Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1118, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 14 December 2016

Efficient bulk mass accommodation of N_2O_5 into neutral aqueous aerosol

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Abstract. An isotope exchange experiment with the short-lived radioactive tracer ^{13}N is used to trace N_2O_5 uptake into nitrate containing aqueous aerosol particles. While uptake of ^{13}N labelled N_2O_5 to deliquesced Na_2SO_4 aerosol is consistent with previous studies, in presence of aerosol phase nitrate efficient exchange of labelled nitrate with the non-labelled nitrate pool was observed. The experiments provide direct evidence for efficient bulk mass accommodation of N_2O_5 into aqueous solution with $\alpha_b > 0.4$ at room temperature, as well as for the fast disproportionation into nitronium and nitrate. While for experimental reasons this study is limited to non-acidic aerosol, it is likely that mass accommodation is not limiting N_2O_5 uptake also under wider ranges of conditions.

1 Introduction

The central role of NO_x in the regulation of the oxidative capacity of the atmosphere is well established. N_2O_5, an important species of the nighttime chemistry of nitrogen oxides, has been identified as one of the major reservoir species and potential sinks of NO_x (Abbatt et al., 2012; Chang et al., 2011). NO_2 reacts with O_3 to form NO_3, which then react together to form N_2O_5 (R1).

$$NO_2 + NO_3 \rightleftarrows N_2O_5 \qquad \text{(R1)}$$

Depending on location N_2O_5 may be removed primarily by heterogeneous hydrolysis to nitric acid or other products on aerosol surfaces, providing thus a nighttime sink for atmospheric NO_x (R2) (Abbatt et al., 2012; Chang et al., 2011).

$$N_2O_5 + H_2O_{(l)} \longrightarrow 2HNO_{3(aq)} \qquad \text{(R2)}$$

Removal of N_2O_5 leads to a reduction of atmospheric NO_x and consequent reduction of tropospheric ozone and thus the oxidative capacity of the atmosphere (Dentener and Crutzen, 1993; Evans and Jacob, 2005). The reactivity of N_2O_5 with aerosols has been of ongoing interest for the past two decades. Laboratory investigations have encompassed measurement of uptake kinetics to a wide array of inorganic aerosols, like H_2SO_4/sulphates (Hallquist et al., 2003; Hanson and Lovejoy, 1994), NaCl/marine aerosol (Gaston and Thornton, 2016; George et al., 1994; Thornton and Abbatt, 2005), nitrates (Hallquist et al., 2003; Wahner et al., 1998) and mineral dust (Karagulian et al., 2006; Wagner et al., 2008). Further constraints have also been derived from field observations of N_2O_5 and aerosol abundance and composition (Bertram et al., 2009; Phillips et al., 2016). The uptake coefficient γ (defined as the as the probability that a gas kinetic collision of a molecule leads to its uptake at the interface) on deliquesced inorganic aerosol is in the 10^{-1}-10^{-2} range. Organic aerosol on the other hand presents a wider range of reactivities, with values approaching those of inorganic aerosols in certain cases such as for malonic acid (Griffiths et al., 2009; Thornton et al., 2003) at around 10^{-2}, while in other cases the uptake coefficients go down to 10^{-3}-10^{-5}, such as for some polycarboxilic acids like citric acid (Gržinić et al., 2015), succinic acid or humic acid (Badger et al., 2006; Griffiths et al., 2009), long chained fatty acids and polyalcohols (Gross et al., 2009) that indicate varying effects of water content and viscosity on the reactivity and kinetic regime. Additionally, coating aqueous particles with insoluble organic films has shown to have an inhibiting effect on N_2O_5 uptake (Anttila et al., 2006; Folkers et al., 2003) by restricting transport from the gas phase to the aerosol phase, reduced solubility in the organic phase or limited water availability. The hydrolysis of $N_2O_5(g)$ is believed to proceed through a multistep process (Behnke et al., 1997; Mozurkewich and Calvert, 1988): molecular solvation (R3) is followed by dissociation into nitronium (NO_2^+, or its hydrated form $H_2ONO_2^+$) and nitrate (R4). The fate of nitronium is governed by competition between the reaction with nitrate to yield molecular N_2O_5 again (R5), the reaction with $H_2O(l)$ to yield HNO_3 (R7) or reactions with other nucleophiles (such as chloride ion) not considered further here.

$$N_2O_{5(g)} \rightleftarrows N_2O_{5(aq)} \qquad (R3)$$

$$N_2O_{5(aq)} \longrightarrow NO^+_{2(aq)} + NO^-_{3(aq)} \qquad (R4)$$

$$NO^+_{2(aq)} + NO^-_{3(aq)} \longrightarrow N_2O_{5(aq)} \qquad (R5)$$

$$NO^-_{3(aq)} + H^+_{(aq)} \rightleftarrows HNO_{3(aq)} \qquad (R6)$$

$$NO^+_{2(aq)} + H_2O_{(liq)} \longrightarrow HNO_{3(aq)} + H^+_{(aq)} \qquad (R7)$$

As long as nitrate is a minority species in the aerosol phase, the loss of N_2O_5 is driven by reaction R7. Depending on the water content, either the transfer of N_2O_5 into the aqueous phase, R3, also referred to as mass or bulk accommodation, or R7 are rate limiting according to current understanding (Abbatt et al., 2012).

