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Secondary organic aerosol formation from acetylene (C_2H_2): seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase

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Abstract

The lightest Non Methane HydroCarbon (NMHC), i.e. acetylene (C_2H_2) is found to form secondary organic aerosol (SOA). Contrary to current belief, the number of carbon atoms, n, for a NMHC to act as SOA precursor is lowered to $n=2$ here. The OH-radical initiated oxidation of C_2H_2 forms glyoxal (CHOCHO) as the highest yield product, and >99% of the SOA from C_2H_2 is attributed to CHOCHO. SOA formation from C_2H_2 and CHOCHO was studied in a photochemical and a dark simulation chamber. Further, the experimental conditions were varied with respect to the chemical composition of the seed aerosol, mild acidification with sulphuric acid (SA, $3<\mathrm{pH}<4$), and relative humidity ($10<\mathrm{RH}<90\%$). The rate of SOA formation is found enhanced by several orders of magnitude in the photochemical system. The SOA yields (Y_{SOA}) ranged from 1% to 20% and did not correlate with the organic mass portion of the seed, but increased linearly with liquid water content (LWC) of the seed. For fixed LWC, Y_{SOA} varied by more than a factor of five. Water soluble organic carbon (WSOC) photochemistry in the liquid water associated with internally mixed inorganic/WSOC seed aerosols is found responsible for this seed effect. WSOC photochemistry enhances the SOA source from CHOCHO, while seeds containing amino acids (AA) and/or SA showed among the lowest of all Y_{SOA} values, and largely suppress the photochemical enhancement on the rate of CHOCHO uptake. Our results give first evidence for the importance of heterogeneous photochemistry of CHOCHO in SOA formation, and identify a potential bias in the currently available Y_{SOA} data for other SOA precursor NMHCs. We demonstrate that SOA formation via the aqueous phase is not limited to cloud droplets, but proceeds also in the absence of clouds, i.e. does not stop once a cloud droplet evaporates. Atmospheric models need to be expanded to include SOA formation from WSOC photochemistry of CHOCHO, and possibly other α-dicarbonyls, in aqueous aerosols.

1 Introduction

Secondary Organic Aerosol (SOA) formation is linked with debates about air quality, visibility, public health, climate, and the oxidative capacity of the atmosphere. Recent experimental findings indicate SOA contributes about 30–60% of the organic component of the aerosols (OA) in urban air, and >70% of OA in rural air and the free troposphere (Zhang et al., 2007). The contribution of SOA to aerosol optical depth (AOD) is estimated to be larger than that of primary organic aerosol (POA) or black carbon (BC) (Tsigaridis et al., 2006). This contribution is likely to increase as (1) current models significantly underestimate SOA production in large and very different compartments of the atmosphere (Heald et al., 2005; de Gouw et al., 2005; Volkamer et al., 2006), (2) current models assume the mass absorption cross-section (MAC) of OA to be zero, while laboratory and field evidence consistently suggests that OA absorbs light (Kirchstetter et al., 2004; Sun et al., 2007; Barnard et al., 2008), and (3) air quality regulations should result into a reduced contribution of sulphate in the future, while SOA precursor emissions are very poorly characterized (Volkamer et al., 2006) and could continue to increase disproportionately compared to sulfate (Tsigaridis and Kanakidou, 2007; Heald et al., 2008). Notably different models agree with respect to the importance of biogenic VOCs for SOA formation on regional and global scales (Griffin et al., 1999; Kanakidou et al., 2000; Chung and Seinfeld, 2002; Lack et al., 2004; Tsigaridis et al., 2006; Henze et al., 2008). These model results are also in general agreement with ^{14}C measurements of organic aerosols at background sites in the US (Klinedinst and Currie, 1999; Bench et al., 2007; Schichtel et al., 2008) and in Europe (Szidat et al., 2006; Lanz et al., 2007; Gelencser et al., 2007). While model predicted and observed SOA tend to agree better in biogenic environments (Tunved et al., 2006), field observations using highly time resolved measurements show no correlation between enhancements of organic aerosol mass and biogenic VOC precursors (de Gouw et al., 2005; Sullivan et al., 2006; Weber et al., 2007), but show an excellent correlation with anthropogenic pollution tracers (de Gouw et al., 2005; Volkamer et al., 2006; Sullivan et al., 2006; Weber et al., 2007). This presents a currently unresolved conflict with the ^{14}C measurements.

SOA is defined as the organic aerosol mass formed in the atmosphere by gas-to-particle partitioning of semivolatile products of the atmospheric oxidation of organic vapors. In the widely established view, partitioning theory (Pankow, 1994a) is employed to describe the partitioning of semivolatile organic vapors only between the gas-phase and the organic fraction of aerosol mass (including the aerosol water attracted into that phase from the hygroscopic properties of SOA) (Seinfeld and Pankow, 2003). This view uses as the key input the vapour pressure of gas-phase oxidation products, which decreases with the number of carbon-atoms of the precursor. Early work suggested the existence of a threshold in the number of carbon atoms, n=7, for a precursor to form SOA (toluene forms SOA, benzene does not) (Pandis et al., 1992). However, more recent experimental studies find SOA formation from benzene (n=6) (Martin-Reviejo and Wirtz, 2005) and isoprene (n=5) (Claeys et al., 2004). Some SOA models have also considered partitioning of SOA species to an aerosol water phase (Pun et al., 2003; Griffin et al., 2005). These models only consider the dissolution of the gas-phase reaction products, do not treat aqueous chemistry explicitly, and the mass fraction of SOA that partitions in this way is typically a few percent of the total SOA; the predominant SOA source in current models is from semivolatile vapors.

SOA formation from acetylene (C_2H_2, i.e. n=2), the lightest non-methane hydrocarbon (NMHC), questions volatility of the gas-phase oxidation products as the only controlling parameter of SOA formation. C_2H_2 oxidation products are at least 6 orders of magnitude too volatile to explain partitioning to aerosols based on physical processes alone (i.e. condensation, absorption). These differences are too large to be explained by organic aerosol activity coefficients, which are thought to modify effective vapor pressures by less than one order of magnitude (Bowman and Melton, 2004). However, C_2H_2 efficiently forms glyoxal (CHOCHO) upon oxidation by OH-radicals. In Mexico City, C_2H_2 oxidation accounts for about 8% to the overall CHOCHO source (Volkamer et al., 2007). An increasing body of experimental evidence (Karpel vel Leitner and

Dore, 1997; Schweitzer et al., 1998; Blando and Turpin, 2000; Sorooshian et al., 2006; Loeffler et al., 2006; Carlton et al., 2007) suggests the processing of CHOCHO and CHOCHO precursors in cloud and fog droplets is an important source for SOA (Ervens et al., 2003; Lim et al., 2005; Warneck, 2005; Ervens et al., 2008). CHOCHO uptake to aerosols forms an alternative pathway for SOA formation in the absence of clouds. Compared to clouds, aerosols contain 3–5 orders of magnitude less liquid water, and aerosol water has therefore been easily rejected as "too small" a volume to dissolve a significant amount of gas-phase organics. The experimental evidence for CHOCHO uptake to particles is more scarce, and far less conclusive (Jang et al., 2002; Kroll et al., 2005; Liggio et al., 2005a; Corrigan et al., 2008). Conflicting evidence exists about the magnitude and mechanism of CHOCHO uptake, as well as the role of acid-catalysis to control CHOCHO reactivity in aerosols. Recent modeling studies deem CHOCHO and methylglyoxal responsible for 5–11 $\mathrm{Tg\,yr^{-1}}$ SOA formation globally, suggesting this SOA source could be comparable to the sum of SOA formed from monoterpenes, sesquiterpenes, isoprene, and aromatics (Fu et al., 2008; Myriokefalitakis et al., 2008). More than 85% of this SOA is deemed to form in clouds, mostly at altitudes below 1.5 km (Fu et al., 2008), where aerosols are mostly aqueous.

Current state-of-the-art SOA models use empirical fits to simulation chamber data to calculate SOA yields and partitioning coefficients (Odum et al., 1997; Robinson et al., 2007). Conditions in these chambers approximate the polluted atmosphere to a considerable extent, i.e. with respect to VOC/$\mathrm{NO_x}$ ratios, $\mathrm{NO_x}$ concentrations, temperatures, the pool of condensable species produced, OH-radical concentrations, light conditions, and oxidation time-scales. However, most SOA observed in chambers is attributed to second- and higher generation oxidation products (Hurley et al., 2001; Kroll and Seinfeld, 2005), while faster SOA formation is observed in the atmosphere (Volkamer et al., 2006; Riddle et al., 2008). Little attention has thus far been paid to the possible effect of the chemical composition of seed aerosol. In particular, most chamber studies of SOA yields to date have either used no seed at all (i.e. homogeneous nucleation of SOA), or added ammonium sulfate (AS) seed to provide a surface area for condensation (Odum et al., 1997; Martin-Reviejo and Wirtz, 2005; Ng et al., 2007; Kroll et al., 2007). Experiments with water containing seed are less common, but have been used to ascertain the effect of ionic strength on the partitioning of semivolatile products (Cocker et al., 2001a, b). More recently it was demonstrated that hydrophobic organic aerosol seed does not participate in the absorption processes that underlie the current concept of vapor-pressure driven partitioning of gas-phase oxidation products to the organic aerosol phase (Song et al., 2007), further increasing the discrepancy between SOA measurements and models. There is currently no systematic study of the effect of chemical composition of seed aerosol on SOA yields.

Here we study directly the SOA formation from C_2H_2 and CHOCHO on different inorganic, organic and mixed inorganic/organic seed aerosols, in a simulation chamber under both photochemical and dark conditions. The relative humidity and chemical seed composition studied resemble an important subset of particles found in the atmosphere.

