



## EC / EUROTRAC-2 Joint Workshop

*“ Shaping the Future of Atmospheric  
Chemistry Research in Europe ”*

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## **An Overview of EUROTRAC-2 - the Final Phase and Beyond (Guest).**

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EUROTRAC is the EUREKA project, studying the transport and transformation of environmentally relevant trace constituents in the troposphere over Europe. The second phase, EUROTRAC-2, started in 1996 and is scheduled to finish at the end of 2002. It involves the scientific work of well over 300 research groups from 30 European countries. The project is organised into 14 subprojects that have clearly formulated goals, coordinated within international and interdisciplinary linked networks of atmospheric research. The goal of EUROTRAC-2 is to provide high quality and relevant scientific results for national and international environmental policy development.

Research work within EUROTRAC-2 has contributed to studies of atmospheric composition change: processes, mechanisms and impacts. The range of the project combining laboratory studies, field measurements and atmospheric models has developed an unparalleled capability for understanding the complex interactions between the sources, transformations and depositions that control the concentrations of trace substances and thus determine their environmental impact.

The process of "Synthesis and Integration" of the results of EUROTRAC-2 is underway and is needed to bring the project to a successful conclusion. The following cross-cutting themes, including both scientific and policy-relevant questions, have been identified:

1. Fluxes of air pollutants at the surface in Europe,
2. Air quality in cities: urban and local issues,
3. Photochemical ozone and its control,
4. Global and regional ozone budget,
5. Tropospheric aerosols and clouds.

The results of EUROTRAC-2 will be presented in its Synthesis and Integration report, a Final Report of the project as a whole as well as a series of reports from the individual subprojects and will culminate in a Final Event in early 2003. Results from basic and applied research are expected to be integrated and prepared for implementation by European policy makers on European, regional and urban scales.

The EUROTRAC community is positioning itself for the future, hoping to take advantage of the new instruments available under the EC 6<sup>th</sup> Framework Programme but also not losing sight of the value of the EUREKA umbrella which has acted as a fore-runner of the new European Research Area in combining national and international funding. Plans for the future will be discussed.

## The Atmospheric Fate of Isopropyl Methyl Ketone (EC-MOST).

A contribution to EC-MOST project (EVK2-CT-2001-00114)

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Methyl isopropyl ketone (MIPK,  $(\text{CH}_3)_2\text{CHC}(\text{O})\text{CH}_3$ ) is a raw material for a number of organic synthesis, it is primary used in the manufacture of dyes, herbicides and pharmaceuticals, therefore it can escape to the atmosphere through evaporation where it can play a role in the photochemical processes. MIPK is also an intermediate product of the atmospheric degradation of other volatile organic compounds. Similarly to other ketones, the atmospheric fate of MIPK in the gas phase is controlled mainly by reaction with OH radicals and photolysis. Up to now a limited number of data are available on these two processes. Therefore, we have conducted a kinetic and mechanistic study on the OH-initiated oxidation of MIPK using two different photoreactors, 200 L Teflon bag irradiated by lamps at LCSR-Orléans and the EUPHORE facility. In addition, we have determined its UV-Visible spectra and studied its photolysis under sunlight conditions at EUPHORE. The obtained data will be presented and discussed.

## **Mechanistic Details of Aromatic Photooxidation derived from the Characterization of Secondary Aerosol Formation (EC-OSOA, Talk).**

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This work presents recent studies on secondary aerosol formation during the photooxidation of toluene in smog chamber experiments under realistic conditions. Experiments were performed in the EUPHORE environmental chamber (Spain) with the objective of investigating the reaction channels responsible for aerosol formation during toluene oxidation and the parameters that may control the total amount of aerosols formed in the aromatic system. Thus, aerosol yields were calculated and the values of the toluene threshold for aerosol formation were analysed for experiments in different toluene/NO<sub>x</sub> regimes together with the gas-phase concentrations of primary oxidation products.

Toluene produces SOA in the presence and in the absence of NO<sub>x</sub> and its aerosol-forming capacity depends significantly on the initial NO and NO<sub>2</sub> content in the system. This could mean that different chemical mechanistic channels are responsible for the particle formation. Under near NO<sub>x</sub>-free conditions the oxidation of toluene reported less concentration of ring fragmentation products, such as methylglyoxal and CO, than under high concentrations of NO<sub>x</sub>. The formation of condensable material, which has been observed in experiments performed under these conditions (NO<sub>x</sub> concentrations < 1ppb), is supposed to be due to the subsequent reactions of ring retaining products (cresols) with the OH radical. When there is initial NO in the system no particle formation is observed indicating that the contribution from the NO<sub>x</sub>-free aerosol-forming channel is significantly reduced at this stage of the oxidation; otherwise, the formation of aerosols should be seen. Moreover, the NO present during the first stage of a classical smog experiment limits the NO<sub>3</sub> radical concentration in the system; thus, the products resulting from reactions with this radical are not produced. Only when the NO is consumed is the particle formation observed, coinciding with the rise in NO<sub>3</sub> concentrations and the formation of nitrocresols. This suggests that the first particles observed in a classical smog chamber experiment with toluene arise from reactions of ring-retaining products such as nitrocresols with OH radicals or ozone. Reactions of NO<sub>3</sub> radicals alone with nitrocresols do not produce condensable products as could be determined in independent experiments performed with o-cresol.

The experimental results obtained by performing photosmog experiments in the atmospheric simulation chamber EUPHORE provide evidence that the presence of initial NO in the aromatic system changes the mechanism favouring the ring fragmentation channel. This circumstance has strong influence on how aerosols are formed during the atmospheric degradation of aromatic compounds.



## A PLP-RF Kinetic Study of the Atmospheric Reactivity of Propene and a Series of 3-Halopropenes with Cl Atoms (GPP9, Talk).

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Chlorine atoms in the troposphere may play a more important role in the oxidation of volatile organic compounds (VOCs) and in the production of ozone than previously thought. These Cl atoms, in polluted coastal regions, may initiate organic oxidation in a manner analogous to that of OH radicals, which is believed to be the dominant loss process of most organic compounds (Finlayson-Pitts, 1993). Hence, measuring accurately the rate coefficients of the reactions involving Cl atoms is very important in order to assess the role of these reactions in atmospheric chemistry at global or regional scales.

In this work we have measured the absolute rate coefficients for the reactions of Cl atoms with propene and a series of 3-halopropenes, at room temperature ( $298 \pm 2$ ) K using a newly constructed laser photolysis-resonance fluorescence (PLP-RF) system. Chlorine atoms were produced in an excess of reagent (propene and 3-halopropenes) and He bath gas, by pulsed 308-nm photolysis of  $\text{Cl}_2$  (*ca.*  $10^{14}$  molecule  $\text{cm}^{-3}$ ) using a XeCl excimer laser and detected by time resolved vacuum UV resonance fluorescence near 134 nm. The time resolved fluorescence signal was first input into a fast preamplifier and then collected with a multichannel scaler and stored in a coupled microcomputer for subsequent kinetic analysis. In order to check this new system, the reaction of Cl with isoprene was also investigated and compared with recent previous results [Notario *et al.*, 1997], being the rate constant determined in excellent agreement in both studies.

The rate coefficients obtained (in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) are: propene  $(1.40 \pm 0.12) \times 10^{-10}$ , 3-fluoropropene  $(3.06 \pm 0.12) \times 10^{-11}$ , 3-chloropropene  $(7.47 \pm 0.76) \times 10^{-11}$ , 3-bromopropene  $(1.23 \pm 0.10) \times 10^{-10}$  and 3-iodopropene  $(1.29 \pm 0.10) \times 10^{-10}$ . These values did not show any significant pressure dependence over the range studied (20-200 Torr).

As far as we know, this work provides the first measurements for the reactions of Cl with the above mentioned series of 3-halopropenes, and also the first absolute determination of the rate constant value for the reaction of Cl + propene at high pressures. The influence of the different halogen atoms substituents on the reactivity of these alkenes with Cl atoms, as well as the atmospheric implications of these measurements, are studied and discussed for the first time in this work. These results are also compared with previous studies carried out in our laboratory on the reactivity of these compounds with  $\text{NO}_3$  radicals [Martínez *et al.*, 1996].

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## Low Pressure Kinetic Study of the BrO Reaction with Methaethiol (GPP9).

Alfonso Aranda, Yolanda Diaz-de-Mera, Diana Rodríguez, Sagrario Salgado and Ernesto Martínez

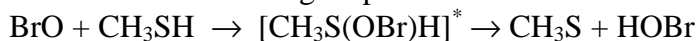
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Text headings: Methyl mercaptan, BrO, troposphere, atmospheric oxidation.

Methyl mercaptan (CH<sub>3</sub>SH) is among the major trace reduced sulfur compounds emitted into the atmosphere. Natural biogenic emissions are the primary sources for this reduced compound [Atkinson et al., 1997]. The primary agents responsible for the gas phase oxidation of CH<sub>3</sub>SH in the troposphere are OH radicals ( $k_{298K} = 3.27 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [3]) and NO<sub>3</sub> radicals ( $k = 8.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) [Urbanski et al., 1999]. Under specific conditions, like in the marine boundary layer, initiation by different halogen compounds may also be important.

