



The influence of
physical state on
shikimic acid
ozonolysis

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The influence of physical state on shikimic acid ozonolysis: a case for in situ microspectroscopy

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Abstract

Atmospheric soluble organic aerosol material can become solid or semi-solid. Due to increasing viscosity and decreasing diffusivity, this can impact important processes such as gas uptake and reactivity within aerosols containing such substances. This work explores the dependence of shikimic acid ozonolysis on humidity and thereby viscosity. Shikimic acid, a proxy for oxygenated reactive organic material, reacts with O_3 in a Criegee-type reaction. We used an environmental microreactor embedded in a Scanning Transmission X-ray Microscope (STXM) to probe this oxidation process. This technique facilitates in situ measurements with single micron-sized particles and allows to obtain Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra with high spatial resolution. Thus, the chemical evolution of the interior of the particles can be followed under reaction conditions. The experiments show that the overall degradation rate of shikimic acid is depending on the relative humidity in a way that is controlled by the decreasing diffusivity of ozone with decreasing humidity. This decreasing diffusivity is most likely linked to the increasing viscosity of the shikimic acid-water mixture. The degradation rate was also depending on particle size, most congruent with a reacto-diffusion limited kinetic case where the reaction progresses only in a shallow layer within the bulk. No gradient in the shikimic acid concentration was observed within the bulk material at any humidity indicating that the diffusivity of shikimic acid is still high enough to allow its equilibration throughout the particles on the time scale of hours at higher humidity and that the thickness of the oxidized layer under dry conditions, where the particles are solid, is beyond the resolution of STXM.

1 Introduction

Atmospheric aerosols are an important focus of environmental research due to their effect on atmosphere, climate and health (Pöschl, 2005). It has been shown that organic matter can account for a significant and sometimes major mass fraction of aerosols,

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depending on location (Kanakidou et al., 2005; Zhang et al., 2007). Around 20–70 % of organic particulate matter is comprised of water soluble organics, such as carboxylic acids, polyols, polyphenols, sugars and other highly functionalized compounds (Rogge et al., 1993; Saxena and Hildemann, 1996; Decesari et al., 2000). It was recently shown that aqueous solutions and solution droplets of such organics are likely to form glasses or highly viscous amorphous semi-solids such as rubbers, gels and ultra-viscous liquids under atmospherically relevant conditions (Murray, 2008; Zobrist et al., 2008; Mikhailov et al., 2009). Additionally, recent experimental findings both from field and laboratory measurements suggest an amorphous solid state for organic aerosols (Virtanen et al., 2010; Saukko et al., 2012). Amorphous solids and semi-solids are highly viscous. Solid glasses have viscosities $\geq 10^{12}$ Pa s (Debenedetti and Stillinger, 2001), while the viscosity of semi-solids is lower ($> 10^{10}$ to $> 10^4$ Pa s) (Mikhailov et al., 2009) but still high compared to liquid water ($\sim 10^{-3}$ Pa s). At high viscosities, diffusion is significantly slower, which is likely to decrease the reaction rate, diminish water uptake, inhibit ice nucleation and influence the formation and growth of SOA (Shiraiwa et al., 2011; Zobrist et al., 2011; Mikhailov et al., 2009; Murray, 2008; Perraud et al., 2012; Shiraiwa and Seinfeld, 2012). Reactions within the bulk of aerosol particles are dependent on diffusion of reactive molecules (oxidant gases) into the bulk. If viscosity is too high, diffusion could become the rate limiting process. Therefore, formation of amorphous solids and semi-solids should severely slow down or even inhibit reactions. This change in reactivity has important implications for the lifetime of particles and their constituents and the particles' physical and chemical properties. It is therefore necessary to thoroughly investigate the existence and extent of the influence of the physical state on reactivity. First indications of such a link between physical state and reactivity were shown by Shiraiwa et al. (2011). In their study, the authors used a kinetic model (KM-SUB) (Shiraiwa et al., 2010) to evaluate experimental data from flow tube experiments of ozonolysis of thin protein films and obtain information on the kinetic regimes as a function of viscosity. The temporal behavior of the reaction rate was interpreted as driven by diffusion in the condensed phase. Since then, only two addi-

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tional studies, both of them using aerosol flow tubes and mass spectrometric detection, have been conducted: a study by Kuwata and Martin (2012) proposing a connection between physical state and the formation rate of organonitrates in α -pinene SOA and one by Zhou et al. (2013), showing that the extent of the reaction of benzo[a]pyrene with ozone (O_3) is limited by diffusion through SOA coatings at humidities of 50 % and lower.

