Coating of Soot and (NH₄)₂SO₄ Particles by Ozonolysis Products of α -Pinene

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Abstract

The ozonolysis of α -pinene in a large aerosol chamber was used to generate secondary organic aerosol (SOA) mass by homogeneous nucleation, or by heterogeneous nucleation, either on soot, or on (NH₄)₂SO₄ seed aerosols. The rate of the α -pinene + ozone reaction and the aerosol yield of ~19% are in good agreement with literature data. The organic coating of soot particles leads to a compaction of the fractal agglomerates expressed by an increase in fractal dimension from 1.9 to 2.1 for Diesel soot, and from 2.0 to 2.3 for spark generated “Palas” soot. The dielectric coating of the soot particles with SOA layers between 2 to 11 nm gives rise to a substantial enhancement of their single scattering albedo, from about 0.2 to 0.5, and increases the effective absorption coefficients of both soot types by ca. 30%. The coating of both soot types increases the hygroscopic growth factors (HGF) to values close below the HGF measured for pure SOA material ($d/d_0 \sim 1.12$ at 90% RH).

Keywords: Aerosol coating, secondary organic aerosol, optical and hygroscopic properties

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1. Introduction

Non-methane volatile organic compounds (NMVOC) are emitted in large quantities from vegetation. Total annual global emissions of biogenic volatile organic compounds (BVOC) are estimated to range from 491 to 1150 Tg C (Müller, 1992; Fehsenfeld et al., 1992; Guenther et al., 1995). Isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), and sesquiterpenes ($C_{15}H_{24}$) comprise the majority of these emissions. The reactions of monoterpenes and sesquiterpenes with OH, O_3 , and NO_3 yield secondary organic aerosol (SOA) mass in highly variable yields. SOA is believed to make up a large fraction of the aerosol over tropical continental regions (Andreae and Crutzen, 1997). For most terpenes, nighttime oxidation by ozone produces significantly higher aerosol yields than the photooxidation at daytime, which is dominated by reactions with OH radicals (Hoffmann et al., 1997; Griffin et al., 1999a). While Andreae and Crutzen (1997) estimated that the global BVOC-derived SOA mass ranges between 30 to 270 Tg/yr, more recent estimates have narrowed this range down to 13 - 24 Tg/yr (Griffin et al., 1999b) and to 61 - 79 Tg/yr (Kanakidou et al., 2000). The dominant SOA forming compounds are monoterpenes of which α -pinene is the most abundant (Geron et al., 2000). Therefore the oxidation of α -pinene has been subject of many recent studies, making it one of the best investigated terpenes. Rate constants for the reactions of OH, O_3 and NO_3 with α -pinene (Atkinson, 1997; Aschmann et al., 1998; Khamaganov and Hites, 2001), the products of the reactions (Alvarado et al., 1998; Christoffersen et al., 1998; Calogirou et al., 1999; Glasius et al., 2000; Yu et al., 1999; Kückelmann et al., 2000; Koch et al., 2000), and their SOA yields (Hatakeyama et al., 1989; Odum et al., 1996; Hoffmann et al., 1997, 1998; Griffin et al., 1999a; Kamens et al., 1999) have been studied intensively, and have led to the development of models describing the formation of SOA (Barthelmie and Pryor, 1999; Jenkin et al., 2000, Pankow et al., 2001; Seinfeld et al., 2001). The ozonolysis of α -pinene is supposed to be one of the major atmospheric sources of SOA. To our knowledge only one other study (Leach et al., 1999) has been done so far in which soot particles were coated with products of the α -pinene ozonolysis. That study focussed on the gas to particle partitioning of semivolatile organic compounds using soot and SOA from the α -pinene + ozone reaction as particle phases.

Organics influence the interaction of aerosols with water vapour in the atmosphere (Novakov and Penner, 1993; Saxena et al., 1995; Shulman et al., 1996). E.g., an organic coating on relatively hydrophobic soot aerosol particles may make them less hydrophobic, thus enhancing their ability to act as cloud condensation nuclei (CCN). Furthermore the optical properties of internally mixed black carbon and non-absorbing (e.g. organic carbon)

aerosol particles differ from those of their external mixtures. They depend mainly on the source and the ageing of initially emitted soot particles (Lioussé et al., 1993, 1995, and 1996). For example, the coating of soot particles with $(\text{NH}_4)_2\text{SO}_4$ is supposed to increase their effective mass absorption coefficient significantly (Fuller et al., 1999).

The aim of the organic coating experiments during the AIDA soot characterisation campaign 1999 was to study the impact of organic coatings on the structure, the optical properties, and the hygroscopic properties of the seed particles. We chose the ozonolysis of α -pinene as a source of SOA because of its atmospheric relevance, and because this is one of the best investigated systems so far.

2. Experimental and Modelling

The AIDA aerosol chamber and its instrumentation are described in two companion papers (Saathoff et al., 2003 a; Schnaiter et al., 2003). The coating experiments were done always in the following sequence: First, the chamber was filled with particle-free humidified synthetic air (~ 45 % relative humidity (RH) at 297 K); second, soot or ammonium sulphate aerosol was filled into the chamber using either two graphite spark generators (GfG 1000, Palas), a 4 cylinder turbo Diesel engine (TDI), or an ultrasonic nebulizer (GA 2400, Sinaptec) using a 0.09 M $(\text{NH}_4)_2\text{SO}_4$ solution; third, the seed aerosol was characterised; fourth, the particles were coated *in situ* by reacting α -pinene with a large excess of ozone. Fifth, the coated aerosol was characterised as described in the following paragraph.

