

# Representation of Secondary Organic Aerosol Laboratory Chamber Data for the Interpretation of Mechanisms of Particle Growth

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Absorptive models of gas-particle partitioning have been shown to be successful in describing the formation and growth of secondary organic aerosol (SOA). Here the expression for particle growth derived by Odum et al. (Odum, J. R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R. C.; Seinfeld, J. H. Gas/particle partitioning and secondary organic aerosol yields. *Environ. Sci. Technol.* **1996**, *30*, 2580–2585) is extended to facilitate interpretation of SOA growth data measured in the laboratory in terms of the underlying chemistry, even when details of the reactions are not well-constrained. A simple (one-component) expression for aerosol growth ( $\Delta M$ ) as a function of the amount of hydrocarbon reacted ( $\Delta HC$ ) is derived, and the effects of changes to three key parameters, stoichiometric yield of condensable species, gas-particle partitioning coefficient, and concentration of preexisting aerosol, are discussed. Two sets of laboratory chamber data on SOA growth are examined in this context: the ozonolysis of  $\alpha$ -pinene and the OH-initiated photooxidation of aromatic compounds. Even though these two systems have a number of significant differences, both are described well within this framework. From the shapes of the  $\Delta M$  versus  $\Delta HC$  curves in each case, the importance of poorly constrained chemistry such as heterogeneous reactions and gas-phase reactions of oxidation products is examined.

## Introduction

Secondary organic aerosol (SOA), particulate matter formed by the condensation of oxidation products of volatile organic compounds (VOCs), is known to constitute a substantial fraction of fine particulate matter in the lower atmosphere. Considerable effort has been devoted to gaining a detailed, quantitative understanding of the formation and growth of SOA in the troposphere, but this has been hampered by difficulties in identifying the individual chemical components of SOA. Even a single precursor hydrocarbon generally yields a large number of condensable products, many of which may not have been identified in laboratory studies. This lack of speciated aerosol data has made it difficult to model aerosol growth accurately from first principles using detailed treatments of gas-phase chemistry and gas-particle partitioning.

Such problems may be partly overcome by describing SOA formation not in terms of its individual components but rather in terms of total particle growth. Absorptive models of gas-particle partitioning (1–3) have been successful in describing laboratory SOA yields and in incorporating such yield measurements into atmospheric models (e.g., ref 4). Such absorptive models generally treat SOA growth as a purely microphysical process in which low-volatility, first-generation VOC oxidation products partition between the gas and absorbing particle phases.

There is now substantial evidence that SOA growth may also be influenced by heterogeneous reactions, so that the condensation of some organics may be reactive as well as absorptive. Such evidence includes the observation of increased aerosol yields under acidic conditions (5–9) and the measurement of high-MW oligomers in SOA (7–11). Although the evidence that heterogeneous reactions may contribute to SOA growth is strong, the reactions themselves remain poorly understood. The detailed chemistry (kinetics, thermodynamics, mechanism) is generally poorly constrained, and significant discrepancies exist between the results from experimental and theoretical studies (5, 12). Therefore, currently it is difficult to assess the influence of heterogeneous reactions on SOA growth quantitatively.

The gas-phase chemistry prior to gas-particle partitioning is believed, in addition, to be significantly more complicated than the formation of condensable products from a single oxidation step. For example, SOA formed in the photooxidation of aromatic hydrocarbons includes compounds such as cyclic anhydrides, organic acids, and polycarbonyls (13–16), highly oxidized compounds that probably are not produced directly in the initial reaction of the parent aromatic hydrocarbon. Instead, they are likely to be formed by photolysis or gas-phase reactions (with OH, NO<sub>3</sub>, or O<sub>3</sub>) of the first-generation products. Such chemistry is currently not well understood, and the relative importance of second-generation products (as well as third-generation products, etc.) as contributors to SOA growth is virtually unknown.

In summary, the chemistry following the initial oxidation reaction of the precursor VOC, in both the gas and particle phases, is poorly constrained, and so its role in SOA formation and growth is not clear at present. In this paper, we present a framework for the representation of laboratory SOA growth data in order to facilitate interpretation of results in terms of such underlying chemistry. This framework is based upon a simple extension of the expression derived by Odum et al. (1) for describing aerosol yield from absorptive gas-particle partitioning. Using an illustrative (one-product) form of this expression, which we show to be a reasonable approximation to the two-component solution, we focus on the dependence of aerosol growth on the concentration of the parent hydrocarbon reacted. This dependence is shown to be affected by changes in three key parameters: the stoichiometric yield of condensable species, the gas-particle partitioning coefficient, and the concentration of preexisting aerosol. We then examine two sets of experimental data on SOA growth within the context of this framework,  $\alpha$ -pinene ozonolysis and photooxidation of aromatic compounds. Although these two cases have significant differences, we show that both can be described using the same general framework outlined here.

**Partitioning Model.** The absorptive gas-particle partitioning model developed by Pankow (2, 3) has been applied to SOA formation and growth by Odum et al. (1), leading to an expression for aerosol yield ( $Y$ ), defined as the ratio of

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aerosol growth to hydrocarbon reacted:

$$Y = M \sum_i \left( \frac{\alpha_i K_i^*}{1 + K_i^* M} \right) \quad (1)$$

in which  $M$  is the mass concentration of the absorbing (aerosol) medium,  $\alpha_i$  is the (mass-based) stoichiometric coefficient for oxidation product  $i$ , and  $K_i^*$  is the gas-particle partitioning equilibrium constant for product  $i$ . We omit the “ $o$ ” subscript (denoting “organic”) used by Odum et al. (1) to indicate that the absorbing medium may also be water in the case of water-soluble compounds (17).

