

Ultrafine particles produced by ozone/limonene reactions in indoor air under low/closed ventilation conditions

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Abstract

Formation of ultrafine particles, $d_p < 100$ nm, from gas-phase reaction of limonene with O_3 was studied. The concentration of reactants was chosen as close to realistic indoor conditions as possible. Two reaction chambers (1 and 14 m³) were used. Particle number concentrations were measured using a CPC and size distributions by using a scanning mobility particle sizer (SMPS) system. Rapid formation of new particles was observed at low concentrations of reactants and close to zero ventilation rates. The maximum number of particles was correlated with the initial rate of formation of reaction products. An excess of O_3 tends to give higher maximum particle concentrations. Modeling work lead to the conclusion that significant nucleation starts when the mixing ratio of “product” from the reaction $\text{Limonene} + O_3 \rightarrow \text{product}_{ox}$ exceeds 0.5–1 ppb. The secondary particles formed by atmospheric chemistry in indoor air contribute to the total particulate matter indoors and should be considered in terms of low-dose long-term exposure.

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1. Introduction

In the last two decades, particulate air pollution has re-emerged as one of the major health issues (Dockery et al., 1993). Numerous studies have shown a connection between particle concentration and health effects. It has been found that mortality

in urban regions and cardiovascular, as well as respiratory hospital admissions are correlated with atmospheric levels of fine (particles with diameter $d < 2.5$ μm , measured as mass concentration $\text{PM}_{2.5}$) and ultrafine ($d < 0.1$ μm) particles (e.g. Donaldson et al., 1998; Wichmann and Peters, 2000; Lippmann et al., 2000; Pope et al., 2002; von Klot et al., 2005; Schultz et al., 2005). Physiological mechanisms and hence which particle properties are causing the adverse health effects are still largely unknown. It has been speculated whether mass-, surface- or

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number concentration, chemical composition or combinations of these are best related to the health effects. Based on results from recent ambient air studies, the particle number and surface area appear to be more appropriate risk indicators than mass concentration (e.g. Penttinen et al., 2001; Nygaard et al., 2004). Most of the studies concern urban ambient air. However, since secondary organic aerosol is involved in both cases, the possibility of health effects caused by indoor aerosol particles must be considered.

The typical individual in Western Europe or the US spends around 90% of the time indoors. Thus, indoor air quality influences human health and well-being (Jenkins et al., 1992; Harrison, 1997). The main outdoor sources of fine and ultrafine particles are combustion processes (vehicle engines, i.e. traffic) and gas-to-particle conversion of pollutants by atmospheric chemical reactions. Particle concentrations indoors tend to reflect those outdoors (e.g. Morawska et al., 2001; Afshari et al., 2005; Matson, 2005). In addition, there are several potential primary indoor particle sources connected to activities such as cooking, tobacco smoking and use of candles.

However, another type of indoor source deserves to be considered, namely chemical reactions of gaseous pollutants with a potential to form products with low vapor pressure (Weschler and Shields, 1997; Weschler, 2001). Atmospheric chemistry of indoor air involves, in principle, the same reaction mechanisms as that of the outside, ambient atmosphere. Only the boundary conditions are different due to significantly different trace gas concentrations in indoor air pollution and the absence of UV light. The time available for chemical reactions indoors is determined by the ventilation rate of the building and by the dry deposition rate of the reactants. The ventilation rate also affects the concentrations of infiltrated and internally generated pollutants. If the pollution sources are located indoors, concentrations will be higher than those outdoors. Reactive substances supplied by ventilation from the outside are e.g. O_3 and NO_2 . Indoor/outdoor concentration ratios vary between 0.1 and 1.0 but are typically around 0.2–0.8 (Monn, 2001). Reaction between O_3 and NO_2 yields NO_3 , a reactive free radical, and both O_3 and NO_3 have considerable reaction rates with unsaturated hydrocarbons. The main outdoor oxidant, the OH radical, has a lifetime so short that transport indoors from the outside is of no concern. However,

it may also be formed indoors in reactions between O_3 and specific unsaturated organic substances (Sarwar et al., 2002). Indoor organic air pollutants originate from sources such as building materials, carpets, paints, cleaning- and hygiene products, plants and flowers. Terpenes are a group of natural, unsaturated organic compounds. Such disparate items as wooden furniture, christmas trees and citrus fruits are known domestic sources of terpenes. They are also common constituents of cleaning products and air fresheners (Nazaroff and Weschler, 2004; Liu et al., 2004). The terpene limonene is one compound that often is present in high concentrations. Typically, the background indoor mixing ratio of limonene is between 5 and 10 ppb (1 ppb = 1 nmol mol^{-1}) (Brown et al., 1994). Several papers report indoor mixing ratios between 0.3 and ~90 ppb (e.g. Wallace et al., 1991; Fellin and Otson, 1993). However, limonene mixing ratios as high as ~175–200 ppb were measured after applying a lemon-scented furniture polish (Wainman et al., 2000) or other cleaning products and air fresheners (Singer et al., 2006a).

