

ABSTRACT

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A Method for Dilute Mixing of Reactants in an Outdoor Aerosol Chamber and the Application to an α -pinene/Ozone System

(Under the direction of Richard Kamens, Donald Fox, and Kenneth Sexton)

Atmospheric aerosols have received increasing attention within the past few years as their role in global climate change is investigated. However, it remains difficult to capture and quantify nucleation events at ambient concentrations in a smog chamber setting. A novel method was developed to mix two dilute reactants at near-ambient concentrations. This method was tested using at the UNC 270 m³ Outdoor Aerosol Chamber in Pittsboro, NC with a dark α -pinene/ozone system at near-ambient concentrations. These results were compared against the UNC Particle Mechanism and scientific literature to test the validity of the method. Further experiments were conducted to examine the role water vapor and background ammonium sulfate seed have in aiding or inhibiting nucleation events.

To all of my teachers.

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LIST OF ABBREVIATIONS AND SYMBOLS

CCN: cloud condensation nuclei

DMA: differential mobility analyzer

f: transfer flow

FID: flame ionization detector

GC: gas chromatograph

EPA: Environmental Protection Agency

SOA: secondary organic aerosols

SO₂: sulfur dioxide

NO: nitrogen monoxide

NO_x: oxides of nitrogen

NO₃: nitrate radical

OH: hydroxyl radical

O₃: ozone

PKSS: photochemical kinetics simulation system

RH: relative humidity

SF₆: sulfur hexafluoride

SMPS: scanning mobility particle sizer

T_d: dewpoint

V: volume

VOC: volatile organic compounds

● α -pinene: alpha-pinene

CHAPTER I

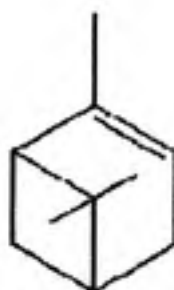
INTRODUCTION

Atmospheric aerosols, the suspended liquid and solid particles that are ubiquitous throughout the troposphere, have received increasing attention within the past few years as their role in global climate change is examined. Biogenic and anthropogenic aerosols have both a direct and an indirect effect on the larger climate; their effects on human health are significant enough that the EPA has put limits on exposure. In the larger climate, aerosols scatter incoming solar radiation and act as cloud condensation nuclei (CCN). An increase in CCN can not only affect the number of clouds and their size, but also whether or not those clouds are able to produce precipitation (Hartmann, 1994; Cruz and Pandis, 1997). Aerosols have been shown to cause adverse health effects in multiple populations, such as the elderly and those with a pre-existing illness. The exact effects of inhalation can vary from aerosol to aerosol and vary greatly according to particle size and chemical composition, but in general they lead to lung irritation and inflammation, bronchial constriction and asthma-like symptoms (U.S. EPA, 2004).

There are two types of aerosols: primary aerosols, which are those emitted into the atmosphere directly, and secondary aerosols, which are formed from atmospheric reactions. Both types of aerosols can be either organic or inorganic in nature. The formation of particle sulfate from gas phase sulfur dioxide (SO_2) is an example of a reaction that can

generate secondary inorganic particle mass. Secondary organic aerosols (SOA), which have both biogenic and anthropogenic sources, are formed from the reactions of volatile organic carbon (VOC) species with ozone (O_3), oxides of nitrogen (NO_x), the nitrate radical (NO_3), and the hydroxyl radical (OH) (Seinfeld and Pandis, 1998). The biogenic contribution to the atmospheric SOA has been recently estimated to be as high as 6.74 Tg yr^{-1} ($1 \text{ Tg} = 10^{12} \text{ g}$) (Goto, 2008). Of this, approximately 44% is due to isoprene, and monoterpenes contribute an additional 11%, which includes alpha-pinene (α -pinene) (Guenther et al, 1995). Of monoterpene emissions, α -pinene dominates, comprising approximately 40% of the total mass (Spirig et al, 2004).

Figure 1: α -pinene



α -pinene ($C_{10}H_{16}$) (Figure 1) is a cyclic alkene that is emitted primarily by coniferous trees. It is highly reactive, due to the four-carbon ring, and its products are of sufficiently low vapor pressure that SOA is easily formed. The reaction of α -pinene with O_3 has been well studied. It has been investigated in the field (Spanke et al, 2001; Boy et al, 2004; Fuentes et al, 2007), and there are multiple laboratory (Bilde and Pandis, 2001; Lee et al, 2004; Jonsson et al, 2006) and chamber studies detailing reaction pathways and the behavior of this reaction

under various conditions (Hatakeyama et al, 1981, 1989; Jang, 1997; Kamens et al, 1999, 2001; Hoppel et al, 2001; Jaoui and Kamens, 2003; Varutbangkul et al, 2006). Kumala et al (2004) organized a comprehensive survey of over one hundred field studies of ultrafine particles. While many of the studies included in this survey do discuss nucleation events, field instrumentation is not yet capable of quantitatively determining the chemical constituents of these particles. Laboratory and chamber experiments over the past three decades have provided additional insights (Hatakeyama, 1981, 1989; Hull, 1981; Kamens et al, 1999) but have been conducted at concentrations that are one to ten orders of magnitude higher than ambient concentrations. This increased concentration is due in large part to detection issues. The individual components of a reaction must be introduced at levels measurable to detection equipment, and the contributions of all compounds must be quantifiable. This creates a different set of problems, which are exemplified in various experiments that have been conducted using α -pinene and O_3 with different levels of background water vapor. Summarized by Jonsson et al (2006), the scientific community is essentially split over whether or not the presence of water vapor has a positive, negative, or null impact on the number of particles created in this system and their resultant mass. Using a flow reactor, some groups (Rohr et al, 2003; Fick et al, 2003) observed that water does not affect the system at all, while others (Berndt et al, 2003) find small effects, whereas Jonsson et al (2006) finds a positive effect. Bonn et al (2002) reported different effects depending on the amount of reactants introduced using a bag reactor, and Cocker et al (2001) reported a positive effect on the amount of mass created.

This paper examines a novel method of introducing reactants and experiments conducted to study the effects of water vapor and seed on nucleation from the dark reaction of α -pinene with ozone. Of special interest was: 1. the effect of water on the final products, 2. how the presence of background particles enhances or inhibits the nucleation process, 3. the ability of the UNC particle mechanism (Kamens et al, 1999) to capture what is seen experimentally, and 4. how these experiments fit within the larger body of scientific evidence.

CHAPTER II

EXPERIMENTAL METHODS

The UNC 270 m³ outdoor dual chamber

Dark-phase reactions were investigated by conducting experiments at night at the UNC outdoor smog chamber facility in Pittsboro, NC. A photograph of the chamber is shown in Figure 2. A complete description of the 270 m³ chamber can be found elsewhere (Lee et al, 2004). The two sides of the chamber are nominally designated as North and South; ductwork runs underneath the chamber to connect them (Figure 3). A schematic of this ductwork can be found in Figure 4. It is through this ductwork that air from one side of the chamber travels to the other side to achieve a diluted mixing.



Figure 2. The UNC Aerosol Chamber



Figure 3. Connecting ductwork between two halves of UNC Aerosol Chamber

In preparation for each experiment, both chambers were flushed for approximately 12 hours with rural air, then purged for a minimum of an additional 48 hours with clean, dry air from a clean air generator. Due to air flow path considerations, O₃ was injected into the

North chamber for all experiments, and α -pinene or d-limonene was injected into the South chamber. Prior to injecting reactants, sulfur hexafluoride (SF_6) was injected into the North chamber only to trace the movement of air from the North side of the chamber to the South side. Ozone was injected using an ozone generator. In the South side of the chamber, nitrogen oxide (NO) was introduced in small amounts to titrate out any traces of O_3 . α -pinene was then vaporized into the South chamber through a heated U-tube. The vapor was carried into the chamber via a nitrogen stream. At the time of introduction into their respective chambers and for two minutes thereafter, all reactants were mixed with a mixing fan located above the injection point inside the chamber. All injections and subsequent mixing took place after sunset to eliminate photochemical effects.

Instrumentation

The rate of reaction plus dilution of α -pinene or d-limonene was measured using a gas capillary chromatograph (GC, Shimadzu model 14A, column: 30 m, 0.25 mm i.d., J&W DB-1, 0.25 m film thickness) in conjunction with a flame ionization detector (FID). A sample was taken every 10 minutes, and it was possible to collect a sample from the South chamber once every 20 minutes. Particle size distributions and volumes were collected using a scanning mobility particle sizer (SPMS) system consisting of two condensation particle counters (TSI CPC, 3025A and 3022, MN, USA) each with a differential mobility analyzer (TSI long DMA, 3070 and 3081, MN, USA). One DMA took samples only from the South chamber, scanning 6 nm to 216 nm. The other switched between the North and South chambers every 10 minutes in accordance with the other sampling instruments and scanned from 14 nm to 660 nm. SMPS sample times were every three minutes, which

included 30 seconds of down scan and 120 seconds of up scan. Ozone was measured by a UV photometric ozone analyzer (Thermo-Environmental Instruments model 49 P/S, Indianapolis, IN, USA). NO and NO_x are measured using a chemiluminescent analyzer (ML9841A, Tyledyne, Los Angeles, CA). Temperature in and around the chambers were measured by temperature probes mounted in each chamber on a white radiation shield and in shaded areas around the exterior of the chamber (R.M. Young Company, Traverse City, MI). Dewpoint (T_d) and relative humidity (RH) were measured continuously inside the chambers with a Relative Humidity Analyzer (Sable Systems RH-100, Las Vegas, NV, USA). Calibrations of all instruments were conducted prior to each experiment. The process used is described in detail elsewhere (Hu et al, 2007).

Ductwork

An illustration of the ductwork connecting the North and South chambers is shown in Figure 4. Air is moved from the North to the South chamber via a 19.3 cm x 6.61 m galvanized duct beneath the chamber floor that connects the two sides. The duct has an inline radial fan (Dayton 6K22, 1725 rpm, ½ hp motor, Dayton 4C659 fan) to transfer air between the North and South chambers. There is a 23.375 in. square HEPA filter (Alpha Cell, Flanders Filters, St. Petersburg FL, USA) downstream of the radial arm fan, so that particles from the North chamber can be removed as air flows into the South chamber. The HEPA filter (23.375 x 23.375 x 12 in.) sits in a 24 in. cube housing. It is rated to filter out at least 99.97% of all particles, and can handle up to 945 cfm.

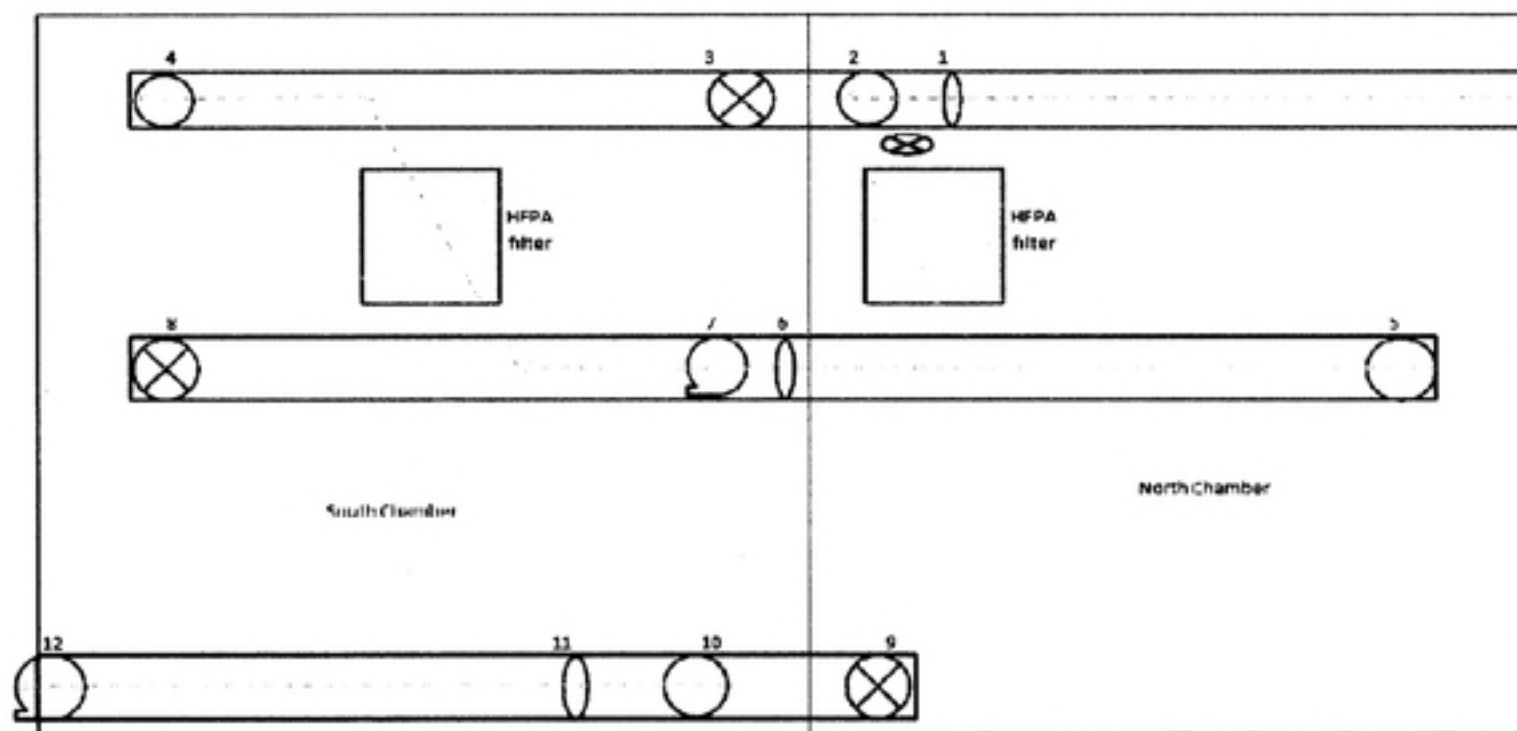


Figure 4. Schematic of ductwork below the chamber.

The flow of air from the North chamber to the South chamber is controlled by a series of blast gate valves 30.5 cm in diameter, which create the path for air to move from the North chamber to the South chamber. They are made from 3.2 mm galvanized sheet metal and are controlled with a screw-actuated stepper motor. Gates are opened in a combination different from that used to vent the chamber in order to force air to move from the North to the South chamber before moving outside. The gate that is immediately upstream of the radial arm fan (Gate 6 in Figure 4) is not opened fully, so the total flow from the North to the South chamber is restricted. Due to this, each experiment has a slightly different rate of transfer. As the air transfer takes place, make up air is drawn from outside the chamber through a 30.5 cm duct into the North chamber. Excess air flowing into the South chamber is vented through a gate valve in the floor and exhausted to the outside.

Experimental results were compared using an α -pinene + O₃ gas-particle chemical mechanism (Kamens and Jaoui, 2001) that was added to the Carbon Bond IV gas-phase chemistry (Gery et al, 1989) and simulations were performed with a photochemical kinetics simulation system (PKSS) written by Jeffries (Jeffries, 1991). This approach was used by Leungsakul et al (2005) to model d-limonene + O₃.

The rate of appearance of either O₃ or SF₆ into the South chamber required an additional reaction in which mass appeared in the South chamber with a rate coefficient equal to the transfer flow (f) divided by chamber volume (V). This is shown through ozone "appearing" with a rate constant (f/V) between the two chambers. The contents of the chamber were assumed to be mixed and were diluted with a first-order rate coefficient of f/V .

CHAPTER III

RESULTS AND DISCUSSION

It is a challenge to simultaneously introduce more than one dilute gas into a smog chamber without diluting a high concentration plume of the second gas in to the first. This may lead to artifacts in observed rates of reaction because the reaction rate, as gases diffuse into to the concentrated plume, will be a function of the high concentration gradient within the plume. This is especially true when attempting to observe particle nucleation. In order to investigate reactions at realistic concentrations, the method used here needs to be evaluated. This requires 1. measurement of the rate coefficients of nonreactive gases during the transfer of gases and particles from one chamber to another; 2. the ability to remove particles that may be inadvertently transferred from one chamber to the other so that nucleation process can be observed; and 3. the ability to model the initial gas phase reactions preceding nucleation, to demonstrate that chamber behavior using this method is consistent with known chemical behavior.

Using Sulfur Hexafluoride (SF_6) as an Unreactive Tracer

When both O_3 and SF_6 are added to the North chamber and flow from the North to the South chamber is begun, a decrease of both O_3 and SF_6 in North chamber is observed followed by an increase of O_3 and SF_6 in the South chamber. Under ideal conditions there would be no losses of SF_6 or O_3 during the transfer; and perfect mixing would exist at all

times in both chambers. This allows the two chambers to be treated as continuously stirred tank reactors (CSTR). Under these conditions, flow into the South chamber is vented to the outside, so a mass balance description of the change in a non-reactive gas such as SF₆ can be described as:

$$-\Delta \text{mass}_{\text{north}} = \Delta \text{mass}_{\text{south in}} = \Delta \text{mass}_{\text{south observed}} + \Delta \text{mass}_{\text{south vented}} \quad (1)$$

SF₆ concentration samples were taken every 10 minutes, alternating between the two chambers, in accordance with the rest of the chamber sampling system. The calculations of rate constants follow.

For a first order process, a change in concentration over time is expressed as:

$$\frac{dC}{dt} = k_{\text{rate}}[-C] \quad (2)$$

where concentration is expressed in units of mass/volume or as a mixing ratio (ppm) and k_{rate} is a rate constant with units of reciprocal time. Dividing Eq. 1 by volume and using the equivalent rates from Eq. 2, one obtains for SF₆:

$$[\text{SF}_6\text{N}] * k_{\text{rateN}} = [\text{SF}_6\text{S}] * k_{\text{rateS observed}} + [\text{SF}_6\text{S}] * k_{\text{rate S vented}} \quad (3)$$

where [SF₆N] is the concentration of SF₆ in the North chamber at a given time, [SF₆S] is the concentration in the South chamber and k_{rate} are the respective rate coefficients. For mass balance purposes, any SF₆ that leaves the North chamber is assumed to be transferred to the South chamber; that is, there are no leaks or other losses in the ductwork. Therefore, $k_{\text{rate N}} = k_{\text{rate S in}}$ and, once the South chamber is fully mixed, $k_{\text{rate S vented}}$ can be considered equal to $k_{\text{rate N}}$ as

$$[\text{SF}_6\text{S}] * k_{\text{rate S observed}} = [\text{SF}_6\text{N}] * k_{\text{rateN}} - [\text{SF}_6\text{S}] * k_{\text{rate S vented}} \quad (4)$$

After the dilution begins and as $[SF_6]_S$ approaches $[SF_6]_N$ one would expect $k_{rate\ S}$ observed to be approximately twice that of $k_{rate\ N}$.

SF_6 GC data was acquired with a strip chart recorder, so peak heights were used as a surrogate for concentrations (Figure 5).

