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Incremental Aerosol Reactivity: Application to Aromatic and Biogenic Hydrocarbons

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The concept of incremental aerosol reactivity is introduced, and the incremental aerosol reactivities of a number of important anthropogenic and biogenic hydrocarbons are investigated for four ambient scenarios. The incremental aerosol reactivity, defined as a change in the secondary organic aerosol mass produced (in μg m^{-3}) per unit change of parent organic reacted (in ppb), is a measure of the aerosol-forming capability of a given parent organic in a prescribed mixture of other organic compounds. The base-case scenario is a mixture of both aromatic and biogenic organics. Reactivity values depend on the choice of the initial organic mixture, so cases are also examined in which all biogenic hydrocarbon concentrations are set to zero and all aromatic concentrations are set to zero. The influence of additional organic aerosol is also investigated. For the compounds studied, incremental aerosol reactivities range from 0.228 μg m^{-3} ppb^{-1} (*m*-xylene) to 10.352 μg m^{-3} ppb^{-1} (α-humulene) for the base case, from 0.234 μg m^{-3} ppb^{-1} (*m*-xylene) to 9.446 μg m^{-3} ppb^{-1} (α-humulene) for the base case in the presence of initial organic aerosol, from 0.133 μg m^{-3} ppb^{-1} (*m*-xylene) to 0.801 μg m^{-3} ppb^{-1} (diethylbenzene) for the zero-biogenic case, and from 0.456 μg m^{-3} ppb^{-1} (linalool) to 6.923 μg m^{-3} ppb^{-1} (α-humulene) for the zero-aromatic case. Using *m*-xylene as a basis, relative incremental aerosol reactivities range from 1.153 (low-yield aromatics) to 3.338 (diethylbenzene) for aromatics in the base case and from 1.349 (low-yield aromatics) to 6.032 (diethylbenzene) in the zero-biogenic case. Using α-pinene as a basis, relative incremental aerosol reactivities range from 0.569 (terpinolene) to 12.843 (α-humulene) for biogenics in the base case and from 0.882 (linalool) to 13.385 (α-humulene) in the zero-aromatic case.

Introduction

Urban fine particulate matter is comprised of a complex mixture of both primary and secondary organic and inorganic compounds and emanates from a wide variety of sources. An important component that can significantly contribute to the fine particulate burden, especially during severe urban smog episodes, is secondary organic aerosol (SOA). Like ozone, secondary organic aerosol results from the atmospheric oxidation of reactive organic gases (ROGs), but whereas the oxidation of most ROGs results in ozone formation, SOA is generally formed only from the oxidation of ROGs comprised of six or more carbon atoms. This is because oxidation products must have vapor pressures that are sufficiently low to enable them to partition into the aerosol phase.

The atmospheric chemical reaction pathways of ROG molecules sufficiently large to lead to SOA are complex, and resulting oxidation products are both numerous and difficult to quantify analytically. The chemical process of organic aerosol formation can be depicted in general terms. Consider the production of semivolatile organic gases, S_1, S_2, ..., from the gas-phase reaction of a parent hydrocarbon, HC, with the OH radical

$$\mathrm{HC} + \mathrm{OH} \xrightarrow{k_{\mathrm{OH}}} ... + \alpha_1 S_1 + \alpha_2 S_2 + ... \qquad (1a)$$

where k_{OH} is the OH reaction rate constant, and α_1, α_2, ... are the stoichiometric product coefficients. (Later these stoichiometric coefficients will be expressed on a mass basis, rather than the usual molar basis.) If the parent hydrocarbon is an alkene, reactions with O_3 and NO_3 radicals are also possible, providing additional pathways for semivolatile product formation

$$\mathrm{HC} + \mathrm{O_3} \xrightarrow{k_{\mathrm{O_3}}} ... + \alpha_{1,\mathrm{O_3}} S_{1,\mathrm{O_3}} + \alpha_{2,\mathrm{O_3}} S_{2,\mathrm{O_3}} + ... \qquad (1b)$$

$$\mathrm{HC} + \mathrm{NO_3} \xrightarrow{k_{\mathrm{NO_3}}} ... + \alpha_{1,\mathrm{NO_3}} S_{1,\mathrm{NO_3}} + \alpha_{2,\mathrm{NO_3}} S_{2,\mathrm{NO_3}} + ... \qquad (1c)$$

The first-generation products, S_1, S_2, ..., may subsequently undergo gas-phase reaction themselves, creating second-generation condensable products, S_{1a}, S_{1b}, ... and S_{2a}, S_{2b}, ..., etc.

$$S_1 + \mathrm{OH} \xrightarrow{k_{\mathrm{OH},S_1}} ... + \alpha_{1a} S_{1a} + \alpha_{1b} S_{1b} + ... \qquad (2a)$$

$$S_2 + \mathrm{OH} \xrightarrow{k_{\mathrm{OH},S_2}} ... + \alpha_{2a} S_{2a} + \alpha_{2b} S_{2b} + ... \qquad (2b)$$

where k_{OH,S_1} and k_{OH,S_2} are the OH-reaction rate constants for the products, S_1 and S_2, respectively.