On the other hand, in presence of significant amounts of nitrate in the aqueous phase, the loss of nitronium ion by reaction with nitrate back to N_2O_5, R5, becomes significant, and the uptake of N_2O_5 becomes lower with increasing nitrate content in the aerosol phase, typically by an order of magnitude. This effect is referred to as the ‘nitrate effect’ (Abbatt et al., 2012; Bertram and Thornton, 2009; Hallquist et al., 2003; Mentel et al., 1999; Wahner et al., 1998).

Most studies conducted related to N_2O_5 reactivity with aqueous aerosol so far were based on measuring the net gas-phase loss of N_2O_5 due to uptake on an aerosol. The kinetics were described with a simplified lumped mechanism by assigning an effective Henry’s law constant, *H*, of N_2O_5 of about 2 M atm^{-1} at room temperature and a net rate coefficient for the overall reaction of N_2O_5 with H_2O to HNO_3 , k_0^{II}, of around 2×10^5 M^{-1} s^{-1} (Ammann et al., 2013), so that the uptake coefficient can be described via the resistor model as given by equation (1).

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{c}{4HRT\sqrt{D_l\, k^{II}[H_2O]}\,[\coth(r/l) - (l/r)]} \qquad l = \sqrt{\frac{D_l}{k^{II}[H_2O]}} \qquad (1)$$

Where α_b denotes the bulk mass accommodation coefficient, c the mean thermal velocity of N_2O_5 in the gas phase, D_l the diffusion coefficient of N_2O_5 in the aqueous phase, usually set to 10^{-5} cm^2 s^{-1} for low viscosity aqueous aerosol, $[H_2O]$ the concentration of H_2O in M, *r* the particle radius and *l* the reacto-diffusive length. α_b was set to about 0.03 at room temperature to explain the apparent levelling off of γ towards high relative humidity (Ammann et al., 2013). The effect of nitrate as mentioned above has been taken into account by using equation (2) instead of a fixed rate coefficient k^{II}:

$$k^{II} = k_0^{II}\left(1 - \frac{k_5[NO_3^-]}{k_5[NO_3^-] + k_7[H_2O]}\right) \qquad (2)$$

This expression requires the knowledge of the concentrations of water and nitrate and the ratio of the two rate coefficients k_5/k_7, for which a value of 0.02 leads to reasonable consistency with available data (Ammann et al., 2013). However, the actual size of the pool of dissolved N_2O_5 (or its dissociated products NO_2^+ and NO_3^-), the true value of the bulk mass accommodation coefficient, α_b, and the rate coefficients for the individual reactions remained obscured. In this study, we make specific use of the short-lived radioactive isotope ^{13}N (Ammann, 2001; Gržinić et al., 2015; Gržinić et al., 2014) to trace the exchange of ^{13}N-labelled nitrate resulting from uptake of labelled N_2O_5 with the non-labelled nitrate pool in the aerosol phase. This allows obtaining a direct estimate of α_b and constraints for the N_2O_5 disproportionation (R4) and the recombination reaction (R5). The tracer method is very sensitive in detecting phase transfer of labelled N_2O_5 at very low gas phase concentrations and thus is able to escape any artefact nitrate effect due to build-up of nitrate during the course of a kinetic experiment for experiments with aerosol without any nitrate initially as discussed by Gržinić et al. (Gržinić et al., 2015). However, this sensitivity comes at the expense of chemical selectivity in the sense that re-evaporating HNO_3 product from an acidic aerosol would interfere with the N_2O_5 measurement as shown in our previous study (Gržinić et al., 2014). We therefore performed the experiments presented here with neutral sodium sulfate and sodium nitrate aerosol to avoid this interference.

2. Experimental section

A detailed description of the experimental method and setup can be found in our previous publications relating to the production of ^{13}N labeled N_2O_5 (Gržinić et al., 2014) and uptake of N_2O_5 on citric acid aerosol (Gržinić et al., 2015). Here we will present a very cursory description of the ^{13}N production method and the changes that have been implemented to the experimental setup for the present uptake measurements.

