Aerosol Formation from the Reaction of α -Pinene and Ozone Using a Gas-Phase Kinetics-Aerosol Partitioning Model

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As a result of new aerosol compositional information, we have implemented an exploratory model for predicting aerosol yields from the reaction of α -pinene with ozone in the atmosphere. This new approach has the ability to embrace a range of different atmospheric chemical conditions, which bring about biogenic aerosol formation. A kinetic mechanism was used to describe the gas-phase reactions of α -pinene with ozone. This reaction scheme produces low vapor pressure reaction products that distribute between gas and particle phases. Some of the products have subcooled liquid vapor pressures which are low enough to initiate self-nucleation. More volatile products such as pinonic acid and pinonaldehyde will not self-nucleate but will partition onto existing particle surfaces. Partitioning was treated as an equilibrium between the rate of particle uptake and rate of particle loss of semivolatile terpene reaction products. Given estimated liquid vapor pressures and activation energies of desorption, it was possible to calculate gas-particle equilibrium constants and aerosol desorption rate constants at different temperatures. This permitted an estimate of the rate of absorption from the gas phase. Gas- and aerosol-phase reactions were linked together in one chemical mechanism, and a chemical kinetics solver was used to predict reactant and product concentrations over time. Aerosol formation from the model was then compared with aerosol production observed from outdoor chamber experiments. Approximately 20–40% of the reacted α -pinene carbon appeared in the aerosol phase. Models vs experimental aerosol yields are shown in Figure 2 and illustrate that reasonable predictions of secondary aerosol formation are possible. The majority of the aerosol mass came from the mass transfer of gas-phase products to the aerosol phase. An important observation from the product data and the model was that as temperatures and aerosol mass changed from experiment to experiment, the composition of the aerosol changed.

Introduction

The atmospheric chemistry of nonmethane biogenic hydrocarbons has received much attention because of their significant global emissions, high photochemical reactivity, and their high aerosol forming potential. Although the potential of aerosol formation from terpenes was noted as early as 1960 (1), the magnitude of the natural contribution by biogenics to the particulate burden in the atmosphere is still not well characterized.

Efforts to represent secondary organic aerosol (SOA) formation in ambient models have been based primarily on experimentally determined fractional aerosol yields (2, 3 and references therein). In general, measured yields for a single compound have shown a wide degree of variation either between or within laboratories (4,5). Odum et al. (3,6) have developed an elegant technique for estimating SOA yields starting with an absorptive gas-particle (G/P) partitioning model (7-9). In this model the overall SOA yield from a single reactant is given as a function of two hypothetical product dependent G/P partitioning coefficients, Kom,i, their associated individual mass-based stoichiometric reaction coefficients, α_i , and the absorbing organic mass concentration, M_0 (µg m⁻³). While this is a very useful advance, it does not address the fundamental atmospheric reactions that bring about secondary aerosol formation. In this paper, we will describe the feasibility of a predictive technique for the formation of secondary aerosols from biogenic hydrocarbons. An advantage of this approach is that it has the ability to embrace the range of different atmospheric chemical and physical conditions that bring about secondary aerosol formation.

Experimental Section

Gas-particle samples for this study were generated in a large outdoor 190 m³ Teflon film chamber (10, 11). All experiments were carried out in darkness to exclude photochemical effects. Rural background air was used to charge the chamber without any additional injections of oxides of nitrogen. Secondary aerosols were created by the reaction of α -pinene with O_3 in the chamber. O3 from an electric discharge ozone generator was added to the chamber over the course of at least an hour with initial concentrations ranging, depending on the experiment, from 0.25 to 0.65 ppm. It was measured using a Bendix chemiluminescent O3 meter (model 8002, Roncerverte,WV) and calibrated via gas-phase titration using a NIST traceable NO tank. O3 addition to the chamber was followed by volatilizing, depending on the experiment, 0.4-1 mL of liquid α -pinene into the chamber atmosphere. The gas-phase concentration of α -pinene was monitored with an online gas chromatograph (Shimadzu Model 8A, column: 1.5 m, 3.2 mm stainless steel packed with Supelco 5% Bentanone 34) using a flame ionization detector and calibrated with a known concentration of a mixture of toluene and propylene.

Gas- and particle-phase α -pinene products were simultaneously collected with a sampling train that consisted of an upstream five-channel annular denuder, followed by a 47 mm Teflon glass fiber filter (type T60A20, Pallflex Products Corp., Putnam, CT) and another denuder. In one of the experiments, a parallel sampling system consisting of a filter, followed by a denuder, was also used. The details of the sample workup procedure and quantitative analysis have been reported in previous manuscripts (10,11). Carbonyl products of α -pinene-O₃ aerosols were derivatized by O-(2,3,4,5,6-pentafluorobenzyl)hydroxyl-amine hydrochloride (PFBHA) as described by Yu et al. (12), and carboxylic acids, using pentafluorobenzyl bromide (PFBBr) as a derivatizing agent as described by Chien et al. (13). (\pm) - α -Pinene, O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA), pentafluorobenzylbromide (PFBBr), decafluorobiphenyl (internal standard for derivatization), cis-

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pinonic acid, n-hexanoic acid, *n*-octanoic acid, hexane-1,6dionic acid, and heptane-1,7-dionic acid were all purchased from Aldrich (Milwaukee, WI).

In one of the experiments the particle size distribution and aerosol concentration for particles ranging from 0.018 to 1.0 μ m were monitored by an Electrical Aerosol Analyzer (EAA) (Thermo Systems, Inc., Model 3030, Minneapolis, MN). Total aerosol number concentration was also measured by a Condensation Nuclei Counter (CNC, Model Rich 100, Environment One Corp., Schenectady, NY).

