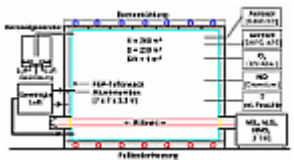
HECONOS



He terogeneous
Co nversion of
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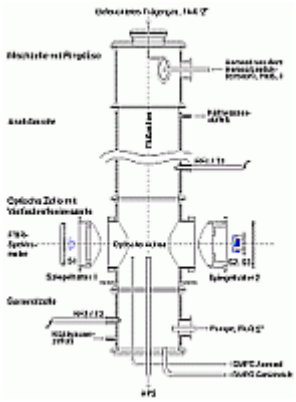

EU-Projekt: ENV4-CT97-0407

Research Area : R&D Environment and Climate

Principal Investigator

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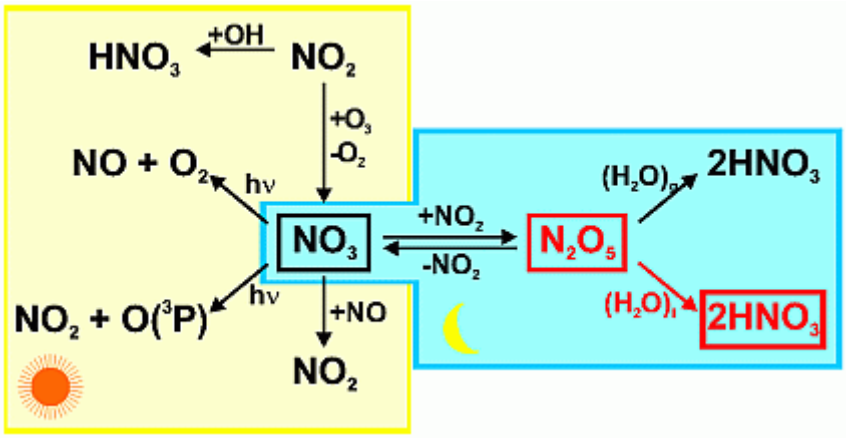
Introduction

Nitrogen oxides are of central importance for the chemistry of the atmosphere. They control the photochemical HOx-cycle and the chemical formation of tropospheric. It is thus important to quantitatively understand the atmospheric nitrogen oxide cycle. An important step in the removal of nitrogen oxides from the atmosphere is the heterogeneous conversion of N_2O_5 to HNO_3 during nighttime. In the continental tropospheric boundary layer this reaction is expected to occur on aqueous inorganic aerosols, but quantitative uptake and conversion rates are scarce and even less is known about the fate of the heterogeneous reaction products. However, a detailed description of the kinetics of the heterogeneous processes and the thermodynamic boundary conditions of product solubility is prerequisite for the implementation of heterogeneous processes in large atmospheric models.



Chemical removal paths for NOx from the atmosphere

The aim of the HECONOS project is to provide a complete mechanistic description of heterogeneous processes for nitrogen oxides on aqueous aerosols. This requires the investigation of heterogeneous

uptake on several aerosol substrates in a wide range of relative humidities and temperatures. The investigation are focussed on the heterogeneous hydrolysis of N_2O_5 on ammonium and sodium sulphates and nitrates, and sulphuric acid. The experimental approach relies on two complementary methods which cover different time scales and spatial scales. The dynamics of the N_2O_5 hydrolysis is investigated in flow tube studies on short time scales which allows for a fast exploration of temperature and humidity regimes. The partitioning of the heterogeneous reaction product is studied in a large aerosol chamber with long contact times between trace gases and aerosol phase. The large spatial scale of the aerosol chamber allows for simultaneous characterization of the gas phase and the aerosol phase.