The ^{13}N short lived radioactive tracer ($T_{1/2} \approx 10$ min.) is produced via the $^{16}O(p,\alpha)^{13}N$ reaction in a gas target by irradiating a 20% O_2 in He flow with 11 MeV protons produced by the Injector II cyclotron at the Paul Scherrer Institute, Switzerland. The highly oxidized ^{13}N labeled species are reduced to ^{13}NO for transport via a 580 m long PVDF capillary tube to the laboratory. Figure 1 shows a schematic of the experimental setup used in this study. ^{13}NO containing gas from the accelerator facility (50 ml/min) is mixed with ~3 ml/min of 10 ppmv non-labeled NO in N_2 from a certified gas cylinder and nitrogen carrier gas (only a very small fraction of NO is labeled with ^{13}N, about 10^{-6} and lower). This gas flow is mixed in the N_2O_5 synthesis reactor with a 50 ml/min flow containing ~8 ppmv O_3 produced by irradiating a 10% O_2 in N_2 gas mixture with 185nm UV light. The reactor is a glass tube of 34 cm length and 4 cm inner diameter, lined with PTFE foil and operated under dry conditions to minimize hydrolysis of N_2O_5 on the walls. The gas phase chemistry of NO with O_3 results in the formation of NO_2, NO_3 and finally N_2O_5 (R1). The resulting gas flow is mixed with a secondary gas flow containing aerosol (720 ml/min) in an aerosol flow tube. This flow tube differs from the one that we used in our previous studies in that it is optimized for measurement of uptake coefficients in the 10^{-1}-10^{-2} range. It consists of a glass tube 39.3 cm in length and 1.4 cm in inner diameter. The inside of the glass tube is coated with halocarbon wax to minimize N_2O_5 losses to the wall by heterogeneous hydrolysis. A PTFE tube (6 mm diameter) is inserted coaxially into the flow tube to act as injector for the N_2O_5 flow. The injector contains holes at the end which allow the N_2O_5 flow to be injected perpendicularly to the aerosol flow. Mixing is assumed to be rapid, and a laminar flow profile is assumed to have been established in the first few cm. A black shroud is used to cover the N_2O_5 synthesis reactor and the aerosol flow tube in order to prevent NO_3 photolysis and thus N_2O_5 loss. Aerosol is produced by nebulizing 0.1% wt. $NaNO_3$, Na_2SO_4 and 1:1 $NaNO_3/Na_2SO_4$ solutions in MilliQ water. The resulting aerosol flow is dried over a Nafion membrane diffusion drier (RH of the drying gas outside is adjusted to 40% RH to prevent efflorescence), passed through an ^{85}Kr bipolar ion source and an electrostatic precipitator to equilibrate the charge distribution and subsequently remove the charged particles, respectively. A humidifier is placed after the ion source to adjust the humidity of the gas flow to the required experimental levels. The overall gas flow exiting from the aerosol fast-flow reactor is split into two flows via a T-connector, one to an SMPS (Scanning Mobility Particle Sizer) system used to characterize the aerosol, consisting of a ^{85}Kr bipolar ion source to re-establish charge equilibrium, a differential mobility analyzer (DMA, TSI 3071) and a condensation particle counter (CPC, TSI 3022). The other part of the gas flow is directed into a parallel plate diffusion denuder system, where the various ^{13}N containing gaseous species (N_2O_5, NO_3 and NO_2) are trapped by lateral diffusion and chemical reaction on a series of parallel, selectively coated aluminium plates: citric acid for trapping N_2O_5 and NO_3, a 1:1 mixture of NDA (N-(1-naphtyl) ethylene diamine dihydrochloride) and KOH for trapping NO_2. The aerosol particles, which have small diffusivity, pass without loss through the denuder system and are trapped on a glass fiber filter placed at the exit. The radioactive decay of ^{13}N is measured by placing a CsI scintillator crystal with PIN diode detectors (Caroll and Ramsey, USA) on each of the denuder traps and the particle filter. ^{13}N decays by β^+ decay and the resulting positron annihilates with an electron with emission of two coincident γ-rays in opposite directions. The resulting signal can be related to the concentration of the species in the gas and particle phase by comparing the NO_2 concentration measured with a NO_x analyzer to the $^{13}NO_2$ and $^{13}N_2O_5$ signals on the denuder plates and particle filter, respectively. Unfortunately, due to experimental limitations, only a limited number of measurements could be performed. The ^{13}N tracer technique is dependent on smooth operation of the accelerator facilities and constant online ^{13}N production to be successful, which is not always the case.

3. Results and Discussion

The measurements were performed at 50% and 70% RH for all three of the solutions in question. The operating procedure is similar to the one reported by Gržinić et al. (Gržinić et al., 2015; Gržinić et al., 2014), although in this case the experiment was performed by measuring the change in signals under variation of the position of the injector (reaction time) and not aerosol surface to volume ratio. Appropriate corrections have been applied to the N_2O_5 signal to account for NO_2 interference on the denuder coating used for N_2O_5 (citric acid) as well as for the small amounts of NO_3 present in the gas phase, as described in our previous studies. Before each experimental run a wall loss measurement was performed without aerosol by moving the injector in 5-10 cm steps along the length of the aerosol flow tube and measuring the gas phase N_2O_5 signal, in order to obtain the pseudo-first order wall loss rate constants (k_w) for each experiment. These values varied between ~3x10^{-2} and ~7x10^{-2} s^{-1}, depending on humidity. Because of the short residence time in the aerosol flow tube and its reduced surface to volume ratio, losses to the wall were less pronounced than in our previous studies. NO_2 concentrations in the system were measured by switching a NO_x analyzer in place of the SMPS system at the beginning of the experiment. By comparing this result to the $^{13}N_2O_5$ and $^{13}NO_2$ signals, the concentration of non-labelled N_2O_5 in the system was calculated, as described in our previous studies (Gržinić et al., 2015; Gržinić et al., 2014). The uptake measurements were performed in a similar fashion to the wall loss measurements, although in this case aerosol was introduced at each step. By using Eq. 3, which describes gas-aerosol phase interaction kinetics, we can estimate the uptake coefficient.

$$\frac{C_p^{(t)}}{C_g^{(t=0)}} = \frac{1-e^{-(k_w+k_p)t}}{1+\frac{k_w}{k_p}} \qquad (3)$$

$$k_p = \frac{S_p \omega \gamma_{eff}}{4} \qquad (4)$$

where $C_g^{(t=0)}$ is the gas-phase N_2O_5 concentration at time zero, $C_p^{(t)}$ is the N_2O_5 concentration in the particle phase, k_w is the wall loss constant, measured as described above, and k_p denotes the apparent first order rate constant for gas-phase loss of N_2O_5 to the aerosol phase, which can be related to the effective uptake coefficient (γ_{eff}) by Equation 4, where S_p is the total aerosol surface area to gas volume ratio and ω is the mean thermal velocity of N_2O_5. Figure 2 shows the appearance of ^{13}N in the aerosol phase as a function of time performed together with least-squares fits using Eq. (3) with γ_{eff} as the only variable.

