MATHEMATICAL MODEL FOR GAS–PARTICLE PARTITIONING OF SECONDARY ORGANIC AEROSOLS

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Abstract—A dynamic model is developed for gas–particle absorptive partitioning of semi-volatile organic aerosols. The model is applied to simulate a pair of m-xylene/NOx outdoor smog chamber experiments. In the presence of an inorganic seed aerosol a threshold for aerosol formation is predicted. An examination of characteristic times suggests conditions where an assumption of instantaneous gas–particle equilibrium is justified. Semi-volatile products that are second-generation, rather than first-generation, products of a parent hydrocarbon cause a delay in aerosol formation due to the delayed rate at which the second-generation products are formed. The gas–particle accommodation coefficient is the principal transport parameter and is estimated to have a value between 1.0 and 0.1 for the m-xylene aerosol. © 1997 Elsevier Science Ltd.

Key word index: Absorption, semi-volatile organics, aerosol yields, aerosol growth

INTRODUCTION

Secondary organic aerosol formation has been identified as an important process in atmospheres where photochemical ozone formation is substantial. Over the past 20 yr smog chamber experiments have been performed to determine secondary aerosol yields for a variety of organic compounds (Grosjean, 1977; Stern et al., 1987; Grosjean and Seinfeld, 1989; Izumi and Fukuyama, 1990; Pandis et al., 1991; Wang et al., 1991a; Odum et al., 1996, 1997). Data obtained from such experiments have been incorporated into models that seek to predict ambient aerosol concentrations (Wang et al., 1991b; Pandis et al., 1992, 1993; Lurmann et al., 1997). Pandis et al. (1993) simulated changes in aerosol size and composition as primary hydrocarbons react to form condensible organic products by assuming that gas-phase products condense upon exceeding their saturation vapor pressure.

However, semi-volatile compounds do partition into the aerosol phase at concentrations below saturation (Pankow, 1994a; Odum et al., 1996, 1997). In this work we present a model for gas–particle partitioning of secondary organic aerosols that incorporates both equilibrium partitioning and full dynamic transport to simulate aerosol formation and growth.

Our goal is to develop a model of sufficient generality to be used as a component of atmospheric models to predict formation of secondary organic aerosols. We seek to address a number of key questions concerning the formation and gas–particle partitioning of secondary organic aerosols: (1) When can the assumption of instantaneous gas–particle equilibrium be invoked? (2) How do observed aerosol yields depend on whether first- or second-generation photooxidation products comprise the condensible species? (3) Under what conditions might homogeneous nucleation of a condensible vapor product be expected to occur? The exact chemical pathways to secondary organic aerosol for most parent hydrocarbons are still uncertain, and because of the large number of compounds identified in those mixtures for which molecular speciation information is available, it is unlikely that all the

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paths of formation of organic aerosol will be elucidated. The generality of gas–particle partitioning theory, however, offers a framework within which secondary organic aerosol formation can be represented without requiring detailed mechanistic knowledge of the photooxidation paths. It is the properties of that theory that we explore here to address the questions posed above.

CONDENSABLE VAPOR FORMATION

A general representation of the chemical process of organic aerosol formation is that semi-volatile organic gases, \( S_1, S_2, \ldots \), are formed by the gas-phase reaction of a parent hydrocarbon, HC, with OH radicals,

\[
HC + OH \xrightarrow{k_{OH}} \ldots + x_1 S_1 + x_2 S_2 + \ldots \tag{1a}
\]

where \( k_{OH} \) is the reaction rate constant, and \( x_1, x_2, \ldots \) are the stoichiometric product coefficients. If the parent hydrocarbon is an alkene, reactions with \( O_3 \) and \( NO_3 \) radicals are also possible, providing additional pathways for condensable vapor formation,

\[
HC + O_3 \xrightarrow{k_{O_3}} \ldots + x_{1, O_3} S_{1, O_3} + x_{2, O_3} S_{2, O_3} + \ldots \tag{1b}
\]

\[
HC + NO_3 \xrightarrow{k_{NO_3}} \ldots + x_{2, NO_3} S_{2, NO_3} + \ldots \tag{1c}
\]

The first-generation products, \( S_1, S_2, \ldots \) may subsequently undergo reaction themselves creating second-generation condensable products, \( S_{1e}, S_{1b}, \ldots \) and \( S_{2e}, S_{2b}, \ldots \).

\[
S_1 + OH \xrightarrow{k_{OH,S_1}} \ldots + x_{1e} S_{1e} + x_{1b} S_{1b} + \ldots \tag{2a}
\]

\[
S_2 + OH \xrightarrow{k_{OH,S_2}} \ldots + x_{2e} S_{2e} + x_{2b} S_{2b} + \ldots \tag{2b}
\]

where \( k_{OH,S_1} \) and \( k_{OH,S_2} \) are the OH radical reaction rate constants for the products, \( S_1 \) and \( S_2 \), respectively.

Once semi-volatile products have been formed, partitioning to aerosol particles will occur. The distribution of organic species between the gas phase and aerosol particles of various sizes depends on both equilibrium and transport considerations.

