

New particle formation during α - and β -pinene oxidation by O_3 , OH and NO_3 , and the influence of water vapour: particle size distribution studies

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Abstract. New particle formation during the oxidation of α - and β -pinene ($C_{10}H_{16}$) by ozone, OH and NO_3 was studied by measuring the particle size distributions with a scanning mobility particle sizer (TSI 3936). The results indicate a drastically higher nucleation potential of the ozonolysis than in the reaction with either OH or NO_3 . On the contrary, the contribution of the individual oxidation reactions to form new aerosol volume was found to depend on the location of the carbon double bond to be oxidised: for the *endocyclic* α -pinene reactions the ozonolysis contributed mostly to the aerosol volume yield, whereas for the *exocyclic* β -pinene reactions the oxidation by O_3 , OH and NO_3 yielded a similar aerosol volume.

In a second part of this study the influence of water vapour on the nucleation in all three possible oxidation routes was examined. The observations revealed only an effect of water vapour during the ozonolysis reactions.

1 Introduction

Around 40 years ago, Went published his article (Went, 1960) on the occurrence of the blue haze observed in remote areas (e.g. smoky mountains, USA) appearing in the morning when photooxidation has already started and vanishing around noon. The author explained the haze effect by the oxidation of terpenes (e.g. monoterpenes; $C_{10}H_{16}$), forming very low-volatile products, that nucleate and scatter the incoming solar radiation bluish in accordance to the Rayleigh theory. Due to the further growth of the new formed particles into the large aerosol size fraction (diameter $d > 100$ nm), the particles change their optical behaviour, scattering the light more whitish as described by the Mie the-

ory (see Finlayson-Pitts and Pitts, 1999; Seinfeld and Pandis, 1998, and cited references therein).

Recent publications support his conclusion reporting nucleation events occurring in the morning hours at remote sites in Finland (Mäkelä et al., 1997), Portugal (Kavouras et al., 1999) and Canada (Leaitch et al., 1999). Therefore, various laboratory studies have been performed to investigate the nucleation potential of different nucleation precursor reactions (e.g. Griffin et al., 1999; Hoffmann et al., 1997; Pandis et al., 1991; Pankow, 1994; Wängberg et al., 1997; Zhang et al., 1992). Although published a long time ago, the observations of Went have not been subscribed to a specific oxidation reaction, such as initiated by ozone, NO_3 or OH, and its products causing the observed nucleation (see, e.g. Jenkin et al., 2000; Koch et al., 2000; Yu et al., 1999). Possible precursors for the detected particle formation are, for example, monoterpenes – non-methane hydrocarbons (NMHC) – emitted by the vegetation in dependence on temperature, solar radiation etc. These will further be oxidised in the atmosphere because of their high reactivity by (a) ozone, (b) the hydroxyl radical (OH) or (c) the nitrate radical (NO_3), producing substances of low-, semi- and high volatility (Seinfeld and Pandis, 1998). The products of low-volatility are believed to be able to nucleate, the semi-volatile products will partition onto the previously formed aerosol particles and the volatile species will remain almost in the gas-phase.

This study tries to compare the particle formation potential (particle number concentration and aerosol volume concentration) of the three different possible oxidation reactions of two selected monoterpenes with different structure types: α -pinene and β -pinene. In this context, α -pinene was chosen as a surrogate for the *endocyclic* monoterpenes, possessing a carbon double bond located inside the C_6 -ring structure, and β -pinene as a surrogate for the *exocyclic* monoterpene class, with the double bond located outside the ring structure. Herein, the location of the double bond might be a critical point in the oxidation mechanism leading to nu-

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Table 1. Rate constants for the reaction of α -pinene and β -pinene with O_3 , OH and NO_3 taken from Atkinson (1997) in $cm^3 \text{ molecule}^{-1} s^{-1}$

Monoterpene	$k_{O_3} \times 10^{17}$	$k_{OH} \times 10^{11}$	$k_{NO_3} \times 10^{11}$
α -pinene	8.66	5.37	6.16
β -pinene	1.5	7.89	2.51

cleation, forming products with a ring-retaining or a ring-opening structure during the oxidation mechanism. This influences the saturation vapour pressure of the produced species (e.g. dicarboxylic acids) that are believed to initiate nucleation. Both monoterpenes have very different rate constants for the reactions (Atkinson, 1997) with ozone, OH and NO_3 as shown in Table 1. In general, the reaction with OH, as well as with NO_3 , is much faster than with ozone, but the former atmospheric concentrations are found to be much lower than the latter, causing a competitive reaction between OH and ozone at daytime, whereas NO_3 and ozone are the dominant sinks of monoterpenes at night (Finlayson-Pitts and Pitts, 1999).

In a second part of this study, the impact of the water vapour concentration on the nucleation occurring during the different oxidation reactions will be discussed because of its elevated atmospheric concentration level and therefore its atmospheric relevance. In this context, a previous study by Bonn et al. (2002) reported a suppressing effect of water vapour on the particle formation process observed during the ozonolysis of monoterpenes. Moreover, Tobias et al. (2000) have found a change in the aerosol composition with increasing relative humidity, analyzed during the reaction of 1-tetradecene with ozone: A decrease of secondary ozonides and an increase of organic peroxides. This might be a possible marker to distinguish between the atmospheric contributions of the different monoterpene oxidation reactions to the observed nucleation in field studies.

2 Experimental

Most of the experiments were performed in an evacuable spherical glass vessel of 0.57 m^3 volume at a temperature of $(295 \pm 2) \text{ K}$ and a total pressure of $(730 \pm 1) \text{ Torr}$ (973 mbar). The reactor has been described previously in detail by Neeb et al. (1995) and will only be mentioned briefly. In all experiments the reactor was filled with purified synthetic air, consisting of 80% nitrogen and of 20% oxygen, prior to the addition of the reactants. No seed aerosol was added in all experiments to maintain a clean background aerosol concentration and to allow homogeneous nucleation. The humidity was measured by a dew point meter (System 3A, Panametrics) located at the top of the glass vessel. To achieve different humid conditions inside the reactor, synthetic air was

passed through a bubbler filled with $18 \text{ M}\Omega$ water (Elgastat) until the planned dew point was reached.

Experiments with two different initial monoterpene concentrations have been performed: experiments with (a) a high initial concentration of 500 ppbv (further referred as 'high concentration' experiment) as well as with (b) a low initial concentration of 50 ppbv (further referred as 'low concentration experiment') (see Table 2).

Additionally, reactions with two different water vapour concentration levels were studied for each single oxidant at both conversion rates: (A) a low humidity level (further referred as 'dry experiment') with a dew point of -80°C ($[H_2O] \approx 3 \text{ ppmv}$, relative humidity = 0%), and (B) a high humidity level (further referred as 'humid experiment') performed at a dew point of 4°C ($[H_2O] \approx 8400 \text{ ppmv}$, relative humidity $\approx 30\%$).

The gas-phase concentrations of the reactants were observed by a Fourier transform-infrared spectrometer (FT-IR, Bruker IFS 28), whereas, the particle phase was physically characterized by a scanning mobility particle sizer (SMPS, TSI 3936) consisting of a long differential mobility analyser (long DMA, TSI 3081) and an ultra-fine particle counter (UCPC, TSI 3025A). The instrument is capable for particle detection in the size range of 7–1000 nm depending on the adjusted sheath flow. The use of a nano-DMA with a particle size range of 3–150 nm instead of the long DMA would have provided an improved detection of very small particles ($d < 10 \text{ nm}$). But on the contrary, all particles with a diameter larger than 150 nm were not been analyzed. This would have caused a remarkable effect on the measured aerosol volume concentration. Consequently, the long DMA was used in this study, although the maximum number concentration measured will be slightly smaller than is real value. Due to the limited reactor volume it was not possible to measure simultaneously with a nano-DMA to include the very small particles in the analysis.

For all experiments samples with a time resolution of 2 min, including 110 s up-scan and 10 s down-scan, were obtained during a total reaction time of 50 min, in which the monoterpene was converted by nearly 100%. The used sample flow rate was 0.5 L min^{-1} diluted with 1.0 L min^{-1} clean air at the UCPC inlet. The sheath flow rate inside the long DMA was set to 5.0 L min^{-1} during the ozone reactions and to 2.0 L min^{-1} during NO_3 as well as during OH reactions to match the particle size distribution best with the measuring range of the instrument.

