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Artifacts in measuring aerosol uptake kinetics: the roles of time, concentration and adsorption

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Abstract

In laboratory studies of organic aerosol particles reacting with gas-phase oxidants, high concentrations of radicals are often used to study on the timescale of seconds reactions which may be occurring over days or weeks in the troposphere. Implicit in this approach is the assumption that radical concentration and time are interchangeable parameters, though this has not been established. Here, the kinetics of OH- and Cl-initiated oxidation reactions of model single-component liquid organic aerosols (squalane, brassidic acid and 2-octyldodecanoic acid) are studied by varying separately the radical concentration and the reaction time. Two separate flow tubes with residence times of 2 and 66 s are used, and [OH] and [Cl] are varied by adjusting either the laser photolysis fluence or the radical precursor concentration ([O_3] or [Cl_2], respectively) used to generate the radicals. It is found that the rates measured by varying the radical concentration and the reaction time are equal only if the precursor concentrations are the same in the two approaches. Further, the rates depend on the concentrations of the precursor species with a Langmuir-type functional form suggesting that O_3 and Cl_2 saturate the surface of the liquid particles. It is believed that the presence of O_3 inhibits the rate of OH reaction, perhaps by reacting with OH radicals or blocking surface sites, while Cl_2 enhances the rate of Cl reaction by participating in a radical chain mechanism. These results have important implications for laboratory experiments in which high concentrations of gas-phase oxidants are used to study atmospheric reactions over short timescales and may explain the variability in recent measurements of the reactive uptake of OH on squalane particles in reactor systems used in this and other laboratories.

1 Introduction

Aerosols are important constituents of the Earth's atmosphere due to their role in climate (Charlson et al., 1989; Hobbs, 1993; Park et al., 2005; Park and Jeong, 2008), atmospheric chemistry (Andreae and Crutzen, 1997), visibility (Baumer et al., 2008;

Eidels-Dubovoi, 2002) and human health (Avol et al., 1979; Ondov et al., 2004; Penn et al., 2005). Organic matter in tropospheric aerosols comprises 10–90% of the fine particulate mass (Andreae and Crutzen, 1997; Putaud et al., 2004; Saxena and Hildemann, 1996). Heterogeneous aging of organic aerosols by atmospheric oxidants such as hydroxyl radicals, nitrate radicals and ozone may modify aerosol properties such as the ability to directly scatter and absorb solar radiation and the ability to act as nuclei for cloud condensation which may indirectly influence the Earth's radiation balance. The rates at which heterogeneous oxidation processes proceed and the products formed as a result of these reactions has become a topic of recent research interest as they can influence the fate and properties of organic aerosols in the troposphere.

Among the most important oxidants responsible for atmospheric radical-initiated oxidation of organic particles in the troposphere are hydroxyl radicals (OH). Chlorine radicals (Cl) are also commonly used as a proxy for OH radicals in the laboratory because they generally react by a similar mechanism and can be generated in higher concentrations, though their significance in the atmosphere is limited. Multiple experiments have shown that both OH and Cl reactions with organic aerosols are very efficient with reactive uptake coefficients (the probability that radical-particle collision will result in reaction) between 0.1 and 0.9 (Bagot et al., 2008; Bertram et al., 2001; Cooper and Abbatt, 1996; Moise and Rudich, 2001; Molina et al., 2004).

Numerous experiments have suggested that secondary chemistry may play an important role in the rapid reactive uptake of radical species into organic aerosol. The reactive uptake coefficient of Cl (Hearn et al., 2007) and OH (Hearn and Smith, 2006; George et al., 2007) on dioctyl sebacate sebacate (DOS) particles has been reported to be greater than unity, and the authors have suggested secondary radical chemistry to explain the rapid loss rate of DOS in these particles. Smith et al. (2009) and Che et al. (2009) have recently published results in which the reactive uptake of OH on squalane particles was studied in two separate reaction chambers that differed in the amount of reaction time and found that at shorter times (∼37 s) and average OH concentrations of 1×10^{10} molecules cm^{-3}, the reactive uptake of OH on Sq particles was

0.3 ± 0.07 (Smith et al., 2009) whereas at longer times (1.5–3 h) and lower OH concentrations (1–7 × 10^8 molecules cm^{-3}) the reactive uptake was 0.51 ± 0.10 (Che et al., 2009). As a possible explanation of the different reactive uptakes measured in these two experiments, Che et al. (2009) have suggested the importance of a secondary loss mechanism at low OH concentrations whereby a radical intermediate, such as RO or RO_2, may abstract a hydrogen from squalane.

A kinetic model, devised by McNeill et al. (2008), predicts that due to secondary radical chemistry and surface renewal processes, decay kinetics may be observed in which time and concentration are not interchangeable variables. This model suggests that laboratory studies employing high radical concentrations (10^{10}–10^{12} molecules cm^{-3}) and short times (seconds to minutes) may not be representative of reactions which occur in the troposphere with much smaller concentrations (∼10^6 molecules cm^{-3}) and long interaction times (days to weeks). Whether time and concentration are equivalent variables in organic aerosol oxidation kinetics, therefore, remains an open question.

In the present work, whether radical concentration and time are interchangeable variables during the OH- and Cl-initiated oxidation reactions of squalane (Sq), 2-ocyldodecanoic acid (2-ODA) and brassidic acid (BA) particles is explored. Two different reactor flow tubes, varying in the internal volume and in the reactant interaction time by a factor of 33, were used to measure the kinetics in two ways: by changing reaction time and by changing radical concentration. To achieve the same radical exposure ([OH] t or [Cl] t) in the two flow tube systems, the radical concentration was varied by the same factor. Further, the influences that the radical precursors (O_3 and Cl_2) have on the measured rates of these reactions are investigated through a systematic study of 2-ODA oxidation as a function of the precursor concentration. Squalane and 2-ODA were chosen for these experiments because they are both branched species which may form liquid particles at room temperature and are representatives of branched, saturated organic molecules found in ambient aerosols. Brassidic acid is an unbranched, unsaturated fatty acid that is able to be supercooled at room temperature (Renbaum and Smith, 2009a, b) and is representative of unsaturated fatty acids in ambient aerosols.

Also, all three species have low vapor pressures at room temperature thus making them amenable to studying the heterogeneous reactions between gas-phase oxidants and condensed phase organics.