2 Experimental

Experiments were conducted in a $7\,m^3$ indoor smog chamber equipped with 64 blacklights, and made of Teflon, with a surface/volume (S/V) ratio of $3\,m^{-1}$. The experimental setup is shown in Fig. 1. The chamber was filled with dry, clean air (Aadco pure air generator, <5 ppbv of hydrocarbons, 0.1% RH), followed by vapour addition of ultrapure water (Milli Q, 18 MΩ) to the desired relative humidity (RH). For all experiments seed aerosol were added prior to the organic by vaporizing dilute salt or salt/organic solutions, and passing the aerosols via a ^{210}Po neutralizer connected to the chamber. All chemicals were purchased from Aldrich, unless otherwise noted. The solutions were made up of either pure compounds (0.1 M) or mixtures of equal mass (about 0.1 M for each solute) of AS (purity 99+%), ammonium bisulfate (ABS, Alfa Aesar, 99.9%), Suwannee River fulvic acid (FA, IHSS), Humic acid sodium salt (tech.), Glycine (>98.5%), Tyrosine (>98.5%). Succinic acid seeds were prepared from vaporizing pure compound (99+%) in a stream of clean air connected to the chamber. C_2H_2 (Airgass, grade 2.6) was further purified by passing a small flow via an acetone-slush bath held at a temperature $T=-85°C$. Concentrations of C_2H_2, CH_3ONO (Taylor et al., 1980), NO (Matheson) were determined from adding known volumes of these gases to the chamber. Typical initial concentrations were $[C_2H_2]$=20 ppm, $[CH_3ONO]$=5 ppm, [NO]=5 ppm. CH_3ONO/NO/UV-light was used to generate OH-radicals. For CHOCHO, the reversible uptake to chamber walls, mixing fans, or sampling lines, has been identified as an uncertainty if experiments are conducted over extended experiment times (Kroll et al., 2005). This uncertainty was minimized here by homogeneously producing CHOCHO inside the chamber from the photo oxidation of C_2H_2 with OH-radicals, thus eliminating the need to actively stir or mix the chamber volume, and systematically reducing experiment time. For the dark experiments authentic CHOCHO samples were prepared from flowing He through heated mixtures of glyoxal trimer dihydrate (GTD) with P_2O_5. About 1% CHOCHO/He mixtures were stable over several days if stored in the dark. The mixing ratio of the bulb was periodically checked from measuring the distinct absorption features of CHOCHO in the UV and visible spectral range, and comparison to resolution adjusted spectra of the absorption cross section of CHOCHO (Volkamer et al., 2005b), and known volumes taken from this bulb were added to the chamber. To convince ourselves that the CHOCHO concentration is reasonably constrained in our photochemical experiments, CHOCHO was measured by means of solid-phase microextraction (SPME) with on-fiber derivatization using o-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA, 98+%) (Baker et al., 2005) in selected experiments. Temperature, RH, NO, NO_y, aerosol size distributions (by Scanning Mobility Particle Sizing, SMPS), and in some experiments CO were periodically monitored over the course of an experiment. Aerosol wall loss was quantified over a period of about an hour prior to each experiment in terms of a volume loss rate τ ($\tau = \Delta \ln (V_t/V_{t=o})/\Delta t = 1.5\times10^{-5}\,\mathrm{s}^{-1}$ in Fig. 2), and aerosol wall loss was corrected in the further analysis. We measured a wall loss-rate for CHOCHO of $3.3\times10^{-5}\,\mathrm{s}^{-1}$ in our setup, or 12% change in the gas-phase CHOCHO concentration over 60 min of experiment time. This loss rate is non-negligible, and comparable to that observed by others (i.e. at EUPHORE, S/V ca. 1.3 m^{-1}, $\tau<6\times10^{-7}$ s^{-1} for dry conditions (Volkamer, 2001); at CALTECH, S/V ca. 1.9 m^{-1}, $\tau=3.2\times10^{-5}$ s^{-1} for 50% RH (Kroll et al., 2005)). Flushing the chamber and filling it with humidified clean air removed NO_y to below the detection limit (about 1 ppb; i.e. dilution factor $>10^4$). The dilution ratio was found smaller for CHOCHO, which is consistent with the release of CHOCHO from the walls, as had been observed previously (Kroll et al., 2005). This CHOCHO memory effect was quantified at 3% for the chamber cleaning procedure used between experiments. CHOCHO measurements compared reasonably well (within 30%) with simulations of the $C_2H_2/CH_3ONO/NO$/light system based on a subset of the Master Chemical Mechanism that accounted for wall-loss. The model was constrained to match the observed rate of NO-to-NO_2 conversions, and reproduced the amount of CO produced in the reaction system within 15%. Based on these model/measurement comparisons we estimate the CHOCHO concentration is known to about 30% in this study. The same model was used to calculate the amount of C_2H_2 reacted.

The experimental conditions were varied to study photochemical and dark reaction systems, and in terms of relative humidity, CHOCHO concentration, seed volume, seed chemical composition, liquid water content (LWC), and the mass of the organic portion of the seed (M_{om}), and are listed for individual experiments in Table 1. LWC of seed aerosols was calculated using an additive approach that sums the amount of water attracted from inorganic and organic components of the seed. The Aerosol Inorganic Model (Wexler and Clegg, 2002) was initiated at representative temperature and RH conditions to calculate LWC for inorganic seed components, accounting for metastable aerosols. For organic components the hygroscopic properties were taken from the literature: succinic acid (Ansari and Pandis, 2000; Peng et al., 2001), Suwannee River fulvic acid (Peng et al., 2001), AA (Chan et al., 2005); hygroscopic properties of humic acid sodium salt were approximated as those of Suwannee River fulvic acid. M_{om} was calculated from subtracting the LWC from the aerosol volume, and converting the volume portions of individual seed components based on their densities d (d_{AS}=1.77 g cm^{-3}; d_{ABS}=1.79 g cm^{-3}; d_{SucA}=1.56 g cm^{-3}; d_{FA}=1.47 g cm^{-3}; d_{HA}=1.72 g cm^{-3}; $d_{Glycine}$=1.46 g cm^{-3}; $d_{Tyrosine}$=1.46 g cm^{-3}). The SOA mass formed was calculated by multiplying the observed volume change by 1.68 g cm^{-3}, which corresponds to the density of glyoxal oligomers in the absence of water (based on the density of 40%$_{w/w}$ glyoxal aqueous solution $d_{Gly40\%}$=1.27 g cm^{-3}).

3 Results

Significant SOA mass is formed from C_2H_2 during all experiments. Figure 2 shows SOA formation for AS+FA seed (experiment #20) as an example. Grey lines indicate the size distribution of seed aerosol. A shift in the size distribution towards larger diameters was observed immediately after C_2H_2 was photochemically oxidized by OH-radicals. The number concentration of particles remained constant in all experiments presented in this work. The aerosol volume growth corresponding to this shift in the aerosol size distribution was used to quantify SOA formation.

The oxidation products from C_2H_2 are very volatile. The products formed in our reaction system are predicted by the model as summarized in Table 2. For room temperature the vapour pressure for all products is well above 1 kPa (CRC Handbook, 2003), i.e. are about 6 orders of magnitude too volatile to explain partitioning to aerosols as the result of physical processes (condensation, sorption into an organic liquid). Also shown are the respective Henry's law coefficients, or lower limits in the case of CHOCHO (Kroll et al., 2005; Sander et al., 2006). As is evident from Table 2, CHOCHO is virtually the only product that partitions to the aerosol aqueous phase; the change in the volume distribution of aqueous seed aerosols is attributed to CHOCHO uptake to the seed aerosol.

3.1 Is SOA formed via partitioning to the organic phase vs. the aqueous phase?

The SOA yield Y_{SOA} is defined as the organic aerosol mass formed divided by the mass of hydrocarbon reacted. In Fig. 3, Y_{SOA} is plotted as a function of M_{om} (panels a, c, e) and as a function of LWC (panels b, d, f). The data has been grouped by individual seed types, which are identified by specific symbols. An excellent correlation is observed between Y_{SOA} and LWC. Sufficient experiments were conducted to demonstrate that Y_{SOA} in fact scales as a linear function of LWC for AS, FA, mixed AS+FA, and ABS seeds. However, no obvious correlation was observed between Y_{SOA} and M_{om}. For example, for AS+FA seed among the highest Y_{SOA} values were observed in experiments with a particularly low M_{om}, while among the lowest Y_{SOA} values were observed at moderately high values of M_{om} (Fig. 3a). For some seed types Y_{SOA} even anti-correlates with M_{om} (e.g. ABS+FA in Fig. 3c). We take this as strong evidence that the aqueous aerosol phase is a chemical reactor for SOA formation from C_2H_2.

3.2 Dependence of SOA yields on seed chemical composition

No new particle formation was observed from the photochemical oxidation of C_2H_2. However, Y_{SOA} from C_2H_2 was non-zero on all seeds studied here. The actual value of Y_{SOA} was found a strong function of the seed chemical composition, as is evident from the considerable scatter of the plotted data points in Fig. 3: Y_{SOA} varied by a factor >20 (i.e. $0.9\% \leq Y_{SOA} \leq 19.8\%$) over the range of experimental conditions investigated. For comparable LWC, e.g. LWC=10 $\mu g\,m^{-3}$, Y_{SOA} varied by more than a factor of 5, and increased in the following sequence: AS+FA+AA (2.7%), AS+FA+AA+SA (3.2%), SucA (3.9%), AS (4.2%), AS+FA+SA (4.8%), ABS (7.3%), ABS+HA (6–21%), ABS+FA (8–17.5%), AS+FA (14.3%), FA (14.4%). For this comparison the observed linear relation with LWC was used for AS, ABS, FA and AS+FA; for AS+FA+SA available data points were interpolated; for SucA, AS+FA+AA, AS+FA+AA+SA, ABS+FA, and ABS+HA linear interpolation through zero was applied (to derive a lower limit in the latter two cases); linear extrapolation between available data points was applied for

ABS+FA, and this data was scaled for ABS+HA (to derive upper limits).

Interestingly, AS seed – by far the most widely used seed in chamber studies of SOA yields to date – showed among the lowest Y_{SOA} from C_2H_2 of any seed investigated. For aqueous AS Y_{SOA} compares to that observed for SucA. However, addition of water soluble FA had a pronounced effect on Y_{SOA} from AS. At comparable LWC, Y_{SOA} is found to be 3.5 times larger for mixed AS+FA than for AS seed (Fig. 3b). Y_{SOA} from ABS is slightly higher than for AS (Fig. 3d). However, the addition of FA (and HA) had less of an effect on Y_{SOA} for ABS than for AS. For example, at LWC=5 μg m^{-3}, the Y_{SOA} for AS+FA is about 8%, i.e. is larger than for ABS+FA (Y_{SOA}=6%), despite the fact that Y_{SOA} is higher for ABS than AS. This suggests that the relevant Y_{SOA} for mixed ABS+FA (and likely ABS+HA) may be closer to the lower limit number of the range extrapolated above.

The lowest yields are observed for seeds containing amino acids (AA) like tyrosine and glycine. Over the timescales accessible by our setup, the presence of AA reduces Y_{SOA} by a factor of 5.3 for AS+FA seed. It is important to note that this conclusion can only be drawn as the LWC for the AA studied here is well known. AA containing seed showed the largest LWC of all experiments conducted, and yielded the largest Y_{SOA} values observed (Fig. 3f). The apparent effect of AA to reduce Y_{SOA} becomes visible only after LWC has been normalized; only then Y_{SOA} is actually comparable to the other seeds studied. The apparent reduction in Y_{SOA} becomes more pronounced over longer timescales. Furthermore, mild acidification with SA leaves Y_{SOA} essentially unaffected for AS+FA+AA seed, but strongly reduces Y_{SOA} for AS+FA seed. Experiments containing AA and SA yielded Y_{SOA} values on the bottom scale of those observed. Similarly low yields were observed on SucA seed. Additional evidence on the role of acid comes from a comparison of ABS+FA and AS+FA seed. ABS behaves more acidic at lower RH, while AS is neutral at any RH. The LWC dependence of Y_{SOA} is primarily determined from varying RH in our work, and hence ABS+FA seed at LWC=3 μg m^{-3} is more acidic than at LWC=5 μg m^{-3}. Interestingly, a factor of 3.5 lower Y_{SOA} is observed for ABS+FA and ABS+HA at LWC=3 μg m^{-3}, while the difference is smaller (factor 1.5) for the less acidic conditions (Fig. 3d). We do not find evidence that would suggest higher Y_{SOA} under acidic conditions. For comparable LWC and over the timescales accessible in our setup Y_{SOA} values from AA, SA or SucA containing seed were lower than Y_{SOA} from AS seed.

