

Influence of Water Vapor on the Process of New Particle Formation during Monoterpene Ozonolysis

Boris Bonn, Gerhard Schuster, and Geert K. Moortgat*

Air Chemistry Division, Max-Planck-Institute for Chemistry, P.O. Box 3060, D-55020 Mainz, Germany

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This study was focused on the investigation of the influence of water vapor on the size distribution of the newly formed aerosol particles during the reaction of monoterpenes and ozone measured by a scanning mobility particle sizer (TSI 3936). Measurements made during reactions of selected exocyclic monoterpenes (β -pinene and sabinene, 1 ppmv) with ozone (0.5 ppmv) showed a decrease of the particle number concentration and total aerosol volume with increasing water vapor. On the contrary, number concentration and total aerosol volume were not affected or less affected by the presence of water vapor during similar experiments with the endocyclic monoterpenes α -pinene and Δ^3 -carene. However, when the reactant concentrations of α -pinene and ozone were lowered to 50 and 110 ppbv, a similar decreasing effect of water vapor on the nucleation was observed as found in the exocyclic monoterpene reactions, whereas an increase of the produced aerosol volume was measured. These observations contradict the assumption that the dicarboxylic acids, such as pinic acid in the case of α - and β -pinene, produced by the unimolecular decomposition of the excited Criegee intermediate, are responsible for the observed nucleation. The dicarboxylic acids should therefore be independent of the concentration of water vapor. On the contrary, we bring evidence that new particle formation proceeds via the stabilized Criegee intermediate. Furthermore, the intermolecularly (e.g., β -pinene) or intramolecularly (e.g., α -pinene) formation of secondary ozonides acting as nucleation precursors explains the observed effect of water vapor. The results of similar experiments with added formic acid and carbonyl compounds are supportive of this assumption.

Introduction

It is 41 years ago since Went¹ reported first the blue haze occurring in the morning hours at remote rural sites. In his conclusion, he explained the occurrence of the haze by the formation of fine aerosol particles initiated by very low volatile products of the oxidation of the biogenic emitted volatile organic carbons (VOC) such as terpenes. These particles scatter the sunlight in accordance to the Raleigh theory and cause the blue light (observations of Tyndall and Haagen-Smit cited in Went¹). The blue effect vanishes with time due to the growing of the aerosol particles and the sunlight is scattered more whitish (Mie scattering). Field observations in Canadian,² Finnish,³ and Portuguese⁴ remote sites support the conclusion of Went, detecting particle formation in the morning, when photooxidation has already started.

Although recent laboratory studies on the ozonolysis of monoterpenes ($C_{10}H_{16}$) have shown that these reactions are the source of significant quantities of secondary organic aerosol (SOA),^{5,6} the particle formation processes and especially the participating species in the first step of nucleation are largely unknown.⁷ This is due to the very small mass of the freshly nucleated aerosol particles with diameters less than 10 nm, too small to be analyzed up to now. Moreover, in most of the published studies,^{6,8–12} performed in smog chambers as well as in the laboratory, the aerosol composition has only been studied at the completion of the reaction by the way of analyzing filter samples. The filter results were then used to draw conclusions on the very first step of nucleation and the initial

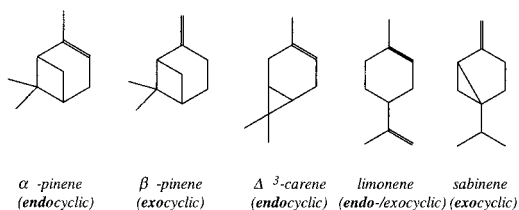
aerosol composition. Consequently, most of the authors^{6,8,9,11–13} believe that the dicarboxylic acids are the initial nucleating substances, because they were the products sampled on the filter with the lowest vapor pressure ($p^{\text{sat}} \leq 5.6 \times 10^{-7}$ Torr).⁶ Therefore, a different analytical tool is needed to observe the process of new particle formation to obtain a better understanding of its initiating steps.

With this respect, some recent publications proposed different nucleation initiating species. Tobias et al.¹⁴ suggest that hydroxyhydroperoxides form new particles under wet conditions in the $O_3 + 1$ -tetradecene reaction. Kamens et al.⁷ used secondary ozonides within their model on the reaction of O_3 and α -pinene formed by the reaction of the C_{10} -CI^{stab} (stabilized Criegee intermediate) of α -pinene with pinonaldehyde to describe particle formation. Moreover, simulations of Kerminen et al.¹⁵ have revealed that at typical environmental conditions substances with saturation vapor pressures lower than 10^{-10} Torr are necessary to start homogeneous nucleation at remote sites with low background aerosol concentrations. This does not conform with the estimated saturation vapor pressures of dicarboxylic acids found in the oxidation of monoterpenes.

To obtain information about the first steps of nucleation, a scanning mobility particle sizer (SMPS) device was used to study the effect of, e.g., water vapor, on the particle formation process. The results presented in this paper on the effect of water vapor on the new aerosol formation during selected endo- (α -pinene, Δ^3 -carene, limonene) and exocyclic (β -pinene, sabinene) monoterpene ozonolysis (see Scheme 1) are explained in terms of CI^{stab} reaction products as nucleation precursors, such as secondary ozonides (SOZ).

* To whom correspondence should be addressed. Phone: (+49) 6131 305476. Fax: (+49) 6131 305436. E-mail: moo@mpch-mainz.mpg.de.

SCHEME 1: Structures of the Different Used Monoterpenes: the *Endocyclic* Monoterpenes α -pinene and Δ^3 -carene Contain One Carbon Double Bond inside a C₆-Ring Structure, whereas the Single Carbon Double Bond of the *Exocyclic* Monoterpenes β -pinene and Sabinene Is Located outside the C₆-Ring Structure (Limonene Contains Two Carbon Double Bonds, One Inside and One Outside the C₆-Ring Structure, but the Ozone Molecule Attacks Predominantly the Double Bond Inside the Ring)



Experimental Section

Experiments were carried out in two different reaction chambers, in order to study the particle formation at different time scales: reaction times larger than 1 min were achieved in an evacuable spherical glass vessel with a volume of 570 L (reactor A), whereas detailed measurements during the first minute of the reaction have been performed in a newly built flow reactor (reactor B).

Reactor A (Spherical Glass Vessel). The experimental setup of reactor A was described in detail previously by Neeb et al.¹⁶ with the exception of the implementation of a scanning mobility particle sizer (SMPS, TSI 3936). Only a brief description will be given here. All experiments were carried out at a temperature of 295 ± 2 K and a pressure of 730 ± 1 Torr using synthetic air (80% nitrogen, 20% oxygen) as a bath gas. Ozone was produced by a mercury pen-ray lamp inside the reactor, prior to the addition of the mixture of the monoterpene and synthetic air (reaction start). The reaction was studied using a Fourier transform infrared spectrometer (FTIR) for the gas-phase analysis and a SMPS to measure the particle size distributions of the aerosol produced. The SMPS consists of an electrostatic classifier (TSI 3080) with a long differential mobility analyzer (LDMA; TSI 3081) and an ultra-fine condensation particle counter (CPC; TSI 3025A) as detector. In order to check the performance of the SMPS, an additional particle counter (TSI 3010) was used. In experiments performed in reactor A, the SMPS system was generally operated with a sample flow of 0.5 L min^{-1} diluted with 1.0 L min^{-1} of purified air at the inlet of the CPC to provide a longer sampling time (around 50 min).

The sheath flow inside the DMA was set to 5.0 L min^{-1} . Usually, 25 scans with a time resolution of 2 min (110 s up-scan and 10 s down-scan) were obtained.

In order to prevent reactions of the terpenes with the OH radicals, which are known to be generated during the ozonolysis of alkenes, *cyclo*-hexane was added as an OH scavenger in all experiments (see Table 1). The humidity was adjusted by passing air through a bubbler filled with 18 M Ω water (Elgastat). Therefore, water vapor was added after the ozone generation process, to avoid observable photonucleation.¹⁷ In this study, two environments of different humidity conditions have been used: (i) a dry environment (in the following referred to as “dry experiment”) with a dew point of -80 °C ($[\text{H}_2\text{O}] = 3$ ppmv) and (ii) a humid environment (referred to as “humid experiment”) with a dew point of 4 °C ($[\text{H}_2\text{O}] \approx 8400$ ppmv). For most investigations, the chosen initial reactant concentrations were 500 ppbv of ozone, 1 ppmv of the monoterpene, and 270 ppmv of *cyclo*-hexane (see Table 1). Alternatively, some studies were performed with 50 ppbv monoterpene initial concentration, as described later in this paper. All substances used were of the highest commercially available purity: α -pinene (Fluka [Sigma-Aldrich Chemistry GmbH (Sigma-Aldrich, Fluka), 82041 Deisenhofen, Germany]: $\geq 99.5\%$), β -pinene (Sigma-Aldrich: $\geq 99\%$), Δ^3 -carene (Fluka: $\geq 99\%$), limonene (Sigma-Aldrich: $\geq 97\%$), sabinene (Roth [Carl Roth GmbH & Co., 76185 Karlsruhe, Germany]: $\geq 96\%$), *cyclo*-hexane (Sigma-Aldrich: $\geq 99.9\%$), acetone (Sigma-Aldrich: $\geq 99\%$), nopinone (Sigma-Aldrich: $\geq 98\%$), *cyclo*-hexanol (Sigma-Aldrich: $\geq 99\%$), *cyclo*-hexanone (Sigma-Aldrich: $\geq 99.8\%$), *para*-formaldehyde (Sigma-Aldrich: $\geq 99\%$), and formic acid (Sigma-Aldrich: $\geq 98\%$).