In writing eq 1, we do not use the absorbing equilibrium constant  $K_p$  (2) but rather a total gas-particle partitioning equilibrium constant,  $K^*$ , which may include contributions from partitioning by both physical absorption and heterogeneous chemical reaction. Although it has typically been assumed that only absorptive partitioning occurs, this assumption is not necessary for the derivation of eq 1 (1). In the simple case of only physical partitioning of a single compound between the gas and aerosol phases ( $X(g) \rightleftharpoons X(a)$ ), the absorbing equilibrium constant may be expressed as

$$K_p = \frac{C_{X(a)}}{MC_{X(g)}} \quad (2)$$

in which  $C_{X(a)}$  and  $C_{X(g)}$  are the mass concentrations of the compound in the aerosol and gas phases, respectively (2). However, if condensed species  $X(a)$  reacts further, forming species  $Y(a)$ , the gas-particle equilibrium shifts further toward the aerosol phase. The total partitioning equilibrium constant,  $K^*$ , for the system  $X(g) \rightleftharpoons X(a) \rightleftharpoons Y(a)$  may be expressed in terms of  $K_p$  (the absorbing equilibrium constant) and  $K_{rxn}$  (the equilibrium constant for  $X(a) \rightleftharpoons Y(a)$ ):

$$K^* = \frac{C_{X(a)} + C_{Y(a)}}{MC_{X(g)}} = \frac{C_{X(a)}}{MC_{X(g)}} + \frac{C_{Y(a)}}{C_{X(a)}} \frac{C_{X(a)}}{MC_{X(g)}} = K_p(1 + K_{rxn}) \quad (3)$$

For more complex chemical reactions, such as dimerization of the condensed species, such a simple expression for  $K^*$  may not exist, but even so,  $K^*$  will always be greater than  $K_p$  (as long as the products of the heterogeneous reactions are less volatile than the reactants). For the case of water-soluble compounds partitioning into aqueous particles,  $K_p$  may be replaced by  $K_H$ , Henry’s Law constant, and  $K^*$  may be replaced by  $K_H^*$ , the “effective Henry’s Law constant” (18).

Although eq 1 has proved useful for interpreting laboratory SOA yield data, the effects of heterogeneous chemistry and reactions of first-generation oxidation products on SOA growth are not immediately obvious in that relation. In addition, for laboratory studies of the gas-particle partitioning of individual hydrocarbons, aerosol yield, as defined above, is not a particularly meaningful quantity. Instead, eq 1 can be rewritten as

$$\frac{\Delta M}{\Delta HC} = (M(0) + \Delta M) \sum_i \left( \frac{\alpha_i K_i^*}{1 + K_i^* (M(0) + \Delta M)} \right) \quad (4)$$

in which yield has been replaced by  $\Delta M/\Delta HC$  (change in aerosol mass concentration divided by change in parent hydrocarbon concentration) and  $M$  by  $M(0) + \Delta M$  (preexisting aerosol mass concentration plus change in aerosol mass concentration). The preexisting aerosol mass concentration,  $M(0)$ , refers only to the fraction of particulate matter that participates in absorptive partitioning (typically organic mass, but also aqueous mass in the case of water-soluble organics)

and not to inert mass, such as solid ammonium sulfate. Equation 4 may then be solved for  $\Delta M$  for any number of condensable products  $i$ . It has been shown (1, 19–21) that laboratory data on SOA formation and growth are generally well-described when just two components are used, with one component usually significantly less volatile than the other.

The two-component form of eq 4 is cubic in  $\Delta M$  and has a very complicated solution (shown in the Supporting Information). However, the solution is substantially simpler when  $M(0) = 0$ ; that is, no absorbing aerosol is present initially, which is the case for most chamber studies of SOA formation and growth. The (physical) solution in that case is as follows:

$$\Delta M = 1/2 \left( \Delta HC(\alpha_1 + \alpha_2) - \frac{1}{K_1^*} - \frac{1}{K_2^*} \right) + \frac{\sqrt{4K_1^* K_2^* (K_1^* \alpha_1 \Delta HC + K_2^* \alpha_2 \Delta HC - 1) + (K_1^* + K_2^* - K_1^* K_2^* \Delta HC(\alpha_1 + \alpha_2))^2}}{2K_1^* K_2^*} \quad (5)$$

Although growth data may be fitted to this expression (22), it may be simplified further. As noted above, in the two-component treatment of SOA growth one component is significantly less volatile than the other. If we treat the second component (with coefficients  $K_2^*$  and  $\alpha_2$ ) as highly non-volatile, then this expression for aerosol growth may be simplified further. At high values of  $K_2^*$ , eq 5 reduces to

$$\Delta M = \frac{1}{2K_1^*} \left( K_1^* \Delta HC(\alpha_1 + \alpha_2) - 1 + \sqrt{1 + 2K_1^* \Delta HC(\alpha_2 - \alpha_1) + (K_1^* \Delta HC(\alpha_1 + \alpha_2))^2} \right) \quad (6)$$

At high values of  $\Delta HC$ ,  $\Delta M$  increases linearly with  $\Delta HC$ , with the proportionality defined by the stoichiometric coefficients ( $\alpha_1 + \alpha_2$ ), as in the one-component solution (discussed below). At low values of  $\Delta HC$ , because component 2 is assumed to partition fully into the aerosol phase, it may be approximated as the “preexisting aerosol mass”. Substituting  $\alpha_2 \Delta HC$  (the amount of component 2) in eq 6 with  $M(0)$ , we obtain