The atmospheric chemistry of terpenes reacting with O_3 has been extensively studied over the past decades, and reaction rate coefficients, reaction mechanisms and principal reaction products are known (Atkinson and Arey, 2003). One aspect of such reactions is the potential of gas-to-particle conversion of reaction products with sufficiently low vapor pressure (Hoffmann et al., 1997). The formation of fine and ultrafine particles from chemical reaction between O_3 and limonene with relevance to indoor environments has been reported from experiments performed either in environmental chambers or in offices/laboratory rooms (Weschler and Shields, 1999; Wainman et al., 2000; Koch et al., 2000; Fan et al., 2003; Rohr et al., 2003; Liu et al., 2004; Leungsakul et al., 2005; Destailats et al., 2006; Zhang et al., 2006; Nøjgaard Kleno et al., 2006; Vartiainen et al., 2006; Tamás et al., 2006; Singer et al., 2006a; Sarwar and Corsi, 2007). The irritating potential of products from limonene and O_3 reaction, expressed as changes in human eye blinking frequency, has been presented (Nøjgaard Kleno et al., 2005).

Here we present results of particle formation experiments from the limonene/ O_3 reaction in environmental chambers simulating low/closed ventilation. The present work extends the concentration ranges, compared to previous work, towards lower reactant concentrations that are relevant to

Scandinavian conditions. Also, this work describes a semi-quantitative attempt to predict the particle formation and to provide a basic set of parameters for a simple, user-friendly indoor particle model. Practical examples, i.e. the effect of peeling an orange and the use of a limonene-containing cleaning product in an office are presented.

2. Experimental setup and procedures

Two environmental chambers were used. The “14 m³ chamber” is made of stainless steel (Weiss Technik, Germany) and has inner dimensions of 2.35 m × 2.6 m × 2.2 m (height × width × depth), a volume of 13.5 m³ and a surface-to-volume ratio (S/V) of 2.5 m⁻¹. The floor and ceiling are made of perforated steel plates since they serve as in- and outlets for an internal air circulating system. Purging air, cleaned by particle- and activated carbon filters, is supplied by a ventilation system. During experiments, the chamber was operated with ventilation and circulation fans shut down in order to obtain close to static conditions. A small mixing fan was placed inside the chamber to ensure complete mixing during the experiments. The air change rate (ACR) in the sealed but mixed chamber was checked by tracer gas experiments and was found to be <0.12 h⁻¹. The experiments further showed that the tracer gas was mixed in the chamber within 5 min after injection. Temperature and relative humidity in the chamber were 23 ± 2 °C and 33 ± 3%, respectively.

The “1 m³ chamber” is made of electro-polished stainless steel with inner dimensions 65 cm × 102 cm × 150 cm (height × width × depth) giving a volume of 0.994 m³ and a S/V = 6.37 m⁻¹. A radial fan for internal mixing is placed in the bottom part of the chamber. The ACR in the sealed but mixed chamber determined by the tracer gas experiment was found to be 0.05 h⁻¹. The chamber can be operated in static or dynamic mode since a flow of clean air can be supplied to the chamber. The chamber can be thermostatted between 15 and 30 °C and the relative humidity can be set between 20% and 80%. Air and gaseous components are supplied to the chamber through mass-flow controllers (model 5850S, Brooks Instruments) and Teflon[®] lines.

Concentrations of limonene were determined by gas chromatographic (GC) analysis of samples collected on stainless steel adsorbent tubes containing 200 ± 1 mg Tenax TA 60–80 mesh (Chrompack,

The Netherlands). The samples were thermally desorbed (Perkin–Elmer ATD 400) into a Hewlett–Packard 5890 GC equipped with flame ionization (FID), and mass selective detection (MS, HP MSD 5972). The capillary column BPX-5 (5% phenyl polysilphenylene-siloxane, SGE), 50 m, 0.32 mm i.d., 1.0 μm film thickness, was placed in the chromatographic oven that was temperature programmed from 60 °C for 2 min, 4 °C min⁻¹ to 150 °C, 8 °C min⁻¹ to 300 °C, hold time 2 min. The injector temperature was set to 280 °C. The carrier gas was ultra-high purity helium. Calibration of the FID was performed by injection of μl-amounts of limonene-in-methanol standards onto adsorbent tubes that were then analyzed in the same way as the samples.

Ozone was generated by UV O₃ generators (HydroAir Bath and Spa Ozonator 20-5133 or UltraViolet Products, SOG-3) operated on air. The concentration of O₃ was monitored by a 42 M O₃ instrument (Environnement, France). The O₃ monitor was calibrated against the NIST Standard Reference Photometer at the Bureau International des Poids et Mesures in Paris, France.