Reactor B (Flow Reactor). Experiments designed for the study of the initial phase of the reaction were performed in a newly built flow reactor (reactor B) shown schematically in Figure 1. It consists of a glass tube of 120 cm length and 5 cm in radius with a fixed sampling line at the bottom of the reactor for the SMPS system. The inlet mixing plunger is movable and provides two flows: (a) the center flow (4 L min^{-1}), consisting of synthetic air and ozone mixture, and (b) the outer flow (1 L min^{-1}), consisting of synthetic air admixed with the terpene, the water vapor (depending on the planned experiment), and eventually additional reactants. The both flows account for a flow rate of 5.0 L min^{-1} in total. This results in a Reynolds number $Re = 70.3$ of the reactor setup (tube) that is a characteristic value for laminar flow conditions. The outer and the center flow were totally mixed during 0.4 s inside the movable plunger under turbulent conditions prior to the inlet

TABLE 1: Experimental Conditions of the First Studies in the Spherical Reactor (A)

monoterpene	sabinene		β -pinene		limonene		Δ^3 -carene	
experiment no.	dry sb1	humid sb2	dry bp1	humid bp2	dry lm1	humid lm2	dry 3c1	humid 3c2
[alkene] ^o	1 ppm	1 ppm	1 ppm	1 ppm	1 ppm	1 ppm	1 ppm	1 ppm
[ozone] ^o	436 ppb	429 ppb	419 ppb	416 ppb	426 ppb	435 ppb	430 ppb	446 ppb
[<i>cyclo</i> -hexane] ^o	276 ppm	276 ppm	276 ppm	278 ppm	286 ppm	276 ppm	278 ppm	276 ppm
[HCOOH] ^o	-	-	-	-	-	-	-	-
dew point	-80 °C	4 °C	-80 °C	4 °C	-80 °C	4 °C	-80 °C	4 °C
monoterpene	α -pinene		α -pinene		sabinene		β -pinene	α -pinene
experiment no.	dry ap1	humid ap2	dry ap3	humid ap4	dry sb3	humid sb4	bp3	ap5
[alkene] ^o	1 ppm	1 ppm	50 ppb	50 ppb	50 ppb	50 ppb	1 ppm	500 ppb
[ozone] ^o	4.6 ppm	4.6 ppm	110 ppb	110 ppb	110 ppb	110 ppb	430 ppb	420 ppb
[<i>cyclo</i> -hexane] ^o	270 ppm	270 ppm	270 ppm	270 ppm	271 ppm	271 ppm	270 ppm	270 ppm
[HCOOH] ^o	-	-	-	-	-	-	1.8 ppm	1.8 ppm
dew point	-73 °C	4 °C	-80 °C	4 °C	-80 °C	4 °C	-80 °C	-80 °C

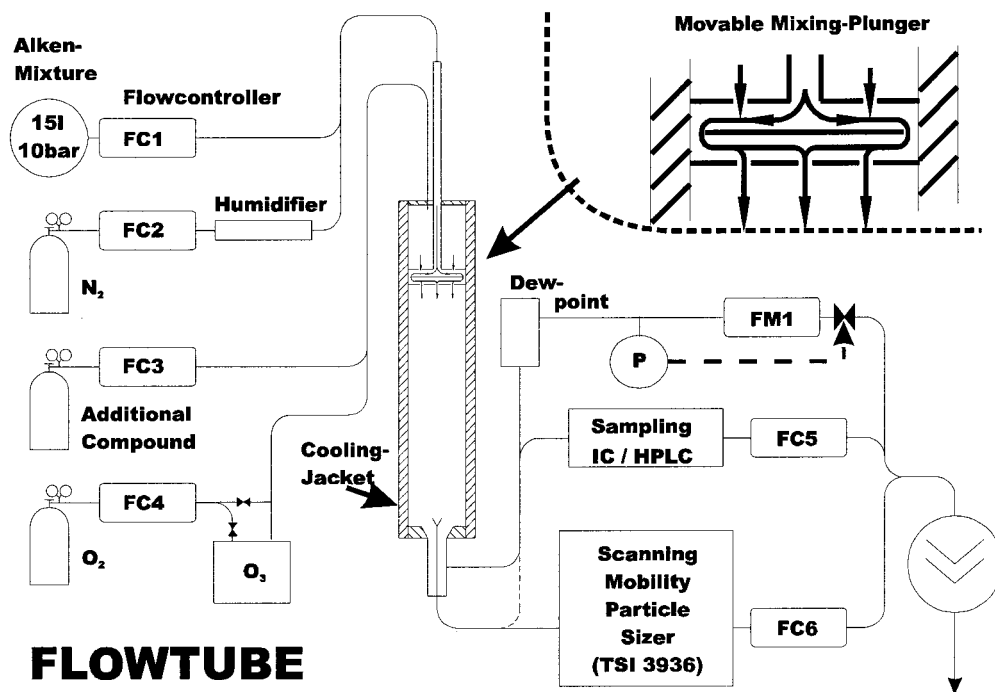


Figure 1. Scheme of the flow tube set-up (reactor B) with the instruments for gas and particle (physical and chemical) analysis.

of the flow tube. During this time, nucleation does not take place. Thereupon, the gas stream enters the reaction chamber through a sieve to achieve laminar flow conditions instantaneously. Because of the laminar nature of the flow, the radial velocity profile $v(r)$ in the stream direction is described by

$$v(r) = 0.16(r_{\max}^2 - r^2)$$

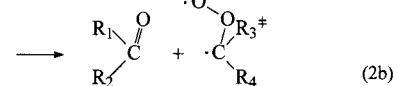
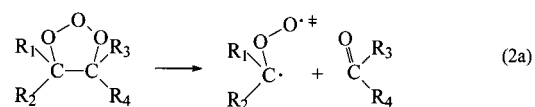
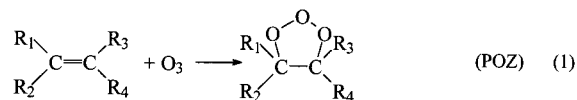
with r the radius in cm, r_{\max} the maximum radius of the reactor (5.0 cm), and v the velocity in cm s^{-1} . Tests made with an CO_2 monitor (Leybold–Heraeus) mounted at the SMPS outlet indicated that laminar flow conditions were reached at 5 cm distance from the mixing plunger. This results in an average velocity of the SMPS outlet of 2.0 cm s^{-1} . Therefore, a reaction time step of one second can be achieved by a displacement of the mixing plunger of 2 cm in the flow tube. Consequently, a reaction progress of maximum of 60 s can be observed in the flow reactor (reactor B). Moreover, thermal convection resulting from mixing etc. can be neglected because of the vertical positioning of the reactor.

Ozone was produced by flushing synthetic air through a cell containing a mercury pen-ray lamp, and its concentration was measured in a second cell by UV absorption at 254 nm prior to the flow reactor.

The terpene and the additional reactants were diluted in synthetic air and stored in stainless steel bottles before added into the outer flow of the reactor. All flows were adjusted by MKS flow controllers. To achieve a certain humidity level inside the flow tube, part of the flow was flushed over heated 18 M Ω water (Elgastat), and the humidity was measured at the outlet of the flow tube by a dew point meter (Panametrics, system 3A). The pressure in the flow reactor was measured adjacent to the sampling outlet and was kept constant at 760 Torr by an adjustable flow controller.

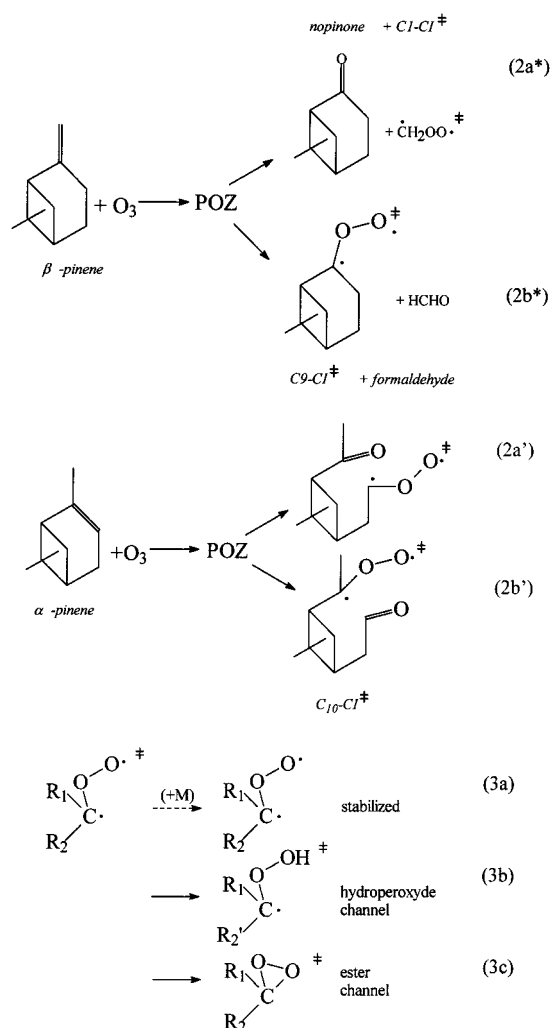
Initial concentrations of ozone and monoterpene were chosen in the range of 100 and 300 ppbv. The sample flow of the SMPS system was adjusted to 1.5 L min^{-1} , and the used sheath flow was 15 L min^{-1} .

Initial Reaction Steps. To understand the particle formation mechanism, first the initial reaction steps must be considered. The reaction of ozone with an alkene proceeds by the general accepted mechanism first suggested by Criegee.¹⁸ The ozone molecule adds to the double bond of the monoterpene to form a primary ozonide (POZ; reaction 1). This



energetically excited POZ is very unstable and decomposes unimolecularly to carbonyl compounds and carbonyl oxide species (2a and b), generally referred as ‘‘Criegee intermediates’’ (CIs).