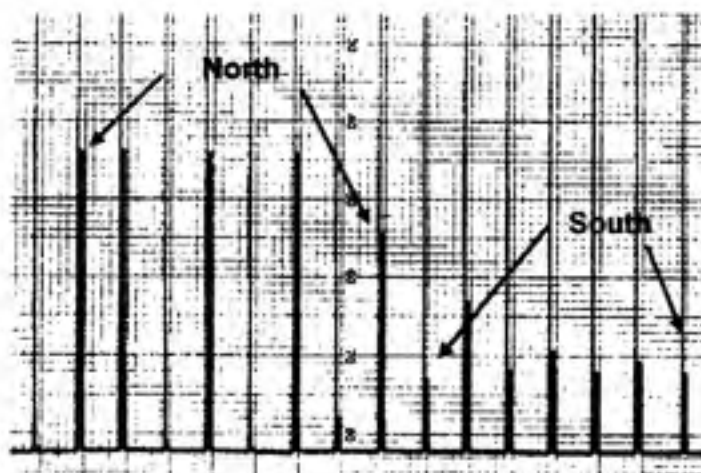


Figure 5: Example of SF_6 GC peak height data using a strip chart recorder (June 12, 2007 experiment). Taller peaks are from the North chamber and shorter peaks from the South. Samples were taken every 10 minutes. Transfer begins after the 4th SF_6 peak in the North chamber, starting from the left.

This permitted an estimate of the SF_6 rate coefficients for the loss of SF_6 from the North chamber. The observed rate coefficients are shown in Table 1.

In this table, Chamber indicates either the North or South side of the smog chamber, and reactant indicates the quantity of each reactant within their respective chamber. Δ particle concentration ($\mu g \cdot m^{-3}$) indicates the change in particle concentration observed over the course of the experiment when there was a nucleation event. Finally, k_{rate} (min^{-1}) is the rate of transfer for each chamber. dlilim is d-limonene, and a-p is α -pinene. By convention, k_{rate} is defined to be positive, so a negative rate is flow out of a chamber, while positive rate is flow into a chamber. The rate coefficients of air leaving the North chamber

range from -0.008 to -0.017. The average $k_{rate\ N}$ was calculated to be -0.012, and with a standard deviation of 0.0034, rate coefficients are similar among experiments. Measured rate coefficients for nonreactive gas entering the South chamber are far less consistent. A wider range is observed, from 0.015 up to 1.645. The average rate coefficient for the South is 0.208, and the standard deviation is 0.0134. A possible reason for this variability is that when air from the North chamber first enters the South chamber, it is not perfectly mixed.

PKSS was used to model the appearance of SF_6 in the South chamber using data from Figure 5. The results of three experiments, the relative concentration of modeled SF_6 compared to observed values over time, are shown in Figure 6. In all cases, the modeled SF_6 concentration was greater than the reported concentration; similar overpredictions were also seen in the O_3/α -pinene model. A correction factor between 0.5 and 0.8 was applied to the individual dilution rates to bring about a closer match between modeled and observed values. For a given day, both the modeled SF_6 and O_3 data differ from observed data by the same amount. This suggests that there was some loss in the system through leaks in the ductwork during the transfer process. Details of individual experiments will be discussed in detail in the modeling section.

Table 1: Summary of Experiments and Transfer Rates*				
Date	Chamber	Reactant	Δ particle concentration ($\mu\text{g}\cdot\text{m}^{-3}$)	Observed k_{rate} (min^{-1})
9-May-07	N	0.2445 ppm O_3		-0.008
9-May-07	S	0.5 ppmC dlim	None	0.015
17-May-07	N	0.251 ppm O_3		-0.015
17-May-07	S	0.017 ppmV a-p	0.5	1.645
23-May-07	N	0.205 ppm O_3		-0.012
23-May-07	S	0.01 ppmC dlim	None	0.025
12-Jun-07	N	0.174 ppm O_3		-0.016
12-Jun-07	S	0.01 ppmV a-p	0.3	0.032
27-Jun-07	N	0.211 ppm O_3		-0.017
27-Jun-07	S	0.01 ppmV a-p	0.04	0.0453
14-May-08	N	0.23 ppm O_3		-0.011
14-May-08	S	0.02 ppmV a-p No clean air used	None	0.023
27-May-08	N	0.27 ppm O_3		-0.011
27-May-08	S	0.02 ppmV a-p Water vapor	None	0.016
26-Jun-08	N	seed particle		-0.009
26-Jun-08	S	in N only	None	0.021
1-Jul-08	N	0.3 ppm O_3		-0.01
1-Jul-08	S	0.03 ppmV a-p Water vapor	None	0.039
10-Jul-08	N	0.1 ppm O_3		-0.008
10-Jul-08	S	0.03 ppmV a-p Background seed	None	0.031

*Indicates reactants and rates of transfer. dlim is d-limonene, a-p is α -pinene, O_3 is ozone

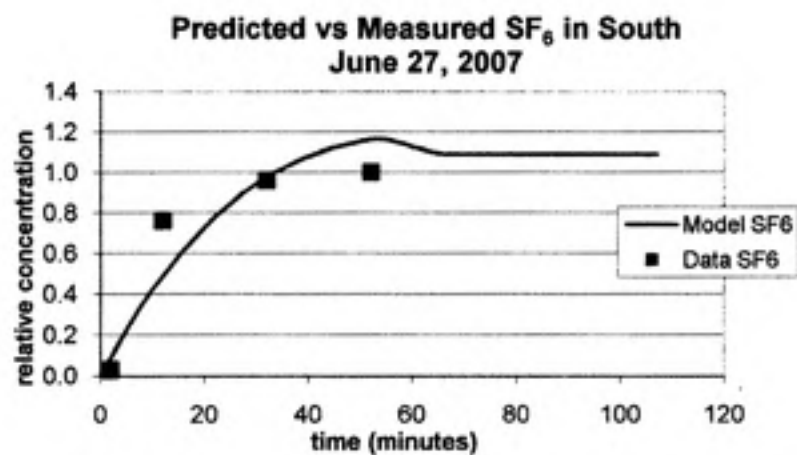
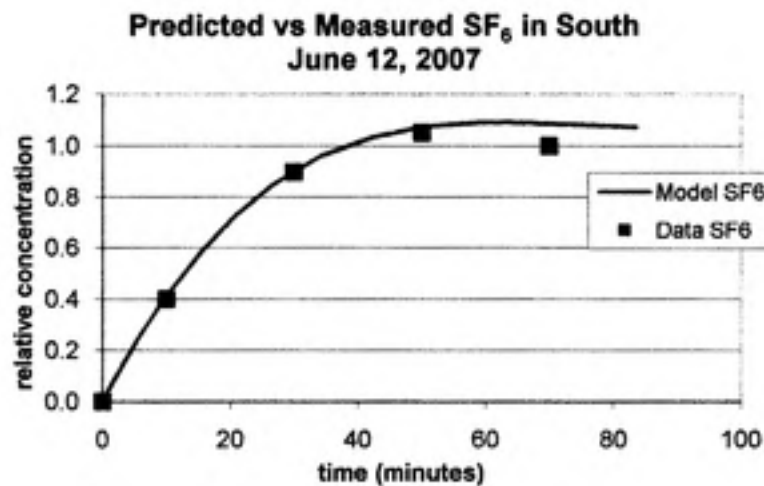
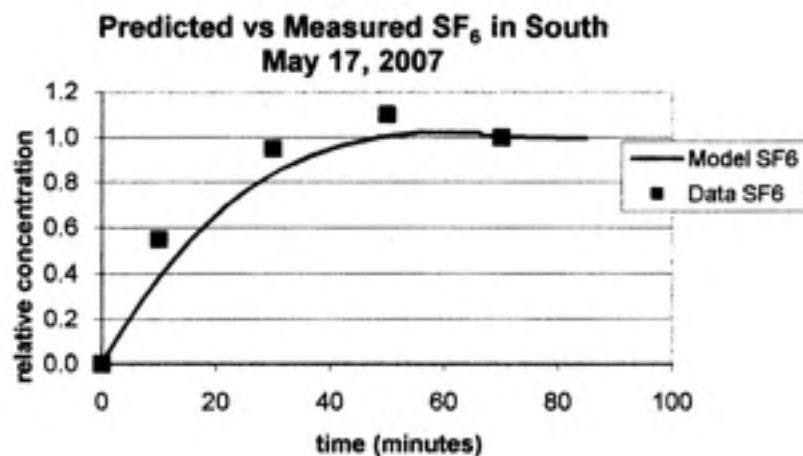


Figure 6: Simulation of SF₆ appearance in the South chamber from the chart data shown in Figure 5 with correction factor of 0.8 applied to all simulations.

It is also useful to calculate the half-life of SF₆ in the North chamber once the transfer has begun (Table 2). Half-life is a good estimate of how long it takes air to be vented out of the South chamber, and can indicate whether α -pinene decay observed on GCs is due to reaction with O₃ or elimination from the chamber.

Table 2: Flow Rate and Half-Life of Air in South Chamber*			
Date	$k_{rate\ N}$	Air Flow (m ³ min ⁻¹)	Half-Life (min)
9-May-07	-0.008	1.088	86.64
17-May-07	-0.015	2.04	46.21
23-May-07	-0.012	1.632	57.76
12-Jun-07	-0.016	2.176	43.32
27-Jun-07	-0.017	2.312	40.77
14-May-08	-0.011	1.496	63.01
27-May-08	-0.011	1.496	63.01
26-Jun-08	-0.009	1.224	77.01
1-Jul-08	-0.01	1.36	69.31
10-Jul-08	-0.008	1.088	86.64

*shows the flow of air from the North chamber to the South chamber, in m³min⁻¹, and the half-life of the air in each chamber. A shorter half-life indicates a faster transfer, while a longer half-life indicates a slower transfer.

The k_{rate} values shown in Table 2 can be applied to Eq. 2 to calculate how much air moves through the two chambers over the course of the transfer. Given that an expression of a rate constant is total flow divided by volume, the observed rate constants can be multiplied by the chamber volume (136m³) to calculate air flow through the ductwork. The estimated transfer flow for the experiments determined in Table 3 ranges from 1.088 to 2.312 m³*min⁻¹. Reaction times for a typical experiment were approximately one hour; at least 50% of the air in the South chamber was diluted by air flowing from the North chamber over this period.

These experiments demonstrate that SF₆ in the North chamber is highly diluted and the decrease in SF₆ concentration in the North chamber combined with an increase in concentration in the South chamber indicates that SF₆ and other gases pass through the HEPA filter and are available for reaction in the South chamber. The modeled data (Figure 6), which compares the simulated and observed increase in SF₆ in the South chamber, shows that there is a good agreement between observations and the modeled data with the application of a correction factor. This suggests that there are losses of SF₆ and other, reactive, gases somewhere in the system, which could be due to leaks in the ductwork or imperfect mixing.

Table 3: Percentage of Air Replaced over the Course of One Hour*				
Date	$k_{rate\ N}$	Air Flow (m ³ min ⁻¹)	Air Moved 1 hr (m ³)	Percentage Diluted
9-May-07	-0.008	1.088	65.28	48%
17-May-07	-0.015	2.04	122.4	90%
23-May-07	-0.012	1.632	97.92	72%
12-Jun-07	-0.016	2.176	130.56	96%
27-Jun-07	-0.017	2.312	138.72	102%
14-May-08	-0.011	1.496	89.76	66%
27-May-08	-0.011	1.496	89.76	66%
26-Jun-08	-0.009	1.224	73.44	54%
1-Jul-08	-0.01	1.36	81.6	60%
10-Jul-08	-0.008	1.088	65.28	48%

* $k_{rate\ N}$ is the rate coefficient at which air leaves the North chamber, also found in Table 1. Air Flow (m³min⁻¹) is $k_{rate\ N} \cdot 136\text{ m}^3$, the volume of the chambers. This value is multiplied by 60 minutes to give the volume of air moved in one hour. The volume is then divided by the chamber volume to give the percentage of South chamber air that has been replaced when nucleation begins.

HEPA Filter Characterization Experiments

An experiment was conducted in order to test the efficacy of the HEPA filter that is situated along the path between the North and South chambers (see Figure 4). This was

done to show that nucleation observed in the South chamber was not influenced by particles entering from the North chamber. Unlike other experiments, this one was conducted during the day as it was not necessary to exclude the effects of photochemistry; photo-reactive elements were not introduced. For this experiment, background meteorological data was taken, as well as O_3 and NO_x data. GCs were not utilized, and only one DMA was used. The DMA operated on high flow mode (15 lpm), and scanned between 6 nm and 216 nm. The sampling system switched between the North and South chambers every ten minutes. Over the course of 40 minutes, $4 \mu\text{g}\cdot\text{m}^{-3}$ of 0.005 M ammonium sulfate $((\text{NH}_4)_2\text{SO}_4)$ salts in 225 mL pure deionized water was added to the North chamber using a medical nebulizer and air supplied from the clean air generator. The volume of particles in both the North and South chamber is shown in Figure 7. Particles injected into the North chamber had a mode at approximately 100 nm, with no particles in post-nucleation mode (5 nm to 20 nm). The particle size distribution across the South chamber was relatively constant over the course of the experiment.

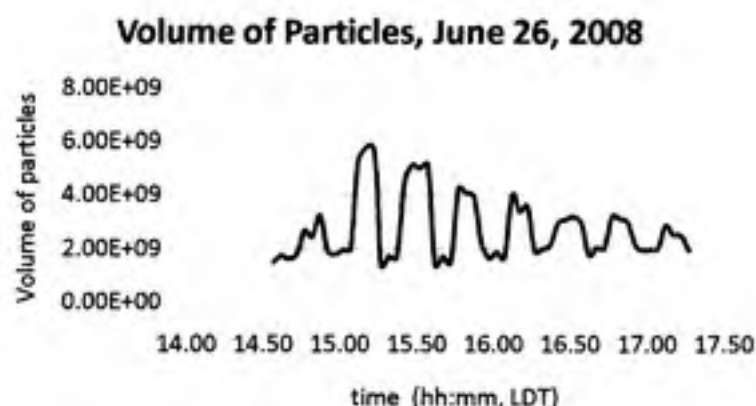


Figure 7. Volume of particles in both chambers, June 26, 2008. Time (x-axis) and volume (y-axis) is in $\text{particles}\cdot\text{m}^{-3}$, which corresponds to $\mu\text{g}\cdot\text{m}^{-3}$. Peaks correspond to scans taken from the North chamber, while troughs are scans taken from the South chamber. Samples from each chamber were taken at 10-minute intervals.

Figure 8 shows particle count size distributions. In this figure, the x-axis indicates the diameter of the particle in nm and the y-axis shows the number of particles per cubic centimeter (cc). The solid line is the distribution in the South chamber, and the dashed line is the distribution in the North chamber. Background scans were taken at approximately 14:00 LDT, and the injection began at 14:45 LDT. The transfer, which is defined as the time at which all gates are fully open and the inline transfer fan is turned on, began at 15:29 LDT.

Together, Figures 7 and 8 show that the HEPA filter effectively removes particles between 6 and 216 nm. In Figure 7, the volume of particles in the North chamber increases from $3 \mu\text{g}\cdot\text{m}^{-3}$ to $6 \mu\text{g}\cdot\text{m}^{-3}$ during the injection period, then decreases back to nearly the original volume over the course of the next two hours. In the transfer period, the volume of particles in the South chamber increases only slightly from $1.5 \mu\text{g}\cdot\text{m}^{-3}$ to $2 \mu\text{g}\cdot\text{m}^{-3}$. This is due to the mode of the particles in the South chamber increasing over the time, from 75 nm to 100 nm. This can be seen in the lower two graphs in Figure 8.

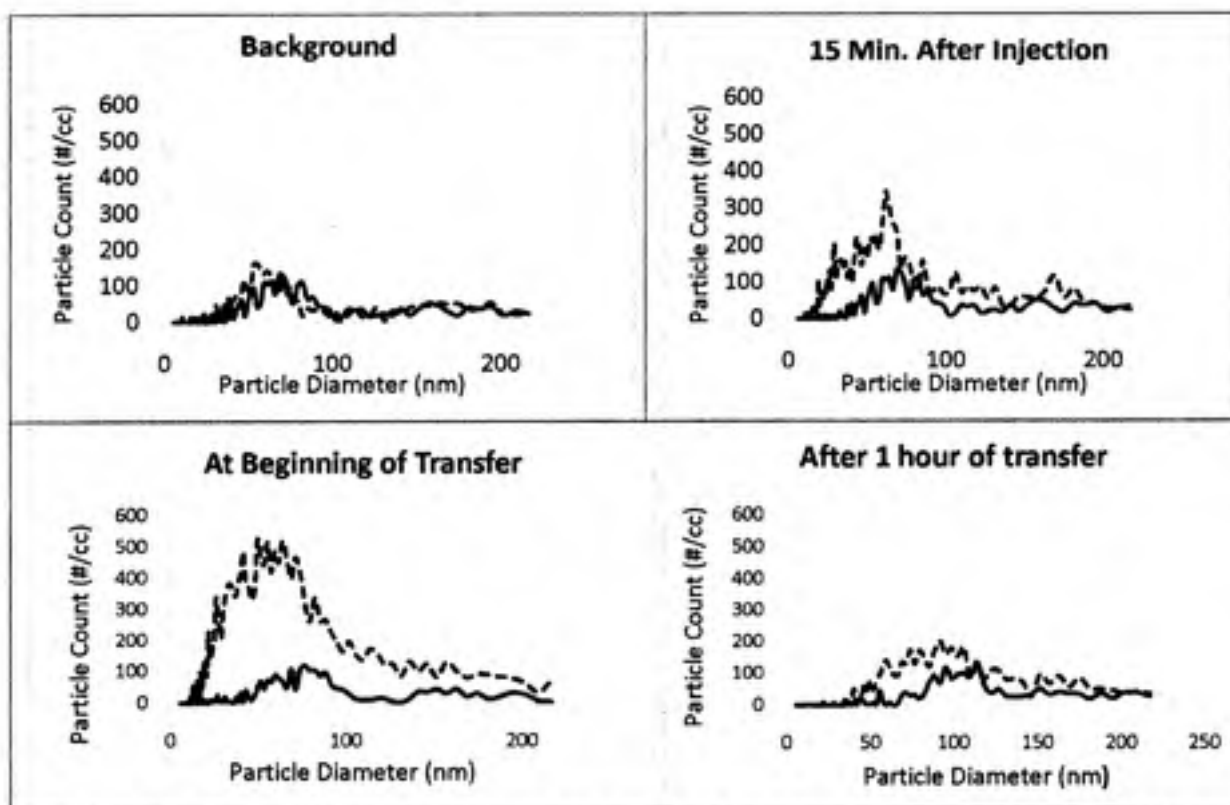


Figure 8: Growth and decay of particles from 6 nm to 216 nm as they are transferred from one chamber to the other through the HEPA filter. Dashed line indicates particle distribution in the North chamber, solid line indicates particle distribution in the South chamber. Addition of ammonium sulfate particles to the North chamber began at 14:45 LDT, and the transfer began at 15:29.

This is likely due to a small percentage of “breakthrough” particles; particles that are not removed by the HEPA filter in addition to outside air that is exchanging with the South chamber at a rate of approximately 1% an hour. Still, it is important to note that the breakthrough particles are not of post-nucleation size (5-20 nm). This means that particle formation observed in the South chamber during nucleation experiments is not due to influences from the North chamber.

Nucleation Experiments

It is important to test the previously described method on a real system. However, a truly accurate facsimile of ambient air is difficult to capture in a chamber system. First, foliar emission rates of α -pinene are highly variable and dependent upon temperature, sunlight, the season, and a host of other variables. It is estimated that across North America, the average monoterpene emission rate is $<0.1\text{--}3.0\text{ ppmC}\cdot\text{h}^{-1}$ (Guenther et al, 1994). As α -pinene comprises approximately 40% of monoterpene emissions (Spirig et al, 2004), α -pinene's individual contribution can be estimated to be $<0.04\text{--}1.2\text{ ppmC}\cdot\text{h}^{-1}$. A lower bound was reported by Haapanala et al(2007); in a boreal forest in early spring α -pinene was reported to be the dominant monoterpene emitted and daytime surface concentrations averaged 37 ppt. In the experiments described here, α -pinene concentrations were between 0.01 and 0.03 ppmC, with nucleation seen at the lowest concentrations. It would be difficult to lower the concentration any further due to current detection limitations. Second is the problem of changing rates of reaction for any additional reactants introduced into the system at the injection point, which has been discussed. Finally, the addition of other factors such as water vapor would only obscure any particle growth that may be seen.

