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Reactions of NO₃ radicals with limonene and α-pinene: Product and SOA formation

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Abstract

Monoterpenes are ubiquitous in forested environments and are subject to reactions with OH radicals, NO₃ radicals and O₃ both within and above forest canopies. While reactions of monoterpenes with OH and O₃ have received considerable attention with regard to their reaction kinetics, reaction products and secondary organic aerosol (SOA) formation those with NO₃ have received relatively little consideration. To redress this imbalance and to try and assess the possible importance of NO₃ + monterpene reactions within forest canopies investigations have been performed on selected monterpenes. The products and aerosol formation from the NO₃ radical initiated oxidation of limonene and α-pinene have been investigated in the EUPHORE photoreactor facility, and the secondary chemistry of the observed major products was then investigated in a large volume laboratory photoreactor. In addition to large yields of yet unidentified organic nitrates, pinonaldehyde and endolim have been identified as the major reaction products of the NO₃ radical initiated oxidation of α-pinene and limonene, respectively. The aerosol formation has been investigated in the presence of different seed aerosols and also water vapour. The reactions lead to the formation of SOA and the results indicate the importance of the chemical character of the seed aerosol in determining the SOA yield in NO₃ + monoterpene reactions. The possible pathways leading to SOA formation and also their potential importance are discussed based on the laboratory results on the reaction of NO₃ with the two major products.
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Keywords: Aerosol; Limonene; Nitrate radical; Products; α-Pinene

1. Introduction

The chemistry of terpenes such as limonene and α-pinene are important in forested environments. Terpenes are a major component of BVOCs emitted in northern Europe (Hakola et al., 2000; Lindfors et al., 2000), representing 50% of gas emissions from citrus plants in the Mediterranean climes (Steinbrecher et al., 1999). Plants unusual to Europe, e.g., Australian *Eucalyptus,* have limonene emissions of more than 30% (He et al., 2000) and limonene represents one of the four highest terpenes emitted in North America. In addition to natural biosynthesis, anthropogenic sources of limonene are becoming increasingly prevalent. Due to environmental concerns over the uses of haloalkanes as

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industrial solvents, this last decade has seen an increase in the use of limonene as a new solvent (Florida JPA, 2000; Florida Chemical Co., 2000).

The atmospheric photooxidation of the monoterpenes have been the subject of many studies and extensive reviews on kinetics, mechanisms and products are available in the literature (e.g., Atkinson, 1994, 1997, 2000; Atkinson and Arey, 1998, 2003; Calogirou et al., 1999; Calvert et al. 2000; Kanakidou et al., 2005). Seinfeld and Pankow (2003) have recently reviewed laboratory studies of secondary particulate matter formation from organic precursors, in particular biogenic hydrocarbons. Most of the studies on the atmospheric chemistry of monoterpenes have focused on their OH radical and ozone initiated oxidation and only a few studies have been performed or considered NO_3 radical-initiated degradation in the analysis of monoterpene/NO_x photooxidation systems (Berndt and Böge, 1997; Bonn and Moortgat, 2002; Hallquist et al., 1999; Hjorth, 1998; Hoffmann et al., 1997; Kanakidou et al., 2005; Griffin et al., 1999a, b; Schuetzle and Rasmussen, 1978; Wängberg et al., 1997).

Based on the rate coefficients and typical median OH, NO_3 and O_3 atmospheric concentrations (Atkinson, 1994, 1997), it can be readily shown that reaction with NO_3 radicals is the most important gas phase loss pathway for α-pinene and limonene during the night time. However, under elevated NO_x conditions reaction with NO_3 can also be significant during the daytime and contribute substantially to the monoterpene decay. Given the potential importance of the NO_3 oxidation channel and the current paucity of data on such reactions the reaction products and SOA formation from the reactions of NO_3 with α-pinene and limonene in particular have been investigated in a laboratory photoreactor and also an outdoor smog chamber with the aim of obtaining a clearer mechanistic picture of the importance of these reactions in forest canopies.

2. Experimental

2.1. EUPHORE photoreactors

Two measurement campaigns were carried out in the chambers of the European photoreactor facility EUPHORE in Valencia during the periods 19–29 November 2001 and 12–22 March 2002. A detailed description of the EUPHORE chambers is given in Becker (1996) and Brockmann et al. (1996).

The analysis in EUPHORE was performed using the following instrumentation: a scanning mobility particle sizer (SMPS) composed of a differential mobility analyser (DMA TSI 3081A) with either a condensation particle counter (CPC) TSI 3022A (provided by EUPHORE) or a TSI 3025A ultrafine CPC (provided by the University of Wuppertal), long-path FT-IR spectroscopy (NICOLET MAGNA 550 in each chamber, optical path length either 326.5 or 553.5 m), long-path DOAS spectroscopy (optical path length 1147 m), on-line gas-chromatography (HP 6890 with FID, Schmitt/Glashütten with ECD, Fisons 8130 with PID/FID, or Fisons TGA with FID), and a series of NO_x and ozone monitors (MONITOR LABS or ECO Physics). In addition, chamber samples were taken on DNPH-coated cartridges and analysed after elution with HPLC–UV/VIS.