2 Materials and methods

2.1 Particle generation

Particles of Sq, 2-ODA and BA were generated through homogeneous nucleation by flowing 0.9 slpm (standard liters per minute) of N_2 through a reservoir containing either Sq, 2-ODA or BA heated to 135–145 °C. The aerosol was then reheated as it flowed through $^1/_2$-inch o.d. glass tubing (4 inches long, 250 °C). Typically, reheating of the aerosol results in narrowing of the particle size distribution from a geometric standard deviation (gsd) of ∼1.4 to a gsd of ∼1.2. As both 2-ODA and BA are solids at room temperature with melting points of 34–36 °C (Knothe, 2002) and 58–59 °C (Chang and Miwa, 1972), respectively, their vapor nucleated and formed supercooled liquid droplets as they cooled to room temperature. After they exited this stage, the squalane, 2-ODA, and BA particles cooled to room temperature and were typically 180–220 nm (gsd = 1.20–1.24), 45–120 nm (gsd = 1.2–1.3), and 90–100 nm (gsd = 1.2–1.3), respectively. The particle size distributions were measured using a scanning mobility particle sizer (SMPS) consisting of a DMA (TSI, Inc. model 3081) and CPC (model 3785, TSI, Inc.).

2.2 Flow tube reactions

A schematic of the experimental setup is shown in Fig. 1. After particle generation, the particles entered one of two flow tube reactors along with N_2, O_2, O_3 or Cl_2 and a gas-phase reference species. Hydroxyl radicals were generated by photodissociation of O_3 using the fourth harmonic (266 nm) from a 10-Hz pulsed Nd:YAG laser (QuantaRay

PRO-250, Spectra-Physics), and residual water vapor in the apparatus was sufficient to react with $O(^1D)$ to generate OH radicals:

$$O_3 + h\nu \rightarrow O\left(^1D\right) + O_2. \tag{R1}$$

$$O\left(^1D\right) + H_2O \rightarrow 2OH \tag{R2}$$

Chlorine radicals were generated by photodissociation of Cl_2 using the third harmonic (355 nm) of the same laser. The concentrations of OH or Cl radicals generated were varied by changing either the concentration of O_3 or Cl_2 or the Nd:YAG laser fluence. The concentration of O_3 in the carrier flow was determined by Beer's Law in a UV absorption cell equipped with a UV pen lamp (254 nm) and a photodiode detector with a 254 nm filter and corrected for dilution upon meeting the particle and O_2 flows. For the Cl_2 concentration dependence experiments, the concentration of Cl_2 in the flow tube was calculated from the flow of Cl_2 from a lecture bottle of known concentration.

Reactions were carried out at atmospheric pressure and 293 K in two separate glass flow tubes with the dimensions 1.1 cm i.d. × 90.0 cm length and 5.1 cm i.d. × 91.4 cm length, and will be referred to from this point forward as the "small" and "large" flow tubes, respectively. Upon exiting the flow tube, gas and particle phase species were analyzed by an Aerosol Chemical Ionization Mass Spectrometer. For the OH experiments, Sq or 2-ODA aerosols (0.9 slpm N_2 flow), O_2 (0.125 slpm for the small flow tube and 0.100 slpm for the large flow tube) and gas-phase reference ($\leq$1 sccm, standard cubic centimeter per minute) were introduced into one inlet port of the flow tube reactor. Ozone, the OH precursor, was generated using a commercial ozone generator (Model L11, Pacific Ozone Technology) and stored on silica gel at −80 °C. By passing a small flow (5–10 sccm) of N_2 over the trapped O_3 and then diluting the O_3 in a N_2 carrier flow (1.48 slpm for the small flow tube and 0.7 slpm for the large flow tube), O_3 was introduced into the second inlet port of the flow tube reactor. The total flow of 1.7 slpm for the large flow tube and 2.5 slpm for the small flow tube thus contained 5–6% O_2. For the Cl experiments, Sq, BA or 2-ODA particles, N_2 carrier flow and O_2 were added as described above, but Cl_2 was added as the radical precursor instead of O_3, and the 1.7 slpm and 2.5 slpm flows for the large and small flow tubes contained 20% O_2. Based on the total flow velocity and the volumes of the two flow tubes, the total reactant interaction times were 2 s and 66 s for the small and large flow tubes, respectively.

For the small flow tube, the beam from the Nd:YAG laser (beam diameter = ~1 cm) was directed down the axis of the flow tube so that the volume of the flow tube was filled with light during the experiments. For the large flow tube, a convex quartz lens with a focal length of 6 cm was positioned so that the beam would expand to approximately one inch in diameter as it passed through the one-inch window and then continue to expand to fill the flow tube within ~4 cm of entering the flow tube. The integrated OH exposure, $[OH]_{avg}\,t$, was determined using mixed-phase relative rates (Hearn and Smith, 2006; Hartz et al., 2007) with gas-phase references of methanol ($k_{OH} = 9.0\ (\pm 0.8) \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$) (Picquet et al., 1998) and 2-hexanol ($k_{OH} = 1.21\ (\pm 0.07) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$) (Wallington et al., 1988) for the reactions of squalane and 2-ODA particle reactions, respectively. Acetone-d_1 was used as the gas-phase reference for Sq + Cl, and its rate constant was measured previously in this lab ($k_{Cl} = 1.83\ (\pm 0.28) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$) (unpublished). Acetone ($k_{Cl} = 2.07\ (\pm 0.31) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$) (Zhao et al., 2008) was used as the gas-phase reference for the 2-ODA + Cl and BA + Cl reactions.

2.3 Collection of particle decay data in the two flow tubes

Use of the small flow tube for studying heterogeneous reactions between gas-phase radicals and organic aerosols has been described in detail elsewhere (Hearn et al., 2007; Renbaum and Smith, 2009a, b). In summary, the reaction time (~2 s) is too short to enable the collection of many data points as the aerosol species concentration decays as a function of time. For this reason, in order collect particle decay data, the radical concentration must be changed either continuously or in discrete steps by adjusting the power of the photodissociation laser or the concentration of the radical precursor. In doing so, it is assumed that changing the radical concentration is equivalent to changing the reaction time in reaching a given radical exposure. The large flow tube used here, however, allows the observation of particle and gas-phase reference decays as a function of time at nearly-constant radical concentration as the particles and gas-phase species exit the flow tube. This "virtual injector" flow tube method will be described in detail in an upcoming paper from this lab. In short, upon introduction of the photodissociation laser either OH or Cl is produced throughout the flow tube and the reaction begins; particles nearest the end of the flow tube exit first with the least amount of time to react with the radical species, while those furthest from the exit of the flow tube have the longest time (66 s) to react. Thus, particle decay data were collected:

1. As a function of radical concentration at fixed time in the small flow tube.
2. As a function of time at a fixed radical concentration in the large flow tube.