Scientific and Technical Goals of the Project

1. Development of experimental set-up and methodology:

- Optimising detection for gas-phase species and in-situ aerosol composition by IR spectroscopic methods: setting up an aerosol calibration tube for simultaneous FTIR absorption and size distribution measurements
- Development of a methodology for automated, quantitative on-line analysis of the aerosol composition in the chamber experiments at FZJ. Time resolution for sampling and chemical analysis less than 20 minutes
- Optimising the separation of gaseous HNO_3 and HONO from air samples by a denuder system to enable interference free sampling of aerosol nitrate and -nitrite in the aerosol chamber experiments at FZJ
- Setting up a flow tube for laboratory measurements of trace gas - aerosol interactions
- Setting up an aerosol generator and aerosol characterisation apparatus for flow tube studies

2. Experimental Studies and Model calculations:

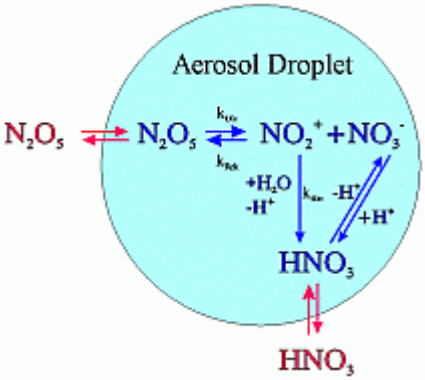
- Investigation of NO_2 and HONO uptake onto sulphuric acid aerosol
- Investigation of NO_2, N_2O_5 uptake onto aqueous sodium and ammonium salt aerosols in the aerosol chamber at room temperature
- Flow tube kinetic measurements with ammonium and sodium salt aerosol at different relative humidities and temperatures for N_2O_5 and
- Evaluation and modelling of flow tube experiments
- Evaluation and modelling of chamber experiments

Major Research Results

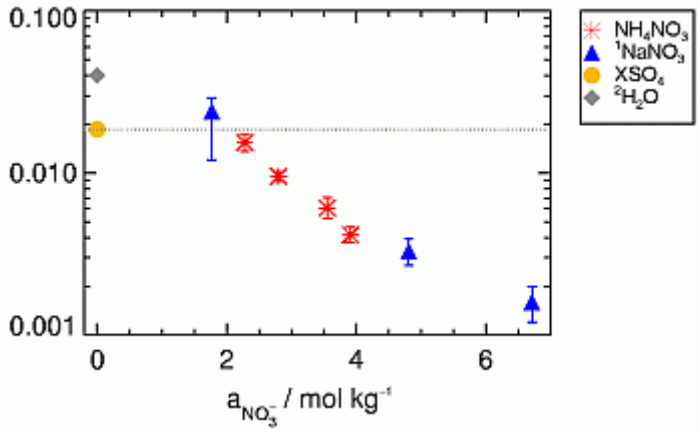
The reaction probabilities γ of N_2O_5 were determined for the following aerosol substrates as function of the relative humidity. The γ determined are of importance in different parts of the troposphere:

i. Na_2SO_4, $NaHSO_4$, and $NaNO_3$ at room temperature (marine and coastal boundary layer)
ii. H_2SO_4 as function of the temperature (marine and continental boundary layer, free troposphere)
iii. $(NH_4)_2SO_4$, NH_4HSO_4 as function of the temperature (rural boundary layer, lower parts of the free troposphere)
iv. NH_4NO_3 at room temperature (continental boundary layer, urban plumes)

The reaction probabilities for the sodium salts and ammonium nitrate were determined for the first time.
At room temperature the reaction probabilities for sulphuric acid and liquid sulphate aerosols are independent of the relative humidity. The heterogeneous hydrolysis of N_2O_5 occurs due to an ionic mechanism with the water independent dissociation of N_2O_5 into NO_2^+ and NO_3^- as rate limiting step. The γ on sulphuric acid (≈0.04) are on average twice that on sulphate aerosol (≈0.02). The uptake of N_2O_5 on sulphuric aerosols is mass accommodation limited.



In contrast to the sulphates systems, the reaction probability of N_2O_5 for nitrate salts decreases by one order of magnitude (γ= 0.02 → 0.002) with decreasing the relative humidity, or more precisely, with increasing nitrate activity in the aerosol droplets. This specific nitrate effect is due to the recombination reaction of the aerosol nitrate with the reactive intermediate NO_2^+, thus directly confirms the ion reaction mechanism. The nitrate effect will possibly become of future importance in urban areas and regions with increasing nitrate fraction in the secondary aerosol (Western Europe, US).