The true uptake coefficients were then obtained by correction for gas phase diffusion of N_2O_5, as described by Pöschl et al. (2007), which leads to considerable corrections for uptake coefficients above 0.1 and particle diameters around 400 nm. The diffusion coefficient was taken as 0.085 cm^{-2} s^{-1} at room temperature and ambient pressure (Tang et al., 2014). Table 1 shows the results obtained for the various aerosols, with corresponding experimental parameters, including γ_{eff} as returned from the fits to the data and γ after the diffusion correction. In absence of aerosol phase nitrate, the obtained results for Na_2SO_4 are comparable to those reported by Mentel et al. (Mentel et al., 1999). In presence of aerosol phase nitrate, uptake of ^{13}N-labelled N_2O_5 is drastically higher than the net uptake of non-labelled N_2O_5 observed in earlier studies by (Hallquist et al., 2003; Mentel et al., 1999; Wahner et al., 1998). A strong dependence on humidity is observed, with an increase by a factor about three from 50% to 70% relative humidity. On mixed Na_2SO_4 / $NaNO_3$ aerosol, the uptake is very close to that of pure $NaNO_3$ aerosol, at both humidities. Since the measured uptake coefficient for labelled ^{13}N into the nitrate containing aerosol is about an order of magnitude larger than previous room temperature estimates of the bulk mass accommodation coefficient, α_b, our results provide a direct indication that gas – aqueous phase exchange of N_2O_5 at room temperature is considerably more efficient than previously thought under comparable conditions.

More insight into the interpretation of the present experiments with ^{13}N labeled N_2O_5 can be obtained by deconvoluting the chemical mechanism of N_2O_5 hydrolysis (R3-7) to take into account the fate of the labelled species. Assuming that the labeled N_2O_5 molecules contain only one ^{13}N atom (due to the very low labeled to non-labeled NO ratio) and under the assumption that no isotopic effects are in play, the chemical mechanism can be assumed to proceed as shown in Figure 3. We first assume that upon dissociation of $^{13}NNO_5$, there is an equal possibility that the ^{13}N label will end up either in the nitronium ion (NO_2^+) or in the nitrate ion (NO_3^-). In the first scenario (left branch of the mechanism) the ^{13}N label ends up on the nitrate ion (R4''). The corresponding non-labelled nitronium ion, if not reacting with H_2O, R7'', may react with nitrate to reform N_2O_5. This N_2O_5 is predominantly non-labeled, since the labeled $^{13}NO_3^-$ ion is lost in the excess nitrate pool present in the aerosol and the likelihood of recombination of the non-labelled nitronium with the labeled nitrate is very small. N_2O_5 re-evaporating to the gas phase is therefore non-labeled. Thus, in this branch, all ^{13}N labels remain in the aqueous phase if evaporation as HNO_3 does not occur, which is unlikely for our neutral aerosol. As evident from the experiments, the net rate of transfer of labelled N_2O_5 into the aerosol nitrate pool is very high.

In the other scenario (right branch) of the mechanism, ^{13}N ends up on the nitronium ion (R4'), and there are two possibilities for its further fate. The $^{13}NO_2^+$ can react with water (R7'), bringing the label into the particulate nitrate pool. Alternatively $^{13}NO_2^+$ can react with NO_3^- from the nitrate pool (R5') to reform $^{13}NNO_5$ which can eventually re-evaporate. Obviously which of these two sub-channels are prevalent depends on water and nitrate concentrations as well as the rate coefficients of the two competing reactions. The water and nitrate concentrations for the conditions of the present experiments were derived from the AIM model (Clegg et al., 1998) and are also listed in Table 1. In presence of nitrate, (R5') is the dominant pathway, as shown by (Mentel et al., 1999) and (Wahner et al., 1998), where values for the ratio k_5/k_7 of 35 and 10, respectively, have been used as fitting parameters to explain the entirety of the nitrate effect. This is consistent with the fact that the net uptake of ^{13}N labelled N_2O_5 is more than an order of magnitude larger than that of non-labelled N_2O_5, indicating that the R5' sub-channel is dominant. Since the uptake coefficient of ^{13}N-labelled N_2O_5 was similar for the aerosol composed of a 1:1 nitrate to sulfate molar ratio mixture and for the pure nitrate aerosol at both humidities, the present results do not allow retrieving rate coefficients for R4, R5 and R7, but indicate that R4 and R5 are fast enough to not become rate limiting, and that R7 is at least an order of magnitude slower than R5, consistent with k_5/k_7 ratios reported earlier. Furthermore, these experiments provide direct evidence that these elementary steps actually exist, because otherwise exchange with the non-labelled nitrate pool would not occur.