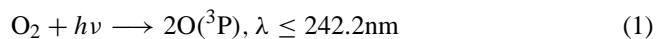
Two additional experiments have been conducted in a flow reactor with a fixed sampling outlet for physical aerosol characterization with a laminar flow profile at pressure of $(760.0 \pm 0.5) \text{ Torr}$ (1013.25 mbar) in order to study artefacts occurring for instance during the reaction of β -pinene with NO_3 . The setup of this reactor is described elsewhere (Bonn et al., 2002) and will not be discussed here in detail. The monoterpene was kept premixed in a stainless steel bottle and admixed with the oxidant in a movable mixing plunger dur-

ing 0.4 s before entering the reaction chamber. Inside of the reactor, the mixture of the reactants diluted in synthetic air was transported with a mean velocity of 2 cm s^{-1} downward the reactor to the fixed sampling outlet, where it was introduced in the SMPS set-up for analysis. In order to achieve best conditions for particle characterization, the sample flow was set to 1.5 L min^{-1} .

The range of uncertainty of the determined values of the particle number as well as the aerosol volume concentration was considered to be affected by the uncertainty of (i) the sampling flow ($\pm 0.01 \text{ L min}^{-1}$) and (ii) of the statistics of the counting as well as of (iii) the sizing of the individual particles. In order to determine the contribution of the sizing uncertainty to the total measurement uncertainty, spherical polystyrene particles with a specific size in the range of 57–460 nm in diameter (Polysciences, USA) were analysed with the SMPS system. The results indicate that this uncertainty was smaller than the size resolution of the instrument. Therefore, the size uncertainty was assumed to be a minor contribution and was not considered further on. On the contrary, the uncertainties caused by the sampling flow and the counting statistics were calculated and given for each value.

2.1 Initial conditions for O_3 -reactions

In order to perform ozonolyses of monoterpenes, ozone was produced inside the spherical reactor by a pen-ray lamp and measured optically at $\lambda = 253.7 \text{ nm}$ as well as by FT-IR. The well-known formation of ozone by photolysis of molecular oxygen is described by the reactions (1) and (2):

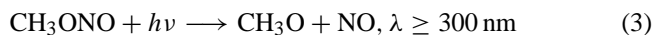


Water vapour was added later on, in order to prevent a detectable photonucleation (Byers Brown, 1995) originating of H_2O -molecules ionized by the radiation. Finally, the monoterpene was introduced diluted in synthetic air. In all ozone experiments, performed in the spherical reactor, cyclohexane (270 ppmv) was present to scavenge more than 90% of the OH-radicals formed in the reaction of the monoterpene with ozone in order to prevent an interfering OH-terpene reaction (Atkinson, 1997). The added cyclo-hexane is very volatile with a saturation vapour pressure of around 120 mbar at room temperature. Its reaction with ozone is by far too slow to affect the studied monoterpene ozonolysis. Additionally, the cyclo-alkane is not able to form aerosol particles under these circumstances.

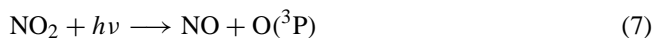
The initial reactant concentrations in the case of α -pinene were: (a) 500 ppbv of the monoterpene as well as of ozone (high concentration) and (b) 50 ppbv of the alkene and 110 ppbv of ozone (low concentration). The initial concentrations chosen in the case of the β -pinene experiments, were (a) 500 ppbv of ozone and 1 ppmv of the monoterpene (high concentration experiment) and were identically to the low-concentration studies performed with α -pinene.

2.2 Initial conditions for OH-reactions

OH-radicals were produced inside the reactor by the photolysis of methyl nitrite (CH_3ONO , 20 ppmv) in the presence of NO (10 ppmv) using a Hg-penray lamp in accordance to the following reaction scheme (Aschmann et al., 1998):



OH radicals are formed by the photolysis of methyl nitrite initiated by reaction (3), forming CH_3O and NO. CH_3O is further oxidised by molecular oxygen and produces formaldehyde and HO_2 (reaction 4), which is converted to the hydroxyl radical by the reaction with NO (reaction 5). The OH radical will further react with the monoterpene or with the primary reaction products. Because of this, the conversion rate of the monoterpene observed by FTIR is an indicator that the OH-reaction with the monoterpene is taking place. Although HO_2 is produced and NO_2 is formed, the production of ozone by the photolysis of NO_2 and the final reaction of $\text{O}({}^3\text{P})$ with O_2 was small and was not able to interfere the studied reaction due to the extremely fast reaction of the monoterpene with the present OH (see Table 1).



Reaction (6) produces nitric acid (HNO_3), that is able to co-condense on the surface of the pre-formed aerosol particles, if its partial vapour pressure reaches the saturation vapour pressure, and therefore might increase the aerosol volume yield.

Although reaction (6) is a minor reaction, it might be able to remarkably affect the total aerosol volume concentration formed during the reaction of the monoterpene with the OH radical at elevated concentration levels of methyl nitrite as well as of NO_2 (first artefact). Moreover, the high concentration of NO, used to enhance the reaction with HO_2 that forms the hydroxyl radical and NO_2 (reaction 5), interferes in the reaction mechanism of the monoterpene oxidation leading to a higher concentration of nitrates as found without NO. These nitrates possibly have a higher saturation vapour pressure (p_{sat}) and consequently cause a reduced nucleation strength (second artefact).

Both points will be discussed in the final section of this article. The use of a different source for OH production such as the photolysis of HONO or H_2O_2 was not possible due to the experimental set-up of the reactor (glass wall, light intensity of the Xenon arc lamp). The concentration of the monoterpene was chosen as follows: (a) 500 ppbv in the 'high concentration' studies and (b) 50 ppbv in the 'low concentration' studies.

Table 2. This table summarizes the initially experimental conditions of each single experiment and its abbreviation in the text. In this context, the abbreviations ‘hce’ and ‘lce’ as used in this table stand for ‘high concentration experiment’ and ‘low concentration experiment’. For each oxidation reaction with one of the monoterpenes two different dew points and two different initial concentrations were used

Experiments performed in the spherical reactor:				
<i>Concentration</i>	<i>Oxidant</i>	<i>Dew point</i>	<i>Abbreviation in the text</i>	<i>Remarks</i>
<i>α-pinene-reactions</i>				
500 ppbv	[O ₃]= 500 ppbv	-78 °C	dry hce of α -pinene and ozone	C ₆ H ₁₂ present to scavenge the formed OH
500 ppbv	[O ₃]= 500 ppbv	+ 4 °C	humid hce of α -pinene and ozone	C ₆ H ₁₂ present to scavenge the formed OH
500 ppbv	OH	-80 °C	dry hce of α -pinene and OH	[CH ₃ ONO]= 20 ppmv, [NO]= 10 ppmv
500 ppbv	OH	+ 4 °C	humid hce of α -pinene and OH	[CH ₃ ONO]= 20 ppmv, [NO]= 10 ppmv
500 ppbv	NO ₃	-80 °C	dry hce of α -pinene and NO ₃	[N ₂ O ₅]= 1 ppmv
500 ppbv	NO ₃	+ 4 °C	humid hce of α -pinene and NO ₃	[N ₂ O ₅]= 1 ppmv
50 ppbv	[O ₃]= 110 ppbv	-80 °C	dry lce of α -pinene and ozone	C ₆ H ₁₂ present to scavenge the formed OH
50 ppbv	[O ₃]= 110 ppbv	+ 4 °C	humid lce of α -pinene and ozone	C ₆ H ₁₂ present to scavenge the formed OH
50 ppbv	OH	-80 °C	dry lce of α -pinene and OH	[CH ₃ ONO]= 20 ppmv, [NO]= 10 ppmv
50 ppbv	OH	+ 4 °C	humid lce of α -pinene and OH	[CH ₃ ONO]= 20 ppmv, [NO]= 10 ppmv
50 ppbv	NO ₃	-80 °C	dry lce of α -pinene and NO ₃	[N ₂ O ₅]= 1 ppmv
<i>β-pinene-reactions:</i>				
500 ppbv	[O ₃]= 1 ppmv	-80 °C	dry hce of β -pinene and ozone	C ₆ H ₁₂ present to scavenge the formed OH
500 ppbv	[O ₃]= 1 ppmv	+ 4 °C	humid hce of β -pinene and ozone	C ₆ H ₁₂ present to scavenge the formed OH
500 ppbv	OH	-80 °C	dry hce of β -pinene and OH	[CH ₃ ONO]= 20 ppmv, [NO]= 10 ppmv
500 ppbv	OH	+ 4 °C	humid hce of β -pinene and OH	[CH ₃ ONO]= 20 ppmv, [NO]= 10 ppmv
500 ppbv	NO ₃	-80 °C	dry hce of β -pinene and NO ₃	[N ₂ O ₅]= 1 ppmv
500 ppbv	NO ₃	+ 4 °C	humid hce of β -pinene and NO ₃	[N ₂ O ₅]= 1 ppmv
50 ppbv	[O ₃]= 110 ppbv	-80 °C	dry lce of β -pinene and ozone	C ₆ H ₁₂ present to scavenge the formed OH
50 ppbv	[O ₃]= 110 ppbv	+ 4 °C	humid lce of β -pinene and ozone	C ₆ H ₁₂ present to scavenge the formed OH
50 ppbv	OH	-80 °C	dry lce of β -pinene and OH	[CH ₃ ONO]= 20 ppmv, [NO]= 10 ppmv
50 ppbv	OH	+ 4 °C	humid lce of β -pinene and OH	[CH ₃ ONO]= 20 ppmv, [NO]= 10 ppmv
50 ppbv	NO ₃	-80 °C	dry lce of β -pinene and NO ₃	[N ₂ O ₅]= 1 ppmv
Experiments performed in the flow reactor:				
<i>Concentration</i>	<i>Oxidant</i>	<i>Dew point</i>	<i>Abbreviation in the text</i>	<i>Remarks</i>
<i>β-pinene-reactions</i>				
500 ppbv	[O ₃]= 500 ppbv	changed	fre with β -pinene and ozone	–
500 ppbv	[NO ₃]= 1 ppmv	changed	fre with β -pinene and ozone	[N ₂ O ₅]= 1 ppmv