GAS–PARTICLE EQUILIBRIUM

Equilibrium gas–particle absorptive partitioning of a semi-volatile organic species \( i \) between the gas phase and an organic phase is described by

\[
p_i = \frac{y_i \gamma_i}{\phi_i} \tag{3}
\]

where \( p_i \) (torr) is the gas-phase partial pressure of species \( i \), \( y_i \) is the mole fraction of species \( i \) in the aerosol phase, \( \gamma_i \) is the activity coefficient of species \( i \) in the aerosol-phase organic mixture, and \( p_i^0 \) (torr) is the vapor pressure of pure species \( i \). The gas-phase partial pressure, \( p_i \), can be converted to the gas-phase mass concentration, \( G_i \) (\( \mu g \) m\(^{-3}\)), by the relationship

\[
G_i = \frac{p_i m_w}{RT} \quad 10^6 \tag{4}
\]

where \( m_w \) (g mol\(^{-1}\)) is the mean molecular weight of the absorbing organic matter, \( R \) \(( = 6.2 \times 10^{-2} \text{ torr m}^2 \text{ mol}^{-1} \text{ K}^{-1}) \) is the ideal gas constant and \( T \) (K) is temperature. The factor \( 10^6 \) accomplishes the appropriate unit conversions. For organic species with similar molecular weights, the aerosol mole fraction, \( y_i \), is given by

\[
y_i = \frac{A_i}{\sum A_k + M_{\text{init}}} \tag{5}
\]

where \( A_i \) (\( \mu g \) m\(^{-3}\)) is the aerosol mass concentration of species \( i \), \( \sum A_k \) (\( \mu g \) m\(^{-3}\)) is the total aerosol mass concentration of all the individual semi-volatile organic species, \( A_k \), and \( M_{\text{init}} \) represents any initially present absorbing organic mass.

Equations (4) and (5) can be substituted into equation (3) and rearranged to yield

\[
\frac{A_i}{\sum A_k + M_{\text{init}}} = \frac{RT}{m_w \gamma_i \phi_i} 10^{-6} = K_i \tag{6}
\]

where \( K_i \) (m\(^3\) \( \mu g^{-1} \)) is defined as the absorption partitioning coefficient of species \( i \) (Pankow, 1994a, b; Odum et al., 1996). The absorption partitioning coefficient incorporates vapor pressure, activity coefficient and molecular weight, providing a single equilibrium parameter for each compound. \( K_i \) is analogous to a Henry's law coefficient in relating gas-phase concentrations of species \( i \) to the mass fraction of species \( i \) in the aerosol phase.

Upon rearrangement, equation (6) can be used to determine the gas-phase concentration of species \( i \) that exists in equilibrium with the particle surface,

\[
G_i^{eq} = \frac{A_i}{K_i (\sum A_k + M_{\text{init}})} \tag{7}
\]

Thus, given a numerical value for the partitioning coefficient, \( K_i \), and the organic aerosol compositions, \( A_i \), the equilibrium vapor concentration at the particle surface may be calculated.

THRESHOLD CONCENTRATION FOR AEROSOL FORMATION

For atmospheric aerosol some amount of organic material is likely always present and \( M_{\text{init}} > 0 \). Under such conditions when a semi-volatile organic product is formed, it immediately begins to partition into the
available organic aerosol. If there is no organic aerosol initially present \((M_{\text{init}} = 0)\), however, absorption partitioning equilibrium theory predicts that a threshold will exist for aerosol formation.

For the case of no initial organic aerosol, an expression that describes gas–particle equilibrium can be derived by rearranging equation (7),

\[ G_i K_i = A_i / \sum_k A_k \]  
and summing over all semi-volatile species \(i\),

\[ \sum_i G_i K_i = \sum_i A_i / \sum_k A_k = 1 \]

The above equation defines a threshold for aerosol formation by specifying the gas-phase concentrations, \(G_i\), required for the existence of an aerosol phase. When \(\Sigma G_i K_i < 1\), this threshold has not been reached and no aerosol phase will be present. Only when gas-phase concentrations exceed the threshold, i.e., when \(\Sigma G_i K_i > 1\), will partitioning to the aerosol phase occur. Once the threshold has been surpassed, the gas and aerosol phases will maintain equilibrium such that \(\Sigma G_i K_i\) remains unity. Thus, until sufficient parent hydrocarbon has reacted to produce gas-phase concentrations that exceed the threshold no aerosol will be formed.

It should be emphasized that the existence of a distinct threshold for aerosol formation is predicted only when no absorbing organic material is initially present. While the threshold prediction is based on the assumption of purely absorptive partitioning, for inorganic or non-absorbing organic particles it is likely that partitioning occurs initially via adsorption until a sufficient organic layer can be formed to allow absorption to occur (Pankow, 1994a).