Results and Discussion

Overview. Conceptually, we began with the development of a kinetic mechanism to describe gas-phase reactions of α -pinene with ozone. This reaction scheme produces low vapor pressure reaction products that distribute between gas and particle phases. Some of the products may have subcooled liquid vapor pressures of $\sim 10^{-6}$ Torr or lower. These are low enough so that if surfaces are not available for sorption from that gas phase, self-nucleation may occur. Once surfaces and their corresponding liquid volumes exist, G/P partitioning becomes the dominant process, and compounds partition from the gas phase onto existing particles. Partitioning can be represented as an equilibrium between the rate of oxidized terpene product uptake and the rate of terpene product loss from the aerosol system. Kinetically, this is represented as forward and backward reactions. The sum of the product mass in the condensed phase equals the aerosol concentration. This was then compared with aerosol concentrations obtained by reacting α -pinene with O₃ in an outdoor chamber.

An α-Pinene-Ozone Gas-Phase Reaction Mechanism. During darkness, the reaction of α -pinene with O₃ is one of the dominant atmospheric loss mechanisms for α -pinene. The electrophilic addition of ozone to the unsaturated carbon-carbon bond of terpenes leads to the formation of an ozonide that rapidly decomposes to energy-rich biradicals often called Criegee biradicals (14). As shown in Scheme 1, the ozonide intermediate generated from the reaction of α -pinene with O₃ will undergo ring opening and yield two species that contain a high energy biradical at one end and an aldehyde or ketone group at the other. One of these biradicals, which will be called Criegee1, quickly reacts to form pinonic acid, norpinonaldehyde, and norpinonic acid (15-19). As will be discussed later, the other biradical, Criegee2, can rearrange to form 2,2-dimethyl,3-carboxyliccyclobutaneethanoic acid (pinic acid), which has recently been reported as an α -pinene-O₃ reaction product (17, 18, 20, 21). The reactions of the energetic Criegee biradicals also lead to the formation of carbon monoxide (CO), carbon dioxide, (CO₂), formaldehyde (HCHO), hydroxyl radicals (OH), and hydroperoxyl radicals (HO₂) (16,22-26). The reaction of α -pinene with OH radicals then leads to the formation of pinonaldehyde and other reaction products (27).

Possible mechanisms for the overall α -pinene-O₃ have recently been presented by Jang and Kamens and Yu et al. (17, 18). Reaction pathways were constructed from experimentally measured products which include pinonaldehyde, norpinonaldehyde, pinonic acid, norpinonic acid, pinic acid, 2,2-dimethylcyclobutane-1,3-dicarboxylic acid (norpinic acid), and hydroxy and aldehyde substituted pionaldehydes and hydroxy pinonic acids. To simplify the mechanism in this study, six generalized semivolatile products were defined: 1. "pinald" to represent pinonaldehyde and norpinonaldehyde, 2. "pinacid" to represent pinonic and norpinonic acids, 3. "diacid" for pinic acid and norpinic acid, 4. "oxy-pinald" for hydroxy and aldehyde substituted pinonaldehydes (called oxo-substituted), 5. "P3" for 2,2-dimethylcyclobutane-3acetylcarboxylic acid, (a pinic acid precursor), and 6. "oxypinacid" for hydroxy and aldehyde substituted pinonic acids. A last group, frag, was employed to account for volatile oxygenated products.

Model Representation of *Criegee1* **Reactions.** In the reaction of ozone with alkenes, alkyl substitution on the carbon atoms participating in the carbon double bond stabilizes the formation of the resulting Criegee biradicals (*28,29*). For the α -pinene-O₃ system, a bias toward the formation of the methyl substituted biradical was assumed with a split ratio of 60:40. A temperature-dependent Arrhenius rate constant for the reaction of O₃ with α -pinene of 1.01 × 10¹⁵ × e^{-732/T} cm³ molecule⁻¹ s⁻¹ was used (*29*), where *T* is in degrees Kelvin. The initial reaction of α -pinene with O₃ is thus represented in eq 1 as

$$\alpha$$
-pinene + O₃ \rightarrow 0.4*Criegee1* + 0.6*Criegee2* (1)

In Scheme 1, 12.5% (\pm 4) of the high energy α -pinene Criegee biradicals are collisionally stabilized (29, 30). We assumed a value of 15%. These stable biradicals (called stabcrieg1 in the mechanism) can react with aldehydes, nitric oxide, nitrogen dioxide, water, sulfur dioxide, and oxygen (29, 31). The reaction of Criegee biradicals with water dominates (29) and in this case yields pinonic acid (pinacid). A rate constant for the reaction of water with a stabilized Criegee radical is on the order of $4 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$ $s^{-1}(\bar{3}1)$. The high-energy *Criegee1* biradical can also undergo rearrangement and stabilize to directly form pinonic acid. Given the recent observation that pinonic acids can account for 20-40% of the aerosol mass (32), 30% of the Criegee1 mass was shunted into the formation of pinacid. Recent studies have suggested similar yields of pinonic and norpinonic acids (17, 32). We have therefore assumed that the group *pinacid* represents approximately equal portions of pinonic and norpinonic acids.

As shown in Scheme 1, the rearrangement of Criegee1 also leads to the formation of norpinonaldehyde (17, 18). The reported ratio of norpinonaldehyde to pinonaldehyde varies from almost zero to 50% (17, 19). A ratio of ~20% was assumed and given the model yields of pinonaldehyde via OH attack on α -pinene in our mechanism, this translated into ~30% of the Criegee1 decomposition. Norpinaldehyde (represented as *pinald* in the mechanism) can then react with OH and in the presence of oxygen form a peroxyacyl radical (pinald-oo). The peroxyacyl radical then reacts with HO₂ (33) to form norpinonic acid and O₃. O₃ formation from this reaction, however, was not included in the mechanism, since it is implicitly represented in the rate constant of $\alpha\text{-pinene}$ with $O_3.$ Given the low yields of the $O(^3P)$ atom from the Criegge decomposition (29), its reaction with α-pinene was not included.

Yu et al. (18) have recently suggested that a hydroxypinonaldehyde (*oxy-pinald*) can also form from *Criegee1*. Using the above *Criegee1* yields for pinonic acid and norpinonaldehyde leaves 25% of the *Criegee1* carbon, and this was



shunted into the formation of *oxy-pinald*. It is proposed (17) that all of these aldehyde compounds undergo OH abstraction of an aldehyde hydrogen and form, via O_2 addition and HO_2 oxidation, hydroxypinonic acids (*oxy-pinacid*).