2.3 Initial conditions for NO₃-reactions

NO₃ reactions were initiated by introducing N₂O₅ (1 ppmv) in the reaction chamber. Therefore, N₂O₅ was generated in a different system by adding ozone to a NO₂ flow. In the following the NO₂ reacts with ozone, forming NO₃ that again reacts with NO₂ producing N₂O₅. This was sampled in a cooling trap at -70°C. Later on, the dinitrogen pentoxide was added to the reactor. Therein, the N₂O₅ molecules further dissociate into NO₂ and NO₃ as well as NO₂ and NO₃ recombine in accordance to the following re-

action (Finlayson-Pitts and Pitts, 1999):



The steady state of reaction (9) is highly temperature and radiation dependent and is shifted with increasing temperature towards the decomposition to NO₂ and NO₃. If the NO₃ molecules react with the terpene, the decomposition of N₂O₅ is strengthened to maintain the equilibrium between both reactions.

Moreover, care has to be taken of the reaction of N₂O₅ with water vapour (reaction 10), that produces two nitric acid molecules and therefore might cause a similar artefact as de-

scribed above for the OH reaction (see first artefact).



The monoterpene and N_2O_5 concentrations were chosen to be (a) 500 ppbv and 1 ppmv and (b) 50 ppbv and 1 ppmv. Again, the observed conversion rate of the monoterpene during an experiment could only be initiated by the reaction with the reaction with NO_3 and was therefore taken as an indicator for the presence of NO_3 . Moreover, the reaction with products such as nopinone or pinonaldehyde is reasonably slow (Hallquist et. al., 1997), so that there is no interference with the primary reaction.

Similar conditions were chosen for two extra flowtube experiments with (a) ozone and (b) NO_3 except the addition of cyclo-hexane during the ozonolysis. In this experiment no OH-scavenger was used.

All initial experimental conditions and their text reference are summarized in Table 2.

2.4 Chemicals

All chemical substances used in this study were of the highest commercial available purity: α -pinene (Fluka: $\geq 99.5\%$), β -pinene (Sigma-Aldrich: $\geq 99\%$), cyclo-hexane (Sigma-Aldrich: $\geq 99.9\%$), NO (UCAR, Belgium: $\geq 99.5\%$), NO_2 (UCAR, Belgium: $\geq 99.5\%$), O_2 (Messer Griessheim: $\geq 99.999\%$), N_2 (Westfalen: $\geq 99.999\%$).

3 Results and discussion

The experiments have been conducted in two different reactors, and therefore will be shown and discussed in two separate sections, Sect. 3.1 including experiments conducted in the static spherical reactor and Sect. 3.2, tackling experiments performed in the dynamic flow reactor. In this context, the presentation and discussion of the individual results are grouped into two subsections: a first subsection, Sect. 3.1.1 covering the contribution of the different dry oxidation reactions to the new particle formation as well as to the aerosol volume production under dry conditions, and a second part, Sect. 3.1.4 describing the effect of water vapour on the results of Sect. 3.1.1.

3.1 Experiments performed in the spherical reactor

3.1.1 Nucleation and aerosol volume formation during the oxidation by O_3 , OH and NO_3

In order to compare the contribution of the individual monoterpene oxidation reactions to nucleation and aerosol volume formation, the focus will be first set on the reactions of the *endocyclic* α -pinene. Later on, similar considerations will be applied using the *exocyclic* β -pinene.

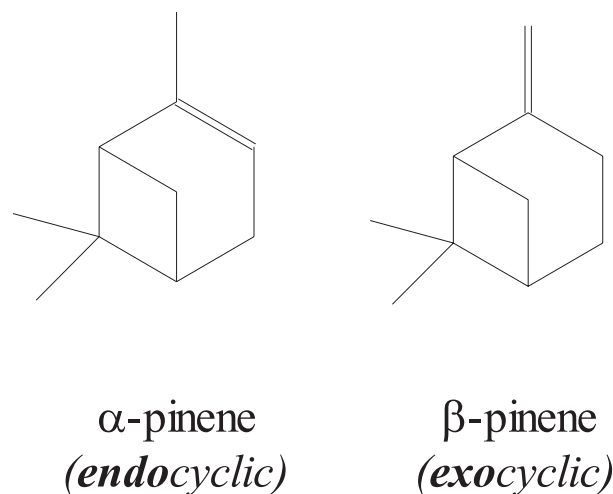


Fig. 1. Chemical structures of the used monoterpenes.

3.1.2 α -Pinene-reactions:

α -Pinene was chosen as a surrogate for the *endocyclic* structured monoterpenes. Its carbon double bond is located inside a C_6 -ring structure as shown in Fig. 1. Therefore, the oxidation reactions, especially by ozone, cause primarily ring-opened structured products, such as pinonaldehyde, possessing different saturation vapour pressures, than found for the *exocyclic* monoterpene reactions with predominantly ring-retaining products, such as nopinone in the case of β -pinene. Although there are a lot of further reaction products, like HCHO or acetone, which are formed by the fragmentation of the terpene molecule during the oxidation process, the predominant products are the large carbonyl compounds pinonaldehyde and nopinone especially with regard to aerosol formation.

At high initial concentrations (500 ppbv of α -pinene) the ozonolysis was found to have a strong impact on new particle formation. This is shown in Fig. 2a (particle size distribution), 2b (particle number concentration) and 2c (total aerosol volume concentration). Due to the low rate constant of the reaction of α -pinene with ozone ($8.66 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Table 1), the reaction proceeds relatively slow, so that it was possible to study the particle formation process in detail. In Fig. 2a each single line represents a single particle size distribution measurement $dN/d \log(d)$ obtained with a time resolution of two minutes. The base line displays the results of blank run performed prior to the monoterpene addition, and represents the situation at reaction time zero.