NO_3 radicals were generated by the thermal decomposition of N_2O_5 ($N_2O_5 \leftrightarrow NO_2 + NO_3$), which was synthesized in a mixing coil by the reaction of NO_2 (diluted with air) with O_3 using an excess of NO_2 to prevent ozone from flushing into the chamber. With this set-up a mixture of N_2O_5, NO_2 and NO_3 flows into the chamber and typical mixing ratios for NO_3 in the low pptV range could be achieved.

In experiments in which an organic seed aerosol was initially present, the BVOC was introduced into the chamber in excess (50–500 ppbV), and a small amount of ozone (~5 ppbV) was added to create organic particles. The initial number concentration of the organic seed aerosol thus created was usually 2000–3000 cm^{-3}. In experiments where ammonium sulphate seed aerosol was used the starting particle concentration was ~20 000 cm^{-3}. After a reasonable time period for mixing or, in the case of an organic seed aerosol for the ozonolysis reaction, N_2O_5 addition was started. After completion of the reaction the data collection for the SMPS system was continued to obtain wall deposition rate constants for the loss of the particulate phase.

In all experiments the initial mixing ratio of the monoterpene was chosen such that at the end of the experiment the ratio $k_{NO_3,VOC}[VOC]/(k_{NO_3,VOC}[VOC] + k_{NO_3,ALD}[ALD])$, where $[VOC]$ = reactant concentration, and $[Ald]$ = concentration of major aldehyde product, was at least 0.97, i. e. the monoterpene was the major reaction partner for NO_3 radicals throughout the experiments and hence

secondary chemistry accounted only for a few percent of the total reaction.

2.2. Wuppertal laboratory chamber

The experiments were performed in a quartz glass photoreactor (6 m long, i.d. 46 cm). Particle measurements were made with a commercial aerosol classifier (DMS TSI 3071A) and two independent particle counters (TSI 3022A, connected to the DMA, and a stand-alone TSI 3025A ultrafine CPC "UCPC"), and long-path FT-IR spectroscopy (either BRUKER IFS 88 or THERMO NICOLET NEXUS, optical path length 484.7 m). A detailed description of the reactor is given in Barnes et al. (1994). The valour over solid N_2O_5 was flushed into the reactor in a flow of dried nitrogen and served as the NO_3 radical source.

In all experiments in EUPHORE and Wuppertal, the measured concentrations of the different reactants and products as well as particles were corrected for loss processes such as wall and leak losses (as in EUPHORE) and secondary reactions of the products with NO_3. Maximum corrections for the gaseous product concentrations at the end of an experiment were typically 10–30%, and for the total particle volume typically 40–50%.

3. Results and discussion

3.1. Product studies in EUPHORE

The yields of the products observed in the reactions of NO_3 with α-pinene and limonene are summarized in Table 1. Calibrated standards were available for pinonaldehyde, endolim (both synthesised for this work), formaldehyde, 4-acetyl-1-methylcyclohex-1-ene, pinan-2,3-oxide, and limonene-1,2-oxide (all purchased). The structures of all compounds are given in Fig. 1. In addition, the spectral features of 3-nitrooxylimonene-2-ol, 2-nitrooxylimonene-3-ol and 3-nitrooxybutane-2-ol

Table 1
Product yields for the reactions of NO_3 with α-pinene and limonene studied in EUPHORE

Product Reactant	Aldehyde (mol-%) this work	Aldehyde (mol-%) literature	Σ $RONO_2$ (%, see text) this work	Σ $RONO_2$ (%) literature
α-pinene	Pinonaldehyde 48.6±9.2	Pinonaldehyde 62±4 Wängberg et al. (1997) Pinonaldehyde 71 Hallquist et al. (1999)	20.2±8.9	14 Wängberg et al. (1997) 19 Hallquist et al. (1999)
limonene	Endolim 28.8±4.3	Endolim 69[a] Hallquist et al. (1999)	67.0±4.5	48 Hallquist et al. (1999)

[a]Tentative because Hallquist et al. (1999) did not have access to authentic standards of endolim.
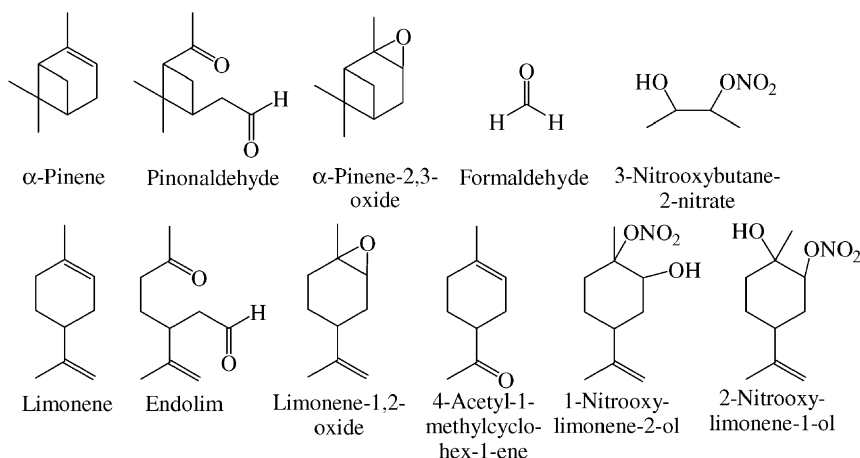