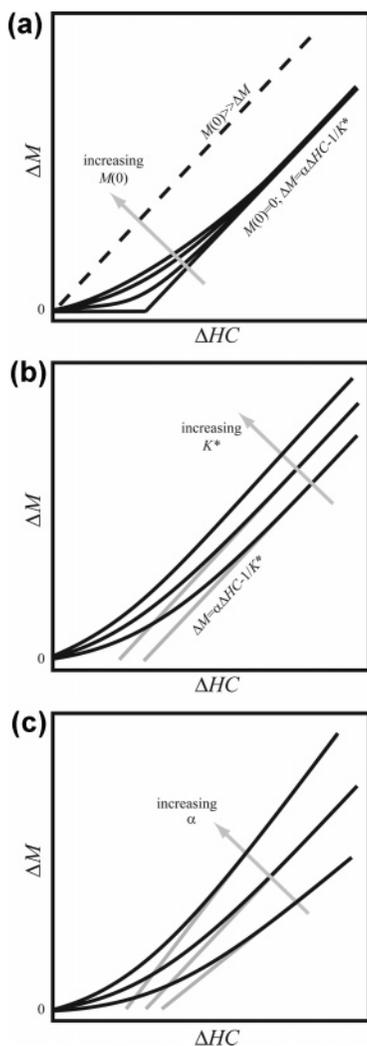
$$\Delta M = \frac{1}{2K_1^*} \left( K_1^* \alpha_1 \Delta HC + K_1^* M(0) - 1 + \sqrt{4K_1^{*2} M(0) \alpha_1 \Delta HC + (1 + K_1^* M(0) - K_1^* \alpha_1 \Delta HC)^2} \right) \quad (7)$$

This expression is very similar to the solution to the one-component form of eq 4 (in which  $M(0)$  may be nonzero):

$$\Delta M = \frac{1}{2K^*} \left( K^* \alpha \Delta HC - K^* M(0) - 1 + \sqrt{4K^{*2} M(0) \alpha_1 \Delta HC + (1 + K^* M(0) - K^* \alpha \Delta HC)^2} \right) \quad (8)$$

(for clarity, the subscript “1” has been removed). Equations 7 and 8 differ only in the sign of the  $K^* M(0)$  term, which is typically small compared to the others. Thus eq 8, the one-component solution to eq 4, serves as a reasonable approximation to the two-component solution, with the effect a second, less volatile SOA component approximated by assuming it partitions fully into the aerosol phase, thereby contributing to the constant  $M(0)$ .

Shown in Figure 1a–c are typical curves of  $\Delta M$  versus  $\Delta HC$  arising from eq 8 for a range of values of  $M(0)$ ,  $K^*$ , and  $\alpha$ . Curves of similar shape have been reported from chamber studies of SOA formation (e.g., refs 22–24) as well as from theoretical simulations of particle growth (25, 26). Plotting



**FIGURE 1. Characteristic plots of aerosol growth ( $\Delta M$ ) vs hydrocarbon reacted ( $\Delta HC$ ). (a) Effect of changes in  $M(0)$ , the concentration of preexisting absorbing medium in the aerosol phase. Dashed line is the special case where  $M(0) \gg \Delta M$ . (b) Effect of changes in  $K^*$ , the total gas-particle partitioning coefficient of the condensable oxidation product. (c) Effect of changes in  $\alpha$ , the stoichiometric yield of the condensable species. Gray lines in Figure 1b and c show limiting behavior at high  $\Delta HC$ , as described by eq 9. See text for details.**

$\Delta M$  versus  $\Delta HC$  using the exact two-component solution (eq 5) yields curves that are very similar to these. Therefore, for simplicity, when examining the dependence of aerosol growth ( $\Delta M$ ) on the amount of parent hydrocarbon reacted ( $\Delta HC$ ), we will refer to this one-component solution. Although it is not an exact description of SOA growth for two components, it captures the qualitative behavior of the two-component solution to eq 4, allowing for the interpretation of mechanisms of particle growth from experimental data.

In Figure 1a, the dependence of growth on the concentration of the preexisting absorbing (aerosol) medium,  $M(0)$ , is shown. In the absence of an initial absorbing phase ( $M(0) = 0$ ), a compound will partition into the particle phase only if its concentration is in excess of its saturation vapor pressure, as shown in the bottom rightmost curve. If  $M(0)$  is nonzero (or, in the two-component solution, if the less volatile component has partitioned strongly into the particle phase), some partitioning may occur even when the compound is formed in quantities below its equilibrium vapor pressure, as described by Pankow (2, 3). Hence, the effects of changes in  $M(0)$  are most pronounced at low values of  $\Delta HC$ , in which

condensable products are formed in subsaturated concentrations and the amount of absorbing medium present is critical for aerosol growth. At higher values of  $\Delta HC$ , in which condensable products are formed in excess of their saturation concentration, all of the condensable products formed will partition into the aerosol phase so that  $\Delta M$  depends linearly on  $\Delta HC$  and is independent of  $M(0)$ . In this case, where  $M(0) \ll \alpha \Delta HC$ , eq 8 reduces to

$$\Delta M = \alpha \Delta HC - \frac{1}{K^*} \quad (9)$$

Hence, most of the curves in Figure 1a converge at high values of  $\Delta HC$ . As discussed above, the linear dependence of  $\Delta M$  on  $\Delta HC$  at high values of  $\Delta HC$  occurs even when more than one condensable compound is formed.