Number concentrations of particles larger than 7 nm were measured continuously with two condensation nuclei counters (CNC 3022A, TSI) and size distributions were measured with a scanning mobility particle sizer (DMA 3071 & CMC 3010, TSI). Samples for total carbon / elemental carbon analysis were collected on preheated quartz fibre filters ($\varnothing$ 47 mm, MK 360, Munktell / $\varnothing$ 25 mm, Schleicher Schüll), and were analysed with coulometric technique (TC) (Coulomat 702, Ströhlein) and a thermal method (Lavanchy et al. 1999). Aerosol extinction was determined periodically at 473 nm by means of an external White type optical cell (75 m folded path length, sensitivity $\sim 10^{-5} \text{ m}^{-1}$). The cell was run in series with a 5 m long optical flow tube which covered the spectral range 230 - 1000 nm at 2.5 nm spectral resolution (sensitivity $\sim 10^{-4} \text{ m}^{-1}$), and with an integrating nephelometer (3563, TSI) which yielded scattering and backscatter parameters at 450 nm, 550 nm, and 700 nm (Schnaiter et al., 2003). Absorption coefficients were determined by analysing filter samples with the integrating plate method (Horvath, 1997). The photoelectron emission charging (222 nm) of soot particles was measured with a photoelectric aerosol sensor (PAS 2000, EcoChem, Bertscher and Siegmann,

1994). This method is highly sensitive to the state of the surface, for example to material adsorbed on the particle surface. A number of studies have shown that ambient particles originating from incomplete combustion of hydrocarbons exhibit the highest photoelectric yield and may, therefore, be selectively detected. For details see (Baltensperger et al., 2001). The active surface area of soot particles was measured with a diffusion charger (LQ1-DC, Matter Engineering AG). This instrument uses a corona discharge to generate ions in the carrier gas. The ions attach to the surface of the particles which are collected in an electrically insulated filter (Matter et al., 1999; Baltensperger et al., 2001). The structure of the aerosol particles which had been collected on polycarbonate filters (47 mm, Nuclepore, type 111106, Corning), were visualised by Scanning Electron Microscopy (SEM, JSM-840, Jeol). The hygroscopic properties of the aerosol were measured with a hygroscopicity tandem differential mobility analyser (HTDMA) (Weingartner et al., 2002). Briefly, in this instrument, the aerosol is first dried to a low relative humidity ($RH < 5\%$) and fed into the first differential mobility analyzer (DMA) where particles of a certain "dry" size are selected ($d = d_0$). After exposure to higher RH (typically $RH = 85$ to 90%), the new particle size distribution is determined with a second DMA combined with a condensation particle counter (CPC), and hygroscopic growth factors (HGF, d/d_0), defined as the ratio of the humidified diameter d to the dry diameter d_0 , are deduced. To ensure a constant temperature within the entire HTDMA system, both DMAs as well as the humidifier are submersed in a water bath at $T = 19^\circ\text{C}$. The applied SMPS technique enabled a precise measurement of the growth factors with a time resolution of 5 min.

After characterising the seed aerosol in the AIDA chamber, about 500 ppb ozone and subsequently (61 ± 3) ppb α -pinene were added by evaporating (5.1 ± 0.2) hPa α -pinene (99%, Aldrich) into a 1-liter glass bulb, and flushing the contents into the chamber with 10 SLM synthetic air for 3 minutes. The end of the flushing procedure marked $t = 0$ on the relative time scale of this series of experiments. Ozone was generated with a silent discharge generator (Semozon 030.2, Sorbios) in pure oxygen (99.999%, Messer Griesheim). The concentrations of α -pinene, sulfate aerosol, ozone, and SF_6 which had been added as an inert dilution tracer were measured by long path FTIR spectrometry (Bruker IFS 66v, 254 m folded optical path, spectral range $4000\text{--}800\text{ cm}^{-1}$, resolution 0.125 cm^{-1}). These determinations were complemented by discontinuous *ex situ* measurements with a commercial ozone monitor (Environment O₃-41M).

The reaction of ozone with α -pinene yields products with very low vapour pressures like pinic acid, pinonic acid, hydroxy pinonaldehyde, and other oxygenated compounds (Yu et al.,

1999). These can either condense on seed particles, or form new particles by homogeneous nucleation, or both, depending on the rate of product formation and the surface area density of the seed aerosol. The experimental data were analysed with an updated version of the aerosol physico-chemical simulation code COSIMA (Naumann and Bunz, 1992; Naumann, this issue) which accounts for the dynamics of fractal particles, their optical properties, and homogeneous as well as heterogeneous chemistry in the aerosol chamber. In the current version a constant volume fractal dimension D of the soot particles had to be assumed. Therefore, a detailed dynamical modelling of the restructuring process induced by the organic coating was not yet possible. However, an improved version of the COSIMA code is under development, which will allow the volume fractal dimension D to be treated as a time-dependent function.

3. Results and discussion

The following results pertain to experiments N° 6 – 10 of the soot characterisation campaign, cf. Table 3 of (Saathoff et al., 2003 a). The initial ozone concentration at $t = 0$ was 500 ppb in all experiments except in experiment N° 7 where it was 385 ppb. The temperatures during these experiments ranged from 296.1 to 297.6 K. The rate constant of the reaction $\text{O}_3 + \alpha\text{-pinene} \rightarrow \text{products}$ is $8.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 1997). Since ozone was always in large excess, the α -pinene concentrations were observed to decrease nearly exponentially with half-lives in the order of 10 minutes. The known or estimated properties of the seed aerosols used in the following experiments as well as their modifications caused by the *in situ* ozonolysis of 61 ppb α -pinene are listed in Table 1.

3.1 New particle formation in the absence of seed aerosol

During experiment N° 10 500 ppb ozone were added to particle-free humidified synthetic air in the AIDA chamber 36 minutes prior to the injection of α -pinene. Reactions of ozone with unknown impurities gave rise to the formation of 10^5 cm^{-3} very small particles, cf. Figure 1, which eventually grew into the detectable size range of the scanning mobility particle sizer (SMPS) (15 - 763 nm). The volume and surface area concentrations of these particles were negligible. After the addition of 61 ppb α -pinene the particle number concentration increased almost instantaneously to almost $2 \times 10^5 \text{ cm}^{-3}$, and a nucleation mode at about 60 nm mobility equivalent diameter was formed, cf. Figure 1 and 2. The particles grew subsequently to diameters of about 110 nm forming a bi-modal size distribution due to coagulation and the ongoing heterogeneous nucleation. The particle surface area and volume which were