Dry Nucleation

A series of three basic α -pinene nucleation experiments were conducted in the summer of 2007 to test the method. Two additional experiments were conducted with d-limonene, but were discarded because the d-limonene reacted and formed particles immediately after injection into the South chamber before the transfer began. This reaction occurred immediately due to d-limonene's faster reaction rate; one current rate coefficient

estimate is $(2.95 \times 10^{-15})\exp(-783/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$, where T is ambient temperature in Kelvin (Khamaganov and Hites, 2001). The reaction time of α -pinene is slower: $(1.492 \times 10^{-15})\exp(-732/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$. The lower reaction rate ensured little to no reaction occurred before the introduction of ozone from the North chamber and subsequent observable nucleation occurred. Hence the primary focus of this work was the reaction of α -pinene with O_3 . The initial conditions of the experiments are summarized in Table 4. In this table, α -pin is the amount of α -pinene introduced into the South chamber in parts per million of carbon (ppmC). O_3 , NO, and NO_2 are provided in parts per million (ppm), and are taken at the beginning of the transfer, which is the time shown in the Begin Time column. The End Time column shows the time at which the number of nucleated particles reaches a peak and coagulation begins. The volume of background particles in the chamber is shown in the Bkgd Vol. column. The initial temperature (Init. Temp) and final temperature (Final Temp) columns show the temperatures at the beginning and ending times, given in degrees Kelvin. Humidity measurements are provided as ppm of water at both the beginning and end of the transfer process for both chambers, and the total number of particles created due to nucleation is provided in the column Total # of Particles. The value shown is the number of particles per cc in the South chamber at the end time. Humidity data is not available for the May 17, 2007 experiment due to a malfunctioning T_d meter.

In these experiments, background trace O_3 in the South chamber was removed by adding ppb levels of NO before α -pinene was injected. Ozone was added to the North chamber, along with SF_6 as a tracer. No additional background seed particles or water vapor

were added, though water vapor from the North chamber entered the South chamber during the air transfer period.

Table 4: Summary of Conditions of Dry Nucleation Experiments*												
Date	α -pin (ppmC)	O ₃ (ppm)	NO (ppm)	NO ₂ (ppm)	Bkgd Vol.	Begin Time	End time	Init. Temp	Final Temp	Init H ₂ O (ppm)	Final H ₂ O (ppm)	Total # of Particles
May 17 2007 N	-	0.2512	0.008	0.0001	2.2e8	20:15	21:11	289.17	284.79	N/A	N/A	2,513
May 17 2007 S	0.017	0.001	0.0267	0.0534	5.3e7							
June 12 2007 N	-	0.1656	0.0001	0.0001	2.5e8	19:31	21:09	299.8	292.4	3115	10296	30,210
June 12 2007 S	0.01	0.003	0.0348	0.0272	4.5e8					5981	8739	
June 27 2007 N	-	0.2113	0.0001	0.0089	4.5e8	19:34	22:05	297.3	294.9	2295	15739	1,113
June 27 2007 S	0.01	0.0001	0.0132	0.037	5.5e7					8239	13558	
May 14 2008 N	-	0.0308	0.0002	0.0015	3.5e9	21:11	0:00	290.7	288.2	11840	12597	-
May 14 2008 S	0.02	0.0228	0.0001	0.0024	1.4e10					11712	12612	

*A-pin is α -pinene injected into the South chamber. O₃, NO, and NO₂ are all given in parts per million (ppm), and the values shown are at the beginning of the transfer. Begin time is the time at which the transfer begins, and End time is the time at which the number of particles peaks. Both times are given in LDT. Bkgd Vol. shows the number of particles per cubic meter in each chamber before the transfer took place. Init. Temp and Final Temp are the temperatures (in Kelvin) corresponding to begin and end time, and Init. H₂O and Final H₂O are ppm of water. Total # of particles indicates the total number of particles created in the South chamber, and is the number of particles at the end time.

Nucleation and Coagulation

Varying numbers of particles were formed due to nucleation in three of the α -pinene experiments. In the May 17 experiment (see Figure 9), particles began to appear at the lowest detectable size (5.72 nm) after approximately 40 minutes. They grew rapidly in number for 25 minutes before reaching their peak at 21:11 LDT. This can be seen in Figure 10. After that time, coagulation began to occur.

An estimate of the change in particle concentration due to coagulation was compared to SMPS observations. To calculate this, the following equation was used (Hinds, 1999):

$$N(t) = \frac{N_0}{1 + N_0 K_0 t} \quad (5)$$

where $N(t)$ is the number of particles at a given time, N_0 is the number of particles at time $t=0$, and K_0 is the coagulation coefficient. An average coagulation coefficient ($\bar{K}$) was calculated, in order to estimate polydisperse coagulation, as a wide range of particle sizes are observed. $\bar{K}$ was calculated using the following equation (Lee and Chen, 1984), as reported in Hinds (1999):

$$\bar{K} = \frac{2kT}{3\eta} \left(1 + \exp(\ln^2 \sigma_g) + \frac{2.49\lambda}{CMD} [\exp(0.5 \ln^2 \sigma_g) + \exp(2.5 \ln^2 \sigma_g)] \right) \quad (6)$$

where k =Boltzmann's constant ($1.39 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$), T =temperature (K), η =viscosity of air, σ_g =geometric standard deviation, λ =mean free path, and CMD = count median diameter. A table was assembled, adapted from Hinds (1999) and detailed in Appendix A, where CMD was calculated from SMPS data taken from the sample with the highest particle count. Entered into this chart were counts at every particle diameter, and this data was used to calculate count mean diameter ($\bar{d}$) (μm) and geometric mean diameter (d_g) (μm). It

was assumed that the distribution of particles was lognormal, so $d_g = \text{CMD}$ (μm). Using this data, it is possible to use the Hatch-Choate equation (Hinds, 1999) to solve for σ_g :

$$\bar{d} = \text{CMD}(0.5 \ln^2 \sigma_g) \quad (7)$$

May 17, 2007 South Chamber Particle Distributions

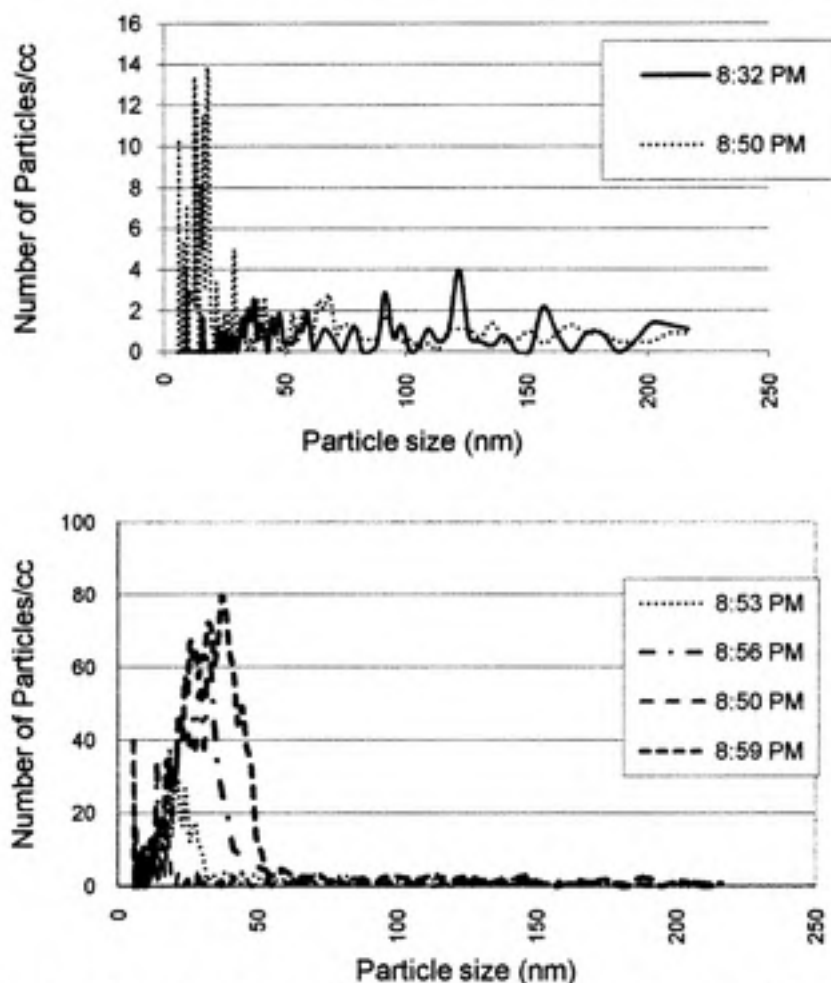


Figure 9: May 17, 2007 South chamber particle distributions. Sequential DMA scans from 6 to 216 nm show particle growth over time. The horizontal axis indicates particle size (nm) and the vertical axis indicates the number of particles per cc.

Table 5: Values Used to Calculate Coagulation*								
Date	Temp	C_c	d_0 (nm)	K_{avg} ($cm^3 s^{-1}$)	$(\bar{d})$ (μm)	d_g	CMD	GSD
17-May-07	291.5	4.48	47.8	3.05E-09	0.03594	0.03072	0.03072	1.7511
12-Jun-07	299.8	9.57	19.4	3.31E-09	0.01904	0.0184	0.0184	1.298878
27-Jun-17	297.3	5.81	34.59	2.84E-09	0.03494	0.03061	0.03061	1.672641

* C_c is the slip correction factor, d_0 is the particle mode at the count maximum, K_{avg} is the average coagulation coefficient, CMD is the count median diameter, and GSD is geometric standard deviation.

The results of Eq. 7 can be used in Eq. 6 to solve for $\bar{K}$ and thus solve for the number of particles expected after a given period of time, in this case, one hour. Values used to calculate coagulation are summarized in Table 5, and the results of this calculation are shown in Figures 10, 12, and 14. The observed particle counts are shown by the line on the graph, and calculated points for one hour and two hours after the nucleation peak are shown by the points. Values are provided next to the points. For the first hour, the observed number of particles differs from the expected number of particles by approximately 35%. This difference is likely because the transfer continued for 33 minutes after the particle count peak was reached. Had the transfer ended at or before the particle peak was reached, the expected and observed values would have been in closer agreement, differing by 12%. This is shown in the second point on the graph, which is adjusted for the observed particles after the first hour.

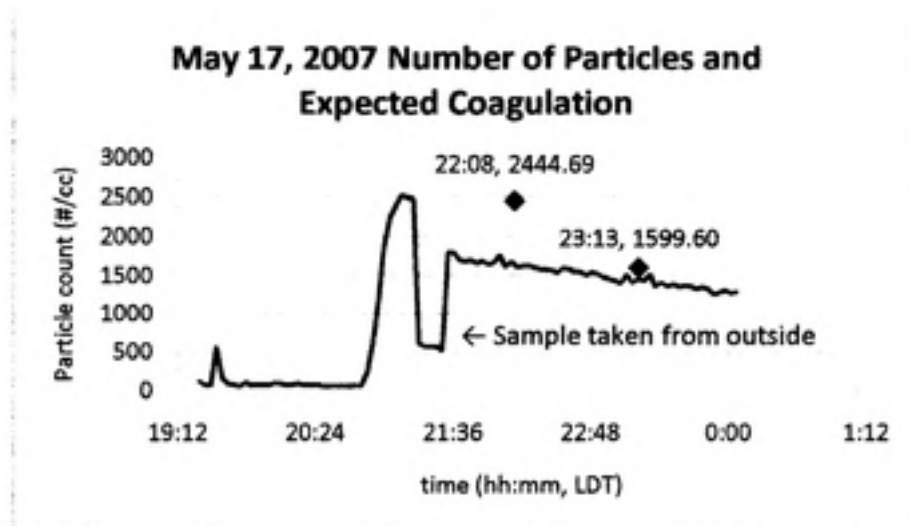


Figure 10. May 17, 2007 Particle Counts and Expected Coagulation. The number of particles over the course of the experiment with predicted particle values using coagulation calculations. The points are calculated particle counts; the values indicate time and the number of particles expected at that time.

More pronounced nucleation was seen in the June 12, 2007 experiment (see Figure 11). In this experiment, homogeneous nucleation began after approximately an hour of transfer, and particles grew rapidly for 40 minutes before reaching a maximum of over 30,000 new particles.

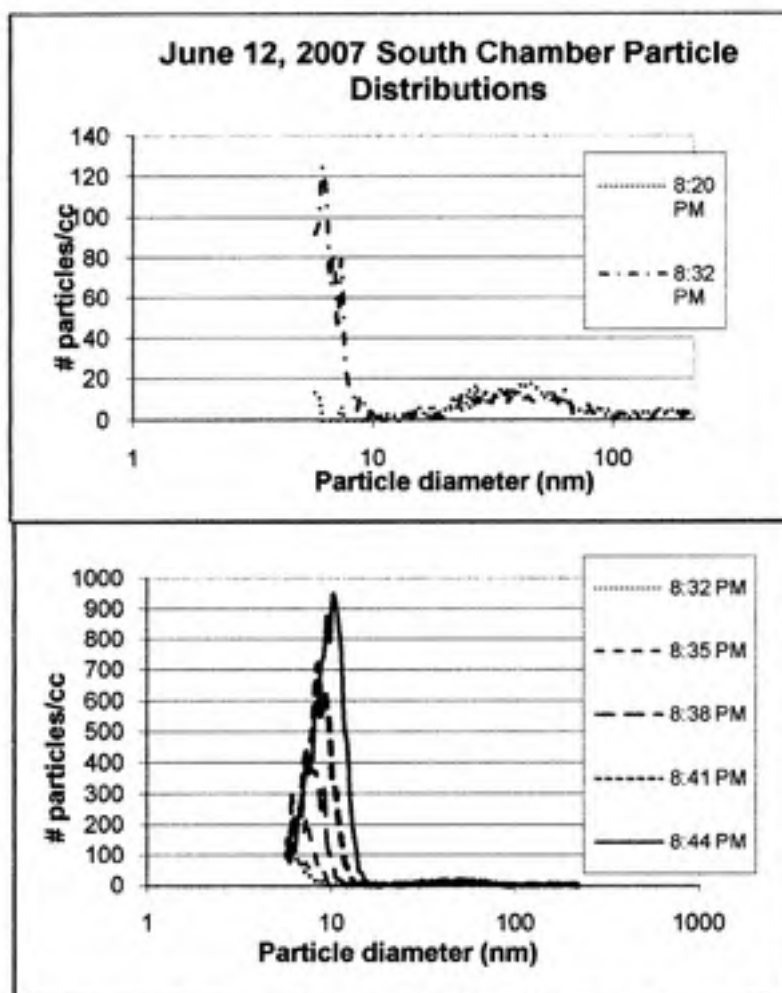


Figure 11. June 12, 2007 South chamber particle distributions. Sequential DMA scans from 6 to 216 nm show particle growth over time Horizontal axis shows particle diameter (nm), vertical axis shows particle count per cubic centimeter.

Expected coagulation numbers were computed using the same method as detailed above, and are shown in Figure 12. In this experiment, calculated expected particle counts are closer to observed data. In the first point, one hour after the observed particle formation peak, the expected number of particles differs from the observed number of particles by just 5%. In the second point, two hours after nucleation ends, the difference between observed and expected particle counts differ by 18%.

June 12, 2007 Number of Particles and Expected Coagulation

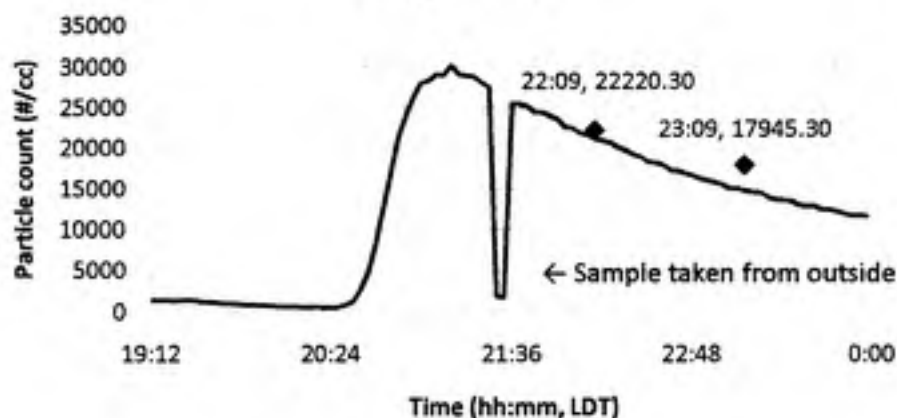


Figure 12. June 12, 2007 Particle Counts and Expected Coagulation. Expected coagulation calculation and observed particle counts. The first point indicates the number of expected particles one hour after the particle count maximum, and the second peak indicates the same after two hours.

The June 27 experiment differs from the previous two in several respects. First, there was no clear observable nucleation burst similar to that of other days; the post-nucleation clusters had a wider range that was maintained through growth and coagulation. Second, there are significantly fewer new particles created in this experiment than in the other two; this experiment produced one-half the particles of the May 17 experiment and one-thirtieth the particles of the June 12 experiment. Particle growth took longer to begin, as well. The transfer began at 19:34 LDT, and particle growth did not begin until 20:55 LDT, nearly 1.5 hours after the transfer began. This onset of growth is the slowest of all three days. Particle growth did not begin until after the air transfer ended at 20:45 LDT.

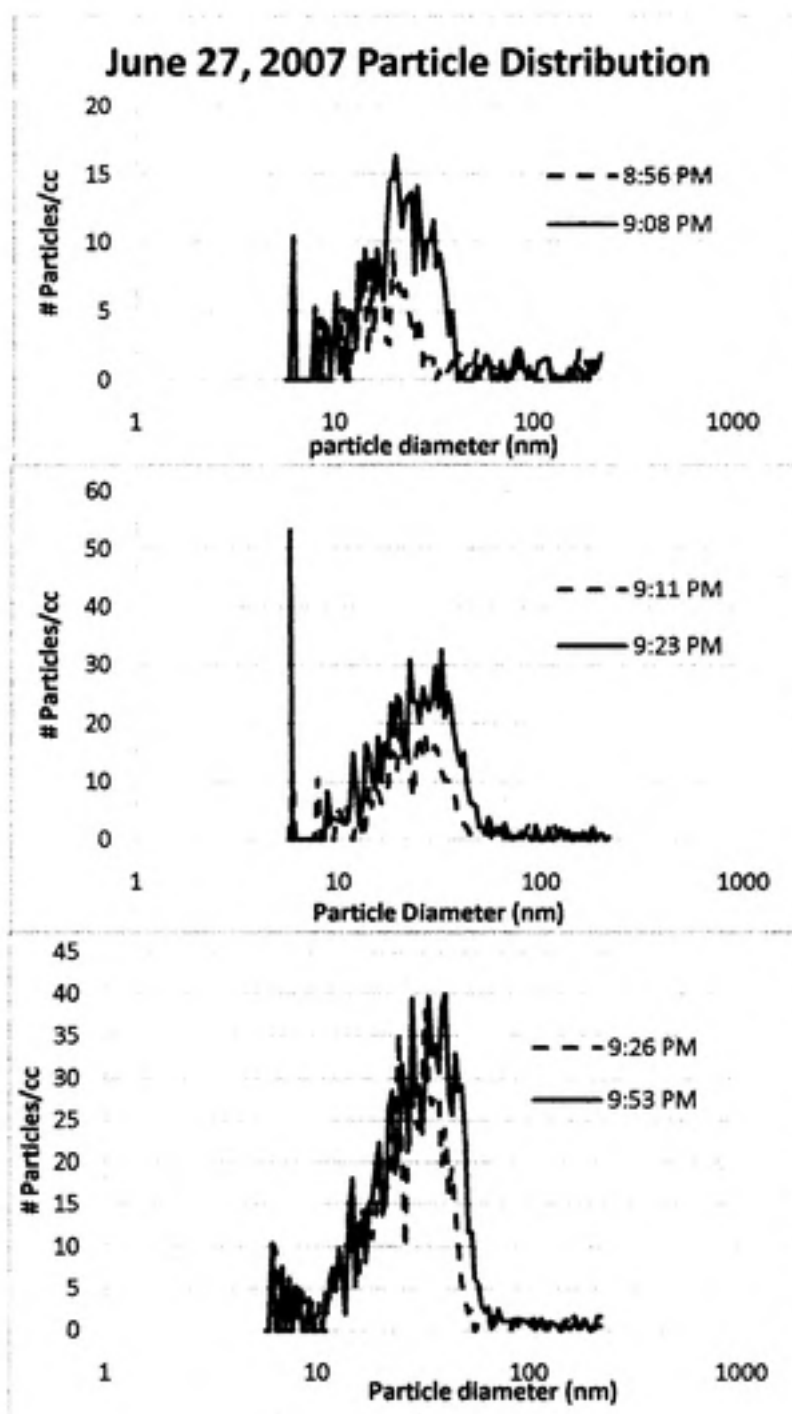


Figure 13. June 27, 2007 particle distribution. Sequential DMA scans from 6 to 216 nm show particle growth over time . Horizontal axis shows particle diameter (nm), vertical axis shows particle count per cubic centimeter.