Dark OH yields from the rearrangements of the Criegee biradicals from $O_3 + \alpha$ -pinene range from 0.76 to 0.85 (34, 35). We used a value of 0.8. HO₂ yields were set slightly higher (0.5) than those used in the Carbon Bond IV mechanism of 0.44 (36), and here it is expected to include other similar RO₂ peroxy radical reactions. Fast first-order rate constants were assigned to the rearrangements of both Criegee biradicals. The above choices led to the following overall reaction sequence of the *Criegee1* biradical:

$$Criegee1 \rightarrow 0.3 pinacid + 0.15 stabcrieg1 + 0.3 pinald + 0.25 oxy-pinald + 0.8 OH + 0.5 HO_2 + 0.3 CO (2)$$

 $stabcrieg + H_2O \rightarrow pinacid$ (3)

$$pinald + OH \rightarrow pinald-oo$$
 (4)

$$pinald-oo + HO_2 \rightarrow pinacid$$
 (5)

Criegee2 Reactions. Possible mechanisms for the Criegee2 biradical have recently been presented (17, 18). To simulate this chemistry, Criegee2 was assumed to collisionally stabilize or rearrange and react via the hydroperoxide channel (C) as shown in Scheme 2 (22, 29, 37). Intermediate A illustrates a stabilization via the ester channel, which leads to the formation of methanol (CH₃OH) and a compound called P3 $(C_9H_{14}O_3)$ in Scheme 2. P3 then reacts to form pinic acid via OH abstraction on the aldehyde hydrogen or continues to react to form the C₈ diacid, 2,2-dimethycyclobutane-1,3dicarboxylic acid. The C₈ diacid represented about 10% of the observed pinic acid (17). We have assumed that the hydroperoxide channel leads directly to a peroxyacyl compound D, which is then oxidized by HO₂ to also form pinic acid. This assumption was made because of the need in the particle portion of the model to rapidly produce low volatility aerosol phase products. This channel also leads (17) to a hydroxypinonaldehyde and an oxopinonaldehyde (oxy*pinald*), which can be further oxidized via OH, O₂, and HO₂ to oxopinonic and hydroxypinonic acids (oxy-pinacid).

For modeling purposes, two generalized intermediate products, called *stabcrieg2* and *crgprod2*, were defined. *Stabcrieg2* represents the reactions of A and *crgprod2* the peroxyacyl compound D in Scheme 2. As with *stabcrieg1*, we assumed a 15% split to *stabcrieg2*. Given the recent observation of substantial pinic acid formation (17) and the uncertainty associated with the yields of *oxy-pinald*, we assumed an almost even split between products leading to the *diacid* and *oxy-pinald*. This permitted the chemistry of Criegee2 to be represented as

$$Criegee2 \rightarrow 0.15 stabcrieg + 0.3 crgprod2 + 0.3 HCHO + 0.55 oxy-pinald + 0.8 OH + 0.5 HO2$$
 (6)

$$crgprod2 + HO_2 \rightarrow diacid + HCHO$$
 (7)

$$stabcrieg1 + H_2O \rightarrow P3 + CH_3OH$$
 (8)

 $oxy-pinald + OH \rightarrow oxy-prepinacid$ (9)

OH Attack on α **-Pinene.** OH radicals from the above Criegee radical reactions will attack the double bond of α -pinene and ultimately form pinonaldehyde (*pinald* in the kinetic mechanism) (27). A yield of pinonaldehyde from α -pinene reaction with OH in the presence of oxides of nitrogen (NOx) of approximately 60% has been reported (16). A small amount of mass was added to the *oxy-pinald* category and the remainder to the volatile fragmentation products category called *frag.* The combined reaction has a rate constant (29) of 12.1 \times 10⁻¹² e^{444/T} cm³ molecule⁻¹ s⁻¹ and is represented as

$$\alpha$$
-pinene + OH \rightarrow
0.6pinald + 0.1oxy-pinald + 0.3frag (10)

As with the other aldehydes mentioned above, *pinald* will undergo OH abstraction of its aldehyde hydrogen to form a peroxyacyl species, *pinald-oo*. This forms pinonic acid, which appears in the mechanism as *pinacid*. Literature values for OH attack on pinonaldehyde range from 2.4 to 9.1×10^{-11} cm³ molecule⁻¹s⁻¹ (*38, 39*). To fit our α -pinene and O₃ decay data, it was necessary to use a value toward the lower end of this range. The Moortgat et al. (*33*) rate constant of $4.3 \times 10^{-13} e^{1040/T}$ cm³ molecule⁻¹s⁻¹ was used for HO₂ reaction with the peroxyacyl to form pinonic acid from pinonaldehyde and was also used for the oxidation of other peroxyacyl radicals to carboxylic acids.

All of the above reactions were linked using a kinetics solver (40) and by convention, rate constant units of min⁻¹ or ppm⁻¹ min⁻¹ for first and second order reactions were used with this package. Units of cm³ molecule⁻¹ s⁻¹ were converted to ppm⁻¹ min⁻¹ by dividing by 6.77×10^{-16} (at 298 K). These reactions were then added to the inorganic chemistry reactions of the Carbon Bond IV photochemical mechanism (36). A temperature table describing the experimental temperature change over time was used by the kinetic solver to calculate the pre-exponential and exponential terms of the rate constant at each time step of a given kinetic simulation.

Particle Nucleation. When α -pinene is vaporized into the chamber, it exits the injection manifold as a very high concentration gas cloud and is mixed into the chamber atmosphere that already contains ozone. Although chamber mixing takes about one minute, the condensation nuclei counter responded as the α -pinene was injected, indicating an immediate formation of condensation nuclei. In the absence of these particle seeds, the system would have to wait for gas-phase concentrations of the least volatile products to reach sufficient supersaturation levels for selfnucleation to occur. The formation rate of these nuclei is dependent on the supersaturation level and the number of molecules needed to form critical clusters (41). The rate of formation can easily span 50 orders of magnitude as the supersaturation level increases from 2 to 7 (41). In our systems we tended to reach supersaturation levels of pinic acid in less than one minute. At this point supersaturation in our systems would rapidly increase to values greater than 50 if gas-phase mass transfer to the particle phase did not occur. To model our data it was only necessary to initiate the migration to the aerosol phase with a small amount of initial

nuclei resulting from the α -pinene injection. This mass was equivalent to $\sim 8 \ \mu g/m^3$ of particulate matter.