When studying the effects of physical state on the reactivity of aerosol particles, direct observation of the bulk reaction would be of an advantage. In Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy, core electrons are excited into unoccupied orbitals, resulting in resonant absorption peaks around the element specific ionization threshold (absorption edge). This resulting fine structure can be used to distinguish different functional groups (Hopkins et al., 2007; Takahama et al., 2007; Pöhlker et al., 2012). Combining this spectroscopic technique with x-ray microscopy offers the possibility to measure chemical maps with high spatial resolution, down to pixel sizes of tens of nanometers (Russell et al., 2002; Maria et al., 2004; Moffet et al., 2010, 2013), which can not be resolved by optical methods such as Raman microscopy (Ivleva et al., 2007; Yeung et al., 2009). Since the ionization edge of carbon lies in the soft x-ray regime, carbon NEXAFS measurements are usually performed in vacuum to avoid absorption of the incident beam by air. To facilitate STXM/NEXAFS measurements of single particles under in situ exposure to various gases, we have developed an environmental microreactor (Huthwelker et al., 2010) based on a design by Drake et al. (2004). Our reactor has so far been used to observe water uptake on ammonium sulfate and mixed ammonium sulfate/adipic acid (Zelenay et al., 2011a) and soot particles (Zelenay et al., 2011c) as well as humidity driven chemical separation of complex organic matter such as fulvic and tannic acid (Zelenay et al., 2011b). A reactor of similar design with an in cell humidity probe was recently developed and characterized by Kelly et al. (2013). We have now utilized our microreactor to observe the ozonolysis of single shikimic acid particles in situ and under different relative humidities, to provide new insights into the dependence of reactivity on physical state. While Drake

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et al. (2004) have already used their cell to monitor oxidation state changes in a silica-supported copper catalyst, this is to our best knowledge the first successful application of STXM/NEXAFS to observe a chemical reaction of an environmentally relevant organic material in situ. The organic compound in question, shikimic acid ((3*R*,4*S*,5*R*)-3,4,5-trihydroxycyclohex-1-ene-1-carboxylic acid, Fig. 1), was chosen as a proxy for oxygenated organic material and has been shown to be present in biomass burning aerosol (Medeiros and Simoneit, 2008). Shikimic acid undergoes humidity dependent changes in physical state (Steimer and Krieger, 2014) and both shikimic acid as well as its first generation ozonolysis products are unlikely to be volatile, making it a suitable compound for a STXM investigation of the influence of physical state on reactivity.

2 Experimental section

2.1 Sample preparation

Shikimic acid ($\geq 99\%$) was purchased from Sigma-Aldrich and used without further purification. Aerosol particles were generated by nebulizing a solution containing a few grams per liter of shikimic acid in ultrapure water ($18\text{ M}\Omega\text{ cm}$, MilliQ) with a custom-built ultrasonic particle generator. The particles were then dried with a Nafion membrane diffusion drier, charge equilibrated by passing them through a Kr-85 source and size-selected using a differential mobility analyzer (DMA) at a voltage of 1.9 kV. The selected particles were counted with a condensation particle counter (CPC) and deposited via impaction on a silicon nitride (Si_4N_3) membrane supported by a Si-window frame, which is attached to the removable front piece of the environmental microreactor.

