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# Viscosity controls humidity dependence of N<sub>2</sub>O<sub>5</sub> uptake to citric acid aerosol

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**Abstract.** The heterogeneous loss of dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) to aerosol particles has a significant impact on the night-time nitrogen oxide cycle and therefore the oxidative capacity in the troposphere. Using a <sup>13</sup>N short-lived radioactive tracer method, we studied the uptake kinetics of N<sub>2</sub>O<sub>5</sub> on citric acid aerosol particles as a function of relative humidity (RH). The results show that citric acid exhibits lower reactivity than similar dicarboxylic and polycarboxylic acids, with uptake coefficients between  $\sim 3 \times 10^{-4}$ – $\sim 3 \times 10^{-3}$  depending on humidity (17–70 % RH). At RH above 50 %, the magnitude and the humidity dependence can be best explained by the viscosity of citric acid as compared to aqueous solutions of simpler organic and inorganic solutes and the variation of viscosity with RH and, hence, diffusivity in the organic matrix. Since the diffusion rates of N<sub>2</sub>O<sub>5</sub> in highly concentrated citric acid solutions are not well established, we present four different parameterizations of N<sub>2</sub>O<sub>5</sub> diffusivity based on the available literature data or estimates for viscosity and diffusivity of H<sub>2</sub>O. Above 50 % RH, uptake is consistent with the reacto-diffusive kinetic regime whereas below 50 % RH, the uptake coefficient is higher than expected from hydrolysis of N<sub>2</sub>O<sub>5</sub> within the bulk of the particles, and the uptake kinetics is most likely limited by loss on the surface only. This study demonstrates the impact of viscosity in highly oxidized and highly functionalized secondary organic aerosol material on the heterogeneous chemistry of N<sub>2</sub>O<sub>5</sub> and may explain some of the unexpectedly low loss rates to aerosol derived from field studies.

## 1 Introduction

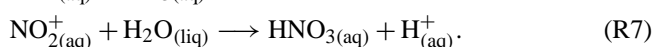
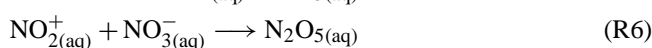
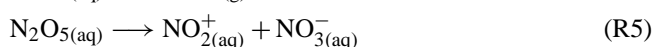
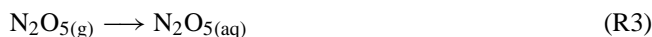
Dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) is an important species of night-time atmospheric chemistry (Abbatt et al., 2012; Chang et al., 2011; Dentener and Crutzen, 1993). Nitrogen dioxide (NO<sub>2</sub>) reacts with ozone (O<sub>3</sub>) to give the nitrate radical (NO<sub>3</sub>). N<sub>2</sub>O<sub>5</sub> is formed via Reaction (R1).



The concentrations of N<sub>2</sub>O<sub>5</sub>, NO<sub>3</sub> and NO<sub>2</sub> are controlled by the temperature-dependent equilibrium (Reaction R1). N<sub>2</sub>O<sub>5</sub> hydrolyzes on any humid surface or in aqueous solution, to give HNO<sub>3</sub> (Reaction R2).



In Reaction (R2), which is considered unimportant in the gas phase, H<sub>2</sub>O represents either adsorbed water, ice or liquid water, present on ground or on airborne particles. The detailed mechanism behind Reaction (R2) that drives heterogeneous uptake of N<sub>2</sub>O<sub>5</sub> on aerosol particles is complex (Hallquist et al., 2003; Mozurkewich and Calvert, 1988; Wahner et al., 1998). The suggested elementary steps of the mechanism are the following:



A reversible disproportionation (Reactions R5, R6) precedes the actual reaction of the nitronium ion NO<sub>2</sub><sup>+</sup> with water (Reaction R7). In case of nitrate already present in the particle phase, uptake is considerably reduced through Reaction (R6), referred to as the nitrate effect (Mentel et al., 1999). The aqueous HNO<sub>3</sub> formed in Reaction (R7) can either deprotonate to yield nitrate or evaporate from the particle according to its volatility and acid–base chemistry with other solutes in the system (Laskin et al., 2012). Water plays an important role in the mechanism, not only for solvation of N<sub>2</sub>O<sub>5</sub> (Reactions R3, R4) and hydration of the nitronium ion, but it is also the main reaction partner of the nitronium ion in absence of other nucleophiles (such as chloride, which are not considered in this work).

Heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> on aerosols acts as a sink for atmospheric NO<sub>x</sub> species, and has therefore a significant impact on ozone production and the oxidative capacity of the atmosphere (Dentener and Crutzen, 1993). N<sub>2</sub>O<sub>5</sub> uptake kinetics on aerosols has thus received substantial interest over the past decades (Abbatt et al., 2012). The loss rate of N<sub>2</sub>O<sub>5</sub> from the gas phase to aerosol particles is expressed in terms of the uptake coefficient,  $\gamma$ , which represents the probability that a gas kinetic collision of a N<sub>2</sub>O<sub>5</sub> molecule leads to its uptake at the interface. Extensive studies on inorganic aerosols or corresponding proxy systems have shown that the primary factors influencing the uptake coefficient in the range of 0.0001 to 0.05 are relative humidity (RH), physical state, particle size, and composition (Abbatt et al., 2012; Davis et al., 2008; George et al., 1994; Hallquist et al., 2003; Hanson and Ravishankara, 1991; Hu and Abbatt, 1997; Karagulian et al., 2006; Mozurkewich and Calvert, 1988; Vandoren et al., 1991; Wahner et al., 1998). Super-saturated liquid particles have shown uptake coefficients up to 1–2 orders of magnitude higher than corresponding solid particles at the same RH, pointing towards the importance of the hydrolysis reaction (Reactions R3–R7) of N<sub>2</sub>O<sub>5</sub> with liquid water present in the bulk of aerosol particles (Hallquist et al., 2003; Thornton and Abbatt, 2005).