As the reaction was initiated by admixing the monoterpene, various products of different volatility non-, semi- and volatile were formed. The non-volatile products reached their saturation vapour pressure and started to nucleate homogeneously. This was observed e.g. during the ozonolysis

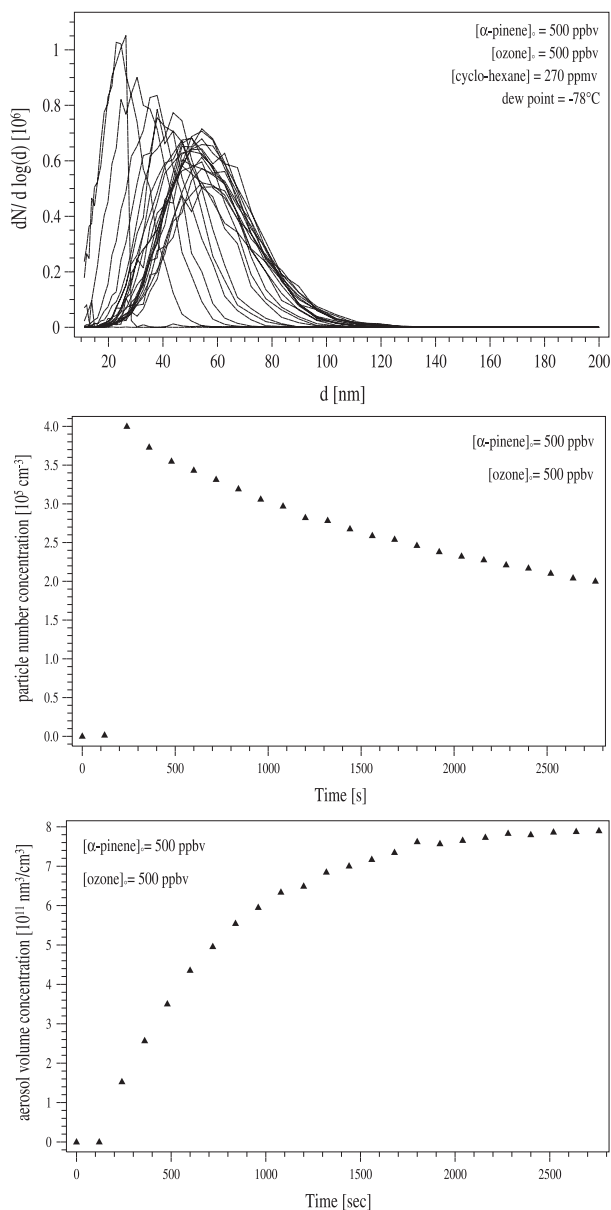


Fig. 2. (a–c) Displayed is the high concentration α -pinene-ozonolysis experiment with added *cyclo*-hexane to prevent interfering reactions of the monoterpene with the produced OH-radicals. Therein, (a) (top) shows 26 particle size distributions measured with a time resolution of 2 min starting with a blank run, covering 50 min of the reaction time. Plotted below are the corresponding particle number (b) (middle) and aerosol volume concentration (c) (bottom) vs. reaction time.

reaction in an intense nucleation during the first two scans with a median around 20 nm limited by the time resolution of the instrument (Fig. 2a and b). At this stage of the reaction, the more volatile products (semi-volatile) were able to condense on the surface of the pre-formed particles and to cause an increase in particle size and aerosol volume. This

behaviour was observed in a broadening and a shift of the particle size distribution to larger diameters (centred around 60 nm in diameter at 50 min reaction time) due to both the coagulation as well as the condensation. In this case, coagulation was pronounced during the nucleation event because of the observed high maximum total number concentration N_{max} of $(4.0 \pm 0.2) \times 10^5 \text{ cm}^{-3}$. During the further progress of the reaction, the particle number concentration drastically decreased and the coagulation process diminished towards the end of the experiment caused by the decreasing total number of particles (Fig. 2b). On the other side, the condensation process intensified during the further reaction as described above, due to the partitioning of the accumulating low- and semi-volatile products in the gas-phase. This process caused the increase of the aerosol volume concentration, which was found to be maximum at the end of the reaction ($V_{\text{max}} = (9.6 \pm 0.2) \times 10^{11} \text{ nm}^3 \text{ cm}^{-3}$) as shown in Table 3.

In contrast to the ozonolysis, the oxidation of α -pinene by OH is much faster ($5.37 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, see Table 1). Because of the time resolution of the instrument and the high reaction rate, only the particle size distributions at the end of the reaction could be measured, when the monoterpene was almost converted. Three of them, obtained at the time 120, 840 and 1200 s, are displayed in Fig. 3a. However, all aerosol number and volume concentrations are shown in dependence on the reaction time, because, on the opposite to the progress of the reaction, the temporal progress of the particle formation is much slower. Moreover, the low number concentration of the particles formed during the reaction increases the measurement uncertainty, which is indicated in the same figure. Plotted below are the total particle concentration (Fig. 3b) as well as the total aerosol volume concentration (Fig. 3c) vs. the reaction time. Although the error bars are quite large due to the measurement uncertainty, both figures indicate the observed delay between the reaction progress and the time needed for particle formation by the clear continuous increase with the observation time.

The reaction products generated an aerosol size distribution with a median diameter of 220 nm, which is more than three times larger than the median diameter of the size distribution observed at the end of the ozonolysis (see above). However, the maximum total aerosol volume concentration formed was found to be approximately four times less ($(2.3 \pm 0.4) \times 10^{11} \text{ nm}^3 \text{ cm}^{-3}$) than was formed during the ozonolysis.

Due to the high reaction rate, we are confronted with the problem that the maximum particle number concentration measured to be $(5.0 \pm 0.4) \times 10^3 \text{ cm}^{-3}$ might have been underestimated, because of coagulation taking place before the first scan. Consequently, the impact of the OH-reaction, observed in the experiments, might have been found smaller than its real value.

The coagulation process itself is generally affected by (i) a high number density, and by (ii) particles of very different

sizes, i.e. very large particles and freshly nucleated ones with very different Brownian velocities so that they will collide.

The observed number concentration during the OH reaction was approximately 100 times smaller at the maximum and 50 times smaller at the end of the OH-reaction than was found during the ozonolysis, in which only a slow coagulation process compared to the time resolution of the instrument was observed (see Fig. 2b). This disagrees with the assumption of a much higher coagulation rate than found during the ozonolysis due to aspect (i): the higher the number density, the faster the coagulation process. Moreover, a slow increasing particle number concentration was measured with proceeding observation time (Fig. 3b). During the ozone reaction new particle formation was quenched at the maximum of the number concentration as shown in Fig. 2b due to the high particle density and the enhanced condensation rate in accordance to the Koehlerian theory (see, e.g. Pruppacher and Klett, 1998). The point of suppression of homogeneous nucleation is therefore not reached in the OH-reaction system as shown in Fig. 3b. On the contrary, the further increase of the particle number concentration, although the monoterpene conversion is already finished, indicates an observable participation of secondary oxidised reaction products in the nucleation process, which seems to be slow compared to the reaction velocity of the monoterpene with OH. An noticeable effect of the second aspect (ii) can be excluded by the observation of a four times smaller aerosol volume concentration generated by the reaction products (Table 3). If there would have been a higher maximum particle number concentration than produced by the ozonolysis, the growth of the particle size distribution would have stopped at smaller median diameters than found during the ozonolysis due to the smaller mass of condensable products ($V_{\max}^{\text{OH}} < V_{\max}^{\text{O}_3}$). With this respect, the maximum particle number concentration is well characterized. On the contrary, the maximum particle number concentration caused by the ozone reaction might be slightly underestimated because of the missing observation with a particle size distribution located at the initial aerosol diameter of 2 nm possessing the highest number density during the nucleation event. But this is not considerably influencing the conclusions of the α -pinene-experiments.

It can be concluded, that the location of the size distribution, observed at the time the monoterpene was converted nearly completely, was rather caused by a higher concentration of *semi*-volatile and gaseous products and a simultaneously reduction of *non*-volatile products. This induced a much lower concentration of the aerosol particles on which the *semi*-volatile products can partition. Because of the higher concentration of the *semi*-volatile OH-reaction products, the aerosol volume of a single aerosol particle grew much larger, so that the final aerosol size distribution was located at larger diameters than found in the ozone reaction. Consequently, the products of the OH-reaction are much more volatile than the products of the ozone reaction.

