td>0.0433</td>
<td>1.9</td>
<td>0.004</td>
<td>6.0</td>
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<tr>
<td>hydroxy carbonaldehydes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>o xo-aldehyde (CO-CHO)</td>
<td>2.97 ( \times 10^{3} )</td>
<td>0.1050</td>
<td>6.4</td>
<td>0.0001</td>
<td>7.9</td>
</tr>
<tr>
<td>hydroxy carbonaldehyde</td>
<td>3.02 ( \times 10^{3} )</td>
<td>0.0261</td>
<td>1.9</td>
<td>0.00002</td>
<td>9.4</td>
</tr>
<tr>
<td>(2,6-dimethyl-4-heptanone)</td>
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</table>

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TABLE 2 (Continued)

Product Predictions for M_o, M_w, and M_t (µg m^-3) for Five SOA Formation Experiments

<table>
<thead>
<tr>
<th>parent hydrocarbon (HC)</th>
<th>0%</th>
<th>20%</th>
<th>40%</th>
<th>60%</th>
<th>80%</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-pinenel, 06/17/98a</td>
<td>40.2</td>
<td>0</td>
<td>40.2</td>
<td>42.7</td>
<td>0.5</td>
</tr>
<tr>
<td>β-pinenel, 06/11/98b</td>
<td>40.4</td>
<td>0</td>
<td>40.4</td>
<td>44.3</td>
<td>0.5</td>
</tr>
<tr>
<td>sabinenel, 06/15/98a</td>
<td>11.1</td>
<td>0</td>
<td>11.1</td>
<td>14.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Δ₃-carenel, 06/15/98b</td>
<td>44.9</td>
<td>0</td>
<td>44.9</td>
<td>45.7</td>
<td>0.5</td>
</tr>
<tr>
<td>cyclohexene, 05/19/99b</td>
<td>43.3</td>
<td>0</td>
<td>43.3</td>
<td>48.6</td>
<td>1.5</td>
</tr>
</tbody>
</table>

* Taken from Pankow et al. (2).

TABLE 3. Model Predictions for M_o, M_w, and M_t (µg m^-3) for Five SOA Formation Experiments

<table>
<thead>
<tr>
<th>Product</th>
<th>Predicted % of M_o</th>
<th>Predicted % of M_w</th>
<th>Predicted % of M_t</th>
<th>Measured % of M_o</th>
<th>Measured % of M_w</th>
<th>Measured % of M_t</th>
</tr>
</thead>
</table>

(a) Predicted Values Based on Concentration Data

- 2-hydroxy-adipic acid: 0.102
- 2-hydroxy-glutaric acid: 0.000
- Adipic acid: 0.000
- Glutaric acid: 0.000
- Malonic acid: 0.000
- Oxalic acid: 0.000
- 3-carene: 0.000
- Pinene: 0.000
- Sabinene: 0.000
- Cyclohexene: 0.000

(b) Predicted Values Based on Mass Balance

- 2-hydroxy-adipic acid: 0.102
- 2-hydroxy-glutaric acid: 0.000
- Adipic acid: 0.000
- Glutaric acid: 0.000
- Malonic acid: 0.000
- Oxalic acid: 0.000
- 3-carene: 0.000
- Pinene: 0.000
- Sabinene: 0.000
- Cyclohexene: 0.000

Almost 40% of the SOA phase at RH = 0%, and so the computed effects of the hypothetically added RH for the Δ₃-carene case are necessarily underestimated.

**Predicted Gas/Aerosol Distributions in Five SOA Systems as a Function of RH**

**General Results.** The RH-added calculations were carried out from RH = 0% to near 100%. (The RH = 0% values correspond to results presented earlier (2).) As noted above, for all of the calculations, it was assumed that only one SOA phase was present across the entire RH range. This assumption was examined by verifying that $\alpha < 1$ for each compound over the entire RH range, where $\alpha$ is mole fraction. This is a necessary, though not sufficient, condition for maintenance of a single phase. It is necessary because as soon as $\alpha = 1$ for any component, a pure phase of that component becomes stable at equilibrium. It is not sufficient, however, because it does not rule out the possibility of two impure phases in equilibrium with one another, as happens for example when two compounds reach their solubility limits in another. Nevertheless, we note that for all of the organic compounds, $\alpha < 0.6$ over the entire RH range. Of course for water, when RH approached 100%, $\alpha$ did approach 1 for all five cases.