Particle number concentration and size distribution were monitored as a function of time using several instruments. A scanning mobility particle sizer (SMPS) consisting of a TSI model 3085 Differential Mobility Analyzer with a TSI 3080 analyzer coupled to a TSI 3010 condensation particle counter (CNC) was used to determine number size distributions. The SMPS is maintained and calibrated on a routine basis. The CNC was operated with a temperature difference between saturator and condenser of 25 °C, giving a lower size detection limit of around 5 nm. The SMPS measured number/size distributions from 5 to 100 nm using 180 s up-scans and a total scan time of 240 s. A “stand alone” CNC (TSI, model 8525, P-Trak) measured total number of particles as 1 min average. According to the technical description, this instrument measures particles with $d > 20$ nm. In addition, an optical particle counter (TSI model 3313, MetOne) was employed to measure particle numbers in the size intervals 0.3–0.5, 0.5–1, 1–3, 3–5 and 5–10 μm. By combination of data from the three instruments it was also possible to estimate particle concentrations in the size range 100–300 nm.

The experiments were conducted as follows: the chamber was purged with clean air corresponding to at least 10 chamber volumes. Background concentrations of O₃, limonene and particles were

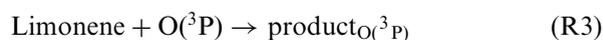
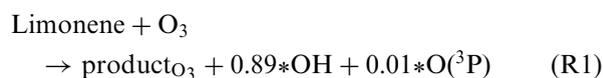
measured before introduction of the reactants. In the 14 m³ chamber, limonene was introduced by evaporating known amounts of the pure liquid into a stream of air that was led into the chamber. Ozone was introduced either as one short injection of air containing several ppm of O₃, or by a continuous low flow of ~5 L min⁻¹ of air containing 600 ppb of O₃. The contribution of the ozone-containing airflow to the ACR in the chamber was negligible (~0.02 h⁻¹). Care was taken to avoid local high concentrations of the reactants. This was done by thoroughly mixing the first component into the chamber air. The second component was then added close to the mixing fan to achieve fast dilution. The O₃ concentration was monitored as 1 min averages. The size distribution and number concentration of the particles formed were followed by the P-Trak instrument and the SMPS system.

In the 1 m³ chamber, O₃ was first added in a flow of 2 L min⁻¹ containing 200–300 ppb ozone until its concentration reached the desired value and then the flow was stopped. Limonene from a diffusion device emitting 4.2 μg min⁻¹ was then added in a 1–2 L min⁻¹ flow of air during 2–15 min to give the desired concentration in the chamber. The emission rate of limonene from the diffusion tube sources was determined by periodic weighing. The experiment was then followed as described above.

The office used for the experiments had a volume of 22 m³ and an ACR of ~2 h⁻¹. The room was not manipulated in any way; the only difference from normal was the presence of the P-trak particle counter and the O₃-monitor. The O₃ concentration attained a value determined by the outside concentration and the ventilation system transmission. The concentration of limonene was determined as described above. Limonene was introduced in the indoor air by peeling one orange or by mopping the floor with a water solution of the cleaning agent, prepared according to the instructions on the product label. The cleaning agent is a popular brand used for all-purpose cleaning of hard surfaces (kitchens, bathrooms, floors, etc.). Limonene is listed among the active ingredients on the product label and its main function is to contribute to the pleasant “lemon scent” when used. The terpene is present at the 0.01% (~100 μg limonene/1 g undiluted agent) level, analysed by GC/FID as a methanol solution. Details of the experimental conditions are presented in Table 1.

2.1. Modeling

The time development of O₃, limonene- and product concentrations were calculated by a simple numerical model by using known O₃ and limonene source fluxes and loss rates through chemical reaction. The wall deposition rate of O₃ and chamber air exchange rate were measured in separate experiments and accounted for in the calculations. The following reaction scheme for limonene and O₃ reaction was used:



with rate coefficient $k_{\text{R1}} = 2.95 \times 10^{-15} \times e^{(-783/T)} \text{ cm}^3 \times \text{s}^{-1} \text{ molec}^{-1}$ (Khamaganov and Hites, 2001) with T in K. The hydroxyl and oxygen radicals that are produced in R1 have reaction rate constants $4.2 \times 10^{-11} \times e^{(401/T)}$ and 7.19×10^{-11} for (R2) and (R3), respectively, five orders of magnitude larger than (R1). Reactions (R2) and (R3) are therefore rate limited by the radical production in (R1). Formation of large secondary ozonides and hydroperoxides from stabilized Criegee intermediates (SCI) is a process that may explain nucleation of new particles (Ziemann, 2003). According to this hypothesis SCI would be proportional to the nucleation rate. At the same time SCI can react with water vapor and CO to form non-nucleating products, making the nucleation rates also proportional to the inverse of the air humidity. We have used information about SCI as described in the reaction mechanism of Leungsakul et al. (2005) and derived Eq. (1) from branching ratios as a simple measure of products that may nucleate.

$$[\text{SCI}] = 0.0015 \times [\text{product}_{\text{O}_3}] + 0.00015 \times [\text{product}_{\text{OH}}] \quad (1)$$

Calculated concentrations of O₃ and limonene were compared with measurements and found to agree well. In this way, ozone and limonene sources, as well as wall deposition and leakage of the chamber were verified and concentration of lumped product ($\text{product}_{\text{ox}} = \text{product}_{\text{O}_3} + \text{product}_{\text{OH}} + \text{product}_{\text{O}(\text{}^3\text{P})}$) in the chamber was calculated.