The goals of these experiments are to determine if the two methods of measuring kinetics yield the same result in both gas-phase and heterogeneous relative rates experiments and to infer from these results whether radical concentration and time are interchangeable variables in studying particle oxidation kinetics. In order to best compare the particle decay data obtained with each flow tube, the OH or Cl concentration in each flow tube was adjusted so that ∼20% of the particle-phase species reacted away over the course of each experiment. Reactions in the small flow tube were performed by discrete measurements where the O_3 or Cl_2 concentration and laser power were set so that upon introducing the laser light into the flow tube, the particle phase species would react by ∼20%. By alternately turning on and off the laser source into the flow tube, the particle phase and gas-phase reference signal were obtained before, during, and after each reaction.

Because the particles have much more time to react with the OH or Cl radicals in the large flow tube it was necessary to use smaller radical concentrations so that after the 66 s residence time only ∼20% of the particle phase species had reacted. This was achieved by adjusting the amount of O_3 or Cl_2 entering the flow tube and the laser power was maintained at the same laser power used in the reactions in the small flow tube above. For the O_3 and Cl_2 concentration dependence experiments, the O_3 and Cl_2 concentrations were fixed and the laser fluence was adjusted in order to reach equivalent radical concentrations in each flow tube.

2.4 Chemical ionization and detection

The flow tube eluent containing aerosol and gas-phase references was sampled into the mass spectrometer through a stainless steel orifice (0.5 mm i.d.) in a heated (180 °C) stainless steel vaporizer tube (1/4 inch o.d., 4 inches long). The vaporized aerosol flow then entered the heated (150 °C) stainless steel ion tube (1/2 inch o.d., 8 inches long, 40 Torr) of the CIMS instrument where it mixed with a 2 slpm flow of N_2 containing $H^+(H_2O)_n$ (where $n = 2,3$) or NO^+ reagent ions generated from a radioactive ^{210}Po source (NRD). When $H^+(H_2O)_n$ ions were used for ionization, small amounts of O_2 were added to the flow through the ^{210}Po source in order to increase the $H^+(H_2O)_n$ ion signal by approximately a factor of two.

For the reactions of 2-ODA and 2-hexanol with OH and for the reactions of 2-ODA, BA and acetone with Cl, proton transfer from $H^+(H_2O)_n$ was used to generate protonated molecular ions. Squalane particles were detected through hydride abstraction and the acetone-d_1 gas-phase reference (for the reaction with Cl) was detected via NO^+-adduct formation, both using NO^+ ions. Methanol, the gas-phase reference used for the OH + Sq reaction, is not efficiently ionized by NO^+ and thus in order to determine the OH exposure after a Sq particle reaction, ionization was rapidly changed to proton transfer via $H^+(H_2O)_n$ by replacing the NO through the ^{210}Po with O_2 and the decay was repeated at the same laser fluence and O_3 flow. This method was repeated approximately ten times and the time between recording respective squalane and methanol decays (the time required to change ionization schemes) was typically 0.5–1 min.

The ions generated as described above were then sampled into the high vacuum region through a 200-µm orifice by means of a small potential gradient (2–5 V) and differential pumping. Ions were filtered using a quadrupole mass spectrometer (ABB Extrel) and detected using a Channeltron electron multiplier (model 4816, Burle).

2.5 Gases and chemicals

Gases used were: N_2 (99.99%, National Welders), O_2 (industrial grade, National Welders), and NO (CP grade, National Welders). Flows were measured and maintained using mass flow controllers (MKS). 2-hexanol, methanol and acetone were purchased from Sigma Aldrich and had purities greater than 99%. Squalane (>99%) and brassidic acid (~99%) were purchased from Sigma Aldrich and MP Biomedicals, respectively, and 2-octyldodecanoic acid (2-ODA) was provided by Jarchem Industies, Inc. (Newark, NJ).

3 Results and discussion

3.1 Reactive uptake experiments in the small and large flow tubes

Reactions between OH and Sq and 2-ODA aerosols and between Cl and Sq, 2-ODA and BA aerosols were studied in each flow tube. The concentration of the O_3 or Cl_2 radical precursor was adjusted in order to reach the same extent of reaction in each flow tube while maintaining a constant laser fluence. The effective reactive uptake coefficients for the gas-particle reactions were calculated using the following equation (Hearn and Smith, 2006):

$$\gamma_{\text{part}} = \left[\frac{d\left([\text{Part}]/[\text{Part}]_0\right)}{d\left([\text{radical}]\bullet t\right)}\right]\frac{4RT}{\bar{c}}\frac{V}{S_A}[\text{Part}]_0 . \quad (1)$$

Here, γ_{part} is the effective reactive uptake coefficient of OH or Cl in the aerosol particle as measured from the rate of loss of the aerosol species and is not corrected for gas-phase diffusion of the radical to the particle. The [radical] term is the concentration of OH or Cl, V/S_a ($= d/6$) is the volume to surface area ratio of the particles determined using the surface-area-weighted particle size data from the SMPS, R is the gas constant, T is the temperature, $\bar{c}$ is the mean speed of OH or Cl, and $[\text{Part}]_0$ is the initial concentration of Sq, 2-ODA, or BA in the unreacted particles. The term in brackets represents the slope of the initial decay of the particle-phase species with respect to radical exposure ($=[\text{radical}]\ t$) which is determined from the measured fractional loss of the gas-phase reference species, $[\text{ref}]/[\text{ref}]_0$:

$$([\text{radical}]\bullet t) = -\frac{1}{k}\ln\left(\frac{[\text{ref}]}{[\text{ref}]_0}\right) \tag{2}$$

where k is the rate constant of the reaction of the reference species with OH or Cl. For the small flow tube measurements, the slope of the initial decay in Eq. (1) is approximated by the discrete change:

$$\frac{d\left([\text{Part}]/[\text{Part}]_0\right)}{d\left([\text{radical}]\bullet t\right)} \cong \frac{\Delta\left([\text{Part}]/[\text{Part}]_0\right)}{\Delta\left([\text{radical}]\bullet t\right)}. \tag{3}$$

Sample decays of 2-ODA aerosol particles as a function of OH and Cl exposure in the two reactor flow tubes are shown in Fig. 2a and b, respectively. From repeated measurements, the average γ_{part} for reactive uptake of OH with 2-ODA and Sq particles and the reactive uptake of Cl with 2-ODA, squalane and BA particles were determined and are displayed in Fig. 3a and b as a function of the average radical concentration, respectively.