2.2 Environmental microreactor

Usage of an environmental microreactor made it possible to expose the particles to various gases within a temperature and humidity controlled environment during microspectroscopy measurements. A detailed description of the reactor can be found

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elsewhere (Huthwelker et al., 2010). Briefly, the microreactor consists of two main parts: a removable front piece, holding the window on which the sample is deposited, and the body. The latter includes a gas in- and outlet and is capped with another window. These windows consist of 5 mm × 5 mm silicon frames with small openings in the center (0.5 mm × 0.5 mm front window, 1 mm × 1 mm back window,) supporting 50 nm thick Si₃N₄ membranes. They are attached to the cell with wax (crystal bond 509, SPI suppliers). The front piece is mounted onto the main body with screws, resulting in a leak tight chamber of about 300 μm × 5 mm × 5 mm inner dimensions which is permeable to x-rays through the windows aligned along the beam axis. The cell was left at room temperature during the present measurements. Temperature was constantly monitored with a thermocouple attached to the reactor body. The atmosphere within the reactor was adjusted by varying the flow of the different gases used in this study. The two main gases were helium (He) and oxygen (O₂) used at ratios from 4 : 1 to 7 : 1. Part of the oxygen was converted to ozone (O₃) using an adjustable O₃ generator based on a mercury UV-lamp resulting in ozone partial pressures of 2.5 × 10⁻⁶ to 6.5 × 10⁻⁶ atm. The O₃ concentration was measured at the exhaust of the reactor with a home-built UV absorption setup, which was calibrated with a commercial ozone analyzer (Model 400E UV Absorption O₃ Analyzer, Teledyne-API). Humidity was adjusted by passing a variable fraction of the He flow through a humidifier. Experiments were conducted at four different relative humidities (RH): 12 %, 52 %, 71 % and 82 %. RH was measured using capacitance sensors at the entrance and exit of the microscope chamber. The sensors were operated at room temperature and regularly compared to a dewpoint sensor (DewMaster, EdgeTech). The relative humidity in the microreactor was calculated from the capacitance sensor output by taking into account the microreactor temperature measured by the thermocouple and the small but measurable pressure drop between inlet and outlet. The pressure within the reactor was set to 150 mbar throughout all experiments.

2.3 STXM-NEXAFS

All measurements were performed at the PolLux beamline (X07DA) of the Swiss Light Source (SLS) at Paul Scherrer Institute, Switzerland. This beamline provides photons with an energy range of 200–1400 eV at an energy resolution ($E/\Delta E$) of about 3000.

5 The endstation is a Scanning Transmission X-ray Microspectroscopy (Raabe et al., 2008) with a spatial resolution of about 40 nm under the conditions of the present experiments. Additional energy calibration of spectra beyond the routine calibration of the beamline was done by comparing the measured lowest energy peak of polystyrene with its literature value (285.18 eV) (Dhez et al., 2003). To convert from transmission
10 to absorption and normalize spectra and images to the incident light intensity, the Lambert–Beer law ($OD = -\ln(I/I_0) = d\mu$) was used. Here OD is the optical density, μ the linear absorption coefficient, d the thickness of the sample, I the transmitted light intensity through the particle and I_0 the incident light intensity. Two different modes of measurement were employed during the experiments. Carbon spectra were measured
15 in image stack mode, in which a series of images is taken at closely spaced energy steps, yielding spatially resolved spectra (Jacobsen et al., 2000). The step sizes for the present experiments were 1 eV in the range of 280 to 284 eV, 0.2 eV in the range of 284.1–290 eV and 1.9 eV in the range of 291–320 eV with a dwell time of 1 ms for each energy. The spatial resolution was either 30×30 or 40×40 pixels over a rectangular
20 area typically 3 to 5 μm . Spatial as well as energy resolution were kept relatively low to increase time resolution and, in addition with the low dwell time, avoid beam damage. For a less noisy, well resolved line spectrum of shikimic acid see Fig S2. To obtain chemical maps, stacks of transmission images with higher spatial resolution (65×65 or 70×70 pixels) were measured at only few selected energies: 279.5 eV, 281.5 eV (pre
25 edge), 284.1 eV, 284.2 eV, 284.3 eV, 284.4 eV ($1s-\pi^*$ transition peak) and 311.0 eV, 319.5 eV (post edge), all with a dwell time of 3 ms. These images were then converted to OD images. The spatial distribution of the double bond of shikimic acid within a particle was assessed by calculating the ratio of the pre-edge subtracted image at peak

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features can be observed: the appearance of a small peak at 286.4 eV and an increase as well as a small shift of the carboxyl peak at 288.2 eV. The appearance of additional oxygen functionality is consistent with secondary chemistry during condensed phase ozonolysis of alkenes (Zahardis and Petrucci, 2007). We refrain from further interpreting these peaks in terms of different conceivable products. Since it is easiest to identify and least likely to be affected by beamline contamination (see Supplement for discussion and an example of a less affected spectrum (Fig. S2)), the decrease of the $1s-\pi^*$ transition peak was chosen to quantitatively follow the progression of the reaction. Note that the spectra are normalized to the averaged absorption between 310 and 320 eV, i.e., total carbon, so that the peak height of the $1s-\pi^*$ transition is proportional to the shikimic acid concentration in an individual particle and differences in particle size are accounted for.