In the special case where the concentration of the absorbing medium is very large relative to any aerosol growth ( $M(0) \gg \Delta M$ ), the one-component form of eq 4 instead reduces to

$$\Delta M = \frac{K^* M(0)}{1 + K^* M(0)} \alpha \Delta HC \quad (10)$$

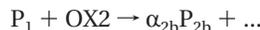
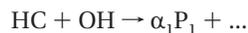
In this case, particle growth is linear with the amount of hydrocarbon reacted for all values of  $\Delta HC$ , shown as a dashed line in Figure 1a. This case is rarely valid for laboratory studies of SOA growth, as most either involve no initial aerosol or start with only inorganic (nonabsorbing) seed particles; one exception is uptake studies of water-soluble organic compounds (WSOCs) by aqueous particles (27). However, particle growth in the atmosphere may often occur under conditions in which preexisting organic aerosol concentration is large relative to  $\Delta M$  and a characteristic particle growth per amount of hydrocarbon reacted may be estimated. This characteristic growth from the oxidation of a particular hydrocarbon, or “incremental aerosol reactivity”, has been discussed in detail by Griffin et al. (28).

Shown in Figure 1b is the effect of changes in  $K^*$ , the total gas-particle partitioning coefficient of the condensing species, on aerosol growth. For a single condensable species at one temperature, the absorbing partitioning coefficient,  $K_p$ , is constant, and any changes in  $K^*$  must be a result of additional chemistry in the particle phase. Naturally, as heterogeneous reactions become increasingly important (as  $K^*$  increases), aerosol growth for a given  $\Delta HC$  increases. This continues to the limit of  $K^* = \infty$ , at which point eq 8 reduces to  $\Delta M = \alpha \Delta HC$ ; all condensable gas-phase compounds partition fully into the particle phase. Similarly, in the two-component solution (eq 5), when both  $K_1^*$  and  $K_2^*$  are large,  $\Delta M = (\alpha_1 + \alpha_2) \Delta HC$ . As in Figure 1a, at high values of  $\Delta HC$  particle growth may be approximated by eq 9 (shown as gray lines), with a simple linear dependence of  $\Delta M$  on  $\Delta HC$ . In this case, absolute growth varies with  $K^*$ , which governs the total partitioning between the gas and particle phases.

Finally, shown in Figure 1c is the effect on the  $\Delta M$  versus  $\Delta HC$  curve of changes in  $\alpha$ , the stoichiometric coefficient of condensable oxidation products. Because the total amount of condensable product formed by the parent oxidation reaction is  $\alpha \Delta HC$ , the dependence of aerosol growth on  $\alpha$  is the same as that for  $\Delta HC$ . Of course, for a given reaction, the stoichiometric yields of all of the reaction products are constant. This characteristic dependence of the  $\Delta M$  versus  $\Delta HC$  curve on different values of  $\alpha$  may therefore be useful in interpreting results from different reactions that form the same (or similar) oxidation products in varying yields, such as aromatic compounds (13).

Moreover,  $\alpha$  refers to stoichiometric coefficients of condensable products only. As described in the Introduction, noncondensing compounds may be formed first, which then

react further to form condensable ones. If changes in reaction conditions lead to significant differences in the relative importance of these further reactions, then the final product distributions may be affected. One example is the case in which a first-generation oxidation product,  $P_1$ , may undergo reactions with one of several oxidants present:

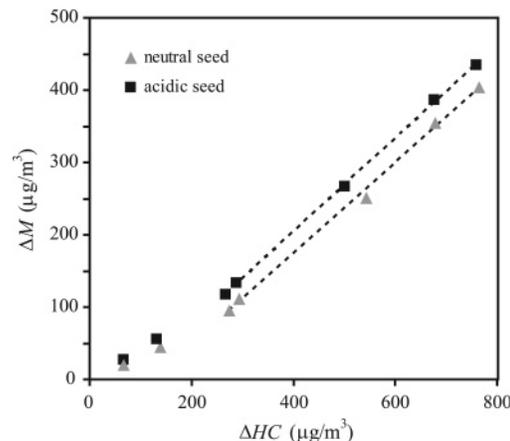


If only one of the second-generation products,  $P_{2a}$ , is condensable, then the overall yield ( $\alpha$ ) of condensable compounds depends not only on stoichiometric coefficients of the individual reactions ( $\alpha_1$  and  $\alpha_{2a}$ ) but also on the relative importance of the two possible oxidation channels of product  $P_1$ . This branching is dependent on the relative concentrations of oxidants OX1 and OX2 so that overall yield ( $\alpha$ ) and therefore particle growth may be highly dependent on specific reaction conditions. This can be the case even if the initial oxidation step is unaffected; we discuss specific examples in a later section.

We have used a simple (one-component) solution to the partitioning equation derived by Odum et al. (1) to express total organic aerosol growth ( $\Delta M$ ) as a function of the amount of parent hydrocarbon reacted ( $\Delta HC$ ). Three key parameters, the initial amount of absorbing medium in the aerosol phase ( $M(0)$ ), the total gas-particle partitioning coefficient of the condensable oxidation product ( $K^*$ ), and the stoichiometric yield of the condensable oxidation product ( $\alpha$ ), each affect the dependence of  $\Delta M$  on  $\Delta HC$  in a characteristic fashion. Although we have focused on only the one-component solution, such responses are general to two-component systems as well. From these characteristic responses, it is then possible to gain an improved mechanistic understanding of the factors that control particle growth, by plotting experimental values of  $\Delta M$  versus  $\Delta HC$  obtained with different hydrocarbons or under different reaction conditions. In the next section we use this framework to examine two sets of laboratory chamber SOA growth data. In the first set, formation of SOA from the ozonolysis of  $\alpha$ -pinene, growth is found to depend on composition of the seed aerosol; in the other, growth from the photooxidation of aromatic compounds varies with  $\text{NO}_x$  concentration. Both data sets are well described using this general framework, allowing us to examine the importance of heterogeneous chemistry and gas-phase reactions of first-generation oxidation products on SOA growth.