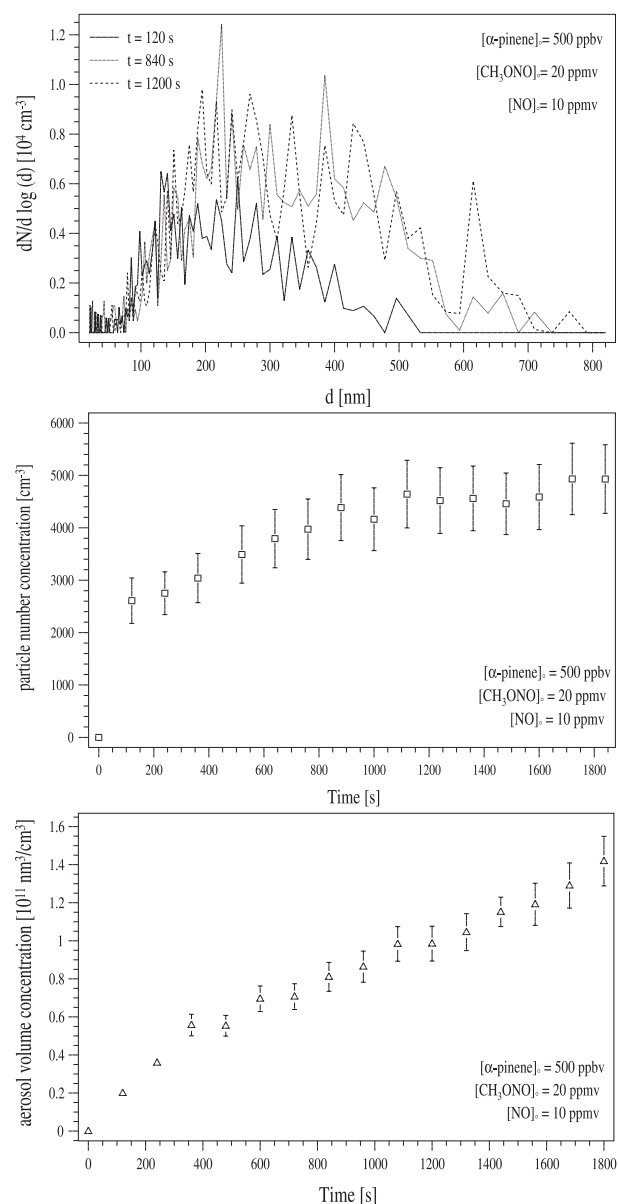


Fig. 3. (a–c) Displayed is the high concentration α -pinene-OH experiment. (a) (top) shows three selected particle size distributions at the reaction time of 120, 840 and 1200 s. By contrast, (b) (middle) displays all the obtained particle number concentrations and (c) (bottom) the aerosol volume concentrations vs. reaction time. The error bars shown in the lower two figures correspond to the measurement uncertainty caused by the counting statistics.

Very similar results as found for the reaction with OH were obtained for the NO_3 experiment with α -pinene. This is indicated in Fig. 4. Most probably, this was caused by a similar increase of the saturation vapour pressures of the formed products leading to a reduced homogeneous nucleation and new aerosol volume formation, such as found for the OH-reaction.

Table 3. Summary of the observed particle number concentration maximum as well as the maximum aerosol volume concentration in all 'hce' with α -pinene. Therein, the column $V_{\max}^{\text{raw data}}$ summarizes the maximum aerosol volume concentration prior to the correction of wall losses and V_{\max}^{corr} : its corrected value

Oxidant	N_{\max} in cm^{-3}	$V_{\max}^{\text{raw data}}$ in $\text{nm}^3 \text{cm}^{-3}$	V_{\max}^{corr} in $\text{nm}^3 \text{cm}^{-3}$
O ₃	$(4.0 \pm 0.2) \times 10^5$	$(7.9 \pm 0.2) \times 10^{11}$	$(9.6 \pm 0.2) \times 10^{11}$
OH	$(5.0 \pm 0.4) \times 10^3$	$(2.1 \pm 0.4) \times 10^{11}$	$(2.3 \pm 0.4) \times 10^{11}$
NO ₃	$(1.7 \pm 0.2) \times 10^3$	$(1.0 \pm 0.1) \times 10^{11}$	$(1.1 \pm 0.1) \times 10^{11}$

All results of the high concentration experiments with α -pinene are summarized in Fig. 5 and Table 3. It is quite obvious from this figure that the ozonolysis, which caused particle size distributions located at small median diameters, dominates the particle formation process, whereas both other reactions caused particle size distributions to be found hardly distinguishable from the base line but centred at much larger median diameters.

The important role of the ozone reaction becomes much more obvious as the initial concentration of the monoterpene was lowered to 50 ppbv. In the low concentration experiments, the ozonolysis was found to be the *only* particle source, whereas the measurements during the OH- as well as during the NO₃ remain in the background aerosol concentration level indicating no nucleation at all.

These findings support strongly the assumption of OH- and NO₃-reaction products with a higher volatility.

3.1.3 β -pinene reactions:

Unlike the oxidation of α -pinene, the observations of new particle formation made during the β -pinene-reactions with ozone, OH and NO₃ revealed different results with regard to the aerosol volume formed. Nevertheless, the ozonolysis is found to dominate the process of homogeneous nucleation again.

Comparing the new particle formation potential (maximum of total particle number formed) of the individual oxidation reactions of β -pinene, the most intense nucleation was observed during the ozonolysis as found for α -pinene, indicating that the reaction occurs with the highest yield of non-volatile products. This is shown by the particle size distribution measurements during the high concentration ozonolysis experiment displayed in Fig. 6. Again, the rate constant of the ozone reaction with β -pinene ($1.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Table 1) is about six times smaller than the one with α -pinene, but the nucleation is much more intensive than for the *endocyclic* compound as shown by Koch et al. (2000). They found in general a

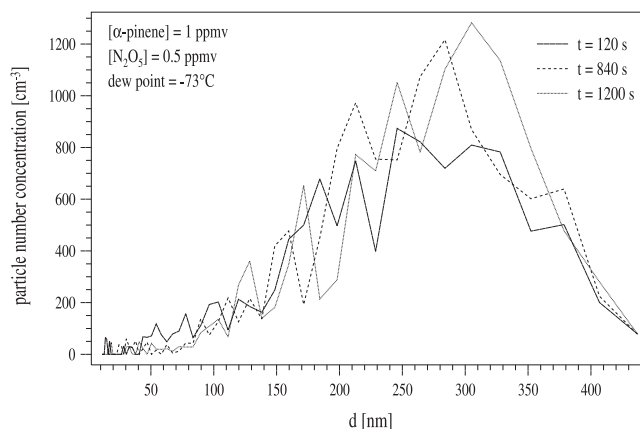


Fig. 4. Particle number size distributions at three reaction time steps (120, 840 and 1200 s), observed during the high concentration experiment of α -pinene with NO₃.

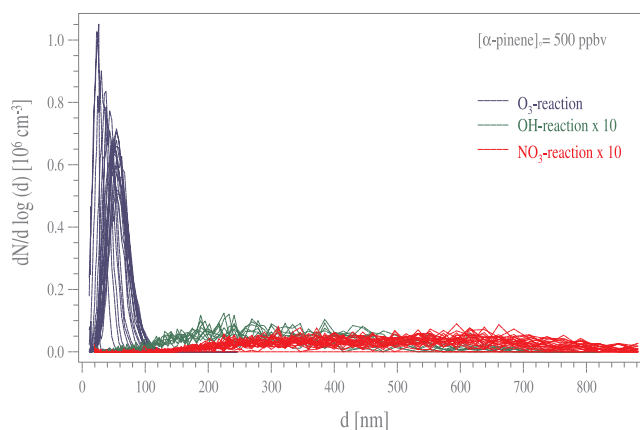


Fig. 5. Summary of all particle size distributions observed during the α -pinene reactions. The ozonolysis (displayed in blue colour) is found to be the dominating process with an intense mode at small diameters. The size distributions observed in OH (green) as well as in NO₃ (red) reactions are multiplied by 10.

higher particle formation rate for *exocyclic* than for *endocyclic* monoterpene-ozone reactions.

The moderate reaction rate allowed a detailed observation of the temporal evolution of the particle size distribution $dN/d \log(d)$ as shown in Fig. 6. Similar to Fig. 2a, a clear nucleation event with a size distribution centered around a particle diameter of 30 nm can be seen during the first two scans. Later on, the particle size distribution was affected by the coagulation process – as described above – enhanced by a maximum detected particle number concentration of $(1.0 \pm 0.1) \times 10^6 \text{ cm}^{-3}$ and the partitioning of semi-volatile and further non-volatile compounds. In this context, the high particle number density, already reached in the reactor, favoured the partitioning of further non-volatile material and suppressed a local supersaturation that is required for homo-

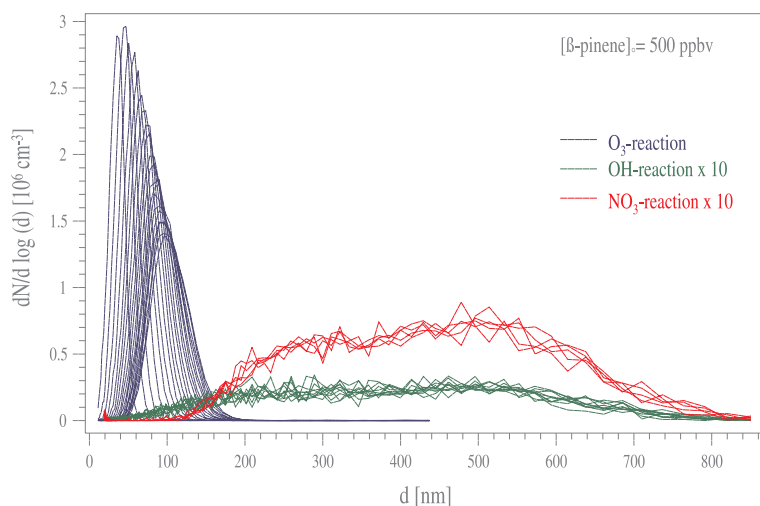


Fig. 6. This figure summarizes all observed particle size distributions during β -pinene reactions with O_3 (blue), OH (green) and NO_3 (red). Easy to find are the narrow size distributions of the ozonolysis centred at diameters smaller than 100 nm, whereas both other reactions caused size distributions, which are multiplied by 10 to make them distinguishable from the base line, found at diameters larger than 150 nm and centred around 450 nm.

geneous nucleation later on.