The structure type of the CIs formed in the reactions 2a and 2b depends on the structure type of the monoterpene: if the carbon double bond is located outside a ring structure (*exocyclic*, e.g., β -pinene), the decomposition of the POZ forms two products. For example, for β -pinene, C_1 -CI and nopinone are produced in reaction 2a* and C_9 -CI and formaldehyde in reaction 2b*. If the carbon double bond is situated inside a ring structure (*endocyclic*, e.g., α -pinene), the ring decomposes to a molecular species with a carbonyl oxide and an aldehydic end (C_{10} -CI) (reaction 2a' and 2b'). The CIs (C_{10} -CIs) are in an energetically excited state denoted by CI^\ddagger , and will further¹⁹ (a) be stabilized by collisions with the bath gas (O_2 and N_2) molecules (reaction 3a), forming stabilized CIs (CI^{stab}) or (b) unimolecularly decompose either via a hydroperoxide (hydroperoxide channel, 3b) or form an ester (ester channel, 3c).



Results and Discussion

H₂O Addition. In this study, the formation of new particles and the evolution of the formed particle size distribution of selected monoterpene ozonolysis were measured by the SMPS under two different conditions of humidity (dry and humid).

A first set of experiments with α -pinene (ap1/2), β -pinene (bp1/2), Δ^3 -carene (3c1/2), limonene (lm1/2), and sabinene (sb1/2) were conducted with 1 ppmv of the terpene, 500 ppbv of ozone, and 270 ppmv of *cyclo*-hexane in the spherical reactor (A), except for α -pinene, where 4.6 ppmv of ozone and 1 ppmv of the monoterpene were used. The experimental details are listed in Table 1.

Exocyclic Monoterpenes and Water Vapor. A typical time evolution of the particle size distribution during experiments with ozone and exocyclic monoterpenes can be seen in Figure 2a. Shown is a β -pinene ozonolysis performed in the spherical reactor (reactor A). Every particle size distribution is obtained within two minutes and is displayed as a single trace. Generally, a nucleation is characterized by particle size distributions $dN/d \log(d)$ with a maximum at very small diameters (diameter $d < 10$ nm) with a high particle number density. Later on, these initial particles coagulate and semivolatile material condenses on the particle surfaces leading to a growth of the aerosol particles and a shift of the size distribution to larger diameters. Both processes cause a decrease in the maximum of the number density and a broadening of the particle size distribution curve. The total particle number concentration (N) is then defined as the integral over the whole size range of a single curve (eq I). The integrals of the particle size distributions shown in Figure

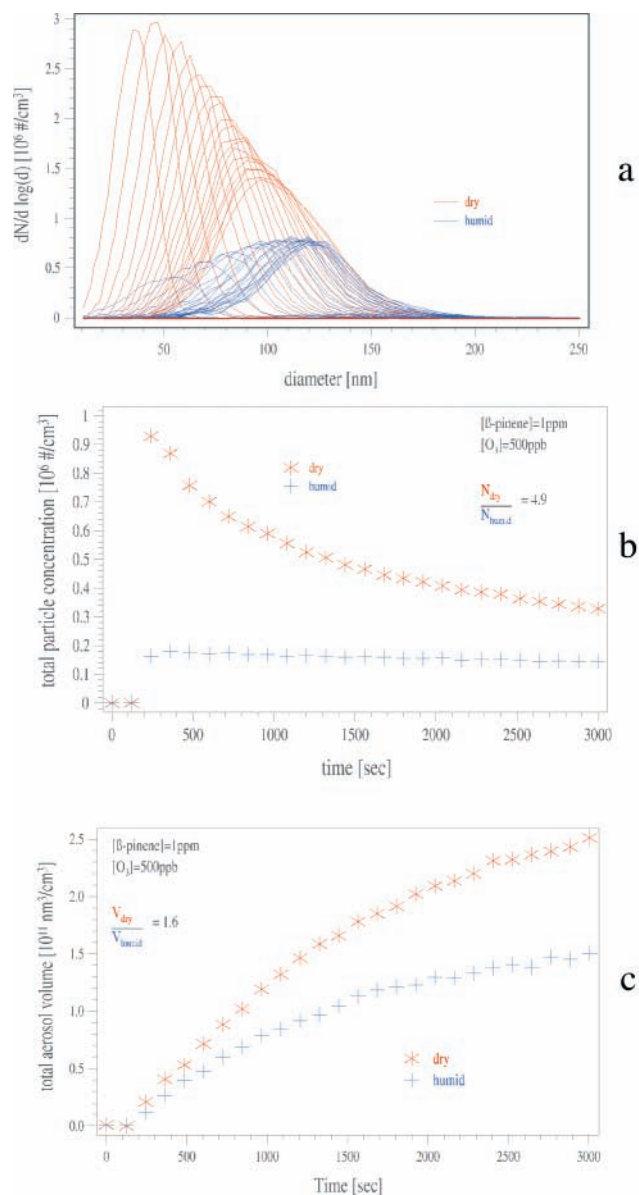


Figure 2. (a) Influence of water vapor on the aerosol size distribution during the ozonolysis of β -pinene in two different experiments performed in the spherical reactor: (pink) with added *cyclo*-hexane under dry conditions and (green) added *cyclo*-hexane under humid conditions. The size distribution at the end of the experiment shifts to larger diameters with increasing water vapor concentration, and the maximum is lowered. (b and c) Similar observations are made for the corresponding total aerosol particle concentration (b) and total aerosol volume (c). The number concentration decreases by a factor of 4.9 with increasing humidity: (dry, *; humid, +). Simultaneously, the total aerosol volume is lowered by a factor of 1.6 with increasing water vapor concentration in the same two experiments.

2a are plotted versus the mean sampling time in Figure 2b. The total aerosol volume is obtained in a similar way by the integral of the volume size distribution $dV/d \log(d)$ (eq II) and is displayed for example in Figure 2c.

$$N = \int_0^{\infty} \frac{dN}{d \log(d)} d \log(d) = \sum_i N_i$$

with N_i as the data point of interval i (I)

$$V = \int_0^{\infty} \frac{dV}{d \log(d)} d \log(d) = \sum_i V_i$$

with V_i as the data point of interval i (II)

TABLE 2: Ratios of the Formed Total Aerosol Volume and the Maximum Formed Total Number Concentration (N_{Max}) under Dry and Humid Conditions for Selected Monoterpenes with the Concentrations A, 1 ppmv (B: 50 ppbv) for the Used Alkene and A, 500 ppb (B: 110 ppb) for Ozone^a

A			
monoterpene	volume (dry)/ volume (humid)	N_{max} (dry)/ N_{max} (humid)	structure (bold: dominating type)
sabinene	2.8 ± 0.2	2.1 ± 0.1	exocyclic
β -pinene	1.6 ± 0.1	4.9 ± 0.4	exocyclic
limonene	1.1 ± 0.1	1.7 ± 0.1	exo-/ endocyclic
α -pinene	1.0 ± 0.1	1.1 ± 0.1	endocyclic
Δ^3 -carene	1.0 ± 0.1	2.5 ± 0.1	endocyclic
B			
monoterpene	volume (dry)/ volume (humid)	N_{max} (dry)/ N_{max} (humid)	structure (bold: dominating type)
sabinene	59 ± 7	not measurable	exocyclic
α -pinene	0.74 ± 0.13	1.8 ± 0.3	endocyclic

^a Although the aerosol volume is influenced different for exo- and endocyclic monoterpenes, the ratio of N_{max} is influenced by the reaction velocity, too. So, β -pinene with the lowest rate constant for the reaction with ozone is influenced most.

Figure 2a displays two ozonolysis experiments for the exocyclic β -pinene using different water vapor concentrations (dry and humid) performed in the spherical reactor. Therein, a nucleation was observed during the second sampling scan (each 120 s) after the admixture of the monoterpene at both conditions.

The nucleation event can easily be seen in Figure 2b, where the total aerosol number concentration is plotted against reaction time for both conditions. It is observed that at first a large particle formation event occurs in the dry experiment (*), at the time when enough very low volatile substances are produced and their saturation vapor pressure is exceeded several times to initiate homogeneous nucleation (Kelvin effect).²⁰ At a later stage in the dry experiment, the particle number concentration decreases because of coagulation and loss processes. In the humid experiment (+), the nucleation intensity is much lower, and because of the smaller maximum particle concentration N_{max} (a factor of 4.9 ± 0.4 less compared to the “dry” experiment, see Table 2a), the coagulation process is less pronounced than in the dry experiment. Time zero corresponds to the particle background level in the chamber measured during the blank run.

In Figure 2c, a similar picture is drawn for the total aerosol volume concentration during the progress of the reaction. After an initial phase (time needed for nucleation), the aerosol volume formation starts in both experiments, most intense in the dry but less in the humid experiment. The decreasing factor of the total aerosol volume formed was determined to be 1.6 ± 0.1 (Table 2a) under humid conditions.