Several reactions of CH<sub>3</sub>SH with halogen compounds have been studied. For the reactions with F, Cl and Br, the obtained values for the rate constant at 298K are  $2.4 \times 10^{-10}$ ,  $1.97 \times 10^{-10}$  and  $2.53 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. Halogen oxides in tropospheric air have been measured with the DOAS technique. For BrO, levels range from 5 to  $60 \times 10^8 \text{ molecule cm}^{-3}$  [Hausmann and Platt, 1994] showing that their reaction towards methyl mercaptan ought to be measured in order to evaluate the potential contribution to the removal of CH<sub>3</sub>SH. So, in this work we report the first absolute kinetic study of the reaction BrO + CH<sub>3</sub>SH → Products, its temperature and pressure dependences, the observation of the products of reaction with the possible mechanism and its atmospheric implication.

The kinetic experiments were carried out using the discharge flow-mass spectrometry technique (DF-MS) over the temperature range 259-333 K and at low total pressure between 0.5 and 3 Torr. BrO radicals were generated inside a movable injector by reaction of bromine atoms with ozone before being introduced into the main reactor:  $\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$   $k_2 = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with  $[\text{O}_3] \gg [\text{Br}]$  to ensure complete consumption of the Br atoms. All the experimental kinetics were carried out under pseudo first-order conditions with CH<sub>3</sub>SH in great excess over BrO with a ratio  $[\text{CH}_3\text{SH}]/[\text{BrO}]$  from 200 to 2000. The kinetic rate constants obtained may be fitted as an Arrhenius expression,  $k = (2.2 \pm 1.9) \times 10^{-15} \exp[(827.87 \pm 254.78)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , with  $k = (3.21 \pm 0.15) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298K. The reaction has been found to be pressure dependent in the pressure range studied. The relative low value of the pre-exponential factor, the negative temperature dependence observed for  $k_1$ , and the increase of this constant with higher pressures clearly suggest the formation of an association complex which can then decompose either back to reactants or to give products



The studied BrO-CH<sub>3</sub>SH reaction should be considered as a potentially efficient atmospheric sink for this reduced sulphur compound. Due to the lack of agreement concerning XO concentrations in the troposphere, the quantification of its contribution is not clear yet.

### References:

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## FT-IR Product Investigations of the OH Initiated Oxidation of Dimethyl Sulphide at Sub-Zero Temperatures (GPP Guest).

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Dimethyl sulphide (CH<sub>3</sub>SCH<sub>3</sub>: DMS) represents one of the most important reduced sulphur compounds emitted by the marine biota to the atmosphere. Chemical transformations of DMS due to its reactions with OH radicals during the day and NO<sub>3</sub> radicals during the night lead to the formation of sulphur containing species, both inorganic and organic in nature, which may significantly contribute to the acidity of the atmosphere. The CCN forming potential of DMS oxidation products make it an important climate modulating species. The products of the reaction of OH radicals with DMS have been extensively studied around room temperature but no studies exist at lower temperatures. In the present work new product investigations of the OH+DMS reaction have been performed in the temperature range 253 K to 273 K at different NO<sub>x</sub> concentrations. Experiments were carried out in a 336 L glass reactor equipped with a system for temperature regulation to within ±1 K from 223 K to 298 K. Dimethyl sulphoxide (CH<sub>3</sub>S(O)CH<sub>3</sub>: DMSO) has been identified as the major reaction product in the oxidative system. The molar formation yields of DMSO have been found to be very sensitive to changes in the initial NO concentration; increasing the NO concentration suppresses DMSO but increases DMSO<sub>2</sub> formation. This is interpreted in terms of an addition reaction between the DMS-OH adduct and O<sub>2</sub> further reaction with NO. The yields of DMSO at the various temperatures support and confirm the results of other studies that the importance of the addition channel increases with decreasing temperature. Formation of sulphur dioxide (SO<sub>2</sub>), dimethyl sulphone (CH<sub>3</sub>S(O)<sub>2</sub>CH<sub>3</sub>: DMSO<sub>2</sub>) and methane sulphonyl peroxy nitrate (CH<sub>3</sub>S(O)<sub>2</sub>OONO<sub>2</sub>: MSPN) in minor quantities has been also observed to occur. The possible atmospheric implications of the findings will be considered.

## FT-IR Investigations of the Gas-Phase Reactions of the NO<sub>3</sub> Radical with a Series of Benzenediol Compounds (GPP).

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The major sink of aromatic compounds in the daytime is their reaction with the OH radical, leading to numerous ring-retaining and ring-cleavage products [1]. In the case of benzene and toluene, which are the major aromatic compounds found in the troposphere, the addition of OH to the aromatic ring is known to produce phenol and cresol isomers, with yields of the order of 20% [2]. The further oxidation of these mono-hydroxylated aromatic compounds is now known to lead to the formation of benzenediols in high yield, about 80% [3], thus rendering them important ring-retaining products in the oxidation of benzene and toluene. Apart for rate constants for the reaction of OH radicals with these compounds [4], nothing is presently known about the atmospheric chemistry of 1,2-benzenediols.

In order to improve our knowledge on the atmospheric chemistry of 1,2-benzenediols we have investigated the kinetics of the reaction of NO<sub>3</sub> radicals with three benzenediols using a relative kinetic technique: 1,2-benzenediol, 3-methyl-1,2-benzenediol and 4-methyl-1,2-benzenediol. Experiments were carried out in two chamber systems with *in situ* FT-IR detection of reactants: a 1080 l quartz glass reactor at Wuppertal University and in the EUPHORE outdoor smog chamber facility in Valencia/Spain. The NO<sub>3</sub> radicals were generated by thermal decomposition of N<sub>2</sub>O<sub>5</sub> and good agreement was found between the rate constants measured in each of the chambers with preliminary rate coefficients of  $(9.4 \pm 3.3)$ ,  $(19.5 \pm 6.8)$  and  $(21.7 \pm 8.0) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  for benzenediol, 3-methyl-1,2-benzenediol and 4-methyl-1,2-benzenediol, respectively, at atmospheric pressure and  $298 \pm 2 \text{ K}$ . Using the kinetic data in combination with an average tropospheric nitrate concentration of  $[\text{NO}_3] = 5.4 \times 10^8 \text{ cm}^{-3}$  [5], leads to very short atmospheric lifetimes ranging from 20 to 8.5 s for these compounds.

This study represents the first determination of NO<sub>3</sub> radical reaction rate coefficients for these compounds. Preliminary results on the products from the reactions of OH and NO<sub>3</sub> with the benzenediols will also be presented.

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## **Tropospheric multiphase reactivity of organic hydroperoxides (GPP).**

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Organic hydroperoxides are major oxidation products of VOCs at very low level of NO<sub>x</sub> in the gas phase. Moreover, they also may be found in aqueous phase since they are highly soluble and they can also be formed in aqueous phase by peroxy-radicals recombination. In addition, they are compounds very reactive. Therefore, these compounds may play a significant role in multiphase tropospheric chemistry and are suspected to have a significant influence on photooxidant such as ozone.

The aim of this study is determine basic data on phase gaseous and aqueous reactivity in view, to assess the role of organic hydroperoxides in tropospheric chemistry.

We investigated the most abundant organic peroxide found in the atmosphere, the MethylHydroPeroxide (MHP) and EthylHydroperoxide (EHP). For each one of these products, their tropospheric fate is studied, as well from the kinetic or the mechanistic point of view, in the two phases where they are present (the gaseous phase and the aqueous phase) and the whole processes in which they are implied (photolysis and oxidation by radical OH).

-Gaseous phase photolysis and OH-oxidation of organic hydroperoxides were investigated in atmospheric simulation chamber. Analysis of reaction products were performed by IRTF. This study reveals that OH-oxidation is the major loss process and photolysis is of negligible importance. OH- oxidation leads mainly to the formation of formaldehyde for MHP and acetaldehyde for EHP.

-The study of aqueous phase fate of organic hydroperoxides was performed in a static photoreactor, equipped with continuous photolysis. Analysis of reaction products were performed by specific chromatographic methods (GC-FID, HPLC-UV, HPLC-fluorimetry and IC-conductimetry).

Aqueous phase OH-oxidation of MHP produce in majority formaldehyde and formique acid and in minority HydroxyMHP. For EHP the products are in majority acétaldehyde and acétic acide and in minority formaldehyde, formique acid and HydroxyEHP. The branching ratios of these products vary with pH. In addition, the reactivity with Fe<sup>II</sup> has been qualitatively investigated.

From these observations, OH-oxidation schemes of organic hydroperoxides in both phase were elucidated. These data will be used to improve the multiphase photochemistry approach controlling the oxidizing capacity of the atmosphere and in particular the ground level of ozone (impact of clouds on the tropospheric ozone budget).