Table 1
Conditions for the individual experiments

Experiment number	Chamber, m ³	Limonene determination	P-trak	SMPS	T, °C	RH, %	[Ozone], ppb	[Limonene], ppb	Particles formed, #cm ⁻³
1	14	GC	+	+	22	~30–35	5.7	27.3	13 000
2	14	GC	+	+	22	~30–35	4.8	16.3	280
3	14	GC	+	+	22	~30–35	9.8	15.0	7300
4	14	GC	–	+	24	~35	5.9	11.0	1340
5	14	GC	+	+	24	~35	10.9	59.7	25 790
6	14	GC	+	+	24	~35	5.6	29.0	11 400
7	14	GC	+	+	24	~35	2.0	25.0	1600
8	14	GC	+	+	24	~35	5.0	12.0	1600
9	1	Calculated	+	–	23	20	23.0	28.7	20 680
10	1	Calculated	+	–	23	20	22.2	27.3	28 950
11	1	Calculated	+	–	23	20	24.3	3.6	430
12	1	Calculated	+	+	23	20	35.7	8.8	47 060
13	1	Calculated	+	–	23	20	13.1	2.5	250
14	1	Calculated	+	–	23	20	41.8	9.9	44 000
15	1	GC	–	+	23	20	23.6	14.2	49 300
16	1	GC	+	+	23	20	89.3	17.9	104 433
Orange	Office	GC	+	–	n.d.	n.d.	8.8	367	134 550
Orange	Office	GC	+	+	25	30	11.6	163	149 400
Orange	Office	GC	+	+	25	30	9.0	343	189 000
Cleaning agent	Office	GC	+	+	25	30	13.4	5.2	600

Chambers are assigned by volume; ozone was monitored in all experiments; in several cases the particle number concentration was measured using only either P-trak or SMPS (+ measured, – no data). Concentration of limonene was determined by GC/FID (GC) or it was calculated from the permeation rate. In experiments 6–8 ozone was added continuously. Initial concentrations of ozone and limonene, and maximum particle number concentration. Particles formed = peak concentration–background concentration. n.d. = not determined.

3. Results and discussion

3.1. Comparison between instruments

The instrument intercomparison was necessary because the P-trak instrument was used as a substitute for the SMPS that was not always available. According to the manufacturer's specifications, a P-Trak is expected to count particles with $d > 20$ nm. When comparing P-Trak data e.g. in Exp. 1 with the time development of number concentrations in various size intervals from the SMPS (Fig. 1), it appears that the P-Trak signal has a greater similarity to the 15 nm SMPS-signal than to the 20 nm SMPS-signal. The best linear fit between P-Trak and size-discriminated SMPS-data occurs for particles larger than 12 nm ($R^2 = 0.995$, $d > 20$ nm, gives $R^2 = 0.52$). Thus, the P-Trak instrument detects particles formed in these specific experiments, down to around 12 nm with great efficiency. The slope of the regression line, i.e. the factor by which P-Trak data should be scaled to coincide with SMPS-data, is 1.38. However, the slopes were found to vary between 1.2 and 2.9, with a tendency towards higher values, i.e. less P-Trak

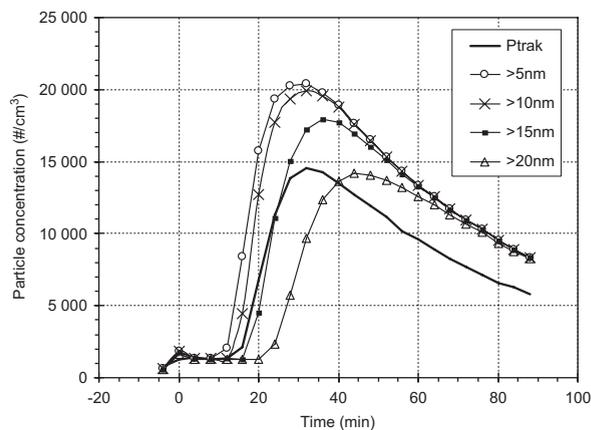


Fig. 1. Particle concentrations measured during experiment no. 1. The diagram shows particle concentrations in selected size intervals calculated from the SMPS-instrument together with the concentration measured by the P-Trak.

sensitivity, at high concentrations (Fig. 2). In experiments where the total particle concentration measured by the SMPS exceeded 100 000 particles cm⁻³, the P-Trak measured increased concentrations of particles even before the formation of particles larger than 12 nm was observed by the SMPS.

This indicates that the P-Trak is sensitive to particles even smaller than 12 nm. A possible cause could be a slight difference in the steepness in the size/detection efficiency curves between the two instruments.

The concentration of particles with a diameter larger than 300 nm, either present in the chamber background or produced by the experiment, was investigated with a MetOne optical particle counter during ten experiments. The contribution of such particles to the particle number and mass concentration was negligible.