The observed difference in the particle formation observed in the β -pinene ozonolysis under dry and humid conditions becomes more obvious by studying the temporal evolution of the particle size distribution during the first seconds of the reaction. These experiments have been performed in the flow reactor (reactor B) shown in Figure 3a–c. The figure displays a sequence of three different time settings (defined by the position of the plunger) during the first minute of the ozonolysis of β -pinene. Figure 3a displays the results at the time at which nucleation starts in the dry experiment, whereas in the humid experiment at the same conditions, no particles are observed ($t_{\text{reac}} = 13$ s). At the next position, 8 s later in the reaction, a beginning of particle formation is detectable under the humid

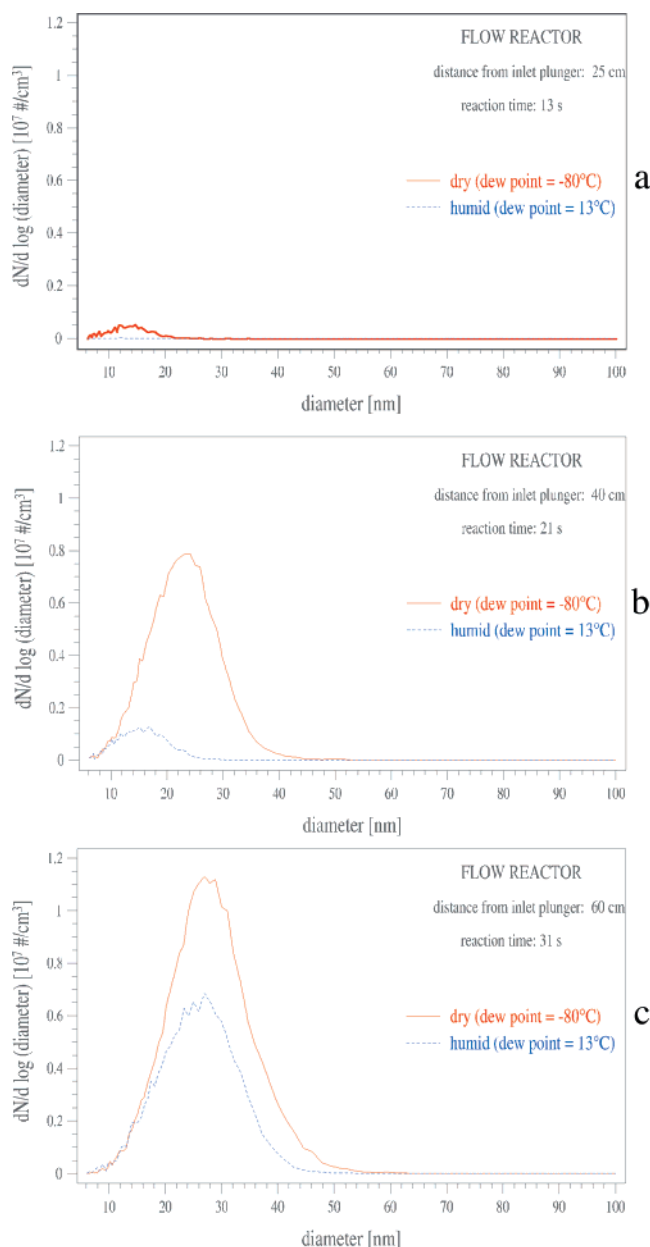


Figure 3. Time sequence of β -pinene ozone experiments in the flow reactor (reactor B). Time-resolved effect of water vapor on the new formed aerosol in β -pinene ozonolysis: (a) start of the nucleation in the dry experiment, but no particles in the humid case (reaction time is 13 s), (b) start of the delayed nucleation in the humid experiment (reaction time is 21 s), and (c) the overtake of the higher size mode (dry) by the lower size mode (humid; reaction time is 31 s).

conditions (Figure 3b). At the same time, the size distribution of the dry experiment is shifted to larger particle diameters because of the growth by condensation and coagulation processes. At a reaction time of 31 s, the maximum of both size distributions (dry and humid experiment) are located nearby the same diameter, although the total particle number concentration is much larger in the dry experiment than in the humid experiment (Figure 3c). The further evolution of the particle size distribution with time can be seen in Figure 2a. The “final” particle size distribution in the humid experiment is located at much larger diameters than the one under dry conditions. These results indicate that the particles formed under humid conditions, although produced at a later stage than the particles in the dry experiment, grow much faster than the particles under dry conditions. This behavior of the particle size distribution can

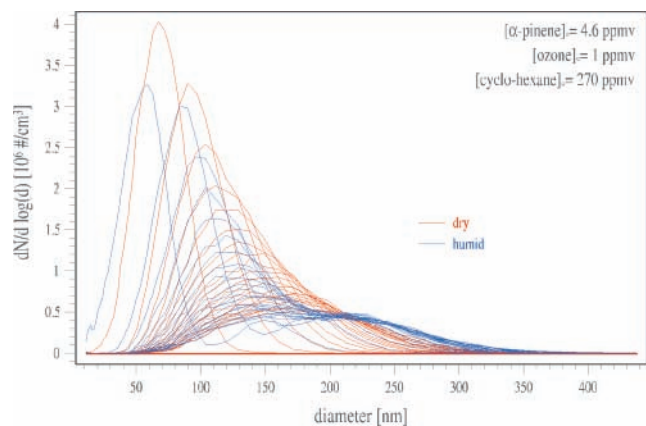


Figure 4. Influence of water vapor on the aerosol particles in α -pinene ozonolysis (spherical reactor).

be explained by the different influence of $[H_2O]$ on (a) the particle number concentration and (b) the total aerosol volume formed. The reduction of the particle number concentration with increasing humidity by a factor of nearly 5 is correlated to a reduction of the aerosol volume by a factor of only 1.6. Therefore, the concentration of the nonvolatile products, initiating the nucleation, is much more affected by water vapor than the concentration of the semivolatile products, condensing on the preexisting aerosol surface and causing their growth. Consequently, the five times less aerosol particles had to uptake the 1.6 times less semivolatile products and grow larger than the aerosol particles of the dry experiment because of the enhanced semivolatile mass per single particle formed.

As a result of the two experiments with β -pinene in the spherical reactor as well as in the flow reactor, it can be stated that water vapor delays nucleation and that it reduces the maximum total number concentration as well as the total produced aerosol volume (bp1/2).

Similar as for β -pinene ozonolysis, even more pronounced particle formations were observed in particle size distributions obtained during sabinene (sb1/2) ozone reactions with added *cyclo*-hexane under dry as well as under humid conditions (not shown). The maximum total number concentration of the aerosol particles formed is found to be reduced by a factor of 2.1 ± 0.1 with increasing humidity, and the total aerosol volume is formed 2.8 ± 0.2 times less under humid conditions than compared to the dry conditions (see Table 2a).

Consequently, water vapor reduces the concentration of the nucleation initiating species and of the condensable material in exocyclic monoterpene ozonolysis.

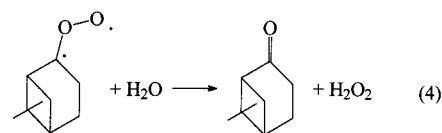
Endocyclic Monoterpenes and Water Vapor. Unlike the β -pinene and sabinene experiments, experiments with the endocyclic monoterpenes α -pinene (ap1/2), Δ^3 -carene (3c1/2), and limonene (lm1/2) in the presence of *cyclo*-hexane displayed little or no effect of water vapor on the aerosol particle concentration and volume. For example, the data sets of the two α -pinene experiments (ap1/2) are presented in Figure 4. In contrast to the particle size distributions obtained, e.g., in β -pinene ozonolysis, there is nearly no effect observable for α -pinene. A nucleation event is observable at nearly the same time for the dry as well as in the humid experiments, and the temporal evolution of the particle size distribution looks very similar for both conditions. This indicates no influence of water vapor on the nucleation as well as on the aerosol volume formation during α -pinene ozonolysis. Similar observations concerning the effect of water vapor concentration on aerosol volume production have been made for Δ^3 -carene. On the other

hand, the nucleation was affected by water vapor (not shown), and the maximum particle number concentration was reduced by a factor of 2.5 ± 0.2 . In the case of limonene ozonolysis, a small effect of increasing $[H_2O]$ was measured (not shown): a reduction by a factor of 1.1 ± 0.1 of the total aerosol volume concentration and a decrease by a factor of 1.7 ± 0.1 of the total number concentration. The influence of the water vapor on the maximum formed number concentration and on the total formed aerosol volume is summarized in Table 2a.

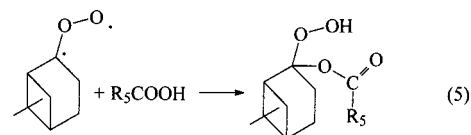
Reactions Involving CI^{stab} . In this context, the different behavior of endo- and exocyclic monoterpene ozonolyses concerning the effect of water vapor on new aerosol volume production has to be discussed. It can be stated that the aerosol volume formed during exocyclic monoterpene ozonolysis is highly sensitive toward the concentration of water vapor, whereas little or no influence is observable in endocyclic monoterpene ozone reactions.

Where the ozonolysis of terpenes is concerned, it is known that water vapor reacts only with the CI^{stab} but not with the CI^{\ddagger} . As a consequence, the production of the initial nucleating substances must occur via the CI^{stab} . However, this mechanism is in contradiction with the current formulation of the nucleation process with respect to the dicarboxylic acids, which are formed via the unimolecular decomposition of the CI^{\ddagger} .^{6–11,13} The latter proposed mechanism should be not affected by water vapor at all.

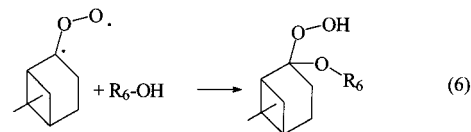
To identify the nucleation initiating species, all of the possible reactions of the CI^{stab} have to be considered.¹⁹ These are considered below using the C_9 - CI^{stab} formed during the ozonolysis of the exocyclic β -pinene as example. All further considerations may also be applied to the C_{10} - CI^{stab} s formed in the endocyclic monoterpene reactions. The C_9 - CI^{stab} is able to react (i) with water vapor (reaction 4) forming a carbonyl compound and H_2O_2 (unpublished data from this laboratory),²¹



(ii) with an acid (reaction 5), forming a hydroperoxy formate,²²

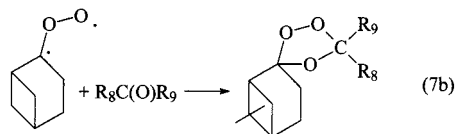
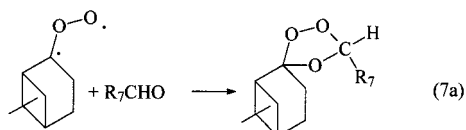


(iii) with an alcohol (reaction 6), forming a hydroperoxy ether,²²

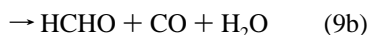


and (iv) with a carbonyl compound (aldehyde or ketone) (reactions 7a and 7b) forming a secondary ozonide (SOZ).