Fig. 1. Molecular structures of the compounds used in this study. Pinonaldehyde, endolim and the three organic nitrates are not commercially available and were synthesized in the laboratory (Spittler, 2001).

were used to estimate the sum of all organic nitrates, $\Sigma RONO_2$, using an integrated absorption cross section. Their spectral features of the $RONO_2$ compounds found in the reaction mixtures are not exactly the same as for the reference compounds. This is, in some degree, probably attributable to the formation of dinitrates and nitroperoxynitrates. For this reason, $\Sigma RONO_2$ is not given in mol%. Since the reaction time was chosen such that even at the end of the experiment the NO_3 radicals reacted predominantly with the terpenes, the observed sum of $RONO_2$ compounds can be interpreted as primary products.

As seen in Table 1, pinonaldehyde has been found as the major product of the reaction of NO_3 with α-pinene along with a significant yield of organic nitrates. For limonene, endolim was the major aldehydic product and very substantial yields of organic nitrates have been estimated. Pinonaldehyde has been previously reported as a major reaction product of the NO_3 + α-pinene reaction by Wängberg et al. (1997) and Hallquist et al. (1999). Endolim was tentatively identified as a major reaction product of the NO_3 + limonene reaction by Hallquist et al. (1999), however, they did not have an authentic standard and could only estimate a yield for this compound by comparison with α-pinene experiments. To our knowledge this work represents the first use of an authentic standard for the quantification of the endolim formation yield from the reaction of NO_3 with limonene.

In the α-pinene experiments sampling of reaction mixtures on DNPH-coated cartridges with subsequent HPLC separation and UV detection was used to determine the pinonaldehyde mixing ratios during some experiments and to compare these data with results obtained with FT-IR. Good mutual agreement between the data obtained using both detection methods was observed. The reason for the different product yields for pinonaldehyde between this study and the studies of Wängberg et al. (1997) and Hallquist et al. (1999) is not clear. The analytical equipment used is almost the same in all cases, and for the FT-IR analyses the same absorption cross-section reported by Wängberg et al. (1997) was used in all three studies. Therefore, we assume that variations in the experimental procedures are responsible for the differences. Wängberg et al. (1997) usually worked with higher α-pinene mixing ratios than here, and both other groups introduced large amounts of N_2O_5 at the

beginning of the experiments, which could lead to difficulties in spectral analysis or to a change in the reaction system. Moreover, Hallquist et al. (1999) calculated the product yields relative to the measured $\Delta[N_2O_5]$ rather than $\Delta[\alpha$-pinene] and assumed a 1:1 stoichiometry which also could be a source of error.

It is difficult to compare the product yields of the limonene experiments with those reported by Hallquist et al. (1999) since they performed only one single experiment in EUPHORE at low initial concentrations. Also, as mentioned previously, they did not have a reference sample of endolim. Instead, they assumed that endolim had spectroscopic features similar to those of caronaldehye and used this analogy in their endolim yield estimate, which is a potentially large source of error.

Wängberg et al. (1997) reported α-pinene-2,3-oxide (Fig. 1, compound 4) as a minor NO_3 + α-pinene reaction product with a yield of $3.0 \pm 0.5\%$ measured with GC-FID after sampling of the reaction mixture in a specially designed syringe. They also quantified β-hydroxy nitrate and a β-keto nitrate with yields of 5.0 ± 0.4 and 3.0 ± 0.2 mol-%. Although we obtained a commercial oxirane sample, we could not detect the compound in our EUPHORE experiments. It is possible that the sampling system and GC set-up used by Wängberg et al. (1997) was more sophisticated than that applied in the present work. Berndt and Böge (1997) also detected α-campholene aldehyde and α-pinene-2,3-oxide as reaction products at pressures lower than 200 mbar. Possible pathways to these products via an excited alkyl radical, rearrangement and subsequent O–NO_2 bond fission are shown in Fig. 2. Both channels are of importance only at low pressures since at atmospheric pressure the initially formed excited alkyl radical is collisionally deactivated and reacts rapidly with molecular oxygen. Problems with detection limits for oxiranes in NO_3 + alkene radical experiments due to small product yields have been reported previously by Canosa-Mas et al. (1999). Fig. 3 shows possible products resulting from NO_3 + limonene via analogous pathways to those outlined Fig. 2.