# Reaction of 1-Methylvinoxy radicals with O<sub>2</sub>: Determination of the equilibrium constant (GPP).

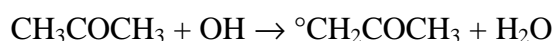
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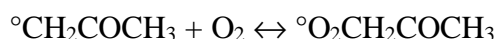
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1-Methylvinoxy radicals are the main product in the first step of the atmospheric degradation of acetone:



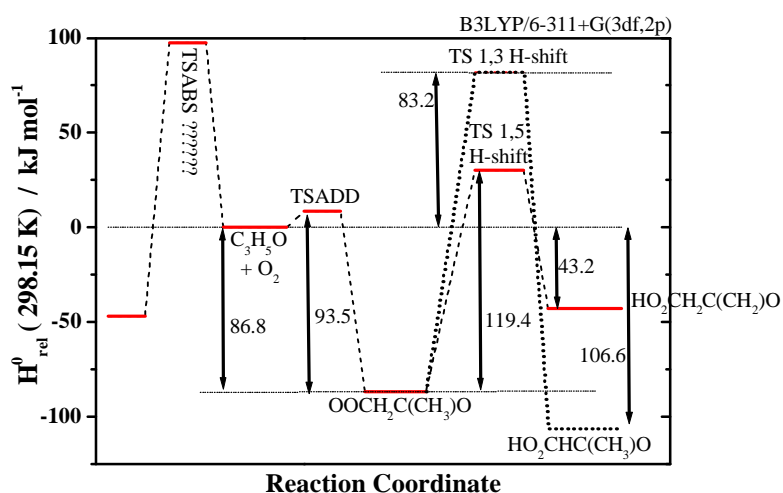
The subsequent fate of this radical under tropospheric conditions is mainly reaction with O<sub>2</sub>:



We have measured the rate constant for this reaction in a large range of pressure and temperature using a laser photolysis set-up, coupled to detection of the radical by laser induced fluorescence.

Biexponential decays, typical for equilibrium reactions, have been observed and the equilibrium constant has been determined in the temperature range 440 - 500 K.

No subsequent reaction of the peroxy radical has been observed. Ab-initio calculations have confirmed the high stability of this radical:



## Reactivity of thiophene and methylthiophenes in the atmosphere: Kinetics study of NO<sub>3</sub> reactions (GPP9).

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Thiophene is a five-member heterocycle ring containing sulphur that have been detected in ambient air emitted in processes of energy also a very large volumes of light hydrocarbons produced from coal carbonisation plants represent a considerable quantity of associated thiophenes. [SickelesII et al., EPA Publication, Cicciolo et al., 1986, Kirton et al., 1991]. The study of the atmospheric chemistry of thiophene and its methyl derivative compounds is important to understand the whole role of the sulphur compounds in the atmospheric global sulphur cycle.

The reactions of thiophene with the atmospheric oxidants OH radical and O<sub>3</sub> have been reported in different works[Atkinson,1989, Atkinson, 1994]. However the investigation about the reactivity of these compound with the NO<sub>3</sub> radical, is scarce. In this sense, we report the temperature kinetic study for the reactions of the nitrate radical with thiophene, 2-methylthiophene, 3-methylthiophene and 2,5-dimethyl-thiophene in a fast flow system by using LIF detection of the NO<sub>3</sub> radical, together with the relative study of this reactions at 298 K, using trans-2-butene as reference compounds. The rate coefficients obtained at 298 K are showed in the following table:

Compound	Absolute rate coefficient k/ 10 <sup>-13</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Relative rate coefficient k/ 10 <sup>-13</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
Thiophene	0.32 ±0.03	0.42 ±0.16
2-methylthiophene	9.98 ±1.70	9.90 ±2.20
3-methylthiophene	9.26±0.69	8.89 ±2.73
2,5-dimethylthiophene	27.5±1.0	23.60± 2.5

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## Features of the Potential Energy Surface for the Reaction of OH Radical with Acetone (GPP).

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Mechanism of the reaction of OH radical with acetone has been studied by quantum chemical computations. Stationary points (including reactant complexes, reaction transition states, intermediate complexes and product complexes) have been characterized on the potential energy surface of the reaction. The MP2 method with 6-31G<sup>\*\*</sup> basis set was employed for geometry optimization. Electronic energies were obtained at the CCSD(T) / 6-311G<sup>\*\*</sup> level of theory. Hydrogen abstraction was found to occur through complex mechanism; no transition state for direct abstraction could be located. Minimum energy path analyses have revealed two distinct pathways which lead to CH<sub>3</sub> (+CH<sub>3</sub>COOH) formation. One of them sets out the abstraction channel and proceeds via intermolecular complexes and the other one involves addition of OH to the carbonyl double bond and subsequent decomposition of the adduct hydroxy-alkoxy radical. The rate limiting steps involve large energy barriers and, consequently, these pathways do not explain the large methyl yields observed experimentally at and below room temperature. Characteristic for the reaction of OH with acetone is the existence of numerous hydrogen-bridged complexes on the potential energy surface that are stabilized by as much as 3.0 - 26.6 kJ mol<sup>-1</sup> binding energy. Some general features and the possible role of these complexes in the mechanism of the reaction are discussed.



## The UV-Visible Spectra and Atmospheric Photolysis of Aromatic Aldehydes (GPP).

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Aromatic aldehydes are emitted to the atmosphere as primary pollutants from motor vehicles and industrial uses, in addition they are produced *in situ* as intermediates in the photooxidation of other aromatic hydrocarbons. Similarly to other aromatic compounds, they may be major contributors to air pollution. In the atmosphere, the potential gas phase removal processes of aromatic aldehydes are photolysis and chemical reactions with OH and NO<sub>3</sub> radicals. These oxidation processes can play an important role in the chemistry of the polluted troposphere. Therefore, in order to quantify the contribution of these aromatic aldehydes to the photochemical reactions in urban and rural areas, it is necessary to know the relative importance of the above processes. In this respect, we have determined, with a high resolution the UV-visible spectra in the laboratory using two different systems and studied the photolysis of benzaldehyde, o-tolualdehyde, m-tolualdehyde and p-tolualdehyde at the EUPHORE facility. The obtained data will be presented and the importance of photolysis as loss process of these compounds compared to other gas phase loss processes in the atmosphere will be discussed.

## Competition Between Various Alkoxy Evolution Process in the Atmosphere (GPP).

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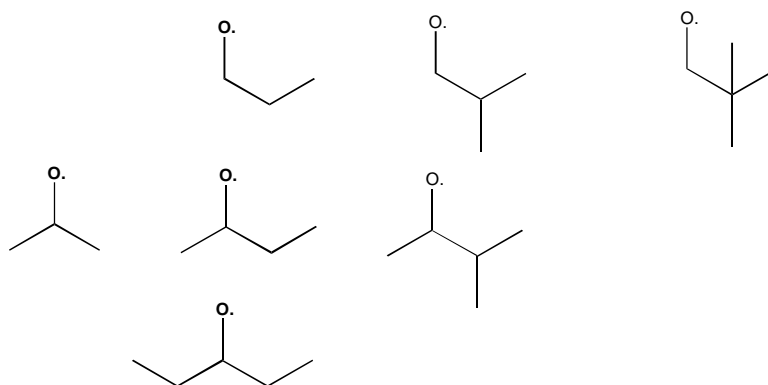
### Abstract.

Alkoxy radicals  $RO\cdot$  are key intermediates in the atmospheric photooxidation of volatile organic compounds, which is leading to the formation of ozone and other oxidation products baneful for environment. In this mechanism, the evolution of alkoxy radicals determines the nature and the concentration of the secondary compounds. These radicals can, depending on the nature of the alkyl group, undergo a  $\beta$ -C-C decomposition, a reaction with  $O_2$  and, for superior alkoxy, a 1-5-H shift isomerization by a 6-member cyclic transition state.

This work aims at studying the chemical evolution of several alkoxy radicals, to measure the ratio between each reaction way by quantification of products issue of each evolution process.

This experiment has been carried out in the evacuable simulation chamber of LISA. Alkoxy radicals has been generated by the photolysis near 420 nm of the corresponding alkyl nitrite. In order to detect minor process, the study was made at several partial pressures of  $O_2$  completed at 1 bar by  $N_2$ . Reactants and products has been detected "in situ" by long path FTIR.

We will present branching ratio  $k_{dec}/k_{O_2}$  for seven branched alkoxy radicals chosen to account the evolution with the structure of the ramification :



We account the influence of the substitution (primary or secondary) of the alkoxy and of the nature of the leaving alkyl group (ethyl, 2-propyl and 2-methyl-2-propyl).