The coagulation calculations for the June 27 experiment are much closer to observed values at both times calculated than the other two experiments. The observed particle count differs from the expected particle count by 13% after the first hour, and by 7% after the second hour. This agreement is good because the air transfer ended before any appreciable particle growth occurred and no newly created particles were exhausted. Taken together, the three coagulation calculations show that, in the absence of the transfer of air, the particle growth and subsequent reduction of particle counts by coagulation agrees with polydisperse coagulation theory as described in literature (Hinds, 1999).

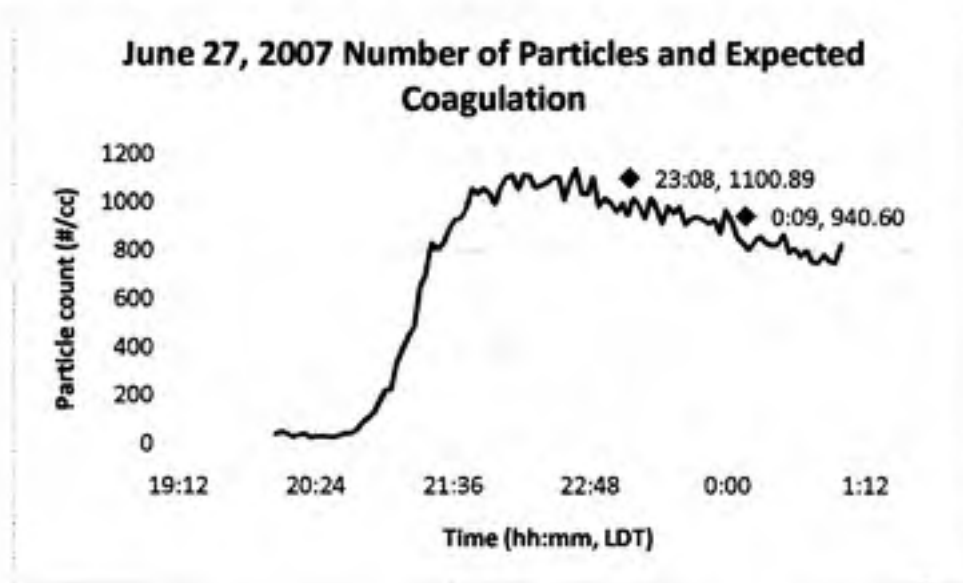


Figure 14. June 27, 2007 Particle Counts and Expected Coagulation. Expected coagulation particle counts and observed particle counts. Points indicate expected particle counts one and two hours after the particle count maximum was reached.

A final nucleation experiment was conducted on 14 May, 2008. This experiment attempted to re-create the previous three experiments using clean rural air from outside, without purging with air from the clean air generator. Experimental conditions are summarized in Table 4. Figure 15 shows the particle count and volume over the course of

the experiment. No nucleation directly attributable to the ozonolysis of α -pinene could be observed. Scans of the South chamber prior to the injection of α -pinene showed particles occurring in the post-nucleation size range with a magnitude of 6×10^2 particles per cc. During the air transfer process, the volume of particles decreased, with a slight recovery of mass once the transfer was completed and all gates were closed. It is possible that nucleation did occur in this experiment and was simply not detectable under these conditions.

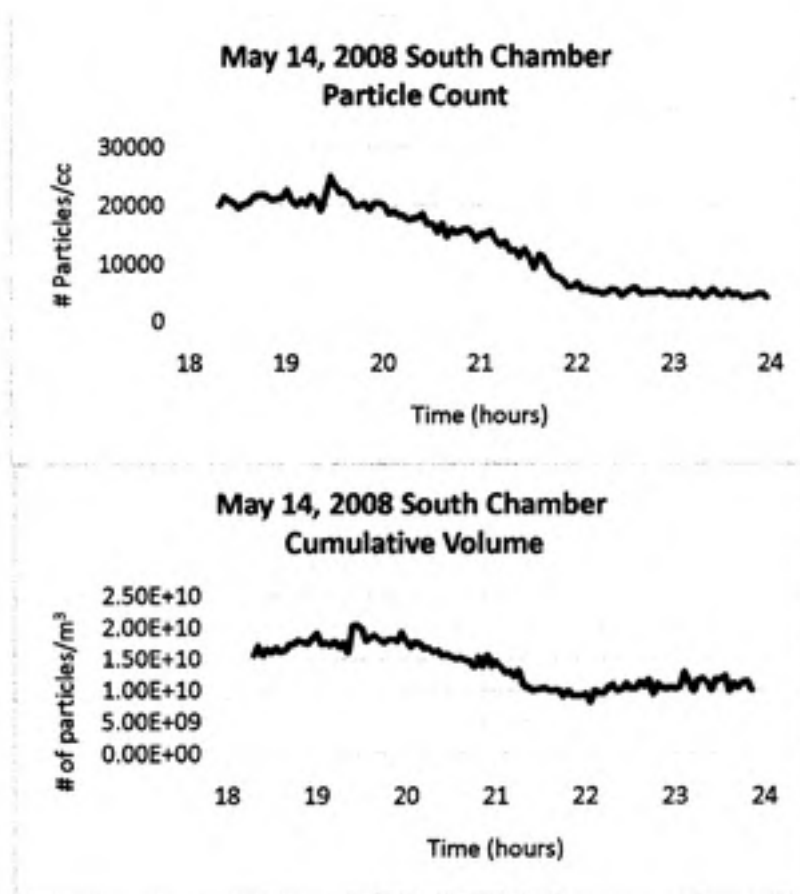


Figure 15: Particle count and volume summary for May 14, 2008 experiment.

Comparison of Experimental Data to Modeled Data

It is extremely difficult to accurately quantify the process of particle formation as it is happening in an outdoor smog chamber. Only the initial reactants and the final products can be described with any accuracy. Intermediate products are better analyzed using a flow reactor system. It is therefore helpful to compare experimental data from an outdoor chamber against a photochemical model containing known chemical processes in a continual dialogue of observations, testing, and feedback. As such, the necessity of comparing observed data to a model is two-fold: first to ensure that what is seen in the field is consistent with known chemistry and second to test the robustness of the model and its applicability to a wide variety of conditions.

For all experiments, observed data was modeled using the Carbon Bond IV (CB-IV) photochemical model (Gery et al, 1989). The model was operated within PKSS (Jeffries, 1991), a collection of programs that, when combined, are a simple box model differential equation solver. In addition to the gaseous compounds from CB-IV, an additional particle mechanism that simulates the degradation of α -pinene as it reacts with O_3 was used (Kamens et al, 1999; Kamens and Jaoui, 2001). This particle mechanism was further edited to remove any reactions that are driven by the presence of sunlight.

All three experiments where nucleation was observed are shown in the figures below (Figures 16, 17, 18). In these figures, "reacted a-pin" shows the amount of α -pinene that is reacted in the system and goes on to form various end products. "apin-zero" shows the rate of decay of α -pinene if none were reacted. "a-pinene" is the modeled rate of

decay, including both reaction and exhaustion from the South chamber. "O3" shows the modeled rate of increase of ozone. Dots indicate observed data. The starting times in the model are defined to be the times that the transfer begins, so in all cases observed data is provided for times earlier than the model start times.

The particle mechanism was altered slightly from its original form. Information providing for the gain of O₃ from the North chamber was added as a simple addition with a reaction rate equal to k_{rate} , found in Table 2, with a correction factor applied. A dilution factor was also added to simulate reactant loss from the South chamber beyond that amount allowed for normal wall loss. The complete mechanism is included in Appendix B.

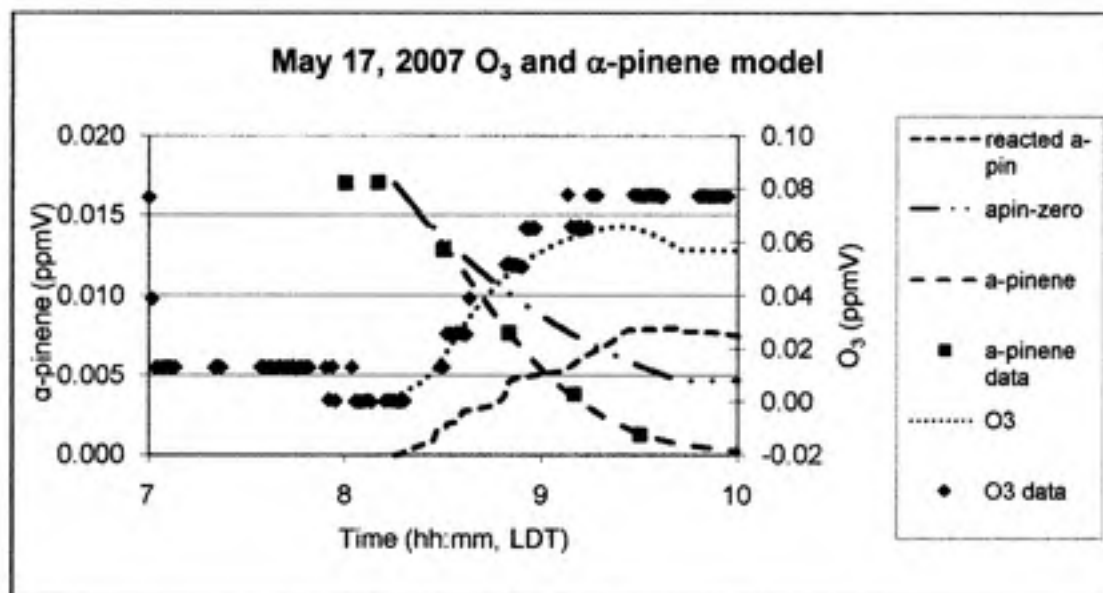


Figure 16.

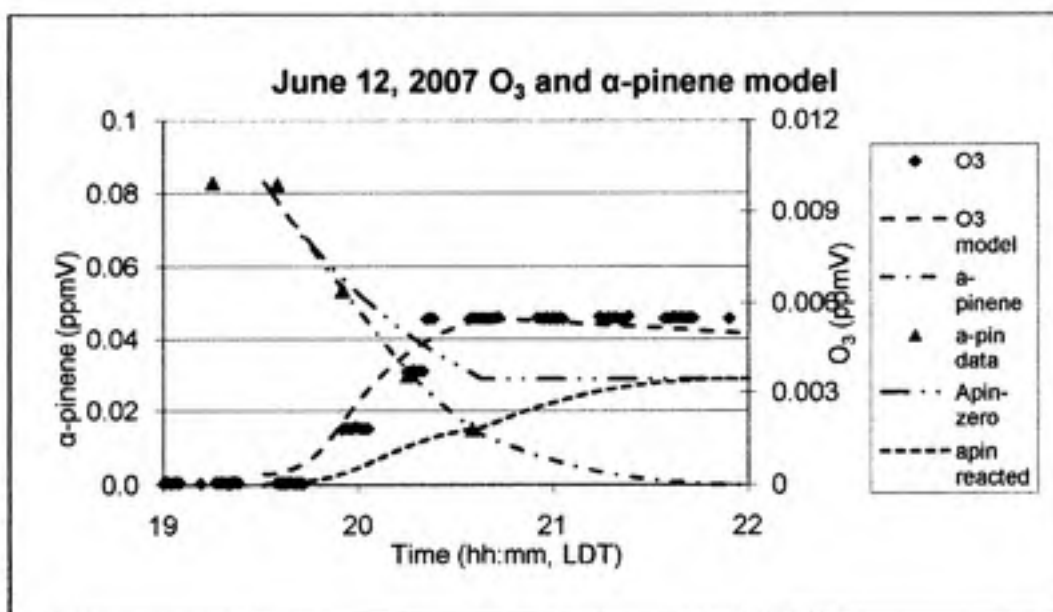


Figure 17.

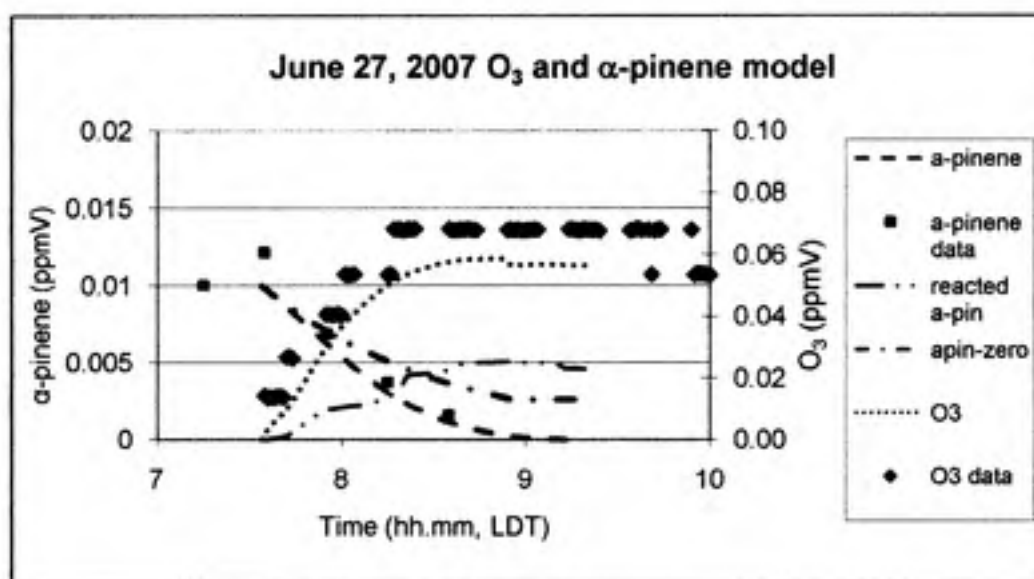


Figure 18.

Figures 16, 17, and 18: α -pinene + O_3 model for the dry experiments. These figures show the model results compared against observed data. Reacted a-pin shows the amount of α -pinene that is reacted in this system and goes on to form end products. Apin-zero shows the rate of decay if α -pinene does not react. A-PINENE is the modeled α -pinene decay, accounting for both reaction and exhaustion pathways. O_3 is modeled ozone. Solid dots indicate experimental data.

These figures show the α -pinene/ O_3 reaction. Discontinuities in the model data occur at the times where the transfer ends. Ozone is under-predicted on two of the three days. It is captured well on June 12, while on May 17 and June 27 it is under-predicted by 20% and 10%, respectively. Other reactants are captured well. The reason for this under-prediction is not readily apparent. It is possible that the model does not capture well the lower concentrations that were used on the later two days; the model was originally written using concentrations 10 to 100 times that used here (Kamens and Jaoui, 2001). Losses due to leakage in the ductwork were accounted for in the correction factor applied to incoming O_3 , but there may be another loss point in the system that is not accurately captured. Specifically there may be additional losses of O_3 in the duct work that is not accounted for in the model. Still, the fact that the modeled data closely follows observations indicates that the model is able to accurately describe the method and that the method is consistent with accepted chemical mechanisms. This is also apparent in Figures 19, 20, and 21, which show gas-phase reaction data.

Figures 19, 20 and 21 show the NO_x/O_3 reaction occurring in the South chamber, along with α -pinene decay data. Modeled results are shown with lines, while observed data are points on the chart. There is good agreement between the two sets of data on all three days and supports the idea that the model accurately reflects what is observed in the South chamber. Consistent with Figure 16, the May 17 data shows the best agreement between observations and modeled values, while the June 12 data shows the worst agreement (Figures 17 and 20).