Nitroperoxy nitrates (e.g. Fig. 2, compound 6) and dinitrates (e.g. Fig. 2, compound 7) may form in both of the reaction systems since at the end of the experiments NO_2 mixing ratios of the order of 100 ppbV were present in the reaction mixtures. As the spectral features of nitrates are very similar it was not possible to distinguish between dinitrates
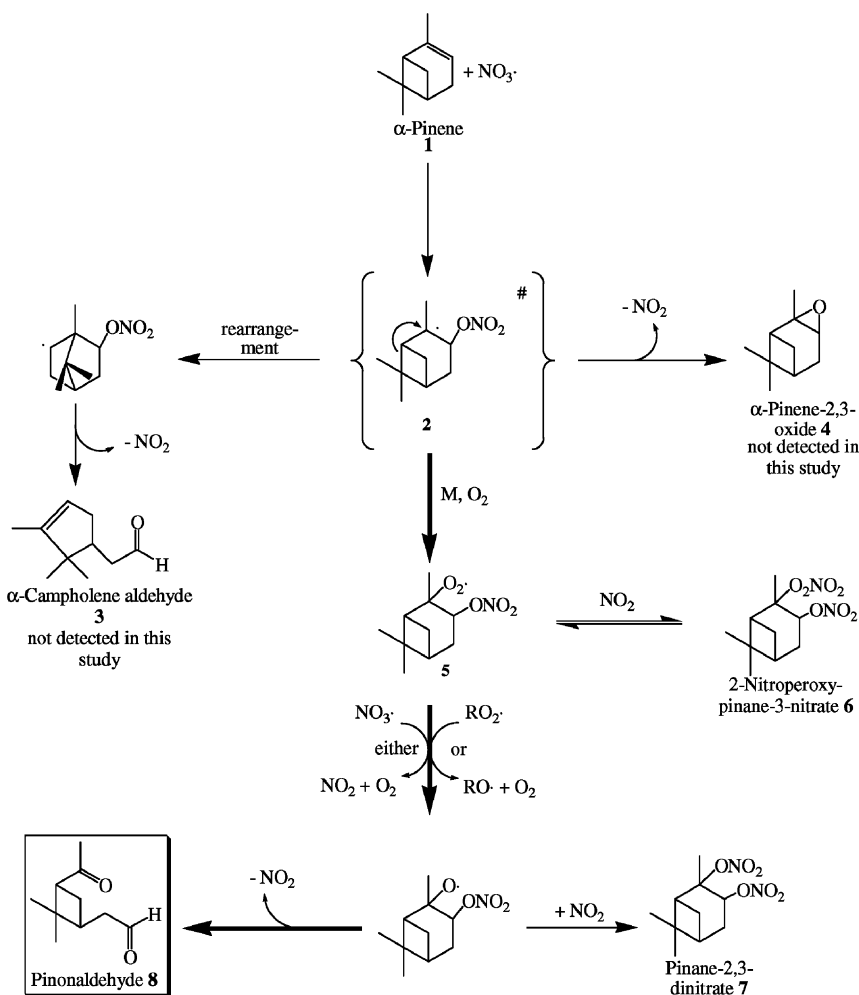
Fig. 2. Simplified reaction mechanism for the $NO_3 + \alpha$-pinene reaction. Reactions of the alkyl groups have been omitted as well as the formation of the less stable alkyl radical and self reactions of peroxy radicals leading to keto or hydroxy nitrates. The boxed compound 8 was identified as a reaction product.

and other $RONO_2$ type compounds. Dinitrate formation, however, is not deemed to be of importance in forested regions and the atmosphere as a whole because of the much lower mixing ratios of NO_2.

In the limonene experiments reported here the endolim yields are slightly smaller than the pinonaldehyde yields in the α-pinene experiments. The remaining carbon in the limonene experiments would appear to be transformed predominantly into $RONO_2$ type compounds. Interestingly, we could not detect products which indicate an attack of NO_3 to the exocyclic double bond in limonene, namely formaldehyde or 4-acetyl-1-methylcyclohex-1-ene (Fig. 3, compound 12) even though formaldehyde is easy to detect even at very small mixing

ratios. This indicates that in electrophilic attack on alkenes NO_3 is more selective than OH or ozone since for the reactions of limonene with OH and ozone formaldehyde and 4-acetyl-1-methylcyclohex-1-ene are well-known major products (e. g. Arey et al., 1990; Grosjean et al., 1993; Hakola et al., 1994; Hjorth, 1998; Larsen et al., 2001). The high selectivity of NO_3 towards different C=C double bonds has previously been reported by Shu et al. (1997) and Martínez et al. (1999) for alkenes with similar structural elements like limonene.