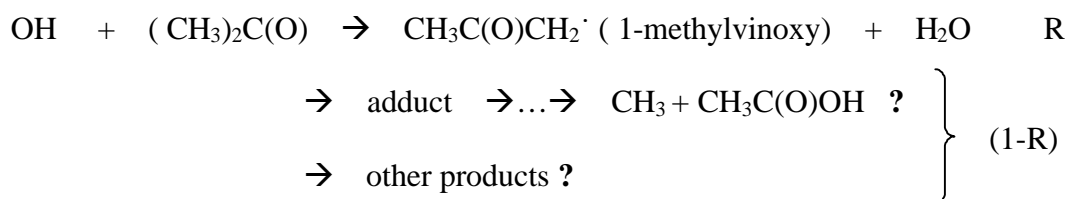
We also study 1-butoxy radical. We have had to synthesis the product of the isomerization, the 4-hydroxy-butanal by ozonolysis of 4-penten-1-ol in gaseous phase and obtain its IR spectrum. And so, we are able to determine the ratio  $k_{isom}/k_{O_2}$ .

## Reaction of OH + Acetone : direct time resolved determination of the branching ratio at room temperature (GPP).

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It has been found recently that acetone is among the most widespread oxygenated VOC in the UTLS (Upper Troposphere Lower Stratosphere). Loss of acetone occurs by both photolysis and reaction with OH; concerning the reaction constant of the latter pathway, all recent measurements have revealed an unusual temperature coefficient (with a broad minimum of the rate constant at room temperature); furthermore, a contradiction exists between two recent groups of measurements (using various techniques) concerning the branching ratio R for the different possible pathways:



Two measurements provide a value of  $R=(0.5 \pm 0.1)$  while the others find  $R \geq 0.95$ .

In view of the importance of accurately knowing the value of R (which significantly influences the mixing ratio of OH and HO<sub>2</sub> in the UTLS), we have performed new measurements using the fast flow technique coupled to a simultaneous detection of OH radicals (by Resonance Fluorescence) and 1-methylvinoxy (by Laser Induced Fluorescence). Our results are clearly in accord with the high value of R (but not exactly R=1). Preliminary results (work in progress) suppose a branching ratio of  $0.8 \leq R \leq 0.95$ .

## Kinetics and Mechanisms for the Oxidation of Oxygenated Organic Compounds (GPP).

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Oxygenated organic compounds are directly emitted into the atmosphere mainly from their use as solvents or as the combustion products of hydrocarbon fuels. For example, alcohols and ethers are used as solvents and fuel additives, and esters and ketones have major applications as solvents. Esters and alkoxy esters are also present in the atmosphere as a result of the tropospheric degradation of ethers and diethers respectively. Reaction with the OH radical is believed to be the major reaction pathway for the tropospheric loss of saturated oxygenated organics. The purpose of this work was to determine the kinetics and mechanisms for the OH radical initiated oxidations of a series of generic alcohols, ethers, ketones, esters and alkoxy esters with the aim of developing structure-activity relationships for their atmospheric degradation. Rate coefficients for the reactions of OH radicals with a series of generic oxygenates were determined using both a pulsed laser photolysis-laser induced fluorescence technique and a conventional photolytic relative rate method. Mechanistic studies on the OH radical initiated oxidation of oxygenates were carried out in laboratory reaction chambers and at the European Photoreactor in Spain.

Rate data obtained for the reaction of OH with alcohols and ethers show that these functional groups increase the rate of H-atom abstraction from the  $\beta$  and  $\gamma$  carbon atoms as well as at the  $\alpha$ -position. It is suggested that the enhancement of reactivity at sites remote from the ether and hydroxy functional groups is a consequence of the stabilisation of the transition state for H-atom abstraction by hydrogen bonding between the attacking OH radical and the oxygen atom of the functional group. In a similar manner, the expected reduction in the rate of hydrogen abstraction by the electrophilic OH radical from carbonyl compounds due to the electron withdrawing effect of the carbonyl group is counterbalanced by stabilisation of the reaction transition states by hydrogen bonding. Thus, carbonyl compounds show higher than expected reactivities. Product distribution studies show that the major products obtained from alcohols and ethers are aldehydes and esters respectively. Degradation of ketones leads to the eventual generation of formaldehyde, acetaldehyde and acetone, although the time scale of the complete oxidation depends strongly on the structure of the ketones. The major products arising from esters are acids and anhydrides. The results from the present study allow the rates and degradation pathways for a large range of oxygenates to be predicted with reasonable accuracy and hence their ozone formation potentials to be estimated.

## **Influence of Organic Aerosol Components on the Heterogeneous Hydrolysis of N<sub>2</sub>O<sub>5</sub> (GPP).**

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An important step in the removal of nitrogen oxides from the atmosphere is the heterogeneous conversion of N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub>. In the planetary boundary layer the hydrolysis occurs on the surface of aqueous aerosols. The heterogeneous N<sub>2</sub>O<sub>5</sub>-hydrolysis is well characterized for aqueous inorganic aerosols (e.g. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>HSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaHSO<sub>4</sub>, NaCl, H<sub>2</sub>SO<sub>4</sub> and pure water). In addition to inorganic components, tropospheric aerosols contain a complex mixture of organic compounds. Organic compounds typically constitute approximately 10 – 70% of the total dry fine particle mass in the atmosphere (Turpin et al., 2000).

These organic aerosol components modify the reactivity of mixed inorganic/organic aerosols. Furthermore, if they act as surfactant, organic components can form an organic coating over the surface of the particles. Such reductions of the surface reactivity or water availability should immediately influence heterogeneous hydrolysis reactions. Experiments in which aqueous inorganic aerosols were coated with the reaction products of  $\alpha$ -pinene demonstrated that organic aerosol components do indeed have a substantial influence on the heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub>. Depending on the thickness of the organic film the reaction probability  $\gamma$  (i.e. the fraction of collisions of N<sub>2</sub>O<sub>5</sub> molecules with the aerosol surface that lead to HNO<sub>3</sub> formation) was reduced by a factor of 2-30 compared to the reference value for purely inorganic aerosols. Within the scope of the CASOMIO project we will quantitatively characterize the effect of organic aerosol components on the reactivity of mixed aerosols. For this purpose we will determine the reactions probability for both mixed inorganic/organic as well as organically coated aerosols.

To further clarify the effect of an organic film on the N<sub>2</sub>O<sub>5</sub> hydrolysis we developed a FACSIMILE model in which we explicitly treat the uptake of N<sub>2</sub>O<sub>5</sub> by the particles. The model consists of a gas phase mechanism for the NO<sub>x</sub>/O<sub>3</sub>/NO<sub>y</sub> chemistry, experimentally determined chamber specific loss terms, chemical reactions in the particles, aqueous phase diffusion and N<sub>2</sub>O<sub>5</sub>/HNO<sub>3</sub> transfer at the gas/liquid interface. The results of the model calculations will be presented.

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## **Theoretical study of the mechanism of the oxidation of benzene in the troposphere. Pathways regenerating OH (GPP).**

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The presence of aromatic compounds in the troposphere is strongly associated with the urban environment and the emission of volatile organic compounds as a result of anthropogenic activity. It has been estimated that their oxidation reactions may be responsible for 30% or so of photochemically produced tropospheric ozone. However, complete degradation mechanisms for aromatic species are still uncertain. In particular, the amount of OH predicted by the kinetic models is lower than observed experimentally.

The first step of the oxidation of benzene is known to be the addition of OH onto the ring to form the hydroxycyclohexadienyl radical ( $C_6H_6-OH$ ). This radical reacts with  $O_2$  to form "democratically" either the peroxy radical adduct or the phenol and  $HO_2$ . We have investigated several chemical transformations of the peroxy radical adduct which can favour the regeneration of OH radicals. To gain insight into the mechanism of these subsequent reactions, quantum chemistry calculations have been performed.

## Generalised Structure-Activity Relationships for the Decomposition and Isomerisation of (Substituted) Alkoxy Radicals. Theory-based Validation (GPP, Talk).

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In general, oxy radicals may undergo  $\beta$  C-C decompositions, 1,5-H migrations, and can react with  $O_2$ . In order to be able to predict, for any VOC, the oxidation routes and the final products of reaction, it is useful to have generalised Structure-Activity Relationships (SARs) for the above mentioned reactions. There are a few available SARs regarding alkoxy radical decomposition (Atkinson, 1997; Méreau et al., 2000; Somnitz and Zellner, 2000), but many are difficult to use as they require the knowledge of reaction enthalpies and/or ionisation potentials. Our aim was to construct a generalised SAR for alkoxy decomposition which expresses the energy barrier  $E_b$  solely in terms of the nature and the number of the (alkyl, oxo or hydroxy-)substituents on the  $\alpha$ - and  $\beta$ -carbon atoms. Our SAR is based on available absolute experimental and quantum chemical  $E_b$  data (Devolder et al., 1999; Méreau et al., 2000; among many others) and on own DFT calculations. Thus, inspired in part by earlier SARs, we developed the following generalised and readily applicable SAR for the barrier height  $E_b$  to  $\beta$  C-C fission in a substituted oxy radical:

$$E_b(\text{kcal/mol}) = 17.5 - 2.1 \times N_\alpha(\text{alk}) - 3.1 \times N_\beta(\text{alk}) - 8.0 \times N_{\alpha,\beta}(\text{OH}) - 8.0 \times N_\beta(\text{O=}) - 12 \times N_\alpha(\text{O=}) \quad (1)$$

where  $N_\alpha(\text{alk})$  is the number of alkyl substituents on the  $\alpha$ -carbon,  $N_\beta(\text{alk})$  the number of alkyl substituents on the  $\beta$ -carbon,  $N_{\alpha,\beta}(\text{OH})$  the number of OH substituents on the  $\alpha$ - and  $\beta$ -carbons together (with a maximum of 1 on either carbon),  $N_\beta(\text{O=})$  the number of oxo functions (0 or 1) on the  $\beta$ -carbon, and  $N_\alpha(\text{O=})$  the number of oxo functions (0 or 1) on the  $\alpha$ -carbon. The standard deviation from the available data is 0.5 to 1 kcal/mol.