Recently, the focus of N<sub>2</sub>O<sub>5</sub> uptake studies has shifted towards organic and mixed inorganic and organic aerosol particles (Anttila et al., 2006; Gaston et al., 2014; Griffiths et al., 2009; Gross et al., 2009; Thornton et al., 2003). Hydrophobic organics may rather form organic surface films or phase separated liquid coatings and thereby may suppress  $\gamma$  for N<sub>2</sub>O<sub>5</sub> significantly compared to pure inorganic aerosols (Badger et al., 2006; Riemer et al., 2009; Thornton and Abbatt, 2005). In turn, particles composed of hygroscopic organics, such as polycarboxylic acids, show uptake coefficient values that in some cases approach those for inorganic aerosols due to their high water content (Griffiths et al., 2009; Thornton et al., 2003), and the humidity-dependent uptake can be understood in terms of the activity of water as reactant (Bertram and Thornton, 2009; Ammann et al., 2013).

Organic aerosols account for a significant fraction of atmospheric particulate mass (Kanakidou et al., 2005). How-

ever there are still significant gaps in our knowledge regarding the chemistry and physical state of organic aerosols (De Gouw and Jimenez, 2009; Kanakidou et al., 2005; Zhang et al., 2007). Recent studies have shown that the previous assumptions of low-viscosity, well-mixed liquid aerosol phases are not always correct, but must be considered depending on environmental conditions such as humidity and temperature. Especially under cold or dry conditions, aerosol particles dominated by organic compounds can exhibit a highly viscous or even glassy state (Koop et al., 2011; Murray, 2008; Renbaum-Wolff et al., 2013; Virtanen et al., 2010; Zobrist et al., 2008). Diffusion in these particles is significantly retarded (Price et al., 2014; Zobrist et al., 2011), leading to severe kinetic limitations in gas-particle partitioning (Shiraiwa et al., 2013; Vaden et al., 2011).

Field measurements (Bertram et al., 2009; Brown et al., 2009) have shown that the observed reactivity of N<sub>2</sub>O<sub>5</sub> on aerosol particles containing organics can be up to a factor of 10 lower than the values predicted by model parameterizations, which are based on laboratory measurements with organic compounds such as malonic acid. Also, a recent laboratory study has shown that uptake of N<sub>2</sub>O<sub>5</sub> to laboratory SOA proxies does not follow exclusively the expected trend with water content based on the correlation of the latter with O : C ratio (Gaston et al., 2014).

For this study we investigated the uptake of N<sub>2</sub>O<sub>5</sub> on citric acid aerosol using the short-lived <sup>13</sup>N radioactive tracer technique developed at the Paul Scherrer Institute (Ammann, 2001; Gržinić et al., 2014). This technique has been used before to study the uptake kinetics of other nitrogen oxides on aerosol particles (Guimbaud et al., 2002; Sosedova et al., 2009; Vlasenko et al., 2009), and we have recently developed a method to produce <sup>13</sup>N-labelled N<sub>2</sub>O<sub>5</sub> for this purpose (Gržinić et al., 2014). Citric acid was used as a proxy for highly oxidized organic species found in secondary organic aerosol (SOA). It has well-known thermodynamic properties and new studies on viscosity and water diffusivity in citric acid have recently become available (Lienhard et al., 2012, 2014). In our study, measurements were conducted over a wide RH range, and several methods were used to estimate the diffusivity of N<sub>2</sub>O<sub>5</sub> in citric acid as a basis for the kinetic analysis.

## 2 Experimental

The experimental method used in this study has been described in detail in our previous publication (Gržinić et al., 2014). N<sub>2</sub>O<sub>5</sub> labelled with the <sup>13</sup>N short-lived radioactive isotope is mixed with citric acid aerosol in an aerosol flow tube. Gas and aerosol phase products are selectively separated and trapped in a parallel plate diffusion denuder system and a particle filter, respectively. The concentration of the various species can be measured simultaneously by monitoring the radioactive decay of the <sup>13</sup>N-labelled species on each

trap over time. A schematic representation of our experimental setup can be found in Gržinić et al. (2014).

## 2.1 Production of <sup>13</sup>N-labelled N<sub>2</sub>O<sub>5</sub>

<sup>13</sup>N ( $\tau_{1/2} \approx 10$  min) is produced online in a flow-through gas-target via the <sup>16</sup>O(*p*, $\alpha$ )<sup>13</sup>N reaction in 10–15 % O<sub>2</sub> in He, at a total flow rate of 1 standard L min<sup>-1</sup> at  $\sim 2$  bar (see Ammann, 2001; Gržinić et al., 2014, for more details). The highly oxidized <sup>13</sup>N-labelled nitrogen species, are reduced to <sup>13</sup>NO over a Mo converter (at  $\sim 380$  °C) and transported from the production site to the laboratory through a 580 m long 4 mm inner diameter polyvinylidene fluoride (PVDF) tube. A small amount of the <sup>13</sup>NO containing gas flow (50 mL min<sup>-1</sup>) is mixed with nitrogen carrier gas and non-labelled NO ( $\sim 2$  mL min<sup>-1</sup>) from a certified gas cylinder (10 ppm in N<sub>2</sub>). O<sub>3</sub> at  $\sim 8$  ppmv is produced by irradiating a flow (50 mL min<sup>-1</sup>) of 10 % O<sub>2</sub> in N<sub>2</sub> with 185 nm UV light in a cylindrical photolysis reactor. The <sup>13</sup>NO and O<sub>3</sub> flows are mixed in the N<sub>2</sub>O<sub>5</sub> synthesis reactor (34 cm long and 4 cm inner diameter, with residence time  $\sim 4$  min), where NO reacts with O<sub>3</sub> to produce first NO<sub>2</sub> and then NO<sub>3</sub>, which then react via Reaction (R1) to form N<sub>2</sub>O<sub>5</sub>. This reactor is covered inside with a thin polytetrafluoroethylene (PTFE) foil to minimize heterogeneous N<sub>2</sub>O<sub>5</sub> losses, and outside by a dark cloth shroud to prevent NO<sub>3</sub> photolysis. Design, performance and consistency of N<sub>2</sub>O<sub>5</sub> production with simulations obtained via a gas kinetic model has been described previously (Gržinić et al., 2014).