For each of the five cases in Table 2, increasing the RH caused monotonic increases in $M_o$, $M_w$, and $M_t$. Adding RH to these systems is therefore predicted to uniformly increase both the amount of condensed organic mass, and the amount of condensed water (Table 3). SOA yields as measured by $Y_o$, $Y_w$, and $Y_t$ are therefore predicted to depend in a significant manner on RH for these parent HCs, and for a fixed value of ΔHC. Significantly more SOA can form in the presence of water than when RH = 0%.

All of the monoterpenes results were similar; Figure 1 presents the $\alpha$-pinene case. Figure 2 presents the cyclohexene case. The effect of increasing RH is predicted to be much stronger for the SOA produced from cyclohexene as the parent HC as compared to the effect on SOA from the four monoterpenes. We ascribe this result to the greater general degree of oxidation (and therefore hydrophilicity) in the products from cyclohexene as compared to the products from the monoterpenes. In fact, some numerical difficulties were encountered in completing the predictions for the cyclohexene system at RH values near 100% because of convergence problems due to the large water uptake in that region. (The mean carbon oxidation state (C) at RH = 0% is +0.01.)
for the SOA from cyclohexene as compared to −1.0 for the SOA from α-pinene.]

Compound-by-compound views of the results of the simulations are presented in Figures 3 and 4 for the α-pinene and cyclohexene cases. These figures present the percentage of each compound that is present in the aerosol phase as a function of RH. Only the products that exhibit \( \phi \geq 100 \% \) over a portion of the RH range are considered. (None of the compounds making up a significant fraction of \( M_o \) was thereby excluded from the figures.) The least volatile compounds in Figures 3 and 4 give the largest values of \( \phi \), and the most volatile compounds give the lowest values of \( \phi \). For all compounds in all five cases, \( \phi \) is greater at RH near 100% than at RH = 0%, although very high RH values are predicted to cause downturns in \( \phi \) for some compounds as RH nears 100% (e.g., adipaldehyde in Figure 4).

A consideration of the effect of compound volatility on \( \phi \) leads to the following three conclusions: (1) the \( \phi \) values of very low p_L value compounds will not be sensitive to changes in RH because high proportions in the SOA phase are not easily affected by changes in \( K_{p,om} \); (2) the \( \phi \) values of very high p_L value compounds may be subject to significant changes with RH, but the low proportion of such compounds in the SOA phase means that those compounds will have only small effects on \( M_o \) and \( M_w \) due to changes in RH; and (3) the \( \phi \) values of intermediate p_L value compounds will be subject to significant changes with RH and will contribute the most to changes in \( M_o \) and \( M_w \) due to changes in RH.

An examination of eq 2 indicates that increases in the F/A ratio (as is required to produce an increase in \( \phi \)) can be accomplished by three different means: (1) a reduction in MWom; (2) a reduction in \( \zeta \); and (3) an increase in f_omTSP (=M_t). The first two means have the effect of increasing \( K_p \), and the third can be viewed as a secondary consequence of generally increased \( K_p \) values. We therefore focus on how increasing RH is predicted to affect the \( K_p \) values by affecting the underlying MWom and \( \zeta \) values.