calculated from the measured number size distributions passed through maximum values of $(35 \pm 7) \text{ cm}^2 \text{ m}^{-3}$ about 20 minutes after the addition of α -pinene, and of $(5.8 \pm 1.7) \times 10^{-5} \text{ cm}^3 \text{ m}^{-3}$ about 20 minutes later. Fitting the measured aerosol volume V with the function $V = V^0 \times (a/(b-a)) \times (e^{-(at)} - e^{-(bt)})$ leads to an estimate of the formed aerosol volume of $65 \times 10^{-6} \text{ cm}^3 \text{ m}^{-3}$. The losses of potential SOA material to the chamber wall can be neglected since the pseudo first order rate of SOA mass formation of about $1/a = 1.4 \times 10^{-3} \text{ s}^{-1}$ is much faster than the upper limit of the wall loss rate for a typical SOA molecule (185 g/mol; 500 pm diameter) of 10^{-4} s^{-1} . This limiting wall loss rate was estimated from the value measured for N_2O_5 , a species exhibiting a high sticking probability, by adjusting the molecular mass while assuming diffusion controlled conditions. The density ρ of the SOA material can be estimated by comparison with compounds such as pinic acid diethyl ester ($\rho = 1.0104 \text{ g cm}^{-3}$), cyclopropanedicarboxylic acid diethyl ester ($\rho = 1.062 \text{ g cm}^{-3}$), or octanedionic acid diethyl ester ($\rho = 0.9811 \text{ g cm}^{-3}$) (Lide, 1999) to be in the order of $\rho = 1 \text{ g cm}^{-3}$. This implies a SOA yield of about $65 \mu\text{g m}^{-3}$. The fractional aerosol yield Y was defined by Odum et al. (1996) as the fraction of the reactive organic gas (here α -pinene) that is converted to aerosol: $Y = \Delta M_{\text{aerosol}} / \Delta M_{\alpha\text{-pinene}}$. Compared to the reacted amount of $61 \text{ ppb} = 343 \mu\text{g m}^{-3}$ α -pinene the $65 \mu\text{g m}^{-3}$ of SOA correspond to an aerosol yield of about 19%, in good agreement with Griffin et al. (1999a) and Yu et al. (1999). However, the temperature in their experiments (308 K) was about 10 K higher. A 10 K decrease in temperature is estimated to increase SOA yields by 20-150%, depending on the assumed evaporation enthalpy (Sheehan and Bowman, 2001). The good agreement with our data may be explained by the fact that Griffin et al. (1999a) measured the size distributions at about 298 K, thus comparable to our conditions. According to Seinfeld et al. (2001) and Cocker et al. (2001) the RH used in our experiments (43 – 35%) should have only a small effect on the SOA yield and thus it should be comparable to the results of Griffin et al. (1999a) obtained at 10% RH.

Assuming an average carbon content of 64 % of the formed organic aerosol (calculated using the particle composition given by Jenkin et al. (2000), about $42 \mu\text{g m}^{-3}$ of particulate carbon were formed. This is much less than the carbon yield calculated from the coulometric analysis of quartz filter samples of $(85 \pm 26) \mu\text{g m}^{-3}$ right after the nucleation event, and of $(49 \pm 15) \mu\text{g m}^{-3}$ 12 hours later (Saathoff et al., 2003 b). The large discrepancy is attributed to the adsorption of semi-volatile ozonolysis products on the quartz fiber filters, which are included in the total carbon determination although they do not contribute to the SOA mass.

The optical properties of the formed SOA in the 230 – 1000 nm range are discussed by Schnaiter et al., 2003. A single scattering albedo of 1 was found for the visible spectral

region, reflecting the non-absorbing nature of the SOA. FTIR spectra of the SOA could not be recorded due to the strong water vapour bands in the spectral range where carboxylic acid functionalities are expected to absorb.

The hygroscopic properties of size-selected SOA particles were measured with the HTDMA operating at $RH \leq 85\%$. In this experiment the RH in the 2nd DMA was continuously changed which allowed measuring humidograms for decreasing and increasing RH conditions. (see Weingartner et al., 2002 for more information). No broadening of the monodisperse size distribution during water uptake was observed, indicating an internally mixed SOA aerosol with homogeneous hygroscopic properties. Figure 3 shows that the $d_0 = 100$ nm particles were characterised by a continuous increase of the HGF with increasing RH. This is in good agreement with the picture of SOA particles consisting of supercooled liquid organic solutions. A clear absence of efflorescence (for $RH > 10\%$) was also observed in a field campaign (Weingartner et al., 2002) where the hygroscopic properties of aged free tropospheric particles were investigated. Whether the absence of efflorescence of the free tropospheric aerosol is caused by organic components or by a mixture effect only is still an open question. However, since no efflorescence was observed for pure SOA particles, SOA might contribute to a distinct reduction of efflorescence RH of atmospheric particles.

It is clearly seen in the inset of Figure 3 that in the early stage of SOA formation the SOA particles showed increasing hygroscopicity with increasing residence time t in the chamber. Freshly produced particles with $t < \sim 2$ h were characterised by significantly lower HGF than the aged particles, indicating that the composition of the SOA particles varies during the first two hours of α -pinene oxidation. At $t = 6$ h, a $HGF = 1.106 \pm 0.002$ (for $d_0 = 100$ nm and $RH = 85\%$) was measured, which remained constant to the end ($t = 12$ h) of the experiment. Particles with $d_0 = 200$ nm which appeared at $t > \sim 4$ h exhibited the same HGF (not shown in Figure 3). Overall, the measured HGF values are in fairly good agreement with measurements performed at an outdoor smog chamber (~ 200 m³) in Valencia, where SOA particles with $d_0 = 50 - 120$ nm produced by ozonolysis of α -pinene experienced an average HGF of 1.070 ± 0.002 at 84.1 % RH (Virkkula et al., 1999).