The product compounds that actually participate in the self-nucleation process are as yet unknown. One possibility is that the stabilized Criegee radical (*stabcrieg1* and *stabcrieg2*) reacts with the carbonyl portion of product compounds to produce an extremely low-pressure secondary ozonide product. These types of products have been observed from an O₃-propylene system by Niki and co-workers and more recently by others for larger molecules (42, 43). It is also possible to form an anhydride from the reaction of the Criegee with a dicarboxylic acid (44). In the α -pinene case, these products would have molecular weights of \sim 350 and be of extremely low volatility. By techniques described later in this paper, vapor pressures lower than 10⁻¹⁵ Torr are estimated and ~1 s after the start of the experiments in this study would exceed supersaturation by \sim 1000-fold. This suggests these compounds would most certainly self-nucleate. In our mechanism these are called "seed1" particles. We assumed that stabilized Criegees would react with all carbonyl products, with a rate constant of $2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1}$ s^{-1} (*31*). For example,

$$stabcrieg1 + pinald \rightarrow seed1$$
 (11)

This process was not very important for the experiments in this study, given the background nucleation levels that resulted during the injection of α -pinene into the chamber. Predictions, using the model developed here, however, suggest a strong influence of these seeds on particle formation when α -pinene has concentrations of ~5 ppb.

A Gas-Particle Model. For a kinetics-based model, it is necessary to calculate the rate constants for sorption and desorption of α -pinene-O₃ products on and off the growing aerosol mass. The ratio of the rate constants for the forward and backward reactions ${}^{i}k_{\text{on}}/{}^{i}k_{\text{off}}$ is equal to the equilibrium constant, ${}^{i}K_{\text{p}}$, for the gas-particle equilibrium of a given partitioning compound.

$${}^{i}K_{p} = {}^{i}k_{on}/{}^{i}k_{off}$$
(12)

Previous investigations by our group (45) show that α -pinene-O₃ aerosols can be treated using an absorptive (gas–liquid) partitioning model (7). ${}^{i}K_{p}$ can be calculated from

$$\log^{i} K_{\rm p} = -\log^{i} p_{\rm L}^{\rm o} - \log^{i} \gamma_{\rm om} + \log[(7.501 RT f_{\rm om})/(10^{9} \,{\rm Mw}_{\rm om})]$$
(13)

where ${}^{i}K_{p}$ has units of ${m}^{3}/{\mu}g$, *T* is the temperature (K), f_{om} is the mass fraction of organic material in particulate matter, Mw_{om} is the average molecular weight of a given liquid medium (g/mol), and $^{i}\gamma_{om}$ is the activity coefficient of a given organic compound i, in a given organic mixture, om. When ${}^{i}p_{\rm L}^{\rm o}$ (the subcooled liquid vapor pressure for a pure compound i) is in Torr and R, the gas constant, has units of 8.31 JK^{-1} mol⁻¹, a conversion factor of 7.501 is necessary. The activity coefficient thermodynamically represents the nonideality of the semivolatile organic compound (SOC) dissolved in the liquid layer of the particle. The activity coefficients of a given SOC vary with the composition of the organic layer associated with the particulate matter. It is reasonable, however, to assume that the activity coefficients of α -pinene products partitioning into particles composed of α-pinene products will be nearly ideal and fairly close to one. This was actually observed for these compounds using a combinatorial calculation technique (46). The fractional mass of organic material in these particles is also close to one. Hence the partitioning expression for ${}^{i}K_{p}$ can be simplified to

$$K_{\rm p} = 7.501 RT / (10^9 \,{\rm Mw_{om}}^{\rm i} p_{\rm L}^{\rm o})$$
 (14)

The average molecular weight of the liquid particle includes any water absorbed from the atmosphere. It is possible to estimate the water uptake for these aerosols (46) and this tends not to exceed 5% of the particle mass. On a molecular basis, however, water can make up 30-50% of the mole fraction. This suggests that compounds such as pinic acid may exhibit liquid-like properties when dissolved in the aerosol bound water.

An implicit assumption in the use of the above equilibrium model is that partitioning from the gas phase takes place into the particle liquid volume. It is this available and accumulating liquid volume, and the mass of products produced in the gas phase, that "drives" the equilibrium between the gas and particle phases. Although surface is not explicitly represented in the model, it is expected that total particle surface changes after the onset of particle formation. Particle size measurements taken with an Electrical Aerosol Analyzer (EAA) show that 4-5 min after the injection of α -pinene (for particles ranging from 0.018 to 1.0 μ m in diameter), the chamber aerosol count, surface, and volume geometric mean diameters were 0.054, 0.095, and 0.151 μ m, respectively. These diameters increased to 0.096, 0.158, and $0.214 \,\mu\text{m}$ over the next 30 min and then increased very slowly over the next 3 h. The EAA total particle surface to total volume ratio after 5 min of reaction was 51 μ m⁻¹ and declined to 33 μ m⁻¹ in 30 min; it then decreased slowly to 26 μ m⁻¹ over the next 3 h. This less than dramatic change in the EAA surfaceto-volume ratio with time and the fact that most of the particle mass was in the measured EAA range suggest that not including surface directly in the model is not a significant problem.