Because of tunneling contributions and other effects, a SAR for 1,5-H shifts is best expressed in terms of Arrhenius parameters for 1 atm and 298 K. We developed the following SAR for the activation energy  $E_A$  of strain-free 1,5-H shifts from an alkane-, alcohol-, or aldehyde C:

$$E_A(1,5\text{-H})(\text{kcal/mol}) = 8.4 - 0.65 \times (99 \text{ kcal/mol} - D_{\text{C-H}}) \quad (2)$$

where 99 kcal/mol is the bond dissociation energy (0 K) of a primary alkane H, and  $D_{\text{C-H}}$  is the bond dissociation energy (0 K) of the migrating H. This SAR was derived in part from the recommended data for 1,5-H shifts in non-cyclic alkoxy radicals (Atkinson, 1997). The expected error is *ca.* 0.5 to 1 kcal/mol.

Validation of the DFT method used by us for quantifying the energetics of these specific reactions will be presented, based mainly on the agreement of the theoretical TST rate coefficients derived therefrom with experimental data.

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## **Ozonolysis of alkenes: Influence of the Structure of the Criegee Intermediate on Carbonic Acid and Particle Formation (GPP).**

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Secondary organic aerosol (SOA) is formed in the troposphere by ozonolysis of biogenic VOC. It influences the properties of global aerosol and therefore has an impact on the Earth's radiation budget as well. The gas phase processes however, which follow the ozonolysis reaction and lead to the formation of the nucleating compounds are so far poorly understood. Therefore, SOA formation during gas-phase ozonolysis has been studied in laboratory investigations on biogenic terpenes and also on simple alkenes as model compounds. A wide range of different primary or secondary products of gas-phase ozonolysis has so far been suggested as potential precursor of nucleation, such as secondary ozonides, dicarboxylic acids and their dimers, and peroxy compounds, such as peroxyhemiacetals or diacylperoxides.

In this work, formation of SOA and of certain classes of reaction products, such as carboxylic acids, is studied for various biogenic terpenes and simple linear and cyclic alkenes, in order to investigate the influences of their structural features. The combined information about the minimal concentrations necessary for nucleation, the nucleation thresholds, and the gas to particle partitioning of reaction products, such as carboxylic acids allows to draw conclusion on the likelihood of potential particle precursors to be formed in the gas phase and to have a sufficiently low vapour pressure for nucleation.

Experiments have been carried out in a flow reactor of 1 m lengths in order to observe SOA formation during the first minute of the reaction, and in a 570 l spherical glass reactor in order to study nucleation or product formation dependent on the reaction time longer than 1 min. Particle size distributions are measured with a scanning mobility particle analyser (SMPS, Model 3936, TSI Inc.), product formation is analysed by ion chromatography or LC-MS-MS.

Threshold concentrations between pure gas phase chemistry and beginning particle formation have been approached in the flow reactor by varying alkene concentrations at constant ozone concentrations and reaction times. The influence of other experimental conditions, such as relative humidity, on SOA and product formation, might as well provide information about gas phase reaction mechanisms and potential SOA formation precursors.



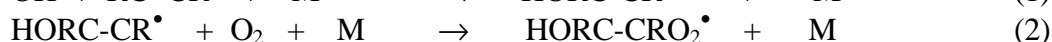
## Chemical Activation in Tropospheric OH-Oxidation of 1-n-alkenes (GPP).

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The mechanism of oxidation of alkenes (general formula RC=CR), mainly initiated by OH-radical addition to the double bond, gives rise to  $\beta$ -hydroxy-alkoxy radicals HOCR-CRO $\cdot$ :



A large part of the energy available from the exothermic reaction (3),  $\text{RO}_2 + \text{NO} \rightarrow [\text{ROONO}]^* \rightarrow \text{RO} + \text{NO}_2$ , is deposited on the nascent alkoxy radical, and a fraction of this radical is formed with sufficient energy to decompose "promptly". Such a process was extensively studied for the case of  $\beta$ -hydroxy-ethoxy and -2-propoxy radicals [Vereecken et al., 1999]. However, the importance of chemical activation in the atmospheric chemistry of larger alkenes and in unimolecular reactions of resulting hydroxy-alkoxy radicals is unknown.

The fraction of chemically activated  $\beta$ -hydroxy-1-alkoxy radicals formed by the OH-radical oxidation of a series of 1-n-alkenes from 1-butene to 1-hexene was evaluated using a four-step procedure based on RRKM-Master Equation analysis and Phase Space Theory. For evaluating the impact of such a chemical activation in tropospheric conditions, the thermal RRKM fall-off behaviour of these alkoxy radicals was calculated.

From these calculations it was concluded: 1) the fraction of  $\text{ROONO}^*$  peroxy nitrile decomposing before thermalisation decreases with increasing the chain-length of this species. However, at 298 K and 1 atm, still 45 % of  $\text{C}_6$  chain-length peroxy nitrile decompose before thermalisation. 2) in the same pressure and temperature conditions, the fraction of hydroxy-alkoxy radicals which undergoes "prompt" reactions decreases from 75 % for  $\text{C}_3$ -radical to 30 % for  $\text{C}_6$ -radical. The hydroxy-ethoxy with higher dissociation barrier height only presents 30 % of prompt dissociation. 3) tropospheric impact is important for this last radical: at the upper troposphere temperature, (220 K), chemically activated radical is predicted to undergo 25 % of dissociation (75 % reaction with  $\text{O}_2$ ), instead of 2.5 % for a thermalised radical. 4) For  $\geq \text{C}_3$  chain-length hydroxy-alkoxy radicals, the thermal dissociation rate constant, at 298 K and 1 atm, being two or three orders of magnitude higher than the pseudo-first order constant of the reaction with  $\text{O}_2$ , the impact of a chemical activation is negligible. At 220 K, owing to the activation energy for unimolecular reactions, the thermal rate constant is lowered and a chemical activation is predicted to produce an enhancement of these reactions.

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## Is the Acetylperoxy Radical $\text{CH}_3\text{C}(\text{O})\text{O}_2$ a Good Model for $\text{RC}(\text{O})\text{O}_2 + \text{HO}_2$ Reactions ? (GPP).

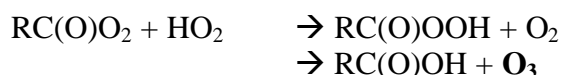
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In the atmosphere, acylperoxy radicals are formed by hydrogen abstraction from aldehydes and combination with  $\text{O}_2$ . Firstly, they may undergo fast reactions with other peroxy radicals and with nitrogen oxides which have a significant influence on ozone formation. Secondly, in polluted atmospheres, the association reaction with  $\text{NO}_2$  may form peroxyacylnitrates  $\text{RC}(\text{O})\text{O}_2\text{NO}_2$  which are recognized as severe irritants of photochemical smog. Moreover, due to their high stability in polluted atmosphere, compared to other peroxy nitrates, they are efficient reservoirs of  $\text{NO}_x$  in troposphere and they contribute to the transport of  $\text{NO}_x$  species far away from sources.

The objective of this study was to investigate the kinetics of  $\text{RC}(\text{O})\text{O}_2 + \text{HO}_2$  reactions as these reactions are important termination reactions as they may lead to the formation of ozone:



We first start to study the reaction of  $(\text{CH}_3)_3\text{CC}(\text{O})\text{O}_2 + \text{HO}_2$  to evaluate the effect of substitution of H atoms by methyl groups on the reactivity of the acetylperoxy radical  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  which is used to now as a model for all acylperoxy radicals in chemical models of the tropospheric chemistry.

Flash photolysis technique coupled to UV absorption spectrometry was used for real time radical monitoring in order to measure the branching ratio of the  $(\text{CH}_3)_3\text{CCHO} + \text{Cl}$  reaction, the rate constant of  $(\text{CH}_3)_3\text{CC}(\text{O})\text{O}_2 + \text{HO}_2$  reaction and the branching ratio leading to the formation of ozone.