In the α-pinene experiments a major product fraction still remains undetected. The formation of SOA cannot explain this result since, as reported below, in all limonene runs the SOA mass yield was higher than in the α-pinene runs, and the product
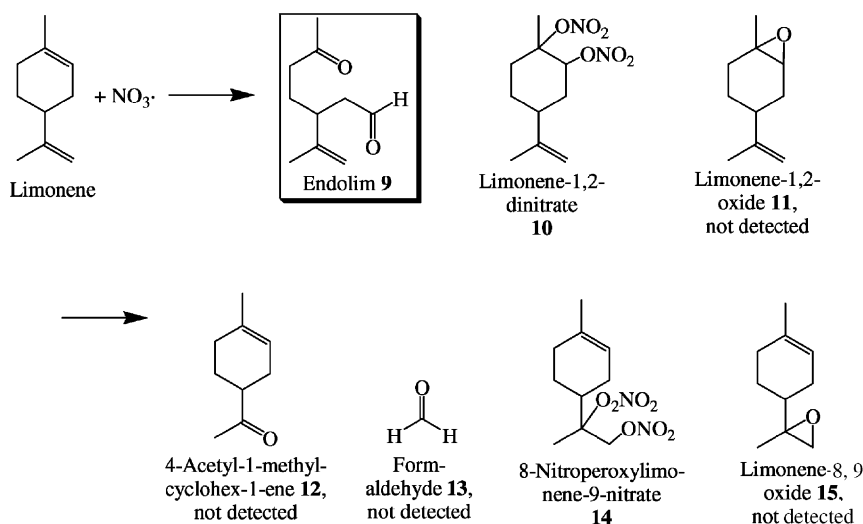
Fig. 3. Possible reaction products from the reaction NO_3 + limonene. Products are formed analogous to the simplified NO_3 + α-pinene mechanism depicted in Fig. 2. The boxed compound 9 was identified as a reaction product.
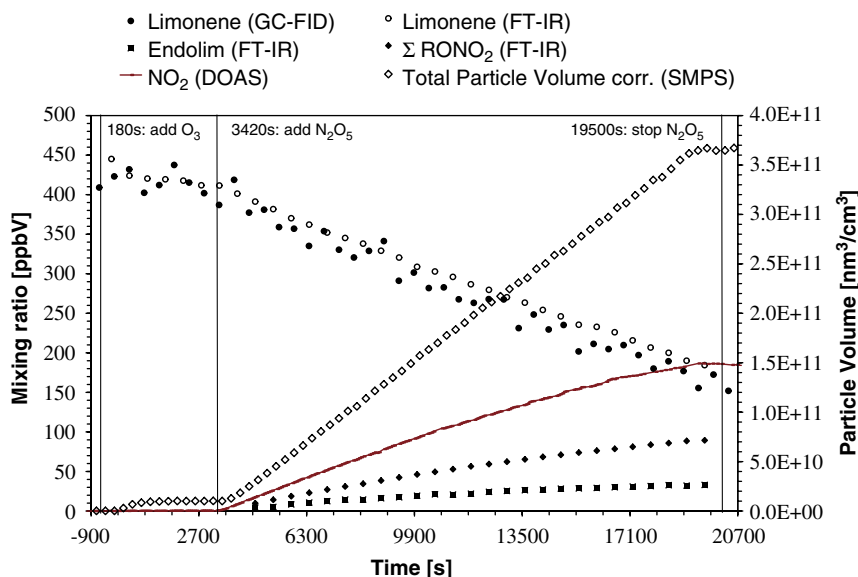

Fig. 4. Typical concentration-time profile for a NO_3 + limonene experiment performed in the EUPHORE photoreactor (26 November 2001) in the presence of an organic seed aerosol.

balance in the limonene studies is significantly better than for the α-pinene systems.

3.2. SOA formation in EUPHORE

Fig. 4 shows a typical concentration-time plot for a EUPHORE experiment on the NO_3 + limonene reaction in the presence of an organic seed aerosol.

After addition of N_2O_5 the total particle volume increases almost immediately and shows a linear temporal behaviour. Fig. 5 depicts the temporal change of the particle volume for the same experiment. During the complete experiment the size distribution function was uni-modal and log-normal which can be interpreted as an unhindered condensation of products and coagulation of the
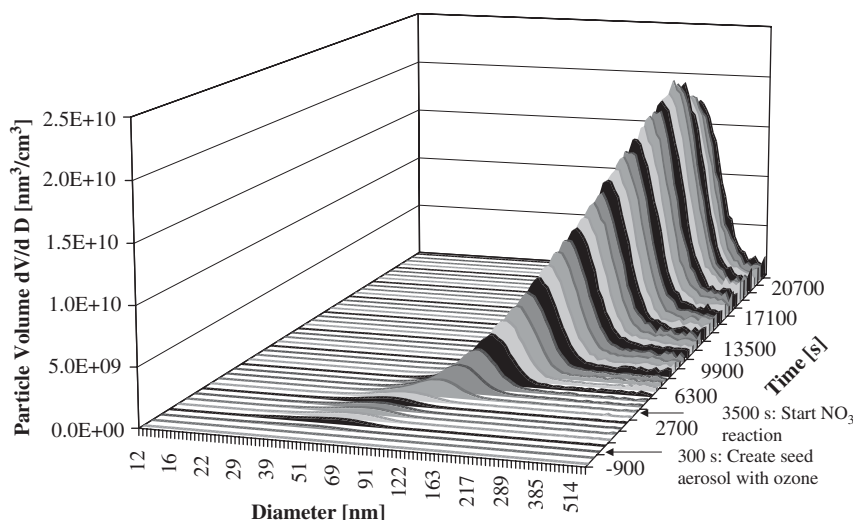
Fig. 5. Typical SMPS plot for the reaction of NO_3 with limonene performed in the EUPHORE photoreactor (26 November 2001). At 300 s 5 ppbV O_3 was added to an excess of limonene to create an organic seed aerosol. After 3500 s the addition of N_2O_5 was started.

smaller particles. Similar behaviour was observed for α-pinene in the presence of an organic seed.