**VAPOR-PARTICLE TRANSPORT**

Transport of a condensable organic species \(i\) from the gas phase to an aerosol particle of diameter \(D_p (\mu m)\), can be described by the flux equation (Wexler and Seinfeld, 1990),

\[ J_i = \frac{2\pi D_p \lambda \tilde{c}_i (G_i - G_i^{eq})}{1 + \frac{8\lambda}{\tilde{c}_i} D_p} \]

where \(J_i (\mu g s^{-1})\) is the rate of mass transfer to the particle surface, \(\lambda (\mu m)\) is the mean free path of air, \(\tilde{c}_i (m s^{-1})\) is the mean molecular speed of species \(i\), \(G_i (\mu g m^{-3})\) is the bulk gas-phase concentration of species \(i\), \(\sigma_i (\text{dyn cm}^{-1})\) is the surface tension of species \(i\) and \(\chi_i\) is the accommodation coefficient. While the overall equilibrium partitioning between gas and aerosol phases is defined by the equilibrium relations, the resulting size distribution of the condensed semi-volatile product cannot be uniquely determined without accounting for size-dependent rates of mass transfer between the gas and aerosol phases. At small particle sizes, \(G_i^{eq}\) may be influenced by the Kelvin effect which accounts for surface curvature. This effect is ordinarily negligible (for a 20 nm diameter particle it represents only a 5% correction to \(G_i^{eq}\)) and is not included in model calculations.

**NUCLEATION**

When vapor transport rates are slow, gas-phase concentrations will increase as semi-volatile compounds build up in the gas phase. If the gas-phase concentration exceeds the saturation vapor pressure, gas to aerosol conversion can occur directly through nucleation. Classical nucleation theory (Oxtoby, 1992) predicts a nucleation rate, \(J_{\text{nucle}} (cm^{-3} s^{-1})\),

\[ J_{\text{nucle}} = \frac{(2\pi N_A)^{1/2} N_A}{\pi m_w} \left( \frac{G_i^{eq} S}{\rho (RT)^2} \right) \times \exp \left( \frac{-16 \times 10^{-21} \pi N_A (m_w)^2}{3 \rho} \frac{\sigma}{RT} \frac{1}{(\ln S)^2} \right) \]

where \(\sigma (\text{dyn cm}^{-1})\) is surface tension, \(N_A (= 6.02 \times 10^{23} \text{mol}^{-1})\) is Avogadro’s number, \(S\) is the saturation ratio and \(\rho (g \text{ cm}^{-3})\) is liquid density. The factor \(10^{-21}\) accomplishes the appropriate unit conversions. The critical cluster size for nucleation, \(n^*\), is given by

\[ g^* = \frac{32 \times 10^{-21} \pi N_A (m_w)^2}{3 \rho} \left( \frac{\sigma}{RT \ln S} \right)^3 \]

**WALL PROCESSES**

Within a smog chamber wall effects are an additional consideration. Particle deposition to the wall of a smog chamber is the net result of turbulent and Brownian diffusion and gravitational sedimentation and is a function of particle size. Particle wall losses can be described as a first-order process with a particle loss coefficient, \(\beta_p (D_p) (s^{-1})\),

\[ \frac{dN(D_p)}{dt} = -\beta_p(D_p) N(D_p) \]

where \(N(D_p) (m^{-3})\) is the number concentration of particles (assumed to be well mixed in the chamber) with diameter \(D_p\) and \(\beta_p (D_p)\) is the loss coefficient for particles with diameter \(D_p\), \(\beta_p\) can be determined theoretically (Crump and Seinfeld, 1981; McMurry and Rader, 1985) or directly from experimental measurements.

There is no evidence of appreciable partitioning of semi-volatile vapors to smog chamber walls. In addition, Storey et al. (1995) have shown that partitioning
to organic particulate matter exceeds that to an inorganic quartz surface by several orders of magnitude. The Teflon surface of a smog chamber is expected to behave similarly to the quartz surface, acting as a poor adsorption medium for organics.

CHARACTERISTIC TIME SCALES

With the basic equations governing gas–particle interaction, characteristic times for each of the above processes may be defined, as summarized in Table I. The characteristic time for semi-volatile product formation, $\tau_p$, is the time scale on which the parent hydrocarbon reacts. This time depends on the OH rate constant, $k_{OH}$, and the OH radical concentration, [OH]. Gas–particle transport is characterized by the time required for vapor diffusion to aerosol particles, $\tau_{GP}$, and is governed by particle number, size, and accommodation coefficient. $\tau_{PW}$ is the characteristic time for particle transport to a chamber wall and depends on the particle loss coefficient, $\beta_p(D_p)$. 

Substituting appropriate values for a typical smog chamber experiment allows the relative time scales to be compared (Table I). With characteristic times on the order of a few hours, formation of semi-volatile products and particle deposition occur relatively slowly as compared to gas–particle transport, which occurs on a time scale of order 1 min. Under these conditions the gas–particle system will be very near equilibrium at all times. It should be recognized, however, that gas–particle transport times are highly dependent on particle number and diameter. It is only appropriate, therefore, to assume instantaneous gas–particle equilibrium when there is sufficient particle surface area to ensure rapid transport.

Exceptions to the assumption of instantaneous equilibrium will arise when there is very little aerosol present or when condensable vapor is formed rapidly by a fast-reacting parent hydrocarbon. For example, an aerosol population with number concentration $500 \text{ cm}^{-3}$ and mean diameter 50 nm results in a gas–particle transport time on the order of 2 h. A parent hydrocarbon, such as d-limonene, with an OH rate constant of $2 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, and an OH concentration of $7 \times 10^6 \text{ molec cm}^{-3}$, results in a characteristic time for semi-volatile product formation, $\tau_p$, of only 10 min. It should be noted, however, that a prolonged state of non-equilibrium for the semi-volatile product is unlikely. Small particles grow quickly resulting in a greatly increased surface area and more rapid gas/particle transport. In extreme cases, where semi-volatile products exceed saturation in the gas phase, nucleation will occur, creating new particles that increase surface area and accelerate transport.