3.2 Coating of (NH₄)₂SO₄ aerosol particles

Experiment N° 8 was done in the same way as experiment N° 10 except that about 710 $\mu\text{g m}^{-3}$ (NH₄)₂SO₄ seed aerosol was present when the reaction of α -pinene with ozone occurred. Figure 4 shows the initial (NH₄)₂SO₄ size distribution with a peak at 450 nm. As can be seen in Figures 4 and 5 the particle number concentration increased rapidly from 8×10^3 cm⁻³ to

$2.6 \times 10^4 \text{ cm}^{-3}$ when 61 ppb α -pinene were added, and a nucleation mode at about 80 nm was formed. This shows that new particle formation was not completely suppressed by the seed aerosol, although an order of magnitude less new particles were formed than in the absence of seed particles. The peak of the nucleation mode shifted eventually from 80 nm to 110 nm. Furthermore, the peak of the $(\text{NH}_4)_2\text{SO}_4$ mode shifted from 450 to 480 nm due to condensation of SOA mass on the seed particles, which dominate the available surface area in spite of the larger number density of the nucleation mode particles. Integration of the volume distribution reveals that about 82% of the formed aerosol volume condensed on the seed aerosol. Figure 5 shows the evolution of the aerosol volume during this coating experiment. From this plot we can estimate (see above) that about $6.8 \times 10^{-5} \text{ cm}^3 \text{ m}^{-3}$ ($68 \mu\text{g m}^{-3}$) of SOA were formed, which is in good agreement with experiment N° 10 (cf. Table 1). Before the coating process started the seed aerosol surface area density was calculated from the measured number size distribution to $(22 \pm 4) \text{ cm}^2 \text{ m}^{-3}$. Distributing the SOA volume homogeneously over this surface leads to an average coating thickness of about $(25 \pm 13) \text{ nm}$. The error was estimated using an uncertainty for the SOA volume of $\sim 30\%$.

Figure 6 a) shows the temporal evolution of the measured HGF during this experiment where, in contrast to the former experiment, the RH was kept constant at $\sim 90.5\%$. At $t < 0$ the uncoated $d_0 = 100$ and 200 nm $(\text{NH}_4)_2\text{SO}_4$ particles experienced a $\text{HGF} = 1.56$ and 1.65 , respectively at $\text{RH} = 90.5\%$. The values at $d_0 = 100 \text{ nm}$ are by $\sim 7\%$ lower than the ones reported by Gysel et al. (2002), which may be due to an unknown contamination of the small $(\text{NH}_4)_2\text{SO}_4$ particles. The measured HGF for freshly emitted $(\text{NH}_4)_2\text{SO}_4$ particles at $d_0 = 200 \text{ nm}$ agree well with theory. After the coating the formerly monomodal growth distribution of the $d_0 = 100 \text{ nm}$ particles transformed into a distinctly bimodal growth distribution, and the two modes are referred to as less and more hygroscopic modes (LHM and MHM). For $d_0 = 200 \text{ nm}$ particles the growth distributions remained monomodal, i.e. only a more hygroscopic mode was present. This difference can be explained as follows: The nucleation mode particles remained mainly smaller than $d_0 = 200 \text{ nm}$, and therefore no external mixture is seen in this size channel. For $d_0 < 200 \text{ nm}$ the coating leads to mixed more hygroscopic $(\text{NH}_4)_2\text{SO}_4/\text{SOA}$ particles which are externally mixed with less hygroscopic "pure" SOA nucleation mode particles. As already seen in experiment 10 an increase in hygroscopic growth of the SOA particles (LHM, $d_0 = 100 \text{ nm}$) was observed mainly within the first 1 – 2 hours after starting the α -pinene oxidation. At $t = 6 \text{ h}$ a HGF of $d/d_0 = 1.121$ at $\text{RH} = 90.3\%$ was measured, which agrees well with SOA particle hygroscopicity from Experiment 10 (Figure 3).

Since HGFs are known for pure SOA particles as well as for the uncoated $(\text{NH}_4)_2\text{SO}_4$ particles and the coated $(\text{NH}_4)_2\text{SO}_4$ particles, one can estimate the volume fraction of the organic coating. Assuming spherical particles and independent additive hygroscopic behaviour of the different components in the mixed particle the volume V of a coated particle at a certain RH is given by

$$V = Gf_1^3 \cdot V_1 + Gf_2^3 \cdot V_2, \quad (1)$$

where the subscripts 1 and 2 stand for the “pure” SOA and $(\text{NH}_4)_2\text{SO}_4$ material, V_1 and V_2 are the corresponding dry volumes, and Gf_1 and Gf_2 the growth factors of the individual substances. From this it follows that the SOA volume fraction ε_1 in the coated particles is given by

$$\varepsilon_1 = \frac{Gf_2^3 - Gf_{\text{mix}}^3}{Gf_2^3 - Gf_1^3}, \quad (2)$$

where Gf_{mix} denotes the growth factor of the coated particles. Volume fractions ε_l calculated with eq. 2 are shown in Figure 6 b) for particles with $d_o = 100$ and 200 nm. Gf_l ($d_o = 100$ nm) is used for particles with $d_o = 200$ nm also, since no large SOA particles were observed in Experiment 8. Two hours after the addition of α -pinene the estimated SOA volume fractions for $d_o = 100$ and 200 nm particles are $\varepsilon_l = 41 \pm 8$ and 28 ± 10 %, respectively. These uncertainties were calculated by error propagation from the uncertainty of the measured growth factors. Dividing the SOA yield by the initial $(\text{NH}_4)_2\text{SO}_4$ mass concentration (see Table 1), gives an upper limit for the average SOA mass fraction of $\sim 10\%$. The volume fractions of $\varepsilon_l = 41 \pm 8$ and 28 ± 10 % corresponds to a SOA mass fraction of 28 ± 5 and 18 ± 6 % for 100 nm and 200 nm particles, respectively, assuming a SOA density of 1 g cm^{-3} . This is not inconsistent because particles larger than 400 nm in diameter give the main contribution to the aerosol mass, and the condensed volume fraction decreases with increasing particle size. The estimated SOA volume fractions correspond to coating thickness of 8 ± 2 and 10 ± 4 nm for 100 -nm and 200 -nm particles, respectively. (see Table 1). The difference to the average value of 25 ± 13 nm (see Table 1) may arise from the fact that the hygroscopicity measurement was done on the edge of the coated particle size mode and from the inaccuracy of the model assumption (independent additive behaviour). Indeed, strong interactions in binary inorganic-organic (e.g. $(\text{NH}_4)_2\text{SO}_4$ with pinonic acid which is a typical product of α -pinene-ozone reactions, see above) particles were observed in recent studies using the HTDMA (Cruz et al., 2000), and the electrodynamic balance technique (Choi et al., 2002). Especially for $(\text{NH}_4)_2\text{SO}_4$ - organic acid mixtures experimental hygroscopic growth factors were often larger than the theoretical value based on the assumption of independent additive

behaviour. Such a positive interaction may also be the reason for the underestimation of the coating thickness in this experiment.

