

DETERMINATION OF PHASE TRANSFER PARAMETERS OF THE ATMOSPHERIC TRACE GASES NITRIC ACID, OZONE, AND DINITROGENPENTOXIDE AT LIQUID SURFACES

M. SCHÜTZE, T. BERNDT and H. HERRMANN

Institut für Troposphärenforschung, Permoserstr. 15, 04303 Leipzig, Germany

Keywords: UPTAKE, NITRIC ACID, DINITROGEN PENTOXIDE, OZONE.

INTRODUCTION

Phase transfer of radicals and trace gases into aqueous tropospheric particles, i.e. the droplets of fog, clouds and rain as well as the aqueous aerosol may significantly alter the respective gas phase budget and hence the oxidation capacity of the troposphere. A new experiment for the experimental determination of uptake (γ) and mass accommodation (α) coefficients has been developed and applied.

EXPERIMENTAL

In order to investigate heterogeneous processes at gas-liquid-interfaces, a new apparatus was developed which is a device for the generation and analysis of single drops inside a flow tube style gas phase reactor. It allows the exposure of the liquid drop to a gas flow containing a trace gas. The analysis of the liquid phase is done by means of optical absorption spectroscopy. For this purpose the light of a broad banded light source is lead to the drop using an optical fiber. After crossing it as an absorption pathway, the light is brought to a broad banded detector by means of a second fiber.

RESULTS

Using this apparatus, the phase transfer of several atmospherically relevant trace gases was investigated. The uptakes of nitric acid and dinitrogenpentoxide on pure water could be observed and quantified by the analysis of the formation of the nitrate ion absorption band at 302 nm (figure 1). For nitric acid uptake coefficients γ in the range of $2.2 \cdot 10^{-3}$ to $5.0 \cdot 10^{-3}$ dependent on the total system pressure were determined. The uptake of dinitrogenpentoxide could be observed with uptake coefficients from $3.7 \cdot 10^{-3}$ up to $9.1 \cdot 10^{-3}$.

The phase transfer of ozone is not observable directly because of the unfavorable relation between its absorption properties and solubility. Sodium iodide was added to the liquid phase as a scavenger for the ozone molecules in order to increase the reactivity in the liquid phase and, by this, make the investigation of the heterogeneous processes possible. From the increase of the absorbance of the triiodide ions which are formed in the oxidation of the iodide by the ozone taken up at the surface, the uptake coefficients on solutions with iodide concentrations between $2 \cdot 10^{-2}$ M and 4 M were determined to $\gamma = 7 \cdot 10^{-6} \dots 6.6 \cdot 10^{-3}$ depending on the concentration.

In order to correct these values for the influence of the gas phase diffusion, a computer program was employed which calculates the time course of the concentration profile of the trace gas in the gas phase during the passage of a spherical drop. By means of this program it is possible to simulate which uptake coefficient in an experiment results from the influence of the gas phase diffusion for a given limiting value without gas phase limitations.

The corrected uptake coefficients γ_{corr} are $(1.0 \pm 0.4) \cdot 10^{-2}$ and $(1.1^{+1.2}_{-0.6}) \cdot 10^{-2}$ for nitric acid and dinitrogenpentoxide, respectively. For these species have a very high solubility respectively reactivity towards water, these corrected uptake coefficients can be identified with the mass accommodation coefficients α for nitric acid and dinitrogenpentoxide, respectively. The value for nitric acid is a little bit lower than previous literature values (Van Doren et al., 1990) while the value for dinitrogenpentoxide agrees very well with measurement made by other authors (Schweitzer et al., 1998).