Secondary organic aerosol yields have been measured for many individual ROGs by a number of researchers over the past decade or more (*1*−*12*). Initially it was believed that each ROG should possess a unique value of its SOA yield (*13*−*15*), but measured yields for an individual ROG exhibited a degree of variation that could not be reconciled in terms of a single, unique SOA yield for each parent ROG. Following Pankow (*16, 17*), Odum et al. (*6*) formulated a framework for explaining observed SOA yield data. They suggested that secondary organic aerosol formation is best described by a gas/aerosol absorptive partitioning model. Within that framework, semivolatile products from the atmospheric oxidation of an ROG can partition into an absorbing organic aerosol phase at a concentration below their saturation concentration, analogous to the partitioning that occurs between the gas and aqueous phases of a water-soluble atmospheric constituent.

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Theory of Secondary Organic Aerosol Formation

Assuming that absorption is the dominant mechanism describing SOA formation, the equilibrium gas-particle partitioning of a semivolatile organic species i between the gas phase and an organic phase can be described with the vapor pressure relation (*18*)

$$p_i = x_i \zeta_i p_i^{\mathrm{o}} \tag{3}$$

where p_i (Torr) is the gas-phase partial pressure of species i, x_i is the mole fraction of species i in the organic aerosol phase, ζ_i is the activity coefficient of species i in the aerosol-phase organic mixture, and p_i^{o} (Torr) is the vapor pressure of species i as a pure liquid (subcooled, if necessary). In this scenario, the organic and inorganic portions of the aerosol remain in separate phases. Assuming ideal behavior for air, the gas-phase partial pressure, p_i, can be converted to the gas-phase mass concentration, G_i (μg m^{-3}), by the relationship

$$G_i = \frac{p_i m_{wi}}{RT} 10^6 \tag{4}$$

where m_{wi} (g mol^{-1}) is the molecular weight of species i, R ($= 6.2 \times 10^{-2}$ Torr m^3 mol^{-1} K^{-1} $= 8.314$ J mol^{-1} 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 (i.e., $m_{wi} = m_w$, the mean molecular weight of the absorbing organic matter) the aerosol mole fraction, x_i, is given by

$$x_i = \frac{A_i}{M_{\mathrm{o}}} \tag{5}$$

where A_i (μg m^{-3}) is the aerosol mass concentration of species i and M_{o} ($=\Sigma A_i$) (μg m^{-3}) is the total aerosol mass concentration of all the individual semivolatile organic species. Equations 4 and 5 can be substituted into eq 3 and rearranged to yield

$$\frac{A_i}{G_i M_{\mathrm{o}}} = \frac{RT}{m_w \zeta_i p_i^{\mathrm{o}}} 10^{-6} = K_i \tag{6}$$

where K_i (m^3 μg^{-1}) is defined as the absorption partitioning coefficient of species i (*6, 16, 17*). 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 concentration of species i to the mass fraction of species i in the aerosol phase. An important implication of eq 6 is that, since, at a particular temperature, K_i is a constant, a greater fraction of each product must partition to the organic phase as the total organic aerosol concentration increases.

Experimental Determination of SOA Yields

The approach that has been most successful to estimate the SOA forming capability of an ROG involves the direct measurement of secondary organic aerosol yields. The SOA yield for a given product i, Y_i, is a measure of the mass of aerosol of a species that is produced from the atmospheric oxidation of an ROG and is defined as

$$Y_i = \frac{A_i}{\Delta \mathrm{ROG}} \tag{7}$$

where ΔROG (μg m^{-3}) is the reacted amount of the ROG. By this definition, the total SOA yield is just the sum of the individual product yields

$$Y = \sum_{i=1}^{N} Y_i \tag{8}$$

In the study of secondary organic aerosol formation, typically a smog chamber is 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. (Dark experiments can also be conducted when O_3 or NO_3 is the oxidizing species.) As the hydrocarbon reacts it forms semivolatile products that condense on the seed particles. If mass transport to the available particles cannot keep up with the rate of product formation or when a seed aerosol is not initially present, the semivolatile products accumulate in the gas phase until supersaturation is reached and nucleation occurs. Studies show that the amount of aerosol produced for a given amount of reacted ROG is independent of whether a seed aerosol is present or not (*18*). Reactions are ordinarily run until the entire initial amount of ROG is consumed. Typically the volume of the initial seed aerosol is small compared to the organic aerosol volume generated.