The situation is somewhat different in the reaction of the C_1 - CI^{stab} (CH_2OO), formed in exocyclic ozonolyses: The reaction with water vapor forms hydroxymethyl hydroperoxyde (HMHP), which is not very stable and further decomposes to formic acid and water (reaction 8).²³ The reaction of the C_1 - CI^{stab} with $HCHO$ leads either to the formation of $HCHO$ and $HCOOH$ (reaction 9a) or to the production of $HCHO$, CO , and water (reaction 9b).¹¹ A formation of a SOZ in the reaction with



HCHO has not been found¹¹ for the C₁-CI^{stab}. However, reactions with higher aldehydes and ketones are known to form SOZ.^{11,21}



Reaction Mechanism Leading to Nucleation. In the following section, the reactions 4, 5, 6, 7a, and 7b will be considered to estimate their contribution to the particle formation process via the CI^{stab}. Because of the required very low vapor pressure to start homogeneous nucleation ($p_{\text{sat}} \leq 10^{-7}$ Torr),⁶ only the large C₉-CI^{stab} as well as the C₁₀-CI^{stab} will be considered at first to act as a precursor of a nucleation initiating substance. The C₁-CI^{stab} will be considered separately.

In the reaction with water (4), an oxygen atom is abstracted and H₂O₂ and a carbonyl compound are formed^{21,23} (e.g., nopinone in the ozonolysis of β -pinene).¹¹ The rate constant of the stabilized CI with H₂O, $k_{\text{CI}}^{\text{H}_2\text{O}}$, is known to be much smaller than^{24,25} the rate constants for reactions 5, 6, 7a, and 7b at similar concentration levels of the competitive partners (acids, alcohols, aldehydes, and ketones). The reaction of CI^{stab} with water can only compete at high [H₂O] with the reaction of CI^{stab} with other partners, when its reaction flux $K_{\text{CI}}^{\text{H}_2\text{O}}$ ($k_{\text{CI}}^{\text{H}_2\text{O}} \times [\text{H}_2\text{O}]$) equals or exceeds the other possible reaction fluxes ($K_{\text{CI}}^{\text{acids}}$, $K_{\text{CI}}^{\text{alcohols}}$, $K_{\text{CI}}^{\text{aldehydes}}$, and $K_{\text{CI}}^{\text{ketones}}$). The results of the different monoterpene ozonolyses at different humidity levels indicate an inhibiting effect of water vapor on the nucleation process. Therefore, reaction 4 is not able to cause the observed particle formation. Because of the competitive aspect of the reaction of water vapor, acids, alcohols, and carbonyl compounds with the CI^{stab}, this effect is enhanced by lowering the reactant concentrations to more atmospherically relevant concentrations. If the initial reactant concentrations are smaller, then the competition between the CI^{stab} with the formed products and the present water vapor will be reduced.

The enhanced inhibiting effect of water vapor on nucleation was observed in further experiments with sabinene (sb3/4) and α -pinene (ap3/4) in the spherical reactor (reactor A) at initial concentrations of 50 ppbv of the monoterpene and 110 ppbv of ozone (see Table 1). The results are displayed in Figures 5 and 6. Although the nucleation in the α -pinene ozonolysis is now influenced by water vapor and the nucleation is reduced (see Figure 5a), the total aerosol volume increases (Figure 5b). Although the error bars are quite high because of the low count rates of the SMPS, it is obvious that in the dry experiment (boxes) many more new particles are produced than in the humid experiment (triangles).

As expected, the inhibiting effect of humidity on nucleation and aerosol volume yield is more pronounced in sabinene ozonolysis with low reactant concentration compared to the

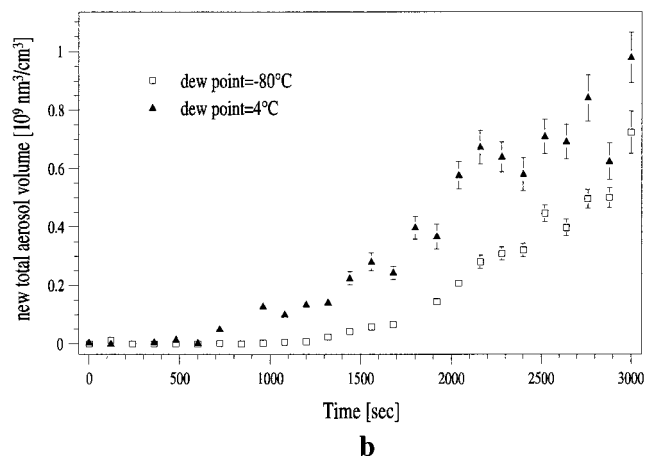
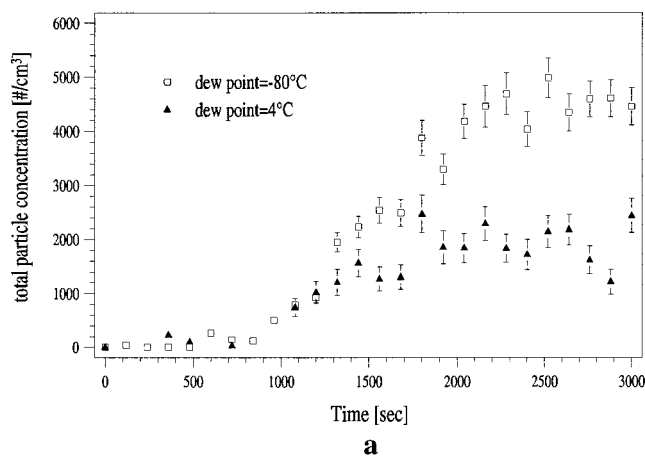


Figure 5. Influence of water vapor on (a) the aerosol number concentration and (b) the total aerosol volume formed in α -pinene ozonolysis at low concentrations (spherical reactor).

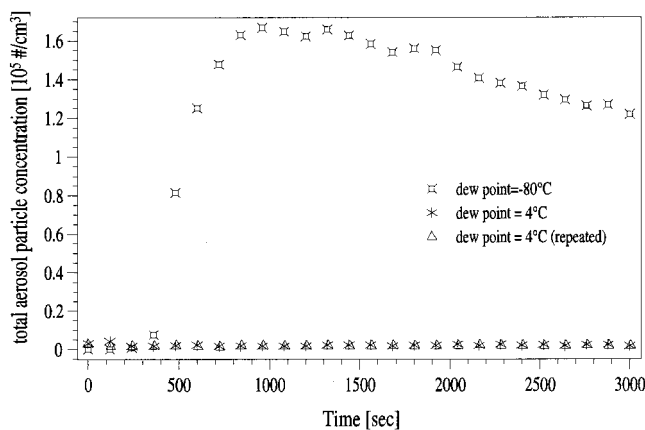


Figure 6. Effect of H₂O on the total number concentration during the sabinene ozonolysis at low concentrations (spherical reactor).

experiments performed with 1 ppmv terpene and 0.5 ppmv ozone, as mentioned above. Adding water vapor nearly suppresses the particle formation during sabinene ozonolysis in the presence of added *cyclo*-hexane (see Figure 6; stars (and triangles) symbolize the humid experiment; cross boxes, the dry experiment).

Products, such as nopinone in the case of β -pinene are not considered to take part in particle formation initiating processes, because of their high saturation vapor pressures ($p^{\text{sat}} = 0.33 \pm 0.02$ Torr at room temperature and atmospheric pressure). Although the nopinone yield increased from 18 to 55% under humid conditions,¹¹ the observed particle concentration de-

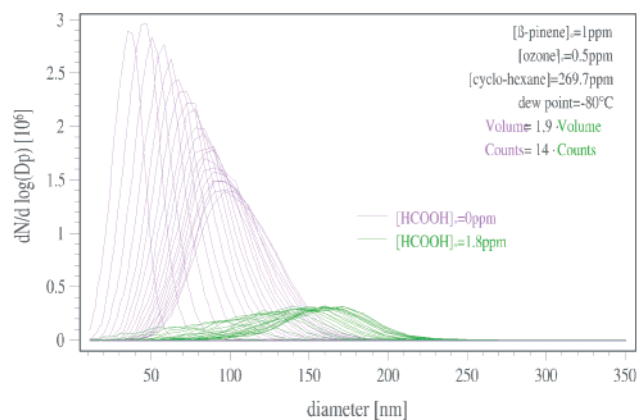


Figure 7. Addition formic acid which depletes particle formation in the β -pinene ozone reaction nearly completely at 1.8 ppmv (spherical reactor).

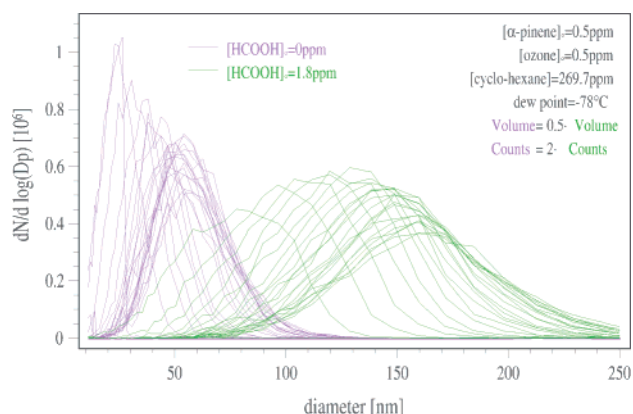


Figure 8. By contrast, the effect of HCOOH in the β -pinene ozonolysis and the effect in the α -pinene ozone reaction which is drastically less (spherical reactor).