## 2.2 Aerosol production

An ultrasonic nebulizer was used to generate an aerosol from a 0.07 % (by weight) solution of citric acid (HQ, Fluka, > 99 %) in MilliQ water. The resulting aerosol particles were dried over a Nafion membrane diffusion drier. Citric acid particles remain in liquid (supersaturated) form over a very wide humidity range (6–90 % RH) and neither crystallization (efflorescence) nor deliquescence has been reported over this range (Peng et al., 2001; Zardini et al., 2008). To avoid possible efflorescence of the aerosol particles in dry air, the sheath gas used in the diffusion drier has been humidified to 15–17 % RH. The resulting aerosol gas flow was passed through a homemade <sup>85</sup>Kr bipolar ion source to establish an equilibrium charge distribution on the aerosol, followed by an electrostatic precipitator to remove all charged particles. This was done to avoid uncontrollable wall losses of charged particles in the insulating aerosol flow tube. A homemade Gore-Tex™ membrane humidifier was placed behind the precipitator for precise adjustment of RH, followed by an elution volume with  $\sim 2$  min residence time to assure gas – particle equilibrium. Measurements were conducted from 17 to 70.3 % RH.

A Scanning Mobility Particle Sizer (SMPS) was used to measure the suspended surface area to gas volume ratio. The

SMPS system consisted of an <sup>85</sup>Kr ion source (to re-establish the equilibrium charge distribution), a Differential Mobility Analyzer (DMA, TSI 3071) and a Condensation Particle Counter (CPC, TSI 3022). Filtered carrier gas was used as sheath gas for the DMA to assure identical RH in the two flows and thus maintain the water content of the particles during size separation. The SMPS was connected immediately after the aerosol flow tube. A capacitance humidity sensor was placed in front of the SMPS to monitor RH.

## 2.3 Aerosol flow tube

The gas flows containing aerosol and N<sub>2</sub>O<sub>5</sub>, respectively, were mixed in a cylindrical flow tube reactor consisting of a perfluoroalkoxy copolymer (PFA) tube with an inner diameter of 7 cm. The inlet and outlet are cylindrical PTFE stops with inverse cones milled into. The stops are equipped with a pneumatic ring to seal the reactor. The inlet and outlet can be moved inside the reactor to vary reaction time. The N<sub>2</sub>O<sub>5</sub> gas flow (102 mL min<sup>-1</sup>) is introduced into the aerosol flow tube along the axis of the reactor. The distance between the N<sub>2</sub>O<sub>5</sub> reactor and the aerosol flow tube was kept short, and the N<sub>2</sub>O<sub>5</sub> reactor was moved along with the inlet into the aerosol flow tube when changing the reaction time. The aerosol flow (720 mL min<sup>-1</sup>) is introduced via a stainless-steel tubular injector (6 mm in diameter) which protrudes from the inlet and is bent in such a way that the injector nozzle is equidistant from the walls of the flow tube. The aerosol flow is injected perpendicularly to the N<sub>2</sub>O<sub>5</sub> gas flow within the flow tube. Reaction times from 10 to 60 s were adjusted. For the flow rate used, a laminar flow profile is assumed to have been established within the flow tube a few cm downstream of the aerosol injector. As with the N<sub>2</sub>O<sub>5</sub> synthesis reactor, a black shroud was used to shield the aerosol flow tube from daylight to prevent NO<sub>3</sub> photolysis and thus loss of N<sub>2</sub>O<sub>5</sub>. The overall system exhaust was pressure controlled at slightly below ambient pressure (960–970 mbar). The aerosol flow tube was kept at ambient temperature, which was controlled by the room ventilation system at  $295 \pm 1$  K.

## 2.4 Separation and detection of <sup>13</sup>N-labelled species

The gas flow from the aerosol flow tube was split with one fraction going to the SMPS system or alternatively a NO<sub>x</sub> (Teledyne T200) or O<sub>3</sub> analyzer (ML 9810) and the other being directed into the parallel plate diffusion denuder system. This system consists of a series of parallel plate sets placed 1 mm apart in an aluminium housing. The plates are prepared with specific coatings and trap the <sup>13</sup>N containing gaseous species (N<sub>2</sub>O<sub>5</sub>, NO<sub>3</sub> and NO<sub>2</sub>) by lateral diffusion and chemical reaction. Aerosol particles pass through the denuder without being trapped and are deposited on a glass fiber filter located at the exit of the denuder system. Citric acid has been used as a denuder coating for N<sub>2</sub>O<sub>5</sub>. Citric acid mixes well with water, has a well-known hygroscopic cycle

(Peng et al., 2001; Zardini et al., 2008), and interferes only weakly with NO<sub>2</sub>; i.e. only marginal amounts are trapped on the denuder plates. Citric acid was used as a coating on the first two denuder plates, the first one capturing N<sub>2</sub>O<sub>5</sub>, while the second one is used to quantify the small NO<sub>2</sub> interference. NO<sub>3</sub>, which is present in small quantities in the gas phase, cannot be separated from N<sub>2</sub>O<sub>5</sub> by this technique and is likewise absorbed on the first denuder plate together with N<sub>2</sub>O<sub>5</sub>. The citric acid coating was prepared by applying a citric acid solution 2 % by weight in 50 / 50 % methanol / water to the plates and allowed to dry at room temperature. The following two denuders were coated with a 1 % N-(1-naphthyl) ethylene diamine dihydrochloride (NDA) solution in 1 % KOH and 10 % water in methanol. NDA reacts efficiently with NO<sub>2</sub> and the basic nature of the solution prevents the re-evaporation of the so formed nitrite. Since NDA is sensitive to O<sub>3</sub>, which is present at around ~ 550 ppbv in our system, two sets of denuder plates were installed in series to extend the operating life. Fresh coatings were prepared and applied every day. An additional gamma detector was attached to the non-coated, 10 cm long, and trapezoidally shaped aluminium inlet to determine the amount of N<sub>2</sub>O<sub>5</sub> trapped there.