3.2 Humidity dependence

The evolution of the $1s-\pi^*$ transition peak with exposure to O_3 was monitored at four different relative humidities: 12 %, 52 %, 71 % and 82 %. This was done by normalizing the peak height measured for one particle after a certain time of oxidation to the average initial height measured in particles prior to oxidation at this humidity (Fig. 3a). The resulting value equals the relative loss of shikimic acid $[Y]_b/[Y]_{b,0}$ where $[Y]_b$ is the current bulk concentration of shikimic acid of the measured particle and $[Y]_{b,0}$ the associated average initial bulk concentration. In other words, for one sample, after taking spectra on a number of particles (2–9) to determine the average signal proportional to the initial concentration $[Y]_{b,0}$, exposure starts at the same time for all particles, but the signal proportional to $[Y]_b$ is quantified for different other individual particles at different times, i.e. $[Y]_b$ is only measured once for each individual particle. Therefore, each data point in Fig. 3 represents the ratio $[Y]_b/[Y]_{b,0}$ for a different particle. Beam damage prevents observing the degradation for the same particle over longer times.

Figure 3 clearly demonstrates that the degradation rate of shikimic acid is depending on humidity. In the following, the degradation rate laws are discussed for different

conceivable kinetic regimes. Assuming a pseudo first order reaction, the depletion rate is linearly dependent on $[Y]_b$ (Eq. 1)

$$\frac{d[Y]_b}{dt} = -k^{II}[O_3]_b[Y]_b = -k^{II}H_{O_3}p_{O_3}[Y]_b = -k_Y^I[Y]_b \quad (1)$$

5 where $[O_3]_b$ equals the O_3 concentration in the aerosol bulk in molL^{-1} , k^{II} the second order rate constant in $\text{M}^{-1}\text{s}^{-1}$, H_{O_3} the Henry constant in $\text{molL}^{-1}\text{atm}^{-1}$, p_{O_3} the absolute pressure of O_3 in the system in atm and k_Y^I the pseudo first order rate constant with respect to shikimic acid depletion in s^{-1} . Solving the differential equation shows that the relative loss as a function of time can be fitted with an exponential decay (Eq. 2).

$$\frac{[Y]_b}{[Y]_{b,0}} = e^{-k_Y^I t} \quad (2)$$

Equation (1) is valid, if the reactants (O_3 and Y) remain well mixed throughout the particle volume and depletion is only limited by the rate of the reaction. This is referred to as the bulk reaction limited case (Berkemeier et al., 2013) or often also referred to as volume limited uptake. In contrast to that, if the reaction is fast compared to diffusion so that O_3 does not reach far into the interior of the particle, the loss rate of $[Y]_b$ exhibits a square root dependence of $[Y]_b$ which is traditionally referred to as reacto-diffusive limitation (Eq. 3),

$$\frac{d[Y]_b}{dt} = -H_{O_3}RT\sqrt{D_{O_3}k_b^{II}\frac{S_p}{V_p}}[O_3]_g\sqrt{[Y]_b} = -k^D\sqrt{[Y]_b} \quad (3)$$

20 where R is the gas constant in $\text{LatmK}^{-1}\text{mol}^{-1}$, D_{O_3} the diffusion coefficient of O_3 in the bulk in cm^2s^{-1} , $[O_3]_g$ the gas phase ozone concentration in molL^{-1} , S_p the particle surface in cm^2 and V_p the particle volume in cm^3 . The relative loss can then be