MODEL IMPLEMENTATION

In the study of secondary organic aerosol formation, typically smog chambers are initially filled with a mixture of NO$_x$, inorganic seed particles, and an aerosol-producing hydrocarbon. The chamber is then exposed to sunlight, or other UV sources, that initiates photooxidation. As the hydrocarbon reacts it forms semi-volatile products that condense on the seed particles. When transport to the particles is slower than the rate of product formation, the semi-volatile products will accumulate in the gas phase and nucleation may occur.

In a simulation of experiments conducted in the Caltech outdoor smog chamber that we will present, gas-phase chemistry is described by the SAPRC90 chemical mechanism (Carter, 1990). The mechanism predicts OH concentrations within the chamber and the resulting OH-reaction rate of the hydrocarbon and its products. Time, date, and location allow one to determine the appropriate actinic flux. Reaction mechanisms for individual hydrocarbons have been modified to include one or more products that are designated as semi-volatile species. These first-generation products may themselves undergo reaction to form second-generation gas-phase products that can also condense. For each condensable product, absorption partitioning coefficients are specified along with estimated surface tensions. For simplicity in evaluating results, all semi-volatile organics are

<table>
<thead>
<tr>
<th>Characteristic time</th>
<th>Typical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation of condensable organic gas</td>
<td>$\tau_p = \frac{1}{k_{OH}[\text{OH}]}$</td>
</tr>
<tr>
<td>Gas–particle transport</td>
<td>$\tau_{GP} = \frac{1 + \frac{8\lambda}{\alpha D_p}}{2\pi N\lambda D_p \beta_p}$</td>
</tr>
<tr>
<td>Particle-wall transport</td>
<td>$\tau_{PW} = \frac{1}{\beta_p}$</td>
</tr>
</tbody>
</table>

Note. [OH] = $7 \times 10^6 \text{ molec cm}^{-3}$
$N = 5 \times 10^7 \text{ cm}^{-3}$, $D_p = 100 \text{ nm}$, $\alpha = 1.0$, $\beta_p = 3 \times 10^{-3} \text{ min}^{-1}$, $k_{OH} = 2 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.
assumed to have a similar molecular weight, density, and accommodation coefficient. A size-dependent particle loss coefficient is used to describe deposition losses to the chamber walls.

The size variation of the aerosol population is represented using discrete size sections. All particles in each section are assumed to have the same chemical composition which is an excellent assumption for a smog chamber. As particles grow, size changes are calculated using the moving section technique (Gelbard, 1990; Kim and Seinfeld, 1990). Specifically, the total change in the aerosol-phase concentration of species $i$, in section $j$, $A_{ij}$ ($\mu g \ m^{-3} \ s^{-1}$), is calculated by combining the flux equation (10) with the particle number concentration in section $j$, $N_j$ ($m^{-3}$),

$$\frac{dA_{ij}}{dt} = N_j 2\pi D_p \lambda \bar{c}_j (G_{ij} - G_{ij}^{eq}) \left(1 + \frac{8}{\pi} \frac{\lambda}{D_p} \right).$$

The equilibrium concentration at the particle surface, $G_{ij}^{eq}$ ($\mu g \ m^{-3}$), is size dependent and is calculated by

$$G_{ij}^{eq} = \frac{A_{ij}}{K_i^{2ns} (\sum_k A_{kj} + M_{init,j})}.$$

For smog chamber experiments, in which there is no initial organic aerosol mass, the above equation can not be used until the threshold for aerosol formation has been reached. In order to simplify the mathematical description of the model, a small amount of non-volatile absorbing organic mass (equal to 0.01% of the inorganic mass) is assumed to be present in each size section,

$$M_{init,j} = 10^{-4} \frac{N_j \pi \rho D_p^3}{6}.$$

This assumption allows equation (15) to be used even before the threshold for aerosol formation has been reached. The initial organic mass used is sufficiently small that there is no recognizable effect on gas–aerosol partitioning predictions.

The change in the gas-phase concentration of semi-volatile species $i$ is governed by

$$\frac{dG_i}{dt} = P_i - \sum_j \frac{dA_{ij}}{dt}.$$  

where $P_i$ ($\mu g \ m^{-3} \ s^{-1}$) is the rate of production of species $i$ from chemical reaction. Taken together, equations (14) and (17) comprise the set of differential equations that define gas-to-particle conversion.