For both α-pinene and limonene log-normal size distribution functions were not established in the absence of seed particles or if $(NH_4)_2SO_4$ seed particles were used in the experiments. In the absence of a seed aerosol the products condensed on the few existing background particles, which are always present in the chamber (N∼10–100 cm^{-3}), and then the particles grew extremely large, often out of the range of the instrument. In the $(NH_4)_2SO_4$ experiments the size distribution function appeared multi-modal indicating a hindered condensation and/or coagulation of semi-volatile products on the existing inorganic material. The size distribution functions only appeared log-normal when organic seed material was initially present.

In order to transform the total SOA volume measured with the SMPS into a particle mass a density of 1.129 ± 0.031 g cm^{-3} has been used which was measured for a model aerosol consisting of two carbonyl compounds and one organic nitrate: endolim, 4-acetyl-1-methylcyclohex-1-ene and 5-isopropenyl-1-methyl-2-nitrooxy-cyclohexanol were mixed in the ratio 49, 41, and 10 mol% and the density of the mixture was then measured. The composition of the model aerosol is based upon a product analysis of OH + limonene (Spittler, 2001).

The derived SOA mass yields have been plotted versus the total particle mass corrected for secondary losses, namely wall deposition and leak losses. An example is shown in Fig. 6. The results have
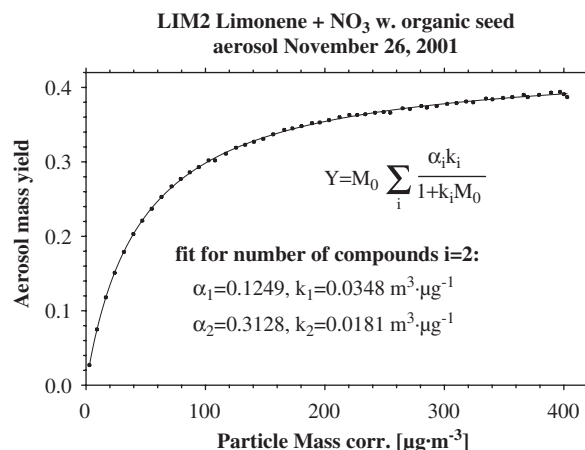

Fig. 6. Partitioning plot for the same limonene + NO_3 experiment as in Fig. 5 assuming that two compounds partition between gas and particle phase. Data points are from the SMPS analysis. K_i: partitioning coefficient, A_i: gas-phase concentration, and F_i: concentration in the particulate phase of compound i. See text for further details.

been fitted using the partitioning model of Odum et al. (1996) who defined partitioning coefficients (termed K_i here) for all compounds i that take part in the gas to particle partitioning process. K_i is based upon the gas-phase concentration A_i, the concentration in the particulate phase F_i, and the total organic mass M_0 which absorbs compound i. Therefore $K_i = F_i/(A_i M_0)$. Odum et al. also showed that the aerosol mass yield Y can be defined as $Y = M_0 \Sigma(\alpha_i K_i/(1 + K_i M_0))$ with a factor α_i that is the product of the stoichiometric yield from compound

Table 2
Measured SOA mass yields for the reactions of α-pinene or limonene with NO_3 radicals in EUPHORE

BVOC/seed	Mass yield (this work) (%)	Mass yield (literature)[a] (%)
α-pinene/organic seed	16.0 ± 3.1	13.5 (Hallquist et al., 1999)
α-pinene/$(NH_4)_2SO_4$	9.2	—
α-pinene/organic/20% RH	4.3	—
Limonene/organic	40.4 ± 4.8	19.2 (Hallquist et al., 1999)
Limonene/$(NH_4)_2SO_4$	20.9	—

[a]The literature values in the right column were published assuming a density of unity and were re-calculated for this comparison using the same "model aerosol" density as in the experiments reported here.

i in the reaction, and the ratio of its molecular weight to that of the parent educt. Therefore, Y is a function of the areosol mass M_0 available for gas-particle partitioning. However, when M_0 rises to infinity (termed M_∞ in our work) Y becomes proportional to α_i. Fig. 6 shows that the aerosol mass yield rises to a limiting value, in the experiment on 26 November 2001 it is approximately 0.4 (= 40 mass-%) when M_0 rises to ∞. These limiting values for the SOA mass yields were given in our experiments. As expected from the model the mass yield approaches a limiting value if the total mass rises infinitely. All values for the SOA mass in this work represent the values extrapolated to M_∞. Best fit results were achieved for the measured yields assuming 2 compounds partitioning between the gas and particulate phase. The results are listed in Table 2.