The data in Fig. 3a show that in the two flow tube experiments, where different OH concentrations were needed to reach the same nominal exposure, the effective reactive uptake coefficient, γ_{part}, increases with decreasing OH concentration. This trend is consistent with the results of Che et al. (2009) and Smith et al. (2009) for OH + Sq aerosols, also shown in Fig. 3a, in which the effective uptake coefficient was larger for the longer-residence-time (1.5–3 h) experiments relative to the shorter-residence-time

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(37 s) experiments. The data in Fig. 3b, on the other hand, show that for the reaction with Cl radicals the effective reactive uptake coefficient increases with decreasing Cl concentration. At first glance, then, it appears as if the rates of reaction are somehow related to the radical concentration implying that experiments conducted by varying reaction time are not equivalent to those conducted by changing the radical concentration.

To investigate this effect further, several measurements of the relative rates of just gas-phase species with OH and Cl were made as well, and it was found that no such discrepancy was observed between the small and large flow tubes. For example, for the OH reactions the rate of 1-butanol relative to that of 2-hexanol was measured to be 0.63 (±0.07) and 0.61 (±0.04) in the small and large flow tubes, respectively, compared to a ratio of 0.72 (±0.07) calculated from published rate constants of these reactions (1-butanol: $k_{OH} = 8.66 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, Wu et al., 2003; 2-hexanol: $k_{OH} = 1.21 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, Wallington et al., 1988). Thus, it appears as if only the rates of the gas-particle reactions, and not the gas-phase-only reactions, are influenced by the radical concentrations. However, it must be noted that in these experiments not only were the radical concentrations different in the two flow tubes, but so were the concentrations of the precursors (O_3 for OH and Cl_2 for Cl); a higher concentration of precursor was used in the small flow tube to generate a higher concentration of the radical. What effect, if any, does the precursor concentration have on the radical uptake kinetics?

3.2 Rate of reaction of 2-ODA with OH with [O_3] held constant

To explore the effects of O_3 and Cl_2 concentrations on the reactive uptake of OH and Cl, respectively, systematic experiments were carried out using 2-ODA particles. Brassidic acid particles were not chosen for this study since BA contains a double bond and thus undergoes reactions with O_3, the OH precursor. Squalane particles were not used because the squalane + OH experiments are relatively time-consuming since different chemical ionization schemes are used to observe the reaction of the squalane (using

NO^+) and methanol, the gas-phase reference species (using $H^+(H_2O)_n$) (see section 2.4). For these reasons, 2-ODA particles were chosen to investigate the effects of precursor species on the reactive uptake of OH and Cl.

The reaction of 2-ODA with OH was performed in the small and large flow tubes using the fluence of the photodissociation laser to control the amount of OH production at fixed O_3 concentrations. Generally, the laser fluence was adjusted such that the 2-ODA reacted by approximately 20% over the length of each flow tube. As before, 2-hexanol was used as the gas-phase reference. The results of one such experiment, where the concentration of O_3 was 3–4 × 10^{15} molecules cm^{-3} are shown in Fig. 4. Now, when O_3 concentration is the same in the two flow tubes, γ_{part} is nearly the same despite the fact that the reaction times and [OH] differed by a factor of 33: $\gamma_{part} = 0.31$ and 0.32 for the small and large flow tubes, respectively. In other words, [OH] and time are truly interchangeable parameters in these gas-particle kinetics experiments as long as the O_3 concentration is fixed. These results suggest that O_3 is affecting the particle reaction kinetics in some way warranting a systematic study as a function of O_3 concentration.

3.3 Rate of reaction of 2-ODA with OH as a function of [O_3]

To better understand the effect that O_3 has on the rate of reaction of 2-ODA particles with OH, γ_{part} was measured as a function of O_3 concentration in the small and large flow tubes (Fig. 5). In these experiments, the laser fluence was used to control [OH] at a fixed O_3 concentration which ranged from 2.7 × 10^{14} molecules cm^{-3} to 8.3 × 10^{15} molecules cm^{-3}. The reactive uptake coefficient initially decreases with increasing [O_3] and then reaches a plateau where a further increase in [O_3] has no effect on the reactive uptake of OH. In order to ensure that this trend was not due to a change in the reactivity of the gas-phase reference species, a gas-phase relative rates experiment using the reactions of 1-butanol + OH and 2-hexanol + OH was performed as a function of O_3 concentration (grey triangles in Fig. 5). No variation in the ratio of the rate constants was observed across the range of ozone concentrations used indicating that the trend observed in the 2-ODA uptake coefficient is, indeed, specific to the particles.

The uptake coefficient data in Fig. 5 are fit well by a Langmuir-type isotherm with the form:

$$\gamma = \gamma_0 \left(1 - \frac{\theta}{f}\right). \tag{4}$$

where γ_o corresponds to the uptake coefficient in the absence of O_3, f is an adjustable parameter which accounts for the incomplete inhibition of the rate of reaction even at the highest values of $[O_3]$, and θ is the fractional surface coverage of O_3:

$$\theta = \frac{K\,[O_3]}{1 + K\,[O_3]}, \tag{5}$$

where K is the O_3 adsorption/desorption equilibrium constant. The fact that this modified Langmuir function fits the data in Fig. 5 well suggests that O_3 is adsorbing to the particle surface where it affects the observed rate of reaction of 2-ODA with OH. The best fit parameters are: $\gamma_o = 0.56$ (± 0.07), $K = 2.60$ (± 1.40) $\times 10^{-15}$ cm^3 molecule^{-1}, $f = 1.86$ (± 0.16).

The value of $\gamma_o = 0.56$ represents the predicted effective uptake coefficient in the absence of any inhibition by adsorbed O_3. Very few experiments exist in which the reactive uptake coefficient of OH on organic films or particles has been measured in the absence of O_3 to which γ_o can be compared. In one such study, Bagot et al. (2008) have determined the reactive uptake of OH on squalane films using 355-nm laser photolysis of a low pressure of HONO to generate OH above the squalane surface. In that study, the reactive uptake coefficient of OH on squalane films was 0.49 ± 0.04 which is comparable to the value of $\gamma_o = 0.56$ (± 0.07) reported here for 2-ODA aerosols. Likewise, these values are similar to the results of Che et al. (2009) in which $\gamma = 0.51$ was measured for reaction of squalane particles with OH over a timescale of 1.5–3 h using a presumably low concentration of O_3 to generate OH, though this concentration was not measured.