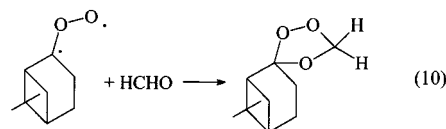
creased drastically, implying the strong inhibition effect of water vapor on nucleation.

HCOOH Addition. To investigate the influence of the acids generated during ozonolysis and to better understand the role of the stabilized Criegee intermediate during nucleation on reaction 5, formic acid was added in α - and β -pinene ozonolyses (experiments bp3 and ap5) in the spherical reactor (reactor A). It is known from previous studies^{11,21} that HCOOH is an effective scavenger for CI^{stab} . Adding HCOOH (initial concentration 1.8 ppmv) during the ozonolysis of β -pinene had a remarkable inhibiting effect on the nucleation (decrease by a factor of 14) and on the total aerosol volume (decrease by a factor of 2; see Figure 7). The data sets of α -pinene indicate a much weaker effect in the presence and absence of formic acid (Figure 8). As shown in Figures 2a and 4, the maximum of the “final” particle size distribution at the end of the β -pinene experiment is located at much larger diameters with added HCOOH than without HCOOH. The effect of HCOOH addition is similar to the described effect of water vapor but much more pronounced because of the higher reactivity of HCOOH with the CI^{stab} compared to the reactivity with H_2O . For the C_1 -CI, an enhanced reactivity of 14000 has been observed.²⁴ Thus, in the case of HCOOH, nucleation is dramatically delayed and the aerosol volume yield is decreased.

Again the difference between the two structure types endo- and exocyclic is evident. Particle formation is much less affected in the endocyclic α -pinene than in exocyclic β -pinene ozonolysis. Consequently, the reaction of the CI^{stab} with an acid is not considered as a mechanism leading to nucleation.

Alcohol Addition. The addition of alcohols (reaction 6) has a similar but less dramatic effect than HCOOH. Experiments with added *cyclo*-hexanol show a similar decrease in the maximum total number concentration as the decrease that is due to water vapor (not shown). With regard to the reaction with the CI^{stab} , the results indicate that alcohol is more effective than water vapor but less effective than formic acid at similar concentrations. The reason is found in the different relative rate constants of the three individual species with the CI^{stab} , as reported e.g. by Tobias et al.²⁸ They calculated a 22 times faster rate constant for the reaction of a linear C_{13} - CI^{stab} with CH_3OH and a 6700 faster rate constant for the reaction of the same CI^{stab} with HCOOH compared to the reaction with water vapor. Therefore, because of the inhibiting effect of alcohols, reaction 6 is not considered as a nucleation initiating reaction step.

Secondary Ozonides. Most probably, reactions 7a and 7b can be considered to lead to new particle formation. SOZs have been found as major products in the dry ozonolysis of β -pinene¹¹ and other alkenes.²¹ Fourier transform infrared (FT-IR) measurements performed in β -pinene studies¹¹ identified SOZ formed by the reaction of the C_9 - CI^{stab} with HCHO (reaction 10) in the gas phase. These authors¹¹ observed a decrease of the SOZ yield with increasing water vapor concentration. Moreover, this SOZ could even be quantified at high water vapor concentrations. Several β -pinene ozone experiments with added aldehydes



and ketones, such as nopinone, *cyclo*-hexanone, acetone, and HCHO, which have been conducted in the spherical reactor (reactor A) as well as in the flow reactor (reactor B), indicate a dependency of the nucleation on the added carbonyl compound (Figure 9a,b).

Upon addition of 1.3 ppmv HCHO (\blacklozenge), particle formation was observed much later than in the reference experiments (no additional compounds, $*$); moreover, the total aerosol volume and the particle concentration were found to be lower. On the contrary, the addition of nopinone (Δ) leads to an earlier nucleation event and an enhanced nucleation rate at the beginning of the reaction, displayed by a steeper onset. As can be seen in Figure 9a, the maximum particle concentration, is somewhat lower than in the reference experiment. This can be explained by the simultaneous enhanced generation of semi-volatile compounds, which co-condense on the existing particles, causing the formation of larger particles and a corresponding increase in the aerosol volume. Consequently, the coagulation process is enhanced, reducing the observed total number concentration.

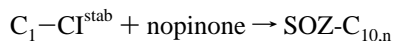
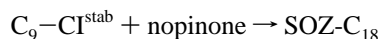
This behavior was confirmed in one experiment where both nopinone (1 ppmv) as well as acetone (4.3 ppmv) were added simultaneously, as displayed in Figure 9a,b (\times). The aerosol volume is reduced compared to the experiments with added nopinone (Δ) or the reference case ($*$); it can be seen that particle formation starts earlier and the maximum particle number concentration reaches nearly the same value as in the reference experiment ($*$).

A further point to be made is the effect of the carbonyl molecule size: the larger the carbonyl compound, the larger the SOZ molecular mass, the lower its vapor pressure, the more pronounced the nucleation, and the larger the aerosol volume

yield. This is evident in the three individual experiments with added nopinone (Δ , 2 ppmv), *cyclo*-hexanone (O, 3 ppmv), and acetone (\square , 10.5 ppmv), see Figure 9.

Generally, it can be concluded from the observations shown above that secondary ozonides formed from the reaction of CI^{stab} with carbonyl compounds (reactions 7a and 7b) participate in the first step of the nucleation process. In the case of exocyclic β -pinene, the production of SOZ is a competitive reaction between all of the produced aldehydes (mainly formaldehyde) and ketones (mainly nopinone), generated by the decomposition of the primary ozonide into a carbonyl oxide and a carbonyl compound.

There are several possible reactions producing SOZ during β -pinene ozonolysis, which should be considered for the nucleation process:



and others, with much lower concentrations. $\text{C}_1\text{-CI}^{\text{stab}} + \text{HCHO}$ does not form a SOZ^{21} as mentioned above.

In the present β -pinene study, it is assumed that the SOZ-C_{18} is the major product causing new particle formation. The two other SOZs ($\text{SOZ-C}_{10,\text{f}}$ and $\text{SOZ-C}_{10,\text{n}}$), formed by the reactions of the $\text{C}_9\text{-CI}^{\text{stab}}$ with HCHO and by the reaction of the $\text{C}_1\text{-CI}^{\text{stab}}$ with nopinone, have been observed in quantitatively large amounts in the gas phase¹¹ and therefore possess a high saturation vapor pressure. They will participate in the nucleation process, but they will not have the main impact. Because of its high molecular mass and its complex structure, the SOZ-C_{18} component is anticipated to have a remarkably low vapor pressure. Kamens et al.⁷ estimated for example a saturation vapor pressure of a SOZ-C_{20} formed in the α -pinene ozonolysis to be lower than 10^{-15} Torr. The saturation vapor pressure of the SOZ-C_{18} component will be somehow similar, and the SOZ-C_{18} will certainly be the dominant key substance leading to nucleation.

If the present reaction mechanism is correct and secondary ozonides are the initial precursors of particle formation, nucleation should also be observable in the ethene ozonolysis in the presence of added large carbonyl compounds, such as nopinone. The reaction mechanism of the ethene ozonolysis is less complex and is understood in more detail²⁴ than the ozonolysis of monoterpenes. Experiments of ethene ozonolysis are known to cause no nucleation at all,²⁷ and the $\text{C}_1\text{-CI}$ s are not able to form dicarboxylic acids.

Indeed, as part of a study performed in the spherical reactor (reactor A), new particle formation has been observed in the presence of initially added nopinone (4.6 ppmv), using $[\text{ethene}]^{\text{initial}} = 4.7$ ppmv and $[\text{ozone}]^{\text{initial}} = 3$ ppmv (Figure 10). In a second experiment using the smaller ketone *cyclo*-hexanone, a delay in particle formation as well as a decrease in nucleation strength (not shown) was observed. This delay can be explained by the formation of a smaller product with a higher saturation vapor pressure than in experiments with added nopinone, causing a longer time to reach the saturation concentration.

In the case of α -pinene (endocyclic monoterpene), an *intramolecular* reaction of the carbonyl oxide and the aldehyde group of the CI^{stab} (reaction 11, see also reaction 2a' and 2b') will form the $\text{SOZ-C}_{10,\text{i}}$; in addition, the *intermolecular* reaction

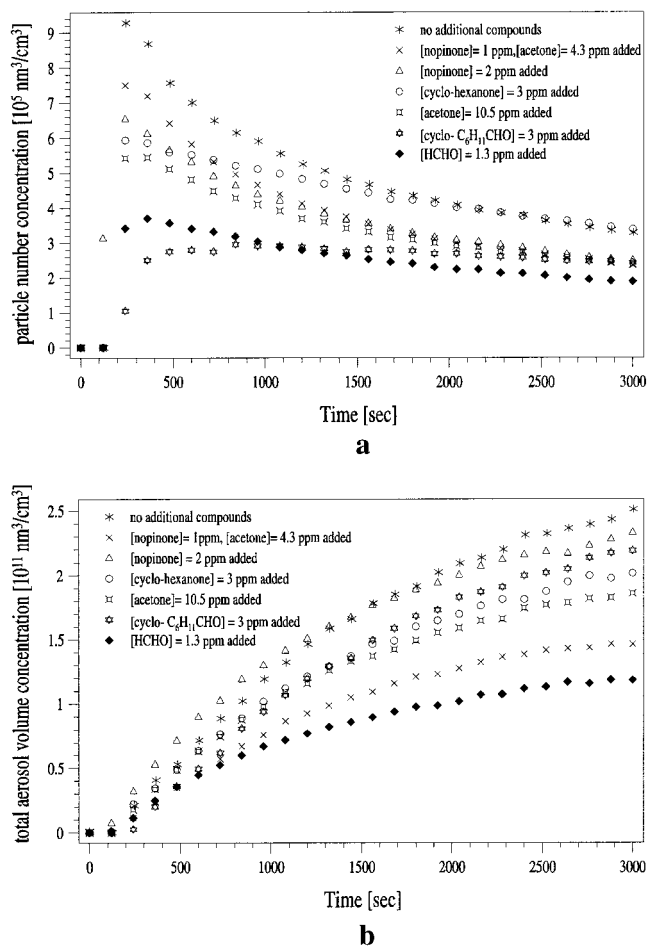


Figure 9. (a) Temporal evaluation of the particle number density during different β -pinene (1 ppmv) ozone (0.5 ppmv) reactions with added *cyclo*-hexane (270 ppmv) and different added carbonyl compounds. Shown is a basic experiment, in which nothing additionally was added (*) for comparison and experiments with different carbonyl compounds: nopinone (1 ppmv, Δ), *cyclo*-hexanone (3 ppmv, \square), acetone (10.5 ppmv, \circ), HCHO (1.3 ppmv, \blacklozenge), and a mixture of nopinone (1 ppmv) and acetone (4.3 ppmv) (\times). A clear dependence of the nucleation intensity on the added carbonyl compounds was observed. (b) Shown is the corresponding aerosol volume formed during the experiments mentioned in (a).