3.3 The timing of SOA formation: photochemical vs dark systems

The volume growth of all seed types investigated can be categorized broadly into two types: (type A) a rapid volume growth is observed upon turning lamps ON (when using photochemical source for CHOCHO from C_2H_2 oxidation), and (type B) slow and continuous growth is observed (independent of the lamps, or in the dark when CHOCHO was added directly). The rate of volume change is found enhanced by a factor of about 200 for type A growth compared to type B growth.

Most experiments showed type A growth in the presence of light, followed by type B growth in the dark (see Table 1). This is illustrated in Fig. 4 for experiments that all used the same AS+FA seed solution. In some experiments the seed was acidified mildly by addition of AA (tyrosine and glycine), or SA to the AS+FA seed solution (pH~4 for the AS+FA+SA seed). Panel (b) shows only experiments that were conducted at different RH, and used the same AS+FA seed, while in panel (c) experiments with addition of acids are shown. The data from panel (a) was normalized in panels (b) and (c) according to Eq. (1):

$$V_{\mathrm{norm,t}} = \frac{V_t}{V_{\mathrm{seed}}} \bullet \frac{100}{[\mathrm{Gly}]_t} \bullet \frac{50}{\%\mathrm{LWC}} \qquad (1)$$

where V_t is the observed volume at time t, V_{seed} is the seed volume before the experiment, $[\mathrm{Gly}]_t$ is the CHOCHO mixing ratio in units of ppb (normalized to 100 ppb here), and %LWC is the percent contribution of LWC to total seed volume (normalized to 50% here). ($V_{\mathrm{norm,t}}-1$) hence represents the volume change in units of percent, if 100 ppb CHOCHO were present in the gas-phase at 75% RH (for AS+FA seed in Fig. 3b; 50% RH for AS, not shown). For experiments #19, #20, and #27 the conditions varied by about a factor of 2 in seed volume, a factor of 2.5 in gas-phase CHOCHO (70–171 ppb) and span a large RH range (16%≤RH≤86%), resulting in a factor of more than 6 difference in the observed volume change (see Table 1 and Fig. 4a). Interestingly, Eq. (1) fully accounts for these significant differences, and the normalized time profiles (Fig. 4b) are indistinguishable within error bars. Similarly, AS, ABS, FA, SucA, mixed ABS+FA and ABS+HA seed showed type A growth, but the absolute volume change depends on the seed type (see Sect. 3.2 below). Normalization according to Eq. (1) accounts for differences in experimental conditions in the case of AS, ABS, FA and AS+FA seed. No dependence was observed on the light level used. Experiments conducted with a factor of 6 reduced light levels gave results that are essentially identical after normalization according to Eq. (1). This demonstrates that for these seeds the photochemical volume growth scales directly proportional to the gas-phase CHOCHO concentration, and the liquid water of the seed, and further suggests that the availability of UV photons does not limit the rate of CHOCHO uptake.

A reference experiment #32 was conducted in the dark chamber, with known amounts of CHOCHO added directly to the chamber. A considerably slower growth rate, and smaller relative volume growth is observed (type B). Notably, experiments #19, #20 (and #12, #17, #26 and #27 – not shown) show a significant volume increase after the lamps were turned OFF. The normalized volume growth rate between dark periods of these experiments agrees quantitatively with that observed in the dark CHOCHO experiment #32, and confirms directly that CHOCHO is a building block for the observed SOA formation. We conclude that type A+B growth is happening for AS+FA seed at high and low RH. Similarly, ABS, FA, mixed ABS+FA and ABS+HA seed showed type A+B uptake behaviour, while AS and SucA seed only showed type A uptake, but did not show continued growth in the dark chamber. Repeated type A volume growth is observed if the lamps were turned ON consecutively, followed by type B uptake during dark periods in between, as illustrated for ABS+HA seed in Fig. 5. The type B growth rate shown here does not represent a fit to the data, but was calculated using the type B growth rate derived from Fig. 4b for AS+FA seed. Interestingly this rate does explain type B growth rates observed for ABS+HA seed as well, despite different CHOCHO and seed volume levels, reflecting that the normalization according to Eq. (1) applies also to type B growth. While type A growth is significantly lower for ABS+HA compared to AS+FA, type B growth rates seem to be controlled largely by gas-phase CHOCHO and LWC of the seed, and appear to be comparable within the measurement precision for both seed types.

Most notably, seeds containing AA like tyrosine and glycine, and/or SA did not show type A growth, despite the fact that the same photochemical system was used. The presence of these acids reduced the amount, and the rate of volume growth as illustrated in Fig. 4c. The normalized growth rate for these acidified experiments agrees reasonably well with type B growth observed for the dark periods of experiments #20 and #32 (type B growth from panel b is reproduced in panel c). We do not find an enhanced rate of volume growth for seeds that were mildly acidified with SA compared to the non-acidified seed. Seeds containing AA show a slightly faster initial volume growth, but this initial growth seems to level off over extended experiment times, and is below the type B growth rate after about 30 min experiment time. It should be noted however, that the smaller relative volume change associated with type B growth poses an experimental challenge that is not compensated easily by extended measurement times. The uncertainties from the correction of aerosol volume loss to the chamber walls and (reversible) uptake of gas-phase CHOCHO to the chamber walls then become dominant error sources. The reduction in uptake rates and relative volume changes for seeds that contained AA or SA however is beyond experimental doubt, and this observation is taken as evidence that the presence of acids reduces the amount of available water, or scavenges any excited states produced from organic photochemistry in the aerosol aqueous phase. The pronounced acceleration of the rate of volume change for neutral seeds suggests that additional CHOCHO uptake is triggered as the result of organic photochemistry in the aerosol aqueous phase. The measured Y_{SOA} number establishes as a result of competing uptake and scavenging rates of the intermediates of SOA formation in the aerosol water.

3.4 Dependence of effective CHOCHO solubility on relative humidity

Given that photochemical volume growth scales proportional to the gas-phase CHOCHO concentration, and LWC (Fig. 4b and Eq. 1), the effective solubility of CHOCHO H_{eff} was calculated from type A volume growth, and values are listed in Table 1. In experiments where also type B growth was observed, H_{eff} was calculated based on the largest volume growth observed. In experiments where type B growth did not level off, H_{eff} is listed as a lower limit number in Table 1. We calculate these H_{eff} values primarily as a means of normalization to facilitate a quantitative discussion between different seeds and experimental conditions, and do not mean to imply any conclusion about the reaction mechanism.

H_{eff} values for AS, ABS, FA and AS+FA are plotted as a function of relative humidity in Fig. 6. H_{eff} values were calculated in two ways: (1) based on the measured seed volume (black open dots) and (2) based on the portion of the seed that was LWC (solid red dots). Calculations of H_{eff} that are based on the measured seed volume give systematically lower values; those H_{eff} values further show an apparent dependence of RH. Notably, this apparent RH dependence is fully accounted after normalization of the LWC portion of the seed. Such calculation gives essentially constant and higher H_{eff} values for all seeds shown, over the entire range of RH probed. This further corroborates that LWC is a crucial quantity for determining the CHOCHO uptake to aerosols; if calculations were based on the overall seed volume the actual H_{eff} value could be underestimated by as much as a factor of 30 (for FA seed, Fig. 6b).

The effect of adding FA to AS seed is illustrated in Fig. 7. The factor of 3.5 higher H_{eff} for AS+FA seed is reflective of the higher Y_{SOA} (Fig. 3b). Interestingly, the two experiments #12 and #20 (AS+FA seed at RH>80%) showed type A+B growth that did not level off over the timescales investigated; the respective H_{eff} values in Table 1 represent lower limit values. For both experiments these lower limit values are higher than the values observed at lower RH (Fig. 7). Both experiments were conducted above the deliquescence RH (DRH) of AS, and the observed H_{eff} value is found to be approximately the sum of H_{eff} values observed for pure AS and FA seed. For experiments below the DRH of AS, H_{eff} values of mixed AS+FA seed were found essentially identical to those of pure FA seed. The higher H_{eff} value for AS+FA seed at RH>DRH deserves further investigation.

4 Discussion and atmospheric relevance

There are currently three laboratory studies that investigate the uptake of CHOCHO to aerosols in the dark (Kroll et al., 2005; Liggio et al., 2005a; Corrigan et al., 2008), and one study reporting field evidence in support of the atmospheric relevance of SOA formation from CHOCHO (Volkamer et al., 2007). Our work is unique for three reasons: (1) the widely used concept of SOA yields is linked directly to a particularly volatile CHOCHO precursor NMHC; SOA formation from C_2H_2 demonstrates directly that the current theory of SOA formation as it is widely used in atmospheric models is incomplete; (2) SOA yields from C_2H_2 show a strong dependence on the chemical composition of seed aerosols, and raise questions whether a similar dependence of SOA yields exists also for other SOA precursors; and (3) we demonstrate that organic photochemistry in the aerosol aqueous phase is needed to accelerate SOA formation from CHOCHO, and dominates over dark processes. We also observe evidence for continued chemical processing of CHOCHO in the dark, but the amounts of SOA produced, and rate of SOA formation by dark processes are much smaller than by the photochemical reactions.

4.1 Comparison with literature values

Kroll et al. (2005) derived H_{eff} based on the total seed volume, and a density of 1 g cm^{-3} for SOA from CHOCHO; both assumptions lead to an underestimate of the actual H_{eff} value. The re-evaluated H_{eff} value comparable to this work is a factor of 3.8 larger, i.e. $H_{\mathrm{eff,\,AS,\,Kroll}}=1\times10^{8}\,\mathrm{M\,atm^{-1}}$ at 50% RH. We find a 40% higher value of H_{eff} for AS in our photochemical system, but the rate of CHOCHO uptake is enhanced by 2–3 orders of magnitude in our photochemical system. Notably the CHOCHO uptake kinetics for AS followed type A growth over the range of relative humidity conditions studied; no type B growth was observed in the following dark period of experiments. This is in contrast to the continued growth observed over several hours in dark systems (Kroll et al., 2005; Liggio et al., 2005a), and surprising, as type B growth rates as those observed by other authors should have been observable in our system. While our results appear to confirm the conclusion for reversible CHOCHO uptake for AS (Kroll et al., 2005) over an extended RH range, the 40% higher uptake in our photochemical system is only marginally within error bars. The difference in amounts and the rate of CHOCHO uptake may reflect either of the following: (1) CHOCHO is irreversibly taken up by photochemical reactions; (2) photochemistry speeds up the reaction rates, but does not alter the reaction products; (3) photochemistry speeds up the reaction rates, consumes building blocks for SOA formation from dark reactions, and forms essentially different products than dark reactions; or (4) a combination of the above. The question of whether CHOCHO uptake to AS is indeed fully reversible, i.e. can indeed be described by Henry's Law, remains to be answered.