**Ozonolysis of  $\alpha$ -Pinene.** Gao et al. (8, 9) have presented aerosol growth data from the prototypical SOA-forming reaction of  $\alpha$ -pinene with ozone, measured over a range of  $\alpha$ -pinene concentrations and using two different seed compositions. Experiments were carried out in the dark in Caltech's dual 28-m<sup>3</sup> Teflon chambers using seed particles of different acidity: 0.03 M  $\text{MgSO}_4$  seed solution for the "neutral" experiments and 0.03 M  $\text{MgSO}_4$  + 0.05 M  $\text{H}_2\text{SO}_4$  for the "acid" experiments. The neutral and acid seeds had calculated pH values of 6.5 and -0.3, respectively (8); experiments were repeated for a range of  $\alpha$ -pinene concentrations (12–135 ppb) for both types of seed. All of the experiments were carried out at 55% relative humidity.

Experimental data, plotted as  $\Delta M$  versus  $\Delta HC$  for both seed types, are shown in Figure 2. Values for  $\Delta M$  were obtained by multiplying the total aerosol volume as measured by the DMA by an assumed density of 1.4 g/mL. Experiments were carried out over a range of initial particle mass concentrations (30–63  $\mu\text{g}/\text{m}^3$ ); no dependence of  $\Delta M$  on the initial particle mass was observed.

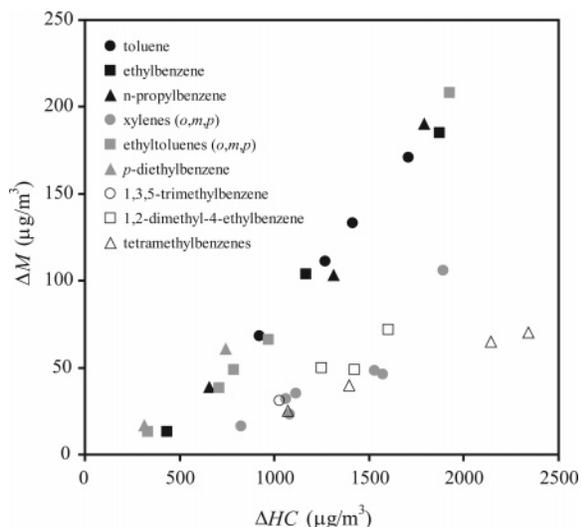


**FIGURE 2.** Aerosol growth ( $\Delta M$ ) as a function of  $\alpha$ -pinene reacted ( $\Delta HC$ ) in the  $\alpha$ -pinene + ozone reaction, for both neutral seed (gray triangles) and acidic seed (black squares). Dashed lines are linear fits to the high- $\Delta HC$  ( $>250 \mu\text{g}/\text{m}^3$ ) data.

For both the acidic and neutral seeds, the curves of SOA growth ( $\Delta M$ ) versus  $\alpha$ -pinene reacted ( $\Delta HC$ ) are of the same general form as those shown in Figure 1. For a given amount of  $\alpha$ -pinene reacted, the growth of SOA is always greater on acidic seed than on the more neutral seed, indicating a larger partitioning coefficient ( $K^*$ ); indeed the shapes of these curves are similar to those shown in Figure 1b. Because the gas-phase products of the ozonolysis reaction are independent of seed composition, equilibrium absorption coefficients ( $K_p$ 's) are the same in both cases; therefore, the greater partitioning into the aerosol phase observed with acidic seed must be a result of an increased importance of heterogeneous reactions. Iinuma et al. (7) and Gao et al. (8, 9) have observed that the proportion of high-MW (oligomeric) products in  $\alpha$ -pinene ozonolysis SOA is larger with more acidic seed, also strongly suggesting that heterogeneous reactions play a greater role in particle growth under acidic conditions.

Although the data presented in Figure 2 may be fit to eq 8, nearly as much information can be obtained by focusing on the high values of  $\Delta HC$  ( $>250 \mu\text{g}/\text{m}^3$ ). For both the neutral and acidic seed, measured values of  $\Delta M$  are linear with  $\Delta HC$ , as described by eq 9 (and illustrated in Figure 1b). Fitting just those data, we obtain fits of  $\Delta M = 0.645\Delta HC - 53.7$  for the acidic seed and  $\Delta M = 0.628\Delta HC - 77.2$  for the neutral seed. The derived values of the stoichiometric coefficients ( $\alpha$ , slopes of the lines) agree to within 3%, consistent with the fact that they should be independent of seed type. At these high values of  $\Delta HC$ , there is a constant difference in  $\Delta M$  of  $\sim 25 \mu\text{g}/\text{m}^3$  between the neutral and acidic seeds, independent of  $\Delta HC$ . This may at least partly explain the observed decrease in relative yield difference (RYD) between the two types of seed as  $\Delta HC$  increases (8). Because aerosol yield is defined as the ratio of aerosol growth to hydrocarbon reacted, a fixed difference between values of  $\Delta M$  will appear as a decreasing yield difference at increasing values of  $\Delta HC$ .