Neutral sulphates incorporate large amounts of HNO_3, up to 30% of the sulphate mass. Thermodynamic model calculations with a Pitzer ion interaction model reproduced the experimentally observed partitioning of HNO_3 quantitatively. The model predicts a shift of the sulphate/bisulphate equilibrium and condensation of water vapour during HNO_3 uptake. Both was verified by in situ low resolution FTIR spectroscopy of the aerosol phase. Increasing scattering extinction in the FTIR spectra indicates that the aerosols are growing on HNO_3 uptake. This could be also detected in the aerosol size distribution measurements. The change of chemical composition, dilution by condensation of water vapor, and particle growth on HNO_3 uptake will change the hygroscopical and optical properties of the chemically processed aerosols. This finding can be important for the direct and indirect radiative forcing induced by aerosols.

Moreover, it could be shown that simple hydrolysis of NO_2 (N_2O_4) or N_2O_3 on acidic, neutral, or alkaline aqueous aerosols cannot explain the amounts of HNO_2 observed in the night time boundary layer.

Publications

- **Folkers, M.**
  Bestimmung der Reaktionswahrscheinlichkeit von N_2O_5 an troposphärisch relevanten Aerosolen.
  Dissertation, Universität zu Köln, 2002

- **Th. F. Mentel, M. Sohn, A. Wahner**
  The Reaction Probability of Dinitrogen Pentoxide on Sodium Salt Aerosols Phys. Chem. Chem. Phys., 1, 5451-5447, 1999

- **M.Hallquist, D.J.Stewart, J. Baker and R.A.Cox**
  Hydrolysis of N_2O_5 on Sub-Micron Sulphuric Acid Aerosols
  J Phys.Chem., 104, 3984-3990, 2000.

- **J.Baker, S.F.M. Ashbourn and R.A.Cox**
  Heterogeneous Reactivity of Nitrous Acid on Sub-micron Sulphuric Acid Aerosol
  Physical Chemistry Chemical Physics , 1, 683-690, 1999.

Conference Contributions

American Geophysical Union Fall Meeting, 2001, San Francisco

- *The partitioning of Nitric Acid between the gas phase and condensed phase of aqueous sulfate aerosols* (poster)
  Th. F. Mentel, M. Folkers, H. Sebald, A. Wahner, H. M. ten Brink and P. A. C. Jongejan
- *Heterogeneous Hydrolysis of Dinitrogen Pentoxide on Aqueous Sulfate Aerosols: Influence of an Organic Coating on the Reaction Probability*
  M. Folkers, Th. F. Mentel, H. Sebald, A. Wahner, H. M. ten Brink, and P. A. C. Jongejan
- *New Flow Tube for in situ Measurements of Optical Spectra and Particle Size Distributions of Aqueous Aerosol Particles of Tropospheric Composition* Th. F. Mentel and H. Sebald
- *Reactive Uptake of Dinitrogen Pentoxide on Aqueous Ammonium Nitrate Aerosols: Dependence on the Nitrate Activity*
  M. Folkers, Th. F. Mentel, H. Sebald, A. Wahner, H. M. ten Brink, and P. A. C. Jongejan

European Aerosol Conference, 2001, Leipzig

- *Heterogeneous Hydrolysis of Dinitrogen Pentoxide on Aqueous Sulfate Aerosols: Dependence of the Reaction Probability on the Aging of the Aerosol Substrate* (Poster)
  M. Folkers, Th. F. Mentel, H. Sebald, A. Wahner, H. M. ten Brink, and P. A. C. Jongejan

European Geophysical Union, 2001, Nizza

- *Heterogeneous Hydrolysis of Dinitrogen Pentoxide on Aqueous Ammonium and Sodium Nitrate Dropets: Dependence of the Reaction Probability on the Nitrate Activity.*
  M. Folkers, Th. F. Mentel, H. Sebald, A. Wahner, H. M. ten Brink, P. A. C. Jongejan
- *Heterogeneous Hydrolysis of Dinitrogen Pentoxide on Aqueous Sulfate Aerosols: Depnedence of the reaction probability on the Aging of the Aerosol Substrate.*
  M. Folkers, Th. F. Mentel, H. Sebald, A. Wahner, H. M. ten Brink, P. A. C. Jongejan
- *Heterogeneous formation of Nitric Acid and its Partitioning between the Gas Phase and Condensed Phase of Aqueous Sulfate Aerosols*
  Th. F. Mentel, M. Folkers, H. Sebald, A. Wahner, H. M. ten Brink, P. A. C. Jongejan
- *FTIR-Spectroscopy of Aerosols*
  H. Sebald, Th. F. Mentel, A. Wahner