3.2. Particle formation

Table 1 presents the experimental conditions, initial concentrations of limonene and ozone and particle number concentrations for the individual experiments. The first type of experiment had both reactants injected into the chamber at the beginning of an experiment (exp. 1–5, 9–16 cf. Table 1). In the second type, an initial injection of limonene was followed by a continuous flow of O₃ into the chamber (exp. 6–8). This strategy produces data e.g. suitable for future model validation.

The temporal development of mixing ratios of gases, number concentration and particle size distributions during the two types of experiments, is shown in Fig. 3. After mixing at time $t = 0$ in the first type of experiment, measurable particle formation begins after an induction time (Fig. 3a) during which time O₃ is lost and gaseous products build up. Nucleation begins, the number concentration reaches a maximum and then drops off. The size

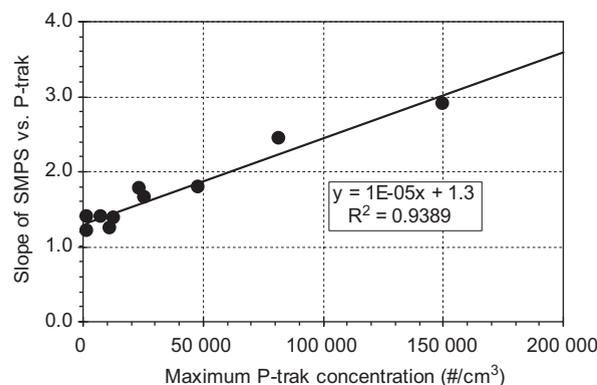


Fig. 2. Slopes of the regression lines obtained when fitting SMPS data for particles with $d_p > 12$ nm to P-Trak data plotted against the maximum particle number concentration in experiment measured by P-Trak.

distribution (Fig. 3b) shows an initial, rapid growth that is reduced concurrently with reduced nucleation rate. Both effects are a result of the falling concentrations of limonene and O₃, thus limiting product formation. In the second type, both nucleation and growth continues during a long part of the experiment (Fig. 3c and d). The rate of reaction (R1) is able to maintain the necessary supersaturation of nucleating compound since the number concentration increases, and at the same time supply material for the particle growth that continues during the experiment. Fig. 3b and d are typical examples of the particle size distributions for all the experiments and they confirm that particles in the ultrafine size region < 100 nm were formed.

The behavior seen above is typical for nucleation of new particles in particle free air. As soon as new particles are formed, they grow by condensation of low volatility reaction products in parallel with continued nucleation. After some time, the particles have grown into the range of instrument sensitivity. As number concentration goes up, the reaction products are, at increasing rate, removed from the gas phase by condensation, slowing down the new particle formation. At the same time, the rate of formation of products decreases as the precursors react away. Also coagulation of particles gradually starts to contribute to particle growth while the number concentration is decreased by this process. Wall loss and slow air leakage out of the chamber are additional loss processes. After some time the loss start to dominate over the sources (Fig. 3a and b).

The maximum number of particles (Table 1) was correlated to initial [O₃]*[limonene] (i.e. proportional to initial product formation rate) in Fig. 4a. Comparable data (static experiments) from Koch et al. (2000) and Nøjgaard Kleno et al. (2006) are plotted in the diagram, and show rather good agreement considering the diversity of experiments. Fig. 4b shows the maximum particle number concentration vs. the initial [O₃]*[limonene] close to the origin. A logarithmic function was fitted to the data ($max. particles = 20482 \times \ln(O_3 \times limonene) - 85195$, $R^2 = 0.67$) and was used to provide an average maximum particle number.

If there is a substantial excess of limonene indoors, a likely event e.g. when household products are used, then the O₃ will be rapidly consumed and further reaction of first generation products cease. However, if there is an excess of O₃, then the system would run out of limonene and there would be