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described by a second order polynomial as a function of time (Eq. 4),

$$\frac{[Y]_b}{[Y]_0} = \left(\frac{-k^D t + 2\sqrt{[Y]_0}}{2\sqrt{[Y]_0}} \right)^2 \quad (4)$$

which is a more general form of the equation described by Worsnop et al. for reacto-
diffusive limitation in spherical particles (Worsnop et al., 2002). In this case $[Y]_{b,0}$ is
needed to fit the data; these concentrations at different humidities were derived from
measurements of the growth of dry shikimic acid particles as a function of humidity
in an electrodynamic balance (EDB) (S. S. Steimer and U. K. Krieger, personal com-
munication, 2014). As one can see from comparison of the fits for the different kinetic
regimes in Fig. 3a, the two regimes can not be distinguished with the available data. By
fitting a linearized version of the respective integrated rate law to the measured data
(Fig. 4), one can determine k_Y^l [s^{-1}] (Eq. 5)

$$\ln \left(\frac{[Y]_b}{[Y]_{b,0}} \right) = -k_Y^l t \quad (5)$$

and k^D [$\text{mol}^{0.5} \text{L}^{-0.5} \text{s}^{-1}$] (Eq. 6)

$$2\sqrt{[Y]_b} - 2\sqrt{[Y]_0} = -k^D t \quad (6)$$

from the slope of the fits. The resulting rate constants are listed in Table 1. Using the
relation of pseudo first order and second order rate constant (Eq. 1) and the description
of the uptake coefficient γ for a bulk reaction limited system (Eq. 7),

$$\gamma_{\text{O}_3} = \frac{4k^{\parallel} H_{\text{O}_3} RT [Y]_b V_p}{\bar{c} S_p} \quad (7)$$

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3.4 Chemical maps

For a highly viscous particle with low diffusion coefficients, a gradient of the condensed phase reactant might build up in the bulk material, as suggested by Shiraiwa et al. (2011) for the case of ozonolysis of a protein. The kinetic analysis at different humidities and the size dependence have also led us to suggest that the reaction occurs within a thin layer close to the surface (for the medium and lower humidities) and that the differences between the humidities would be attributed to a change in diffusion coefficient by four orders of magnitude. It would thus be conceivable to assume that the diffusion coefficient of shikimic acid could become low enough so that the diminished exchange within the bulk phase leads to a gradient within the particles. Therefore, we extracted chemical maps showing the distribution of the double bond throughout the particles at various steps of the oxidation process at 13 % RH, 52 % RH and 71 % RH. Figure 6a–c show the progress of the oxidation for different particles at 71 % RH. These figures again clearly show that the concentration of the double bond decreases with an increasing O_3 dose (Sect. 3.1). In Fig. 6c, one can clearly see that the smaller particle of the two is oxidized to a larger degree than the larger one (Sect. 3.3). This decrease occurs homogeneously throughout the particle, as would be expected for particles at high humidity, where the diffusivity of shikimic acid is likely large enough to allow sufficient exchange throughout the particle, in spite of the fact that the actual reaction occurs within the reacto-diffusive depth of O_3 . The radial profiles in Fig. 6d support this conclusion. Also at 52 % RH no gradient was apparent in spite of measurable overall degradation. Plots e to g in Fig. 6 on the other hand depict the progress of oxidation at 12 % RH. No oxidation is observable, as also seen from the radial profiles in Fig. 6h. Progression of the reaction from the surface towards the interior was obviously too slow to be observed within the duration of the experiment, and the layer of oxidized material too thin to become apparent within the resolution of the method. As estimated above, the reacto-diffusive length of O_3 would be 0.9 nm at this humidity. Accordingly, the integrated analysis of many more particles shown in Fig. 3 likewise does not show

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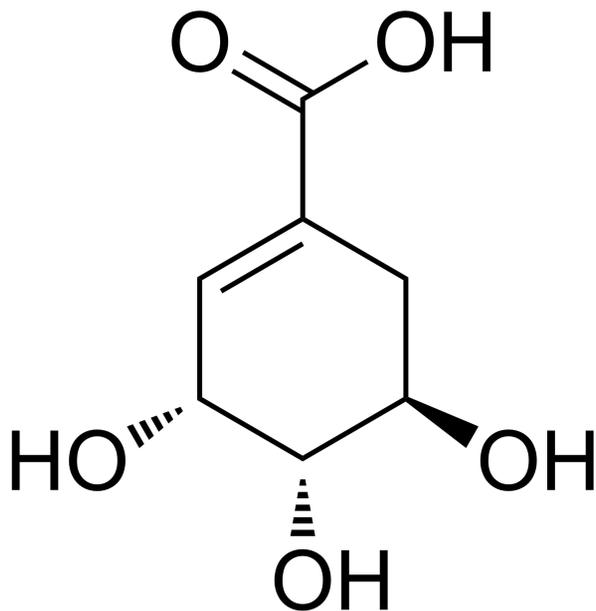


Fig. 1. Structure of shikimic acid.