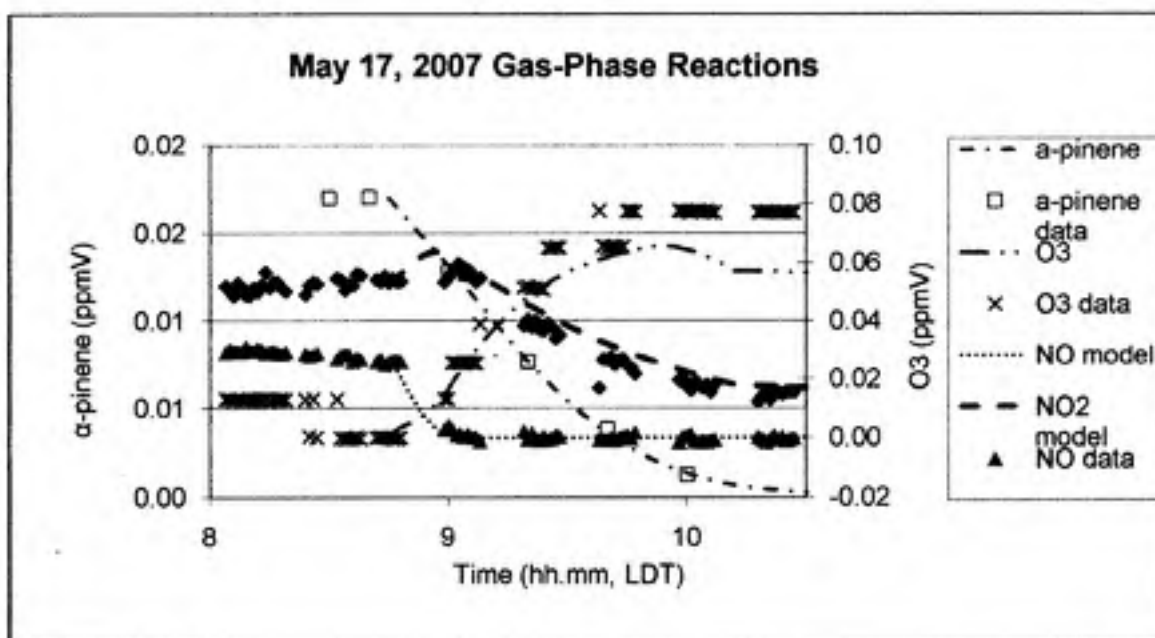


Figure 19. Comparison of modeled gas-phase reactions to observed data from May 17, 2007 experiment

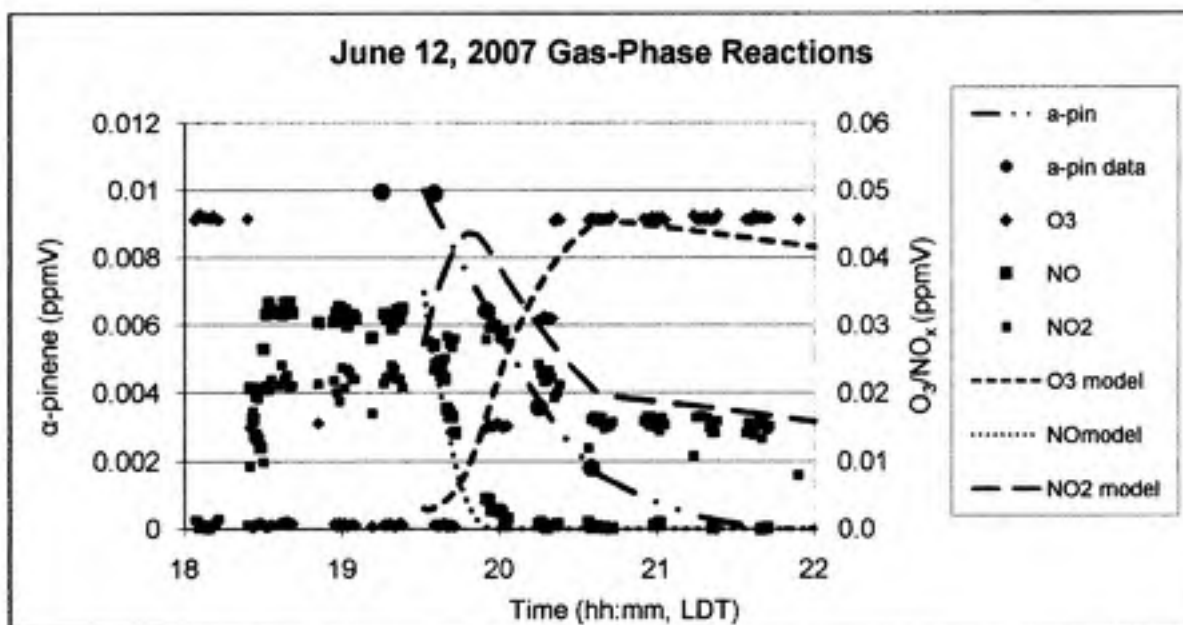


Figure 20. Comparison of modeled gas-phase reactions to observed data from June 12, 2007 experiment.

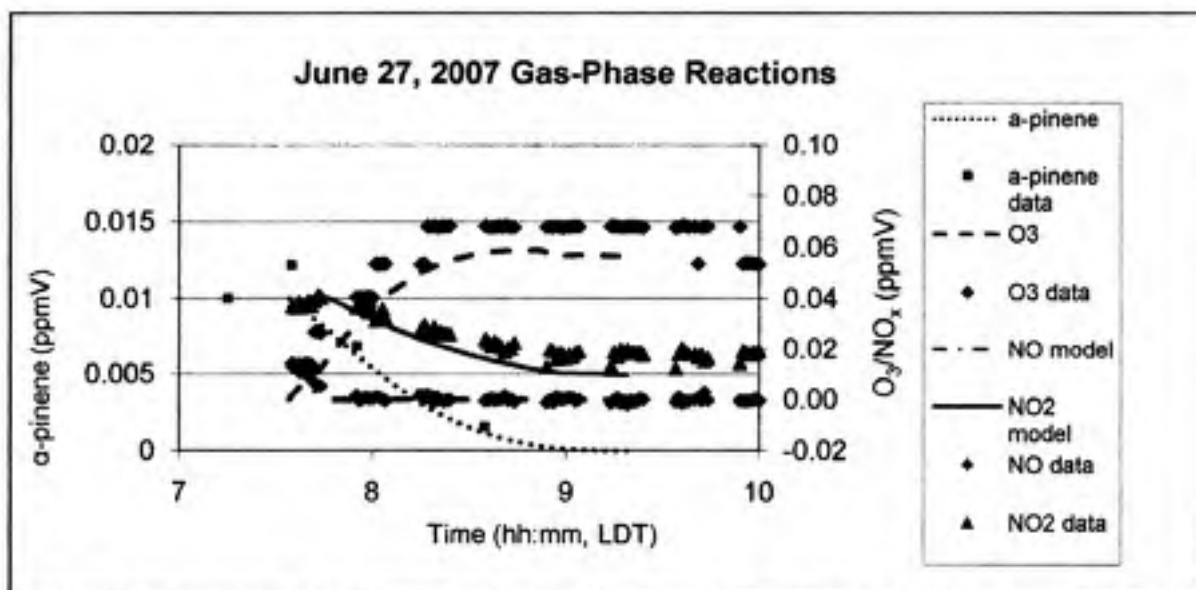


Figure 21. Comparison of modeled gas-phase reactions to observed data from June 27, 2007 experiment.

One of the unknowns in this set of experiments is why different numbers of particles were produced on different days when initial conditions were so similar. Part of the difference may be ascribed to the different transfer rates. According to Table 2, June 27 had the highest transfer rate, and therefore reactants had a shorter residence time in the South chamber before being exhausted. This is one possible reason why the number of particles produced on June 27 was so low. Further, June 27 is possibly the most humid day of the three successful nucleation attempts. By contrast, the June 12 experiment, where the most nucleated particles were observed, was dry. Without dew point data on May 17, it cannot be definitively stated that water (H_2O) inhibits nucleation. Further experiments were conducted to investigate the role water and background seed particles may have in influencing the number of particles that are created during a nucleation event.

Criegee Radicals

Ozone attacks α -pinene at either end of the carbon double bond in the six-carbon ring. The site of attack partially determines the ultimate products of ozonolysis, as the ozone opens up the carbon ring and there is either an aldehyde or a ketone on the other end. The first product of reaction, however, is an unstable, highly reactive intermediate compound called a Criegee biradical or Criegee Intermediate (CI) after the German scientist who proposed them (Finlayson-Pitts and Pitts, 2000). These Criegee radicals can collisionally stabilize and become what is known as a Stabilized Criegee Intermediate (SCI), and go on to react with other components, or they can degrade into the final products of ozonolysis. Water vapor is one of the primary reactants with a SCI, in the absence of other radical species (Finlayson-Pitts and Pitts, 2000), as it has the shortest lifetime with water, and water is ubiquitous throughout the atmosphere. Reaction rates are calculated to be between 1×10^{-15} and 2×10^{-19} ($\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$). Atkinson (1994) also supports the idea that water is a primary reactant for stabilized Criegee radicals. The reaction of a SCI with water can compete with the primary reactions that generates pinic and norpinic acid and norpinonaldehyde, the first-generation products of the reaction of α -pinene and O_3 (shown in Figure 22 below)

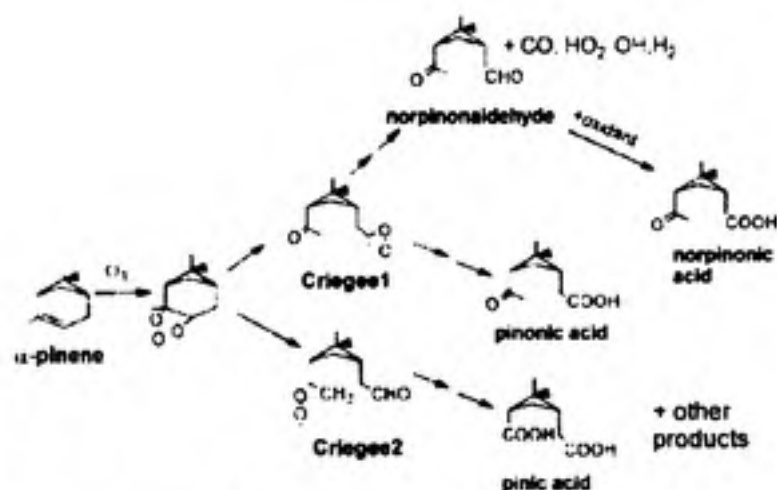


Figure 22. Reaction pathways of α -pinene ozonolysis. (Image source: Kamens et al, 1999)

Humid Experiments

Two varieties of humid experiments were conducted in order to observe the effect of water on the O_3/α -pinene nucleation system. In the experiment conducted on May 27, 2008, the chambers were vented with rural air for 48 hours, and clean air was injected into the South chamber only for 24 hours. Water vapor was added to the South chamber using a commercially available humidifier. This was followed by NO to titrate out any O_3 , then 0.02 ppmC α -pinene. Ozone and SF_6 were injected into the North chamber. In the second variation conducted on July 1, 2008, both chambers were vented with rural air for 24 hours, and the South chamber was cleaned using air from a clean air generator for 72 hours. In both experiments, particles in the North chamber were filtered out using the in-line HEPA filter, but water vapor was not. The conditions of both experiments are summarized in Table 6. Ending times are defined as the time a particle maximum was observed.

Table 6. Summary of Experimental Conditions of Humid Experiments*												
Date	a-pin (ppmC)	O ₃ (ppm)	NO (ppm)	NO ₂ (ppm)	Bkgd Vol.	Begin time	End time	Init Temp	Final Temp	Init H ₂ O (ppm)	Final H ₂ O (ppm)	Total # of particles
May 27 2008 N	-	0.2717	0.003	0	6.0e8	22:30	0:03	295.1	293.8	9728	12453	3,433
May 27 2008 S	0.02	0.0133	0.0076	0.0231	4.8e8					5964	10163	
July 1 2008 N	-	0.3026	0.0017	0.0007	2.5e8	21:15	23:06	289.8	287.2	11566	9879	6,861
July 1 2008 S	0.03	0.0098	0.0038	0.0386	2.0e8					5050	8709	

* A summary of the conditions during the experiments where humid conditions were created. Columns are the same as described in Table 4. On May 27 experiment, water vapor was added to the South chamber, and in the July 1 experiment, the North chamber was kept at ambient humid conditions.

In these experiments, particle creation and growth was clearly observed, as seen in Figure 23, which shows the change in volume over the course of the experiments.

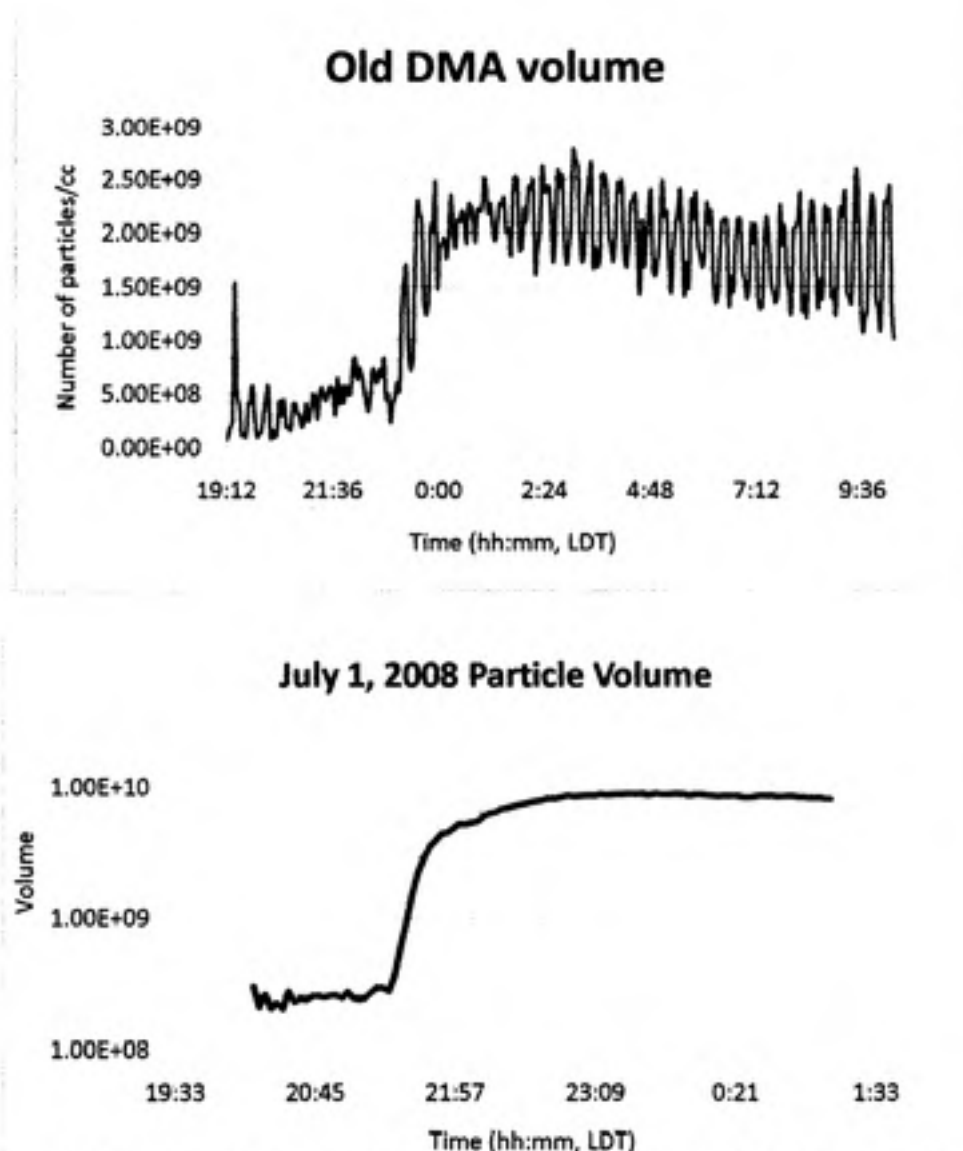


Figure 23. Change in volume over the course of the experiment for humid experiments conducted on May 23, 2008 and July 1, 2008. The horizontal axis indicates time and the vertical axis indicates the number of particles per cc. Upper graph shows volume of both North and South chambers, switching between the two every 10 minutes. This accounts for the "saw tooth" appearance. The South chamber volume is the lower edge of the line.

What separates these experiments with higher humidities from the dry ones discussed above are the way in which particles grew. In the dry experiments, post-nucleation particles were clearly seen, but in the wet experiments, this was not observed. Rather, on the May 27 experiment there was a burst of particles with a mode of 25 nm, which developed into a bimodal response which grew until a count maximum was reached. This particle growth also took longer to begin to occur. In the dry nucleation experiments, nucleation was completed after approximately an hour, and in the wet experiments, it took about an hour and a half for growth to reach a maximum. Particle growth is shown for both days in Figures 24 and 25.

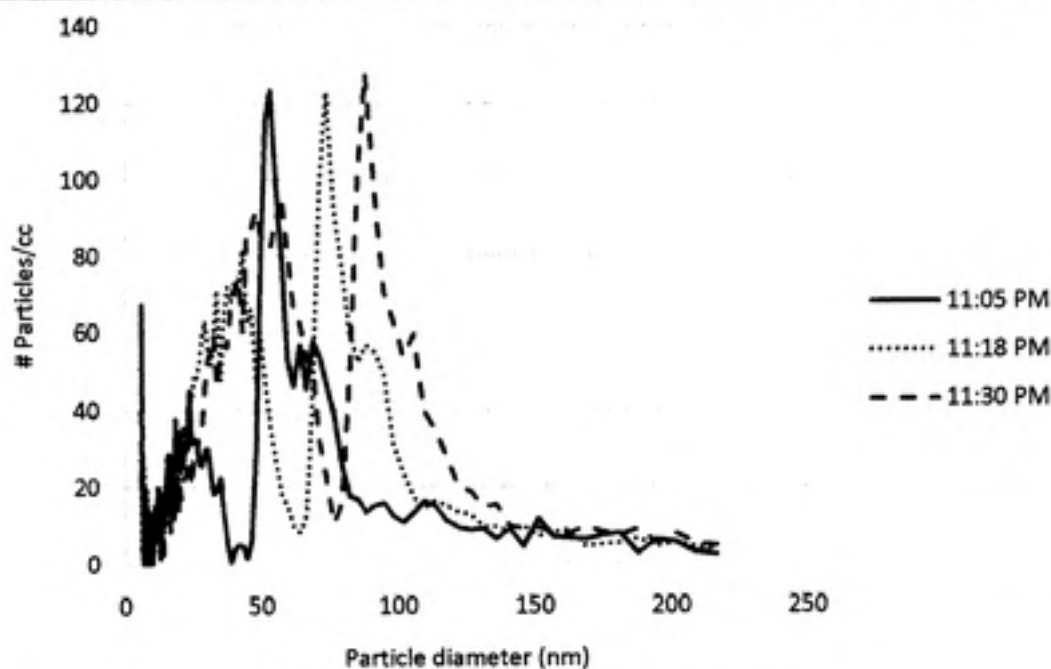
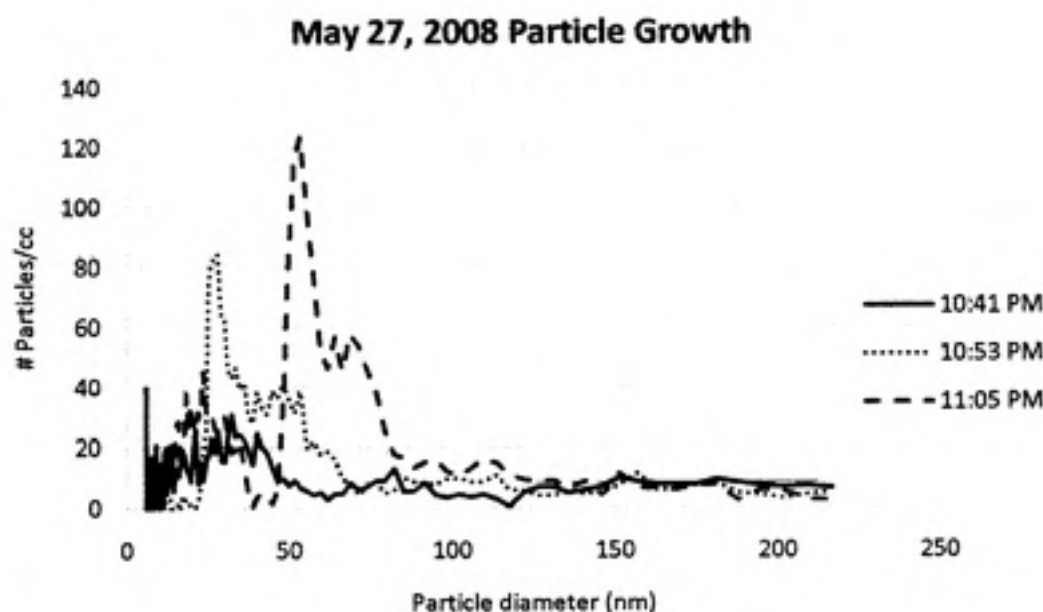


Figure 24. DMA scans showing particle growth on May 27, 2008. Horizontal axis indicates particle diameter (nm), and vertical axis shows the number of particles per cc. There is a peak of particles at 25 nm, which develops into a bimodal peak, with modes at 50 and 100 nm.