Estimating $K_{\rm p}$. To estimate ${}^{i}K_{\rm p}$ it is necessary to have knowledge of ${}^{i}p_{\rm L}^{0}$. For the aldehyde, acid-carbonyl, and diacid products of the α -pinine-O₃ system, ${}^{i}p_{\rm L}^{0}$ information is scarce. There are some vapor pressure data, however, for nonandionic acid, a linear alkanoic diacid with the same carbon number as pinic acid (47). At 560 K it has a vapor pressure of 100 Torr, and at 498 K, 10 Torr. Using the simple form of the Clausius-Clapeyron equation at 295 and 270 K, vapor pressures of 6.0×10^{-6} and 2.3×10^{-7} Torr can be estimated for nonandionic acid. An expanded form of the Clausius-Clapeyron (48) equation can also be used to estimate vapor pressures at ambient Kelvin temperatures (*T*), from boiling point (*T*_b) and entropy of vaporization ($\Delta S_{\rm vap}T_{\rm b}$) information.

$$\ln {}^{\mathrm{i}}p_{\mathrm{L}}^{\mathrm{o}} = \frac{\Delta S_{\mathrm{vap}}T_{\mathrm{b}}}{R} \left[1.8 \left(1 - \frac{T_{\mathrm{b}}}{T} \right) + 0.8 \left(\ln \frac{T_{\mathrm{b}}}{T} \right) \right] \quad (15)$$

Entropies of vaporization can be estimated from the boiling points for organic compounds and boiling points from chemical structural semiempirical additive techniques (49). For nonandionic acid, a boiling point of 696 K at 760 Torr and an entropy of vaporization of 91 J/mol were computed. When these values were used in eq 14, estimated subcooled liquid vapor pressures for nonandionic acid at ambient temperatures of 295 K and 270 were 3.3 \times 10^{-6} and 9.6×10^{-8} Torr. These results are remarkably close to the vapor pressures (6.0 \times 10^{-6} and 2.3 \times 10^{-7} Torr) estimated above from the experimental data in ref 47. Similar results were also obtained for the C9 monoacid, only in this case the vapor pressure was 2 orders of magnitude lower than the diacid, nonandionic acid. Given this agreement, Fishtine correction factors for molecular polarity were not included as a multiplier on the entropy term in eq 13 (50). For the $\alpha\mbox{-pinene}$ product pinic acid, a boiling point of 698 K and entropy of vaporization of 91.0 J/mol were estimated. This

TABLE 1. Experimental Outdoor Chamber Conditions Used To Produce α -Pinene-O₃ Aerosols

run ID	date	temp (K)	RH (%)	O ₃ (ppm)	α-pinene (ppmV)	TSP (µg/m ³) (max concn)	MW _{om}
А	Aug. 5, 1996	296-294	55-66	0.60	0.82	2190	142
В	July 15, 1996	296-295	90-100	0.25	0.35	504	106 ^a
С	Mar. 11, 1997	288-279	62-92	0.65	0.60	1860	114
^a Using the	e composition for the Au		nent (see ref 17).				

gave subcooled liquid vapor pressures of 3.0 \times 10 $^{-6}$ Torr at 295 K and 8.9 \times 10 $^{-8}$ Torr at 270 K.

Computed vapor pressures were then used in eq 14 to calculate iKp. Based on our measurement of a-pinene-O3 aerosol particle composition and water uptake as a function of humidity (46), average molecular weights of the particles were calculated for each experiment and are shown in Table 1. To simplify calculations, an average molecular weight (Mwom) of 120 was used. Using the experiment specific Mwom values did not have any impact on the modeling results discussed later in this manuscript. As mentioned previously, units of ppmV (40) were used in the kinetics solver for gasphase compounds, and thus units of $m^3/\mu g$ for iK_p were converted to their equivalent 1/ppmV units. When the average Mwom was combined with estimated vapor pressures in eq 14, ⁱ K_p values for pinic acid of $5.1 \times 10^{-2} \text{ m}^3/\mu g$ (or 390 L/ppmV) at 295 K and 1.6 m³/ μ g (or 1.3 \times 10⁴ L/ppmV) at 270 K were obtained.

Estimating Rates of Particle Sorption and Desorption. It is expected that the gas-phase uptake by the particles will not be overly temperature sensitive, since the rate constant, k_{on} , for the gas-phase uptake by particles varies with temperature to the 1/2 power

$$^{i}k_{\rm on} \alpha \left(RT/2\pi MW_{\rm i}\right)^{1/2} \tag{16}$$

where MW_i is the molecular weight of the partitioning gas phase compound. The rate of loss from a particle, however, will be strongly temperature dependent, where the rate constant, k_{off} , for loss of a compound from the liquid particle phase has the form

$${}^{\mathrm{i}}k_{\mathrm{off}} = \beta \mathrm{e}^{-E_{\mathrm{a}}/RT} \tag{17}$$

Here, E_a is the activation energy or energy barrier required for desorption from the particles and β is a preexponential factor. E_a can be calculated from the following general expression by Glasstone (*51*) for evaporation from a pure liquid surface

$$j_{\text{evap}} = \eta \kappa \frac{k_{\text{b}}T}{h} \exp \frac{-\Delta \phi}{k_{\text{b}}T} \equiv \eta \kappa_{\text{evap}}$$
(18)

where j_{evap} is the molecular flux across the surface (molecules cm⁻² s⁻¹); κ is a transmission coefficient (assumed \approx 1); $k_{\rm b}$ is Boltzmann's constant (1.381 \times 10⁻²³ Joules/K); *h* is Planck's constant (6.626 \times 10⁻³⁴ Joules s); $\Delta \phi$ is the energy barrier a single molecule must overcome to evaporate from the surface (Joules); and η is the number of molecules exposed on the liquid surface (number/cm²). By dividing eq 18 by the particle radius, k_{evap} becomes k_{off} in eq 17. Using recent k_{off} data (52) for fluorene and phenanthrene for diesel soot particles (0.51 and 0.37 s⁻¹) and k_{off} for fluoranthene (0.03 s⁻¹) calculated for this study from this same data set, E_a values of 73.9, 74.6, and 80.7 kJ/mol were estimated from eq 18 for these three compounds. Interestingly, the values for phenanthrene and fluoranthene are close to the pure liquid enthalpy values as reported by Pankow (53). If one assumes a direct relationship between PAH activation energies and their respective $\log^{1} p_{\rm L}^{0}$ values, then very crude estimates of E_a values can be made for example, for pinic acid, pinonic acid, and *cis*-pinonaldehyde from their estimated vapor pressures. These were calculated as 84.4, 79.2, and 71.4 kJ/mol, respectively, for these three compounds. As will be discussed later the model is not very sensitive to these choices within \pm 5 kJ/mol.