The total SOA yield from an ROG that generates N semivolatile products is computed as follows. The total concentration of product i, C_i, is proportional to the total amount of parent organic that reacts, ΔROG

$$\alpha_i \Delta \mathrm{ROG} = C_i \tag{9}$$

C_i is also equal at any time to the sum of the gas- (G_i) and aerosol- (A_i) phase concentrations of i.

$$C_i = A_i + G_i \tag{10}$$

Combining these relations with the definition of the gas-particle partitioning constant, K_i, gives the expression for the total yield in terms of the individual product mass-based stoichiometric coefficients, α_i, partitioning coefficients, K_i, and the organic aerosol mass concentration, M_{o}

$$Y = M_{\mathrm{o}} \sum_{i=1}^{N} \frac{\alpha_i K_i}{1 + K_i M_{\mathrm{o}}} \tag{11}$$

Note that in the limit of small organic aerosol mass concentration or high volatility of the products

$$Y \sim M_{\mathrm{o}} \sum_{i=1}^{N} \alpha_i K_i \tag{12}$$

the SOA yield is directly proportional to M_{o} and that in the limit of large M_{o} or low volatility of the products

$$Y \sim \sum_{i=1}^{N} \alpha_i \tag{13}$$

the total yield is independent of M_{o} and is just the sum of the mass-based stoichiometric coefficients of the products.

It is important to distinguish between aerosol yield, Y, and stoichiometric coefficients, α_i. Stoichiometric coefficients depend on the gas-phase chemical mechanism and represent the total amount of semivolatile product formed, in both gas and aerosol phases, per amount of parent hydrocarbon reacted. The yield, on the other hand, which measures only the semivolatile products that have partitioned into the aerosol phase, depends on both the gas-phase reaction mechanism as well as 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 (except in the limits discussed previously,

TABLE 1. Aerosol Formation Parameters α_i and K_i (m^3 μg^{-1}): Values Obtained in the Caltech Smog Chamber (*6*−*9*, *12*)

hydrocarbon	α_1	K_1	α_2	K_2
Aromatic Compounds				
low-yield aromatics	0.038	0.042	0.167	0.0014
high-yield aromatics	0.071	0.053	0.138	0.0019
m-xylene	0.030	0.032	0.167	0.0019
diethylbenzene	0.083	0.093	0.220	0.0010
methylpropylbenzene	0.050	0.054	0.136	0.0023
Biogenic Compounds				
Δ^3−carene	0.054	0.043	0.517	0.0042
β-caryophyllene	1.000	0.0416	-	-
α-humulene	1.000	0.0501	-	-
limonene	0.239	0.055	0.363	0.0053
linalool	0.073	0.049	0.053	0.0210
ocimene	0.045	0.174	0.149	0.0041
α-pinene	0.038	0.171	0.326	0.0040
β-pinene	0.130	0.044	0.406	0.0049
sabinene	0.067	0.258	0.399	0.0038
α- & γ-terpinene	0.091	0.081	0.367	0.0046
terpinene-4-ol	0.049	0.159	0.063	0.0045
terpinolene	0.046	0.185	0.034	0.0024

as in eq 13). Partitioning coefficients, stoichiometric coefficients, and organic aerosol mass are required in general to determine the SOA yield.

Ozone-forming potential of organics is determined based on atmospheric reaction mechanisms (*19*, *20*). In principle, aerosol-forming potential could be calculated based on a similar atmospheric oxidation mechanism that includes all significant semivolatile product species. The relative aerosol-forming potential of a group of organics could, this way, be determined based on their oxidation products and the thermodynamic properties of these products. This ab initio approach represents a goal that is not yet attainable because of incomplete knowledge of the semivolatile oxidation products of the important aerosol-forming compounds. Thus, it is necessary to rely on experimentally measured aerosol yields. Aerosol yields Y are expressed theoretically as a function of the available M_o through eq 11. Observed aerosol yields as a function of M_o can be fit to eq 11 by specifying the stoichiometric coefficients, α_i, and gas-particle partitioning coefficients, K_i, of each of the semivolatile products of oxidation of the parent organic.