The rate constant measured in this work ( $k = (4.62 \pm 0.52) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ) appears to be three times larger than that measured for the  $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$  reaction (Tomas *et al.*, 2001). It suggests that rate constants of  $\text{RC}(\text{O})\text{O}_2 + \text{HO}_2$  reactions are increasing with the acylperoxy radical substitution. The next step will be the study of isobutyraldehyde to check the trend observed in this work.

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# A kinetic and mechanistic study of the OH and NO<sub>2</sub> initiated oxidation of 2,4-hexadiene in the gas phase (GPP).

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Conjugated dienes play a significant role in the chemistry of the atmosphere. Isoprene (mainly emitted from biogenic sources), is believed to have the highest global emissions of all non-methane hydrocarbons (Guenther et al., 1995), and a number of conjugated dienes are emitted as highly reactive components of vehicle exhaust (e.g., Jemma et al., 1995). The dominant atmospheric sink for conjugated dienes tends to be reaction with the OH radical. However, the reactions with NO<sub>2</sub> have also received attention due to their possible role in thermal initiation of free radical catalysed NO-to-NO<sub>2</sub> conversion during urban winter pollution episodes (Shi and Harrison, 1997; Harrison et al., 1998; King et al., 2002). Whereas kinetic data are available for reactions of OH and NO<sub>2</sub> with a number of conjugated dienes (e.g. Atkinson, 1994; King et al., 2002), OH product studies appear to be limited to 1,3-butadiene and isoprene. There are no reported studies of the products of NO<sub>2</sub>-initiated oxidation, although Shi and Harrison (1997) have demonstrated that the chemistry involving 1,3-cyclohexadiene and 1-methyl-1,3-cyclopentadiene leads to oxidation of NO to NO<sub>2</sub>.

To extend the available database on the atmospheric chemistry of conjugated dienes, the reactions of OH and NO<sub>2</sub> with 2,4-hexadiene at 296(±2)K have been investigated using long-path FTIR spectroscopy. The rate constant for the reaction with OH was determined using the relative rate technique, yielding a value of  $1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The rate constant for the reaction with NO<sub>2</sub>, determined from the observed decay of 2,4-hexadiene under pseudo-first order conditions, was  $3.0 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The results are compared with existing kinetic data for these reactions (Atkinson, 1994; Ohta et al., 1986). Acetaldehyde (CH<sub>3</sub>CHO), crotonaldehyde (CH<sub>3</sub>CH=CHCHO) and 2,5-dimethylfuran were detected as products of the OH initiated oxidation, and probable mechanisms leading to the generation of these products are presented. In the presence of NO, the NO<sub>2</sub>-initiated oxidation leads to the partial generation of HOx radicals (probably in conjunction with nitrohexenone products), and the partial loss of radicals, most probably due to the formation of nitrohexenyl nitrates. In this system, therefore, 2,4-hexadiene is removed simultaneously by reaction with both NO<sub>2</sub> and OH. A detailed chemical mechanism has been developed which is able to explain the observed time dependence of 2,4-hexadiene, NO, NO<sub>2</sub> and of a number of oxidised products.

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## Isomerization of 1-Butoxy Radicals (GPP, Talk).

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Alkoxy radicals are important reactive intermediates in the atmospheric degradation of volatile organic compounds. In the atmosphere, they undergo either unimolecular transformation (decomposition/isomerization,  $k_{uni}$ ) or reaction with  $O_2$  ( $k_{O_2}$ ):

- (1a) thermal decomposition ( $k_{dis}$ ,  $\rightarrow$  aldehyde/ketone + alkyl/H)  
 (1b) isomerization ( $k_{iso}$ ,  $\rightarrow$  hydroxyaldehyde/hydroxyketone)  
 (2) reaction with  $O_2$  ( $k_{O_2}$ ,  $\rightarrow$  aldehyde/ketone +  $HO_2$ )

Depending on the branching ratio  $k_{uni}/(k_{O_2} \times [O_2])$ , different products are formed with different effects on atmospheric chemistry.

The 1-butoxy radical is a model compound for large alkoxy radicals where isomerization via a six-membered transition state is possible (e.g. Niki et al., 1981; Lendvay and Viscoltz, 1998). It has been suggested that 4-hydroxybutanal is a stable product of this isomerization; however, identification of 4-hydroxybutanal (Niki et al., 1981; Atkinson et al., 1996) was not very straightforward so far. In this work, evidence is presented from product IR spectra that 4-hydroxybutanal is indeed a product of the isomerization of 1-butoxy, and that comparable amounts of 2-hydroxytetrahydrofuran are also formed under laboratory conditions. At present, kinetic experiments are performed to examine if isomerization to cyclic compounds can be a general loss reaction of hydroxyaldehydes and hydroxyketones in the troposphere.

The experiments are performed in a 200 L photochemical reaction chamber from quartz. 1-butyl iodide is photolyzed at 254 nm in the presence of  $O_2$  and NO, and the yields of the products butanal, 4-hydroxybutanal and 2-hydroxytetrahydrofuran are measured. 2-hydroxy-tetrahydrofuran was synthesized by hydrolysis of dihydrofuran. The IR absorption coefficient of 4-hydroxybutanal was determined by mass balance in experiments at low partial pressures of oxygen. From the yields of butanal (channel 2) and 4-hydroxybutanal+2-hydroxytetrahydrofuran (channel 1b)), the ratio  $k_{iso}/k_{O_2}$  has been determined at room temperature. Experiments are under way to measure the temperature dependence of  $k_{iso}/k_{O_2}$ .

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## Nitrate Formation in the Reaction of 1-Nonylperoxy Radicals with NO (GPP).

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Alkylperoxy radicals are important intermediates in the atmospheric degradation of volatile organic compounds. Peroxy radicals mainly react with NO or other RO<sub>2</sub> radicals, depending of the air mass being NO<sub>x</sub> rich or not:



The ratio  $k_{1a}/k_{1b}$  has been investigated mainly by Atkinson and coworkers (Atkinson et al., 1982; Atkinson et al., 2001), showing that this ratio increases from close to zero for R = CH<sub>3</sub> to  $\geq 0.2$  for R = heptyl and larger. In the experiments of Atkinson, alkanes were reacted with OH radicals, and the mixture of isomeric nitrates formed in reaction (1b) was analyzed by GC-FID and GC-MS analysis.

In this work, the yield of 1-nonyl nitrate (channel 1b) has been measured by long-path IR absorption, and the branching ratio  $k_{1a}/k_{1b}$  was determined from this yield and the conversion of the precursor compound 1-nonyl iodide.

The experiments are performed in a temperature controlled 200 L photochemical reaction chamber from quartz. 1-nonyl iodide is photolyzed at 254 nm in the presence of O<sub>2</sub> and NO. The IR spectra of other products show hydroxy-, nitrate-, and carbonyl functions and can be assigned to 1-nonanal and the products following the isomerization of the 1-nonyloxy radical.

At 298 K,

$$k_{1a}/(k_{1a}+k_{1b}) = 0.25 \pm 0.02$$

has been derived, in good agreement with results of Atkinson et al. (2001) for R = 2-, 3- and 4-octyl.

Preliminary experiments at temperatures above and below room temperature show a systematic decrease of  $k_{1a}/(k_{1a}+k_{1b})$  with temperature; these investigations are being continued..

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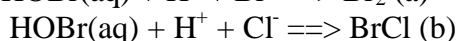
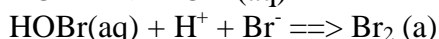
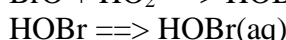
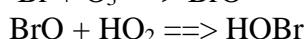
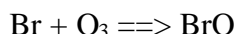
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## The Interaction between Sea-Salt Aerosol and Marine Gaseous Chemistry (HEP).

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Wolf-Ulrich Palm\* and Cornelius Zetzsch

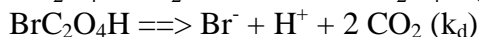
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Using an aerosol smog-chamber technique (teflon bags), the activation of Br<sup>-</sup> and Cl<sup>-</sup> to atomic Br and Cl in sea-spray aerosol was investigated in laboratory experiments. No activation was observed in the presence of O<sub>3</sub>, hydrocarbons and NaCl aerosol alone. By adding Br<sup>-</sup> to the aerosol, the chain reaction:



was verified. The step from reaction (a) to (b) is accompanied by a decrease of the Br<sup>-</sup>/Cl<sup>-</sup> ratio from 1/600 to less than 1/2000. In the absence of sulphate, the chain is initiated by the reaction of OH(aq) with Br<sup>-</sup>. The pH value decreases to 3.5 to 4 during the first minutes of the experiment (in the absence of NO<sub>x</sub> or SO<sub>2</sub>). This is caused by the formation of oxalic acid from alkanes and toluene. At this pH-value the uptake coefficient of HOBr was evaluated to be  $\gamma_{\text{HOBr}} = (3 \pm 1.5) \cdot 10^{-3}$ .