Kroll et al. (2005) had suggested that the uptake of CHOCHO to AS is controlled by ionic strength. This appears to be somewhat unlikely based on the anti correlation between ionic strength and the missing CHOCHO sink observed in Mexico City (Volkamer et al., 2007). Based on the results from this work, any effect of ionic strengths is much smaller than the effect of organic photochemistry to enhance CHOCHO uptake to aerosols.

There is one study available for discussion of SucA. Corrigan et al. (2008) did not observe any CHOCHO uptake in the dark under conditions where SucA is believed to be dry and solid (up to 54% RH). Our study was conducted at slightly higher RH (61% RH), and SucA containing about 36%$_{v/v}$ LWC showed type A uptake kinetics in the photochemical system. Consistent with findings by Corrigan et al. (2008) we did not observe type B growth in the dark, when the aqueous seed was exposed to about

90 ppbv CHOCHO. It appears unlikely that aerosol water associated with dicarboxylic acids catalyzes any irreversible reaction with CHOCHO under dark. Interestingly the uptake kinetics, and amounts of CHOCHO related growth for AS and SucA are directly comparable. In analogy to AS, we conclude that any irreversible reaction of CHOCHO with SucA in our system must be driven by photochemical reactions. Alternatively, the reaction rate to form oligomers from CHOCHO in the associated water phase could be strongly enhanced by photochemistry, yet follow a reversible mechanism. It remains to be elucidated whether the photochemically enhanced uptake of CHOCHO to AS and SucA follows a reversible or irreversible reaction mechanism.

The reaction of amines to form covalent N-C bonds has been exploited by analytical techniques for the detection of carbonyls including CHOCHO for a long time (Koshy et al., 1975; Yu et al., 1995b). Little is known however about the extent to which gas-phase reactions of amines play a role in the formation of particles, or affect the atmospheric chemistry of CHOCHO. More information is available on amino acids, which have recently been shown to catalyze the formation of oligomers from acetaldehyde via aldol condensation (pathway 1), or a Mannich Pathway (pathway 2) (Noziere and Cordova, 2008). While similar reactions may also trigger aldol condensation of α-dicarbonyls, the rate limiting step for both pathways consists in the formation of enamine, which may proceed also in the case of CHOCHO, as the additional aldehyde group in water undergoes rapid gem-diol chemistry. For acetaldehyde, pathway 2 was shown to dominate over pathway 1 at molar concentrations above 0.15 M arginine. For glycine, the most abundant AA in atmospheric particles, the rate of enamine formation is lower by about a factor of four than for arginine (Noziere and Cordova, 2008). Under the molar concentrations of glycine (and tyrosine) used in this study (about 2–4 M), the AA concentration is sufficiently high that any enamine that may form from CHOCHO would likely react via a Mannich pathway. Glycine concentrations used in this study are about two orders of magnitude higher than those found in atmospheric particles (up to 0.02 M) (Zhang and Anastasio, 2003; Matsumoto and Uematsu, 2005; Noziere and Cordova, 2008); however, our concentrations are low compared to those employed in

Corrigan et al. (2008), where essentially pure solid AA were used. Under such particular experimental conditions Corrigan et al. (2008) argue that the presence of particle phase nucleophiles, sulfate and acidity all appear to increase CHOCHO uptake. However, growth factors observed on sodium sulfate are larger than growth factors on any AA. Arginine and glutamic acid experiments are the only AA systems that showed enhanced uptake over sodium chloride, which was chosen as a reference seed that only forms glyoxal oligomers in the associated water phase (no reactions with sodium chloride are expected). The observed growth factors on sodium chloride were larger than for glycine and other AA studied, including one of the two glutamic acid experiments. Overall, the enhancements attributed to AA catalysis over salt solutions were, if observable, rather small. In our study addition of glycine and tyrosine to AS+FA seed did reduce the rate of CHOCHO uptake by 2–3 orders of magnitude compared to experiments in the absence of AA in the photochemical system. We observe growth rates in the dark to be comparable in the presence and absence of AA, and do not find evidence that the most abundant AA in atmospheric aerosols, i.e. glycine, enhances the reactivity of CHOCHO in aerosols.

Similarly, acid catalyzed heterogeneous reactions of CHOCHO are found second to photochemical reactions to enhance the CHOCHO uptake to particles. For the mildly acidified seeds investigated here (see Table 1) the photochemical rate of CHOCHO uptake is reduced by several orders of magnitude compared to identical seeds that were not acidified with SA. Differences in experimental conditions may explain results different from those observed by (Jang et al., 2002); those experiments were conducted with more acidic particles in a photochemical reaction system. An acid effect on CHOCHO uptake was also observed by Liggio et al. (2005a) and Corrigan et al. (2008), while – consistent with our results – no acid effect was observed by Kroll et al. (2005). Notably, in the apparent correlation of the growth rate with pK_a (Corrigan et al., 2008) the strongest acid studied (oxalic acid) was an outlier to any apparent acid trend. Oxalic acid and SucA showed negligible CHOCHO uptake in the dark, despite rather high RH. This is consistent with the absence of type B growth on SucA observed here, and our finding that addition of SA had no effect on the rate of CHOCHO uptake in the dark. The apparent correlation of growth rate with pK_a could hence equally be interpreted as LWC controlled CHOCHO uptake, and competing acid effects, as concluded in this work. LWC is not well constrained in Corrigan et al. (2008), and such interpretation seems likely also in light of the growth rate data for glycine and glutamic acid, which appears to be internally consistent only if regarded in context to the presumably higher LWC at higher RH. The reduced uptake of CHOCHO to acidified aqueous solutions observed in this work and Corrigan et al. (2008) appears to be analogous to the observation of reduced methylglyoxal uptake on more acidic solutions (55–85$\%_{w/w}$ SA) (Zhao et al., 2006), which suggested a competition of acid for liquid water, and recognized the relevance of liquid water rather than acid as catalyst for SOA formation. Our study directly confirms such competition exists also for CHOCHO uptake due to organic photochemistry in aerosol water. At the pH found in atmospheric particles throughout the troposphere, acidity is also an inhibiting factor in SOA formation. In terms of the CHOCHO reactivity enhancements, we conclude that sulfate is second to organic photochemical reactions; the presence of nucleophiles and SA reduces this reactivity.

4.2 Do SOA yields depend on the seed chemical composition also for other VOCs?

Most studies of SOA yields to date used either no seed at all (e.g. Hurley et al., 2001, and references therein), or added AS seed in an attempt to overcome barriers in the Gibbs free energy towards homogeneous nucleation of semivolatile vapors, or ascertain the effect of ionic strength on the partitioning of semivolatile products (Odum et al., 1997; Cocker et al., 2001; Kroll et al., 2007). AS seed has been shown to accelerate the rate of SOA formation, but does not affect the SOA yield compared to experiments conducted in the absence of seed (Kroll et al., 2007). Notably, our observation of rapid photochemical SOA formation on AS could contribute to this acceleration, though AS is among those seeds that forms least SOA in this work. Cocker et al. (2001a, b) did not observe any measurable effect of RH on SOA yields from a-pinene, m-xylene and

1,3,5-trimethylbenzene, and attributed this to the existence of two separate SOA and aqueous salt phases in a single particle. This interpretation of phase separation is supported also by thermodynamic model considerations (Chang and Pankow, 2006). Consequently, experiments using seeds composed of inorganic aqueous salts, SOA, or mixtures of both will not be particularly sensitive to any aqueous phase organic photochemistry, as the amount of liquid water associated with SOA is much smaller than that associated with aqueous salts. Notably, the OH-radical initiated oxidation of 1,3,5-trimethylbenzene does not form CHOCHO as oxidation product, and CHOCHO yields from a-pinene are very small. Also, CHOCHO yields from m-xylene are low compared to other alkylbenzenes (see Table 1 in Volkamer et al., 2007), reducing the sensitivity of all three systems further towards effects as those observed in this study. Regardless, CHOCHO and glyoxylic acid were identified in Cocker et al. (2001b) among the aerosol phase products. There is no currently known mechanism to produce glyoxylic acid via a gas-phase oxidation mechanism, while it is a known product from aqueous phase oxidation of CHOCHO and other precursors (Ervens et al., 2003). The observation of glyoxylic acid among the constituents in SOA gives direct evidence that the molecular formation routes for SOA formation appear to have been affected by the presence of small amounts of water (either from multiphase chemistry at the interface between aqueous salt phases, or in water associated with SOA); CHOCHO and glyoxylic acid accounted for about 0.1% each of the extracted SOA mass from m-xylene under dry conditions.

To the best of our knowledge ours is the first study that systematically investigated the dependence of Y_{SOA} on seed chemical composition. Unless SOA generated in chambers is equally water soluble as SOA generated in the atmosphere, our findings point to a possible bias in current simulation chamber data: a reduced interface for organic photochemistry in externally mixed SOA and water phases (within the same particle), compared to a greatly enhanced interface in bulk aqueous aerosols containing water soluble organic carbon (WSOC). WSOC is a major component of the seeds studied here, as well as the SOA produced in the atmosphere (Sullivan et al., 2006;

Weber et al., 2007). If a similar effect of seed chemical composition was confirmed also for other SOA precursor VOCs, this would significantly increase the predicted amount of SOA formed on local, regional and global scales.

4.3 Can CHOCHO uptake be described by Henry's Law?

Whether or not the partitioning of CHOCHO to aerosols can be described by Henry's Law is directly tied to the question whether the uptake mechanism is reversible or irreversible. The relevance of this question is illustrated from discussion in Volkamer et al. (2007): reversible CHOCHO uptake as described by Kroll et al. (2005) can explain several 10 ng m^{-3} of SOA mass for the typical urban CHOCHO concentrations found in Mexico City (Volkamer et al., 2005a); irreversible CHOCHO uptake (Liggio et al., 2005a) predict several 10 μg m^{-3} SOA. The missing CHOCHO sink to form SOA is closer to the upper end of this range, and can explain a significant fraction of the missing SOA source (Volkamer et al., 2006, 2007). Notably, this conclusion was reached without making any assumption about the reaction mechanism, reflecting that the uncertainty related to SOA formation from CHOCHO on aerosols spans several orders of magnitude.