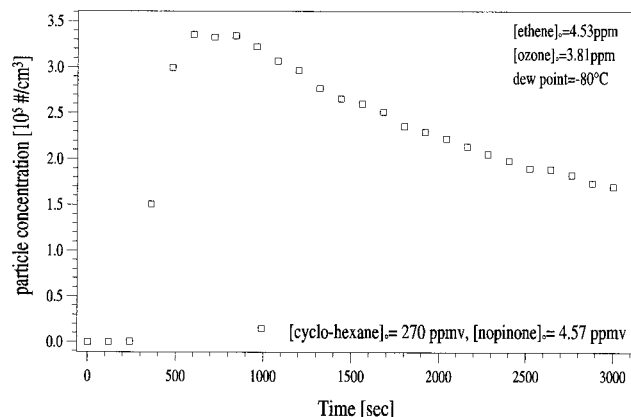
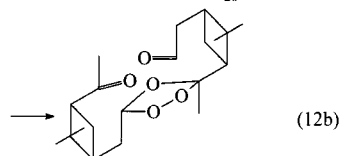
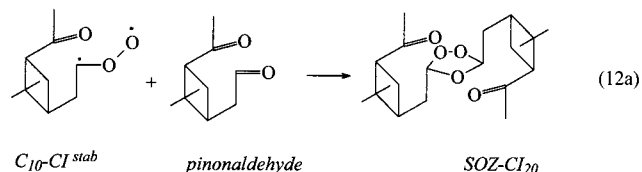
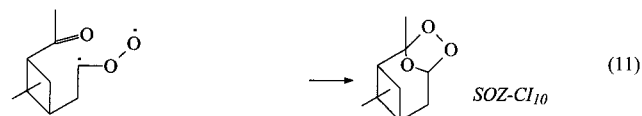


Figure 10. Total particle number concentration plotted vs time in an ethene ozonolysis experiment with previously added nopinone (4.6 ppmv). A nucleation event was observed in contradiction to an ethene ozone experiment without any additional substances.

of the CI^{stab} and a carbonyl compound such as pinonaldehyde (reaction 12a and 12b) will produce SOZ-C_{20} . Note that only one of the two diastereomers of $\text{C}_{10}\text{-CI}^{\text{stab}}$ is shown.



Our results support the intramolecular formation of SOZ- $C_{10,i}$ and its important role on the nucleation process, and not the contribution of the large SOZ- C_{20} formed by bimolecular reaction 12. Evidence was found in new experiments with added HCHO (1 ppmv) or nopinone (1 ppmv) during α -pinene ozonolysis (see the Supporting Information). If SOZ- C_{20} plays a dominant role in the nucleation process, the addition of excess small carbonyl compounds, such as HCHO, will affect the particle concentration and nucleation time: The estimation of the saturation vapor pressure⁷ of the SOZ- C_{20} to be lower than 10^{-15} Torr corresponds to an extremely low volatile product, which is able to initiate self-nucleation. The addition of excess HCHO will cause the predominant formation of a SOZ from the reaction of the C_{10} -CI^{stab} with HCHO (SOZ- C_{11}). This SOZ- C_{11} is supposed to have a higher saturation vapor pressure than the SOZ- C_{20} and therefore will initiate a less pronounced nucleation.

The new results of α -pinene ozone experiments with added HCHO (1 ppmv, +) revealed no remarkable difference with the reference experiment (\square) in nucleation time and intensity. Only a small temporal delay of the nucleation was observed in the experiment with added HCHO, caused by the higher saturation vapor pressure of the ring-opened SOZ.

It was reported by Criegee¹⁸ that for liquid-phase studies the intramolecular reaction between the aldehydic and the carbonyl-oxide ends of the C_{10} -CI^{stab} was the fastest and dominant reaction, whereas the reaction of the C_{10} -CI^{stab} with an external aldehyde was faster than with a external ketone. With respect to this, the intramolecular formation of SOZ has not been observed in the liquid phase ozonolysis of cyclic alkenes with the double bond inside a C_6 ring²⁸ because of the instability of an eight-atomic-ring structure. In this case, Criegee²⁹ reported the formation of oligomere ozonides (CI^{stab} self-reactions) in the liquid-phase ozonolyses.

On the contrary in our study, a SOZ was observed by FTIR and displayed similar spectroscopic features as the SOZ- C_{10f} formed by reaction of C_9 -CI^{stab} with HCHO during the β -pinene ozonolysis.¹¹ Because of the much lower collision frequency of molecules in the gas-phase compared to the liquid phase, the existence of the intramolecular SOZ is more likely.

Another point to be made concerns the molecular mass of the SOZ- C_{10} formed in the endocyclic monoterpene ozonolysis, which is comparable to the products formed in the reaction with for example an acid such as HCOOH. Because of the functional groups and its molecular mass, the latter products should have a slightly higher vapor pressure and might affect nucleation in the scavenger studies in the laboratory.

TABLE 3: Rate Constant for the Reaction with Ozone²²

monoterpene	$k \times 10^{17}$ [cm ³ molecule ⁻¹ s ⁻¹]
Δ^3 -carene	3.7
limonene	20
α -pinene	8.66
β -pinene	1.5
sabinene	8.6

Assuming that the C_9 -CI^{stab} forms a SOZ (SOZ- C_{18}) by reacting with nopinone in a significant amount, it is probable that the exocyclic β -pinene may have a stronger tendency in dry environments to nucleate than the endocyclic α -pinene. This is due to the higher yield of the CI^{stab} (24.9% for β -pinene and 12.5% for α -pinene)³² and the higher SOZ- C_{18} molecular mass of β -pinene compared to the SOZ- C_{10} of α -pinene. Although the rate constant of the α -pinene ozonolysis is 6 times faster than the rate constant of the β -pinene + ozone reaction (Table 3), the much larger SOZ- C_{18} will possess a higher nucleation potential than the SOZ- C_{10} . This tendency was reported by Koch et al.⁶ They show a drastically smaller nucleation potential and a much larger nucleation time of the α -pinene compared to the β -pinene ozone reaction.

Some additional comments have to be made relating the different intensity of the effect of water vapor on the nucleation process during either exocyclic or endocyclic monoterpene ozonolyses. The influence of H₂O is only affected by the concentration of the different competitive partners reacting with CI^{stab}. Therefore, different formation rates and product yields of carbonyl compounds, acids, etc. will cause different results with regard to particle formation.

In this context, an anticorrelation of the influence of water vapor on nucleation (Table 2) and the rate constant of the ozone reaction with the monoterpene (Table 3)³¹ was found, for example, for the ozonolysis of β -pinene (high influence of H₂O, slow reaction) and of sabinene (smaller influence of water vapor, faster reaction). This is in agreement with the previous explanation, because the reaction fluxes of the CI^{stab} with the individual partners (acids, alcohols, water vapor, and carbonyl compounds) depend on the rate constant and the concentration of the individual partners. A smaller ozonolysis rate constant will cause a slower increase of the concentrations of reaction products participating in the reaction with CI^{stab}. By contrast, the concentration of water vapor is dominant all of the time. Consequently, the initial phase of the reaction, which affects the nucleation process at the most, is more sensitive toward H₂O concentration. Therefore, one explanation for the highest reduction of the total number concentration in the case of β -pinene can be ascribed to its lowest rate constant in the reaction with ozone (see Table 3), so that water vapor is able to influence most effectively the competitive reaction mechanism.

Finally, a possible self-reaction of the CI^{stab} with regard to particle formation cannot be totally excluded. However, this reaction is not likely to occur because of the low concentrations of the CI^{stab} and the higher concentrations of the competitive reaction partners. Very little is known about the CI^{stab} self-reaction in the gas phase, except that which was reported in liquid-phase studies by Criegee and Lohaus.²⁸

In conclusion, the different effect of water vapor on the nucleation in exo- and endocyclic monoterpene ozonolyses (e.g., β - and α -pinene) is probably caused by the intramolecular addition of an aldehydic group to the carbonyl-oxide in the endocyclic monoterpene ozone reaction. The rate constant of this reaction is supposed to be much faster than the one of the

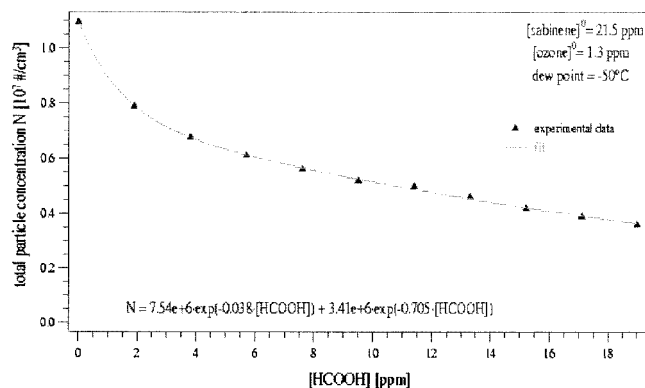


Figure 11. Total particle number concentration as a function of added formic acid concentration at a fixed time step in the flow tube reactor. A sum of two exponential decay functions fits the exponential values in a good agreement. No constant factor adding to the exponential functions is needed.

intermolecular SOZ formation. Therefore, large carbonyl compounds, such as nopinone in the case of β -pinene, have to add intermolecularly because of the structure of the exocyclic monoterpenes. Consequently, the competitive reaction scheme is more sensitive toward water vapor in the exocyclic case.