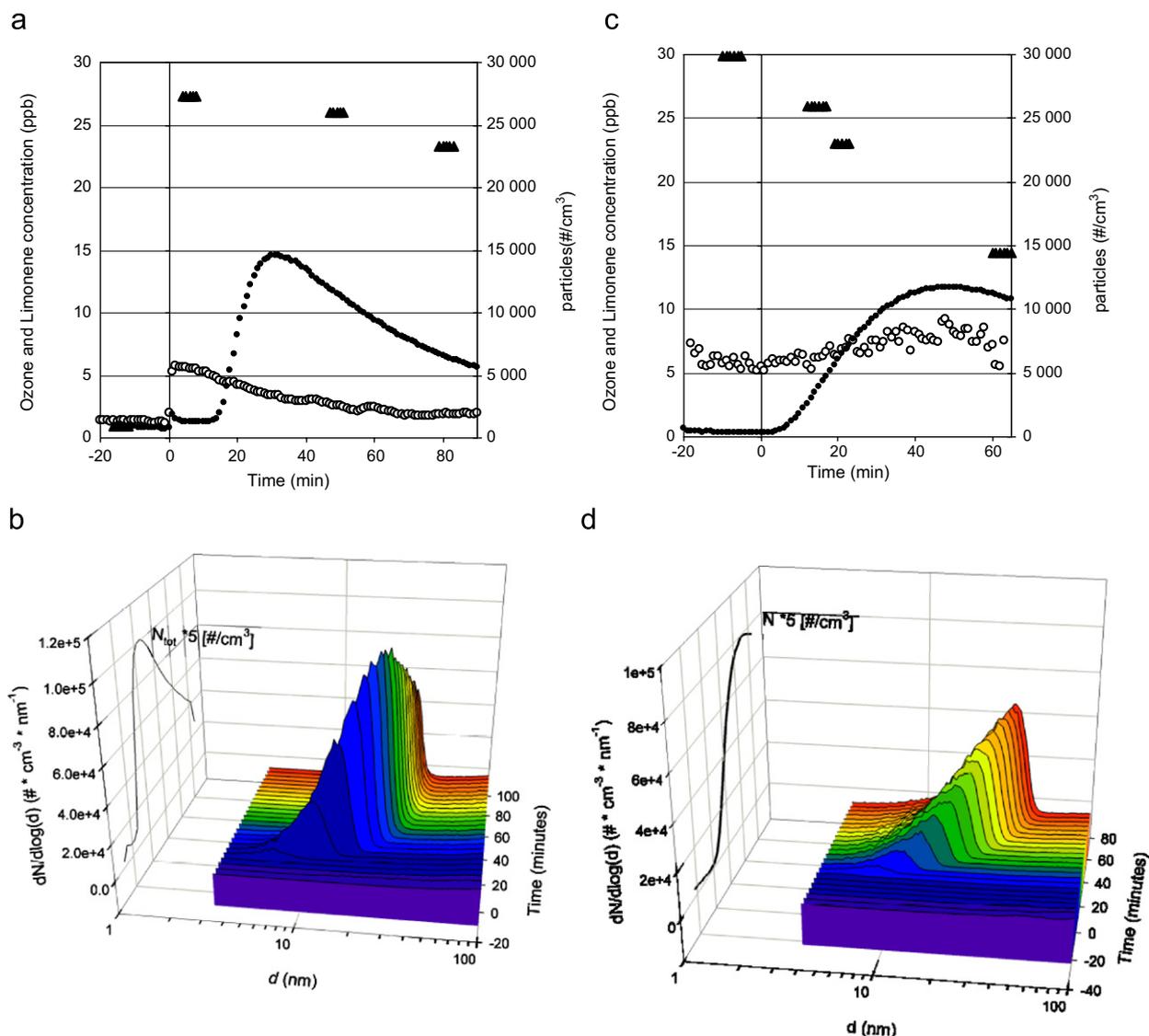


Fig. 3. Temporal development of mixing ratios of ozone (open circles), limonene (triangles), and of total concentration of particles measured by the P-Trak instrument (filled circles) in: a—experiment with instantaneous injection of ozone (data from experiment no. 1), c—continuous injection of ozone (data from experiment number 6). Development of particle number distributions in time (SMPS data) with the total particle concentrations–time development on the YZ plane, b—instantaneous injection (corresponds to a) and d—continuous ozone injection (corresponds to b). Ozone addition starts at time = 0. Note the background O₃ concentration in the chamber.

enough O₃ to attack the second, remaining double bond in the first generation products, either in the gas phase or through heterogeneous reaction (e.g. Zhang et al., 2006). The product distribution and thus the aerosol properties would therefore be expected to differ between the two cases. The data points in Fig. 4b laying below the “average” line have [O₃]/[limonene] ratios <1 while the points laying above the line have ratios >1. This is consistent with the hypothesis that excess O₃ will be attacking the remaining double bond in first

generation product molecules and producing second generation, low volatility products that also nucleate particles.

New particle formation according to the kinetic theory (e.g. Laakso et al., 2004) needs a certain supersaturation of the nucleating product to form particles with size large enough to overcome the critical Kelvin diameter. The main products from the limonene-O₃ reaction have been identified and appear not to fulfill the criteria for homogeneous nucleation (Atkinson and Arey, 2003). Candidate