The resulting shift of the particle size distribution to larger median diameters and a broadening of the curve can be seen in the figure. The mode of the particle size distribution at the end of the experiment was located around 100 nm in diameter. This latest observed particle size distribution corresponds to a maximum aerosol volume concentration V_{\max} of $(3.0 \pm 0.2) \times 10^{11} \text{ nm}^3 \text{ cm}^{-3}$ (Bonn et al., 2002, see Table 4).

By contrast, the reaction initiated by OH led to a much less intensive nucleation (see Fig. 6). Because of the much faster rate constant of the OH reaction $k_{OH} = 7.89 \times 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Table 1), only the particle size distributions at the end of the reaction, when most of the monoterpene was converted, could be observed. It was centred at a larger diameter of around 400 nm as found in the ozonolysis reaction and resulted in a maximum particle number concentration of around $1.7 \times 10^4 \text{ cm}^{-3}$. The detected aerosol volume yield was around two times larger than found in the ozonolysis experiment, which differs from the α -pinene-results: a maximum of $(6.7 \pm 1.0) \times 10^{11} \text{ nm}^3 \text{ cm}^{-3}$ was measured. Although care has to be taken in order to obtain the maximum number concentration correctly, similar considerations as performed for the reaction of α -pinene with OH, also exclude an underestimation of the observed nucleation due to coagulation. Although the aerosol volume concentration was found to be slightly higher than its value observed during the reaction with ozone, the aspect (ii) of coagulation did not affect the observation because of the small particle number concentration of the OH experiment and its observed very slight increase with proceeding observation time, when the monoterpene was already converted. This contradicts an observable coagulation process between the end of the reaction of β -pinene with OH and the first scan.

These findings indicate a reduction of the non-volatile species concentration and an enrichment of semi-volatile

Table 4. Summary of the observed maximum particle number concentrations N_{\max} as well as the maximum aerosol volume concentration V_{\max} uncorrected ('raw data') as well as corrected ('corr.') for wall losses found in all high concentration experiments for the oxidation of β -pinene

Oxidant	N_{\max} in cm^{-3}	$V_{\max}^{\text{rawdata}}$ in $\text{nm}^3 \text{ cm}^{-3}$	$V_{\max}^{\text{corr.}}$ in $\text{nm}^3 \text{ cm}^{-3}$
O_3	$(1.0 \pm 0.1) \times 10^6$	$(2.5 \pm 0.2) \times 10^{11}$	$(3.0 \pm 0.2) \times 10^{11}$
OH	$\approx 1.7 \times 10^4$	$(6.0 \pm 0.9) \times 10^{11}$	$(6.7 \pm 1.0) \times 10^{11}$
NO_3	$\approx 2.0 \times 10^4$	$(3.8 \pm 0.2) \times 10^{11}$	$(4.2 \pm 0.2) \times 10^{11}$

substances as compared to the ozonolysis.

The situation found in the NO_3 reaction with β -pinene is somewhat similar as displayed in Fig. 6. The maximum number concentration N_{\max} of $\approx 2 \times 10^4 \text{ cm}^{-3}$ as well as the totally formed aerosol volume of $(4.2 \pm 0.2) \times 10^{11} \text{ nm}^3 \text{ cm}^{-3}$ were found in a comparable amount as observed during the reaction with OH. A summary of all the observed particle size distributions, maximum total number and aerosol volume concentrations, formed during the high concentration β -pinene-experiments, is given in Fig. 6 and Table 4.

Although the ozonolysis of β -pinene caused the highest maximum number concentration once more, the situation changed for the aerosol volume produced. Concerning the aerosol volume formation, the OH reaction as well as the NO_3 reaction dominated the production process. However, the artefact of co-condensation of nitric acid might lead to a small overestimation of the aerosol volume concentration formed during the reactions with either OH or NO_3 . Consequently, the values obtained have to be taken as an upper limit.

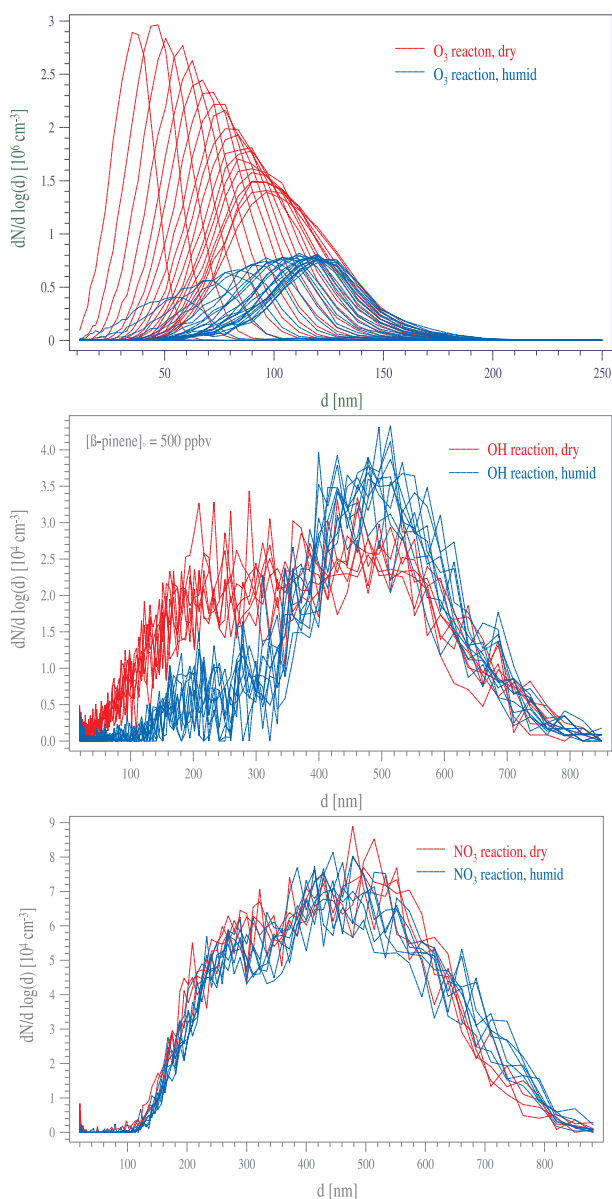


Fig. 7. (a–c) Shown are the particle size distributions for a ‘dry’ (red) and a ‘humid’ (blue) experiment for each β -pinene oxidation reaction. (a) (top) by Bonn et al. (2002) displays the ozonolysis experiments with the clear effect of water vapour, (b) (middle) shows the OH and in (c) (bottom) the NO_3 experiments are plotted.

3.1.4 Influence of water vapour on the nucleation process

In their recent study Bonn et al. (2002) have shown that care has to be taken, when the laboratory results obtained at a dew point of -80°C are transferred to atmospheric conditions because of the suppressing effect of water vapour on the nucleation during monoterpene ozonolyses. Consequently, in a second part of this article, the influence of water vapour on the nucleation caused by the three observed oxidation reactions was studied. Therefore, the observed nucleation origi-

nating by the reactions of the monoterpenes with OH as well as of NO_3 was investigated in additional experiments with added water vapour and compared with the results of Bonn et al. (2002) for the nucleation observed during the ozonolyses. Thereby, it was found that only the nucleation process caused by ozonolysis was affected by the concentration of H_2O , whereas the particle size distributions observed during the reactions of α -pinene as well as of β -pinene with OH or NO_3 remained unchanged.