When a vapor concentration exceeds its equilibrium vapor pressure, nucleation may occur. The nucleation rate is calculated with equation (11). If the nucleation rate exceeds an arbitrary threshold level of $10^{-2} \ cm^{-3} \ s^{-1}$, the nucleated particles are assigned to a new size section. The diameter of particles in the nucleation section is that of the critical nucleus size, $g^*$. These particles subsequently grow along with the initially present seed particles.

| Table 2. Initial conditions for m-xylene smog chamber experiments carried out in Pasadena, California on 4 August 1995* |

<table>
<thead>
<tr>
<th>Side A</th>
<th>Side B</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-Xylene</td>
<td>1008 ppb</td>
</tr>
<tr>
<td>Propene</td>
<td>200 ppb</td>
</tr>
<tr>
<td>NO</td>
<td>957 ppb</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>686 ppb</td>
</tr>
<tr>
<td>$N_0$</td>
<td>$9.7 \times 10^9$ cm$^{-3}$</td>
</tr>
<tr>
<td>$D_p$</td>
<td>0.1 $\mu$m</td>
</tr>
</tbody>
</table>

*Start time 9:00 am (PDT). Temperature 40 ± 5 °C.

SIMULATION OF SMOG CHAMBER EXPERIMENTS

The performance of the model can be demonstrated by simulating a set of smog chamber experiments, also illustrating the general behavior and physics involved with aerosol growth and providing a realistic scenario for examining the influence of the various equilibrium and transport parameters. We will simulate a pair of experiments performed on 4 August 1995 in the Caltech outdoor smog chamber.* The chamber was divided into two approximately 20 m$^3$ sides that were both filled with (NH$_4$)$_2$SO$_4$ seed particles and mixtures of m-xylene, propene, NO and NO$_2$. Initial conditions for both sides of the chamber are listed in Table 2. One side contained 510 ppb of m-xylene and 820 ppb NO$_x$, while the other contained 1008 ppb m-xylene and 1643 ppb NO$_x$. Both sides had similar propene concentrations, aerosol populations, and VOC/NO$_x$ ratios, so that the key difference between the two chambers was the m-xylene concentrations.

In the photooxidation of m-xylene the semi-volatile vapor species are expected to be second-generation products of the m-xylene. One compound that has been observed as a component of the organic aerosol from m-xylene is m-toluic acid (Forstner et al., 1997), which is the product of reaction of a first-generation reaction product. The m-xylene-OH reaction is assumed to produce a first-generation product, $S_1$, that reacts with OH ($k_{OH} = 6.8 \times 10^{-11}$ cm$^3$ mole$^{-1}$ s$^{-1}$) to form two semi-volatile second-generation products, $S_{1a}$ and $S_{1b}$.

The condensable vapors $S_{1a}$ and $S_{1b}$ are not intended to represent specific products of the m-xylene photooxidation, and the parameters used in the simulation are those found to best fit the experimental data. The products are generated with stoichiometric coefficients, $x_{1a}$ and $x_{1b}$, of 0.03 and 0.14, respectively.

* The model includes 74 gas-phase species, with up to six condensable organic species that partition between the gas and aerosol phases. The aerosol population is represented by 39 size sections with 23 for initially present seed particles, 15 for nucleation size sections and 1 section to track aerosol mass deposited to the chamber walls.
Absorption partitioning coefficients, $K_{1a}$ and $K_{1b}$ for $S_{1a}$ and $S_{1b}$ were set at 0.06 m$^3$ µg$^{-1}$ and 0.002 m$^3$ µg$^{-1}$. These values for the stoichiometric and partitioning coefficients are close to those estimated by Odum et al. (1996) from a series of m-xylene experiments.

Molecular weight, $m_w$, of 150, density, $\rho$, of 1.5 g cm$^{-3}$, and surface tension, $\sigma$, of 25 dyne cm$^{-1}$ were assumed for both semi-volatile products as representative of typical aromatic products. The accommodation coefficient for particles was set at 0.2 to fit the experimental observations. The size dependence of the particle deposition loss coefficient, $\beta_p(D_p)$, was based on theoretical predictions for Teflon-walled chambers (McMurry and Rader, 1985) with the absolute value scaled to match observed particle losses. A summary of the parameters used to simulate the two experiments is given in Table 3.

Figure 1 compares the simulations of aerosol growth with experimental observations for Side A. In Fig. 1a the simulated particle number concentration steadily declines as particles are lost to the chamber walls; this behavior matches that observed since the particle wall deposition rate was adjusted to fit the data. More importantly, the predicted aerosol volume matches the experimental observations. For the first hour no noticeable aerosol growth occurs and aerosol volume decreases due to deposition. During the next two hours aerosol volume increases from approximately 30 to 250 µm$^3$ cm$^{-3}$ as semi-volatile product deposits on the seed particles. After 3 h aerosol volume levels off and begins to decrease as growth slows while deposition continues.

The evolving aerosol size distribution is simulated closely (Fig. 1b). Initially, when growth is small, the distribution moves only slightly to larger particle diameters and the peak height decreases as a result of deposition. As growth begins, the size distribution shifts to larger diameters, the peak height increases, and the distribution exhibits the characteristic narrowing as small particles grow faster than larger particles. Near the end of the experiment when growth slows, the peak height of the distribution decreases again due to deposition.