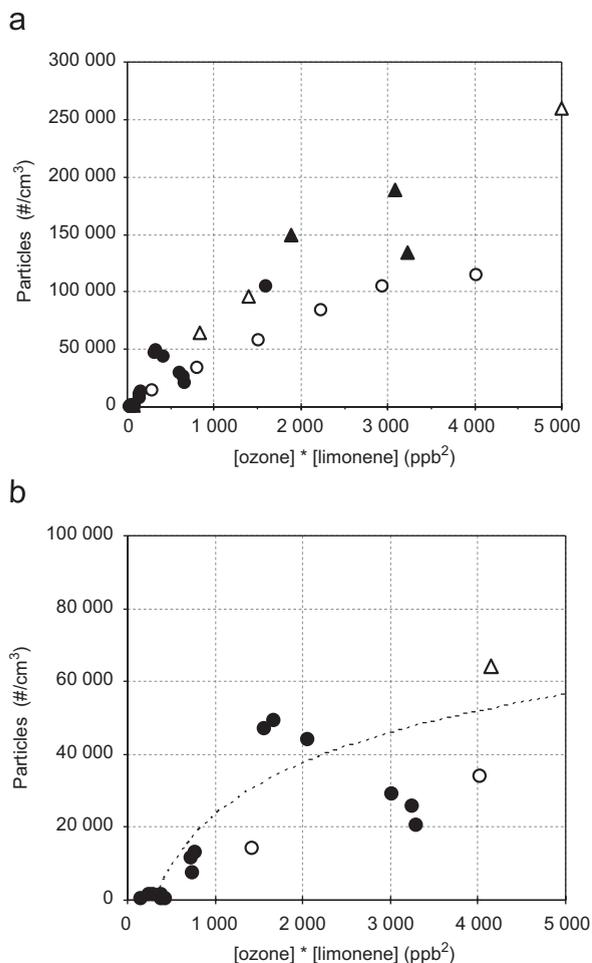


Fig. 4. Maximum particle number concentrations plotted against product of initial ozone and limonene mixing ratios. Filled circles—chamber experiments, filled triangles—orange or cleaning agent experiments, open circles—data published by Nøjgaard Kleno et al. (2006), open triangles—data published by Koch et al. (2000); (a) all data and (b) initial part of the diagram for [ozone*limonene] < 1000 ppb².

species for nucleation are estimated to have equilibrium vapor pressures of the order of 10^{-11} – 10^{-10} bar (Koch et al., 2000; Moldanová and Ljungström, 2000; Ziemann, 2003; Leungakul et al., 2005). Thus, it is concluded that the first generation nucleating species are formed in low yield in a side reaction of (R1). Di- or tri-substituted C₉–C₁₀-compounds could have the required properties, especially if two of the substituents are carboxylic acid- or hydroperoxy groups.

There is not enough information available about the identity of low-yield, low vapor pressure products to warrant an attempt to set up a detailed particle formation model. However, an attempt to

predict the particle formation by calculating the mixing ratio of the lumped reaction products $\text{product}_{\text{ox}}$ from reaction (R1)–(R3) at the time of observation of new particles was made using the simple model (experimental section). As a hypothesis we would expect that the nucleation of new particles appears when the $\text{product}_{\text{ox}}$ exceeds a certain threshold concentration product_0 . The value of the threshold concentration product_0 obtained in experiments was scattered between 0.5 and 4 ppb. Fig. 5 shows positive correlation of product_0 to the rate of formation of SCI as defined by Eq. (1). The increase of product_0 values at higher initial concentration of reactants, and consequently higher rate of formation of SCI, can most likely be explained by the time delay between the actual time of particle formation and the time when these particles are first registered by the SMPS instrument: At higher rates of $\text{product}_{\text{ox}}$ and SCIs formation more gaseous product is formed before the particles, more numerous than in a low rate of SCIs formation case, grow by condensation to the diameter observed by the instrument. Three experiments did not give any particles and have product_0 between 0.5 and 1.5 ppb. Taking experimental uncertainties and model simplification into account, significant nucleation appears to start when the mixing ratio of product_0 exceeds 0.5–1 ppb at RH ~20%. It is suggested that this rather easily evaluated criterion may be used to decide if significant aerosol formation is expected.

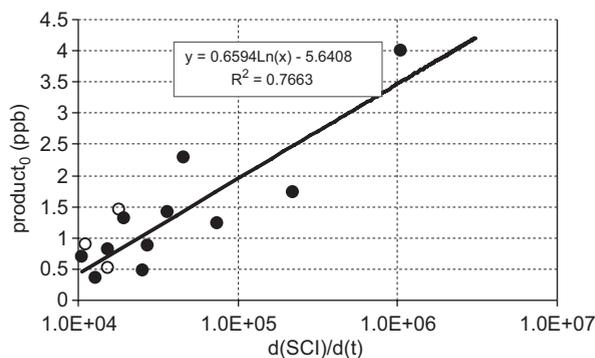


Fig. 5. Mixing ratio of the reaction product from (R1) in the chamber, calculated by the model at the time of observation of new particles; product_0 plotted against the rate of increase of nucleating SCIs (filled circles) and maximum mixing ratio of product_0 plotted against the maximum rate of increase of SCIs in experiments that did not give new particle formation (open circles).