In stopped flow experiments, the reduction of Br<sub>2</sub> by oxalic acid was observed to occur through a two-step mechanism:



with the following rate constants and ratios of rate constants,  $k \pm 2\sigma$ :  $k_c k_d / k_c = (2.9 \pm 0.3) \cdot 10^{-4} \text{ s}^{-1}$ ,  $k_c / k_d = 7000 \pm \frac{13000}{3000} \text{ M}^{-1}$ ,  $k_c = 2 \pm \frac{4}{1} \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_d > 0.1 \text{ s}^{-1}$ ,  $k_c > 600 \text{ M}^{-1} \text{ s}^{-1}$ . Oxalic acid may be responsible for the inhibition of the chain reaction observed at the end of the experiments.

In separate wetted-wall flow tube experiments it was found that the formation of BrCl from the uptake of Br<sub>2</sub> on NaCl solution is independent of pH below pH values of 5, decreasing for higher pH values. After the initial injection of less than 1.4 ppb NO no effects on the production rate of atomic Cl and the Br explosion were observed. At higher injections the halogen activation increases significantly. Iodide is transformed to iodate very fast, and its effect on halogen activation is small in contrast to that of bromide.

Externally mixed metal oxide aerosols (model aerosols for outbursts of desert dust) are found to increase the production of atomic Cl from sea-spray. In those experiments halogenated products like bromoacetone, 1,1-dibromoacetone and phosgene were generated from the degradation of nonhalogenated alkanes and toluene.

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## Interaction of Trace Gas Species of Atmospheric Interest with Ice (HEP).

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Ice provides an important substrate for heterogeneous chemistry in the stratosphere, the upper troposphere, but also in the cold regions of the planetary boundary layer. We investigate the interaction of trace gas species of atmospheric interest with ice in the laboratory. Two experimental techniques are available to monitor compounds in the gas phase, the use of short-lived radioactive tracers (such as  $^{13}\text{N}$ ) to label the trace gas molecules at very low concentration (Ammann, 2001) and Atmospheric Pressure Chemical Ionisation Mass Spectrometry, APCI-MS, (Guimbaud et al., 2002).

Currently, we are evaluating the adsorption enthalpy of acetone on ice using a chromatographic technique similar to that applied by Bartels et al. (2002) to investigate the adsorption of nitrogen oxides on ice, combined with Proton Transfer Reaction Mass Spectrometry (PTR-MS) for the monitoring of acetone in the gas phase. Indeed, In the upper troposphere, and under dry conditions ( $\text{H}_2\text{O} < 100$  ppm), the photolysis of acetone becomes the main source of  $\text{HO}_x$  production dominating the one from the reaction of  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$  (Jaegle et al., 2001). Sources and mainly sinks of acetone need to be quantified in order to simulate properly the concentration of the main atmospheric oxidant ( $\text{HO}_x$ ). Ice cirrus clouds are suggested to be one of the acetone sinks. Some preliminary data will be presented and compared to other data obtained by our partners of the EC 5<sup>th</sup> FP project Cut-Ice.

Furthermore, ice cores represent the only direct paleo-atmospheric archives which allow to study the coupling of changes in atmospheric composition and climate and to assess the ongoing global change. However, interpretation of the archives relies significantly in the bi-directional physical transfer between air and snow and in photochemical reactions (involving heterogeneous processes as well) in the upper firn. Physical and chemical processes have an important influence on ice cores air composition on top of the ice and thus an impact on the understanding of paleo-atmospheric archives. Thus, future perspectives related to interactions of species of atmospheric interest with ice (and snow) will be discussed.

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## Mechanism leading to SOA-particle formation in the oxidation of biogenic alkenes (HEP, Talk).

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It is established that secondary organic aerosol (SOA) is formed during the reaction of ozone with biogenic alkenes. This laboratory study on the SOA particle size distribution tries to describe the mechanism for the homogeneous particle formation during the ozonolysis of terpenes. Therefore, experiments with an *endo*- as well as with an *exocyclic* monoterpene ( $\alpha$ - and  $\beta$ -pinene) and ozone have been performed with additional compounds such as water vapour, alcohols and carbonyl compounds, to examine the effect of the terpene structure on the nucleation mechanism.

Experiments were performed in a spherical glass vessel of 570 L volume at atmospheric pressure. The particle size distribution was measured by a scanning mobility particle sizer, including a long DMA and an ultra-fine particle counter, with a time resolution of two minutes. All reactions were conducted with an initial monoterpene concentration of 500 ppb and different concentrations of the added substances. In addition, cyclohexane was present during all experiments to prevent interfering reactions of the produced OH-radicals.

The results indicate that the homogeneous nucleation process during the ozonolysis of terpenes is controlled by the formation of large secondary ozonides and can be suppressed by the addition of water vapour. These nucleating secondary ozonides are formed differently in *endo*- and *exocyclic* reactions: *intramolekular* in *endocyclic* and *intermolekular* in *exocyclic* monoterpene ozonolyses (Bonn *et al.*, 2002).

Consequently, the nucleation during endocyclic monoterpene reactions is found to be less pronounced than during exocyclic ozonolyses due to the smaller secondary ozonides formed.

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## Uptake Of Trace Gas Species To Solid And Liquid Atmospheric Particles (HEP, Talk).

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Trace gas aerosol interactions will continue to play an important role in atmospheric chemistry. They are directly affecting aerosol composition, but also their physical, chemical and radiative properties, and thus provide one link between chemistry and climate change issues.

Uptake of species of atmospheric interest (e.g.,  $\text{HNO}_3$ ) to airborne aerosol particles is studied in a flow reactor in the laboratory. Submicron particles are generated using a nebulizer for water soluble material such as sea-salt or organics, and a solid aerosol generator for dust. They are characterized with a Scanning Mobility Particle Sizer (SMPS) consisting of a differential mobility analyser (DMA) and a condensation particle counter (CPC).

Two experimental techniques are available to monitor compounds of atmospheric interest, a) the use of short-lived radioactive tracers  $^{13}\text{N}$ ,  $^{86}\text{Br}$ , and  $^{11}\text{C}$  to label gas phase molecules at very low concentration (Ammann, 2001), and b) Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI-MS).

Uptake of  $\text{HNO}_3$  to deliquescent sea-salt aerosol particles was studied under a wide range of  $\text{HNO}_3$  concentration (Guimbaud et al., 2002). Between 1 and 60 ppbv, the uptake coefficient was constant at  $0.5 \pm 0.2$  within the first few seconds, whereas at higher concentrations of about 600 ppbv, the uptake coefficient rapidly dropped to 0.1 after about 1 second. This drop was due to complete release of chloride as  $\text{HCl}$ . The equilibrium conditions for these experiments were explored using the North American Aerosol Inorganics (AIM) model, which accounts for the activities of the concentrated solution of the deliquescent aerosol. It is concluded that the rates of uptake at low concentration were limited by the mass accommodation coefficient as both the diffusion in the liquid phase or the rate of release of  $\text{HCl}$  were not rate limiting. In a similar way, uptake of  $\text{HOBr}$  on deliquescent sodium bromide particles was found to be limited by a mass accommodation coefficient of  $0.6 \pm 0.2$  (Wachsmuth et al., 2002). Presently, we have started to investigate the uptake of  $\text{HNO}_3$  to mineral dust aerosol particles in a similar flow reactor, and first results will be presented.

In this paper we will present the experimental set up to generate the aerosols, the analytical technique to monitor species of atmospheric interests, results currently obtained and future experimental perspectives.

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## **Reaction of HNO<sub>3</sub> with mineral dust and aerosol particles (HEP).**

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## Formation of surface radicals in heterogeneous reactions of solid paraffin wax with OH, Cl and O (HEP).

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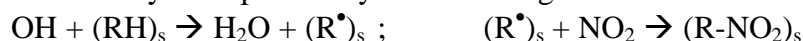
Heterogeneous reactions between atmospheric species OH and Cl and condensed organics should form surface organic radicals (SORs). This changes the hygroscopicity and CCN properties of organic aerosols. Here we present the first evidence of the SORs formation in reactions of OH, Cl and O with alkane  $(\text{CH}_3)_2(\text{CH}_2)_{2n}$  (melting range 346-353 K). Typical concentrations of gas radicals  $\sim 10^{11} \text{ cm}^{-3}$ ,  $P \sim 1 \text{ Torr}$ ,  $T = 293 \text{ K}$ . The gas phase EPR was used to detect OH, Cl, O. SORs were detected by ESR. The Cl and  $\text{Cl}_2$  consumption was studied simultaneously with HCl formation by quadrupole mass spectrometer (MS).

### Kinetic evidence of SORs formation

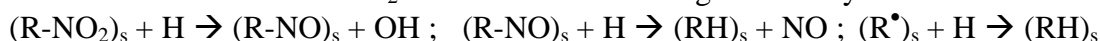
#### I.1. Consumption and regeneration of paraffin wax.