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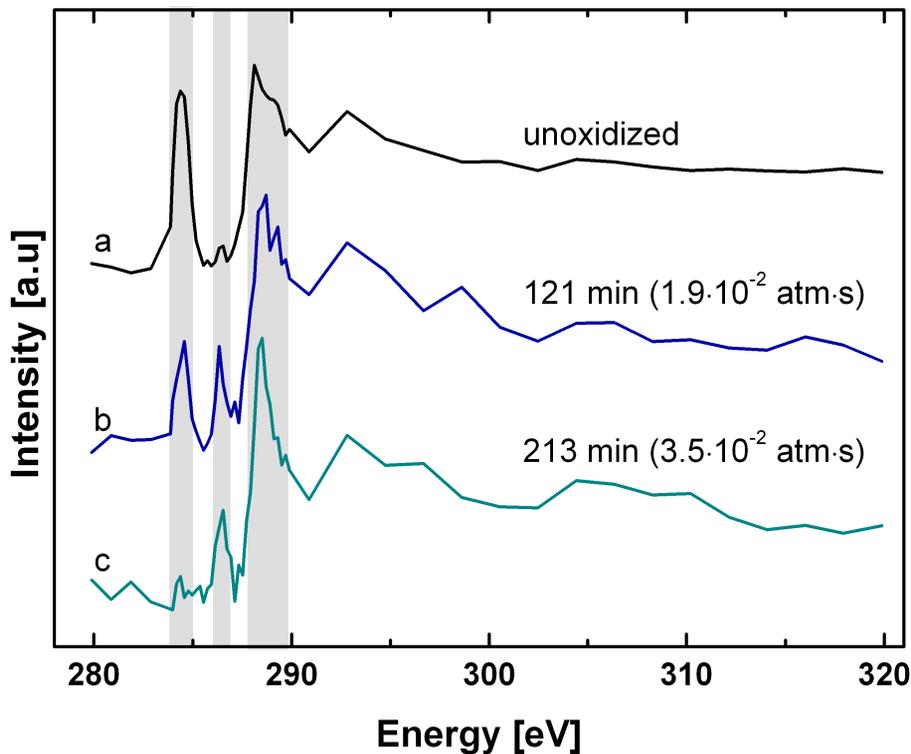


Fig. 2. Averaged spectra of single particles before and after oxidation at a relative humidity of 82 %. The grey areas denote regions in which spectral changes can be observed. The main feature of the oxidation is the decrease of the $1s-\pi^*$ peak at 284.4 eV.

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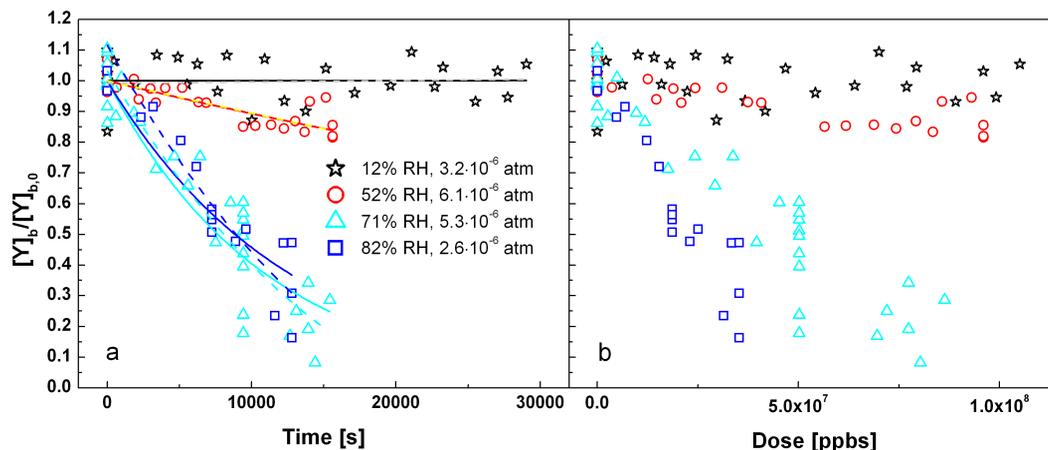