The adsorption/desorption equilibrium constant of O_3 on the 2-ODA particle surface deduced from the Langmuir fit in Fig. 5 is $K = 2.6\ (\pm 1.4) \times 10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}$ and is comparable to the adsorption/desorption equilibrium constant obtained from experiments of O_3 adsorption on other organic surfaces (Mmereki and Donaldson, 2003; Kwamena et al., 2004, 2007; Mmereki et al., 2004). In particular, Kwamena et al. (2007) describe the Langmuir-Hinshelwood adsorption of O_3 on various liquid organic aerosols, and for supercooled liquid azelaic acid aerosols they report a value of $K = 2.2 \times 10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}$. This good agreement is not surprising, as both the azelaic acid particles used in that study and the 2-ODA aerosols used here are supercooled liquid organic carboxylic acid particles.

The parameter f in the modified Langmuir function used to fit the data is a measure of the degree to which the reactive uptake coefficient is affected by the presence of O_3 at the particle surface. A value of $f = 1$ would represent a Langmuir adsorption isotherm for which the reaction is completely inhibited at saturation (when $\theta = 1$), whereas a value of $f > 1$ represents incomplete inhibition even at saturation. In the fit to the data in Fig. 5, the value of f is 1.86 (±0.16) indicating that when O_3 has reached its surface saturation concentration, the reaction between OH and 2-ODA still proceeds at 54% (=1/1.86) of the rate if O_3 were absent (γ_0). This partial hindrance of the reaction could be due to: (1) the existence of a layer of O_3 that acts as a barrier between OH and the 2-ODA particle surface which slows but does not inhibit the reaction, or (2) the incomplete coverage of the surface by O_3 islands or other such phenomena whereby OH can still react with 2-ODA that is not covered by O_3. An O_3 layer may act as either a physical barrier, where only OH that is able to diffuse through the O_3 layer may react with 2-ODA, or a chemical barrier which reacts with OH to form HO_2. From gas-phase rate constants of OH and HO_2 reactions with analogous organic species (Lloyd, 1974; Ohta, 1984; Atkinson et al., 1982; Gierczak and Ravishankara, 2000) it is expected that the conversion of OH to HO_2 would slow considerably, if not halt entirely, the reactive loss of 2-ODA. The formation of island-like structures of O_3 would be feasible if O_3 self-adsorption is favored relative to O_3 adsorption to the 2-ODA surface once a critical concentration of O_3 exists at the surface.

3.4 Rate of reaction of 2-ODA with Cl as a function of [Cl_2]

Unlike the reaction of OH with 2-ODA, for which the rate of reaction decreased at higher OH concentration, it was found that the apparent uptake coefficient for the Cl reaction with 2-ODA increased with Cl concentration (Fig. 3b). Is it possible that this trend is related to the concentrations of Cl_2 used in those experiments in a similar way that the rate of OH reaction was influenced by the concentration of O_3? To investigate this possibility, γ_{part} was measured as a function of Cl_2 concentration (shown in Fig. 6) with the laser fluence adjusted in each experiment to achieve approximately 20% reaction of the 2-ODA. Experiments were conducted in both the small flow tube and in the large flow tube, and it was found that the effective reactive uptake coefficients are equal at a given Cl_2 concentration even though [Cl] and reaction time differed by a factor of 33 in the two flow tubes. Thus, [Cl] and time are equivalent and interchangeable variables in measuring the reactive uptake of Cl on 2-ODA particles for a given Cl_2 concentration.

As seen in Fig. 6, the reactive uptake coefficient increases with increasing [Cl_2] and then reaches a plateau where a further increase in [Cl_2] has little to no effect on the observed rate of reaction. As with the OH uptake dependence experiments, these data are well represented by a Langmuir-type isotherm (Eq. 4) with: $\gamma_o = 0.92$ (±0.07), $K = 1.72$ (±1.23) × 10^{-15} cm^3 molecule^{-1}, and $f = -1.42$ (±0.30). To ensure that the observed change in the rate of 2-ODA reaction was not due to a change in the reactivity of the gas-phase reference species, a gas-phase relative rates experiment of Cl + methanol and Cl + n-propanol was performed. The ratio of the rate constants was measured to be 2.62 (±0.16), in good agreement with the ratio of 2.91 ($^{+0.74}_{-0.59}$) calculated from the values recommended in the IUPAC Gas Kinetic Data Evaluation (Atkinson et al., 2006). The fact that the ratio is independent of [Cl_2] indicates that the trend observed in the 2-ODA uptake coefficient is, indeed, specific to the particles.

The observed Langmuir-type dependence indicates that Cl_2 is adsorbing to the surface of the particle with a concomitant enhancement in the rate of loss of 2-ODA. The most likely cause of this enhancement is from a radical chain mechanism in which the alkyl radicals (R) formed from the initial reaction of Cl + 2-ODA react with Cl_2 to re-form a Cl radical and an alkylchloride product, RCl. In fact, evidence for the formation of the RCl product is observed by the appearance of a peak at $m/z = 347$ amu ([(Sq-H + Cl)H$^+$]) in the mass spectrum (not shown). The Cl radical that is formed from the R + Cl_2 reaction can then react with another 2-ODA molecule thereby enhancing its rate of loss. In essence, there is a higher Cl concentration at the surface than is calculated based on the gas-particle collision rate derived from the measured rate of loss of the gas-phase reference, and this increases the effective uptake coefficient. This secondary loss of 2-ODA also explains why effective uptake coefficients greater than one are measured. Further evidence for this radical chain mechanism was observed in reactions carried out in the absence of O_2 in which the effective uptake coefficient was measured to be as high as 10 (not shown), presumably because the competitive R + O_2 reaction was eliminated allowing the chain to propagate to a larger extent. The value of the uptake coefficient in the absence of the enhancement from the adsorbed Cl_2 can be estimated from the γ_o parameter obtained from the Langmuir isotherm fit: $\gamma_o = 0.92$ (±0.07). Thus, the reaction between Cl radicals from the gas phase and the 2-ODA occurs at nearly the gas-particle collision rate, consistent with analogous reactions in the gas phase which typically occur near the gas-kinetic collision rate (Atkinson et al., 2006). The parameter f in the Langmuir fit represents the degree to which the rate of 2-ODA reaction increases or decreases because of the adsorbed Cl_2. The best fit value for f is -1.42 (± 0.30) indicating that the adsorbed Cl_2 enhances the rate of 2-ODA loss (because $f < 0$) by a factor of 70% (=1/1.42), which is effectively a measure of the radical chain length.