From eq 18, the preexponential factor, β , in eq 17 is equal to $k_{\rm b}T/h$, and at 298 K is 6.21×10^{12} s⁻¹. It is also of interest to note that for solids, a parameter similar to β is equal to the inverse of the molecular vibrational frequency (*54,55*) and has an approximate value of $10^{-12}-10^{-13}$ s. If an average value of 5×10^{-13} is used for the solid vibrational frequency, its reciprocal equals 2×10^{12} s⁻¹, and this is within a factor of 3 of the β values calculated above for liquids. From the computed $E_{\rm a}$ values for the α -pinene products, ${}^{i}k_{\rm off}$ can now be obtained from eq 17, and given estimated ${}^{i}K_{\rm p}$ values from eq 14, ${}^{i}k_{\rm on}$ can be computed from eq 12. As indicated above, $k_{\rm on}$ does not significantly change with temperature, and an average value computed from K_p and $k_{\rm off}$ over a temperature range of 285–305 K was used.

At this point it is useful, for illustrative purposes, to describe the partitioning of the product, pinonic acid (*pincid*). The initial aerosol surfaces available for partitioning come from background aerosols called *seed* or from self-nucleating particles called *seed1*. Newly formed low vapor pressure products such as gas-phase pinic acid (*diacid_{gas}*) migrate to these nuclei and contribute their mass to the particle phase (*diacid_{parl}*). This creates more mass for additional partitioning. To conserve mass and distinguish between *seed* and newly formed diacid particle mass, *seed* appears on both sides of the equation.

$$diacid_{gas} + seed \rightarrow diacid_{nart} + seed$$
 (19)

The migration of gas-phase pinonic acid ($pinacid_{gas}$) to the diacid particle phase ($diacid_{part}$) can thus be represented as

$$pinacid_{gas} + diacid_{part} \rightarrow pinacid_{part} + diacid_{part}$$

 $k_{on} = 29.7 \text{ min}^{-1}$ (20)

To maintain equilibrium, *pinacid_{part}* back reacts or "off-gases" from the particle to give back gas-phase pinonic acid.

$$pinacid_{part} \rightarrow pinacid_{gas}$$

$$k_{off} = 3.73 \times 10^{14} \exp(-9525/T) \min^{-1} (21)$$

Similarly, when gas-phase pinonaldehyde partitions to the particle phase, it will "see", in this example, particles composed of *seed*, *diacid*_{part}, and *pinacid*_{part}, and it will partition onto all three of these. A similar set of reactions can be written for all of the partitioning products. The rate constants are given in $ppm^{-1} min^{-1}$ for second-order processes and min^{-1} for first-order reactions (Table 2). All the reactions and rate constants used to demonstrate the feasibility of this approach are reproduced in Table 2. By keeping track of the amount of mass that appears in the particle phase from each of the products, an estimate of the overall particle mass yield can be made over a range of temperature conditions.

TABLE 2. Gas and Particle Phase Reactions Used To Simulate Secondary Aerosol Formation^{a-c}