Over the last several years, SOA yields for over 30 aromatic and biogenic organics have been measured in the California Institute of Technology outdoor smog chamber (Table 1). In these experiments, M_o is generated completely by photooxidation of the parent. To fit the observed yields to eq 11, the mix of semivolatile oxidation products for each parent compound has been represented by two empirical products, characterized by parameters α_1, K_1, α_2, and K_2. It has been determined that observed yields cannot be fit by assuming only a single product and that use of three products is superfluous (*6*). (An exception are those compounds with extremely large yields, which can be represented by a single product.) Roughly speaking, one of the empirical semivolatile products tends to represent a relatively lower vapor pressure compound and the other a relatively higher vapor pressure compound. In Table 1, low-yield aromatics (those with multiple methyl substituents) represent those species that fall on the lower of two curves of Y versus M_o described by Odum et al. (*7, 8*). Correspondingly, high-yield aromatics (those with only one methyl substituent) represent the species falling on the higher of the two curves.

It must be noted that this theory assumes that secondary products are unable to form a solution with existing inorganic seed aerosol. Accounting for the interactions among the organic compounds themselves allows it to be shown that such products can condense onto seed aerosol at concentrations lower than the saturation concentration of the compound (*21*). There is a threshold amount of parent compound that must react to form secondary organic aerosol by absorption, defined as $\Delta\mathrm{ROG}^*_j$; after consumption of $\Delta\mathrm{ROG}^*_j$, products condense onto seed aerosol to form an initial organic layer that can then act as an absorptive medium. At this point, absorption becomes the dominant mechanism governing the partitioning of secondary products and, therefore, determining yield, as in the atmosphere. Adsorption of products is not considered here as it has been shown that absorption is the dominant mechanism associated with SOA formation in the ambient (*22*).

Odum et al. (*6, 7*) showed, moreover, that aerosol formation from the photooxidation of a mixture of parent hydrocarbons can be predicted simply from the SOA yields for the individual parent compounds. This suggests that, at least for the case of a pure organic absorbing phase, oxidation products of different parent hydrocarbons are as soluble in a mixed organic product phase as in an organic phase consisting exclusively of their own oxidation products.

The experimentally determined SOA yields reported by Odum et al. (*6, 7*) and Griffin et al. (*12*) have been measured at relative humidity (RH) less than 5%. At this level of RH the seed aerosol, $(\mathrm{NH_4})_2\mathrm{SO_4}$, is dry, and the resulting organic aerosol is water-free. Because organic products will likely be most soluble in their own liquids, SOA yields measured at essentially 0% RH can be expected to represent an upper limit to the aerosol partitioning that will result. While many SOA products are water soluble (*23*), they are not expected to be more soluble in an aqueous mixture than in a pure organic phase.

Threshold Concentration for SOA Formation

For the purpose of illustration, assume that two semivolatile products are formed from the parent organic ROG_j

$$\mathrm{ROG}_j + \text{oxidant} \rightarrow \alpha_{1j}S_1 + \alpha_{2j}S_2 \tag{14}$$

where $\alpha_{i,j}$ represents the mass-based stoichiometric factors described earlier. Therefore by a mass balance

$$G_1 + A_1 = \alpha_{1j}\Delta\mathrm{ROG}_j \tag{15a}$$

$$G_2 + A_2 = \alpha_{2j}\Delta\mathrm{ROG}_j \tag{15b}$$

where G_i and A_i represent the gas- and aerosol-phase mass concentrations of product i, respectively, and $\Delta\mathrm{ROG}_j$ represents the amount of ROG_j consumed. As shown earlier, their gas-phase concentrations would be defined by

$$G_1 = \frac{x_1\zeta_1 p_1^o m_{w1}}{RT}10^6 \tag{16a}$$

$$G_2 = \frac{(1 - x_1)\zeta_2 p_2^o m_{w2}}{RT}10^6 \tag{16b}$$

where x_1 represents the mole fraction of the first compound in the binary solution. If it is assumed that m_{w1} is approximately equal to m_{w2}, this mole fraction is given by

$$x_1 = \frac{A_1}{A_1 + A_2} \tag{17}$$

Combining eqs 15−17, replacing vapor pressure with the expression for the equilibrium partitioning coefficient given in eq 6, and setting each ζ_i equal to one, since an ideal solution is assumed, results in a quadratic expression for x_1 in terms of $\alpha_{1,j}$, $\alpha_{2,j}$, $K_{1,j}$, $K_{2,j}$, and $\Delta\mathrm{ROG}_j$. This expression has real and positive roots. When solved subject to the constraints that