Open questions are the effects of organic compounds on the efflorescence (ERH) and deliquescence relative humidity (DRH) of mixed inorganic-organic particles. Various phenomena have been reported by Cruz et al. (2000), Lightstone et al. (2000), and Choi and Chan (2002). At the end of this experiment ($t > 12\text{h}$) the RH dependence of the HGFs under increasing RH conditions was investigated. Observed HGFs ($d_0 = 200\text{ nm}$) were smaller than 1.03 for $\text{RH} < 70\%$, i.e. the $(\text{NH}_4)_2\text{SO}_4$ remained solid and the small water uptake is attributed to the hygroscopic growth of the SOA coating. At $\text{RH} \geq 80\%$ coated particles were completely deliquescent similar to pure $(\text{NH}_4)_2\text{SO}_4$ particles ($\text{DRH} = 80\%$, Gysel et al., 2002). Although in the RH range $70\% < \text{RH} < 80\%$ no measurements of HGFs are available one can still conclude that a possible reduction of the DRH by the organic coating is smaller than 10%. The effect of the organic coating on the ERH was not investigated.

3.3 Coating of Diesel soot aerosol particles

In experiment N° 7 (78 ± 23) $\mu\text{g C m}^{-3}$ Diesel soot and 385 ppb ozone were present in the AIDA chamber when 61 ppb α -pinene were added. Three hours of prior interaction with initially 500 ppb ozone had changed the surface properties of the Diesel soot particles significantly, as evidenced by the increase of oxygen-containing hydrocarbon fragments in the particle mass spectra which are presented in the companion paper of Kirchner et al. (2003). The change in surface properties caused a decrease of the photoemission signal from 2200 to 650 fA. However, the influence of the ozone soot interaction on the hygroscopic and optical properties of the Diesel soot particles was negligible.

Diesel soot aerosol offers a significantly larger specific surface area than the ammonium sulphate seed aerosol of experiment N° 8. Typical Diesel exhaust particles have specific surface areas of about $100\text{ m}^2\text{ g}^{-1}$ (Kittelson, 1998). For example, the standard reference material 2975 (Diesel particulate matter) of the National Institute of Standards & Technology (NIST) has a certified specific surface area of $91\text{ m}^2\text{ g}^{-1}$ determined by N_2 adsorption (BET method). However, this specific surface area must be clearly distinguished from the active surface area which is measured by the diffusion charger. To take this into account we used the measured size distribution and mass concentration of the seed aerosol as input for the COSIMA model (Naumann, 2003) and calculated the accessible or active surface area of Diesel soot to $60\text{ m}^2\text{ g}^{-1}$ (cf. Table 1). Comparing this value with the signal of the diffusion charger led to a calibration factor of $\sim 5.2 \times 10^{-7}\text{ cm}^2\text{ cm}^{-3}\text{ fA}^{-1}$ for Diesel soot aerosol.

As evidenced in Figure 7, dramatic changes in most of the measured aerosol parameters occurred when α -pinene was added to the Diesel soot - ozone mixture. Besides new particle formation a significant amount of oxidation products of α -pinene must have condensed on the Diesel soot particles. This is concluded from the fact that the volume density of the nucleation mode of $(12\pm6)\times10^{-6} \text{ cm}^3 \text{ m}^{-3}$ accounted for only about 18 % of the expected SOA yield of $65\times10^{-6} \text{ cm}^3 \text{ m}^{-3}$ (assumed to be similar as in the two reference experiments N° 8 and 10), and is in sharp contrast to the observed shift of the Diesel soot mode from 245 nm to 222 nm after the coating event. The decrease of the mobility equivalent particle diameter results from the compaction of the fractal soot agglomerates, due to capillary forces exerted by the SOA which forms a supercooled liquid coating. The compaction is confirmed by electron micrographs of particles collected before and after the coating event (Figure 8) and by the significant narrowing of the Diesel particle mode (Figure 7): the mode width decreased from $\sigma = 1.67$ before to $\sigma = 1.34$ after the coating event.

The compaction can also be expressed in terms of fractal dimensions of the Diesel soot particles before and after the coating event: the COSIMA model calculates an increase of the fractal dimension from $D = 1.9$ to $D = 2.1$ upon coating. The value for the initial fractal dimension agrees perfectly with the one reported by Nelson et al. (1990) and Harris and Maricq (2002), but is lower than found by Weingartner et al. (1997) possibly due to the use of different Diesel engine types with different exhaust gas treatment and different operation conditions.

Figure 9 shows a comparison of COSIMA calculations of aerosol mass, surface, and number concentration with measured values. The parameters used for the COSIMA calculations are summarised in Table 2. The calculation for the uncoated Diesel soot aerosol was initialised 3.6 hours before the coating event, assuming $D = 1.9$ as determined from experiment N° 2 (Wentzel et al., 2003). The calculation for the coated Diesel soot was started 3.2 hours after adding α -pinene to the aerosol assuming that the coating process was completed. The initial monomer diameter of 22.0 nm was increased with a coating layer of 8.3 nm to 38.6 nm, assuming that 82% of the low volatile oxidation products had condensed on the surface of the soot particles, see above. The fractal dimension of the compacted soot particles was determined by taking advantage of the fact that the mobility equivalent diameter of a fractal-like cluster is related to its number of monomers and thus to its mass by a scaling law in terms of D (Naumann, 2003). The mass concentration related to the soot mode of the size distribution was estimated to be $123 \mu\text{g m}^{-3}$ by continuing the COSIMA calculation for the uncoated aerosol to 3.2 hours and adding a SOA coating of $53 \mu\text{g m}^{-3}$. Transforming the

soot mode of the measured mobility size distribution into a size distribution based on the number of monomers and comparing its average bulk density weighted integral with the estimated mass concentration then uniquely fixes the value of the fractal dimension to $D = 2.1$, leaving no adjustable parameter for the COSIMA simulation.