The <sup>13</sup>N containing species that were trapped on the denuder plates, inlet and particle filter were measured by monitoring the radioactive decay of <sup>13</sup>N. A CsI scintillator crystal with integrated PIN diode detector (Carroll and Ramsey, USA) was placed on each of the traps. <sup>13</sup>N, a well-known β<sup>+</sup> emitter, decays with emission of a positron which, upon annihilation with an electron, emits two coincident γ-rays in opposite directions. These γ-rays are detected by the scintillators and the signal is converted to the flux of the <sup>13</sup>N containing gaseous species into the respective traps using the inversion procedure reported elsewhere (Kalberer et al., 1996). The flux into a trap can be calculated using Eq. (1):

$$I_j = \frac{A_{j(i)} - A_{j(i-1)} \exp(-\lambda(t_i - t_{i-1}))}{1 - \exp(-\lambda(t_i - t_{i-1}))}, \quad (1)$$

where  $I_j$  is the flux into trap  $j$ ,  $A_{j(i-1)}$  and  $A_{j(i)}$  are two consecutive activity measurements performed at times  $t_{i-1}$  and  $t_i$ , and  $\lambda$  is the decay constant for <sup>13</sup>N ( $\lambda = 0.00116 \text{ s}^{-1}$ ). The measured flux is proportional to the gas phase concentration of the respective species. By comparing the value of the gas phase NO<sub>2</sub> concentration measured with the NO<sub>x</sub> analyzer to the <sup>13</sup>NO<sub>2</sub> and <sup>13</sup>N<sub>2</sub>O<sub>5</sub> signals measured at the denuder traps and the particle filter, it is possible to calculate the concentration of N<sub>2</sub>O<sub>5</sub> in the gas phase and its degradation products in the particle phase. The overall signal of N<sub>2</sub>O<sub>5</sub> in the gas phase was obtained by adding the inlet and first citric acid coated denuder plate signals and subtracting the second citric acid denuder signal (NO<sub>2</sub> interference). To correct for the small amounts of NO<sub>3</sub> present in the gas phase the signal was multiplied with the N<sub>2</sub>O<sub>5</sub> / (NO<sub>3</sub> + N<sub>2</sub>O<sub>5</sub>) ratio obtained via the gas kinetic model described in our previous study (Gržinić et al., 2014).

Additional information on coating preparation, traps and measurement efficiencies can be found in our previous publications (Ammann, 2001; Gržinić et al., 2014; Guimbaud et al., 2002).

### 3 Results and discussion

#### 3.1 Uptake coefficient of N<sub>2</sub>O<sub>5</sub> as a function of relative humidity

A typical experiment was performed as follows: after a period of stabilization, during which all flows were switched on, but the nebulizer switched off, the NO and NO<sub>2</sub> concentrations were measured via the NO<sub>x</sub> analyzer connected to the system (in place of the SMPS), before turning on the O<sub>3</sub> generator. Concentrations around 9–10 ppbv of NO were obtained in the aerosol flow tube reactor. From the measured gamma-ray detector signals of N<sub>2</sub>O<sub>5</sub> and NO<sub>2</sub>, after switching on the O<sub>3</sub> generator, typically, a maximum initial concentration of ~ 5 ppbv of N<sub>2</sub>O<sub>5</sub> was calculated. Next, a wall loss measurement was performed by changing the length of the aerosol flow tube and thus the reaction time, which is shown in the first part of the exemplary record of an experiment in Fig. 1. Typical pseudo-first order wall loss rate constants,  $k_w$ , were ~  $9 \times 10^{-3}$  and ~  $3 \times 10^{-2} \text{ s}^{-1}$  for low and high humidity, respectively, indicating strong wall loss of the labelled N<sub>2</sub>O<sub>5</sub> molecules.  $k_w$  was remaining constant over time after an initial passivation period. After the wall loss measurement was completed, the SMPS was connected to the system and the reactor length was adjusted to enable a 60 s reaction time within the aerosol flow tube. The wall loss measurement was routinely performed for each set of aerosol experiment.

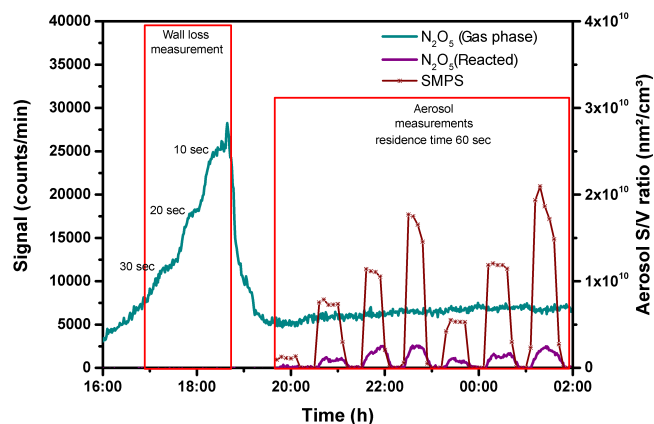
At this point the nebulizer was switched on to generate citric acid aerosol for 25–30 min and then switched off again for an interval of the same duration. The aerosol surface area was varied by changing the vibration frequency of the piezoelectric membrane in the ultrasonic nebulizer, leading to data as shown in Fig. 2.

The gas-aerosol interaction kinetics can be described by Eq. (2):

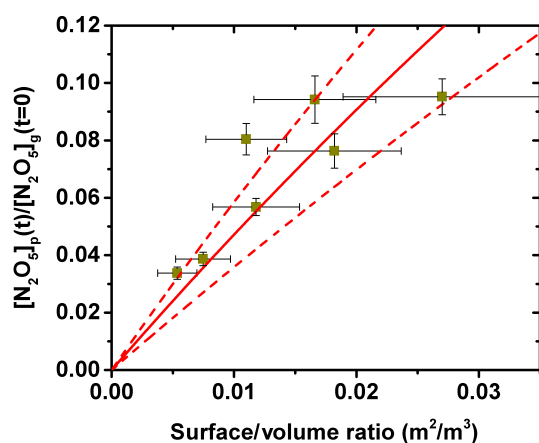
$$\frac{C_p^{(t)}}{C_g^{(t=0)}} = \frac{1 - e^{-(k_w + k_p)t}}{1 + \frac{k_w}{k_p}}, \quad (2)$$

where  $C_g^{(t=0)}$  is the gas-phase N<sub>2</sub>O<sub>5</sub> concentration at time zero,  $C_p^{(t)}$  is the N<sub>2</sub>O<sub>5</sub> concentration in the particle phase at the end of the reactor,  $t = 60 \text{ s}$ ,  $k_w$  is the wall loss rate constant, measured as described above, and  $k_p$  denotes the apparent first order rate coefficient for loss of N<sub>2</sub>O<sub>5</sub> from the gas phase due to its heterogeneous reaction with the aerosol phase. Equation (3) relates  $k_p$  to the uptake coefficient,  $\gamma$ :

$$\gamma = \frac{4k_p}{S_p \omega} \quad \omega = \sqrt{\frac{8RT}{\pi M}}, \quad (3)$$