Because an analysis of the mixing ratios of the monoterpenes was problematic in the presence of water due to saturation of the absorption signal in large sections of the infrared spectrum by the water only a single experiment for α-pinene has been conducted in the presence of water (20% RH). This experiment yielded only 4.3% particle mass, which is substantially less than was typically observed in the presence of organic seed particles. Two possible processes could explain this observation. Firstly, the presence of H_2O could change the gas-phase mechanism for the $NO_3 + α$-pinene reaction yielding more volatile products than in the absence of water vapour. Some change in the chemical mechanism is supported by the observed decreased pinonaldehyde yield of 38.7% indicating a scavenging of the intermediate peroxy radicals by another process. Second, the water vapour could be taken up on the SOA and could change the chemical potential of organic compounds shifting the gas -particle partitioning equilibrium of organic compounds towards the gas phase. This is supported by the studies of Aumont et al. (2000) and Nozière et al. (2001) which showed a discernable but clearly limited solubility of monoterpene reaction products in water. It is also possible that a mixture of both processes is responsible for the observed lowered SOA mass yield in the presence of water vapour. The result is, however, in contradiction with the studies of Bonn and Moortgat (2002) who report that addition of water vapour had no effect on the observed particle size distribution during their $NO_3 +$ limonene studies.

Fig. 7 shows the relationship between the observed SOA mass yields (using the yield extrapolated to M_∞) and the corresponding product yields. The SOA and product yields show a positive correlation. Although similar physical properties (e.g. vapour pressures and polarities) are expected for pinonaldehyde and endolim the limonene experiments gave considerably higher SOA masses than the α-pinene experiments despite the fact that the pinonaldehyde yields are higher than the endolim yields. This negative correlation for the large carbonyl products as well as the positive correlation for the $RONO_2$ products is an indication that the SOA mass may be mainly attributable to organic nitrates $RONO_2$ and not to carbonyl compounds. Organic nitrates have previously been observed in field measurements (Schuetzle et al., 1975; Schuetzle and Rasmussen, 1978; Mylonas et al., 1991; Nielsen et al., 1995, 1998; Cornell et al., 2001), and in smog-chamber simulations large partitioning coefficients for organic nitrates have had to be taken into account to explain the observations (Kamens and Jaoui, 2001).

3.3. Wuppertal laboratory reactor results

In the Wuppertal reactor, the focus of the experiments was the investigation of the secondary chemistry occurring in the NO_3 oxidation of the
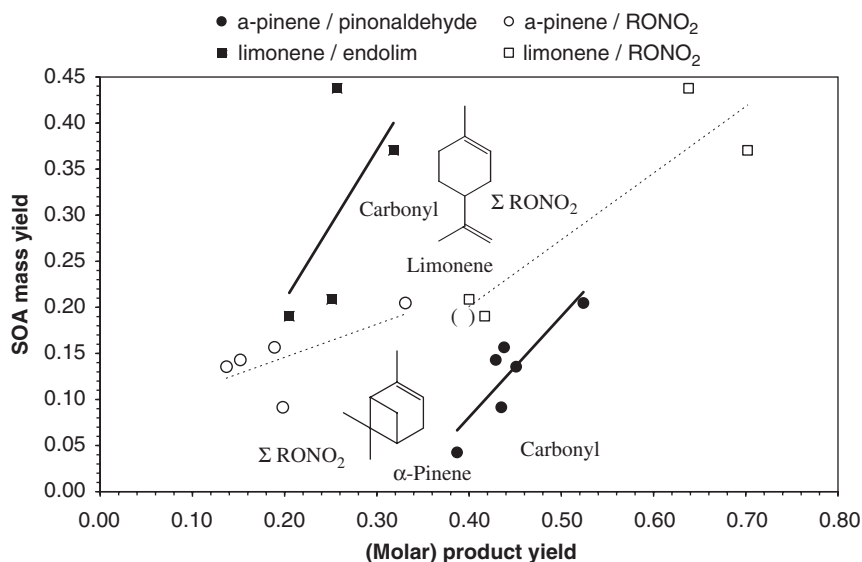
Fig. 7. Relationship between the measured product yields (molar yields only for the carbonyl products) and the observed SOA mass yields. For the limonene/$RONO_2$ data set the points in brackets ($\square$) are from the experiments with the $(NH_4)_2SO_4$ seed the other points are from the experiments with an organic seed. For the α-pinene/ $RONO_2$ data set ($\bigcirc$) points are shown for only five of the six experiments, in the experiment performed with 20% RH an accurate estimation of the $RONO_2$ yield was not possible due to interference in the infrared spectrum by absorptions from water.

monoterpenes. The observed major products pinonaldehyde and endolim were separately introduced into the 6 m reactor and oxidized by NO_3. The FT-IR data were used to record concentration-time profiles for reactants and products, and to determine ΔVOC, i.e., the amount of reactant aldehyde consumed by N_2O_5. The UCPC was usually operated with a time resolution of 2 s and provided information on the exact time of formation of new particles. With the combination of FT-IR and UCPC the threshold mixing ratios for particle formation could be determined.

The mixing ratios of pinonaldehyde and endolim were corrected for their wall deposition and leak losses caused by the analytical sampling and were then fitted with an appropriate function to describe their decay. From the UCPC data the time at which particle formation occurred could be measured, and from the fitted aldehyde data, the concentration of aldehyde required to be oxidized before particle formation is observed could be calculated.