For AS seed, Kroll et al. (2005) reproduced experiments by Liggio et al. (2005a) over extended experiment times, and observed that initial CHOCHO uptake slowed and reached a plateau after several hours. They concluded that CHOCHO uptake to aqueous AS is reversible. This implies that the chemical bonds formed when CHOCHO reacts with sulfate in the dark (Liggio et al., 2005c), or forms oligomers in aerosol water (Kroll et al., 2005; Hastings et al., 2005; Liggio et al., 2005c) are not stable and appear to be broken already at ambient temperatures. Corrigan et al. (2008) observed continued growth upon exposing CHOCHO to (mostly dry) aspartic acid, sodium sulfate, arginine, glutamic acid aerosols (among others) in a dark chamber, and attribute this growth to reactions of CHOCHO with sulfate, nucleophiles (AA), and oligomer formation in thin water layers associated with mostly dry aerosols. The apparent growth rate appears to decrease with time, and it is not clear at present if it converges towards a plateau. It should be noted that the results by Corrigan et al. (2008) on dry seed (0<LWC<4%$_{w/w}$ showed most growth) and in the dark are somewhat difficult to compare with our results on mostly aqueous aerosols, where AA and/or SA largely reduce the photochemistry enhanced aerosol growth rate (see also Sect. 4.1). Our findings that photochemical aerosol growth directly scales with (1) the CHOCHO concentration, and (2) the LWC for any given seed type are compatible with Henry's Law behavior, but allow no definite conclusion whether such growth is reversible or irreversible (see Sect. 4.1). About half our experiments showed continued growth in the dark over accessible time scales; however, about an equal number showed no such growth. While an increasing number of studies now provide evidence that CHOCHO partitions to aerosols in amounts larger than expected, it remains to be demonstrated convincingly whether such CHOCHO uptake proceeds by a reversible or irreversible mechanism. Notably, we choose to present our results in terms of H_{eff} values primarily for means of a quantitative comparison with other studies, and for discussion purposes, and do not mean to imply that photochemical CHOCHO uptake is necessarily reversible.

4.4 Atmospheric implications

It is of interest to place the results from the present work into perspective in terms of our understanding of the mechanism of SOA formation in the atmosphere. Traditional SOA models struggle with predicting the fast timing and the large amount of SOA produced in the atmosphere (Heald et al., 2005; de Gouw et al., 2005; Johnson et al., 2005; Volkamer et al., 2006; Riddle et al., 2008). Recent experimental work has further demonstrated that only a portion of the organic aerosol seems to participate in the absorption processes for semivolatile oxidation products (Song et al., 2007). This evidence further increases the already substantial mismatch between SOA predictions and observations. Traditional SOA models contain a high bias with respect to the predicted amount of SOA from semivolatile oxidation products in the atmosphere.

4.4.1 Conceptual expansion of SOA models: the photochemical solubility-reactivity scale

Most SOA models represent SOA formation as the result of the gas-phase oxidation of VOCs to form semivolatile products that partition by absorption (dissolution) into an organic particle phase (Odum et al., 1997; Seinfeld and Pankow, 2003; Robinson et al., 2007). These models follow (Pankow, 1994a), according to which only the organic mass fraction of the aerosol (M_{om}) contributes to absorbing semivolatile gases; the partitioning coefficient for an absorptive process is expressed as a function of physical and thermodynamic properties of the semivolatile compound:

$$K_{p,i} = \frac{RTM_{om}}{MW\xi_i p_i^0} \tag{2}$$

where R is the ideal gas constant, T is temperature, M_{om} (see above), MW is the mean molecular weight of the absorbing aerosol phase, ξ_i is the activity coefficient of compound i in this phase, and p_i^o is the vapor pressure of compound i as a pure liquid. M_{om} is defined to include any liquid water that is attracted due to hygroscopic properties of organic material (see Eq. 4 in Seinfeld and Pankow, 2003). According to Eq. (2) aerosol components other than M_{om}, such as crustal material, inorganic aerosol, and liquid water attracted by inorganic aerosol do not contribute to SOA formation. In this view, for any given SOA precursor NMHC there is one set of Y_{SOA} and M_{om} data pairs; i.e. Y_{SOA} is treated as a chemically inert quantity that should not depend on the chemical seed composition. The seed role is limited to accelerating SOA formation by providing a surface for condensation.

In this work the Y_{SOA} values for any given seed do not correlate with M_{om}, but instead show an excellent correlation with LWC (see Fig. 3, and Sect. 3.1). Moreover, at any given M_{om} the Y_{SOA} is found to vary as a strong function of the chemical seed composition (see Sect. 3.2), providing direct evidence that SOA formation from C_2H_2 is controlled by heterogeneous chemistry. Internal mixtures of inorganic and water soluble organic aerosol (fulvic and humic type matter) increase Y_{SOA} over pure inorganic aerosol. This highlights an important function of inorganic aerosol, namely to attract LWC, and thus increase the reactor volume where organic photochemistry causes the Y_{SOA} enhancements over pure salt solutions. Such SOA largely escapes the parameterization of SOA yields derived in simulation chamber experiments of other SOA precursors (see Sect. 4.4.4).

Vapor pressure as the only parameter to control SOA formation clearly is insufficient to explain SOA formation from C_2H_2, and the variability of SOA yields at fixed M_{om} observed in this study. SOA models require a conceptual expansion to also reflect SOA formation via the photochemical and dark solubility – reactivity scale in aqueous aerosols. The implementation of such SOA formation in atmospheric models requires knowledge of partitioning coefficients (e.g. effective Henry's law constants, reactive uptake coefficients), the oxidation mechanism and chemical kinetics of reactions that foster and inhibit SOA formation, ideally under conditions that resemble those found in the atmosphere.

4.4.2 Aerosol vs. cloud water as a chemical reactor

The chemical environment in aerosol water is fundamentally different from that in cloud or fog water, because (1) the liquid water content of aerosols is 3–5 orders of magnitude smaller than in clouds/fog droplets, and (2) the smaller diameter of aerosols results in 2–3 orders of magnitude higher surface to volume ratio for aerosols compared to cloud/fog droplets. The different chemical environment in aqueous aerosols compared to cloud/fog droplets is illustrated in Fig. 8. Based on measurements of the effective Henry's law constants of dilute solutions of CHOCHO in water $H_{eff}=4.2\times10^5$ M atm^{-1} (Ip et al., 2008[1]), and seawater $H_{eff}=3.6\times10^5$ M atm^{-1}(Zhou and Mopper, 1990), CHOCHO should partition in appreciable amounts only to clouds/fog, but not to aqueous aerosols. Even the higher CHOCHO solubility in aqueous AS par-

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[1] Ip, H. S. S., Huang, X. H. H., and Yu, J. Z.: Effective Henry's Law Constant of Glyoxal, Glyoxylic Acid, and Glycolic Acid, Geophys. Res. Lett., submitted, 2008.

ticles, $H_{\mathrm{eff}}=2.6\times10^{7}\,\mathrm{M\,atm^{-1}}$ at 50% RH (Kroll et al., 2005), does not significantly affect the gas-phase CHOCHO budget in the absence of clouds. However, the presence of dissolved organic matter can photochemically enhance the CHOCHO uptake. Using our measured effective solubility of CHOCHO in aqueous fulvic acid particles, $H_{\mathrm{eff}}=5.1\times10^{8}\,\mathrm{M\,atm^{-1}}$, and assuming $10\,\mu\mathrm{g\,m^{-3}}$ of aerosol liquid water, about 11% of the CHOCHO will be in the particle phase. For Mexico City, where organic aerosols comprise the largest fraction of fine particulate mass (Salcedo et al., 2006), our laboratory results predict up to 20% of the CHOCHO will partition to aerosols. Clearly, aerosols can affect the gas-phase CHOCHO budget to a measurable extent despite their small LWC.

The aerosol aqueous phase as a chemical reactor is distinctly different from cloud water. Notably, the source of oxidants is different. H_2O_2 does not partition in appreciable amounts to aerosols; however, OH-radical uptake from the gas-phase provides a significant source of oxidants in particles (Ervens et al., 2003). Also, compared to the micro- to milli-molar dilute solutions characteristic of cloud or fog water (Carlton et al., 2007), reaction rates of CHOCHO are likely to be accelerated in 0.1–10 M solutions characteristic of aqueous aerosols. The nature of oligomer formation is non-linear (Barsanti and Pankow, 2005), and requires experiments to be conducted under essentially different conditions that resemble aerosols.

4.4.3 Anthropogenic vs. biogenic SOA sources

Global simulations indicate that biogenic NMHC oxidation is the major global source of SOA and this source has been enhanced by humans due to the anthropogenic increases in gas-phase oxidant and primary particle levels (Kanakidou et al., 2005; Fuzzi et al., 2006). This view is supported by ^{14}C measurements, which attribute a modern carbon age to most OA found in the atmosphere. However, field observations show no correlation between enhancements of OA mass and biogenic precursors (de Gouw et al., 2005; Sullivan et al., 2006; Weber et al., 2007), but instead show an excellent correlation with anthropogenic pollution factors (de Gouw et al., 2005; Volkamer et al., 2006; Sullivan et al., 2006; Weber et al., 2007). Such conflicting evidence from ^{14}C data and correlative analysis of time series data is difficult to resolve within the purely physical (vapor pressure driven) framework of SOA formation that underlies most SOA models; such models necessarily maintain the ^{14}C signature of precursors also in the ^{14}C signature of the semivolatile oxidation products. It should be noted, however, that a primarily modern ^{14}C age of OA is not necessarily indicative of biogenic NMHC precursors. Rather our interpretation of the information content of ^{14}C measurements depends on the framework that we choose to think about SOA formation. If, for example, the framework for SOA formation was expanded to include heterogeneous (photo) chemistry, other factors could increase or decrease particulate phase reactivity of SOA building blocks. While the possibility for such bias in the interpretation of ^{14}C age could in principle be caused by a biogenic or anthropogenic trigger of SOA formation, only an anthropogenic trigger to enhance SOA formation from biogenic NMHC is compatible with the available field evidence (de Gouw et al., 2005; Volkamer et al., 2006; Sullivan et al., 2006; Weber et al., 2007; Riddle et al., 2008). Further, there is no experimental evidence as yet that would demonstrate convincingly that equal amounts of OA are formed from biogenic NHMC precursors in the presence and absence of anthropogenic pollution factors.