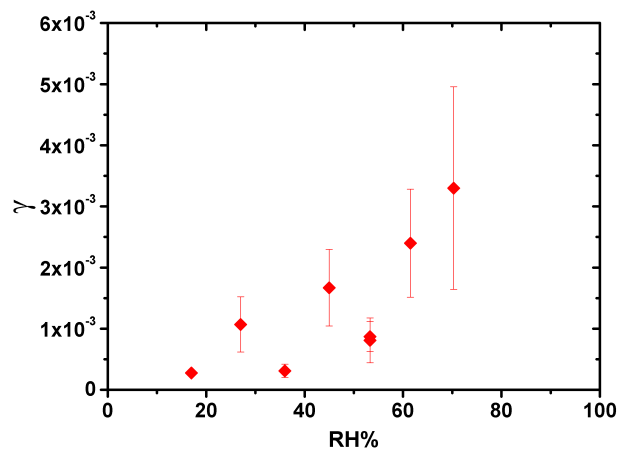
**Figure 1.** Exemplary traces of inverted detector signals for an experiment: teal: gas-phase <sup>13</sup>N<sub>2</sub>O<sub>5</sub> signal; purple: particle-phase <sup>13</sup>N signal; red: SMPS signal (aerosol surface / volume ratio).



**Figure 2.** Normalized particle-phase N<sub>2</sub>O<sub>5</sub> concentration vs. aerosol surface area to gas volume ratio for the experiment from Fig. 1. The data points represent experimental data; vertical error bars represent a 95 % confidence interval, horizontal error bars represent the S/V measurement error (30 %), the full red line is the fitted series determined by least-squares fitting of Eq. (2) to experimental data, the dashed red lines are 95 % confidence intervals.

where  $S_p$  is the total aerosol surface area to gas volume ratio obtained with the SMPS,  $\omega$  is the mean thermal velocity of N<sub>2</sub>O<sub>5</sub>,  $R$  is the gas constant,  $T$  is the absolute temperature and  $M$  is the molar weight of N<sub>2</sub>O<sub>5</sub>. Equation (2) was then used to fit the experimental data as shown in Fig. 2 with  $\gamma$  being the only variable. Note that this procedure of varying the aerosol surface area to volume ratio gave better reproducibility and lower scatter than varying the interaction time. The resulting  $\gamma$  values ranged from  $3 \times 10^{-4}$  to  $\sim 3 \times 10^{-3}$  over the RH range of 17 to 70 % as shown in Fig. 3.

The uncertainty in  $\gamma$  arises primarily from the fact that aerosol uptake rates ( $k_p$ ) were smaller than wall loss rates ( $k_w$ ) as well as from the systematic error associated with the measurements of surface to volume ratio of the aerosol by the



**Figure 3.** Uptake coefficient of N<sub>2</sub>O<sub>5</sub> on citric acid as a function of RH. Error bars represent 95 % confidence bounds. The measured values can be found in Table S1 of the Supplement.

SMPS ( $S_p$ ), which amounts to  $\sim 30$  %. The 95 % confidence interval from replication (as can be seen in Fig. 2) does not strongly influence the overall uncertainty for  $\gamma$ . There are a few factors that may have influenced the scatter among the measurements at different RH. We have noticed that a small but variable number of very large particles fell outside the measurement range of the DMA, which for our settings was limited to particle diameters up to 806 nm. Additionally, two separate batches of citric acid (from the same manufacturer) have been used to prepare the solutions, and possible contaminations, which might induce phase separation or crystallization, may have affected the physical properties and reactivity of the resulting aerosol.

Compared to other aqueous polycarboxylic acids (Griffiths et al., 2009; Thornton et al., 2003) the uptake coefficient on citric acid is more than an order of magnitude lower. As mentioned in the experimental section, care was taken to avoid crystallization by using a humidified gas flow to equilibrate the solution droplets resulting from the nebulizer to the lowest RH used in the experiments. Therefore, the low uptake coefficients are unlikely to represent uptake to crystalline citric acid. With respect to the humidity range, the primary limitations were wall loss (at high RH) and potential efflorescence of the aqueous aerosol (at RH at or below 6 %, Peng et al., 2001).

As a consistency test we measured the uptake coefficient of N<sub>2</sub>O<sub>5</sub> on deliquesced ammonium sulfate aerosol at 52 % RH as described by (Gržinić et al., 2014) and obtained an average value of  $(1.4 \pm 0.4) \times 10^{-2}$ , similar to other studies compiled by Ammann et al. (2013).

### 3.2 Physical state, reaction mechanism, and parameterization

The data in Fig. 3 show a gradual increase of the uptake coefficient with increasing RH, consistent with the expected increase in water content. Literature data suggest that citric acid particles form supersaturated solutions down to low RH (Peng et al., 2001; Zardini et al., 2008). Recent experiments have demonstrated high viscosity of highly supersaturated citric acid solutions, obtained either from the kinetics of shape change of coalescing droplets (J. Reid and C. Cai, personal communication, 2015, and using the method described by Power et al., 2013) or via the hygroscopic growth kinetics in single levitated droplets (Lienhard et al., 2014). It is thus not surprising that the observed uptake coefficient of N<sub>2</sub>O<sub>5</sub> of around 10<sup>-4</sup> at low humidity is comparable to succinic acid or oxalic acid in their effloresced (and thus solid) form Griffiths et al. (2009). The difference between low and high humidity is also similar to that of solid (effloresced) vs. liquid (deliquesced) inorganic aerosol (Hallquist et al., 2003), but as mentioned above, the gradual increase observed here is consistent with the absence of a sharp deliquescence step and thus probably the result of continuously changing water content and hence diffusivity of N<sub>2</sub>O<sub>5</sub> within the particles. This is in line with previous observations of the gradually changing water content in amorphous organics (Mikhailov et al., 2009).