**Effects on \( K_p \) of RH-Induced Changes in MWom and \( \zeta \).** At constant temperature and pressure, the total derivative of \( K_p \) is given by

\[
\frac{dK_p}{dMW_{om}} = \left( \frac{\partial K_p}{\partial MW_{om}} \right)_{\zeta} dMW_{om} + \left( \frac{\partial K_p}{\partial \zeta} \right)_{MW_{om}} d\zeta
\]

(12)

By eq 2,

\[
\left( \frac{\partial K_p}{\partial MW_{om}} \right)_{\zeta} = -\frac{760RTf_{om}}{10^3 p_{L_{om}} MW_{om}^2} = -\frac{K_p}{MW_{om}}
\]

(13)
and

\[
\left( \frac{\partial K_p}{\partial \zeta} \right) = \frac{-760RTf_{om}}{10^9p_{L,C}^2MW_{om}} = \frac{K_p}{\zeta}
\]  

(14)

so that

\[
dK_p = -K_p \left[ \frac{dMW_{om}}{MW_{om}} + \frac{d\zeta}{\zeta} \right]
\]  

(15)

or

\[
dK_p = -K_p \left[ d \ln MW_{om} + d \ln \zeta \right]
\]  

(16)

We therefore obtain that

\[
\frac{dK_p}{dRH} = -K_p \left[ \frac{d \ln MW_{om}}{dRH} - \frac{d \ln \zeta}{dRH} \right]
\]  

(17)

or alternatively

\[
\frac{d \ln K_p}{dRH} = -\frac{d \ln MW_{om}}{dRH} - \frac{d \ln \zeta}{dRH}
\]  

(18)

The first term in eq 17 (including the minus sign) is a measure of the RH-induced effect on $K_p$ caused by changes in $MW_{om}$, the average molecular weight of the om phase. The second term (including the minus sign) is a measure of the RH-induced effect on $K_p$ caused by changes in $\zeta$. The derivatives within these two terms were estimated by finite difference using the output from the RH-dependent model runs. The results indicate that $\frac{dK_p}{dRH}$ is positive over the entire RH range for all of the compounds considered; that is, increasing the RH leads to increases in $K_p$ and therefore an increase in the overall extent of partitioning to the aerosol.

For the cases considered, the contribution to $\frac{dK_p}{dRH}$ from the $MW_{om}$ term is always positive. This is due to the very low MW of water as compared to the MW values of the oxidation products: adding water to the SOA phase uniformly drives down the value of $MW_{om}$. Figures 5–7 show the two terms (along with the sum as given by eq 17) for three products of the oxidation of $\alpha$-pinene, namely pinic acid, pinonic acid, and hydroxy pinonic acid. Figures 8 and 9 are similar plots for oxalic acid and adipic acid, which are two products from the oxidation of cyclohexene.

The contribution to $\frac{dK_p}{dRH}$ from the $\zeta$ term is more complex than the contribution from the $MW_{om}$ term. In
particular, three behaviors can be identified. Type I: uniformly positive (that is, \( \frac{\mathrm{d} \ln \sigma}{\mathrm{d} \text{RH}} \) is uniformly \(<0\)) across the RH range (e.g., hydroxy pinonic acid in Figure 7 and oxalic acid in Figure 8). Type II: at first positive (\( \frac{\mathrm{d} \ln \sigma}{\mathrm{d} \text{RH}} < 0 \)) at low RH, then negative (\( \frac{\mathrm{d} \ln \sigma}{\mathrm{d} \text{RH}} > 0 \)) as more and more water is taken up by the SOA phase (e.g., pinic acid in Figure 5). Type III: uniformly negative (\( \frac{\mathrm{d} \ln \sigma}{\mathrm{d} \text{RH}} > 0 \)) (e.g., pinonic acid in Figure 6 and adipic acid in Figure 9). Another possible behavior, type IV (at first negative (\( \frac{\mathrm{d} \ln \sigma}{\mathrm{d} \text{RH}} > 0 \)) at low RH, then positive (\( \frac{\mathrm{d} \ln \sigma}{\mathrm{d} \text{RH}} < 0 \))) is not observed in Figures 5-9. Type I behavior is what might be expected for a more hydrophilic compound; type II behavior is what might be expected for a less hydrophilic compound.