Fig. 3. (a) Depletion of shikimic acid as a function of exposure time via the decrease in the normalized OD at 284.4 eV (relative loss). The depletion was measured at four different relative humidities. The lines show the respective fits for that humidity assuming pseudo first order decay (black, red, blue and cyan, solid line) and reacto-diffusive limitation (grey, yellow, blue and cyan, dashed line). (b) Depletion of shikimic acid as a function of O_3 dose via the decrease in the normalized OD at 284.4 eV at four different relative humidities.

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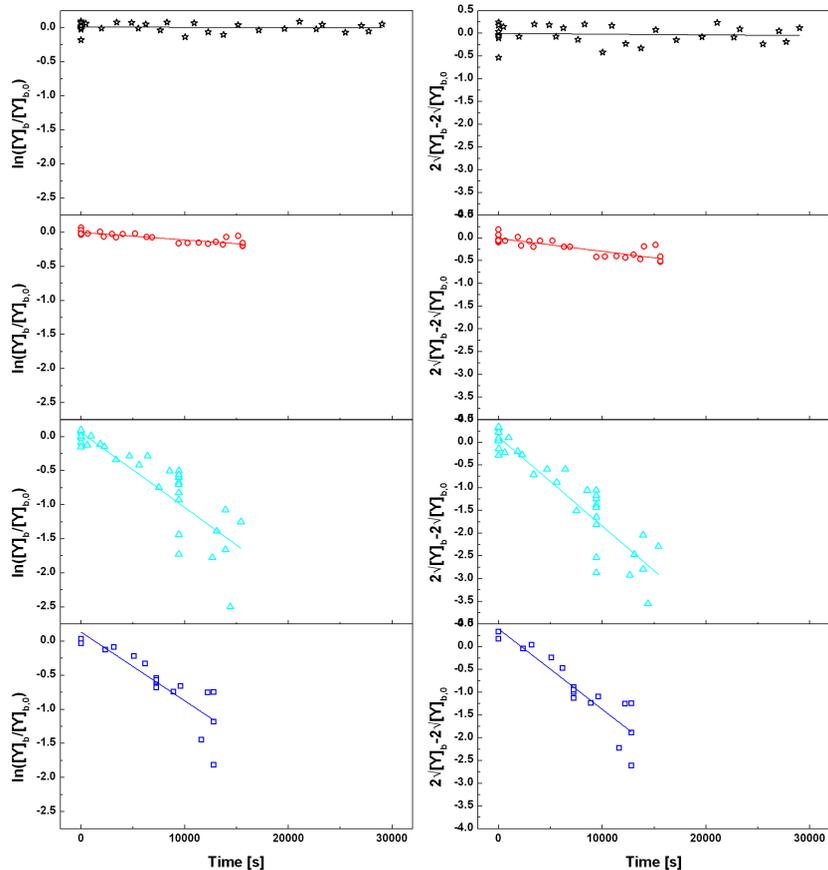


Fig. 4. Linearized plots for pseudo first order volume limited (left) and reacto-diffusion limited reaction (right): linearized plots for the reacto-diffusive case: 12 % RH (black stars, 3.2×10^{-6} atm), 52 % RH (red circles, 6.1×10^{-6} atm), 71 % RH (light blue triangles, 5.3×10^{-6} atm) and 83 % RH (blue squares, 2.6×10^{-6} atm). The slope of the linear fit equals the corresponding rate constant.