The measured uptake coefficient increases with RH (water content) as the increase in water concentration promotes the reaction of $^{13}NO_2^+$ with water (R7') while at the same time a decrease in nitrate concentration suppresses the $^{13}NNO_5$ reformation sub-channel (R5'). However, as argued above, in presence of nitrate at several M, the dominant fate of the label in the right branch of the mechanism is the reformation of labeled N_2O_5. In such a situation the measured uptake coefficient would be only slightly larger than $\alpha_b/2$, with $\alpha_b/2$ contributed by the left branch of the mechanism shown in Fig. 3, and a minor contribution from the right branch. Our results therefore strongly indicate that α_b must be about twice as high as the uptake coefficient of ^{13}N-labelled N_2O_5 measured for $NaNO_3$ and $NaNO_3/Na_2SO_4$ aerosols and thus $\alpha_b>0.4$ when including the uncertainties related to aerosol surface to volume ratio and correction for gas phase diffusion. The only systematic uncertainty not considered in this is the assumption that isotope effects do not influence the symmetry of the disproportionation reaction (R4).

Interestingly, the measured uptake coefficient is more sensitive to the water activity, irrespective of whether it is pure nitrate or mixed nitrate / sulfate particles, than to the fractional nitrate content. In spite of the fact that the expected ratio $k_7[H_2O]/k_5[NO_3^-]$ (see Table 1) increases substantially from pure nitrate to mixed nitrate / sulfate, still bulk accommodation and the efficient exchange of the label with the non-labelled nitrate pool dominates the behavior, indicating that α_b might increase by a factor of three from 50 to 70 % RH. In combination with the insensitivity to composition (water molarity increases much less), this suggests that salting effects should be considered for N_2O_5 to effectively reduce its solubility (and maybe also α_b) for high ionic strength.

Obviously for this technique to work a nitrate pool has to be available and it has to be substantial enough to 'trap' the ^{13}N tracer and prevent its release. In other words, this method traces uptake of N_2O_5 into the non-limiting pool of aqueous nitrate. In absence of nitrate, R7' and R7'' dominate in both branches, and the measured uptake coefficient for the ^{13}N labelled N_2O_5 is comparable to that reported with other techniques for the same aerosol, in the range of a few 10^{-2} for Na_2SO_4 in this study or for $(NH_4)_2SO_4$ reported by Gržinić et al. (2014), both consistent with available literature. For comparison, calculated uptake coefficients based on the parameterization and values from the IUPAC evaluation (Ammann et al., 2013), implemented in equation (1) and (2), are also listed in Table 1.

Conclusion and atmospheric implications

Highly efficient uptake of ^{13}N-labelled N_2O_5 into nitrate containing aqueous aerosol was observed and attributed to the exchange of ^{13}N labeled nitrate as disproportionation product of N_2O_5 with the nitrate pool in the aqueous phase. This allows deriving a very large value for the bulk mass accommodation coefficient for N_2O_5 into an aqueous aerosol at room temperature of $\alpha_b > 0.4$ at high relative humidity. This also provides direct evidence that the fast disproportionation into nitrate and nitronium actually occurs, and thus also supports the arguments behind the nitrate effect. The observed behavior of ^{13}N-labelled N_2O_5 is similar to that observed by Wachsmuth et al. (Wachsmuth et al., 2002), where $^{83-86}$Br isotopes have been used to determine the bulk accommodation coefficient of HOBr on aqueous bromide containing aerosol. The large value of α_b obtained for N_2O_5 at room temperature implies that other limiting processes must be at work to explain the insensitivity of the uptake coefficient to water content at high relative humidity (Abbatt et al., 2012; Griffiths et al., 2009; Thornton et al., 2003), which was partly interpreted as accommodation limitation. Possible other aspects may be the temperature dependence of the solubility of N_2O_5 or salting effects, for which also strong indications come from this study to explain the strong water activity dependence of the observed uptake coefficient of ^{13}N labelled N_2O_5. At least this study would exclude any accommodation limitation and supports previous indications that reaction and diffusion limit uptake of N_2O_5 to low viscosity aqueous aerosol (Gaston and Thornton, 2016). The absence of accommodation limitation also helps rationalizing results from field experiments (Phillips et al., 2016; Wagner et al., 2013), where under some conditions uptake coefficients constrained by combined N_2O_5 and aerosol measurements are larger than those suggested by laboratory studies available to date.

Acknowledgements

The authors would like to thank the staff of the PSI accelerator facilities and of the isotope production facility IP-2 for their invaluable help during experimental work. Technical support by M. Birrer is much appreciated. This study was supported by the Swiss National Science Foundation (grants no. 130175 and 149492).

The Supplement related to this article is available online

References

Abbatt, J. P. D., Lee, A. K. Y., and Thornton, J. A.: Quantifying trace gas uptake to tropospheric aerosol: recent advances and remaining challenges, Chem. Soc. Rev., 41, 6555-6581, doi: 10.1039/C2CS35052A, 2012.

Ammann, M.: Using 13N as tracer in heterogeneous atmospheric chemistry experiments, Radiochim. Acta, 89, 831-838, 2001.

Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI – heterogeneous reactions with liquid substrates, Atmos. Chem. Phys., 13, 8045-8228, doi: 10.5194/acp-13-8045-2013, 2013.

Anttila, T., Kiendler-Scharr, A., Tillmann, R., and Mentel, T. F.: On the reactive uptake of gaseous compounds by organic-coated aqueous aerosols: Theoretical analysis and application to the heterogeneous hydrolysis of N_2O_5, J. Phys. Chem. A, 110, 10435-10443, 2006.

Badger, C. L., Griffiths, P. T., George, I., Abbatt, J. P. D., and Cox, R. A.: Reactive uptake of N_2O_5 by aerosol particles containing mixtures of humic acid and ammonium sulfate, J. Phys. Chem. A, 110, 6986-6994, 2006.