The global source of α-dicarbonyls is estimated to be at least 185 Tg yr^{-1} (Fu et al., 2008). The CHOCHO source is estimated at 45–83 Tg yr^{-1}, and largely due to secondary sources (17% from C_2H_2, 70% from biogenic NMHCs) (Myriokefalitakis et al., 2008; Fu et al., 2008); an additional oceanic source (Wittrock et al., 2006) is currently largely uncertain. Aerosol uptake to form SOA could determine 75–95% of the atmospheric fate of CHOCHO in polluted air, and form about an equal amount of SOA as the sum of semivolatile oxidation products from traditional anthropogenic and biogenic SOA precursor NMHC in Mexico City (Volkamer et al., 2007). CHOCHO, and other α-dicarbonyls, are deemed responsible for 5–11 Tg yr^{-1} SOA production on global scales, which is comparable to the sum of SOA formed from monoterpenes, sesquiterpenes, isoprene, and aromatics (Fu et al., 2008; Myriokefalitakis et al., 2008); these estimates underestimate the role of aerosols, and will further increase based on the results of this study. WSOC accounts for a major portion of OA in urban and rural areas (Sullivan et al., 2006; Weber et al., 2007). Our observation of fast SOA formation from WSOC photochemistry of CHOCHO is consistent with field evidence of fast SOA formation due to first generation oxidation products, and helps explain part of the missing SOA source in Mexico City (Volkamer et al., 2006). However, our results fall short by a factor of 8–17 to explain the CHOCHO sink to form SOA in Mexico City (Volkamer et al., 2007).

Given the large mismatch between predicted and observed SOA on local and global scales, little trust should be placed in the dominance of biogenics on global scales based on these models alone. Clearly, the source of α-dicarbonyls, and the uncertainty associated with their atmospheric fate, is large enough to affect the interpretation of ^{14}C measurements on scales from local to global. Anthropogenic precursors could be responsible for about one third of the global SOA production (Volkamer et al., 2006). Our results support the expanded definition of SOA formation, according to which SOA sources include gas-to-particle partitioning in the organic- and aqueous phase, organic phase processing, aqueous phase processing, and multiphase processing (i.e. surface and bulk) (Volkamer and Kanakidou, 2007).

4.4.4 On the issue of double-counting SOA from CHOCHO

The parameterization of SOA yields that underlie current SOA models possibly could include SOA formed from CHOCHO in these chamber experiments. Is CHOCHO SOA double counted here? It appears unlikely for the following reasons: (1) the SOA source from CHOCHO closely compares to (and slightly exceeds) that of all other currently studied SOA precursor NMHC (Volkamer et al., 2007; Fu et al., 2008); all SOA would need to be CHOCHO related. This is obviously not the case, as most aerosol products that have been identified to date at the molecular level are unrelated to CHOCHO (Yu et al., 1995a; Forstner et al., 1997; Cocker et al., 2001). (2) Most chamber experiments were conducted under dry experimental conditions, and on AS seed. Such conditions essentially preclude SOA formation via the aerosol aqueous phase. AS showed among the lowest Y_{SOA} values in this study. In the presence of relative humidity there is consistent experimental and theoretical evidence (Cocker et al., 2001a, b; Chang and Pankow, 2006) that strongly suggests that WSOC photochemistry is greatly reduced in current chamber data due to phase separation effects (see also Sect. 4.2), (3) The aerosol mass spectra of SOA generated in the presence of aqueous AS seed in chambers (Bahreini et al., 2005) are different from OOA spectra observed in ambient air (Zhang et al., 2005), and SOA generated from CHOCHO uptake to AS (Liggio et al., 2005a). Notably, CHOCHO uptake to AS accounts only for 2–3% of the missing CHOCHO sink to form SOA in ambient air (Volkamer et al., 2007); WSOC photochemistry is likely to result in different aerosol mass spectra than CHOCHO uptake to AS. Further, the differences in the mass spectra of (Zhang et al., 2005; Bahreini et al., 2005) appear to be largest for masses that have a high contribution from oxygen containing products (e.g. m/z 28, which corresponds to CO). (4) The oxygen-to-carbon ratio (O/C) for the di-hydrated CHOCHO monomer is O/C=2, and this ratio approaches O/C=1 for longer chain oligomers; O/C is likely to be high also for the presently unidentified products. As noted in Volkamer et al. (2007) SOA from CHOCHO will increase predicted O/C ratios (see Dzepina et al., 2008[2]). While the high O/C ratios of CHOCHO related SOA compare favorably to the O/C=0.9 observed in ambient aerosol, the range of observed values in chamber experiments from toluene, 1,3,5-trimethylbenzene, isoprene, α-pinene is much lower, i.e. $0.3<\mathrm{O/C}<0.4$ (Aiken et al., 2008). It is these low O/C ratios that are currently parameterized in atmospheric SOA models. Finally, (5) SOA generated in chambers is more volatile than ambient SOA (Huffman et al., 2008[3]).

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[2] Dzepina, K., Tulet, P., Griffin, R. J., Volkamer, R., Taylor, J. L., Madronich, S., Aumont, B., Camredon, M., Ulbrich, I., Zhang, Q., and Jimenez, J. L.: Comparison of Several Secondary Organic Aerosol (SOA) Models for a Mexico City case study of 9 April 2003, Atmos. Chem. Phys. Discuss., in preparation, 2008.

[3] Huffman, J. A., Aiken, A. C., and Jimenez, J. L.: Volatility of primary and secondary organic aerosols in the field contradicts current model representations, Environ. Sci. Technol.,

Thereby, the more oxidized fraction of the aerosol is least volatile. Typical values for the heat of vaporization ΔH of SOA generated from toluene in chambers range between $11<\Delta H<31\,\mathrm{kJ\,mol^{-1}}$ (Takekawa et al., 2003; Offenberg et al., 2006). The ΔH of SOA generated from single component CHOCHO aerosol is $\Delta H=13.3\,\mathrm{kJ\,mol^{-1}}$ (Offenberg et al., 2006). While the volatility of CHOCHO related SOA is difficult to separate from the convoluted volatility of ambient or chamber generated organic aerosol, the CHOCHO related SOA is likely to lower the effective volatility of ambient aerosol. Conversely, increasing the CHOCHO related portion of SOA in chamber experiments (see Sects. 3.2 and 4.3) and ambient aerosol (Volkamer et al., 2007) will likely bring the predicted and observed volatility of SOA in closer agreement (see Dzepina et al., 2008[2]).

Overall, it appears likely that the predominant fraction of CHOCHO related SOA escapes the current parameterizations of SOA yields from chamber experiments (e.g. Odum et al., 1997; Ng et al., 2007) that underlie current estimates of SOA formation from atmospheric models (Kleeman and Cass, 2001; Chung and Seinfeld, 2002; Kanakidou et al., 2005; Fuzzi et al., 2006; Henze et al., 2008).

5 Conclusions

The formation of Secondary Organic Aerosol (SOA) from C_2H_2, the lightest Non Methane HydroCarbon (NMHC), is surprising, because all currently known oxidation products are at least six orders of magnitude too volatile to condense or partition into the aerosol organic phase to any appreciable extent. SOA formation from C_2H_2 highlights the importance of heterogeneous chemistry in SOA formation. Our results point out the particular role of organic photochemistry in aerosol water as a SOA source from CHOCHO, and possibly other α-dicarbonyls.

This is to our knowledge the first systematic study of the effect of seed chemical composition and photochemistry on SOA yields, and the rate of SOA formation. The

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submitted, 2008.

seed particles investigated here are representative for a large subset of aqueous atmospheric particles. Experiments were conducted for seed composed of pure ammonium sulfate (AS), ammonium bisulfate (ABS), fulvic acid (FA), succinic acid (SucA), and mixtures of AS+FA, ABS+FA, ABS + humic acid (HA), AS+FA + aminoacid (AA); selected seeds were further mildly acidified (3<pH<4) with sulphuric acid (SA). We find SOA yields from C_2H_2 do not correlate with the organic mass portion of the seed aerosol, and instead – for any given seed type – correlate in a linear way with aerosol liquid water content (LWC). The inorganic aerosol component of seed aerosols largely determines the LWC. For a given LWC the SOA yields for mixed inorganic/water soluble organic carbon (WSOC) seed aerosols are about four times larger compared to pure inorganic aerosol, but are comparable for the pure water soluble organic seed aerosol. Further, the rate of SOA formation is about a factor of 200 higher in photochemical conditions compared to dark experiments. Hence, it appears that the inorganic aerosol component primarily determines the reactor size, where WSOC photochemical reactions cause the increased SOA yields. Any ionic strength effects of concentrated salt solutions appear to be secondary to providing a sizable photochemical reactor.

The implications for our understanding of atmospheric processes are significant: (1) Atmospheric SOA models currently widely represent SOA yields from experiments conducted in the absence of seed, or in the presence of pure AS seed. Here we find the highest SOA yields for internally mixed inorganic/WSOC seed particles due to organic photochemistry in the bulk LWC of the particles. Most SOA precursors for which their chemical identity is known to date are major sources for CHOCHO, and other α-dicarbonyls. Hence, any low bias in the currently available SOA yield data might explain a significant portion of the missing SOA source in current atmospheric models. (2) The effective Henry's Law constants H_{eff} for CHOCHO are sufficiently high to compensate for the 3-5 orders of magnitude smaller amount of liquid water associated with atmospheric particles compared to clouds/fog. We demonstrate that WSOC photochemistry of CHOCHO – and possibly other α-dicarbonyls – is a SOA source already in the absence of clouds/fog. Most notably, the SOA formation associated with these gases does not stop once a cloud droplet has evaporated, as inferred by current SOA models that represent cloud processing, but rather proceeds also in the absence of clouds, possibly even at an enhanced rate as aerosols are more concentrated solutions compared to clouds. (3) Organic photochemistry in the aerosol aqueous phase enhances the rate of CHOCHO uptake by three orders of magnitude over reactions triggered by atmospherically relevant AA and/or SA; also the uptake is enhanced for internally mixed inorganic/water soluble organic seed aerosol compared to pure concentrated salt solutions. This is relevant, as the atmospheric fate of α-dicarbonyls to form SOA depends on the competition between the rate of uptake to particles compared to other gas-phase loss rates. The rate of CHOCHO uptake to particles in our photochemical system is fostered by AS, ABS, SucA, FA, HA, but reduced by the presence of atmospherically relevant AA like glycine, and SA. This might indicate competing reactions in the early stages of photochemical reactions in the aqueous aerosol phase. (4) Our results explain up to 360 ng m^{-3} of the missing SOA source in Mexico City as CHOCHO related (Volkamer et al., 2006), and account for up to 6–12% of the missing CHOCHO sink in Mexico City (Volkamer et al., 2007). While our results reduce the existing imbalance in current gas-phase CHOCHO budgets, they fall short by a factor of 8–17 to explain the CHOCHO imbalance in the Mexico City atmosphere; most of the imbalance in gas-phase CHOCHO cannot be explained as yet based on the currently available laboratory data.

There is an urgent need for further laboratory studies to determine the reaction mechanism, kinetics, and products of this organic photochemistry. Atmospheric SOA models need to be expanded to explicitly represent the aerosol aqueous phase chemistry in form of dark and photochemical reactions in the presence and absence of clouds.

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Table 1. Experimental conditions.