Exclusion of Nucleation Pathways via the CI*. To investigate the contribution to nucleation from other processes (e.g., via CI[‡]), experiments with an efficient CI^{stab} scavenger such as HCOOH have been performed at a fixed reaction time in the flow reactor (reactor B). The nucleation of precursor species other than the CI^{stab} will be independent of the concentration of added HCOOH and remain constant with increasing HCOOH. On the contrary, if the particle formation is initiated by CI^{stab}, an exponential decrease of the nucleation intensity will be observable with increasing HCOOH. For a nucleation-initiating species with very low volatility (vlvSPECIES), the nucleation strength and the total particle number density N is directly related to the concentration of vlvSPECIES. The higher their concentration, the higher the number of the newly formed particles N . This is expressed in eq III, in which the total particle number concentration is described as a function of the concentration of formic acid (CI^{stab} dependent part of the nucleation) and a constant (CI^{stab} independent part of the nucleation):

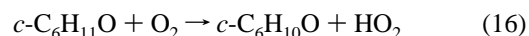
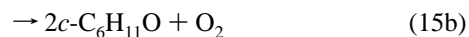
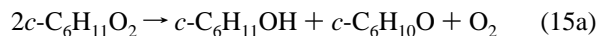
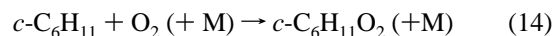
$$[\text{vlvSPECIES}] \propto N = f([\text{HCOOH}]) + \text{constant} \quad (\text{III})$$

The analysis of the total particle number vs the CI^{stab}-scavenger HCOOH concentration for the exocyclic sabinene is plotted in Figure 11. The results can be fitted and are found to be in good agreement with a sum of two exponential decay functions (see Figure 11). The fit results in a constant, which equals zero. By contrast, the measured decline of the total number concentrations associated with one or more nonvolatile nucleating species can be simulated quite well with the assumption of the CI^{stab} as a nucleation precursor.

Effect of *cyclo*-Hexane Addition. Finally, the effect and the consequences of the addition of *cyclo*-hexane has to be discussed in the context of influencing the nucleation process. The addition of large amounts (up to 270 ppmv) of *cyclo*-hexane ($c\text{-C}_6\text{H}_{12}$) scavenges the OH radicals, preventing them to react with monoterpenes. Therefore, the concentration of *cyclo*-hexane was chosen in such a way that more than 95% of the OH radicals are scavenged.

Initially, an H atom is abstracted from *cyclo*-hexane by OH, forming a *cyclo*-hexyl radical (reaction 13). Thereupon, molecular oxygen adds (reaction 14) to the *cyclo*-hexyl radical

forming a *cyclo*-hexylperoxy radical. The self-reaction of the *cyclo*-hexylperoxy radical leads to *cyclo*-hexanol and *cyclo*-hexanone (reaction 15a) or forms *cyclo*-hexanone (reaction 16) via the oxy radical (reaction 15b):³²



The interference of *cyclo*-hexane on the nucleation process is shown in Figure 9a,b. First, the addition of *cyclo*-hexanone (o) to the ozonolysis of β -pinene reduces the total particle number concentration compared to the reference experiment (*) because of the smaller molecular mass and the higher saturation vapor pressure of the ozonide SOZ-C₁₅. Second, the addition of *cyclo*-hexanol also causes a decrease in nucleation intensity because of the reaction of the CI^{stab} with the alcohol. Therefore, observations in experiments with added *cyclo*-hexane indicate a slightly delay of nucleation compared to experiments with no scavenger. With respect to this, the influence of *cyclo*-hexane on the reaction mechanism, causing a reduction of the new formed aerosol, is similar to the effects caused by the addition of alcohols and small ketones. This effect will lead to a decrease of the concentration of substances with very low saturation vapor pressure that lead to nucleation and further cause a delay in new particle formation and a decrease of the total aerosol volume yield.

Summary and Conclusion

In this study, the influence of water vapor on the new particle formation in monoterpene ozonolysis was examined by using a SMPS. The results reveal a decrease of total formed aerosol volume at high concentrations (1 ppmv terpene, 500 ppbv ozone) in exocyclic monoterpene reactions but no detectable change in endocyclic alkene reactions. Moreover, the total number concentrations were substantially affected by the presence of H₂O during (exocyclic) β -pinene and sabinene ozonolysis studies and less during endocyclic Δ^3 -carene and α -pinene ozonolyses. These effects are enhanced by lowering the reactant concentrations at constant humidity. At much lower concentrations of the endocyclic α -pinene (of 50 ppbv and 110 ppbv of ozone), the measurements show a reduction in the nucleation intensity but an increase in the total aerosol volume with enhanced water vapor concentration. Moreover, the smaller the conversion rate of the exocyclic terpenes, the more reduced the new aerosol formation is. This can be explained by the slower production of the competitive reaction partners of the CI^{stab}, whereas water vapor is present from the beginning.

To our knowledge, no study has been performed on the influence of water vapor on the mechanism of new particle formation during biogenic alkene ozone reactions. A few studies have been performed on the hygroscopicity of the final SOA particles (e.g., by Virkkula et al.³⁵), having found growth factors of around 1.1 (less hygroscopic) for the “final” aerosol particles, by comparing dry to humid (ca. 90% relative humidity) environments for all aerosol particles sampled during monoterpene ozonolysis. The relative humidity in our study was 30%, so the particles will not uptake a significant amount of water

vapor. The behavior of the SOA yield at different relative humidity conditions was the subject of an ozonolysis study by Seinfeld et al.,¹² performed in the presence of added seed aerosol ((NH₄)₂SO₄), a strong hydrophilic salt. They have observed an increase of the aerosol volume with increasing humidity for the monoterpenes α -pinene, β -pinene, sabinene, Δ^3 -carene, and *cyclo*-hexene especially in the range of 80–100% relative humidity, which is far from the humidity level in the present study. By contrast, our study was focused on the effect of the *absolute* humidity on (a) the nucleation initiation process without using seed aerosol and (b) the aerosol volume yield. Consequently, a direct comparison between the two studies is rather difficult.

The results of this study lead to the conclusion that the CI^{stab} is a central intermediate in SOA formation from monoterpene ozone reactions. This is confirmed by further studies with added HCOOH, which indicate a much stronger reduction in total number concentration and volume than with added water vapor. Indeed, it seems that the pathway of nucleation includes the involvement of CI^{stab} and not of CI⁺, as was speculated in earlier studies.^{6,8,9,11–13} Our results are explained in terms of secondary ozonides, formed in bimolecular reactions of the CI^{stab} with carbonyls (such as the ketone nopinone in the case of β -pinene forming the large SOZ-C₁₈) in exocyclic terpene reactions. In endocyclic monoterpene reactions, nucleation occurs by the way of intramolecular reactions of the CI^{stab} forming SOZ-C_{10i}.

The assumption of SOZ to act as nucleation precursor species has been proposed previously in the theoretical work of Kamens et al.⁷ to explain the observed nucleation within their model. An evidence of this assumption has not been brought forward. Our results support strongly the general assumption of SOZs that act as nucleation precursors in order to describe the observations of this study. However, the results indicate the importance of different SOZs formed during the ozone reactions, as described by Kamens et al.⁷

Atmospheric Implications

To discuss the atmospheric relevance of this laboratory study on particle size distributions, the comparison with field measurements is important. There are two publications by Clement et al.³⁴ and by Boy and Kulmala³⁵ examining the possible explanations for the occurrence of nucleation events at a measuring station in the Finnish forest (Hyytiälä). The published data sets indicate a remarkable decrease of the nucleation events and intensity with increasing absolute humidity (considering both relative humidity and temperature) as observed in the laboratory. Scandinavian absolute humidity levels e.g. at measuring sites used in the publications of Clement et al.³⁴ as well as of Boy and Kulmala³⁵ are comparable to the levels used in this study. With respect to this, some of the conclusions from this laboratory work can be transferred to the atmosphere.

The observed effect of water vapor on the endo- and exocyclic monoterpene oxidation has several consequences for the atmosphere:

(a) Because of the atmospheric concentration levels of monoterpenes, ozone, and water vapor, new particle formation as a result of exocyclic monoterpene ozonolysis is not likely to occur at high concentrations of H₂O (absolute humidity). Therefore, the particle formation of exocyclic terpenes is favored under dry conditions. Consequently, the description of new particle formation potentials of selected exocyclic monoterpenes by chamber studies in dry environments is an overestimation because of their relatively high concentration used in the chamber studies.

(b) The reaction of ozone with endocyclic monoterpenes (e.g., α -pinene) should be able to initiate a nucleation in the atmosphere with a nucleation potential, which is sensitive on the environmental humidity and their ad-hoc concentrations.

Consequently, our description of particle formation in this study can lead to an overestimation of the nucleation potential from the monoterpene oxidation, because of the inhibiting effect of water vapor on particle formation. However, specific oxidation products are able to participate in the growth of currently not-detectable aerosol particles (radius < 1 nm) as formulated in the article of Kulmala et al.³⁶ and might have an impact on the (heterogeneously) new particle formation even if they do not nucleate by themselves.

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Supporting Information Available: Figures showing the ozonolysis of α -pinene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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