gas phase reactions	min ⁻¹ or ppm ⁻¹ min ⁻¹	reference
1. α -pinene + O ₃ \rightarrow 0.4 Criegee1 + 0.6 Criegee2	1.492 exp-732/ <i>T</i>	(29)
2. Criegee1 \rightarrow 0.3pinacid _{gas} + 0.15stabcrieg1 + 0.8OH +	1 × 10°	
$0.5HO_2 + 0.3pinald_{gas} + 0.250Xy-pinald_{gas} + 0.3CO$	1 × 106	
$0.35HCHO + 0.15stabcriec2 + 0.80H + 0.5HO_{2}$	Τ Χ ΤΟ',	
4. stabcried 1 + $H_2O \rightarrow pinacid_{cas}$	6×10^{-3}	(31)
5. stabcrieg2 + H ₂ O \rightarrow P3 _{ras} + CH ₃ OH	6×10^{-3}	(31)
6. $P3_{gas} + OH \rightarrow predi-oo$	35450	(38)
7. oxy -pinald + OH \rightarrow oxy-prepinacid	35450	(38)
8. predi-oo + HO ₂ \rightarrow diacid _{gas}	677 exp1040/ <i>T</i>	(38)
9. crgprod2 + HO ₂ \rightarrow diacid _{gas}	677 exp1040/ <i>T</i>	(33,38)
10.oxy-prepinacid $+HO_2 \rightarrow oxy$ -pinacid	677 exp1040/ <i>T</i>	(33)
11. OH + α -pinene \rightarrow 0.6pinald _{gas} + 0.1oxy-pinald + 0.3frag	17873 exp444/ <i>T</i>	(29)
12. pinald + OH \rightarrow pinald-oo	35450	(38)
13. pinald-oo + HO ₂ \rightarrow pinacid _{gas}	6// exp1040//	(33)
14. dlacid _{gas} {Walls} →	$6 \times 10^{-7} \exp 2445/1$	(10,56)
15. OXY-pinacid _{gas} {Walls} \rightarrow	$6 \times 10^{-7} \exp 2445/T$	(10,56)
10. $\mu(ac)ugas \{walls\} \rightarrow 17$ ovy pipald (walls) \rightarrow	$4 \times 10^{-7} \exp(2445/T)$	(10,56)
17. $Oxy-pinalogas \{waits\} \rightarrow$ 18. pinald	$4 \times 10^{-7} \exp(2445/T)$	(10,50)
10. pinalogas (waits)	2.3 × 10 exp2443/1	(10,50)
partitioning reactions	min ⁻¹ or ppm ⁻¹ min ⁻¹	reference
22. stabcrieq1 + pinald _{gas} \rightarrow seed1	29.5	(42)
23. stabcrieg2 + oxy-pinald _{gas} \rightarrow seed1	29.5	(42)
24. stabcrieg2 + HCHO \rightarrow oxy-pinald	29.5	(42)
25. pinacid _{gas} + seed1 \rightarrow seed1 + pinacid _{part}	29.7	
26. pinacid _{gas} + diacid _{part} → diacid _{part} + pinacid _{part}	29.7	
27. pinacid _{gas} + seed \rightarrow seed + pinacid _{part}	29.7	
28. pinacid _{gas} + pinacid _{part} \rightarrow pinacid _{part} + pinacid _{part}	29.7	
29. pinacid _{gas} + pinacid _{part} \rightarrow pinacid _{part} + pinacid _{part}	29.7	
30. pinacid _{gas} + 0xy-pinald _{part} \rightarrow 0xy-pinald _{part} + pinacid _{part} 21. pinacid + P2 \rightarrow P2 + pinacid	29.7	
31. pinacid _{gas} + r_{part} + r_{part} + $pinacid_{part}$ 32. pinacid_{res} + ovy-pinacid_{res} \rightarrow ovy-pinacid_{res} + pinacid_	29.7	
32. pinacid _{gas} \rightarrow pinacid _{gas}	$3.73 \times 10^{14} \text{ exp-}9525/T$	
34 , diacid _{gas} + pinacid _{gas} \rightarrow pinacid _{gas} + diacid _{gas}	106	
35. diacid _{part} \rightarrow diacid _{nas}	$3.73 \times 10^{14} \exp(-10285/T)$	
36. pinald _{gas} + oxy-pinacid _{part} \rightarrow oxy-pinacid _{part} + pinald _{part}	5.94	
37. pinald _{part} → pinald _{gas}	$3.73 \times 10^{14} \exp - 8598/T$	
38. oxy-pinald _{gas} + $P3_{part} \rightarrow P3_{part} + oxy-pinald_{part}$	21.7	
39. oxy-pinald _{part} → oxy-pinald _{gas}	$3.73 \times 10^{14} \exp{-9341/T}$	
40. $p3_{gas} + oxy-pinacid_{part} \rightarrow oxy-pinacid_{part} + p3_{part}$	19 9	
41. $p_{3part} \rightarrow p_{3gas}$	17.7	
	$3.73 \times 10^{14} \exp{-9282/T}$	
42. $oxy-pinacid_{gas} + seed1 \rightarrow seed1 + oxy-pinacid_{part}$	$3.73 \times 10^{14} \text{ exp-9282/}T$ 116	
42. oxy-pinacid _{gas} + seed1 → seed1 + oxy-pinacid _{part} 43 oxy-pinald _{part} → oxy-pinacid _{gas}	$3.73 \times 10^{14} \exp{-9282/T}$ 116 $3.73 \times 10^{14} \exp{-10353/T}$	
 42. oxy-pinacid_{gas} + seed1 → seed1 + oxy-pinacid_{part} 43 oxy-pinald_{part} → oxy-pinacid_{gas} 44. diacid_{part} {walls} → 45. Oc (walls) → 	$3.73 \times 10^{14} \exp{-9282/T}$ 116 $3.73 \times 10^{14} \exp{-10353/T}$ 0.0008 0.0005	

^a Rate constants are at 298 K. To convert the second-order rate constant in cm³ molecule⁻¹ s⁻¹ in the text to ppm⁻¹ min⁻¹ divide the rate constant in cm³ molecule⁻¹ s⁻¹ by 6.77 × 10⁻¹⁶. ^b Exp in the temperature-dependent reactions is the natural base e, in the rate equation, $k = Be^{-A/T}$. The gas constant *R* is imbedded in *A* so that $A = E_a/R$. ^c The partitioning reactions for pinald, oxy-pinald, diacid, and oxy-pinacid are the same as for the pinacid but, to save space, are only given for k_{off} and one particle species. stabcrieg1 and stabcrieg2 reactions are illustrated for pinacid_{gas}, and oxy-pinacid_{gas} and HCHO but are the same for the other carbonyls. Loss of product gases to the chamber walls were estimated from observed pyrene loss at 297 and 271 K (10, 56). Reactions not referenced were determined in this study. All reactants were diluted from the chamber at a rate determined with an SF₆ tracer. A typical loss was 0.0005 min⁻¹. Other specific measured or estimated losses such as O₃, particles and α -pinene product to the walls were adjusted for the SF₆ loss rate.

Experiential Data and Model Fits. Three experiments (A, B, and C in Table 1) were conducted under different temperatures and spanned a total temperature range of 279-296 K. The individual temperature profiles for each experiment were used as inputs to the individual simulations. It was not possible to obtain an α -pinene concentration at the instant of injection. This is because there is a need for chamber mixing on the order of \sim 1 min, and sampling (2-8 min), during which time reaction takes place. Hence the initial α -pinene concentration was based on the mass of α -pinene injected into the chamber. This was not an issue with the initial O₃ concentration data, since O₃ was injected into the chamber prior to α -pinene, and O₃ measurements were taken as α -pinene was injected. In Figure 1, it can be seen that $\alpha\mbox{-pinene}$ reacts faster than $O_3,$ and this is due to the additional reaction of α -pinene with the OH radical. As shown in Figure

1, reasonable fits to the experimental data for the reaction of gas-phase α -pinene with O₃ with the mechanism shown in Table 2 were observed.