Figure 10 shows a 95% decrease of the photoemission signal of Diesel soot compared to the signal before the coating event. This indicates that the SOA coating significantly reduces the probability of photoelectron emission. Also shown in Figure 10 is the aerosol surface area measured by the diffusion charger (DC). Note that the instrument exhibited a problem: the signal started to decrease each time the instrument was switched from particle-free reference air to aerosol from the AIDA chamber although the surface area of the particles was essentially constant. However, this does not invalidate the following observation: during the coating process the signal increased almost instantaneously by about $2 \text{ cm}^2 \text{ m}^{-3}$. This indicates that the emerging surface area of the nucleation mode overcompensated the loss of Diesel soot surface area due to compaction of the particles. Calculating the surface area from the size distribution measured 35 minutes after the coating process yields a surface area density of about $9 \text{ cm}^2 \text{ m}^{-3}$ for the nucleation mode. Therefore we estimate an active surface area density loss due to the compaction of the soot agglomerates of about $7 \text{ cm}^2 \text{ m}^{-3}$. This value is perfectly reproduced by the COSIMA simulations.

As shown by Schnaiter et al. (2003), the coated particles scattered more like Mie-type particles and exhibited a strongly enhanced extinction coefficient. Figure 11 shows furthermore that the coating led to a strong increase of the single scattering albedo from about 0.2 to 0.5, as well as to a change in the wavelength dependence of the scattering coefficient and to a 30-% increase of the absorption coefficient. The latter effect has been predicted in model calculations, e.g. by Fuller et al. (1999), and Jacobson (2001). Aethalometer measurements by Weingartner et al. (2003) are also consistent with an absorption increase of the coated Diesel soot particles by 30-40%. The initial rise of the backscatter ratio and of the Angström exponent is attributed to the compaction of the soot agglomerates. This is followed by condensational growth, as evidenced by the subsequent decrease of the backscatter ratio and the Angström exponent.

The temporal evolution of the measured HGF of uncoated and coated Diesel soot particles at $(89.7 \pm 0.5) \% \text{ RH}$ are shown in Figure 12. Uncoated diesel soot particles show a hydrophobic behaviour: 100-nm particles are characterised by no hygroscopic growth, whereas 200-nm particles reduce their diameter by about 1.2%. This is different to findings from another study (Weingartner et al., 1997) where freshly emitted diesel soot particles were

characterised by a slight hygroscopic growth ($d/d_o = 1.01$ for a similar fuel sulphur content). The smaller fractal dimension of the particles used in this study may favour capillary condensation in the cavities of larger aggregates, enhancing the potential for compaction of the particles.

As seen in Figure 12, the coating of the diesel soot particles leads to a sudden change of their hygroscopic properties. During this experiment the growth factor distribution at $t > 0$ remained monomodal. The addition of α -pinene leads to a significant increase of the HGF within the first hour. Particles with $d_o = 100$ showed a HGF of 1.11 at RH = 90%. Since the number concentration of the 100 nm size fraction is dominated by homogeneously nucleated SOA particles (cf. Figure 7) it is not surprising that the measured HGF is close to the value for the pure SOA particles (HGF = 1.12 at RH = 90.3%). Particles with $d_o = 200$ nm consist mainly of coated diesel soot and showed a HGF of 1.08 at RH = 90%. This increase is attributed to a reduction of the compaction potential of the dry particles (see above) and the water uptake of the SOA coating.

3.4 Coating of spark generated (“Palas”) soot aerosol

In experiment N° 9 (111 ± 34) $\mu\text{g C m}^{-3}$ of spark generated “Palas” soot and ~ 500 ppb ozone were present in the AIDA chamber when 61 ppb of α -pinene were added. As can be seen in Figure 13, and in perfect agreement with the Diesel soot experiment N° 7, the addition of ozone to “Palas” soot aerosol 15 minutes before the coating event resulted in a 70% decrease of the photoemission signal. However, a small influence of the ozone soot interaction on the hygroscopic and optical properties of the “Palas” soot particles was observed and could clearly be separated from the impact of the coating. Due to the very large surface area density of the “Palas” soot aerosol (Table 1), which exceeded that of experiment N° 7 by at least a factor of three, new particle formation was almost completely suppressed in experiment N° 9, cf. Figures 13 and 14. Helsper et al. (1993) determined the size of the primary particles to 5 nm and the specific surface area of spark generated soot to $395 \text{ m}^2 \text{ g}^{-1}$ with the BET method. For the “Palas” soot aerosol used in this investigation an average primary particle diameter of 7.3 nm was determined by Wentzel et al. (2003). Kuznetsov et al. (2003) determined the specific surface area by N_2 thermodesorption / gas chromatography to $(310 \pm 30) \text{ m}^2 \text{ g}^{-1}$. These differences may be due to different operating conditions of the spark discharge generators, which are known to influence the soot particle structure (Schwyn et al., 1988).

The active surface area of “Palas” soot was calculated with the COSIMA model (Naumann, 2003) on the basis of the measured size distribution and mass concentration to $150 \text{ m}^2 \text{ g}^{-1}$, cf. Table 1. Thus, the diffusion charger measurements could be calibrated by a factor of about $5.6 \times 10^{-7} \text{ cm}^2 \text{ cm}^{-3} \text{ fA}^{-1}$ for this soot type, very similar to the factor for Diesel soot.

Dramatic changes in most of the measured aerosol parameters were observed when α -pinene was added to the “Palas” soot - ozone mixture. The volume of the extremely weak nucleation mode was negligible in comparison with the expected SOA yield of $65 \times 10^{-6} \text{ cm}^3 \text{ m}^{-3}$ (assumed to be similar as in the two reference experiments N° 8 and 10). Condensation of this amount of SOA on the “Palas” soot seed aerosol led to a compaction of the fractal agglomerates, as evidenced by the shift of the “Palas” soot mode from 255 to 175 nm, and a concomitant narrowing of the mode from $\sigma = 1.60$ to $\sigma = 1.40$, cf. size distributions shown in Figure 14. The coating-induced change of the agglomerate structure, which is confirmed by SEM pictures shown in Figure 15, can also be expressed in terms of fractal dimensions of the “Palas” soot particles before and after the coating event. The COSIMA model calculates an increase of the fractal dimension from 2.0 to 2.3 upon coating.