A_1 and A_2 are greater than or equal to zero, it can then be shown that the threshold value of the parent organic that must be oxidized to form aerosol, ΔROG_j^* (μg m^{-3}), is (*21*)

$$\frac{1}{\Delta\text{ROG}_j^*} = \sum_{i=1}^{2} \alpha_{i,j} K_{i,j} \tag{18}$$

Using the $\alpha_{i,j}$ and $K_{i,j}$ values for the organics given in Table 1, it is possible to calculate ΔROG_j^* for each compound. These values will be used to define a base-case scenario and are described later.

Formation of Organic Aerosol from a Mixture of Hydrocarbons

Odum et al. (*6*−*8*) showed that the amount of organic aerosol produced from a mixture of parent hydrocarbons can be predicted as long as each ΔROG_j and the appropriate $\alpha_{i,j}$ and $K_{i,j}$ values are known. For a given M_{oT} (where the subscript T denotes total), the total yield for a parent hydrocarbon j can be calculated from eq 11

$$Y_j = M_{oT} \sum_i \left(\frac{\alpha_{i,j} K_{i,j}}{1 + M_{oT} K_{i,j}} \right) \tag{19}$$

The amount of aerosol formed specifically from that parent of interest can then be calculated using this yield by

$$M_{oj} = Y_j \Delta\text{ROG}_j \tag{20}$$

Summing the amount of aerosol generated by each parent in the mixture and adding any initial aerosol, M_{init}, gives the total amount of organic aerosol or

$$M_{oT} = \sum_j M_{oj} + M_{\text{init}} \tag{21}$$

Finally, combining eqs 19−21 results in

$$1 = \sum_j \Delta\text{ROG}_j \sum_i \left(\frac{\alpha_{i,j} K_{i,j}}{1 + K_{i,j} M_{oT}} \right) + \frac{M_{\text{init}}}{M_{oT}} \tag{22}$$

in which M_{oT} can be found iteratively if M_{init} is known. In this expression, ΔROG_j is actually equal to $\chi_j[\text{ROG}_j]_0$ where χ_j is the fraction of the parent hydrocarbon that reacts and $[\text{ROG}_j]_0$ is the initial concentration of ROG_j. For this study, it is assumed that χ_j is 1 for all species due to the high reaction rates of the species of interest and to avoid the need for complicated gas-phase modeling.

Incremental Aerosol Reactivity

The incremental ozone reactivity of a parent compound is defined as the ratio of the incremental change in the amount of ozone formed (relative to the ozone formed from oxidation of a base-case mixture) that results from an incremental change in the concentration of the compound of interest in the mixture to the change of the compound's concentration itself (*19*). Such measurements are useful when ozone control strategies require some sort of numerical ranking of the parent compounds of interest. Analogously, *incremental aerosol reactivity* for a parent organic ROG_j and a given initial mixture of organics and NO_x, IAR_j (μg m^{-3} ppb^{-1}), can be defined as

$$\text{IAR}_j = \frac{\delta M_{oT}}{\delta \Delta\text{ROG}_j} \tag{23}$$

the ratio of δM_{oT} (μg m^{-3}), the incremental change in total organic aerosol mass that results from an incremental change in the amount of parent hydrocarbon j that reacts, $\delta\Delta\text{ROG}_j$ (ppb), to $\delta\Delta\text{ROG}_j$ itself. δM_{oT} is calculated as the difference between the total amount of organic aerosol mass formed when the amount of parent j in the mixture is varied incrementally and the total amount of organic aerosol formed in the given initial case (base, base plus initial aerosol, zero-biogenic, or zero-aromatic case in the present situation). Because the initial amount of ROG_j is assumed to react completely, $\delta\Delta\text{ROG}_j$ is just the difference between the initial concentrations of parent reacting in the two scenarios. IAR_j values are then simply found as the slope of a plot δM_{oT} versus $\delta\Delta\text{ROG}_j$ if this ratio is linear.