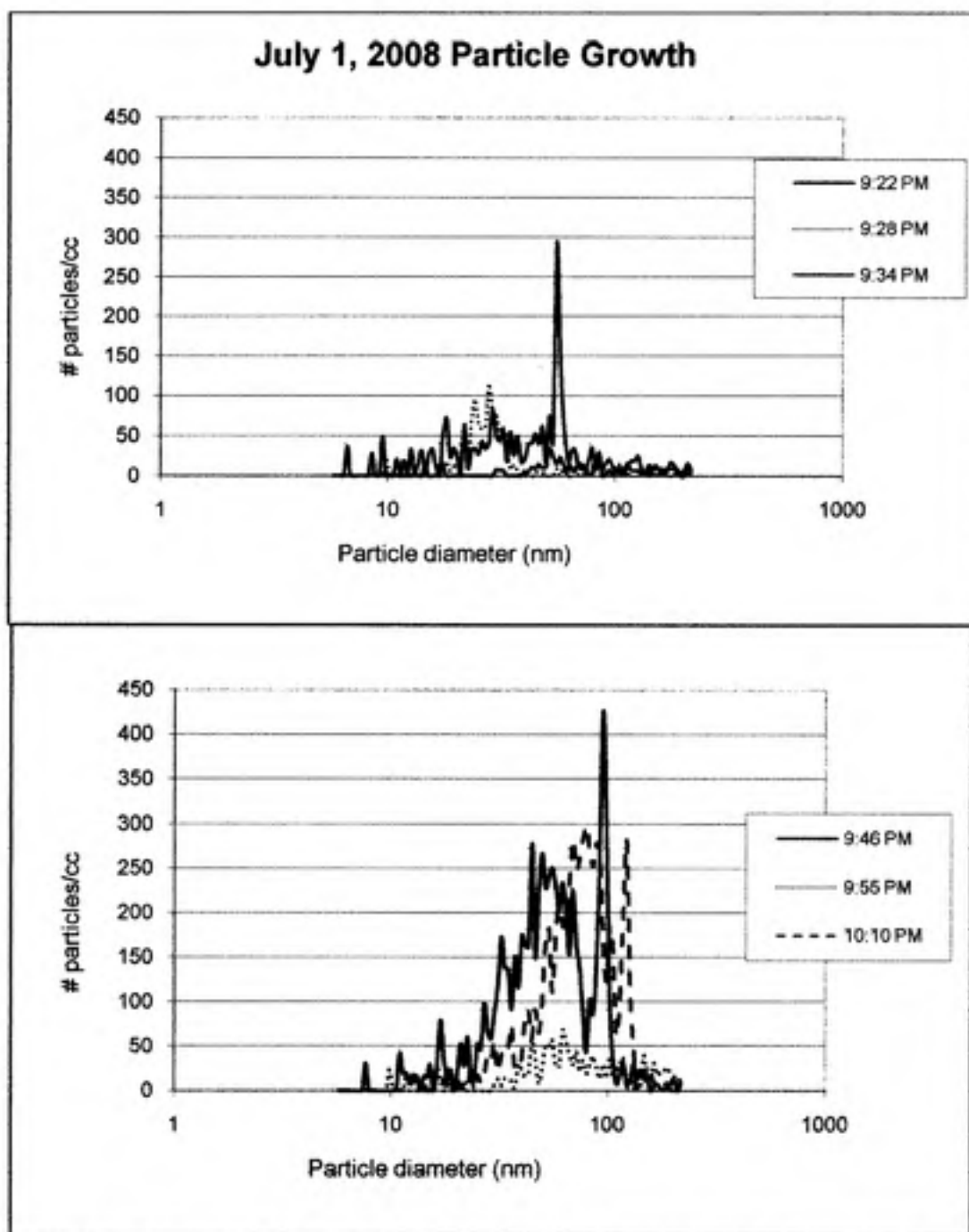


Figure 25: Particle growth on July 1, 2008 experiment. Scans were done between 5 and 216 nm. Particle mode appears at 50 nm, then develops into a bimodal scan with peaks at 50 nm and 100 nm.

These experiments were also compared against the UNC Particle Mechanism.

Results are shown in Figures 26 and 27. On both days, modeled α -pinene and O_3 tracked

the observed data well. This is likely due to the higher concentrations of reactants used in these experiments.

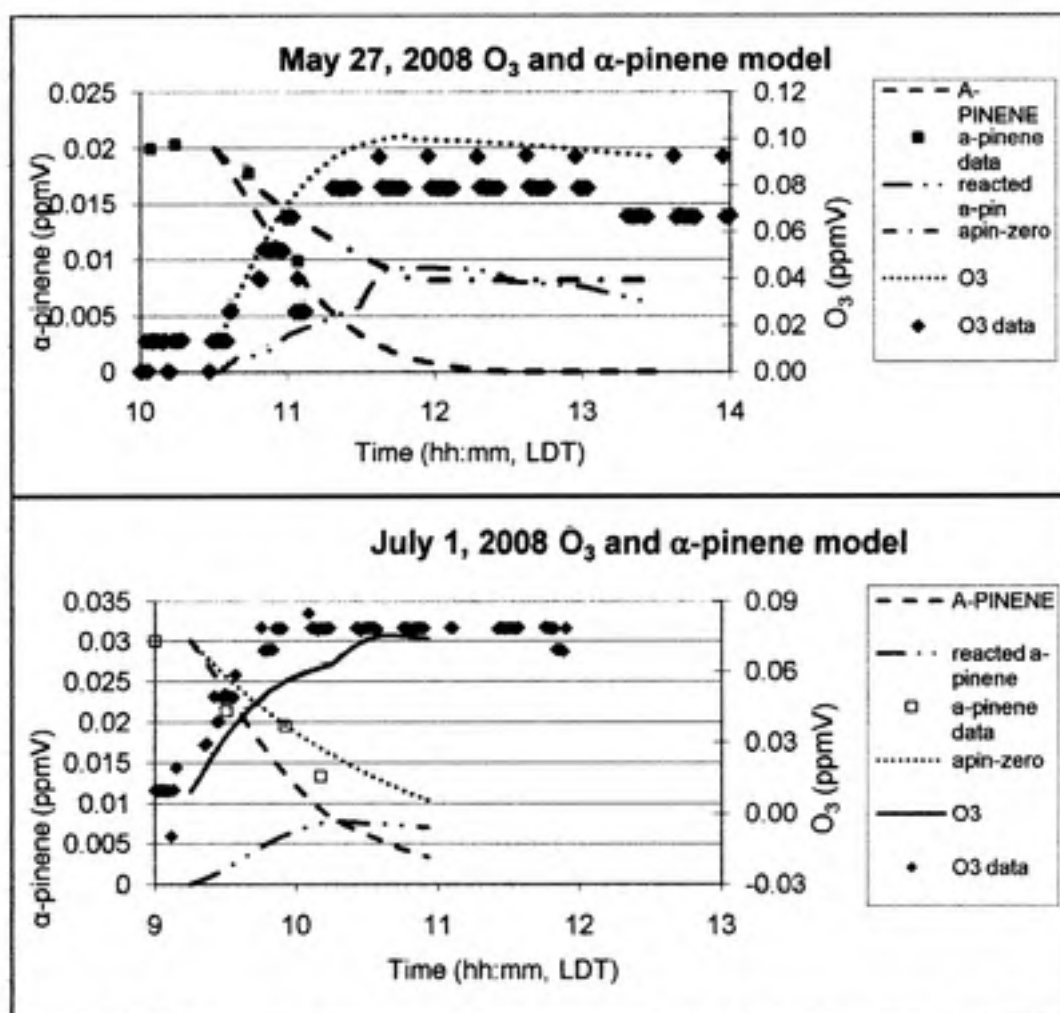


Figure 26. Comparison of Modeled α -pinene and O_3 to Observed Data for Humid Experiments. modeled data are lines, observed data noted by markers.

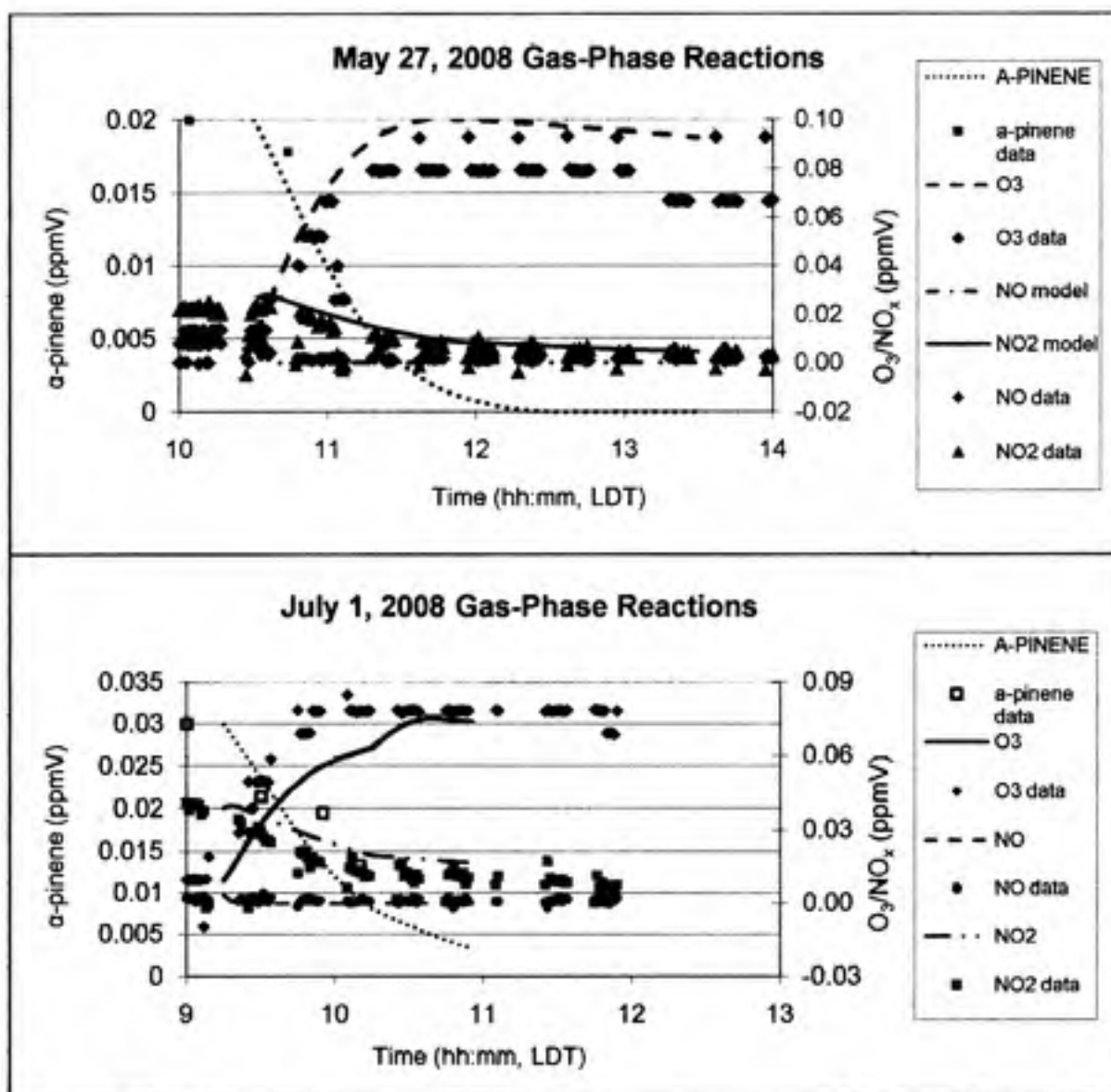
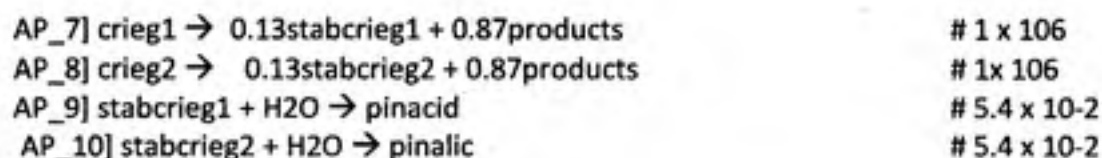


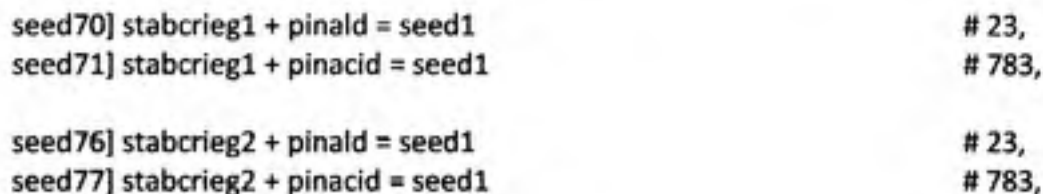
Figure 27. Gas-phase reactions for humid experiments. Comparison of observed gas-phase reaction data to UNC particle mechanism.

Of particular interest in these two experiments as compared to the previous four are the integrated reaction rates for each of the experiments. The integrated reaction rate shows the reaction pathways, products and concentrations in the α -pinene/ O_3 system for a given set of initial conditions. This is of interest because if water is competing with gaseous compounds for Criegee Intermediates, this will result in different products than if no water

were present. The interaction of water with Criegee Intermediates is captured in the mechanism with the following reactions:



These reactions chemically describe the reactions diagrammed in Figure 22 and the interaction of water with stabilized Criegee Intermediates. Crieg1 and Crieg2 represent Criegee intermediates, differentiated by which part of the α -pinene double carbon bond was initially broken. Pinacid represents pinonic and norpinonic acid; pinald represents pinonaldehyde and norpinonaldehyde, and stabcrieg represents a stabilized Criegee Intermediate. The reaction rate coefficient is the number following the # sign, with units of min⁻¹ for first order reactions (AP-7 and AP-8) and ppm⁻¹min⁻¹ for second order reactions (AP-9 and AP-10). Of interest are reactions the reactions "Seed 70, 71, 76 and 77" in the mechanism, shown below:



These reactions are the primary competition with reactions AP-9 and AP-10 above. Stabilized Criegees can either react with water to form acid or react with acid to create seed particles, which in turn create nuclei. Integrated reaction rates were calculated for the

reactions detailed above. The results were compared to determine whether more α -pinene reacted through the acid-forming pathway or the seed-forming pathway under various humidities. This comparison is shown in Table 7, below.

Date	Chamber Conditions	H ₂ O (ppm)*	Criegee 1 H ₂ O/Pinacid	Criegee 2 H ₂ O/Pinacid
17-May-07	dry	N/A	4.06E+03	3.66E+03
12-Jun-07	dry	7115.4	5.20E+03	7.80E+03
27-Jun-07	dry	10197.8	5.88E+03	8.81E+03
27-May-08	humid	8111.6	2.62E+04	3.93E+04
1-Jul-08	humid	7509.8	7.47E+02	7.48E+02
10-Jul-08	dry seed	7892.8	1.17E+03	1.16E+03

*H₂O is calculated as an average over the course of the transfer time.

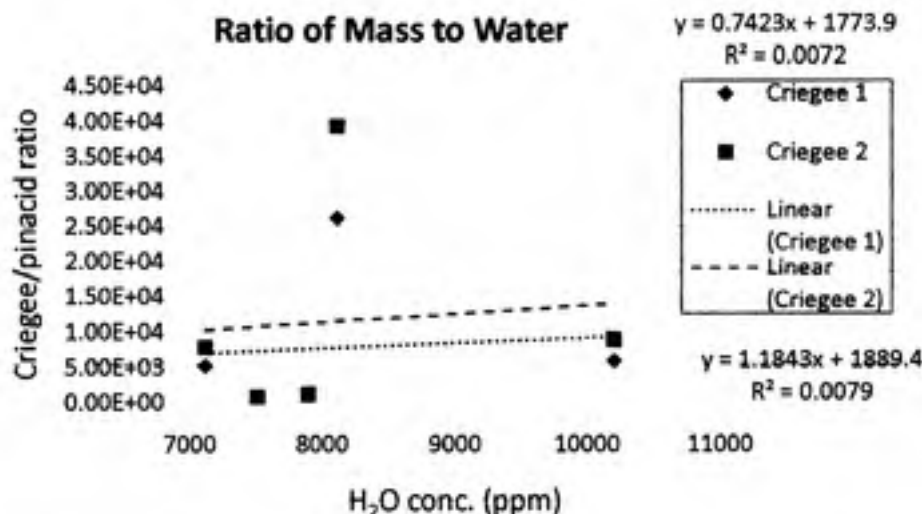


Figure 28. Ratio of Criegee Intermediate/acid mass as a function of humidity.

A regression calculation on this data shows that there is a slight positive relationship between the relative humidity and the amount of Criegee Intermediates reacting with water as opposed to acid. However, the R^2 value shows no statistical significance, as only 7% of the data can be described with this equation. Therefore, it cannot be positively stated

that water inhibits the formation of nuclei by reacting with Criegee Intermediates. This finding supports other findings in the larger scientific community. Bonn et al (2002) reports a similar finding-that water has no real effect on particle number or volume at a concentration of 1 ppm α -pinene with 4.46 ppm O_3 , a dry/humid number ratio of 1.1 and a volume ratio of unity.

Seed Experiments

To further distinguish the ambient conditions that encourage or inhibit nucleation, an experiment was conducted in which $4.5 \mu\text{g}\cdot\text{m}^{-3}$ of 0.005 M ammonium sulfate salt in 225 mL of pure deionized water was added to the South chamber using medical nebulizers and air from the clean air generator. Prior to the experiment, the chamber was vented with rural air for 12 hours, then purged with air from the clean air generator for 24 hours. The background particle volume of the chambers was $0.04 \mu\text{g}\cdot\text{cm}^{-3}$ and $0.15 \mu\text{g}\cdot\text{cm}^{-3}$ in the North and South chambers, respectively, prior to the injection of ammonium sulfate. Other background information is summarized in Table 8.

No nucleation was observed during the course of this experiment; the particle count peak was obtained during the injection of the background seed (Figure 29). The particle distribution (Figure 30) shows similar data. The four times shown in the figure are at the particle count peak, the beginning of the transfer process, the end of the transfer, and one hour later. This shows that particles did not begin to form even after the data transfer ended. This could have been due to the low concentration of ozone that was transferred.

Table 8: Summary of Experimental Conditions of Background Seed Experiment*												
Date	α -pin (ppmC)	O ₃ (ppm)	NO (ppm)	NO ₂ (ppm)	Bkgd Vol.	Begin time	End time	Init Temp	Final Temp	Init H ₂ O	Final H ₂ O	Total # of particles
July 10 2008 N	-	0.116	0.0005	0.0023	4.5e7	0:40	1:24	296.2	295.4	5178	12118	2,096 [†]
July 10 2008 S	0.03	0.012	0.0034	0.0219	4.5e9					5421	9380	

*same as other two tables (add the data)

[†] the number of particles at end time. This is less than the number of particles at the begin time.

July 10, 2008 Particle Counts

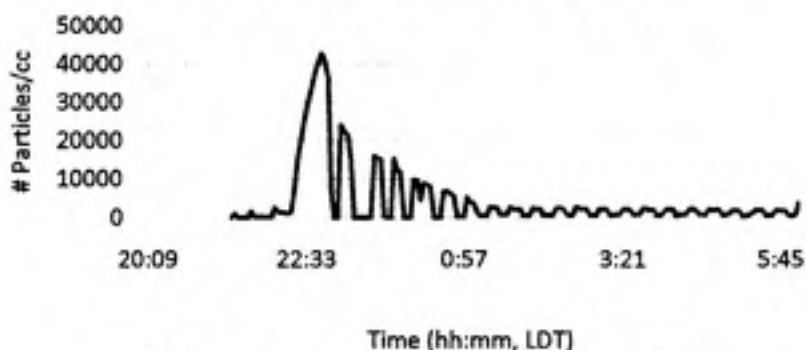


Figure 29. Particle count for July 10, 2008 experiment.