For moderate uptake rates and submicron particles, where gas-phase diffusion constraints can be neglected, the N<sub>2</sub>O<sub>5</sub> uptake coefficient can be described according to the resistor model (Davidovits et al., 1995) with Eq. (4):

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_b} = \frac{1}{\alpha_b} + \frac{\omega}{4HRT\sqrt{D_1k^I}} \left( \coth q - \frac{1}{q} \right)^{-1}, \quad (4)$$

where  $\alpha_b$  is the bulk accommodation coefficient,  $H$  is the Henry's law constant,  $R$  is the gas constant,  $T$  is the absolute temperature,  $D_1$  is the liquid-phase diffusion coefficient,  $k^I$  is the apparent first-order loss rate constant for N<sub>2</sub>O<sub>5</sub> in the liquid phase,  $\omega$  is the mean thermal velocity of N<sub>2</sub>O<sub>5</sub> molecules in the gas phase and  $q$  is the reacto-diffusive parameter which accounts for the competition between reaction and diffusion within the particle. The reacto-diffusive parameter is defined by Eq. (5):

$$q = \frac{l}{r}, \quad (5)$$

where  $r$  is the radius of the particle and  $l$  is the reacto-diffusive length, defined by Eq. (6):

$$l = \sqrt{\frac{D_1}{k^I}}. \quad (6)$$

The reacto-diffusive length is the characteristic distance that a molecule diffuses within a particle before reacting, which

brings about a size dependence of  $\gamma$  when  $l$  is comparable to or larger than the radius of the particle ( $q > 1$ ). Equation (5), in which the complex mechanism (Reactions R3–R7) is lumped into the net Reaction (R2) by treating only one dissolved N<sub>2</sub>O<sub>5</sub> species undergoing a bimolecular reaction with liquid phase water, provides a reasonable parameterization to describe uptake of N<sub>2</sub>O<sub>5</sub> to laboratory generated aerosol particles (Ammann et al., 2013). An analytical expression has been suggested to also take into account the nitrate effect (Griffiths et al., 2009; Bertram and Thornton, 2009). Since we have worked at low N<sub>2</sub>O<sub>5</sub> concentrations (5 ppbv), where the maximum HNO<sub>3</sub> concentration expected in the particle phase was  $\sim 10^{-3}$  M, we could safely neglect this.

The Henry's law constant for N<sub>2</sub>O<sub>5</sub>, an important variable in Eq. (4), is unknown for organic polycarboxylic aerosol particles. However, in several studies (Badger et al., 2006; Robinson et al., 1997; Thornton et al., 2003), a generic value of  $H = 2 \text{ M atm}^{-1}$  has been suggested for liquid aerosol particle solutions. Recommended values (Ammann et al., 2013) for aqueous organic aerosols have been used for  $\alpha_b$  (0.035) and  $k^{\text{II}}$  ( $1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ), which is the apparent second-order rate constant for the reaction of N<sub>2</sub>O<sub>5</sub> with water, and  $k^I = k^{\text{II}}[\text{H}_2\text{O}]$ . The recommended values are based on several studies with dicarboxylic and polycarboxylic acids (Badger et al., 2006; Griffiths et al., 2009; Thornton et al., 2003). Note that as evident from Eq. (4), experiments allow to safely constrain only the product  $H \times \sqrt{(k^I)}$ , so that the rate constant values are linked to the choice of  $H$ .

Since water is the main reactant for the hydrolysis of N<sub>2</sub>O<sub>5</sub>, the parameterization relies heavily on the water concentration as a function of RH. Mass growth factor values (and consequently mass fractions) for citric acid and water were obtained from Zardini et al. (2008), while the citric acid solution densities have been obtained from several sources, each relating to the particular parameterization used for viscosity further below (Laguerie et al., 1976; Lienhard et al., 2012; Peng et al., 2001).

For the diffusion coefficient  $D_1$  of N<sub>2</sub>O<sub>5</sub> in an aqueous solution, previous studies were based on an estimate of  $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (Badger et al., 2006; Griffiths et al., 2009; Hallquist et al., 2003; Thornton et al., 2003), independent of water activity. Together with the other parameters, this leads to a reasonable agreement of the parameterization based on Eq. (4) with the measured data for malonic acid. However, as it turns out, the parameterization would largely overpredict the reactivity for citric acid. Citric acid solutions exhibit a substantially higher viscosity; i.e. for a solution of 1.04 M, the reported viscosity (Laguerie et al., 1976) of CA is  $1.49 \times 10^{-3} \text{ Pa s}$ , while for malonic acid it is  $1.09 \times 10^{-3} \text{ Pa s}$  (Chmielewska and Bald, 2008), close to that of water ( $0.91 \times 10^{-3} \text{ Pa s}$ ). It is therefore likely that the lower uptake coefficients of N<sub>2</sub>O<sub>5</sub> in citric acid compared to those for malonic acid are caused by lower diffusivity in the



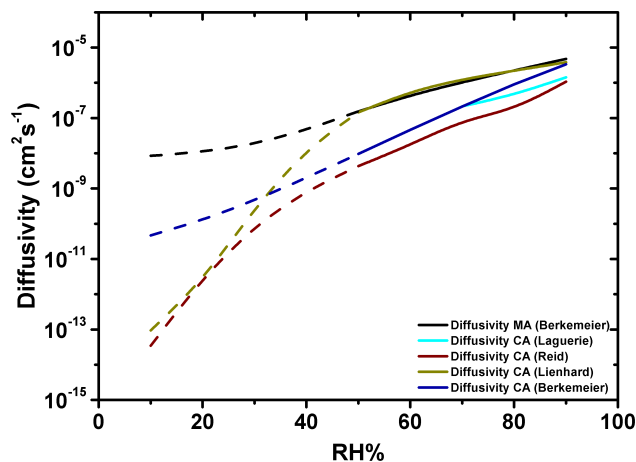
more viscous solution. Since the diffusivity of N<sub>2</sub>O<sub>5</sub> is not known in either medium, we used four methods for its estimation, based either on measured viscosities or on measured or estimated diffusivity of H<sub>2</sub>O. If the viscosity is known,  $D_1$  for N<sub>2</sub>O<sub>5</sub> can be calculated by applying the Stokes–Einstein relation (Eq. 7):