The concept of mean carbon oxidation state may have some applicability here since hydrophilicity will tend to be correlated with this parameter (see Table 4). In general, for a series of compounds with the same number of carbon atoms, it can be expected that polarity (and therefore hydrophilicity) will increase as \( C \) increases. For example, for the SOA formed from \( \alpha \)-pinene, within the three products considered above, hydroxy pinonic acid at \( C(-0.8) \) and pinic acid at \( C(-0.7) \) have higher mean carbon oxidation states than pinonic acid at \( C(-1) \). For the SOA formed from cyclohexene, oxalic acid at \( C(+3.0) \) is considerably more oxidized than adipic acid at \( C(-0.3) \).

<table>
<thead>
<tr>
<th>compd</th>
<th>mean carbon oxidation state</th>
<th>behavior type in SOA from ( \alpha )-pinene</th>
<th>behavior type in SOA from cyclohexene</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydroxy pinonic acid</td>
<td>( C(-0.8) )</td>
<td>type I</td>
<td></td>
</tr>
<tr>
<td>pinic acid</td>
<td>( C(-0.7) )</td>
<td>type II</td>
<td></td>
</tr>
<tr>
<td>pinonic acid</td>
<td>( C(-1) )</td>
<td>type III</td>
<td></td>
</tr>
<tr>
<td>oxalic acid</td>
<td>( C(+3.0) )</td>
<td>type I</td>
<td></td>
</tr>
<tr>
<td>adipic acid</td>
<td>( C(-0.3) )</td>
<td>type III</td>
<td></td>
</tr>
</tbody>
</table>
The specific effects of RH on the values of pinonic, pinonic, and hydroxy pinonic acids in the α-pinene system are illustrated in Figure 10. For the SOA from α-pinene, the value of MW at RH = 0% is predicted to be about 183. We note here that more than half of the mass of that SOA is predicted to be made up of a combination of pinic acid (MW = 186) and norpinic acid (MW = 170). As RH increases above 0% and water is thereby added to that SOA, the value of MW decreases uniformly with a slope of about −1 (i.e., a decrease of about 1 g mol⁻¹ for every percent increase in RH). For the SOA from cyclohexene, the value of MW at RH = 0% is predicted to be about 137; more than half of the mass of that SOA is predicted to be made up of a combination of 2-hydroxyglutaric (MW = 148) and 2-hydroxyadipic acid (MW = 162). As RH increases above 0% and water is added to that SOA, MW decreases uniformly, with a slope that is again close to −1.

The specific effects of RH on the values of the five compounds in Figures 5–9 are summarized in Figure 11. The curve for each of the five compounds is labeled as exhibiting type I, II, or III behavior. Near RH = 0%, four of the five compounds exhibit predicted values that are close to 1 in the two relevant SOA mixtures (SOA from α-pinene at RH = 0% for pinonic, hydroxy pinonic, and pinic acids, and SOA at RH = 0% from cyclohexene or adipic acid). Oxalic acid was predicted to exhibit a value that lies between 1.5 and 1.0 over the entire RH range in SOA from cyclohexene. Thus, as a first approximation, we conclude that it may prove reasonable to make the assumption that ζ = 1 for many compounds making up SOA mixtures. That oxalic acid exhibits a predicted value in the SOA from cyclohexane at RH = 0% that is somewhat greater than 1 is likely a result of the fact that other, less polar compounds are predicted to dominate in that SOA at low RH. The predicted values of ζ for the two cases are presented as a function of RH in Figure 12. In the SOA from cyclohexene, the predicted value of ζ remains close to unity over the entire RH range. In the SOA from α-pinene, ζ remains within 1.6 and 1.8 over the entire RH range.

**Strength of Increasing RH in Increasing SOA Mass.** As seen in Figure 1, the dependence of M on RH is predicted to be only moderate for SOA formed at 306 K from ΔHC = 244 g m⁻³ of α-pinene. The upper x-axis in Figure 1 indicates that the same increase in M that is caused by raising RH from 0 to 50% can be effected by holding RH constant at 0% and increasing ΔHC by 13% (from 244 to 276 g m⁻³). Similar results were obtained for the three other monoterpenes considered. The effect of RH in the cyclohexene case (Figure 2) is much stronger, and a 27% increase in ΔHC (from 460 to 584 g m⁻³) is needed to obtain the same increase in M that is caused by raising RH to 50%.