Our experimental data show that 20-40% of the reacted α -pinene carbon appeared in the aerosol phase. Approximately 30% of the aerosol mass was generated via the *Criegee1* pathway. This pathway produces higher volatility products than *Criegee2*. OH attack on α -pinene generates pinonal-dehyde and ultimately pinonic acid. This channel accounts for ~10% of the model aerosol. Model simulations of the measured particle concentration in mg/m³ are shown in Figure 2. The experimentally measured aerosol concentrations with the denuder-filter-denuder system ranged from 350 to 2700 μ g/m³. The parallel filter-denuder sampling system gave particle concentrations that were within 5% of the denuder-filter denuder system. Again, reasonable model



FIGURE 1. Reaction of α -pinene (triangles) with O₃ (squares) in 190 m³ outdoor chamber; symbols are data and lines are model simulations. Letters correspond to experiments in Table 1.

fits to the experimental secondary aerosol data for all three experiments (A–C) were possible, even though α -pinene and O₃ from these experiments exhibited very different time– concentration behaviors (Figure 1). Electrical aerosol analyzer data (EAA) were available for run B in Figure 2, and the initial rate of mass flow to the particle phase in the model seems to follow the total EAA volume (mass) build up. This suggests that it is only necessary to "seed" the model with condensation nuclei, after which almost all of the resulting aerosol mass will come from gas-phase mass transfer to the particle phase. An initial aerosol concentration resulting from the initial mixing of α -pinene and O₃ of 8 µg/m³ was used for all the experiments.

Quantitative product data to guide the development and testing of the mechanism for the reaction of α -pinene + O₃ are very scarce. Our experimental product measurements (17) from the combined samples of each experiment accounted for ~50% (±15%) of the observed aerosol yields where pinic acid, pinonaldehyde, and pinonic acid were the major aerosol phase products. Although hydroxypinonaldehydes and hydroxypinonic acids were detected in trace amounts, it is expected, based on the Criegee fragmentation scheme, that these would also contribute substantially to the aerosol mass.

An important observation from the product data was that as temperatures decreased from experiment A to experiment C, the contribution of the pinic acid mole fraction of measured aerosol products decreased from 77 to 61%, while the importance of the pinonaldehyde mole fraction increased from 13 to 30% (*17*). Although not as much *pinald* compared to *diacid* was predicted in this study for the particle phase, the general trend is supported by the model product distributions (Figure 3). The model predictions also suggest



FIGURE 2. Comparison of experimental (squares) and model aerosol concentrations (lines) with model reacted α -pinene concentrations (triangles). Experimental conditions listed in Table 1. The total electrical aerosol (EAA) volumes in graph C (solid circles) were scaled to approximate the experimental concentrations.



FIGURE 3. Simulated particle phase products for a warm and cool α -pinene + O₃ experiment: *diacid* = large \blacksquare , *pinald* = \blacktriangle , *pinacid* = \blacktriangledown , *oxy-pinald* = \ominus , *pa* = small \blacksquare .

that the composition of the secondary aerosol changes with temperature and particle concentration. This is because higher volatility compounds tend to partition to the aerosol phase more under cool conditions and high particle concentrations than under warm conditions and lower particle concentrations.

As with pinonaldehyde, it was expected that as experimental conditions cooled, much more pinonic acid would be observed on the particle phase than under warm experimental conditions. Measured pinonic acid compounds, however, only constituted 4% of the mole fraction products (17), and this did not change dramatically between experiments A and C. It is possible, although yet unknown, that storage of the samples before analysis resulted in a loss of *pinacid* compounds. That more pinonic and norpinonic acid should have been observed in our experiments is corroborated by the recent observations of Kavouras et al. (*32*). These authors show that $\sim 20-40$ of the aerosol mass over a Eucalyptus forest in Portugal was composed of pinonic and norpinonic acids.

Impact of Model Inputs and Choices. Many of the choices made in this manuscript will influence the amount of aerosol generated and the timing of model events compared to outdoor data. The choice of a 60:40 split for the formation of *Criegee2* over *Criegee1* is reasonable based on the observations of Grosgean et al. (*28*). At 295 K increasing or decreasing the split to 70:30 or 50:50 changed the model particle yield by $\sim \pm 10\%$. At 285 K there was less of an effect. The splits used to obtain norpinonic acid, *diacid*, and *oxy-pinald* product yields are speculative and must await further product verification. In addition, we assumed that the rate constant for the OH attack on pinonaldehyde (*38*) was applicable to the oxidation of *P3* and *oxy-pinald* and that the Moortgat rate (*33*) used for HO₂ oxidation of small aldehydes to carboxylic acids was also applicable to larger radicals.

Vapor pressure estimates are at best within an order of magnitude. When vapor pressures were lowered for all product compounds by \sim 1 order of magnitude, aerosol yields were overestimated by 40–100%; when vapor pressures were increased by a factor of 10, aerosol yields were underestimated by a factor of 2. It is also possible that vapor pressures were not uniformly under- or overestimated. For example, an alcohol group can increase Fishtine correction factors to 1.3 (*50*). This would lower vapor pressure calculations in eq 15. If this were the case, it would suggest that hydroxy pinonaldehyde products would partition to the particle phase to a greater extent than suggested by our model.

Estimates for activation energies (E_a) are based on a completely different class of compounds (PAHs) than the products used in this study. The effect of changing Ea values by \pm 5 kJ/mol, and adjusting $k_{\rm on}$ and $k_{\rm off}$ accordingly, was explored. Uniformly increasing E_a for all partitioning compounds by 5 kJ/mol tended to slow the onset of aerosol formation and only slightly decrease aerosol yields. This was almost unnoticeable in the high concentration experiments A and C but delayed aerosol formation by \sim 7 min in the warm July experiment. Decreasing E_a by 5 kJ/mol did not seem to have any effect on aerosol fits. The high concentration experiments A and C were not sensitive to the choice of initial seed concentrations over the range of $5-40 \ \mu g/m^3$. Effects were greatest with the low concentration experiment B, where lower seed values $(1-5 \,\mu g/m^3)$ tended to delay the onset of particle production. Last, under warm conditions (295 K), the impact of increasing the temperature by 10 degrees K was to decrease particle yields by \sim 30%. This effect may be even greater in systems that generate lower aerosol levels. Decreasing the temperature by 10 degrees from 295 K increased the aerosol yield by 25-50%, with the greatest effect observed for the low concentration experiment B. At \sim 285 K in experiment C, these kinds of temperature changes caused a 20-25% change in aerosol formation. In closing there are many uncertainties in this proposed approach that will probably require a number of years to sort out. We feel,

however, that the feasibility of a new secondary aerosol modeling approach has been demonstrated, and in doing so, it highlights significant areas of research which should be undertaken.

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