The observed mass yields in these secondary reactions were measured as a function of the initial mixing ratio. In the case of endolim, a mass yield of $70.0 \pm 3.4\%$ was calculated as a limit for large initial mixing ratios. This high value is an indication that the further oxidation of endolim is a major

contributor to the total SOA mass occurring in the NO_3 oxidation of limonene. The threshold value for endolim was below 2 ppbV in all experiments. The total number of particles in the endolim experiments exceeded the upper detection limit of the ultrafine particle counter used ($100\,000\,cm^{-3}$) and the volume size distribution function dV/dD typically showed mono-modality with maxima between 100 and 200 nm.

The threshold values of the reaction of endolim + NO_3 are much lower than those determined previously for the OH reaction (Spittler, 2001), which, in combination with its higher mass yield, shows the significant potential of NO_3 radical monoterpene reactions with respect to particle formation.

In previous Wuppertal studies on pinonaldehyde oxidation with NO_3 the introduction of the compound led to a large number of particles ($> 20\,000\,cm^{-3}$) because of the high viscosity of the aged pinonaldehyde sample used at that time. In those experiments a broad size distribution function was established during the experiments, and a total mass yield of 2–3% was calculated. GC analyses showed no impurities in the pinonaldehyde sample and the reason for the aerosol formation on introduction of pinonaldehyde is unclear. In order

to avoid the formation of such an unintentional seed aerosol pinonaldehyde was freshly synthesized and used directly in the experiments. Under conditions with initial particle concentrations of the order of $10\,cm^{-3}$ the total number concentration of particles during the reaction of pinonaldehyde with NO_3 reached $70\,000\,cm^{-3}$, but the volume distribution function dV/dD had maxima at very small diameters ($\sim 30\,nm$). So the overall volume of the particulate phase was very small and the total mass yield was below 1%. This clearly shows that the further oxidation of pinonaldehyde by NO_3 is not significant for the total SOA mass and, therefore, other compounds need to be considered as major participants in the formation of particles in α-pinene experiments with NO_3. The threshold value for nucleation was below $2\,ppbV$ as for endolim.

The measured threshold values for nucleation in the endolim and pinonaldehyde experiments with NO_3 need to be compared with the mixing ratios of the parent monoterpenes and the corresponding values for the reactions with O_3. Most field studies on monoterpenes report mixing ratios that are measured as median values over large, well-mixed volumes. In forested canopies under the treetops and near the leaf surface, however, the mixing ratios of monoterpenes might exceed $1\,ppmV$, and under conditions of slow transport (in the absence of airflow) the major products can accumulate and could reach mixing ratios of the same order of magnitude as used in the experiments presented here. On the other hand, Koch et al. (2000) reported threshold values for nucleation in α-pinene and limonene experiments with ozone of $2.5\,ppbV$ with a similar experimental method as used in this study. This is a strong indication that under normal tropospheric conditions with approximately $30\,ppbV$ of ozone only the reaction with O_3 will form new particles. Other oxidation channels of α-pinene and limonene will predominately influence the total aerosol mass.

4. Conclusion

In the EUPHORE reactor, pinonaldehyde and endolim were identified as the major reaction products of the α-pinene and limonene oxidation by NO_3, respectively, together with large amounts of yet unidentified organic nitrates. Previously reported compounds like α-pinene oxide could not be identified indicating their minor importance at

normal pressure. In the limonene experiments, formaldehyde and 4-acetyl-1-methylcyclohex-1-ene could not be detected although these compounds are known to be formed during the limonene oxidation by OH or O_3. This result can be explained by the stronger selectivity of the NO_3 radical in comparison to OH and ozone and needs to be implemented in present chemistry models. By measuring the ratio between 4-acetyl-1-methylcyclohex-1-ene and endolim in air parcels the relative importance of NO_3 reactions could be determined during field campaigns.

The oxidation reactions led to the formation of secondary organic aerosol under all experimental conditions. However, the SOA mass was lower if $(NH_4)_2SO_4$ was used as a seed aerosol and also appeared multi-modal. Water vapour was also found to strongly decrease the aerosol mass for $NO_3 + \alpha$-pinene either by changing the reaction mechanism favouring the formation of more volatile compounds or by water uptake into the particulate matter resulting in an increased presence of low-volatile products in the gas phase. These results indicate the importance of the chemical character of the seed aerosol strongly in determining the SOA yield from $NO_3 +$ monoterpene reactions. This behaviour needs to be implemented into computer models. As an organic seed is more likely in a forested canopy without air transport from coastal or agriculturally used areas it is recommended for future studies to use exclusively organic seed particles.

The results indicate that the total SOA mass formed during limonene oxidation by NO_3 occurs mainly through the secondary chemistry of its major product endolim. In contrast, pinonaldehyde the major oxidation product from $NO_3 + \alpha$-pinene, has a small SOA mass yield, implying that other compounds will have more influence on the total particle mass in α-pinene experiments. The question as to whether these pathways are important for the atmospheric formation of SOA or not can only be answered in cooperation with field measurements. However, the formation of new particles from monoterpenes after heavy rainfalls or comparable events will mostly occur via the ozonolysis channel.

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