Exp #	RH	Glyoxal [ppb]	Seed-V [μcm^3 m^{-3}]	dV [μcm^3 m^{-3}]	LWC^a [%]$_{v/v}$	M^b_{om} [μg m^{-3}]	H^c_{eff} [10^7 M atm^{-1}]	Uptake type
AS						average	13.8±2.4	
13	46	160	10.5	3.1±0.5	41.7	10.9	12.8±2.1	A
9	49	117	6.6	1.5±0.3	44.3	6.5	12.6±2.5	A
18	56	137	13.0	5.8±2.0	49.9	11.5	18.9±7.1	A
7	88	143	20.7	10.6±1.1	78.5	7.9	13.2±1.4	A
FA						average	51.7±19	
19	16	171	18.5	1.8±0.5	3.2	14.7	52±14	A+B
14	51	158	25.0	6.0±3.5	8.6	16.8	51±29	A
AS+FA						average	49.7±8.1	
17	49	162	12.0	10.0±0.5	29.1	6.9	51.4±2.8	A+B
11	54	100	9.7	5.5±1.1	32.2	5.4	51.1±11	A
27	66	70	26.2	11.3±0.5	39.7	12.9	44.5±6.7	A+B
26	67	121	22.8	19.3±1.2	40.2	11.2	50.5±10	A+B
12	82	91	8.0	8.2±2.5	52.6	3.1	>62.2±22	A+B
20	86	70	13.6	11.4±0.9	56.9	4.8	>60.8±13	A+B
32^d	50	100	49.7	>11	29.7	25.7	>21.5	B
AS+FA+acids								
15^e	60	189	63.7	>20.9	45.0	37.6	>11.2	B
16^f	49	167	201	>42.0	31.9	149	>11.4	B
34^g	52	173	57.0	>11.6	44.4	23.6	>7.7	B
35^g	53	64	17.1	>6.3	45.0	7.1	>37.6	B
SucA								
6	61	88	106.9	14.6±1.9	35.8	107.1	12.5±1.7	A
ABS						average	37.0±6.3	
23a	24	108	8.8	1.9±0.2	17.7	13.0	33.2±4.0	A
23b	24	185	8.8	4.3±0.4	17.7	13.0	42.9±6.7	A
8	51	141	4.2	4.6±1.0	46.4	4.0	48.4±12	A+B
21	61	92	15.2	6.7±1.3	55.0	12.2	29.8±6.6	A+B
ABS+FA								
24a	28	118	23.4	1.8±0.2	12.3	16.6	>15.7	A+B
24b	28	193	23.4	3.2±1.0	12.3	16.6	>16.8	A+B
22a	62	99	14.0	5.7±1.5	33.8	7.5	>35.3	A+B
22b	62	179	14.0	12.9±2.6	33.8	7.5	>44.2	A+B
ABS+HA								
25b	40	55	13.5	>1.4±0.3	20.2	9.5	>27.4	A+B
25a	40	139	13.6	>2.6±0.2	20.2	9.5	>19.5	A+B

[a] calculated using the Aerosol Inorganic Model II, see details in the text; [b] converted using density values as given in the text; [c] converted using density of 40% aqueous solution of CHOCHO (1.27 g/cm^3); [d] CHOCHO added; type B uptake in the dark, not included in the average; [e] AS+FA+tyrosine+glycine; [f] AS+FA+SA+tyrosine+glycine; [g] AS+FA+SA.

Table 2. Products formed in the $C_2H_2/CH_3ONO/NO_x$/light system, effective Henry's law coefficients. Values in the right column have been normalized to CHOCHO.

Product	*n*	Conc. [ppb]	$H(298\,K)_{eff}$ [$M\,atm^{-1}$]	$(Conc \times H_{eff})_{norm}$ [rel.units]
C_2H_2	2	22 000	0.041	3.5×10^{-7}
CHOCHO	2	100	2.6×10^{7}	1
HCHO	1	320	3200	3.4×10^{-4}
HCOOH	1	61	8900	2.0×10^{-4}
CH_3NO_3	1	6	2	4.6×10^{-9}
CO	1	93	0.00098	3.5×10^{-11}
HNO_3	0	28	2.1×10^{5}	2.3×10^{-3}
HONO	0	300	50	5.8×10^{-6}

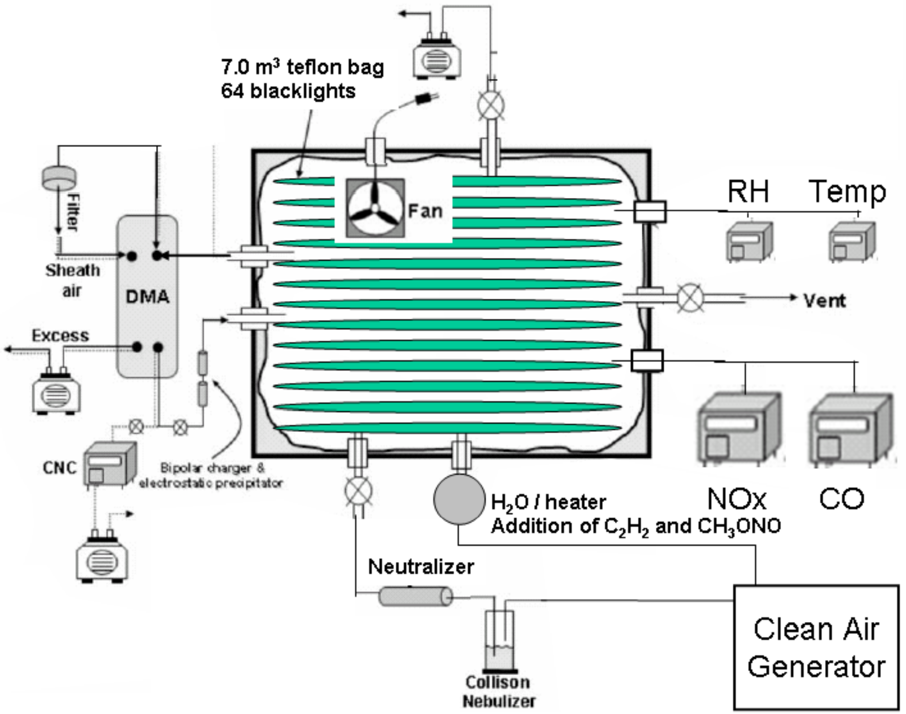

Fig. 1. Experimental setup used in this study.

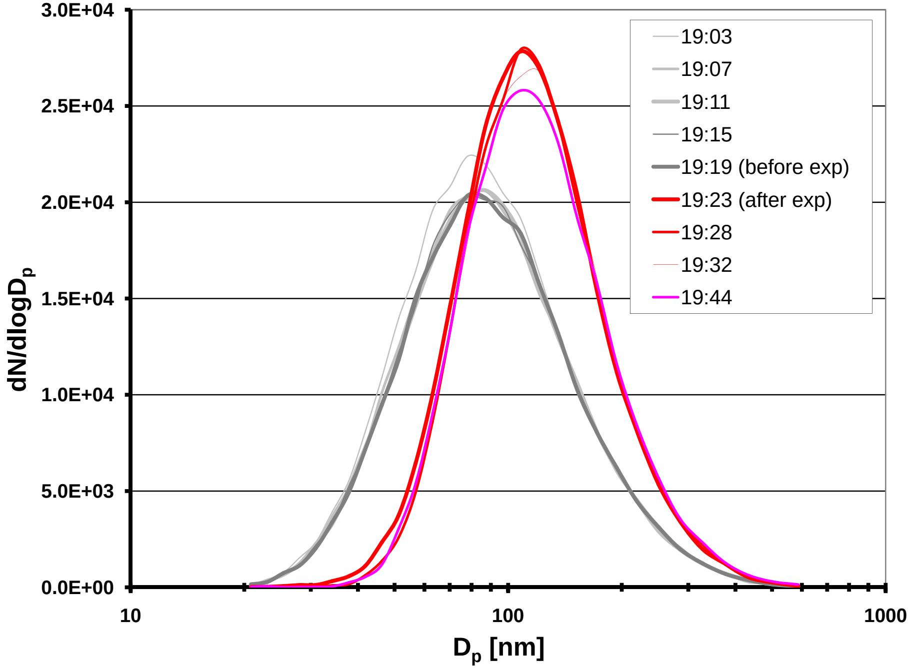

Fig. 2. SOA formation in the photochemical oxidation of C_2H_2. The size distribution of the seed aerosol (grey lines) shifts towards larger diameters immediately after C_2H_2 is photochemically oxidized to produce CHOCHO (red lines). Data from experiment #20 (AS+FA) is shown here.

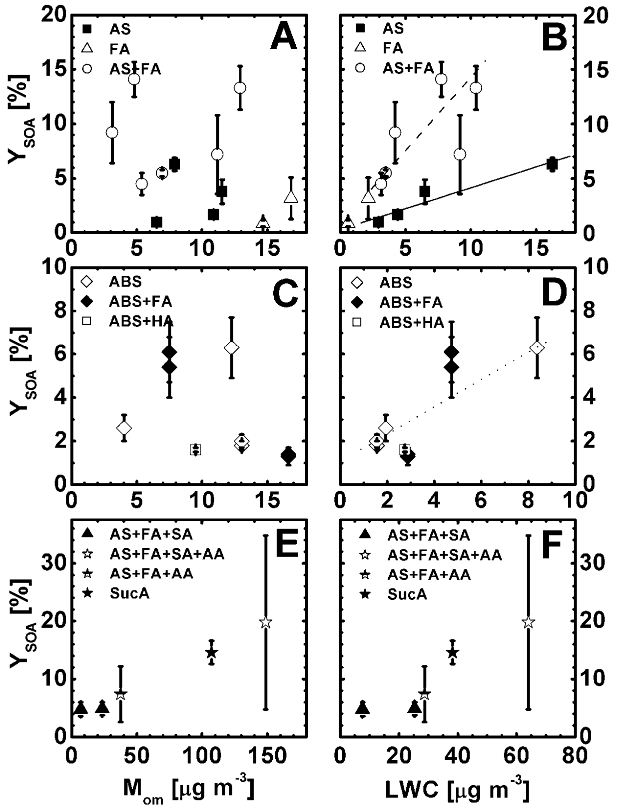

Fig. 3. SOA yield (Y_{SOA}) as a function of organic seed mass, M_{om} (panels **a**, **c**, **e**) and liquid water content, LWC (panels **b**, **d**, **f**). No obvious correlation is found between Y_{SOA} and M_{om}, but Y_{SOA} correlates well with LWC for all seed-types studied. For pure AS (solid line), AS+FA (dashed line), and pure ABS (dotted line) sufficient experiments were conducted to demonstrate that the increase in Y_{SOA} with LWC is linear.