Behnke, W., George, C., Scheer, V., and Zetzsch, C.: Production and decay of ClNO2, from the reaction of gaseous N_2O_5 with NaCl solution: Bulk and aerosol experiments, J. Geophys. Res., 102, 3795-3804, doi: 10.1029/96jd03057, 1997.

Bertram, T. H. and Thornton, J. A.: Toward a general parameterization of N_2O_5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmos. Chem. Phys., 9, 8351-8363, 2009.

Bertram, T. H., Thornton, J. A., Riedel, T. P., Middlebrook, A. M., Bahreini, R., Bates, T. S., Quinn, P. K., and Coffman, D. J.: Direct observations of N2O5 reactivity on ambient aerosol particles, Geophys. Res. Lett., 36, 2009.

Chang, W. L., Bhave, P. V., Brown, S. S., Riemer, N., Stutz, J., and Dabdub, D.: Heterogeneous Atmospheric Chemistry, Ambient Measurements, and Model Calculations of N_2O_5: A Review, Aerosol Sci. Technol., 45, 665-695, doi: 10.1080/02786826.2010.551672, 2011.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system H^+-NH_4^+-Na^+-SO_4^{2-}-NO_3^-- Cl^--H_2O at 298.15 K, J. Phys. Chem. A, 102, 2155-2171, 1998.

Dentener, F. J. and Crutzen, P. J.: Reaction of N_2O_5 on tropospheric aerosols: Impact on the global distributions of NOx , O3, and OH, J. Geophys. Res., 98, 7149-7163, doi: 10.1029/92JD02979, 1993.

Evans, M. J. and Jacob, D. J.: Impact of new laboratory studies of N_2O_5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH, Geophys. Res. Lett., 32, 2005.

Folkers, M., Mentel, T. F., and Wahner, A.: Influence of an organic coating on the reactivity of aqueous aerosols probed by the heterogeneous hydrolysis of N_2O_5, Geophys. Res. Lett., 30, 2003.

Gaston, C. J. and Thornton, J. A.: Reacto-Diffusive Length of N_2O_5 in Aqueous Sulfate- and Chloride-Containing Aerosol Particles, J. Phys. Chem. A, 120, 1039-1045, doi: 10.1021/acs.jpca.5b11914, 2016.

George, C., Ponche, J. L., Mirabel, P., Behnke, W., Scheer, V., and Zetzsch, C.: Study of the Uptake of N_2O_5 by Water and NaCl Solutions, J. Phys. Chem., 98, 8780-8784, 1994.

Griffiths, P. T., Badger, C. L., Cox, R. A., Folkers, M., Henk, H. H., and Mentel, T. F.: Reactive Uptake of N_2O_5 by Aerosols Containing Dicarboxylic Acids. Effect of Particle Phase, Composition, and Nitrate Content, J. Phys. Chem. A, 113, 5082-5090, 2009.

Gross, S., Iannone, R., Xiao, S., and Bertram, A. K.: Reactive uptake studies of NO3 and N_2O_5 on alkenoic acid, alkanoate, and polyalcohol substrates to probe nighttime aerosol chemistry, Phys. Chem. Chem. Phys., 11, 7792-7803, 2009.

Gržinić, G., Bartels-Rausch, T., Berkemeier, T., Türler, A., and Ammann, M.: Viscosity controls humidity dependence of N_2O_5 uptake to citric acid aerosol, Atmos. Chem. Phys., 15, 13615-13625, doi: 10.5194/acp-15-13615-2015, 2015.

Gržinić, G., Bartels-Rausch, T., Birrer, M., Türler, A., and Ammann, M.: Production and use of 13N labeled N_2O_5 to determine gas–aerosol interaction kinetics, Radiochimica Acta, 102, 1025–1034, doi: 10.1515/ract-2014-2244, 2014.

Hallquist, M., Stewart, D. J., Stephenson, S. K., and Cox, R. A.: Hydrolysis of N_2O_5 on sub-micron sulfate aerosols, Phys. Chem. Chem. Phys., 5, 3453-3463, 2003.

Hanson, D. R. and Lovejoy, E. R.: The Uptake of N_2O_5 onto Small Sulfuric-Acid Particles, Geophys. Res. Lett., 21, 2401-2404, 1994.

Karagulian, F., Santschi, C., and Rossi, M. J.: The heterogeneous chemical kinetics of N_2O_5 on CaCO3 and other atmospheric mineral dust surrogates, Atmos. Chem. Phys., 6, 1373-1388, 2006.

Mentel, T. F., Sohn, M., and Wahner, A.: Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, Phys. Chem. Chem. Phys., 1, 5451-5457, 1999.

Mozurkewich, M. and Calvert, J. G.: Reaction probability of N_2O_5 on aqueous aerosols, J. Geophys. Res., 93, 15889-15896, doi: 10.1029/JD093iD12p15889, 1988.

Phillips, G. J., Thieser, J., Tang, M., Sobanski, N., Schuster, G., Fachinger, J., Drewnick, F., Borrmann, S., Bingemer, H., Lelieveld, J., and Crowley, J. N.: Estimating N_2O_5 uptake coefficients using ambient measurements of NO_3, N_2O_5, $ClNO_2$ and particle-phase nitrate, Atmos. Chem. Phys., 16, 13231-13249, doi: 10.5194/acp-16-13231-2016, 2016.