The challenge in actually computing values of the incremental aerosol reactivity lies in specifying the gas-phase organic parent concentrations. (Since complete consumption of each parent compound is assumed and yield parameters are experimentally determined, the need for gas-phase mechanisms is obviated.) A first choice one might make is a set of typical ambient concentrations in, say, an urban area. While such a choice can certainly serve to define conditions for the calculation, such an approach lacks the generality desirable in computing IAR_j values. In addition, aerosol formation parameters are available only for a select few of the compounds that are part of the complex mixture of gas-phase organic precursors in the atmosphere. Because the presence of additional organic aerosol precursors increases the potential for aerosol formation, simply using the ambient concentrations of those compounds for which yield data is available would significantly underpredict a compound's ability to form aerosol. However, a unique parameter associated with each organic is its threshold concentration for SOA formation, ΔROG_j^* as defined in eq 18, suggesting specification of the initial mixture based on ΔROG_j^* values. Because less parent is required to react to form aerosol in the presence of other aerosol-forming compounds than when the compound exists by itself, however, the individual ΔROG_j^* values need to be reduced in order to produce an initial mixture that leads to a concentration level relevant to ambient conditions. If ΔROG_j^* values are not reduced, the base case would lead to a prediction of organic aerosol concentration that is greater than 650 μg m^{-3}. The degree to which the ΔROG_j^* values should be reduced to define the initial mixture introduces, however, an unavoidable element of arbitrariness into the specification of the mixture for the IAR calculation. The goal is to select a fraction of the ΔROG_j^* that leads to predicted aerosol levels that are in the range of those observed in ambient atmospheres. By using $\Delta\text{ROG}_j^*/4$ for the anthropogenic compounds (the aromatic species listed in Table 1) and $\Delta\text{ROG}_j^*/8$ for the biogenic compounds, we find that these values are the smallest whole fractions that lead to aerosol formation in the cases when all biogenics equal zero and when all aromatics equal zero, respectively.

Since the biogenic species are more efficient aerosol precursors than the aromatic species, the concentrations of the biogenics need to be decreased from the individual threshold values by a factor of 8, rather than 4. This approach produces a base-case scenario that may be atmospherically realistic for a polluted urban area receiving some influence from biogenic species. These base-case mixing ratios (ppb) that result from this choice of conditions are given in Table 2 for 308 K (approximately the temperature at which the aerosol yield parameters for each of these compounds were derived). In the base case, anthropogenic species contribute approximately 75% of the total amount of carbon ($\text{ppbC}_{\text{aromatics}}/(\text{ppbC}_{\text{aromatics}} + \text{ppbC}_{\text{biogenics}})$). Since the incremental aerosol reactivities are expected to be dependent on the initial case chosen, to investigate reactivities for a range of scenarios, two additional cases are defined. The first is the so-called zero-biogenic case, in which all biogenic concentrations have been set to zero; correspondingly, in the zero-aromatic case the concentrations of all aromatic species are set to

TABLE 2. Base Case Mixing Ratios (ppb) for the Hydrocarbons of Interest

hydrocarbon	mixing ratio	hydrocarbon	mixing ratio
Aromatic Compounds			
low-yield aromatics	32.58	diethylbenzene	5.94
high-yield aromatics	17.06	methylpropylbenzene	15.65
m-xylene	46.67		
Biogenic Compounds			
Δ^3−carene	5.17	α-pinene	2.98
β-caryophyllene	0.37	β-pinene	3.01
α-humulene	0.31	sabinene	1.24
limonene	1.54	α- & γ-terpinene	2.56
linalool	4.95	terpinene-4-ol	2.88
ocimene	2.75	terpinolene	2.70

zero. For these cases, M_{init} is assumed to be zero. A fourth case uses base-case concentrations and assumes that M_{init} is equal to 10 μg m^{-3}.

Solving eq 22 for the four cases results in values of M_{oT} of 37.43, 5.31, 6.39, and 54.97 μg m^{-3}, respectively. The base-case result is not unrealistic for a polluted area during a smog episode. In this base case, 51.1% of the organic aerosol formed is attributable to the oxidation of aromatics, with the remainder resulting from the biogenic precursors. It is interesting to note that simply adding the zero-aromatic and zero-biogenic cases together does not produce the base-case value, indicating the nonlinearity associated with SOA formation and the increased potential for aerosol formation when the products of one parent hydrocarbon interact with products of the oxidation of other compounds.