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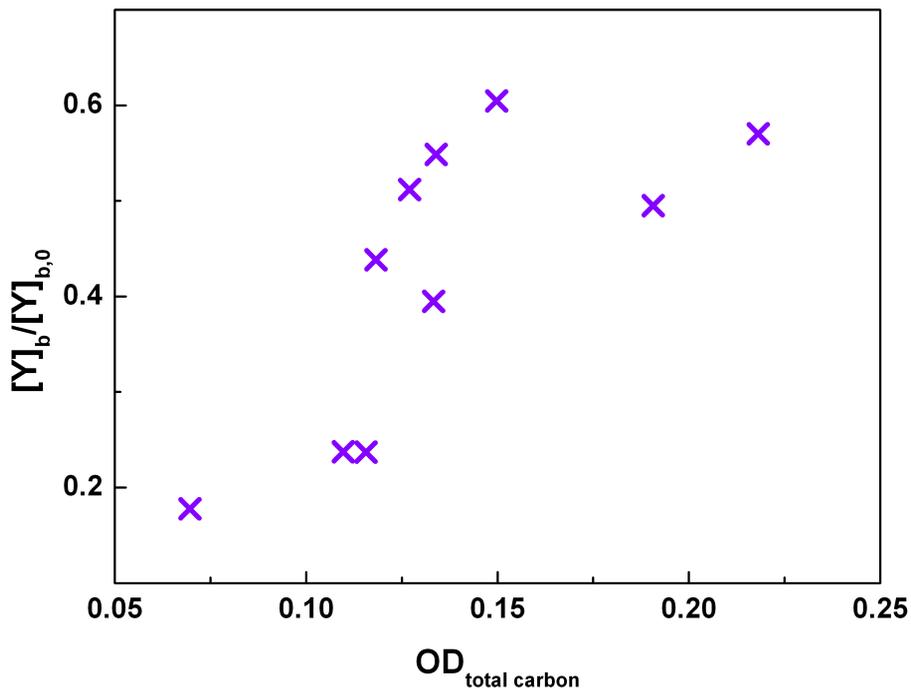


Fig. 5. Size dependence of the oxidation rate: the amount of material already oxidized differs for particles of different thickness, all oxidized at 71 % RH with an ozone dose of $5.0 \times 10^{-2} \text{ atm s}^{-1}$.

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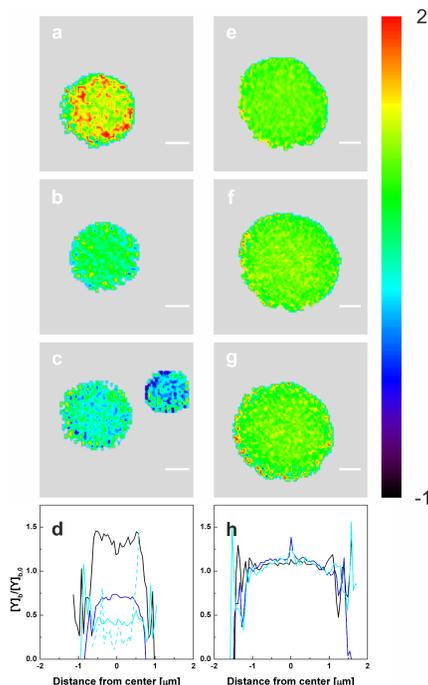


Fig. 6. Depletion of shikimic acid via the decrease of OD at the maximum of the $1s-\pi^*$ transition peak around 284.4 eV normalized to total carbon. **(a–c)** show the progress of the reaction for four different particles at 71% RH at O_3 doses of 0 atm s^{-1} **(a)**, $5.0 \times 10^{-2} \text{ atm s}^{-1}$ **(b)** and $7.7 \times 10^{-2} \text{ atm s}^{-1}$ **(c)**. **(d)** depicts the respective radial profiles of the particles: **(a)** (black line), **(b)** (dark blue line) and **(c)** (light blue lines, solid (larger particle) and dashed (smaller particle)). **(e–g)** show the progress of the reaction for three different particles at 13% RH with O_3 doses of 0 atm s^{-1} **(e)**, $1.4 \times 10^{-2} \text{ atm s}^{-1}$ **(f)** and $7.9 \times 10^{-2} \text{ atm s}^{-1}$ **(g)**. **(h)** depicts the respective radial profiles: **(e)** (black line), **(f)** (dark blue line) and **(g)** (light blue line). The scale bar denotes 500 nm. The images show that no observable concentration gradient has formed at either humidity.

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