Uptake of NO_3 on liquid surfaces

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Introduction

NO_3 which is formed in the reaction of NO_2 with ozone can reach concentration levels up to 10^9 molecules per cm^3 in the night time atmosphere. Its gas phase reactions with many compounds, e.g. olefins, are fast and may represent import loss pathways at night. In wet atmospheric particles such as cloud drops, NO_3 can initiate radical reactions leading to the oxidation of S(IV) compounds and to halogen activation from Cl^- and Br^- (Finlayson-Pitts & Pitts, 2000). The phase transfer of the radical across atmospheric liquid surfaces such as cloud droplets can act as an import loss or sink process for either phase.

Fig. 1: Single drop hanging on a pipette's tip inside a flow tube gas phase reactor

Single drop experiment

A single drop experiment (Schütze & Herrmann, 2002) was used for the investigation of the transfer from the gas phase into an aqueous drop. It consists of a flow-tube reactor including a section for generation and analysis of single liquid drops. The drops are suspended on the tip of a pipette, see Figure 1. The light of a broad banded source is fed through an optical fibre inside the pipette to its tip. After passing the drop as an absorption path way the light is coupled into a second fibre which leads to a diode array spectrometer for detection. This set-up allows *in situ* monitoring of the liquid phase concentrations.

Set-up I

The basic flow tube shown in Fig. 2 is 30 cm long and 2.13 cm in diameter. It was fed with humidified Helium as a carrier gas through the main inlet. N_2O_5 was introduced via the lateral precursor inlet and thermolized by an electrical heater right before entering the main tube. This produced NO_3 (beside NO_2). The concentration of NO_3 is determined after reaction with

Fig. 2: Schematic diagram of the basic flow tube reactor

an organic which is introduced at the position of the drop through the movable inlet. The concentration of the organic is monitored by GC-FID. The drops were made of aqueous solutions of the dye Alizarin Red S (ARS) which acted as a scavenger for the NO_3 that entered the liquid phase. The strong absorbance of the dye was followed for quantification of the uptake.

Set-up II

The basic flow tube was extended by a heated pre-reactor upstream the main tube and by an UV-VIS absorption cell downstream. NO_3 was produced from the reaction of NO_2 and O_3 at 393 K in the pre-reactor (1 m long, 3.5 cm i.d.). It was detected by its absorption at 662 nm. For the determination of the other N-containing species present, the UV-VIS cell was replaced by a FT-IR spectrometer equipped with a white cell. The drops consisted of aqueous NaCl solutions. The uptake of the NO_3 radical

Fig. 3: Schematic diagram of the extended flow tube reactor including heated pre-reactor and UV-VIS (FT-IR) absorption cell. The result of a model simulation of the reaction system is shown in the inset

was monitored by the absorption of the nitrate ions formed in the drop after reaction of NO_3 with Cl^- or other constituents of the solution.

Uptake on ARS solutions

A drop of ARS solution exposed to a NO_3 containing gas flow shows a time dependent absorbance as shown in Fig. 3.
Around 430 nm the absorbance is decreasing indicating the degradation of the dye. At wavelengths below 400 nm the absorbance is increasing which is attributed to the formation of products from the reaction of NO_3 with

Fig. 3: Time dependent absorbance of a drop of ARS solution exposed to gas phase NO_3

the dye. The uptake of NO_3 was monitored by following the decaying absorbance of ARS.
The measured time course of the absorbance at 450 nm (corrected by the absorbance at 600 nm) depending on the initial ARS concentration is presented in Fig. 4. For the lowest dye concentrations, a decreasing slope indicates some kind of saturation effect. Nevertheless, this is not the case for the highest concentrations used.
An uptake coefficient of

$$\gamma_{NO_3} = (2.7 \pm 0.8) \cdot 10^{-3}$$

was calculated from the initial slopes of these plots. After correction for the effect of the limited gas phase diffusion, a lower limit for the mass accommodation coefficient is obtained:

$$\alpha_{NO_3} \geq 2.4 \cdot 10^{-3}$$

Fig. 4: Plot of the ARS absorbances at 450 nm for the different dye concentrations used. For comparison, all plots are normalized with the measured gas phase NO_3 concentration.

c_{ARS} [10^{-3} mol l^{-1}]:
0.15
0.29
0.61
1.17
2.35

Gas phase composition

NO_2 reacted with an excess of ozone to form NO_3. Nevertheless, no NO_3 was found in the UV-VIS cell if the heater of the pre-reactor was switched off (**Case A** in Fig. 5). This is due to the reaction of NO_2 with NO_3 which forms N_2O_5. A mixture of N_2O_5 and HNO_3 was found using FT-IR. The occurrence of nitric acid is attributed to the conversion of N_2O_5 on the reactor walls which carry small amounts of water even under very low relative humidities (RH).
When the heater is switched on (**Case B**) the N_2O_5 decomposes very rapidly. Consequently, the measured NO_3 concentration accounts for more than 90 % of the initial NO_2.
Upon increasing the relative humidity to 90 %, the NO_3 concentration dropped to less than 60 % of the initial NO_2 concentration (**Case D**). **NO_3 seems to be converted efficiently on the humid reactor walls. Surprisingly, the lost NO_3 was recovered as HNO_3 in the gas phase!**
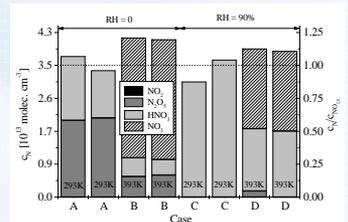
Fig. 5: Gas phase composition measured by UV-VIS and FT-IR spectroscopy.
Case A: RH = 0; T_{heater} = 293 K
Case B: RH = 0; T_{heater} = 393 K
Case B: RH = 90%; T_{heater} = 293 K
Case B: RH = 90%; T_{heater} = 393 K

Uptake on NaCl solutions

After uptake on solutions of NaCl, the NO_3 radical reacts with chloride to form the NO_3^- ion.
This was used to quantify the uptake of NO_3. Fig. 6 shows the resulting uptake coefficients γ_{meas} depending on the chloride activity a_{Cl^-}. Extrapolating γ_{meas} to $1/a_{Cl}^{-0.5} = 0$ (corresponding to an infinitely fast liquid phase reaction) and correcting for the limiting effect of gas phase diffusion yields a value for α_{NO_3}:

$$\alpha_{NO_3} = (4.2^{+2.2}_{-1.7}) \cdot 10^{-3}$$

This is consistent with the ARS measurements.

Fig. 6: Uptake of NO_3 on NaCl solutions, plot of $1/\gamma_{meas}$ versus $a_{Cl}^{-0.5}$.

Literature

Finlayson-Pitts, B.J., Pitts, J.N.Jr. (2000). *Chemistry of the Upper and Lower Atmosphere*. New York, Academic Press
Schütze, M., & Herrmann, H. (2002). Determination of phase transfer parameters for the uptake of HNO_3, N_2O_5 and O_3 on single aqueous drops, *Phys. Chem. Chem Phys.*, 4, 60-67.

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