For each parent organic in each case, individual initial organic concentrations were varied by ±5% and ±10%. Equation 22 was used to calculate the total mass of organic aerosol formed in each situation, and IAR$_j$ values were then calculated using eq 23. For example, in the base case, M_{oT} is 37.43 μg m^{-3}. The M_{oT} values that result from eq 22 if the concentration of *m*-xylene (base case concentration of 46.67 ppb) is decreased by 10%, decreased by 5%, increased by 5%, and increased by 10% are 36.37, 36.90, 37.96, and 38.50 μg m^{-3}, respectively. The corresponding δM_{oT} values are thus −1.06, −0.53, 0.53, and 1.07 μg m^{-3}. These are associated with $\delta\Delta$ROG$_j$ values of −4.667 , −2.334, 2.334, and 4.667 ppb. The slope of the plot of δM_{oT} versus $\delta\Delta$ROG$_j$ is IAR$_j$. For *m*-xylene in the base case, this slope is 0.228.

There exists a wide range of IAR$_j$ values for the compounds of interest in each case (Table 3). For the base case, IAR$_j$ values range from 0.228 to 0.761 μg m^{-3} ppb^{-1} for the aromatics considered and from 0.459 to 10.352 μg m^{-3} ppb^{-1} for the biogenic compounds investigated. These ranges are 0.234−0.694 and 0.399−9.446 μg m^{-3}, respectively, when initial organic aerosol is present. Because these represent only small changes (−13 to 5%) compared to the base case, M_{init} is assumed to be zero for the zero-aromatic and zero-biogenic cases. In the zero-biogenic case, the IAR$_j$ values for the aromatics exhibit a range of 0.133−0.801. It is interesting to note that all of the compounds except diethylbenzene have lower IAR$_j$ values in the zero-biogenic case than in the base case. Diethylbenzene exhibits a 5% decrease in its IAR$_j$ value between the zero-biogenic and base cases, whereas the other aromatics show a 26−72% increase going from the zero-biogenic to the base case. In the zero-aromatic case, the IAR$_j$ of the biogenic compounds range from 0.456 to 6.923. Similar to the behavior of the aromatics in the zero-biogenic case, all the biogenics except one, terpinolene, have lower IAR$_j$ values in the zero-aromatic case than in the base case. Terpinolene exhibits an IAR$_j$ value that is 7.5% lower in the base case when compared to the zero-aromatic case. The other biogenic compounds exhibit an increase of 10−129%.

TABLE 3. Incremental Aerosol Reactivities (μg m^{-3} ppb^{-1}) for Parent Organic Compounds

hydrocarbon	base case	base case with initial aerosol	zero-biogenic case	zero-aromatic case
Aromatic Compounds				
low-yield aromatics	0.263	0.260	0.179	na
high-yield aromatics	0.410	0.391	0.326	na
m-xylene	0.228	0.234	0.133	na
diethylbenzene	0.761	0.694	0.801	na
methylpropyl-benzene	0.466	0.450	0.358	na
Biogenic Compounds				
Δ^3−carene	1.106	1.161	na	0.484
β-caryophyllene	9.670	9.025	na	6.071
α-humulene	10.352	9.446	na	6.923
limonene	2.361	2.257	na	1.388
linalool	0.751	0.703	na	0.456
ocimene	0.625	0.581	na	0.531
α-pinene	0.806	0.806	na	0.517
β-pinene	1.527	1.527	na	0.777
sabinene	1.166	1.133	na	0.971
α- & γ-terpinene	1.310	1.287	na	0.803
terpinene-4-ol	0.556	0.487	na	0.507
terpinolene	0.459	0.399	na	0.496

It should be noted that the R^2 associated with each plot of δM_{oT} versus $\delta\Delta$ROG$_j$ was essentially unity.

The contrary behavior of diethylbenzene and terpinolene is best explained by considering Y as a function of M_o. While Y increases as the amount of material reacted (and therefore M_o) increases (a positive effect on IAR$_j$), it becomes less dependent on M_o. This means that dY/dM_o decreases as M_o increases (a negative effect on IAR$_j$). However, because of the link to α_i and K_i values, the dependence of these effects on M_o varies considerably among the compounds of interest. Diethylbenzene and terpinolene are the two compounds with the fastest decreasing dY/dM_o values, meaning that the negative effect is greatest for these species. For diethyl benzene and terpinolene, this negative effect is greater than the positive effect of increasing M_o, and IAR$_j$ decreases when comparing the zero-biogenic and zero-aromatic cases, respectively, to the base case. Basically, the increase in yield due to an increased amount of reaction, and, therefore, an increased amount of material available to act as an absorptive medium, is not large enough to counteract the change in dY/dM_o, as it is for all other compounds. This behavior is also linked to the fact that diethylbenzene and terpinolene are present only in small amounts in the scenarios defined in this study.