From the intercepts, equal to  $1/K^*$ , the total partitioning equilibrium coefficient,  $K^*$ , is calculated to be  $\sim 45\%$  greater with acidic seed than with neutral seed. As mentioned above, this difference most likely arises from the increased importance of heterogeneous reactions in the acidic case. However, the cause of this difference is not entirely clear, and details of the heterogeneous chemistry are poorly constrained. Reactions believed to be responsible for oligomer formation, such as aldol condensation, dehydration, and acetal/hemiacetal formation, are known to be acid-catalyzed, but this implies a difference in kinetics only. Although a difference in the rate of particle growth between the acidic and neutral



**FIGURE 3.**  $\Delta M$  vs  $\Delta HC$  for the photooxidation of a number of aromatic compounds, as measured by Odum et al. (19). Symbol color indicates level of alkyl substitution: monosubstituted (black), disubstituted (gray), or tri- and tetrasubstituted (open). In some cases, isomers are lumped together (as in the case of *o*-, *m*-, and *p*-xylenes), which accounts for much of the observed scatter for a single aromatic.

cases is indeed observed (8), a difference in total growth is observed to continue over long times, which simple differences in heterogeneous reaction rates cannot explain. The difference in total growth may arise from other factors, such as differences in ionic strength; further studies are certainly necessary.

**Photooxidation of Aromatic Compounds.** The radical-initiated oxidation of aromatic compounds, a major contributor to SOA formation in anthropogenically dominated environments, has been studied extensively in terms of both total aerosol yields (19, 22–24) and identification of individual aerosol chemical components (13–16). Typically, studies are carried out by UV irradiation of hydrocarbon/ $\text{NO}_x$  mixtures; the hydroxyl radicals formed react with the aromatic compound, initiating oxidation. Shown in Figure 3 are  $\Delta M$  versus  $\Delta HC$  curves from the photooxidation of a number of aromatic compounds, as measured by Odum et al. (19). As discussed by Odum, the aromatics clearly fall into two categories, “high yield” aromatics, singly substituted aromatics, ethyltoluenes, and *p*-diethylbenzene, and “low-yield” aromatics, xylenes and tri- and tetra-substituted benzenes. Because the data for the low-yield aromatics do not extend to very high values of  $\Delta HC$ , it is not clear from the plot whether the difference between the two classes of compounds arise from differences in formation yields ( $\alpha$ ) or partitioning coefficients ( $K^*$ ) of the condensable compounds (or some combination of the two). However, the remarkable agreement in particle growth among the various high-yield aromatics suggests that in those cases the primary condensing compounds are the same or very similar. It is not clear why structurally similar compounds such as xylene and ethyltoluene behave so differently; quantitative measurements of aerosol and gas-phase products from each parent aromatic may help in addressing this question.

The general shapes of the  $\Delta M$  versus  $\Delta HC$  curves in Figure 3 for aromatic compounds are fundamentally different from those in Figure 2 for  $\alpha$ -pinene ozonolysis. In Figure 2, particle growth is observed even at very low amounts of reacted hydrocarbon, but for most of the compounds shown in Figure 3, the curves suggest negligible aerosol growth at such low concentrations. This case is represented in Figure 1a by the  $M(0) = 0$  case (lower rightmost curve), indicating that, unlike in the case of  $\alpha$ -pinene ozonolysis, there are no highly

nonvolatile reaction products that immediately partition into the particle phase upon reaction initiation. Therefore, an organic aerosol phase into which other semivolatile compounds can partition will not form until later in the reaction, when a threshold concentration of reacted hydrocarbon has been reached.

This threshold concentration (or “latent consumption”) has been observed in other studies of photooxidation of aromatic compounds as well (22–24), as a time lag (typically an hour or more) between reaction initiation and aerosol growth. As discussed by Hurley et al. (24), such a time lag may be a result of either of two factors: all condensable products are formed in concentrations below their saturation vapor pressures, so they do not partition into the aerosol phase (this includes the less volatile compound in the two-component model), or condensable products are formed as second-generation products. Assuming the reaction conditions are constant, the latter effect is a purely kinetic one: given sufficient time, the same amount of aerosol will be formed, regardless of whether it is from condensation of first- or second-generation products (25).

Changes in reaction conditions, however, may affect the relative concentrations of different oxidants so that the gas-phase chemistry of first-generation products may be affected. For example, both Hurley et al. (24) and Song et al. (22) have shown that for the OH-initiated oxidation of aromatic compounds (toluene and *m*-xylene, respectively) aerosol yields are highly dependent on gas-phase reaction conditions, even for a fixed amount of hydrocarbon reacted and in the absence of seed particles. For a given amount of aromatic reacted, SOA growth is suppressed strongly by increased levels of  $\text{NO}_x$ . In these cases, the differences in the  $\Delta M$  versus  $\Delta HC$  curves for toluene photooxidation under low- and high- $\text{NO}_x$  conditions are consistent with changes in the stoichiometric coefficient,  $\alpha$ , with different slopes at high values of  $\Delta HC$  (as in Figure 1c). As described in a previous section, the stoichiometric yields may vary if changes in reaction conditions affect the branching ratios in multistep reaction mechanisms.

This is likely to be the case when  $[\text{NO}_x]$  is varied in chamber studies of SOA growth by UV irradiation of hydrocarbon mixtures. As discussed by Hurley et al. (24), changes in  $[\text{NO}_x]$  affect the relative concentrations of oxidants OH,  $\text{NO}_3$ , and  $\text{O}_3$ : high  $\text{NO}_x$  levels would tend to increase  $\text{NO}_3$  and suppress ozone (and, under some conditions, OH). The chemistry of first-generation oxidation products is poorly understood, but if they react with ozone (or OH) to produce a greater amount of condensable product than is formed in the reaction with the nitrate radical, particle growth should be greater at lower  $\text{NO}_x$  concentrations, which is consistent with observations. Song et al. (22) showed that increased ozone or nitrate radical concentrations alone cannot explain the observed changes in SOA yields; therefore aerosol growth from first-generation oxidation products may be governed by a complex competition between reaction with those oxidants, reaction with OH, and photolysis. An alternate (though similar) possibility is that  $\text{NO}_x$  concentration controls the fate of peroxy radical intermediates by changing the branching between reaction with NO and reaction with  $\text{HO}_2$  or  $\text{RO}_2$ . Reaction with NO produces mostly alkoxy radicals, which may decompose to smaller (and more volatile) compounds, whereas reaction with  $\text{HO}_2$  or  $\text{RO}_2$  may form acids, peracids, peroxides, and alcohols, which may partition efficiently into the aerosol phase. In this case, the “first-generation products” are not the first set of molecular oxidation products but rather the peroxy radical intermediates formed from the initial OH-aromatic reaction.