![Fig. 1. Simulated and observed aerosol growth for the 1008 ppb m-xylene experiment. (a) Particle number concentration (cm$^{-3}$) and volume concentration (µm$^3$ cm$^{-3}$) as a function of reaction time (min). (b) Particle size distributions at various times.](image)

Table 3. Partitioning and transport parameters for m-xylene smog chamber simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_1$</td>
<td>0.03$^a$</td>
</tr>
<tr>
<td>$X_2$</td>
<td>0.14$^a$</td>
</tr>
<tr>
<td>$K_1$</td>
<td>0.06 m$^3$ µg$^{-1}$</td>
</tr>
<tr>
<td>$K_2$</td>
<td>0.002 m$^3$ µg$^{-1}$</td>
</tr>
<tr>
<td>$m_w$</td>
<td>1.50$^b$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>1.5 g cm$^{-3}$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>25 dyne cm$^{-1}$</td>
</tr>
<tr>
<td>$k_{OM}$</td>
<td>6.8 x 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$z$</td>
<td>0.2$^c$</td>
</tr>
</tbody>
</table>

$^a$ Based on estimates for m-xylene (Odum et al., 1996).
$^b$ Assumed values for organic aerosol.
$^c$ Adjusted to fit experimental results.

Similar results for the Side B experiment are shown in Fig. 2. As with the Side A experiment, total aerosol volume (Fig. 2a) initially decreases, then undergoes a period of growth, achieves a maximum value and ultimately decreases. The size distributions in Fig. 2b also exhibit these periods dominated by particle deposition and aerosol growth. Maximum aerosol growth for the 1008 ppb side, 220 µm$^3$ cm$^{-3}$, is about a factor of 4 higher than that for the 510 ppb side, 50 µm$^3$ cm$^{-3}$, as a result of the larger production of semi-volatile products and the shift in the gas-particle partitioning equilibrium as more organic aerosol is formed. Model predictions fit the observed experimental data quite well.

In both the 510 and 1008 ppb m-xylene simulations, the same set of equilibrium and transport parameters was used. The ability of the model to accurately reproduce total aerosol mass and aerosol size distributions for both experiments suggests that these parameters provide a meaningful representation of secondary organic aerosol formation from m-xylene. These parameters may not be applicable, however, to all m-xylene systems as under different reaction conditions, i.e. temperature, reactant concentrations, VOC/NOx ratio, etc., the system chemistry and equilibrium will...
The sensitivity of the model to the various equilibrium and transport parameters will be determined by varying the values of key parameters. In so doing we seek to examine the qualitative nature of gas-particle partitioning and answer the following questions: (1) How do the absorption partitioning coefficients influence the equilibrium aerosol yield? (2) What changes in the timing of aerosol growth and overall aerosol yield are expected when the semi-volatile organics are second-generation, instead of first-generation, products? (3) Which parameters most directly control the rate of mass transfer between the gas and aerosol phases? (4) Under what conditions can equilibrium be assumed and when is nucleation expected to occur?

Reaction conditions and parameters from the 1008 ppb m-xylene experiment (see Tables 2 and 3) are used with a few modifications as a base case scenario. In order to distinguish between transport and equilibrium related delays in aerosol growth the condensing organic compounds used in the base case, $S_1$ and $S_2$, are first-generation, as opposed to second-generation, photooxidation products of m-xylene. Second-generation products cause a delay in aerosol growth in addition to those associated with slow mass transfer and the predicted equilibrium threshold. First-generation products, therefore, are used in the base case, eliminating kinetic related delays. The particle accommodation coefficient, $\beta$, is assumed unity to ensure equilibrium conditions for the base case. Finally, the particle loss coefficient, $\gamma_p(D_p)$, is zero to remove the effect of particle deposition and thereby represent ambient atmospheric conditions more clearly.

Concentrations of the two semi-volatile products, $S_1$ and $S_2$, in both the gas-phase, $G_1$ and $G_2$, and the aerosol phase, $A_1$ and $A_2$, are shown in Fig. 3, for the base case simulation. $S_1$ is the less volatile of the two products with an absorption partitioning coefficient of 0.06 m$^3$ µg$^{-1}$, compared to 0.002 m$^3$ µg$^{-1}$ for $S_2$. $S_2$ however is produced in greater abundance than $S_1$ with stoichiometric production rates of 0.03 and 0.14 for $S_1$ and $S_2$, respectively. Initially the gas-phase concentrations, $G_1$ and $G_2$, increase linearly, with no aerosol partitioning. Then after approximately 0.08 ppm of hydrocarbon has reacted, aerosol growth ensues, dominated at first by the lower volatility product, $S_1$, and later by the more volatile and more abundant $S_2$. When aerosol growth begins, the vapor concentration, $G_1$, of the lower volatility product $S_1$ reaches a maximum and slowly declines to a steady value, while $G_2$ continues to increase but eventually also approaches a steady concentration.

Partitioning of the individual semi-volatile products is shown in Fig. 4a and b. The heavy solid line in each figure represents the total amount of semi-volatile product formed and increases linearly with a slope equal to the stoichiometric coefficient. The dashed line shows the equilibrium aerosol concentration. The area below this line represents the aerosol phase, while the area above the dashed line represents
the gas phase. Below the threshold of 0.08 ppm hydrocarbon reacted, virtually no aerosol phase exists and almost all of the semi-volatile product is found in the gas phase. Once the threshold is exceeded aerosol concentrations increase. For the lower volatility product, $S_1$, partitioning occurs quite readily and as $\Delta HC$ increases most of $S_1$ is found in the aerosol phase. The more volatile product, $S_2$, remains in the gas phase longer and as an aerosol phase, composed primarily of $S_1$, builds up does $S_2$ undergo significant partitioning.