Poschl, U., Rudich, Y., and Ammann, M.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions - Part 1: General equations, parameters, and terminology, Atmos. Chem. Phys., 7, 5989-6023, 2007.

Tang, M. J., Cox, R. A., and Kalberer, M.: Compilation and evaluation of gas phase diffusion coefficients of reactive trace gases in the atmosphere: volume 1. Inorganic compounds, Atmos. Chem. Phys., 14, 9233-9247, 2014.

Thornton, J. A. and Abbatt, J. P. D.: N_2O_5 reaction on submicron sea salt aerosol: Kinetics, products, and the effect of surface active organics, J. Phys. Chem. A, 109, 10004-10012, 2005.

Thornton, J. A., Braban, C. F., and Abbatt, J. P. D.: N_2O_5 hydrolysis on sub-micron organic aerosols: the effect of relative humidity, particle phase, and particle size, Phys. Chem. Chem. Phys., 5, 4593-4603, 2003.

Wachsmuth, M., Gäggeler, H. W., von Glasow, R., and Ammann, M.: Accommodation coefficient of HOBr on deliquescent sodium bromide aerosol particles, Atmos. Chem. Phys., 2, 121-131, doi: 10.5194/acp-2-121-2002, 2002.

Wagner, C., Hanisch, F., Holmes, N., de Coninck, H., Schuster, G., and Crowley, J. N.: The interaction of N_2O_5 with mineral dust: aerosol flow tube and Knudsen reactor studies, Atmos. Chem. Phys., 8, 91-109, 2008.

Wagner, N. L., Riedel, T. P., Young, C. J., Bahreini, R., Brock, C. A., Dubé, W. P., Kim, S., Middlebrook, A. M., Öztürk, F., Roberts, J. M., Russo, R., Sive, B., Swarthout, R., Thornton, J. A., VandenBoer, T. C., Zhou, Y., and Brown, S. S.: N_2O_5 uptake coefficients and nocturnal NO_2 removal rates determined from ambient wintertime measurements, J. Geophys. Res., 118, 9331-9350, doi: 10.1002/jgrd.50653, 2013.

Wahner, A., Mentel, T. F., Sohn, M., and Stier, J.: Heterogeneous reaction of N_2O_5 on sodium nitrate aerosol, J. Geophys. Res., 103, 31103-31112, 1998.

Table 1. Experimental parameters and results

Aerosol	$NaNO_3$	$NaNO_3$	$NaNO_3$/ Na_2SO_4	$NaNO_3$/ Na_2SO_4	Na_2SO_4	Na_2SO_4
Molar mixing ratio	-	-	1:1	1:1	-	-
Temperature (K)	295±1	295±1	295±1	295±1	295±1	295±1
RH (%)	50±1	70±1	51±1	70±1	51±1	70±1
Average S/V ratio (m^2/m^3)	5.66×10^{-3}	5.00×10^{-3}	3.36×10^{-3}	4.76×10^{-3}	3.42×10^{-3}	3.00×10^{-3}
γ_{eff} (^{13}N-N_2O_5)	0.057	0.18	0.054	0.17	0.0052	0.025
Error[a]	±0.004	±0.02	±0.008	±0.02	±0.002	±0.003
γ (^{13}N-N_2O_5) [b]	**0.067**	**0.29**	**0.063**	**0.26**	**0.0053**	**0.027**
Total error [c]	±0.02	±0.1	±0.02	±0.2	±0.002	±0.008
$[H_2O]$ (M) [d]	28.5	38.2	34.4	41.6	38.6	43.8
$[NO_3^-]$ (M) [d]	13.1	8.78	4.60	3.29	0	0
$k_7[H_2O]/k_5[NO_3^-]$ [e]	0.044	0.087	0.15	0.25	-	-
γ (non-labelled N_2O_5) [f]	0.0050	0.010	0.013	0.019	0.044	0.047

[a] 95% confidence level of the fit of eq. (3) to the data as shown in Fig. 2

[b] corrected for diffusion in the gas phase

[c] including 30% uncertainty related to the aerosol surface to volume ratio

[d] from AIM model (Clegg et al., 1998) k^{II} calculated according to $1\text{x}10^5$ M^{-1} s^{-1}

[e] $k_7/k_5 = 50$

[f] calculated using equations (1) and (2), with $k_0^{II} = 10^5$ M^{-1} s^{-1} and H = 2 M atm^{-1}