In either case, stoichiometric yields ( $\alpha$ ) may change with reaction conditions when particle formation occurs via condensation of second-generation oxidation products. This

will not be the case if condensable products are purely first-generation: aromatic compounds are unreactive toward ozone and NO<sub>3</sub> (29), so loss of hydrocarbon ( $\Delta HC$ ) is a result of reaction with OH only. Therefore, if only first-generation oxidation products were condensable, the stoichiometric coefficient ( $\alpha$ ) would be independent of radical concentration.

It should be noted that in this case  $\alpha$  refers to the overall yield for an entire reaction mechanism rather than for a single step. Although studies of hydrocarbon oxidation over a wide range of experimental conditions may allow for the quantification of this overall yield for different radical concentrations, the use of stoichiometric yields for single reactions, which do not rely on a particular set of reaction conditions, would be ideal. This requires a better understanding of the chemistry of the first-generation reaction products; in particular, laboratory studies of particle growth from the reaction of such compounds with single oxidants would be very useful. Although such studies may be possible for relatively stable, isolable compounds identified as intermediates in VOC oxidation, in many cases the first-generation oxidation products cannot be isolated easily, or have not yet been identified. In these cases, in which stoichiometric coefficients can only be determined from the oxidation of the precursor VOC, it is especially important that experiments are carried out using HC/NO<sub>x</sub> ratios and photon fluxes as close to tropospheric levels as possible.

Because we are currently not able to study (or even in some cases identify) many of the relevant intermediates and products in SOA formation, accurate modeling of the explicit chemistry leading to particle formation and growth is not yet possible. Simplified models of gas-particle partitioning, such as the Odum/Pankow partitioning model (1–3), are therefore necessary for describing laboratory growth data and applying them to atmospheric models. We have expanded this treatment so that it not only describes aerosol growth as a function of the amount of hydrocarbon reacted but also provides insight into the underlying chemistry of SOA formation. In particular, the importance of heterogeneous chemistry and further reactions of oxidation products may be assessed using this framework. The effects of such reactions often cannot be distinguished using the standard yield curve approach (22); however, such chemistry is currently not understood well enough for the explicit inclusion into full chemical models of SOA formation and growth. The approach described in this work allows for a better understanding of the contributions of such reactions, even when details of the reactions remain poorly constrained. We note that for this approach to be useful, SOA growth experiments need to be carried out over a wide range of hydrocarbon concentrations. Although time-dependent measurements of  $\Delta M$  versus  $\Delta HC$  over the course of a single aerosol growth experiment (22–24) might be sufficient, this requires that the gas-phase chemistry of oxidation products goes to completion (and gas-particle partitioning equilibrium is reached) nearly instantaneously. Further work on the kinetics of these processes is necessary to establish whether applying the equilibrium approach described here to time-dependent data is appropriate.

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## Supporting Information Available

Two-component solution to eq 4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Literature Cited