The adsorption/desorption equilibrium constant of Cl_2 on the 2-ODA particle surface deduced from the Langmuir fit in Fig. 6 is $K = 1.72$ $(\pm 1.23) \times 10^{-15}$ cm^3 molecule^{-1}. There is currently a lack of adsorption/desorption coefficients in the literature for Cl_2 on organic surfaces, but as there are no chemical reactions (and thus no chemisorption) between Cl_2 and 2-ODA, adsorption is due to physisorption. Physisorption is expected even for nonpolar adsorbents on nonpolar surfaces because of the attraction of the *instantaneous* dipole moments in the surface species and adsorbent arising from the instantaneous positions of the nuclei and electrons. For adsorbent species with near-zero *permanent* dipole moments, such as Cl_2 and O_3, the attraction to a mostly non-polar surface such as 2-ODA (although 2-ODA is slightly polar due to the presence of a carboxylic acid moiety, the long carbon chains are essentially nonpolar) is expected to result in physisorption of Cl_2 and/or O_3 to the particle surface. Because the permanent dipole moments of O_3 and Cl_2 are on the same order of magnitude, it is expected that the Cl_2 adsorption/desorption coefficient would be similar to that of O_3, which was measured in the OH experiments to be $K = 2.60\ (\pm 1.40) \times 10^{-15}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}$. Thus, the adsorption/desorption equilibrium constant obtained from the modified Langmuir isotherm for Cl_2 on 2-ODA, $K = 1.72\ (\pm 1.23) \times 10^{-15}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}$, is reasonable.

It may seem counterintuitive that a lightweight, volatile halogen, Cl_2, would adsorb to the surface of a liquid 2-ODA particle instead of dissolving in it. To further investigate the plausibility of this, experiments were performed in which Br_2 was added to the flow tube along with Cl_2 to determine whether Br_2 would adsorb and affect the rate of 2-ODA loss. Br_2 was used to decouple the effect of adsorption from the radical reactions since the Br radicals generated by photolysis of Br_2 should not react with the gas-phase reference, acetone, or the particles; for example, the Br + acetone rate constant is estimated to be only $1.0 \times 10^{-20}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ at 298 K (King et al., 1970), and reactions between Br and gas-phase organic compounds are typically orders of magnitude slower than analogous reactions with Cl (Bierbach et al., 1996; Finlayson-Pitts et al., 1999; Ezell et al., 2002). However, the Br_2 is expected to interact with the surface in a similar way as Cl_2 does thereby providing a probe of surface adsorption. The effective uptake coefficient measured from the 2-ODA loss decreased from $\gamma = 1.23$ in the absence of Br_2 to $\gamma = 0.94$ in the presence of $2 \times 10^{14}\ \mathrm{molecules\ cm}^{-3}$ of Br_2 (Fig. 6 open square), a statistically-significant difference at the 99% confidence level. This decrease could have resulted from either or both of two possibilities: (1) Br_2 at the surface "deactivates" the Cl radicals by reacting with them:

$$Cl + Br_2 \rightarrow BrCl + Br, \tag{6}$$

or (2) Cl_2 is displaced by Br_2 at the surface thereby reducing the significance of the $R + Cl_2$ reaction in the radical chain mechanism. Either way, the decrease observed in the 2-ODA reactivity indicates that Br_2 has adsorbed to the particle surface, and by extension implies that the Cl_2 adsorption inferred from the Langmuir-type plot (Fig. 6) is reasonable. While it would have been interesting to study this effect as a function of $[Br_2]$ to see if Br_2 also saturates the surface, it was not possible to increase it without adversely influencing the $H^+(H_2O)_n$ reagent ion signal.

4 Implications and conclusions

No difference is observed in the reaction kinetics of 2-ODA aerosols with OH or Cl when the decay profiles are constructed by changing the radical concentration (small flow tube) or the reaction time (large flow tube) as long as the precursor (O_3 or Cl_2) concentration is the same in both cases. Thus, it is appropriate to consider the radical concentration and reaction time as interchangeable parameters with the product of the two, the exposure (=[OH] t or [Cl] t), being conserved. Consequently, it seems reasonable to extrapolate results from laboratory aerosol flow tube studies, in which reactions are studied with high radical concentrations on the timescales of seconds to minutes, to atmospheric processes, which involve much lower radical concentrations and occur over several days to a few weeks.

However, it has also been observed that the rates of reaction are functions of the concentrations of the precursor species, O_3 or Cl_2. It was inferred from these dependencies that these species affect the reactivity of the radicals by adsorbing to the surface of the liquid particles. This finding has implications for many gas-particle uptake experiments since high concentrations of precursors are almost always required to carry out the reactions on the seconds-minutes timescale. For example, in the case of OH reaction with 2-ODA particles, extrapolation of the high-[O_3] uptake coefficients to the atmosphere, where O_3 concentrations rarely exceed 250 ppbv (Kleinman et al., 2002) (still 50 times smaller than the smallest concentration used here) would underestimate the rate by 50%. The only way to determine the magnitude of this artifact is to carry out a systematic study as a function of O_3 concentration.

The adsorption of O_3 is also believed to be responsible for the slower rate of reaction observed for squalane in the small flow tube ($\gamma = 0.10$) compared to the large flow tube ($\gamma = 0.28$) (Fig. 3a) where higher [O_3] was used in the small flow tube. Interestingly, O_3 adsorption may also explain the range of values reported by Wilson and co-workers (Che et al., 2009; Smith et al., 2009) for the reaction of OH + squalane in which they also used O_3 photolysis to generate OH (shown for comparison in Fig. 3a); in an aerosol flow tube study (with a residence time of 37 s), they report a value of $\gamma = 0.30$, and in a continuous flow stirred tank reactor (residence time of 1.5–3 h), they report a higher value of $\gamma = 0.51$. It seems reasonable that they probably used a larger O_3 concentration in the shorter flow tube study and that O_3 adsorption resulted in a smaller uptake coefficient, but O_3 concentrations were not reported in either study. Likewise, the effect that Cl_2 has on the rate of reaction with Cl radicals does not seem to be unique to reactions with 2-ODA particles; the effective uptake coefficients measured for brassidic acid and squalane particles were also approximately 50% larger with high [Cl] (and high [Cl_2]) in the small flow tube as compared to with low [Cl] (and low [Cl_2]) in the large flow tube (Fig. 3). Thus, adsorption of both O_3 and Cl_2 precursors appears to occur regardless of particle composition, at least in these studies, and must be taken into account in similar experiments.

In the atmosphere, O_3 concentrations are orders of magnitude smaller than those for which adsorption effects were observed to be significant in this study. However, if volatile species such as O_3 and Cl_2 exhibit a Langmuir-type adsorption on the surfaces of organic particles, it seems reasonable that other inert gas-phase species present at much higher concentrations in the troposphere may demonstrate similar behavior.