$$D_1 = \frac{k_B T}{6\pi\eta r}, \quad (7)$$

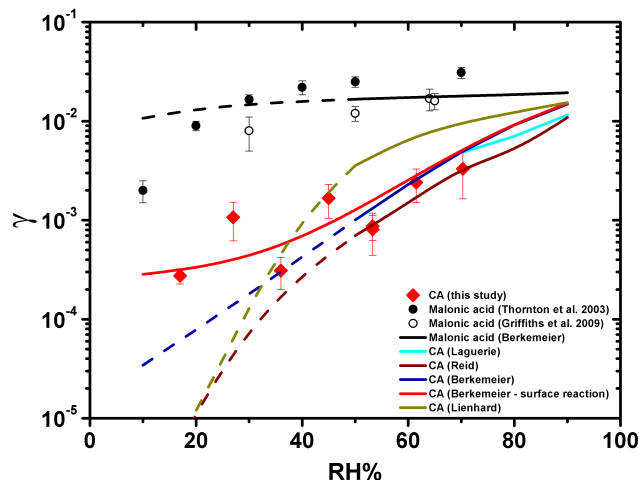
where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\eta$  is the viscosity, and  $r$  is the radius of the N<sub>2</sub>O<sub>5</sub> molecule assumed spherical (2.5 Å). Uncertainty remains with respect to the effective molecular radius to be used, since the identity of the solute for the rate limiting step is not clear (dissolved N<sub>2</sub>O<sub>5</sub> or NO<sub>2</sub><sup>+</sup>). Additionally, for high viscosity (at low RH), the use of the Stokes–Einstein relation may be questioned: Power et al. (2013) suggested that the diffusivity of water in sucrose droplets decouples from the viscosity at viscosities around 1 Pa s, and at 10 Pa s the diffusivity calculated by Eq. (7) departs from measured values already by an order of magnitude. For the cases, where the diffusivity of H<sub>2</sub>O is known or estimated, we also used Eq. (7) to estimate the diffusivity of N<sub>2</sub>O<sub>5</sub> by accounting for change in molecular size.

The results are summarized in Fig. 4. The different parameterizations are represented by solid lines, and by dashed lines where the use of the Stokes–Einstein relation may not be granted. The first one (labelled “Laguerie”) is based on viscosity measurements by Laguerie et al. (1976). The viscosity parameterization in this case covers a range of citric acid concentrations up to ~4.3 M, which in our case corresponds to RH values > 70 %. More recent measurements of viscosity of citric acid were provided by C. Cai and J. Reid (personal communication, 2015) from a combination of optical tweezers and electrodynamic balance (EDB) experiments covering a range of 3 to 73 % RH (labelled “Reid” in Fig. 4). The third method is based on an estimate of the diffusivity of H<sub>2</sub>O in the organic matrix, which is in turn based on the principal parameterization for the one of H<sub>2</sub>O in sucrose from Zobrist et al. (2011). This method uses the measured glass transition and hygroscopicity data to infer diffusion properties of a target substance (e.g. citric acid) by extrapolation from a known reference substance (e.g. sucrose) (Berkemeier et al., 2014) (labelled “Berkemeier” in Fig. 4). The same method has been used to estimate the diffusivity of N<sub>2</sub>O<sub>5</sub> in malonic acid. Finally, Lienhard et al. (2014) determined the diffusivity of H<sub>2</sub>O in citric acid solution droplets by measuring the kinetics of the size change in response to step changes in RH in an EDB. The data are parameterized via an empirical Vignes-type equation (Lienhard et al., 2012, 2014).

The result of calculating the uptake coefficient according to Eq. (4) and using diffusion coefficients estimated according to these four methods is presented in Fig. 5. The solid and dashed shape of the lines again indicate the validity or not, respectively, of the Stokes–Einstein relation as a basis



**Figure 4.** Diffusivity of N<sub>2</sub>O<sub>5</sub> in malonic and citric acid solutions as calculated according to four parameterization methods – black: Berkemeier (for malonic acid); teal: Laguerie; red: Reid; green: Lienhard; blue: Berkemeier; see text for details. Calculated values for a RH range between 10 and 90 % can be found in Table S2 of the Supplement.



**Figure 5.** Parameterization of N<sub>2</sub>O<sub>5</sub> uptake on citric acid aerosol according to Eq. (4) (lines) based on diffusivities estimated by the four parameterization methods: teal: Laguerie; dark red: Reid; green: Lienhard; blue: Berkemeier. Dashed lines indicate the RH range where the Stokes–Einstein relation (Eq. 7) is not strictly applicable. The red line represents the extended parameterization including a surface reaction term (Eq. 8), based on the Berkemeier H<sub>2</sub>O diffusivity estimates. The black line represents the parameterization for malonic acid using the same kinetic parameters and diffusivity data estimated using the Berkemeier method for malonic acid; red diamonds: uptake coefficients measured in this study; solid circles: uptake coefficients for malonic acid according to Thornton et al. (2003); open circles: uptake coefficients for malonic acid according to Griffiths et al. (2009).

for diffusivity estimation. Figure 5 also shows data for liquid (supersaturated) malonic acid particles (Griffiths et al., 2009; Thornton et al., 2003) and the calculated uptake coefficient based on Eq. (4), using the corresponding estimate of N<sub>2</sub>O<sub>5</sub> diffusivity. Thornton et al. (2003) have reported malonic acid efflorescence to occur at < 7 % RH and deliquescence at 69 % RH, and have performed experiments on solid malonic acid particles for comparison, which are not included here.

The parameterization based on the Lienhard et al. H<sub>2</sub>O diffusivity data starts to deviate strongly from the rest as well as from the measured citric acid uptake coefficients above 30 % RH, overestimating the uptake by about a factor of 3–4. We note that the Vignes-type parameterization used by Lienhard et al. (2014) was constrained by measurements of the diffusivity of water below 40 % RH only at max. 281 K. Since H<sub>2</sub>O is much smaller than N<sub>2</sub>O<sub>5</sub>, the diffusivity of N<sub>2</sub>O<sub>5</sub> may exhibit a different slope as a function of humidity. The parameterization based on the Laguerie viscosity data is limited by the small range of solution compositions covered by measurements (RH > 70 %). The other parameterizations (Berkemeier, Reid) follow the measured values for the uptake coefficient fairly well down to about 50 % RH, indicating that the changing viscosity and associated changes in diffusivity as a function of RH control the uptake coefficient of N<sub>2</sub>O<sub>5</sub>. At lower RH the measured data seem to level off, which may be related to the decoupling between viscosity and diffusivity below 10 Pa s (Debenedetti and Stillinger, 2001; Power et al., 2013). However, this decoupling would rather lead to lower diffusivity of N<sub>2</sub>O<sub>5</sub> than expected based on the Stokes–Einstein equation and thus fails to explain the higher than expected reactivity at low RH.