Surface Exchange Conference, 2000, Edinburgh

- *Heterogeneous conversion of dinitrogen pentoxide and partitioning of nitric acid in the presence of aqueous aerosols* (poster)
  Th. F. Mentel, M. Folkers, H. Opitz, A. Wahner, H. M. ten Brink, P. A. C. Jongejan

Bunsentagung 2000, Würzburg

- *Heterogeneous hydrolysis of dinitrogen pentoxide on aqueous ammonium nitrate and sulfate aerosol droplets: reaction probability of dinitrogen pentoxide* (poster)
  M. Folkers, Th. F. Mentel, H. Opitz, A. Wahner, H. M. ten Brink, P. A. C. Jongejan
- *Heterogeneous hydrolysis of dinitrogen pentoxide on aqueous sulfate aerosol droplets: partitioning of nitric acid between gas phase and condensed phase* (poster)
  Th. F. Mentel, M. Folkers, H. Opitz, A. Wahner, H. M. ten Brink, P. A. C. Jongejan

EGS-2000, Nice

- *Hydrolysis of N2O5 on electrolyte Aerosols* (poster)
  David J. Stewart *, Mattias Hallquist and R. Anthony Cox

FZ Karlsuhe, IMK, 2000

- *Heterogene Hydrolyse von N2O5 an wässrigen Aerosoloberflächen: Simultane Messungen in der Gasphase und in der Aerosolphase* (invited lecture)
  Th. F. Mentel, M. Folkers, H. Opitz, A. Wahner, H. M. ten Brink, P.A.C. Jongejan

The First Informal Conference on Reaction Kinetics
June 17 to 19, 2000, Helsingør, Denmark

- *Uptake of N2O5 on Sub-Micron Sulphuric Acid Aerosols - Temperature and Humidity Dependence* (poster)
  Mattias Hallquist, David J. Stewart, and R. Anthony Cox

2nd Gentner Symposium on Geoscience, 1999, Nazareth

- *Partitioning of nitric acid between the gas phase and the condensed phase of aerosols: experimental observations for aqueous sodium sulfate aerosols* (invited lecture)
  Th. F. Mentel, M. Folkers, H. Opitz, A. Wahner, H. ten Brink, P.A.C. Jongejan
- *Nitrate Effect in the heterogenoeus hydrolysis of dinitrogen pentoxide* (poster)
  A. Wahner, Th. F. Mentel

CMD in Aachen 1999

- *Uptake of N2O5 on Sub-Micron Sulphuric Acid Aerosols - Temperature and Humidity Dependence* (poster)
  Mattias Hallquist, David J. Stewart, and R. Anthony Cox

IGAC, 1999, Bologna

- *Nitrate effect in the heterogenoeus hydrolysis of N2O5* (poster)
  A. Wahner, Th. F. Mentel

Bunsentagung 1999, Dortmund

- *Nitrateffekt in der heterogenen Hydrolyse von N2O5 an wässrigen Aerosolen* (oral)
  Th. F. Mentel and A. Wahner

EGS-99, Den Haag

- *"Hydrolysis of N2O5 on Sub-Micron Sulphuric Acid Aerosols"* (oral)
  Mattias Hallquist*, David J. Stewart, Jacob Baker and R. Anthony Cox

CMD-Workshop in Karlsruhe 1998

- *Nitrate Effect in the Heterogeneous Hydrolysis of Dinitrogen Pentoxide* (oral)
  A. Wahner, Th. F. Mentel, M. Sohn
- *The Reaction Probability of Dinitrogen Pentoxide on Sodium Salt Aerosols* (poster)
  Th. F. Mentel, M. Sohn, A. Wahner
- *The Reaction of Nitrogen Oxide and Nitrogen Dioxide With Water* (poster)
  Th. F. Mentel, S. Nass, H. Opitz, A. Wahner