Perhaps N_2, O_2, Ar, H_2O or CO_2, for example, adsorb to the surface of particles and influence rates of gas-particle reactions. In fact, indirect evidence for the adsorption of O_2 to liquid dioctyl sebacate (DOS) particles was observed previously in this lab (Hearn et al., 2007). In that study, Cl radicals reacted with DOS particles, and the yield of the ketone product initially increased with increasing $[O_2]$ and then approached an asymptote at higher $[O_2]$ (Fig. 7 in that paper, Hearn et al., 2007). The dependence on $[O_2]$ was described well by a Langmuir-type functional form, and it was inferred that a reaction to create the ketone product was occurring at the surface of the particles:

$$RO\bullet + O_2 \rightarrow \text{ketone} + HO_2. \tag{7}$$

However, the effect that O_2 had on the rate of reaction was not measured, and further work is required to determine whether species such as O_2, N_2 and H_2O might influence rates of gas-particle reactions under tropospheric conditions.

This work has shown that radical concentration and time can be considered interchangeable parameters in laboratory studies of gas-particle kinetics. However, it has also demonstrated that rates of gas-particle reactions can be influenced dramatically by the adsorption of inert species such as O_3 and Cl_2. This effect may not be specific to O_3 and Cl_2, and the high concentrations of other precursors that are often used in laboratory studies may also alter the gas-particle kinetics. For example, HONO photolysis can also be used to generate OH radicals, but it is not clear to what extent HONO adsorbs to particle surfaces and how it modifies the uptake kinetics. Clearly, careful consideration of the high concentrations of precursor species used to create radical species in the laboratory must be made in order to accurately extrapolate laboratory results to the troposphere. Finally, this study has examined only single-component, model liquid particles. Likely, the extent and importance of adsorption is dependent on the chemical and physical properties of the particles, but more work is needed to explore this.

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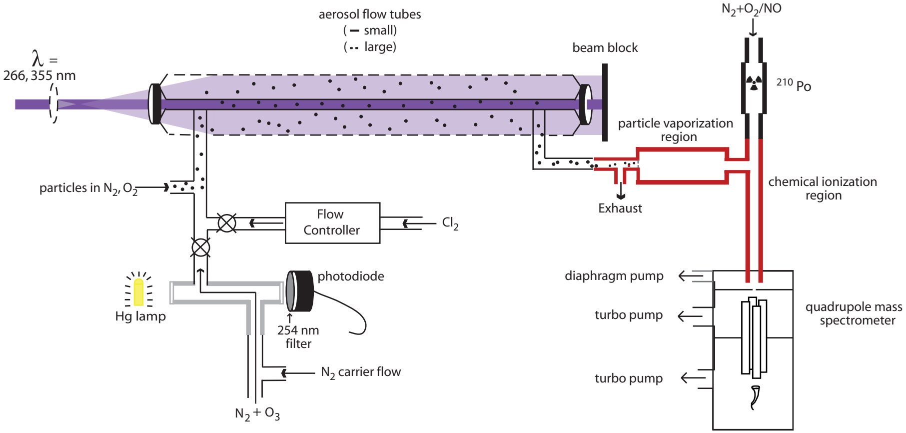

Fig. 1. Schematic diagram of the experimental setup to collect particle kinetic decays with: (1) fixed reaction time of 2 s (small flow tube) or (2) variable reaction time up to 66 s (large flow tube). The chemical ionization schemes used for particle and gas-phase reference detection are described in the text.

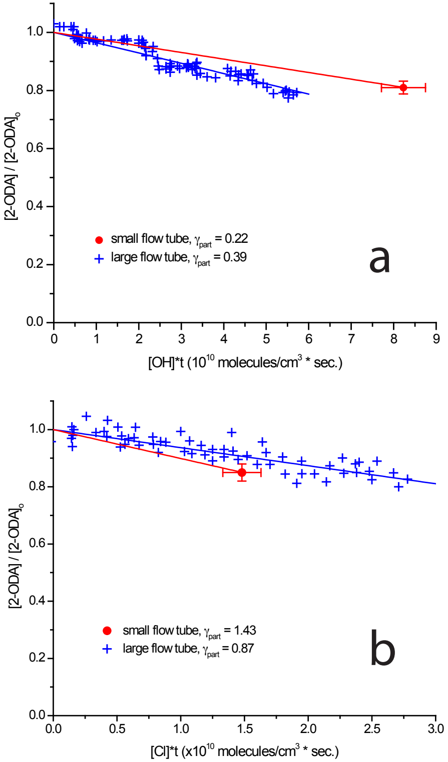

Fig. 2. **(a)** Sample 2-ODA particle decays from small and large flow tubes. For the examples shown, γ_{part} for OH on 2-ODA particles were 0.22 (50 nm particles) and 0.39 (58 nm particles) for the small and large flow tubes, respectively. **(b)** Sample 2-ODA particle decays from small and large flow tubes. For the examples shown, γ_{part} for Cl on 2-ODA particles were 1.43 (52 nm particles) and 0.90 (58 nm particles) for the small and large flow tubes, respectively. These reactive uptake coefficients were not corrected for limitation of uptake by gas phase diffusion.

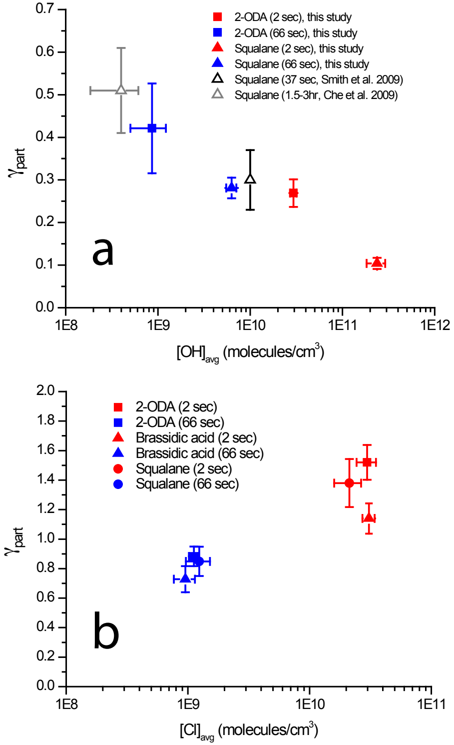

Fig. 3. **(a)** Effective reactive uptake coefficient, γ_{part}, of OH on 2-ODA particles and Sq particles in the large and small flow tubes as a function of OH concentration. The data of Che et al. (2009) and Smith et al. (2009) are shown for comparison. **(b)** Effective reactive uptake coefficient, γ_{part}, of Cl on 2-ODA, Sq, and BA particles in the large and small flow tubes as a function of Cl concentration.