Figure 16 shows a comparison of COSIMA calculations of aerosol mass, surface, and number concentration with measured values. The parameters used for the COSIMA calculations are summarised in Table 2. The calculation for the uncoated “Palas” soot was initialised 1.5 hours before coating. The calculation for the coated “Palas” soot was started 1.8 hours after adding α -pinene to the aerosol, assuming that the coating process was completed. The initial monomer diameter of 7.3 nm was increased with a coating layer of 2.1 nm to 11.5 nm following the same reasoning as for the Diesel soot coating experiment N° 7. A fractal dimension $D = 2.0$ determined from experiment N° 3 was assigned to the uncoated particles. Its increase to $D = 2.3$ due to agglomerate restructuring was determined in a manner similar to the Diesel soot case. Again there was no adjustable parameter in the COSIMA simulation of the dynamics of the coated particles.

In Figure 13 a 95-% decrease of the photoemission signal of “Palas” soot compared to the value before the coating event can be seen, confirming that the probability of photoelectron emission is significantly reduced by the SOA coating, as previously found for Diesel soot. This is why the usual linear relationship between photoemission signal and diffusion charger signal (Baltensperger et al., 2001) does not hold when the surface properties of soot particles are modified. Figure 13 shows that the active surface area measured by the diffusion charger decreased from $140 \text{ cm}^2 \text{ m}^{-3}$ to $60 \text{ cm}^2 \text{ m}^{-3}$, comparable to the value calculated from the measured number size distribution. This is a much stronger decrease in the active surface area

than had been estimated for the Diesel soot agglomerates. The result reflects the structural differences of both soot types: spark generated soot agglomerates are composed of many small monomers, while Diesel soot agglomerates consist of less but larger primary particles. For example, considering a mobility equivalent diameter of 200 nm, a Diesel soot particle is estimated to consist of about 200 monomers, and a “Palas” soot agglomerate of about 1900 monomers. These estimates are based on the formalism presented by Naumann (2003), and on the parameters listed in Table 2. Clearly, the fragile structure of “Palas” soot agglomerates gives rise to a much larger compaction potential.

Figure 17 shows the changes in optical properties induced by coating “Palas” soot aerosol with non-absorbing SOA (Schnaiter et al., 2003). The single scattering albedo increased from about 0.2 to 0.57 comparable to the Diesel soot experiment N° 7 (Fig. 11). Significant differences are also observed for the backscatter ratio and the Angström exponent. In contrast to experiment N° 7 with Diesel soot aerosol, there is no subsequent drop of the “Palas” soot backscatter ratio or Angström exponent after their strong increase at the onset of the coating process. These differences might be a result of the different compaction properties of the two soot types. Since the Angström exponent depends mainly on the size of the scatterer this behaviour might reflect the ability of partially collapsed “Palas” soot aggregates to absorb larger quantities of supercooled liquid SOA, thus inhibiting substantial growth of the particles by condensation. This interpretation is supported by a wavelength dependent drop of the backscatter ratio observed in the Diesel soot experiment N° 7 (Fig. 11) since scattering of blue light is more size-sensitive than scattering in the red part of the visible spectrum. The differences in the Angström exponent can be interpreted as well by a lower compaction and thus an earlier onset of condensational particle growth in case of the Diesel soot coating experiment. Note the different Angström exponents of uncoated Diesel and “Palas” soot aerosols in Figs. 11 and 17, which point towards different optical properties of these materials (Schnaiter et al., 2003). Particle coating increased the absorption coefficient of “Palas” soot aerosol by 30 %; comparable to the Diesel soot experiment N° 7. Aethalometer measurements by Weingartner et al. (2003) revealed an increased absorption of 30 to 60% increasing with decreasing wavelength. An absorption enhancement of a few ten percent for both types of soot due to a thin organic coating is in reasonable agreement with theoretical predictions by Fuller et al. (1999). Further details are reported by Schnaiter et al., 2003.

The structural differences between Diesel and “Palas” soot agglomerates are also seen in different hygroscopic behaviours. Figure 18 shows the temporal evolution of the measured HGF at $(90.1 \pm 0.4) \% \text{ RH}$ for uncoated ($t < 0$) and coated ($t > 0$) $d_0 = 100$ and 200 nm “Palas”

soot particles. These particles remained internally mixed after the coating. Uncoated “Palas” soot particles experienced a significantly higher restructuring than Diesel soot particles, i.e. particles with $d_0 = 100$ and 200 nm reduced their diameter by 6.8 and 8%, respectively. This behaviour is explained by the fact that “Palas” soot aggregates are composed of more primary particles having a smaller size than Diesel soot aggregates (see above). This provides more cavities for water absorption resulting in a higher restructuring. The magnitude of the observed restructuring agrees well with measurements performed by Weingartner et al. (1995), where the restructuring of “Palas” soot particles was investigated over a larger size range, and the size dependence of d/d_0 was attributed to size dependent particle morphology.

The coating of $d_0 = 100$ and 200 nm particles increased the HGF from 0.932 and 0.92 to ~ 1 and ~ 0.95 , respectively. The fact that a growth factor < 1 is measured for coated $d_0 = 200$ nm particles indicates that the compaction potential was not fully exhausted by the SOA coating.

4. Conclusions

The secondary organic aerosol (SOA) yield found in these experiments for the ozonolysis of α -pinene is in reasonable agreement with values reported in the literature. Convincing evidence has been presented that the coating of fractal soot particles with non-absorbing material, which is one of the dominant ageing processes in the atmosphere, induces important changes of the physical, hygroscopic, and optical properties of the particles: coating leads to a substantial compaction of the fractal soot agglomerates. This enhances sedimentation, but decreases coagulation rates. In our chamber experiments the airborne lifetime of coated Diesel soot aerosol decreased by about one forth compared to the COSIMA reference calculation for uncoated aggregates. The active surface area of Diesel soot particles was diminished by only about 10%. The deposition of more hygroscopic condensable ozonolysis products of α -pinene on soot agglomerates results in a increase of the growth factor at 90 % RH. This increase of the HGF corresponds to $\sim 65\%$ to 95% of the growth of pure SOA particles ($d/d_0 = 1.12$).