In spite of the uncertainties related to the diffusivity estimates, the uptake coefficient parameterized by Eq. (4), while well describing the measurements at higher RH, thus clearly underestimates the measurements at low RH. To assess the validity of the reacto-diffusive regime, we consider the reacto-diffusive length (Table 1), which remains much smaller than the particle dimensions, especially towards low humidity, due to the strong reduction in diffusivity. Thus no size effects are expected. In turn, Eq. (4) assumes that water, the reactant for N<sub>2</sub>O<sub>5</sub>, remains well mixed. Even for 15 % RH, using the diffusivity parameterization closest to our measured results (Berkemeier), the diffusivity of H<sub>2</sub>O is about  $1.34 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ , and the characteristic time for diffusion across a particle,  $t = d_p^2/D_{\text{H}_2\text{O}}$ , becomes about 0.75 s, which is significantly shorter than the residence time in the flow tube. Other effects, such as salting in of N<sub>2</sub>O<sub>5</sub> (thus effectively increasing  $H$ ) or an increase in the apparent rate constant  $k^{\text{II}}$  are also not likely. Therefore, we suggest that at low RH, uptake of N<sub>2</sub>O<sub>5</sub> becomes limited by its hydrolysis on the surface, which is not included in Eq. (4). Including a surface reaction term to the uptake model would lead to

**Table 1.** Reacto-diffusive lengths calculated using diffusivity values obtained via the four above mentioned parameterizations.

| RH [%] | Reacto-diffusive length (nm) |      |            |          |
|--------|------------------------------|------|------------|----------|
|        | Laguerie                     | Reid | Berkemeier | Lienhard |
| 30     | –                            | 0.09 | 0.21       | 0.16     |
| 50     | –                            | 0.49 | 0.74       | 2.88     |
| 70     | 3.03                         | 1.83 | 2.96       | 7.21     |
| 90     | 6.33                         | 5.26 | 9.63       | 10.29    |

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_s + \left(\frac{1}{\Gamma_{\text{sb}}} + \frac{1}{\Gamma_{\text{b}}}\right)^{-1}}, \quad (8)$$

where  $\alpha_s$  is the surface accommodation coefficient, and  $1/\Gamma_{\text{sb}}$  represents the resistance for surface to bulk transfer (Ammann et al., 2013), which together constitute the bulk accommodation coefficient  $1/\alpha_{\text{b}} = 1/\alpha_s + 1/\Gamma_{\text{sb}}$ . The value of  $\Gamma_{\text{sb}}$  has been estimated by assuming that surface accommodation is not rate limiting and setting  $\alpha_s$  to 1 and keeping  $\alpha_{\text{b}}$  at 0.035 as above.  $\Gamma_s$  is the limiting uptake coefficient for the surface reaction.  $1/\Gamma_{\text{b}}$  represents the bulk reaction-diffusion resistance given in Eq. (4).

The red line in Fig. 5 represents the result of applying Eq. (8), keeping the bulk reactivity parameters as before for the Berkemeier diffusivity estimates for citric acid and setting the value of  $\Gamma_s$  to  $2.5 \times 10^{-4}$ , which leads to good agreement with the observed data. The value of  $\Gamma_s$  falls into the range of uptake coefficients observed on effloresced malonic, succinic or oxalic acids (Griffiths et al., 2009; Thornton et al., 2003). Even at low RH, adsorbed water is abundant on a polar surface like citric acid, so that surface hydrolysis of N<sub>2</sub>O<sub>5</sub> on high viscosity citric acid may indeed become the rate limiting step at low RH.

#### 4 Conclusions and atmospheric impact

We have conducted measurements of N<sub>2</sub>O<sub>5</sub> uptake to citric acid aerosol over an atmospherically relevant RH range at room temperature. Our results have shown that uptake coefficients change by roughly 1 order of magnitude ( $\sim 3 \times 10^{-4}$ – $3 \times 10^{-3}$ ) between low (17 %) and high (70 %) RH. The results can be described under the assumption that citric acid remains a supersaturated liquid, even at low RH, and exhibits an increased viscosity at low water content. Reactive uptake is found to be governed by reacto-diffusive limitation with the reacto-diffusive length decreasing under the influence of increased viscosity (and thus decreased diffusivity) from a few nm to the sub-nanometer range. Thus, the decreasing uptake coefficients with decreasing RH are well explained by the parameterization of N<sub>2</sub>O<sub>5</sub> uptake by the bulk reacto-diffusive uptake regime at RH above 50 %, essentially driven



by the decreasing diffusivity of N<sub>2</sub>O<sub>5</sub>. At low RH, estimating the diffusivity of N<sub>2</sub>O<sub>5</sub> from the measured diffusivity of H<sub>2</sub>O or the measured viscosity is problematic due to the decoupling between viscosity and diffusivity at high viscosity. However, even when taking these uncertainties into account, the reactivity observed at low RH cannot be explained by reaction in the bulk of the particles. We conclude that surface hydrolysis dominates uptake at low relative humidity.

Secondary organic aerosol (SOA) is likely to exhibit a similar, or even higher viscosity compared to citric acid used here as model compound (Renbaum-Wolff et al., 2013). Thus high viscosity at low RH could explain the discrepancy between N<sub>2</sub>O<sub>5</sub> reactivity in field measurements and model predictions based on laboratory measurements. A recent study (Gaston et al., 2014) suggested that the organic O : C ratio in mixed inorganic-organic aerosols may be used as an indicator of N<sub>2</sub>O<sub>5</sub> reactivity, based on a trend of increasing uptake coefficient with increasing O : C ratio. However, citric acid and some high O : C mixtures containing citric acid and other highly functionalized oxidized organic compounds were an exception to this trend. Hence, while O : C ratio can serve as an indicator for reactivity towards N<sub>2</sub>O<sub>5</sub> at low O : C, this trend might be reversed for highly oxidized organic compounds forming high viscosity aqueous solutions. Parameterization of N<sub>2</sub>O<sub>5</sub> reactivity in atmospheric models should thus not only rely on particle O : C, but should also have means to take into account high particle viscosity.

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