This is shown, for example, in the case of the *exocyclic* monoterpene β -pinene (high concentration experiments) in Fig. 7a (ozone-reaction, taken from, Bonn et al., 2002), 7b (OH-reaction) and 7c (NO_3 -reaction). Therein all particle size distributions observed under dry conditions are displayed in red, whereas all particle size distributions measured under humid conditions are plotted in blue.

With regard to the effect of water vapour concentration on nucleation during ozone reactions, it has to be added that Bonn et al. (2002) observed not only a decreasing maximum particle number concentration but also a nucleation delay with increasing water vapour concentration. They explained this effect by the competitive reaction of the stabilized Criegee intermediate CI^{stab} – formed during the ozone reaction with the monoterpene – with either water vapour, alcohols, acids or carbonyl compounds. The latter reaction of the CI^{stab} with carbonyl compounds was found to initiate the observed nucleation.

On the contrary, particle size distributions observed during both, ‘dry’ as well as ‘humid’ OH and NO_3 experiments, were found to be identical, within the range of uncertainty. This is shown e.g. for the NO_3 reaction in Fig. 7c. This different behaviour of the reactions with either O_3 or OH and NO_3 with respect to water vapour can be explained by different reaction mechanisms and products leading to nucleation during the different oxidation reactions.

The formation of dicarboxylic acids, such as pinic acid, has been observed during the oxidation of α -pinene and β -pinene by all three reactions (Jenkin et al., 2000; Koch et al., 2000; Larsen et al., 2001). According to the postulated mechanism, these authors assume reactions involving radical intermediates (RO_2 , RO , HO_2 , NO , etc), isomerization reactions, etc., which are not believed to be affected by water vapour. It seems possible that dicarboxylic acids initiate nucleation in the case of OH- and NO_3 -reactions, but not during the ozonolysis, where products of lower volatility are generated as observed by Bonn et al. (2002). These will start to nucleate earlier and suppress particle formation by dicarboxylic acids during the ozonolysis.

In this context of the influence of water vapour on the ozonolysis induced nucleation, a similar but slightly different behaviour of *endocyclic* monoterpene compared to *exocyclic* reactions was observed by these authors. Whereas the *exocyclic* reactions are affected strongly by the increase of water vapour, the *endocyclic* monoterpene-ozonolyses are only slightly influenced by water vapour. In the case of the

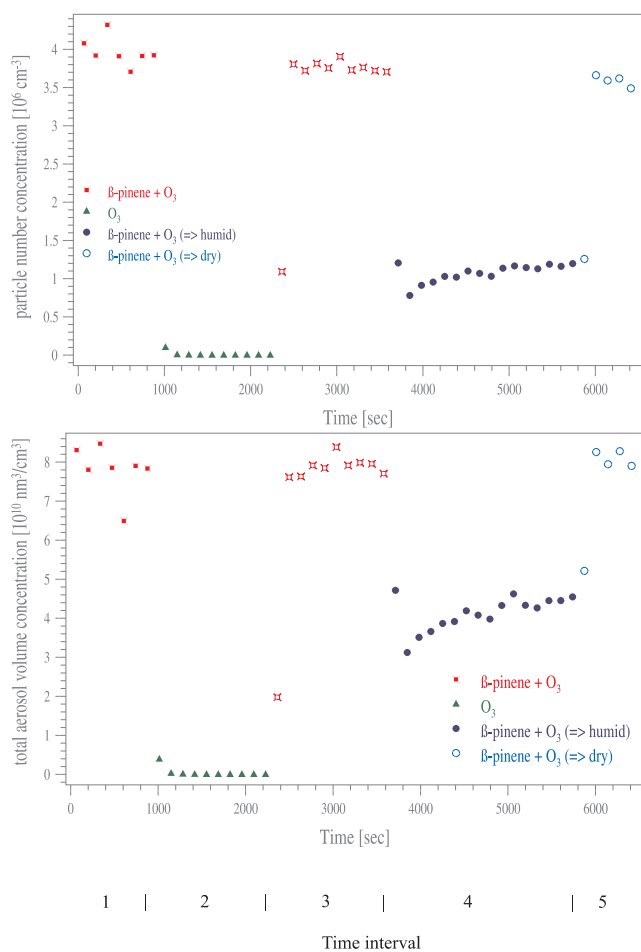


Fig. 8. Shown are the particle number concentration (upper part) and the aerosol volume concentration measurements (lower part) obtained during a β -pinene ozonolysis experiment performed at a fixed reaction time in the flow reactor. In this experiment, different experimental conditions were adjusted: the monoterpene flux was turned on (interval 1, 3, 4 and 5) and off (interval 2), and the humidity was increased in interval 4. Steady state conditions were reached nearly immediately.

endocyclic reactions the effect of water vapour was found much weaker and occurred predominantly at lower concentrations, which was explained by a less competitive involvement of water in the formation of secondary ozonides (*inter- or intramolecular*) that are believed to cause the observed homogeneous nucleation. Consequently, these intercomparison between the three different oxidation reactions can be used to distinguish between the different reactions, for example, occurring in smog chamber studies.

3.2 Experiments performed in the flow reactor

Additionally, two β -pinene experiments, one with O_3 (Fig. 8) and one with NO_3 (Fig. 9) were conducted in a flow reactor, in order to be able to compare and discuss probably oc-

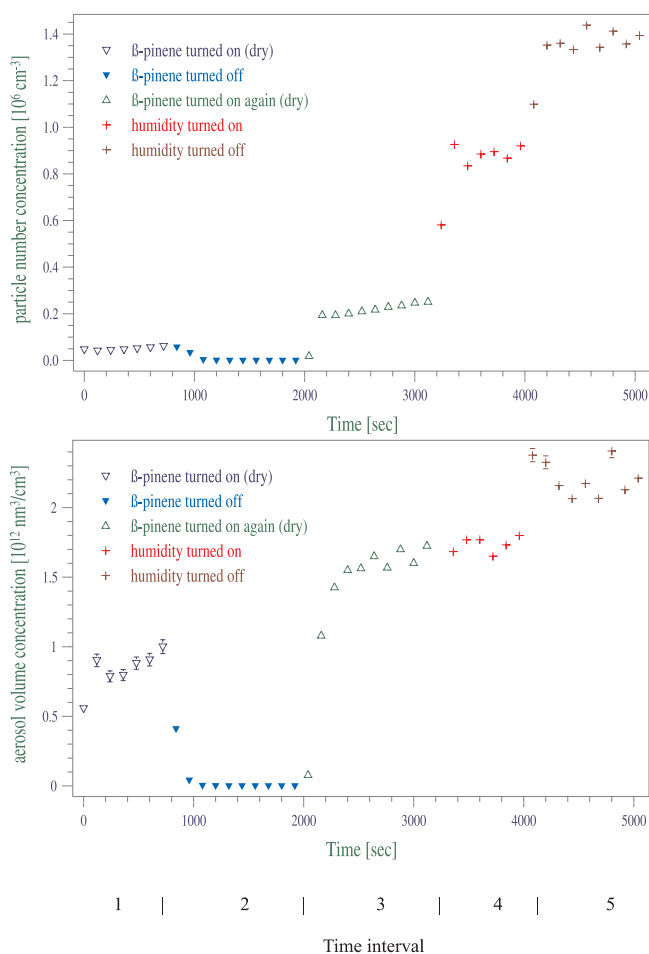


Fig. 9. Shown are similar experimental conditions as presented in Fig. 8 during the reaction of β -pinene with NO_3 . From the plot of the concentration measurements as well as from the aerosol volume concentration, a clear reactor surface artefact with a remarkable memory effect have been observed.

curing artefacts observed in both reaction systems, and to draw mechanistic conclusions regarding single particle formation. During some experiments in the spherical reactor with β -pinene and NO_3 , conducted prior to the ones of this study, we observed artefacts that occurred during the experiment, and which are able to influence succeeding experiments. In this context, it was possible to reach a much higher particle concentration level during an experiment with 50 ppbv conversion rate than with 500 ppbv conversion rate, if the experiment with 500 ppbv conversion rate was performed first, if the reactor was not cleaned very carefully previously! In order to investigate this phenomenon, a flow reactor setup was chosen, which provides steady-state conditions at a fixed sampling outlet. In this way the continuously observation at a fixed reaction time was possible. Therefore, both experiments were initiated and adapted to achieve a better knowledge of the process causing the observed artefact.