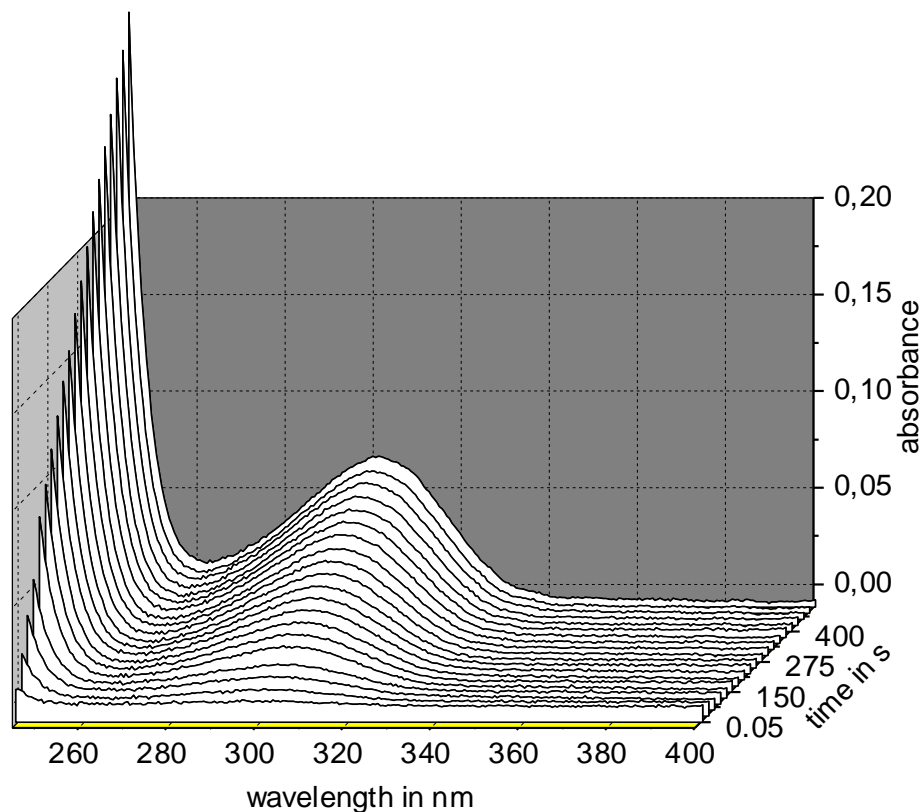


Figure 1. Time course of the absorbance of a drop being exposed to a gas phase containing nitric acid or dinitrogenpentoxide

The extrapolation of the concentration dependent uptake coefficients for ozone to an infinite iodide concentration and subsequent correction of this value for gas phase diffusion yield a lower limit for α of $4 \cdot 10^{-3}$ in agreement with literature values (Magi et al., 1997; Utter et al., 1992).

Another application of the new apparatus is the investigation of chemical kinetics in liquid phase. There are two different possibilities. Firstly, rate constants for the reaction of a species that is taken up from the gas phase and a second species present in the liquid phase can be determined if the uptake of the first species is governed by its reactivity towards the second one. This rate is obtained from the dependence of the corrected uptake coefficient for the first species on the concentration of the second reactant. The rate of the reaction of ozone with iodide was determined by this method to be $k = (2,5 \pm 0,5) \cdot 10^9 \text{ M}^{-2} \text{ s}^{-1}$ assuming a rate law with second order in the iodide concentration. Secondly, the ratio of reaction rate constants for a species that is taken up with two different reactants present in the liquid can be determined if the uptake rate is independent on the concentration of the two reactants, e.g. when the reactivity towards one of them is high enough to make the uptake independent on liquid phase processes. In this way, the ratios of the rates of the reactions of dinitrogenpentoxide with phenol and iodide to the rate of the water reaction were determined to be $4,9 \pm 0,7$ and 40 ± 4 , respectively.

REFERENCES

- Schweitzer, F., P. Mirabel and C. George (1998). Multiphase Chemistry of N_2O_5 , ClNO_2 , and BrNO_2 , *J. Phys. Chem. A* **102**, 3942.
- Van Doren, J.M., L.R. Watson, P. Davidovits, D.R. Worsnop, M.S. Zahniser and C.E. Kolb (1990). Temperature Dependence of the Uptake Coefficients of HNO_3 , HCl , and N_2O_5 by Water Droplets
- Magi, L., F. Schweitzer, C. Pallares, S. Cherif, P. Mirabel, and C. George (1997). Investigation of the Uptake Rate of Ozone and Methyl Hydroperoxide by Water Surfaces, *J. Phys. Chem.* **101**, 4943
- Utter, R.G., J.B. Burkholder, J.H. Carleton, and A.R. Ravishankara (1992). Measurement of the Mass Accommodation Coefficient of Ozone on Aqueous Surfaces, *J. Phys. Chem.* **96**, 4973