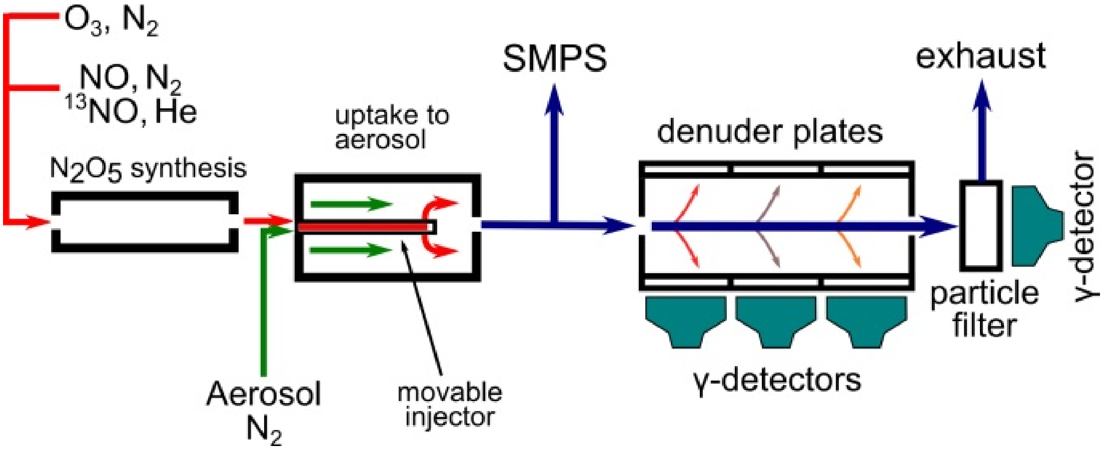

Fig. 1. Schematic of the modified experimental setup used in this study

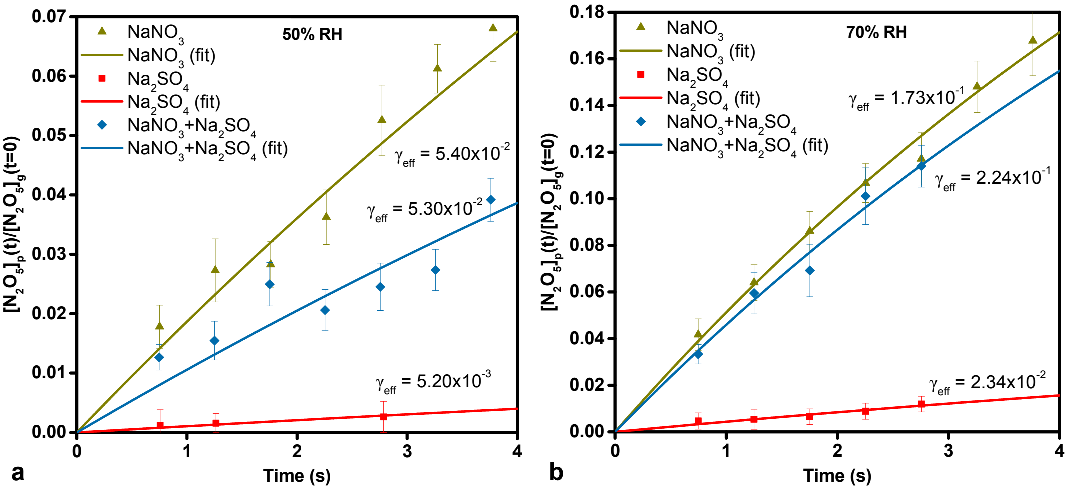

Fig. 2. Normalized particle-phase N_2O_5 concentration vs. time graph for the experiments performed at 50% RH (a) and 70% RH (b). The data points represent the measurement data, the error bars represent the standard deviation of the measurements, the curves are a least-squares fit of Eq. 1 to the measured data.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1118, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 14 December 2016

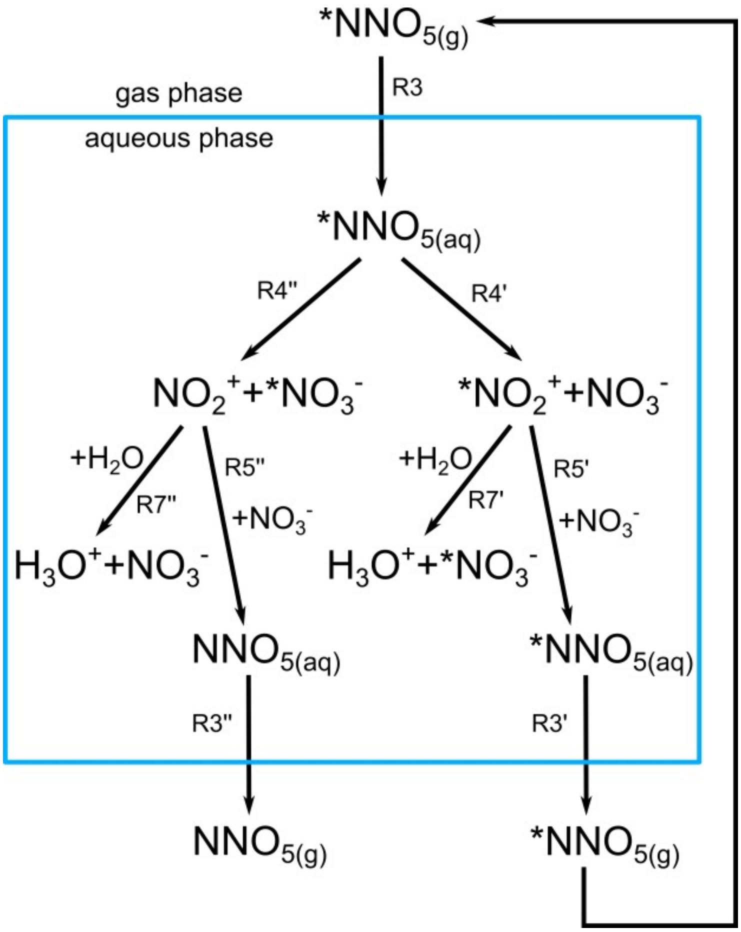

Fig. 3. The chemical mechanism of ^{13}N labeled N_2O_5 hydrolysis in nitrate containing solutions. *N refers to ^{13}N.