Aerosol formation by a reacting hydrocarbon can be described in terms of an aerosol yield, $Y$ ($\mu g \ m^{-3} \ ppm^{-1}$) (Grosjean and Seinfeld, 1989; Odum et al., 1996),

$$Y = \sum_{i} \frac{A_i}{\Delta HC} = \sum_{i} \frac{x_i \ K_i \ (\sum_k A_k + M_{\text{inh}})}{1 + K_i \ (\sum_k A_k + M_{\text{inh}})} \quad (18)$$

where $\Sigma A_i$ ($\mu g \ m^{-3}$) is the total organic mass in the aerosol phase generated from the parent hydrocarbon and $\Delta HC$ ($\mu g \ m^{-3}$) is the amount of the parent hydrocarbon that has reacted. The aerosol yield is most meaningful when it represents equilibrium conditions for first-generation products of the parent hydrocar-

bon. As indicated previously, gas–aerosol transport in the base case scenario for the $m$-xylene experiments is sufficiently rapid to assume equilibrium conditions at all times during the smog chamber experiment. Figure 5 shows how the aerosol yield for the base case changes as hydrocarbon continues to react. The yield is dependent on the amount of organic mass present into which semi-volatile gases may be absorbed. When little hydrocarbon has reacted, and little semi-volatile product has been formed, the yield is negligible, but as more hydrocarbon reacts and organic aerosol forms, partitioning equilibrium shifts to the aerosol phase and yields increase.

It is important to distinguish between aerosol yield, $Y$, and stoichiometric coefficients, $x_i$. Stoichiometric coefficients depend on the gas-phase chemical mechanism and are assumed constant; they represent the total amount of semi-volatile product formed, in both gas and aerosol phases, per amount of parent hydrocarbon reacted. The yield, on the other hand, which measures only the semi-volatile product that has partitioned into the aerosol phase, is not constant but will vary depending on the amount of organic mass available as an absorption medium. Stoichiometric coefficients by themselves are therefore not sufficient to predict the amount of aerosol formation. Partitioning coefficients, and organic aerosol mass are also required to determine the correct aerosol concentrations and yields.

**Effect of absorption partitioning coefficient**

The effect of the values of the absorption partitioning coefficients, $K_1$ and $K_2$, on the equilibrium aerosol yield is presented in Figure 6. When both $K_1$ and $K_2$ are large ($10^{-1} \ m^3 \ mu g^{-1}$), the yield curve is composed of two distinct regions. At higher organic mass concentrations, the yield is more or less constant, while at low organic mass the curve appears initially to increase linearly from zero. Large partitioning coefficients are indicative of relatively low volatility products with an equilibrium that favors the aerosol phase.
As long as there is organic aerosol mass into which the semi-volatile product may be absorbed, virtually all of it will partition into the aerosol phase. The asymptotic aerosol yield seen at high organic mass values represents the maximum yield based on complete gas-to-particle conversion. At low organic mass concentrations, gas- and aerosol-phase concentrations are comparable and the aerosol yield depends directly on the amount of organic mass available as an absorption medium.

For intermediate volatility products ($K_1 = K_2 = 10^{-2} \text{ m}^3 \mu\text{g}^{-1}$), the transition between the two regions is less sharp and at high organic mass the yield is still increasing. In this case, equilibrium is shifted more to the gas phase relative to the large $K$ case and at equal organic mass concentrations, less of the condensable product is found in the aerosol phase. At higher volatility ($K_1 = K_2 = 10^{-3} \text{ m}^3 \mu\text{g}^{-1}$), nearly linear behavior is observed for the organic mass levels shown. Here the gas–particle equilibrium favors the gas phase and most of the condensable product remains as a vapor. When $K_1$ and $K_2$ differ ($K_1 = 10^{-1} \text{ m}^3 \mu\text{g}^{-1}, K_2 = 10^{-3} \text{ m}^3 \mu\text{g}^{-1}$) the resulting yield curve is simply an additive combination of the individual values, weighted by the stoichiometric coefficients for each species.

Given experimentally determined yield data, partitioning and stoichiometric coefficients for a parent hydrocarbon can be evaluated by fitting the theory to the data (Odum et al., 1996, 1997). The resulting parameters are, however, strictly valid only when the yield data represent equilibrium conditions. When gas–aerosol transport is slow or when condensing species are secondary products, time-dependent yields may not accurately predict these parameters. For this reason, coefficients should be estimated from yields determined at the conclusion of experimental runs when the parent hydrocarbon has finished reacting, conversion to secondary products is complete, and equilibrium between gas and aerosol phases has been attained. Coefficients determined in such a manner are extremely useful as a simplified approximation of a complex array of condensable organics most likely involved in partitioning, for which individual identification and parameter determination is not feasible.