The ozone concentration was unintentionally low for this experiment because the ozone generator malfunctioned during the course of the experiment, and only one third of the intended ozone concentration was actually injected into the North chamber. Combined with any losses in the transfer process, very little O_3 actually entered the South chamber. This is shown in the experimental data in Figure 31. The model does a poor job of capturing the α -pinene decay on this day, as well. At this time, it is unknown why the fit is poor.

It is possible that the model does not capture the low concentrations of O_3 ; in fact, on this day the model actually under-predicts O_3 concentrations, in contrast to every other experiment where it is over-predicted. It is also possible that the transfer process is not described well, and α -pinene is being exhausted from the South chamber at a faster rate than predicted.

July 10, 2008 Particle Distribution

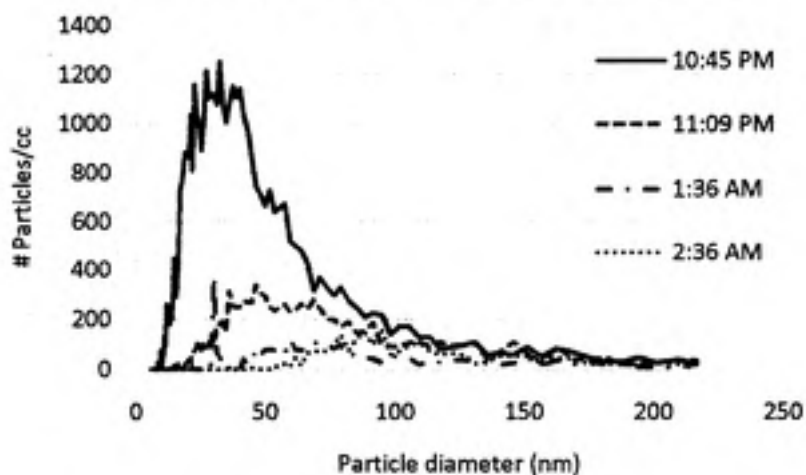


Figure 30. Particle distribution for July 10, 2008 experiment.

July 10, 2008 O₃ and α -pinene Model

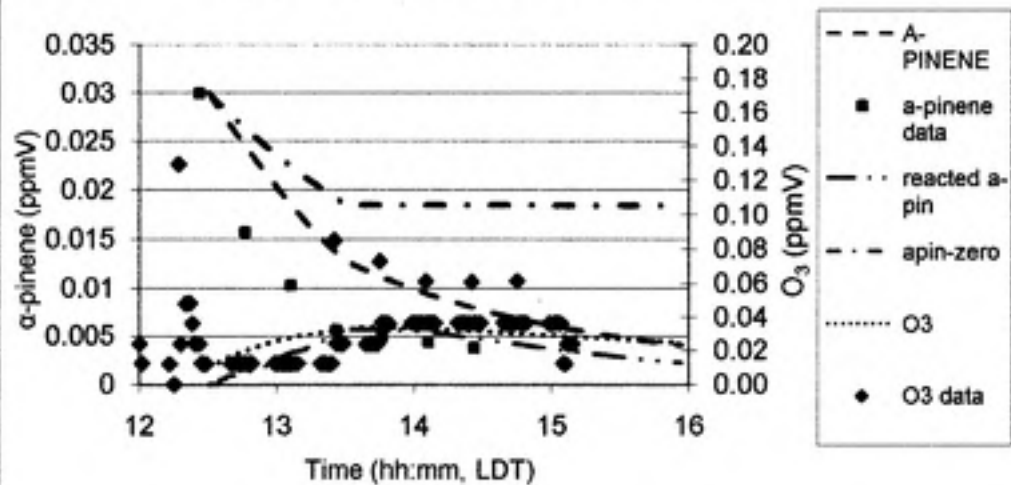


Figure 31. July 10, 2008 α -pinene/O₃ model.

CHAPTER IV

CONCLUSIONS AND FUTURE WORK

A novel method was developed to introduce and mix two dilute compounds in an outdoor smog chamber environment. It was then tested using a variety of α -pinene/ O_3 nucleation experiments with varying levels of water vapor and background seed. The method was shown to be useful for this system, as nucleation was observed at concentrations approaching those found in the ambient atmosphere. Observations were compared to an existing photochemical mechanism to test the robustness of the method. There appears to be some source of reactant loss in the system, though the observed reaction rates agreed well. This was corrected for with the application of a factor to the dilution rate in the Particle Model. However, the source and mechanism of loss should be determined and corrected.

Additional α -pinene nucleation experiments were conducted to test the effects of water vapor and background ammonium sulfate seed on nucleation. Water vapor was found to have no statistically significant effect on the reaction mechanism. Background seed also had no observable effect on nucleation. Further experimentation is needed to determine if the effect of water on nucleation is real or not. Experiments should be conducted at very low humidities to provide a stronger base for comparison within the data set.

In addition to the clarification of the air transfer process described above, a future area of investigation include the application of this method to a blend of biogenic compounds to include isoprene, α -pinene, d-limonene and Δ^3 -carene in proportion to concentrations seen in the ambient atmosphere.

APPENDIX A

CALCULATION OF PARTICLE STATISTICS USING DMA DATA

This chart was used to calculate particle statistics for use with Hatch-Choate equations discussed in Chapter III. Column 1 is the midpoint diameter, defined to be the diameter reported by the DMA. Column 2 is the count, the number of particles at that diameter. Column 3 is the product of Columns 1 and 2. Column 4 is the squared difference between the midpoint diameter and the count mean diameter, multiplied by the number of particles of that diameter. Column 5 is the natural logarithm of the midpoint diameter, and Column 6 is the count fraction for a particular diameter- the number of particles of a given diameter divided by the total number of particles. This chart was supplied with counts at the particle count maxima for the three dry nucleation days.

Count-Based Data

1	2	3	4	5	6	7	Cumulative	# of std
Mid,d	Count, n	n x d	(da-d) ² x n	ln(d)	n x ln(d)	n/Σ(n)	Count	dev from
							Fraction	mean
5.72549	13.3	76.1	11350.4093	1.7	23.2	0.01	0.01	-2.27
5.93523	0	0.0	0.0	1.8	0.0	0.00	0.01	-2.27
6.15265	10.4	64.0	8617.8	1.8	18.9	0.01	0.02	-2.04
6.37804	0	0.0	0.0	1.9	0.0	0.00	0.02	-2.04
6.61169	8.4	55.5	6740.34490	1.9	15.9	0.01	0.03	-1.91
6.8539	0	0.0	0.0	1.9	0.0	0.00	0.03	-1.91
7.10497	0	0.0	0.0	2.0	0.0	0.00	0.03	-1.91
7.36525	0	0.0	0.0	2.0	0.0	0.00	0.03	-1.91
7.63506	5.7	43.5	4249.3	2.0	11.6	0.01	0.03	-1.83
7.91476	0	0.0	0.0	2.1	0.0	0.00	0.03	-1.83
8.2047	0	0.0	0.0	2.1	0.0	0.00	0.03	-1.83
8.50526	0	0.0	0.0	2.1	0.0	0.00	0.03	-1.83
8.81683	0	0.0	0.0	2.2	0.0	0.00	0.03	-1.83
9.13982	0	0.0	0.0	2.2	0.0	0.00	0.03	-1.83
9.47464	0	0.0	0.0	2.2	0.0	0.00	0.03	-1.83
9.82172	0	0.0	0.0	2.3	0.0	0.00	0.03	-1.83
10.1815	6.3	64.1	3861.4	2.3	14.6	0.01	0.04	-1.76
10.5545	3	31.7	1783.8	2.4	7.1	0.00	0.04	-1.73
10.9411	5.6	61.3	3225.0	2.4	13.4	0.00	0.05	-1.68
11.3419	5.3	60.1	2951.1	2.4	12.9	0.00	0.05	-1.63
11.7574	5	58.8	2686.9	2.5	12.3	0.00	0.06	-1.59
12.1881	2.4	29.3	1242.2	2.5	6.0	0.00	0.06	-1.57
12.6346	0	0.0	0.0	2.5	0.0	0.00	0.06	-1.57

13.0975	4.2	55.0	2003.6	2.6	10.8	0.00	0.06	-1.54
13.5773	4	54.3	1825.2	2.6	10.4	0.00	0.06	-1.51
14.0746	6	84.4	2611.9	2.6	15.9	0.01	0.07	-1.47
14.5902	7	102.1	2898.4	2.7	18.8	0.01	0.08	-1.43
15.1247	10.4	157.3	4083.0	2.7	28.2	0.01	0.09	-1.37
15.6788	11.1	174.0	4117.5	2.8	30.6	0.01	0.10	-1.31
16.2531	6.9	112.1	2409.2	2.8	19.2	0.01	0.10	-1.27
16.8485	10.5	176.9	3436.2	2.8	29.7	0.01	0.11	-1.22
17.4658	13	227.1	3968.9	2.9	37.2	0.01	0.12	-1.16
18.1056	15.2	275.2	4307.0	2.9	44.0	0.01	0.14	-1.10
18.7688	14.9	279.7	3895.9	2.9	43.7	0.01	0.15	-1.04
19.4564	18.1	352.2	4338.6	3.0	53.7	0.02	0.16	-0.97
20.1691	21.8	439.7	4755.5	3.0	65.5	0.02	0.18	-0.90
20.908	25	522.7	4921.5	3.0	76.0	0.02	0.21	-0.82
21.6739	20.9	453.0	3677.5	3.1	64.3	0.02	0.22	-0.76
22.4679	14.7	330.3	2286.2	3.1	45.7	0.01	0.24	-0.71
23.291	21	489.1	2849.1	3.1	66.1	0.02	0.26	-0.66
24.1442	21.3	514.3	2481.9	3.2	67.8	0.02	0.27	-0.60
25.0287	34.4	861.0	3378.4	3.2	110.8	0.03	0.31	-0.51
25.9455	30.8	799.1	2491.1	3.3	100.3	0.03	0.33	-0.43
26.896	32.9	884.9	2128.2	3.3	108.3	0.03	0.36	-0.35
27.8813	23.6	658.0	1175.5	3.3	78.5	0.02	0.38	-0.30
28.9026	35.8	1034.7	1304.4	3.4	120.4	0.03	0.41	-0.22
29.9614	28.9	865.9	716.0	3.4	98.3	0.03	0.44	-0.15
31.059	36.3	1127.4	546.4	3.4	124.7	0.03	0.47	-0.07
32.1968	33.2	1068.9	249.6	3.5	115.3	0.03	0.50	0.00
33.3762	31.6	1054.7	77.2	3.5	110.8	0.03	0.53	0.07
34.5989	38.6	1335.5	4.5	3.5	136.8	0.03	0.56	0.16
35.8664	37.1	1330.6	31.9	3.6	132.8	0.03	0.60	0.24

37.1803	45.4	1688.0	228.1	3.6	164.2	0.04	0.64	0.35
38.5423	44.7	1722.8	580.5	3.7	163.2	0.04	0.68	0.45
39.9542	35.3	1410.4	888.0	3.7	130.2	0.03	0.71	0.54
41.4178	29.1	1205.3	1221.6	3.7	108.4	0.03	0.73	0.62
42.9351	38.4	1648.7	2455.4	3.8	144.4	0.03	0.77	0.73
44.5079	31.3	1393.1	2866.1	3.8	118.8	0.03	0.79	0.82
46.1384	27.7	1278.0	3474.5	3.8	106.1	0.02	0.82	0.91
47.8286	28.6	1367.9	4751.8	3.9	110.6	0.03	0.84	1.01
49.5807	37.1	1839.4	7953.8	3.9	144.8	0.03	0.88	1.15
51.397	29.8	1531.6	8072.1	3.9	117.4	0.03	0.90	1.29
53.2798	24.9	1326.7	8376.2	4.0	99.0	0.02	0.92	1.43
55.2316	18.1	999.7	7453.6	4.0	72.6	0.02	0.94	1.56
57.2549	14.5	830.2	7221.2	4.0	58.7	0.01	0.95	1.67
59.3523	11.6	688.5	6913.9	4.1	47.4	0.01	0.96	1.79
61.5265	6.1	375.3	4312.1	4.1	25.1	0.01	0.97	1.86
63.7804	3.1	197.7	2578.7	4.2	12.9	0.00	0.97	1.90
66.1169	1.2	79.3	1166.5	4.2	5.0	0.00	0.97	1.92
68.539	1.7	116.5	1919.3	4.2	7.2	0.00	0.97	1.94
71.0497	3	213.1	3912.0	4.3	12.8	0.00	0.98	1.99
73.6525	0.7	51.6	1049.1	4.3	3.0	0.00	0.98	2.00
76.3506	1.2	91.6	2057.9	4.3	5.2	0.00	0.98	2.02
79.1476	1.8	142.5	3518.0	4.4	7.9	0.00	0.98	2.05
82.047	1.2	98.5	2663.0	4.4	5.3	0.00	0.98	2.07
85.0526	0.7	59.5	1758.0	4.4	3.1	0.00	0.98	2.08
88.1683	0.4	35.3	1133.4	4.5	1.8	0.00	0.98	2.09
91.3982	2.1	191.9	6694.1	4.5	9.5	0.00	0.98	2.14
94.7464	1.3	123.2	4650.0	4.6	5.9	0.00	0.98	2.17
98.2172	2.1	206.3	8408.7	4.6	9.6	0.00	0.99	2.22
101.815	1	101.8	4472.4	4.6	4.6	0.00	0.99	2.24

105.545	1.8	190.0	8973.4	4.7	8.4	0.00	0.99	2.30
109.411	1.1	120.4	6100.7	4.7	5.2	0.00	0.99	2.33
113.419	0.6	68.1	3695.5	4.7	2.8	0.00	0.99	2.35
117.574	0.1	11.8	682.9	4.8	0.5	0.00	0.99	2.35
121.881	0.6	73.1	4535.4	4.8	2.9	0.00	0.99	2.38
126.346	0.7	88.4	5848.7	4.8	3.4	0.00	0.99	2.40
130.975	0.3	39.3	2766.9	4.9	1.5	0.00	0.99	2.42
135.773	0.2	27.2	2033.5	4.9	1.0	0.00	0.99	2.42
140.746	0	0.0	0.0	4.9	0.0	0.00	0.99	2.42
145.902	0	0.0	0.0	5.0	0.0	0.00	0.99	2.42
151.247	0.9	136.1	12174.8	5.0	4.5	0.00	0.99	2.46
156.788	1.3	203.8	19301.4	5.1	6.6	0.00	0.99	2.53
162.531	0.9	146.3	14651.8	5.1	4.6	0.00	1.00	2.58
168.485	0	0.0	0.0	5.1	0.0	0.00	1.00	2.58
174.658	0.9	157.2	17569.3	5.2	4.6	0.00	1.00	2.64
181.056	0.9	163.0	19215.2	5.2	4.7	0.00	1.00	2.71
187.688	0.9	168.9	20999.1	5.2	4.7	0.00	1.00	2.80
194.564	0.5	97.3	12740.1	5.3	2.6	0.00	1.00	2.86
201.691	0.5	100.8	13903.2	5.3	2.7	0.00	1.00	2.93
209.08	0.5	104.5	15162.6	5.3	2.7	0.00	1.00	3.03
216.739	1.4	303.4	46271.9	5.4	7.5	0.00	1.00	#NUM!

Sums -> 1132.8 39578.6 459054.5 3876.0

Count	Mean	34.93874
	SD	20.13944
Geometric	Mean	30.61758

APPENDIX B

UNC PARTICLE KINETICS SOLVER SYSTEM MECHANISM

Please note that this is an example mechanism. All mechanisms differ slightly with regard to the rate in which O₃ was added to the chamber. This was determined using the rate of SF₆ movement.

Reactions are broken into sections according to type, and numbered sequentially. Reaction rates are provided after the # sign. Arrhenius rate factors are in the format XYZ @ ABC, where the @ symbol is equivalent to an exponential factor, and the division of temperature is implied.

Individual components of this mechanism are discussed in further detail by Jeffries (1991) and Jaoui and Kamens (2003).

Title= A-pinene nighttime + particle chemisity + Carbon Bond 4.2 + UNCCHAM.RXN;

!*****

UNITS:

Afactor=ppm_min;

IgnoreSpecies:

CO2 ;

!

! I == INORGANIC CHEMISTRY

{ a) NO2 photolysis }

{TABLE= HVNO2;}

REACTIONS=

la2] O = O3

83830 e^(1175/T),

la3] O3 + NO = NO2

2.643 x 10³ e^(-1370/T),

la4] O + NO2 = NO

1.375 x 10⁴,

la5] O + NO2 = NO3

230.284 e^(687/T),

la6] $O + NO = NO_2$ # 323.31 $e^{(602/T)}$;

{ b) NO3 CHEMISTRY

{TABLES= HVNO3NO, HVNO3NO2;}

REACTION=

lb1] $O_3 + NO_2 = NO_3$ # 176.00 $e^{(-2450/T)}$,
lb3] $NO_3 + NO = 2.0 * NO_2$ # 19086 $e^{(250/T)}$,
lb4] $NO_3 + NO_2 = NO + NO_2$ # 36.6 $e^{(-1230/T)}$,
lb5] $NO_3 + NO_2 = N_2O_5$ # 784.88 $e^{(256/T)}$,
lb6] $N_2O_5 = NO_3 + NO_2$ # $2.11 \times 10^{16} e^{(-10897/T)}$,
lb7] $N_2O_5 + H_2O = 2.0 * HNO_3$ # 2.96×10^{-6} ;

{ c) OZONE photolysis }

{TABLES= HVO3O3P, HVO3O1D;}

TABLES= NORTH03;

REACTIONS=

lc3] $O_1D = O$ # $1.147 \times 10^5 e^{(390/T)}$,
lc4] $O_1D + H_2O = 2.0 * OH$ # 3.26 ,

lc5] $O_3 + OH = HO_2$ # 2343.8 $e^{(-940/T)}$,
lc6] $O_3 + HO_2 = OH$ # 21.0 $e^{(-580/T)}$,
lc6a] = O_3 # 0.015789 * NORTH03;

HONO CHEMISTRY

{COEFF= HONO_NO2R=0.171;}

{from ratio of rates on July 13, 1986 UNC Site}

REACTIONS=

ld1] $NO + NO \{+ O_2\} = 2.0 * NO_2$ # $2.60 \times 10^{-5} e^{(530/T)}$,
ld2] $NO + NO_2 + H_2O = 2.0 * HONO$ # 1.6×10^{-11} ,
ld3] $HONO + HONO = NO + NO_2 + H_2O$ # 1.5×10^{-5} ,
ld4] $OH + NO = HONO$ # 655.44 $e^{(806/T)}$,
ld6] $OH + HONO = NO_2 + H_2O$ # 9770;

NO/NO2 WITH RO2 CHEMISTRY

REACTIONS=

le1] $HO_2 + NO = OH + NO_2$ # 5482.1 $e^{(242/T)}$,
le2] $HO_2 + NO_2 = PNA$ # 164.0 $e^{(749/T)}$,
le3] $PNA = HO_2 + NO_2$ # $2.876 \times 10^{15} e^{(-10121/T)}$,
le4] $OH + PNA = NO_2$ # 1909 $e^{(380/T)}$,
le5] $OH + NO_2 = HNO_3$ # 1536.78 $e^{(713/T)}$,

!e6] OH + HNO3 = NO3 # 7.6 e^(1000/T) ;