- (1) Odum, J. R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R. C.; Seinfeld, J. H. Gas/particle partitioning and secondary organic aerosol yields. *Environ. Sci. Technol.* **1996**, *30*, 2580–2585.
- (2) Pankow, J. F. An absorption-model of gas-particle partitioning of organic-compounds in the atmosphere. *Atmos. Environ.* **1994**, *28A*, 185–188.
- (3) Pankow, J. F. An absorption-model of the gas aerosol partitioning involved in the formation of secondary organic aerosol. *Atmos. Environ.* **1994**, *28A*, 189–193.
- (4) Chung, S. H.; Seinfeld, J. H. Global distribution and climate forcing of carbonaceous aerosols. *J. Geophys. Res.* **2002**, *107*, 4407, doi10.1029/2001JD001397.
- (5) Jang, M.; Kamens, R. M. Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst. *Environ. Sci. Technol.* **2001**, *35*, 4758–4766.
- (6) Jang, M.; Czoschke, N. M.; Lee, S.; Kamens, R. M. Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions. *Science* **2002**, *298*, 814–817.
- (7) Iinuma, Y.; Böge, O.; Gnauk, T.; Herrmann, H. Aerosol-chamber study of the  $\alpha$ -pinene/O<sub>3</sub> reaction: influence of particle acidity on aerosol yields and products. *Atmos. Environ.* **2004**, *38*, 761–773.
- (8) Gao, S.; Ng, N. L.; Keywood, M.; Varutbangkul, V.; Bahreini, R.; Nenes, A.; He, J.; Yoo, K. Y.; Beauchamp, J. L.; Hodyss, R. P.; Flagan, R. C.; Seinfeld, J. H. Particle phase acidity and oligomer formation in secondary organic aerosol. *Environ. Sci. Technol.* **2004**, *38*, 6582–6589.
- (9) Gao, S.; Keywood, M.; Ng, N. L.; Surratt, J.; Varutbangkul, V.; Bahreini, R.; Flagan, R. C.; Seinfeld, J. H. Low-molecular weight and oligomeric components in secondary organic aerosol from the ozonolysis of cycloalkenes and  $\alpha$ -pinene. *J. Phys. Chem. A* **2004**, *108*, 10147–10164.
- (10) Kalberer, M.; Paulsen, S.; Sax, M.; Steinbacher, M.; Dommen, J.; Prevot, A. S. H.; Fisseha, R.; Weingartner, E.; Frankevich, V.; Zenobi, R.; Baltensperger, U. Identification of polymers as major components of atmospheric organic aerosols. *Science* **2004**, *303*, 1659–1662.
- (11) Tolocka, M. P.; Jang, M.; Ginter, J. M.; Cox, F. J.; Kamens, R. M.; Johnston, M. V. Formation of oligomers in secondary organic aerosol. *Environ. Sci. Technol.* **2004**, *38*, 1428–1434.
- (12) Barsanti, K. C.; Pankow, J. F. Thermodynamics of the formation of atmospheric matter by accretion reactions—Part I: aldehydes and ketones. *Atmos. Environ.* **2004**, *38*, 4371–4382.
- (13) Forstner, H. J. L.; Flagan, R. C.; Seinfeld, J. H. Secondary organic aerosol from the photooxidation of aromatic compounds: Molecular composition. *Environ. Sci. Technol.* **1997**, *31*, 1345–1358.
- (14) Yu, J.; Jeffries, H. E.; Sexton, K. G. Atmospheric photooxidation of alkylbenzenes—I. Carbonyl product analyses. *Atmos. Environ.* **1997**, *31*, 2261–2280.
- (15) Edney, E. O.; Driscoll, D. J.; Weathers, W. S.; Kleindienst, T. E.; Conner, T. S.; McIver, C. D.; Li, W. Formation of polyketones in irradiated toluene/propylene/NO<sub>x</sub>/air mixtures. *Aerosol Sci. Technol.* **2001**, *35*, 998–1008.
- (16) Jang, M.; Kamens, R. M. Characterization of secondary organic aerosol from the photooxidation of toluene in the presence of NO<sub>x</sub> and 1-propene. *Environ. Sci. Technol.* **2001**, *35*, 4758–4766.
- (17) Seinfeld, J. H.; Erdakos, G. B.; Asher, W. E.; Pankow, J. E. Modeling the formation of secondary organic aerosol (SOA). 2. The predicted effects of relative humidity on aerosol formation in the  $\alpha$ -pinene-,  $\beta$ -pinene-, sabinene-,  $\Delta^3$ -carene- and cyclohexene-ozone systems. *Environ. Sci. Technol.* **2001**, *35*, 1806–1817.
- (18) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics*; John Wiley: New York, 1998.
- (19) Odum, J. R.; Jungkamp, T. P. W.; Griffin, R. J.; Forstner, H. J. L.; Flagan, R. C.; Seinfeld, J. H. Aromatics, reformulated gasoline, and atmospheric organic aerosol formation. *Environ. Sci. Technol.* **1997**, *31*, 1890–1897.
- (20) Griffin, R. J.; Cocker, D. R., III; Flagan, R. C.; Seinfeld, J. H. Organic aerosol formation from the oxidation of biogenic hydrocarbons. *J. Geophys. Res.* **1999**, *104*, 3555–3567.

- (21) Keywood, M. D.; Varutbangkul, V.; Bahreini, R.; Flagan, R. C.; Seinfeld, J. H. Secondary organic aerosol formation from the ozonolysis of cycloalkenes and related compounds. *Environ. Sci. Technol.* **2004**, *38*, 4157–4164.
- (22) Song, C.; Na, K.; Cocker, D. R., III. Impact of the hydrocarbon to NO<sub>x</sub> ratio on secondary organic aerosol formation. *Environ. Sci. Technol.* **2005**, in press.
- (23) Izumi, K.; Fukuyama, T. Photochemical aerosol formation from aromatic hydrocarbons in the presence of NO<sub>x</sub>. *Atmos. Environ.* **1990**, *24A*, 1433–1441.
- (24) Hurley, M. D.; Sokolov, O.; Wallington, T. J.; Takekawa, H.; Karasawa, M.; Klotz, B.; Barnes, I.; Becker, K. H. Organic aerosol formation during the atmospheric degradation of toluene. *Environ. Sci. Technol.* **2001**, *35*, 1358–1366.
- (25) Bowman, F. M.; Odum, J. R.; Seinfeld, J. H.; Pandis, S. N. Mathematical model for gas-particle partitioning of secondary organic aerosols. *Atmos. Environ.* **1997**, *31*, 3921–3931.
- (26) Depchanya, W.; Eusebi, A.; Kimura, Y.; Allen, D. T. Secondary organic aerosol formation from aromatic precursors. 1. Mechanisms for individual hydrocarbons. *Environ. Sci. Technol.* **2003**, *37*, 3662–3670.
- (27) Kroll, J. H.; Ng, N. L.; Murphy, S. M.; Varutbangkul, V.; Flagan, R. C.; Seinfeld, J. H. Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds. *J. Geophys. Res.*, submitted for publication, 2005.
- (28) Griffin, R. J.; Cocker, D. R., III; Seinfeld, J. H. Incremental aerosol reactivity: Application to aromatic and biogenic hydrocarbons. *Environ. Sci. Technol.* **1999**, *33*, 2403–2408.
- (29) Calvert, J. G.; Atkinson, R.; Becker, K. H.; Kamens, R. M.; Seinfeld, J. H.; Wallington, T. J.; Yarwood, G. *The Mechanisms of the Atmospheric Oxidation of Aromatic Hydrocarbons*; Oxford University Press: Oxford, U.K., 2002.

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