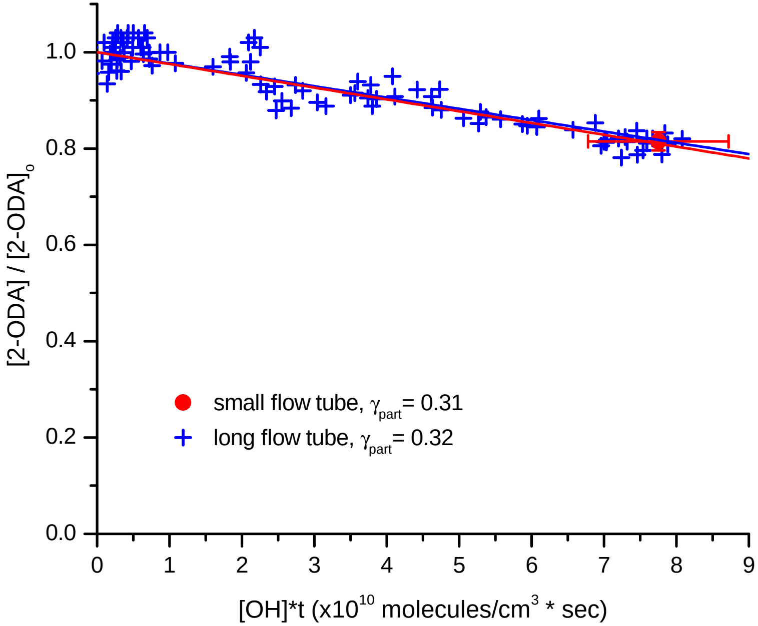

Fig. 4. 2-ODA decay from reaction with OH in the small and large flow tubes with $[O_3] = 3–4 \times 10^{15}$ molecules cm^{-3}.

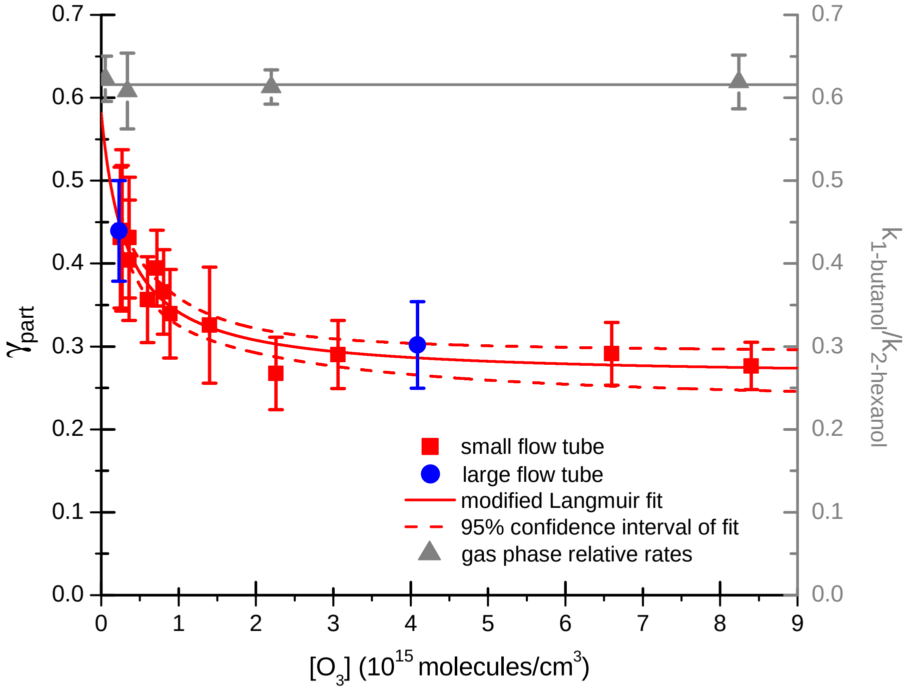

Fig. 5. Effective reactive uptake coefficient, γ_{part}, of OH on 2-ODA particles as a function of O_3 concentration. The Langmuir-type adsorption isotherm used to fit the data, Eq. (4), is also shown with 95% confidence intervals. The best fit parameters are: $\gamma_o = 0.56$ (±0.07), $K = 2.60$ (±1.40) $\times 10^{-15}$ cm^3 molecule^{-1}, and $f = 1.86$ (±0.16). Also shown are the results of a gas-phase relative rates experiment in which the ratio of the rate constants of 1-butanol and 2-hexanol reacting with OH was determined as a function of $[O_3]$.

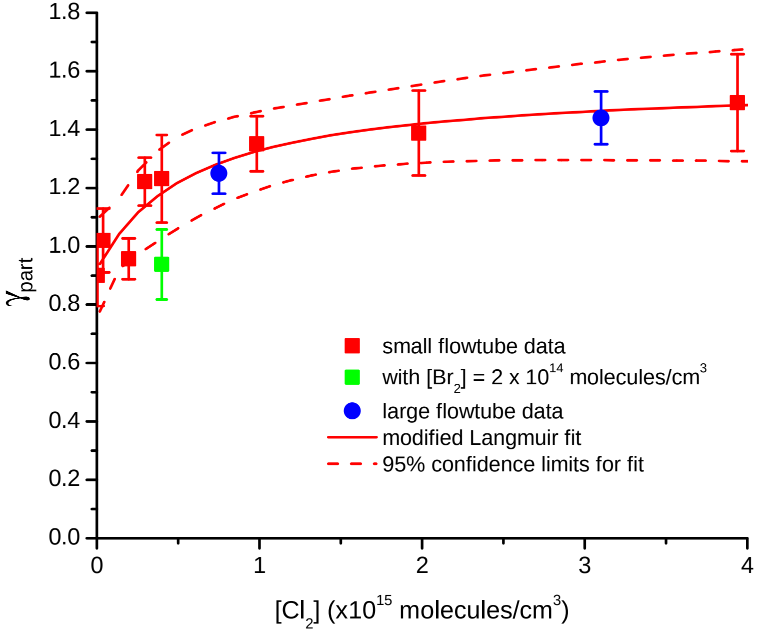

Fig. 6. Effective reactive uptake coefficient, γ_{part}, for Cl on 2-ODA particles as a function of Cl_2 concentration. The Langmuir-type adsorption isotherm used to fit the data, Eq. (4), is also shown with 95% confidence intervals. The best fit parameters are: $\gamma_o = 0.92$ (±0.07), $K = 1.72$ (±1.23) × 10^{-15} cm^3 molecule^{-1}, and $f = -1.42$ (±0.30). Br_2 adsorption decreases the observed rate of reaction.