! f) HO2 TERMINATION REACTIONS
{TABLE= HVH2O2;}

REACTIONS=

!f1] HO2 + HO2 = H2O2 {+ O2} # 87.39 e^(1150/T) ,

!f2] HO2 + HO2 + H2O =
H2O2 + H2O # 7.69 x 10⁻¹⁰ e^(5800/T) ,

!f4] OH + H2O2 = HO2 + H2O # 4719.8 e^(-187/T) ,

!f5] OH + CO = HO2 # 322.0 ,

!f6] OH + CH4 = XO2 + HCHO + HO2 # 3.55 x 10³ e^(-1710/T) ,

! ***** C1 == ALDEHYDE CHEMISTRY*****

TABLE= HVHCHOR, HVHCHOS ;

REACTIONS=

C1_3] HCHO + OH = HO2 + CO # 15000 ,

C1_4] HCHO + O = OH + HO2 + CO # 43019.2 e^(-1550/T) ,

C1_5] HCHO + NO3 = HNO3 + HO2 + CO # 0.93 ;

C2 : HIGHER ALDEHYDE CHEMISTRY

TABLE= HVCCHOR, HVPINALD;

REACTIONS=

C2_2] CCHO + O = C2O3 + OH # 17394.7 e^(-986/T) ,

C2_3] CCHO + OH = C2O3 # 10372.2 e^(250/T) ,

C2_4] CCHO + NO3 = C2O3 + HNO3 # 3.7 ;

SpeciesAlias:

RCHO=CCHO;

PAN CHEMISTRY

REACTIONS=

PAN_1] C2O3 + NO =
NO2 + XO2 + HCHO + HO2 # 7915.0 e^(250/T) ,

PAN_2] C2O3 + NO2 = PAN # 0.000118 e^(5500/T) ,

PAN_3] PAN = C2O3 + NO2 # 5.616E18 e^(-14000/T) ,

PAN_4] C2O3+ C2O3 = 2*XO2 +
2*HCHO + 2*HO2 # 3700 ,

PAN_5] C2O3+ HO2 = 0.79*HCHO + 0.79*XO2

+ 0.79*HO2 + 0.79*OH # 9600 ;

MG == DICARBONYL CHEMISTRY

TABLE= HVMetGly;

REACTIONS=

MG_2] OH + MGLY = XO2 + C2O3 # 26000 ;

ETHENE CHEMISTRY

REACTIONS=

ETH_1] O + C:C = HCHO + 0.70*XO2 {+ CO}
+ 1.70*HO2+ 0.30*OH # 15400 e^(-792/T),

ETH_2] OH + C:C = XO2 + 1.56*HCHO + HO2
+ 0.22*RCHO # 3000 e^(411/T),

ETH_3] O3 + C:C = HCHO {+ 0.42*CO} + 0.12*HO2
18.56 e^(-2633/T),

! ***** Dark A-PINENE GAS Phase CHEMISTRY*****

REACTIONS=

AP_0] apin-zero= # 1 x 10⁻⁶,

AP_1] OH + apine = ap-oo # 17873 e^(444/T), {Atkinson, 1997, p 236, Table 15}

AP_2] ap-oo + NO = 0.77*NO2 + 0.52*pinald + 0.77*HO2
+ 0.25*XO2 + 0.18*HCHO + 0.23*OH-apNO3 + 0.065*acetone
+ 0.18*vol-oxy # 6056 e^(180/T), {Jenkin, 1997, p 88, table 5,
f factor =1}

Ap_3] ap-oo + ap-oo = 0.7*pinald + 0.12*HCHO
+ 1.431*vol-oxy + 0.3*HO2 # 222 e^(416/T), {Jenkin, M.E. et al, 1997;
table 8, p 91, combo of tertiary
and secondary R-oo with beta hydroxy;}

AP_4] apine + NO3 = apNO3-oo # 517 e^(818/T),

AP_5] apNO3-oo + NO = 0.56*pinald + 0.19*OH-apNO3+ 0.06*acetone
+ 0.26*XO2+ 0.81*NO2 + 0.19*HCHO + 0.183*vol-oxy + 0.81*HO2
6056 e^(180/T)

AP_6] apine + O3 = 0.4*crieg1 + 0.6*crieg2 # 1.492 e^(-732/T),

AP_7] crieg1 = 0.49*pinacid + 0.13*stabcrieg1 + 0.8*OH + 0.3*HO2
+ 0.39*pinald + 0.01*oxypinald + 0.03*O + 0.19*CO
1 x 10⁶,

AP_8] crieg2 = 0.4*crgprod2 + 0.08*oxypinald + 0.433*vol-oxy
+ 0.13*stabcrieg2 + 0.8*OH + 0.3*HO2 + 0.03*O + 0.4*HCHO
1 x 10⁶,

AP_9] stabcrieg1 + H2O = pinacid # 5.4 x 10⁻²,

AP_10] stabcrieg2 + H2O = pinalic # 5.4×10^{-2} ,
 AP_11] stabcrieg1 + NO = pinald + NO2 # 10340, {avg kerr and clavert, 1984 and atk-lloyd, 1984}
 AP_12] stabcrieg1 + NO2 = NO3 + pinald # 148, {avg, Kerr-clav,1984 and atk-lloyd, 1984, Manzanares, 1987}
 AP_13] stabcrieg2 + NO = pinald + NO2 # 10340, {avg kerr and clavert, 1984 and atk-lloyd, 1984}
 AP_14] stabcrieg2 + NO2 = NO3 + pinald # 148, {avg, Kerr=clav,1984 and atk+lloyd, 1984, Manzanares, 1987}
 AP_15] crgprod2 + HO2 = 0.8*diacid + 0.2*oxypinacid # $635 e^{(1040/T)}$,
 AP_16] ap-oo + HO2 = 0.5*ap-ooH + 0.5*vol-oxy # $384 e^{(1250/T)}$, {2.6e-13e1250/T;jenkin, 1997, p90,98 }
 AP_17] ap-ooH + OH = ap-oo # $2836 e^{(190/T)}$, {jenkin, 1997 p 96,react 52b see 98, 90 too}
 AP_19] ap-oo + XO2 = vol-oxy # 59,
 AP_19a] apNO3-oo + XO2 = OH-apNO3 # 59,
 AP_19b] apNO3-oo + HO2 = OH-apNO3 # $384 e^{(1250/T)}$,
 AP_19c] apNO3-oo + ap-oo = 0.35*OH-apNO3 + 0.35*pinald + 1.431*vol-oxy + 0.15*HCHO + 0.15*HO2 # $222 e^{(416/T)}$,

PINONALDEHYDE CHEMISTRY

pin_21] pinO2 + NO = 0.765*pinald + 0.85*HO2 + 0.865*NO2 + 0.135*OH-apNO3 + 0.015*XO2 # $6056 e^{(180/T)}$,
 pin_22] C8O2 + NO = 0.84*NO2 + 0.711*vol-oxy + 0.8*HO2 + 0.16*OH-apNO3 + 0.04*XO2 # $6056 e^{(180/T)}$, {jenkin, 1997, p89, table 5, f=1}
 pin_23] C8O2 + C8O2 = 1.77*vol-oxy + 1.2*HO2 # $2.41 e^{(1961/T)}$,
 pin_24] pinald + OH = 0.8*pinald-oo + 0.1*C2O3 + 0.1*acetone + 0.1*C8O2 + 0.3*XO2 # 134417,
 pin_25] vol-oxy + OH = 0.5*acetone + 0.3*C2O3 + 1.3*XO2 + 0.5*C8O2 # 10000,
 pin_26] pinacid + OH = 0.5*C2O3 + 0.5*acetone + 1.3*XO2 + 0.5*C8O2 # 13000,
 pin_27] pinald + NO3 = 0.8*pinald-oo + 0.1*acetone + 0.3*XO2 + 0.1*C2O3 + 0.1*C8O2 + HNO3 # 79.76,
 pin_28] pinald-oo + NO = pinO2 + CO2 + NO # $6056 e^{(180/T)}$, {jenkin, 1997, p 89, table 5 f = 2.7}

pin_29] pinald-oo + NO2 = pinald-PAN # 3885 e^(380/T),
 pin_30] pinald-PAN = 0.95*pinald-oo+ 0.015*oxypin-oo
 +0.035*pred-oo+ NO2 # 1.067E11 e^(-8864/T),

 pin_31] pinald-PAN + OH = PAN + C8O2 # 13000,
 pin_32] pinald-oo + pinald-oo = 1.4*pinO2 + 0.6*pinacid
 # 25111 e^(416/T), {Jenkin 1997 bottom of
 table 8, p 91}
 pin_33] pinO2 + pinO2 = 1.48*pinald + 0.355*vol-oxy +
 1.2*HO2 # 2.4 e^(1961/T), {Atkinsion, 1997, p226, table 8,
 Lightfoot etal, ref 76}
 pin_34] pinald-oo + HO2 = 0.4*pinacid + 0.6*pin-ooH + 0.4*O3
 # 635 e^(1040/T), {Lightfoot, atmos envir, 26a,
 1805-1964,/fs1992}
 pin_36] pin-ooH + OH = pinO2 # 2836 e^(190/T), {Jenkin, 1997 p 96, eq 53a}
 pin_36a] pinO2 + XO2 = 0.8*vol-oxy +0.6*HO2 +0.6*CO2
 + 0.18*pinald # 59, {atkinson 1997,p 226 table 8; 0.4e-13,
 no temp coef}
 pin_37] pinO2 + HO2 = pin-ooH # 310 e^(1320/T), {Jenkin, 1997 p 90, Table 6,
 see cyclo c-5}
 pin_38] C8O2 + HO2 = vol-oxy # 310 e^(1320/T),
 pin_38a] C8O2 + XO2 = 0.88*vol-oxy
 + 0.6*HO2 # 59,
 pin_39] pinald-oo + ap-oo = vol-oxy +
 pinald # 7533 e^(272/T), {Atkinson 1997, P226, table8,
 CH300+ CH3C(O)O2 see path a that
 dominates}
 pin_40] pinald-oo + XO2 = pinO2 # 7522 e^(272/T),
 pin_41] pinald-oo + apNO3-oo = vol-oxy
 + OH-apNO3 # 7522 e^(272/T),
 PIN_41] pinald-oo + pinO2 = 0.7*pinO2 + 0.3*pinacid+
 0.9*pinald +0.44*vol-oxy # 7522 e^(252/T),

OXYPINALDEHYDE CHEMISTRY

opin_42] oxypinO2 + NO= 0.72*oxypinald + 0.8*HO2 +
 0.82*NO2 + 0.18*OH-apNO3 # 6056 e^(180/T),
 opin_43] oxyC8O2 + NO = 0.84*NO2 +0.711*vol-oxy +
 0.8*HO2 +0.16*OH-apNO3 # 6056 e^(180/T),
 opin_44] oxypinald + OH = 0.8*oxypin-oo + 0.1*C2O3
 + 0.3*XO2 # 134417,
 opin_45] oxypinald + NO3 = 0.8*oxypin-oo +0.12*C2O3

+ 0.36*XO2 + 0.08*acetone + 0.08*HO2

79.76,

opin_46] oxypin-oo + NO = NO2 + oxypinO2

6056 e^(180/T),

opin_47] oxypin-oo + NO2 = pinald-PAN

0.00015 e^(5500/T),

opin_48a] oxypin-oo + XO2 =

oxyC8O2 {+CO2}

59,

opin_49] oxypinO2 + oxypinO2 = 1.48*oxypinald + 0.355*vol-oxy

+ 1.2*HO2

55111 e^(416/T),

opin_50] oxypinO2 + HO2 = pin-ooH

211 e^(1380/T),

opin_51] oxypin-oo + HO2 = 0.4*oxypinacid +

0.6*pin-ooH

635 e^(1040/T),

PINALIC ACID CHEMISTRY

pinal_55] pinalic + OH = 0.71*predi-oo + 0.4*XO2 + 0.2*acetone

+ 0.2*C8O2

134417,

pinal_56] pinalic + NO3 = 0.8*predi-oo + 0.2*acetone

+HNO3

79.76,

pinal_57] predi-oo + NO = C8O2 + NO2

6056 e^(180/T),

pinal_58] predi-oo + NO2 = pinald-PAN

0.00015 e^(5500/T),

pinal_59] predi-oo + predi-oo = 1.4*C8O2 + 0.6*pinalic

+ 1.2*HO2

25111 e^(417/T),

pinal_61] predi-oo + HO2 = 0.4*diacid + 0.6*pin-ooH

635 e^(1040/T), {lightfoot, 1992, atmos environ}

wall losses

wall_62] diacid {walls} =

6 x 10⁻⁷ e^(2445/T),

wall_63] oxypinacid {walls} =

6 x 10⁻⁷ e^(2445/T),

wall_64] pinacid {walls} =

4 x 10⁻⁷ e^(2445/T),

wall_65] oxypinald {walls} =

4 x 10⁻⁷ e^(2445/T),

wall_66] pinalic {walls} =

4 x 10⁻⁷ e^(2445/T),

wall_67] pinald {walls} =

2.5 x 10⁻⁷ e^(2445/T),

wall_68] OH-apNO3 {walls} =

7 x 10⁻⁷ e^(2445/T),

wall_69] pinald-PAN {walls} =

7 x 10⁻⁷ e^(2445/T),

PARTITIONING REACTIONS

seed70] stabcrieg1 + pinald = seed1

23,

seed71] stabcrieg1 + pinacid = seed1

783,

seed72] stabcrieg1 + oxypinald = seed1

23,

seed73] stabcrieg1 + pinalic = seed1

783,

seed74] stabcrieg1 + HCHO = oxypinald

23,

seed75] stabcrieg1 + oxypinacid = seed1

783,

seed76] stabcrieg2 + pinald = seed1	# 23,
seed77] stabcrieg2 + pinacid = seed1	# 783,
seed78] stabcrieg2 + oxypinald = seed1	# 23,
seed80] stabcrieg2 + HCHO = oxypinald	# 23,
seed81] stabcrieg2 + oxypinacid = seed1	# 783,
seed82] diacid + diacid = seed1	# 0.05,
P83] diacid + seed = seed + part	# 70,
P84] diacid + seed1 = seed1 + part	# 70,
P85] diacid + part = part + part	# 70,
P86] diacid + part1 = part1 + part	# 70,
P87] diacid + part2 = part2 + part	# 70,
P88] diacid + part3 = part3 + part	# 70,
P89] diacid + part4 = part4 + part	# 70,
P90] diacid + part5 = part5 + part	# 70,
P91] diacid + part7 = part7 + part	# 70,
P92] part = diacid	# $3.73 \times 10^{14} e^{(-10285/T)}$,
P93] pinacid + seed1 = seed1 + part1	# 40,
P94] pinacid + part = part + part1	# 40,
P95] pinacid + seed = seed + part1	# 40,
P96] pinacid + part1 = part1 + part1	# 40,
P97] pinacid + part2 = part2 + part1	# 40,
P98] pinacid + part3 = part3 + part1	# 40,
P100] pinacid + part5 = part5 + part1	# 40,
P101] pinacid + part7 = part7 + part1	# 40,
P102] part1 = pinacid	# $3.73 \times 10^{14} e^{(-9650/T)}$,
P104] pinald + part = part + part2	# 30,
P106] pinald + part1 = part1 + part2	# 30,
P108] pinald + part3 = part3 + part2	# 30,
P109] pinald + part4 = part4 + part2	# 30,
p110] pinald + part6 = part6 + part2	# 30,
P111] pinald + part5 = part5 + part2	# 30,
P112] pinald + part7 = part7 + part2	# 30,
P113] part2 = pinald	# $3.73 \times 10^{14} e^{(-9000/T)}$,
P114] oxypinald + seed1 = seed1 + part3	# 65,
P115] oxypinald + part = part + part3	# 65,
P116] oxypinald + seed = seed + part3	# 65,
P117] oxypinald + part1 = part1 + part3	# 65,
P119] oxypinald + part3 = part3 + part3	# 65,
P121] oxypinald + part5 = part5 + part3	# 65,
p122] oxypinald + part6 = part6 + part3	# 65,
P123] oxypinald + part7 = part7 + part3	# 65,
P124] part3 = oxypinald	# $3.73 \times 10^{14} e^{(-10100/T)}$,
P126] pinalic + part = part + part4	# 40,

P128] pinalic + part1 = part1 + part4	# 40,
P130] pinalic + part3 = part3 + part4	# 40,
p132] pinalic + part5 = part5 + part4	# 40,
p133] pinalic + part6 = part6 + part4	# 40,
p134] pinalic + part7 = part7 + part4	# 40,
P135] part4 = pinalic	# $3.72 \times 10^{14} e^{(-9650/T)}$,
P136] oxypinacid + seed1 = seed1 + part5	# 74,
P136] oxypinacid + seed = seed + part5	# 74,
P137] oxypinacid + part = part + part5	# 74,
P138] oxypinacid + part1 = part1 + part5	# 74,
P140] oxypinacid + part3 = part3 + part5	# 74,
P142] oxypinacid + part5 = part5 + part5	# 74,
p142] oxypinacid + part6 = part6 + part5	# 74,
P143] oxypinacid + part7 = part7 + part5	# 74,
P144] part5 = oxypinacid	# $3.73 \times 10^{14} e^{(-10335/T)}$,
p145] pinald-PAN + seed1 = part6 + seed1	#40,
p147] pinald-PAN + part = part6 + part	#40,
p148] pinald-PAN + part1 = part6 + part1	#40,
p149] pinald-PAN + part3 = part6 + part3	#40,
P150] pinald-PAN + part4 = part6 + part4	#40,
p151] pinald-PAN + part5 = part6 + part5	#40,
p152] pinald-PAN + part6 = part6 + part6	#40,
p153] pinald-PAN + part7 = part6 + part7	#40,
p155] part6 = pinald-PAN	# $3.73 \times 10^{14} e^{(-9200/T)}$,
p156] OH-apNO3 + seed1 = part7 + seed1	#40,
p158] OH-apNO3 + part = part7 + part	#40,
p159] OH-apNO3 + part1 = part7 + part1	#40,
p160] OH-apNO3 + part3 = part7 + part3	#40,
p162] OH-apNO3 + part5 = part7 + part5	#40,
p163] OH-apNO3 + part6 = part7 + part6	#40,
p164] OH-apNO3 + part7 = part7 + part7	#40,
p165] part7 = OH-apNO3	# $3.73 \times 10^{14} e^{(-9200/T)}$,
P166] part {walls} =	# 0.0008,
P167] part1 {walls}=	# 0.0008,
P168] part2 {walls}=	# 0.0008,
P169] part3 {walls}=	# 0.0008,
P170] part4 {walls}=	# 0.0008,
P171] part5 {walls}=	# 0.0008,
P172] part6 {walls} =	# 0.0008,
P173] part7 {walls} =	# 0.0008,
P174] seed {walls} =	# 0.0008,
P175] seed1 {WALLS}=	# 0.0008,
W176] O3 {walls} =	# 0.0005,
W177] O3 +part = part	# 4×10^{-3} ,

W178] O3 + seed1 =
 W179] O3 + part1 = part1
 W180] O3 + part2= part2
 W181] O3 + part3= part3
 W182] O3 + part4= part4
 W183] O3 + part5= part5
 W184] O3 + part6= part6
 W185] O3 + part7= part7

4 x 10⁻³,
 # 4 x 10⁻³,
 # 4 x 10⁻³,
 # 4 x 10⁻³,
 # 4 x 10⁻³,
 # 4 x 10⁻³,
 # 4 x 10⁻³,
 # 4 x 10⁻³;

Operator Chemistry

REACTIONS=

XO_1] XO2 + NO = NO2
 XO_3] XO2 + XO2 =
 XO_4] XO2 + HO2 =

4431 e^(280/T),
 # 369 e^(190/T),
 # 561 e^(800/T);

EndMechanism;

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