Relative Incremental Aerosol Reactivity

One may also define *relative incremental aerosol reactivities,* where IAR$_j$ is reported relative to that of a reference compound. We can select a single reference compound for the entire mixture of aromatics and biogenics studied, or we can choose one compound from each category as the reference compound. We choose to do the latter because these compounds are emitted from different sources, although one can clearly report all relative incremental aerosol reactivities with respect to a single compound if so desired. *m*-Xylene and α-pinene, compounds that are prevalent in ambient air and that have been investigated extensively experimentally, are convenient reference compounds for aromatics and biogenics, respectively. With these reference compounds, relative incremental aerosol reactivities are defined as either

TABLE 4. Relative Incremental Aerosol Reactivities

hydrocarbon	base case	zero-biogenic case	zero-aromatic case
Aromatic Compounds (Basis: *m*-Xylene)			
low-yield aromatics	1.153	1.349	na
high-yield aromatics	1.799	2.453	na
m-xylene	1.000	1.000	na
diethylbenzene	3.338	6.032	na
methylpropylbenzene	2.046	2.693	na
Biogenic Compounds (Basis: α-Pinene)			
Δ^3–carene	1.373	na	0.935
β-caryophyllene	11.997	na	11.737
α-humulene	12.843	na	13.385
limonene	2.929	na	2.684
linalool	0.932	na	0.882
ocimene	0.775	na	1.026
α-pinene	1.000	na	1.000
β-pinene	1.894	na	1.501
sabinene	1.446	na	1.878
α- & γ-terpinene	1.626	na	1.553
terpinene-4-ol	0.690	na	0.981
terpinolene	0.569	na	0.958

$$\mathrm{RIAR}_j = \frac{\mathrm{IAR}_j}{\mathrm{IAR}_{m-\mathrm{xylene}}} \tag{24a}$$

or

$$\mathrm{RIAR}_j = \frac{\mathrm{IAR}_j}{\mathrm{IAR}_{\alpha-\mathrm{pinene}}} \tag{24b}$$

for aromatics and biogenics, respectively (Table 4). From this definition, $\mathrm{RIAR}_{m-\mathrm{xylene}}$ and $\mathrm{RIAR}_{\alpha-\mathrm{pinene}}$ are equal to 1.0. It should be noted that the ratio of $\mathrm{IAR}_{\alpha-\mathrm{pinene}}$ to IAR $_{m-\mathrm{xylene}}$ under the base-case conditions considered here is 3.535.

For the base case, RIAR_j values range from 1.153 for low-yield aromatics up to 3.338 for diethylbenzene and from 0.569 for terpinolene up to 12.843 for α-humulene. In the zero-biogenic case the range of values shifts compared to the base case to 1.349 for the low-yield aromatics up to 6.032 for diethylbenzene. In the zero-aromatic case, RIAR_j values range from 0.882 for linalool up to 13.385 for α-humulene. The RIAR_j value of each aromatic increases in the zero-biogenic case when compared to the base case. This simply means that the other aromatic compounds will form aerosol more readily than *m*-xylene and that this difference is more pronounced at lower values of M_o. The RIAR_j values of these aromatics also retain the same rank when comparing the base and zero-biogenic cases (i.e., low-yield aromatics < high-yield aromatics < methylpropylbenzene < diethylbenzene). The same cannot be said for the biogenic species. Of the compounds investigated, six have RIAR_j values that decrease in the zero-aromatic case when compared to the base case (Δ^3-carene, β-caryophyllene, limonene, linalool, β-pinene, and the terpinene isomers), and five have values that increase (α-humulene, ocimene, sabinene, terpinene-4-ol, and terpinolene). This shows that relative to α-pinene, the tendency of the biogenic compounds to form aerosol is more strongly dependent on M_o. This is supported by the fact that the relative rank of the RIAR_j values of these compounds varies significantly between the two cases. These differences can be explained using arguments similar to those presented earlier regarding yield as a function of M_o, the behavior of the derivative of this function, and the amount of each compound present in these scenarios.

Because of the link between IAR_j values and the chosen initial conditions, RIAR_j values depend on this choice as well. However, significant changes (a decrease of 20% or an increase of 33%) in the concentrations in the base case chosen here result in small changes (average of 5% and −8%, respectively) in the associated RIAR_j values, indicating the robustness of the methodology used to determine the incremental aerosol reactivity. The relative ranks of these values in the altered base cases remain virtually unchanged, as well. Only in the case in which concentrations are increased by 33% is there a slight discrepancy; sabinene and Δ^3-carene, which have very similar RIAR_j values in the base case, switch places in the ranking in this scenario.

Acknowledgments

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