The only parameters changed were (a) the concentration of the monoterpene (on or off) as well as (b) the humidity during different time intervals of the experiment.

It can be seen from the measurements of the particle number concentration plotted in the upper graph of Fig. 8 and of the aerosol volume concentration (lower graph, Fig. 8) during the ozonolysis that particles ($N \sim 4 \times 10^6 \text{ cm}^{-3}$) are formed as the monoterpene flux was turned on at time zero (interval 1, filled red points) and the measurements of both parameters scattered around constant values. At 900 s observation time, as soon as the monoterpene flux was turned off (interval 2, green triangles) the particle number concentration and the aerosol volume concentration dropped immediately to the background levels and recovered to their values at 900 s, as expected for steady-state conditions when turned on again at 2000 s (interval 3, open red points).

Next, the humidity level was increased at 3700 s (interval 4, filled blue dots) and the particle number and the volume concentration decreased as reported by Bonn et al. (2002). The delay of stable measurement data at this point is due to the response time of the reactor to reach the planned humidity level. In the final time interval 5 (open blue dots) the water vapour was turned off and both the number as well as the volume concentration recovered very fast to its previous values before increasing the water vapour content. Consequently, the flow reactor runs at stable conditions.

On the contrary to the ozonolysis experiment, the reaction of β -pinene with NO_3 (Fig. 9) led to a multitude of surface artefacts, to be expected to occur also on the surface of smog chambers.

Although the reaction of β -pinene with NO_3 is very fast (Table 1), and the monoterpene is almost converted prior to the sampling outlet, the number concentration as well as the aerosol volume concentration increased continuously with observation time. As the β -pinene-flux is turned off at 720 s similar to the ozonolysis experiment, the number and the aerosol volume concentration decline much slower towards the background concentrations (interval 2, filled blue down triangles) than found during the ozonolysis. As the terpene flux was turned on again at 1920 s, the number and the aerosol volume concentration increase rapidly to the values measured at 720 s, immediately before the β -pinene-flux was turned off, and increased to higher levels. This behaviour continued and was enhanced during the change of the humidity level (intervals 4 and 5, red crosses) indicating a memory artefact inside the reactor. This memory effect must have been caused by products attached to the reactor wall, which will evaporate later on. In the gas phase, these products will be possibly oxidised in a second reaction by NO_3 to form clusters, which serve in the following as nucleation precursors. These precursors originate either from nitric acid formed by the reaction of N_2O_5 with water vapour (reaction 8) that is present ($\sim 3 \text{ ppmv}$) even in the dry experimental periods, or from oxidised organic species that react further on forming secondary products of lower volatility.

With regard to the aerosol number concentration Wängberg et al. (1997) observed a broad range of number concentrations for the same initial conditions during their studies at the European PHotoREactor (EUPHORE) in Valencia (Spain). In order to suppress the artefact, these authors have introduced N_2O_5 prior to the experiment to finish ongoing oxidation reactions of formed products that were still in the chamber (wall etc), so that these cannot contribute to homogeneous nucleation. With this procedure the effect was decreased dramatically.

Consequently, a similar procedure was used during the present study to reduce the same artefacts with regard to number and aerosol volume concentration increase as much as possible. This procedure lead to identical measurement datasets for identical experimental setup in the range of uncertainty, so that no further artefacts can be expected to occur than the ones mentioned above. But, as it can be seen from Fig. 9, the time required for the recovery of the reactor is much larger than 5 min. During our experiments N_2O_5 was introduced prior to the experiment and resided in the chamber one hour before the reactor was evacuated for a second time during the dry as well as during the humid experiments.

With respect to the observations of Wängberg et al. (1997) and of this study, a nucleation initiated by nitric acid and water vapour can be ruled out because of the suppression during the second phase of the NO_3 -experiment. Therefore, primary products, which will be further oxidised, are involved in the process that causes the observed artefact.

Finally, the results of both the OH as well as the NO_3 -experiments with different humidities lead to the conclusion that nitric acid formed especially in the 'humid' case did not affect the aerosol volume much. Consequently, this artefact is found to be less important. The high concentration of NO might have affected the results in the dry as well as in the humid experiments with OH, but the depletion of particle formation at the high concentration of 50 ppbv conversion rate makes the OH reaction negligible regarding atmospheric new particle formation. Therefore further studies on the input of NO-concentration on especially the aerosol volume yield are needed.

3.2.1 Comparison to literature

There is one recent publication by Griffin et al. (1999) which also tackles the contribution of the different oxidation reactions (O_3 , OH and NO_3) of monoterpenes to secondary organic aerosol (SOA) formation. The authors have used a large outdoor smog chamber and have performed photo-smog experiments as well as ozonolyses and NO_3 reactions of several monoterpenes. The photosmog experiment was conducted at usual smog chamber conditions with NO_x concentrations higher than 10 ppbv, which lead to ozone production during their experiments. Because of the simultaneous presence of multiple oxidants, a direct separation of the contribution to SOA mass production by the different re-

action mechanisms was not possible due to missing marker species with well known reaction yields. Therefore, they run a model representing the reaction mechanisms occurring inside the chamber with various parameters, such as saturation vapour pressures and product yields with high uncertainties as found in the literature (e.g. pinonaldehyde: 0.06 (Larsen et al., 2001) $\leq Y \leq 0.87$ (Nozière et al., 1999)). In their study they used dried air containing 2000 ppmv of water vapour at minimum that is roughly 1000 times higher than used in our 'dry' experiments. This has affected their measurements remarkably during the ozonolysis. Additionally, former reaction products like HCOOH might have evaporate from the walls and reduce the observed nucleation measurably during the ozonolysis as described by Bonn et al. (2002). Moreover, they added seed aerosol that diminished homogeneous nucleation. On the contrary, a scavenger was not added in most of the studies. These points can be addressed to further papers tackling the SOA formation in smog chamber experiments like Pandis et al. (1991); Zhang et al. (1992); Odum et al. (1996); Hoffmann et al. (1997); Yu et al. (1999).

Due to the addition of seed aerosol in the smog chamber studies, a comparison is only possible for the aerosol volume concentration but is rather difficult due to the non-identical initial conditions.

In our reactor no sunlight was used and the artefacts occurring during the NO_3 -reactions were suppressed. With this set-up it was possible first to study the particle formation for each oxidant separately without the use of models at very low water vapour concentrations. This enables us to analyze the influence of water vapour on the results.

The comparison of this study and the one of Griffin et al. (1999) lead to the following statements: Concerning the reactions of α -pinene their general conclusion is somewhat similar to the results of the present study. On the contrary, their findings concerning the β -pinene-reaction differ significantly from our results. This is most probably caused by the artefacts described above, which was observed to be much smaller during α -pinene- than during β -pinene-reactions. Therefore, we believe that the present values are much closer to reality.

4 Conclusions

In this study on the contribution of the different reactions of α -pinene (endocyclic monoterpene) and β -pinene (exocyclic monoterpene) with O_3 , OH and NO_3 , it was found that the ozonolysis dominates the homogeneous nucleation process and is probably the only atmospheric relevant organic source for new particle formation, because of the atmospheric concentrations of monoterpenes lower than 1 ppbv (Fuentes et al., 2000). On the contrary, the aerosol volume forming potentials of the individual reactions are similar for monoterpenes containing an *exocyclic* double bond, and dominated

by the ozonolysis during reactions of *endocyclic* monoterpenes.

Therefore, models describing the *initial new particle formation* in the real atmosphere caused by monoterpenes only have to take the ozone reactions into account, whereas all products of every single monoterpene reaction has to be included to describe the *growth* of the aerosol particles.

Finally, a different effect of humidity was found on the nucleation occurring during the different reactions with O_3 , OH, and NO_3 . As published by Bonn et al. (2002), the nucleation during the ozonolysis of monoterpenes is negatively affected by the concentration of water vapour, but the monoterpene reaction with OH as well as with NO_3 is not. If this effect is atmospheric relevant, it will be enhanced because of the different concentration levels of monoterpenes and ozone and the reaction products in the laboratory and the real atmosphere. Consequently the reaction of the stabilized CI with water vapour will dominate the competitive reaction mechanism of the stabilized CI in the atmosphere.

In fact, Clement et al. (2000), Buzorius et al. (2000) and Boy and Kulmala (2001) have made similar observations to those found in the present study during field measurements at the very remote site of Hyytiälä in Finland. They found a reducing effect of water vapour on nucleation, as it can be described by the observations during the ozonolysis.

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