A second perspective from which to consider the predicted effect of water on SOA formation may be obtained as follows. In the α-pinene system represented in Figure 1, by the time that RH = 50%, a value of M₃ of 2 μg m⁻³ equal to only 5% of the initial M₃ (40 μg m⁻³) has been absorbed by the SOA phase. This small amount of water, however, causes a 20% increase in M₃ (from 40 to 48 μg m⁻³). Thus, although the value of M₃ is relatively low at RH = 50%, its low MW allows X₃ to quickly become large enough to significantly affect MW₉.

Predictions obtained by the methods presented above can be compared with experimental results when the aerosol is a mixture of organics and water only, i.e., without any seed aerosol having been present. Of the five systems studied here, only the α-pinene–O₃ system has been investigated experimentally in the absence of seed aerosol and at RH values above zero. In particular, for these conditions, in two separate chamber-based experiments, Cocker et al. (11) observed the SOA yields at RH = 0% and 303 K. Then, using a tandem differential mobility analyzer, the growth in particle size was measured (in the presence of the gas-phase organic com-
pounds) when the RH was raised first to 50%, then to 85%. In the two experiments, the values of \( M_o \) at RH = 0% were 110 and 185 \( \mu g \) m\(^{-3}\). The growth factors observed by Cocker et al. (11) in the two experiments were not statistically different, and were found to be 1.12 and 1.30, respectively, for the two RH values (Table 5). These water uptake experiments were modeled here by first taking the \( \alpha \) values for \( \alpha \)-pinene from Table 2 and determining the values of \( \Delta H_C \) required to produce \( M_o = 110 \) and 185 \( \mu g \) m\(^{-3}\) at RH = 0% and 303 K. Since the vapor pressures of organic compounds decrease by a factor of roughly 2 for every 10 K decrease in temperature, all of the vapor pressure values for the \( \alpha \)-pinene products were reduced for these model runs by a factor of \( \sqrt{2} \) due to the 5 K difference between the Table 2 temperature and the 303 K used by Cocker et al. (11). The required \( \Delta H_C \) values to achieve \( M_o = 110 \) and 185 \( \mu g \) m\(^{-3}\) at RH = 0% and 303 K were determined to be 519 and 784 \( \mu g \) m\(^{-3}\), respectively. The corresponding predicted growth factors for the two hypothetically added RH values are given in Table 5. The agreement at RH = 50% is very good, but the model underpredicts the observed growth factor at RH = 85%. It is significant to note that the predicted growth factors at both RH values are slightly less in the system with the larger organic concentration. This is a result of the fact that a larger \( M_o \) value will make the SOA phase less hydrophilic: a larger \( M_o \) value allows larger amounts of more volatile and therefore less polar products to condense. Given the uncertainties inherent in measured and predicted growth factors, the agreement in Table 5 is encouraging.

**Final Comments.** The five systems investigated here are characterized by products of ozone oxidation that are likely to be generally representative of those formed in various SOA systems of interest. The products studied reflect relevant ranges in both carbon oxidation state and vapor pressure. In the five systems, the predicted increases with increasing RH in the organic portion of the SOA yield are principally attributable to the water-uptake-related decrease in average molecular weight of the absorbing organic/water phase. This effect is expected to be a general characteristic of SOA systems. The effect of RH on organic compound activity coefficients is more complex, as well as compound dependent, and depends on the specific molecular nature of each compound of interest. Nevertheless, in the five systems investigated here, the predicted activity coefficient values for the dominant organic compounds in the SOA phases studied were not found to deviate considerably (within a factor of 1.5) from unity over the entire range of RH. If that finding extends to other organic aerosols of interest, it may be a source of significant simplification for efforts to describe SOA formation in models of atmospheric aerosols.

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**Literature Cited**


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