Effect of second-generation product formation

When the semi-volatile organics are not first-generation products, $S_1$, but second-generation products resulting from OH-reaction of first-generation products, $S_{1a}$ and $S_{1b}$, as in reaction (2a), the OH rate constant of the first-generation product, $k_{OH,SI}$, becomes a controlling factor in aerosol growth. Figure 7 shows how the equilibrium aerosol concentration of the second-generation products $S_{1a}$ and $S_{1b}$ is affected by varying $k_{OH,SI}$. Gas–particle partitioning and stoichiometric coefficients for the semi-volatiles $S_{1a}$ and $S_{1b}$ are taken as the same as those used in the base case for the first-generation products $S_1$ and $S_2$. Compared to the case in which the semi-volatile products are first-generation, when the aerosol results from second-generation products a time delay of varying magnitude is exhibited, with a greater delay for smaller values of $k_{OH,SI}$. This delay is not a mass transport effect but reflects simply the slower rate at which the second-generation products are formed. Given a sufficiently fast secondary reaction, no difference would be observed in aerosol concentrations from either first- or second-generation semi-volatile products. At sufficiently long time the second-generation concentrations approach the first-generation curve.

Effect of accommodation coefficient

The accommodation coefficient, $\alpha$, is the principal transport parameter. Figure 8 demonstrates how aerosol growth is affected by the value of the accommodation coefficient. As was noted earlier, when there is sufficient initial particle surface area, mass transport from the gas to aerosol phase is rapid and conditions approach equilibrium. For $\alpha$ values exceeding 0.1,
equilibrium is achieved essentially instantaneously, but at lower values of $z$, mass transfer becomes the limiting factor in particle growth. For $z = 0.001$ and 0.003, transport is initially slowed until particle growth leads to sufficient surface area that equilibrium is eventually reached. For the case of $z = 0.001$, mass transfer is sufficiently slow that the vapor concentration of semi-volatile product $S_1$ reaches supersaturation and nucleation occurs. Upon nucleation a large number of small particles are formed that rapidly increase in surface area as they grow, actually allowing the system to reach equilibrium faster than in the $z = 0.003$ case where nucleation did not occur. This is an unexpected consequence of the effect of the accommodation process.

Effect of initial surface area

As in the case of the accommodation coefficient, initial aerosol surface area, $SA_{ini}$, has a significant effect on the rate of gas–particle partitioning. Figure 9 shows the predicted aerosol growth behavior for different initial aerosol surface areas. At high initial surface area, the system is at equilibrium at all times; for lower initial surface area, mass transport is slower, and if initial surface area is sufficiently small, semi-volatile product concentrations can accumulate to the point where nucleation will occur.

Effect of surface tension

Whereas the accommodation coefficient and initial surface area help determine when saturation levels can be reached, the surface tension of the semi-volatile product most directly controls the level of supersaturation at which nucleation will occur and the nature of the resulting nucleation burst. The lower the surface tension, the more facile is nucleation; at higher surface tension values nucleation slows considerably such that further increasing the surface tension has no observable effect. When nucleation does occur, gas–particle equilibrium may actually be reached more quickly because of the immediate addition of particle surface area, but the effect is much less dramatic than that seen for changes in accommodation coefficient or initial surface area.

Effect of molecular weight and density

The molecular weight, $m_w$, and density, $\rho$, of the semi-volatile products have no significant effect on aerosol mass concentration. Molecular weight values ranging from 100 to 300 g mol$^{-1}$ and density values between 1 and 3 g cm$^{-3}$ produce almost identical aerosol mass curves. Aerosol volumes and vapor pressures inferred from partitioning coefficients will depend directly on $\rho$ and $m_w$, but since partitioning coefficients and aerosol concentrations are both expressed in mass units, model predictions are not sensitive to the exact values used for molecular weight and density.

**SUMMARY**

A comprehensive model is presented for the dynamic process of gas–particle partitioning of semi-volatile organics generated from the oxidation of atmospheric hydrocarbons. Partitioning of the organic products is governed by gas–particle equilibrium and transport. Vapor transport to aerosol particles, nucleation and particle deposition are accounted for by the model, allowing the aerosol size distribution to be predicted both in the ambient atmosphere and in a laboratory smog chamber. When inorganic seed particles are present, gas–particle partitioning exhibits a threshold for aerosol growth. Until sufficient hydrocarbon reacts to create a concentration of condensable products that will exist in equilibrium with an organic aerosol phase, no aerosol is formed.

A set of partitioning and transport parameters have been determined that fit observed aerosol yields in two simultaneous outdoor smog chamber experiments with m-xylene. Based on the time delay for the onset of aerosol growth and the observed yield curves,
the condensing vapor species from m-xylene are predicted to be second- rather than first-generation products of the photooxidation. This conclusion is supported in part by some observed products of m-xylene oxidation.

An evaluation of the model's sensitivity to the various input parameters allows one to understand the nature of secondary organic aerosol formation and gas-particle partitioning in general. The smog chamber system is predicted to have been at gas-particle equilibrium because of the relatively high particle concentrations. The particle accommodation coefficient may also be estimated to have a value between 1.0 and 0.1. Significantly lower values would have resulted in more gradual aerosol growth, particularly initially, an effect not evident in the experimental data. Non-equilibrium conditions may arise when particle surface areas are not large enough to ensure rapid gas-particle transport (SA < 1000 µm² cm⁻³) or when the aerosol precursor is a fast-reacting hydrocarbon. Such conditions, however, are not typically expected to persist as particle growth or nucleation will increase surface area and accelerate the approach to equilibrium.

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