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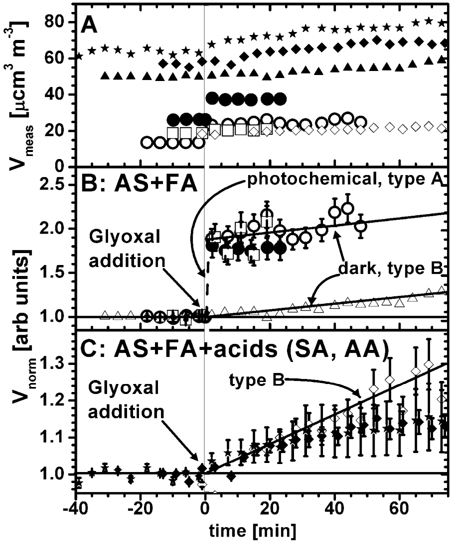

Fig. 4. Kinetics of SOA formation from C_2H_2. Panel **(a)**: time-series of experiments #15 (solid stars), #19 (open squares), #20 (open circles), #27 (solid circles), #32 (solid triangle), #34 (solid diamond), #35 (open diamond); see Table 2 for experimental conditions. Panel **(b)**: The normalized volume (see Eq. 1) accounts for differences in gas-phase CHOCHO concentrations, and liquid water content of the seed. For AS+FA seed two distinctly different rates of SOA formation are observed if CHOCHO is produced from the photochemical source (#19, #20, #27, type A, dashed line) or added in the dark (#32, type B, solid line). Type A uptake kinetics is observed for pure AS, ABS, FA, mixed ABS+FA and ABS+HA seed (not shown). Panel **(c)**: Type B kinetics is observed for AS+FA seed acidified with AA (#15) or SA (#34, #35); use of the photochemical source does not accelerate the uptake for these seeds (the solid line from panel (b) is reproduced here for comparison purposes).

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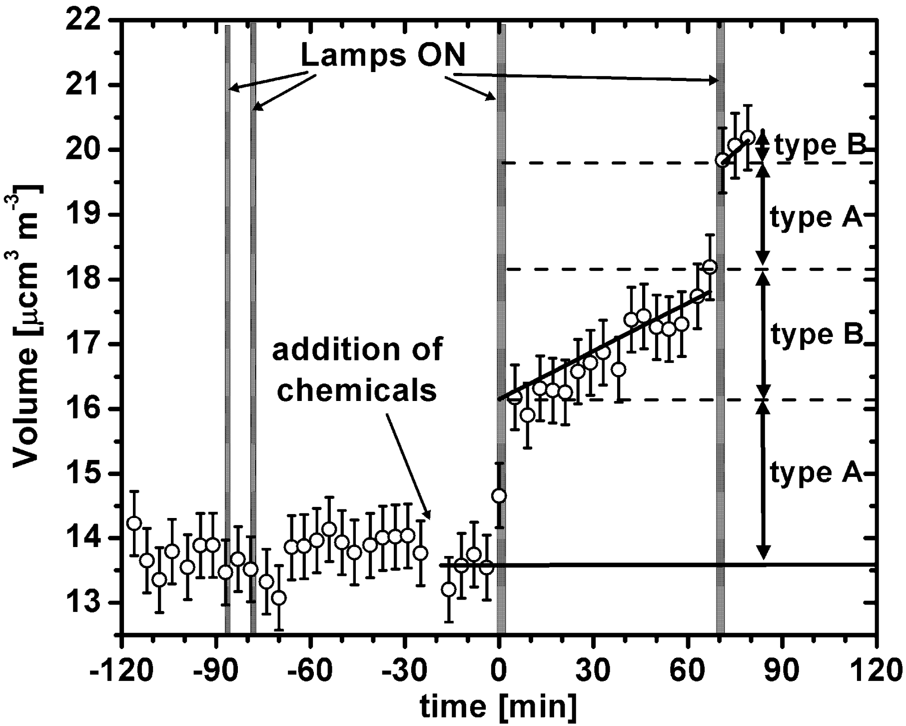

Fig. 5. Time series of the aerosol volume for type A uptake kinetics. Data from experiment #20 (ABS+HA) is shown here. No effect is observed if the seed is exposed to light in the absence of reagents in the chamber. After addition of chemicals to the gas-phase, an immediate shift in aerosol volume is observed when C_2H_2 is photochemically oxidized (twice here), followed by type B growth in the dark. Type B growth as parameterized in Fig. 3 for AS+FA can explain that observed for ABS+HA seed (solid line), see text. The rapid volume growth during periods when the light is turned ON is proportional to the amount of CHOCHO produced, and inversely proportional to LWC of the seed aerosol.

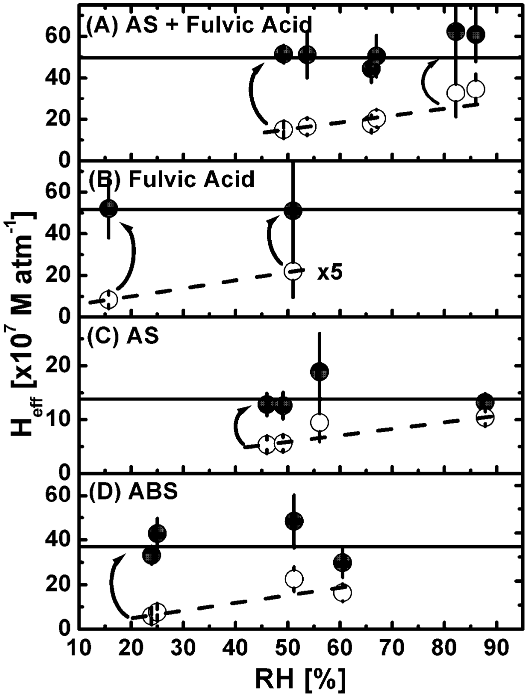

Fig. 6. RH dependence of the effective Henry's law constants, H_{eff}, of CHOCHO for different seed aerosols: **(a)** Ammoniumsulfate mixed with fulvic acid (AS+FA), **(b)** Fulvic acid (FA), **(c)** Ammoniumsulfate (AS), **(d)** Ammoniumbisulfate (ABS). Open symbols represent values of H_{eff} derived under the assumption that CHOCHO partitions to the overall seed volume (case 1). Solid symbols represent values of H_{eff} derived under the assumption that CHOCHO partitions only to the portion of the seed volume that corresponds to aerosol liquid water (case 2). The apparent RH dependence of H_{eff} in case 1 is fully accounted in case 2, presenting direct evidence that CHOCHO uptake proceeds through the aerosol aqueous phase.

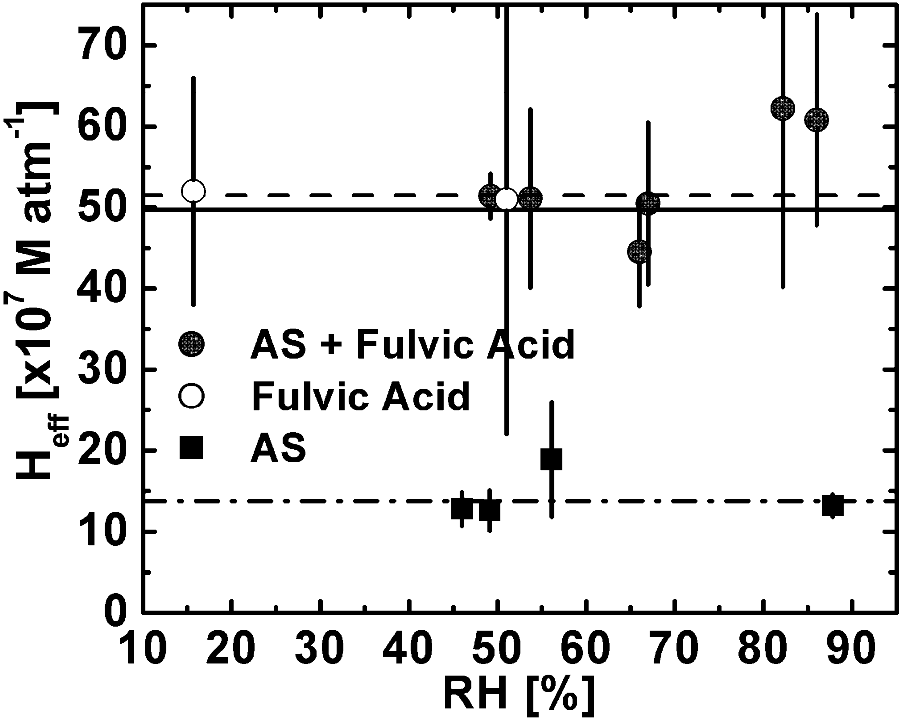

Fig. 7. Water soluble organic carbon (WSOC) photochemistry enhancement of CHOCHO partitioning to AS+FA and pure FA aerosols compared to pure salt solutions (AS).

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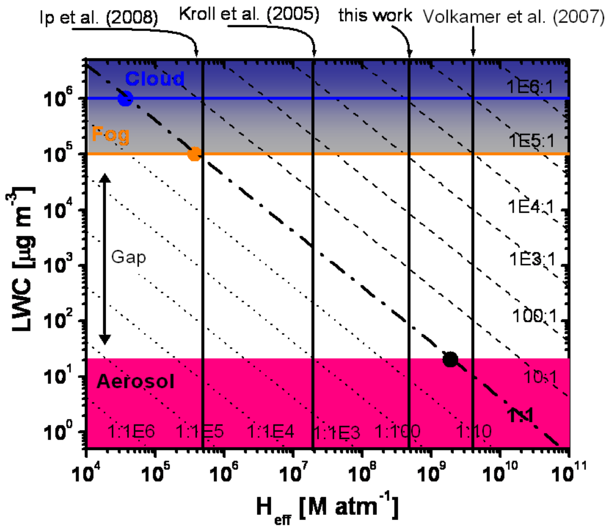

Fig. 8. Partitioning of water soluble molecules to cloud/fog vs aerosol liquid water. The LWC of clouds (blue line) and fog (orange line) is 3–5 orders of magnitude larger than that of aerosols (pink area). H_{eff} values on the order of 3.5×10^4 M atm^{-1} (blue dot), 3.5×10^5 M atm^{-1} (orange dot) and 2×10^9 M atm^{-1} (black dot) characterize equal parts in the gas- and dissolved phase for clouds, fog and aerosols, respectively. Dotted lines indicate H_{eff}-LWC pairs that favor the gas-phase; dashed lines indicate H_{eff}-LWC pairs where the dissolved phase is the dominant reservoir (the partitioning ratio, defined as dissolved/gas-phase, is indicated next to each line). The vertical lines represent H_{eff} values as measured for CHOCHO in **(a)** bulk water (Ip et al., 2008[1]), **(b)** metastable AS aerosols (Kroll et al., 2005), **(c)** metastable AS+FA aerosols (this work), and **(d)** aqueous ambient aerosols in Mexico City (Volkamer et al., 2007). Aerosols are distinctly different aqueous/multiphase chemical reactors than clouds/fog.