4. Implications for indoor air and conclusions

The next-to-unavoidable experiments to see if the laboratory results apply also to “real life” were made in an office. The measured O_3 concentration was around 10 ppb resulting from an outdoor concentration of around 30 ppb that is typical for winter-time, rural southern Sweden. Such an everyday activity as peeling (and consuming) an orange gave rise to a number concentration exceeding those observed in any of the experiments as presented in Fig. 6 (cf. Table 1). The increase is transient and the particle concentration decreased to its original indoor level in about 1 h. The concentration decrease is mainly caused by the ventilation but also by wall loss and coagulation. At the onset of nucleation, $product_0$ was calculated to ca. 1 ppb, in good agreement with the criterion given above. The much-discussed effect of cleaning products in connection with particle formation (e.g. in Nazaroff and Weschler, 2004; Liu et al., 2004; Singer et al., 2006b) is illustrated in another example. The detergent was diluted according to the instructions and after wet mopping the floor in the office, the increase in the limonene-mixing ratio was moderate, ~ 5 ppb. The increase in particle concentration was very small, ~ 600 particles cm^{-3} (Fig. 7). Here, the calculated mixing ratio of $product_0$ was calculated to around 0.3 ppb, indicating that no large increase in particle concentration should be expected. This

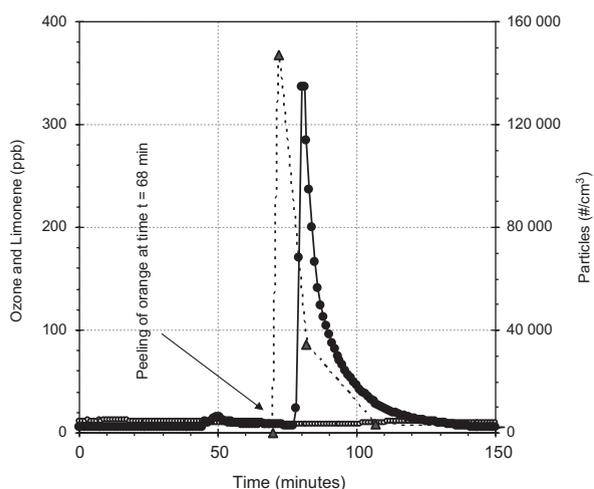


Fig. 6. Particle formation in an office room as a result of peeling an orange in presence of indoor ozone. Particle number concentration was measured by the P-Trak instrument. Open circles: ozone, filled circles: particles, filled triangles: limonene.

means that using this limonene source under typical Scandinavian winter conditions does not necessarily cause elevated particle concentrations.

The office used for the experiments had 1000–4000 particles cm^{-3} as a background value while O_3 mixing ratios were between 5 and 20 ppb during 1 week in November/December 2006. During summer, the concentration can reach 50 ppb.

Thus, when the concentration of limonene is increased sufficiently, the particle number concentrations increase by a factor of 10–20 over the typical background levels. The increase is of transient character due to ventilation and particle coagulation and deposition processes. Typical realistic indoor air concentration of limonene of < 10 ppb and of 10–20 ppb O_3 will produce ultrafine particles although at relatively low concentrations. The contribution of ultrafine particles from the O_3 /limonene reaction is not significant to the total mass load of particulate matter indoors. However it will add to the long-term exposure of humans to ultrafine particles.

There is large amount of work published on indoor formation of fine and ultrafine particles from reaction between limonene and O_3 (cf. Section 1). In some cases, however, the initial concentrations of the reactants cannot reasonably be considered as “indoor realistic”. Other referenced investigations are not comparable with this work as the experiments were performed in ventilated chambers.

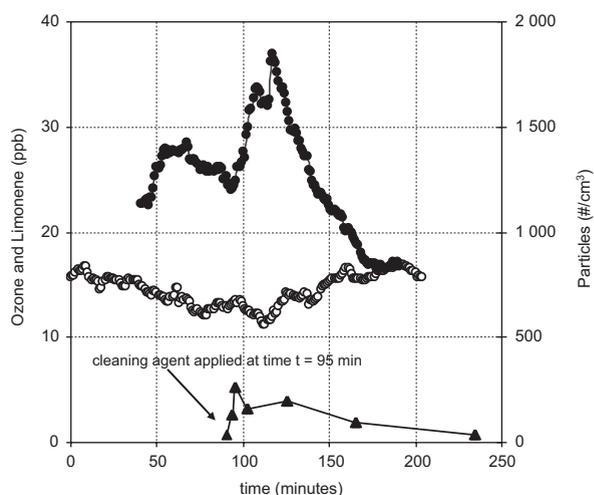


Fig. 7. Particle formation in an office room as a result of application of the cleaning agent in the presence of indoor ozone. Particle number concentration was measured by the P-Trak instrument. Open circles: ozone, filled circles: particles, filled triangles: limonene.

The present work falls in the low-concentration end, both when initial reactant concentrations and resulting maximal particle concentrations are concerned.

The experiments clearly show that nucleation and growth of particles take place from the O₃/limonene reaction, even at the low levels of reactants used in the present study. The formation rate is strongly dependent on reactant concentration and, less strongly so on the O₃/limonene ratio. Thus, there is a good possibility that particles formed from secondary reactions in indoor air may contribute to human everyday exposure to particles. Even if the contribution from the secondary organic particles to the indoor particle levels is not very large, there is certainly an issue of low-dose long-term exposure to be considered.

Since the precise product distribution, identity of minor products and relevant rate coefficients for describing the reactions are largely unknown, it is impossible today to set up a detailed model of the particle formation. However, with the information presented here and in earlier studies, it should be possible to construct a simple, parameterized model to predict aerosol formation and likely concentration ranges, given source strengths of reactants and ACRs of the space considered.

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