Being an extremely strong absorber of sunlight, atmospheric soot aerosol gives rise to significant direct positive climate forcing. According to the results presented in this study, the positive forcing calculated for e.g. external mixtures of non-absorbing material and soot may be significantly modified when the soot particles are coated with transparent material such as SOA mass: apart from increasing the single scattering albedo, particle coating was found to enhance the effective absorption cross section of soot aerosol significantly. The dependence of this important phenomenon on the thickness of the coating will be studied in the near future.

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TABLES

Table 1. Aerosol surface and coating estimates, see text for details.

Experiment N°	10	8	7	9
Seed aerosol type	none	(NH ₄) ₂ SO ₄	Diesel soot	“Palas” soot
Initial carbon mass concn. [μg m ⁻³]	-	710±70	78±23	111±34
Specific surface area [m ² g ⁻¹]	-	3	91 ^a	(310±30) ^b
Active specific surface area [m ² g ⁻¹]	-	3	60 ^c	150 ^c
Initial surface area concn.[cm ² m ⁻³]	-	22±4	(47 – 71) ^d	(167 - 342) ^d
SOA volume concn. [cm ³ m ⁻³]	6.5×10 ⁻⁵	6.8×10 ⁻⁵	~ 6.5×10 ⁻⁵	~ 6.5×10 ⁻⁵
Formed SOA mass [μg m ⁻³]	65	68	~ 65	~ 65
m _{cond.} /(m _{nucl.} + m _{cond.})	1.0	~ 0.8	~ 0.8	~ 1.0
Coating thickness ^e [nm]	-	25±13	7 - 11	2 - 4
Coating thickness (HTDMA) ^f [nm]	-	10±4	-	-

^a NIST Standard reference material 2975, 2000; ^b Kuznetsov et al., 2003; ^c Naumann, 2003; Xiong et al., 1992 ; ^d based on Fuchs and BET surface area, respectively, ^e condensed SOA volume / initial surface area, ^f for d₀ = 200 nm particles.

Table 2. Parameters used in COSIMA calculations.

Exp. N°	Soot type	Fractal Dimension	Monomer Diameter [nm]	Volume filling factor	Density [g cm ⁻³]	Overlap factor
7	Diesel	1.9	22.0	1.05	1.7	0.15
7	Coated Diesel	2.1	36.4	0.36	1.33	0.48
9	“Palas”	2.0	7.3	1.43	2.0	0 ^a
9	Coated “Palas”	2.3	11.0	0.55	1.46	0.34

^a no overlap of monomers assumed since this parameter is unknown.

FIGURE CAPTIONS

Fig. 1: Evolution of the size distribution and number concentration of the pure organic aerosol formed upon ozonolysis of α -pinene without seed aerosol in experiment N° 10.

Fig. 2: Evolution of the aerosol volume calculated from the measured size distribution during experiment N° 10. Additionally the evolution of the number concentration and the depletion of the α -pinene concentration are shown.

Fig. 3: Humidogram of SOA particles (dry diameter $d_0 = 100$ nm) produced by ozonolysis of α -pinene. The inset shows a magnification of the upper RH range and the numbers next to the points denote the ageing time (in minutes) after the addition of α -pinene.

Fig. 4: Evolution of the size distribution and number concentration of $(\text{NH}_4)_2\text{SO}_4$ and organic aerosol formed upon ozonolysis of α -pinene in experiment N° 8.

Fig. 5: Evolution of the aerosol volume calculated from the measured size distribution during experiment N° 8. Additionally the evolution of the number concentration and the depletion of the α -pinene concentration are shown.

Fig. 6.: Temporal evolution of the measured hygroscopic growth factor (HGF) of $d_0 = 100$ nm and $d_0 = 200$ nm for the less and more hygroscopic modes (LHM and MHM) during experiment N° 8 for a RH of $\sim 90.5\%$ (a). Evolution of the calculated SOA volume fraction (b).

Fig. 7: Evolution of the size distribution and number concentration of Diesel soot and organic aerosol formed upon ozonolysis of α -pinene in experiment N° 7.

Fig. 8: SEM pictures of Diesel soot before (left) and after coating (right) with α -pinene oxidation products in experiment N° 7.

Fig. 9: Evolution of measured aerosol mass, surface, and number concentrations during experiment N° 7 compared to values calculated with the COSIMA model.

Fig. 10: Evolution of the number concentration, surface area and photoelectric yield during experiment N° 7.

Fig. 11: Evolution of the single scattering albedo, Angström exponent, backscatter ratio, and absorption coefficient of Diesel soot coated by ozonolysis of α -pinene in experiment N° 7.

Fig. 12: Hygroscopic growth factor (HGF) of $d_0 = 100$ nm and $d_0 = 200$ nm Diesel soot particles vs. ageing time. The coating of the particles starts at $t = 0$. The RH responsible for this growth is also shown and lies between 89.2 and 91%.

Fig. 13: Evolution of the number concentration, surface area and photoelectric yield during experiment N° 9.

Fig. 14: Evolution of the size distribution and number concentration of “Palas” soot and organic aerosol formed upon ozonolysis of α -pinene in experiment N° 9.

Fig. 15: SEM pictures of “Palas” soot before (left) and after coating (right) with α -pinene oxidation products in experiment N° 9.

Fig. 16: Evolution of measured aerosol mass, surface, and number concentrations during experiment N° 9 compared to values calculated with the COSIMA model.

Fig. 17: Evolution of the single scattering albedo, Angström exponent, backscatter ratio, and absorption coefficient of “Palas” soot coated by ozonolysis of α -pinene in experiment N° 9.

Fig. 18: Temporal evolution of hygroscopic growth factors (HGF) of $d_0 = 100$ nm and $d_0 = 200$ nm “Palas” soot particle (left axis). The coating of the particles starts at $t = 0$, and a $HGF < 1$ is attributed to a shrinking of the particles. The actual RH at the measurement of d is also shown and lies between 89.8 and 90.5% (right axis).

Fig.1

Fig. 2

Fig. 3

Fig.4

Fig.5

Fig.6

Fig.7

Fig. 8

Fig.9

Fig.10

Fig.11

Fig.12

Fig.13

Fig.14

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Fig.16

Fig.17

Fig.18