The uptake coefficient  $\gamma$  of OH on paraffin wax was measured using the coated insert/flow tube technique combined with EPR method. Hydroxyl radicals were produced in reaction of H atoms with  $\text{NO}_2$  in excess of  $\text{NO}_2$  over H:  $[\text{H}] = [\text{OH}] \sim (3-5) \times 10^{11} \text{ cm}^{-3}$ ,  $[\text{NO}_2] \sim 10^{13} \text{ cm}^{-3}$ . The OH uptake probability decreases with exposure time reaching its steady-state value after few tens of seconds. When  $\text{NO}_2$  flux is stopped and then added again the  $\gamma$  value sharply increases first to its initial value and then come back to the previous lower steady-state value.

Such behavior may be explained by the following reaction scheme. In presence of  $\text{NO}_2$  :



index s — surface. When  $\text{NO}_2$  is OFF the alkane is regenerated by H atom reactions:

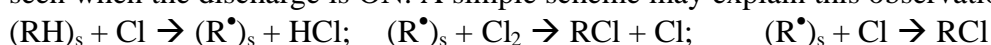


The estimated initial  $\gamma$ -value is close to that obtained by (Bertran et. al.,2001)

#### I.2. Reaction Cl + $(\text{RH})_s$ in excess of $\text{Cl}_2$

$[\text{Cl}] \sim (0.5 - 2) \times 10^{11} \text{ cm}^{-3}$ ;  $[\text{Cl}_2] \sim 40 \times 10^{11} \text{ cm}^{-3}$ ; discharge of  $\text{Cl}_2$  in He.

More than one HCl molecule is formed when one Cl atom is consumed.  $\text{Cl}_2$  consumption is also seen when the discharge is ON. A simple scheme may explain this observation:



#### Direct ESR detection of SORs

When the paraffin wax was placed inside the ESR cavity and irradiated with atomic oxygen or chlorine, the ESR spectra of SORs were detected. The spectra are similar in both cases and most probably belong to the  $\text{RO}_2$  radicals.

#### Future studies

Further study of OH,  $\text{NO}_2$ ,  $\text{NO}_3$ , Cl reactions with organic matter important for cloud formation will be carried out. On-line analysis of gas and surface radicals as well as gas products will be also done. The off-line analysis of organic surface after irradiation (contact angle, XPS, FTIR) will be performed.

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## Aerosol Flow Tube Studies of Trace Gas Uptake to Mineral Dust (HEP, Talk).

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A recent study estimates that 1600-2000 Tg of mineral aerosol are emitted annually into the atmosphere (Ginoux *et al.*, 2001). As shown by modelling studies (Zhang *et al.*, 1994; Dentener *et al.*, 1996), mineral aerosol can strongly influence atmospheric chemistry, especially the budgets of NO<sub>x</sub>, HO<sub>x</sub> and O<sub>3</sub>. These modelling studies revealed the need for reliable data quantifying the heterogeneous uptake of trace gases onto mineral dust particles.

Recent laboratory studies determining uptake coefficients for the interaction between trace gases and dust used the Knudsen reactor technique (e.g. Börensén *et al.*, 2000; Hanisch and Crowley, 2001). The main disadvantages of this technique, however, are the use of bulk substrates instead of airborne particles and the inability to simulate atmospheric relative humidities.

These problems are overcome by the use of the aerosol flow tube technique. In this study we present results for the uptake of HNO<sub>3</sub> onto airborne mineral aerosol, using an aerosol flow tube coupled to a chemiluminescence detector and an optical particle counter for the determination of the concentrations of HNO<sub>3</sub> and mineral aerosol, respectively. Uptake coefficients for this reaction were measured and the influence of relative humidity on the reaction was investigated.

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## **The number of surface functional groups of secondary organic aerosols (SOA) generated under laboratory conditions (HEP).**

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The goal of this work is to probe, *via* heterogeneous reactions, the surface of SOA particles generated under well controlled laboratory conditions. These investigations let us determine the nature and the abundance of surface functional groups. SOA particles are generated from the (photo) oxidation of VOC's (toluene, limonene) in the presence of O<sub>3</sub> at 1 atmosphere of air using a (filtered) 150W high-pressure Xe arc lamp. SOA production takes place in an atmospheric pressure flow cell whose gas phase is monitored using a differentially pumped quadrupole mass spectrometer. The size distribution of SOA aerosol has been characterized by a Differential Mobility Analyzer (DMA). Particle counts of several 10<sup>5</sup> particles cm<sup>-3</sup> were routinely achieved. The flow is taken across a PTFE filter during one to two hours at constant throughput leading to typical sample masses of a few mg. Photo acoustic spectroscopy (IR) was performed to determine the nature of the surface functional groups. Finally, to determine the abundance of these surface functional groups, heterogeneous reactions have been used to measure their absolute numbers in relation to the mass or surface area of the filtered SOA particles. We have interrogated the surface in a Knudsen flow reactor using NO<sub>2</sub>, O<sub>3</sub>, N(CH<sub>3</sub>)<sub>3</sub> and NH<sub>2</sub>OH as probe molecules.

## **Heterogeneous Reactivity of Diesel and Synthetic Soot: a Single Particle Mass Spectrometry Investigation (HEP).**

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A need for characterization of aerosol particles, especially black carbon, has been recognized due to their role in atmospheric chemistry. During heterogeneous reactions not only reactive gas phase compounds are consumed and gaseous reaction products are formed but also the particle surface is processed, which alters its properties. For example, freshly emitted hydrophobic Diesel soot has been shown to become more hygroscopic upon oxidation.

A previously described single particle mass spectrometer was equipped with a new ionization laser and a modified particle detection unit, which enables analysis of particles of all sizes simultaneously. Previously, particle sizes were stepwise manually scanned and at each size several hundred particles were sampled to have a statistically relevant number of spectra.

In several laboratory studies different types of soot aerosol particles were produced and investigated. Two measurement campaigns were conducted at the 84 m<sup>3</sup> aerosol chamber AIDA at the research center in Karlsruhe, Germany. Soot particles from a spark generator or a commercial diesel engine were exposed to species which interact with particles in the atmosphere, such as NO<sub>2</sub> or the reaction products of  $\alpha$ -pinene + O<sub>3</sub>. The particles were characterized before and after the reactions and in some experiments comparisons to other measurement techniques could be made. During mixing experiments of diesel soot and ammonium sulfate aerosol, single particle mass spectrometry was used to differentiate between internal and external mixtures.

## Heterogeneous Conversion of NO<sub>2</sub> on Secondary Organic Aerosol Surfaces: A Possible HONO Source? (HEP)

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Nitrous Acid (HONO) is an important precursor for OH-radicals in the atmosphere not only early in the morning but also during daytime due to the photolysis:  $\text{HONO} + h\nu \rightarrow \text{NO} + \text{OH}$ . In addition, HONO is an important in-door pollutant. Although it is expected that heterogeneous pathways are responsible for the formation of HONO in the atmosphere, the exact nature of the formation process is not well understood. From field measurements formation on ground surfaces and on aerosol surfaces have been proposed. Several laboratory studies postulated the heterogeneous conversion of NO<sub>2</sub> on soot surfaces as a possible HONO source. Soluble organics on the soot surface were found to be responsible for the reaction (Stadler and Rossi, 2001). However, the integrated yield of the non-catalytic reaction was found to be too small to explain atmospheric HONO levels (Kleffmann et al., 1999, Arens et al., 2001). Very recently, heterogeneous HONO formation on aqueous surfaces containing semi-volatile organics emitted from a diesel engine was reported (Gutzwiller, 2002). The results indicate that organics adsorbed on humid surfaces might be responsible, at least in part, for heterogeneous HONO formation in the atmosphere. However, up to now it is unknown, whether HONO formation by heterogeneous conversion of NO<sub>2</sub> on secondary organic aerosol surfaces is of importance. Secondary organic compounds can represent the major constituents of atmospheric particles and thus heterogeneous HONO formation on these surfaces may be a more significant HONO source compared to soot surfaces.

Accordingly, heterogeneous conversion of NO<sub>2</sub> on secondary organic aerosol surfaces formed in the reaction of different hydrocarbons with OH-radicals and/or ozone in an aerosol flow reactor was investigated under atmospheric conditions. HONO was detected by ion chromatography or by a new, very sensitive HONO instrument (LOPAP) developed at our institute, while NO<sub>2</sub> was measured by a commercial NO<sub>x</sub> monitor.

No NO<sub>2</sub> uptake and no HONO-formation was observed in any of the different reaction systems investigated. Upper limits of  $<10^{-6}$  and  $<10^{-7}$  were found for the uptake coefficients of NO<sub>2</sub> and the reactive uptake coefficients for the formation of HONO on different organic aerosol surfaces, respectively. These results indicate that HONO formation on secondary organic particles do not represent an important HONO source in the atmosphere, which is in good agreement with recent vertical gradient measurements from which a significant contribution of aerosols to atmospheric HONO formation was excluded (Kleffmann et al., 2002).

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## Chemical Reactivity and Transformation of Aerosol Particles: Experimental Investigation and Mechanistic Description (HEP, Talk).

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Air particulate matter contains a wide range of substances, which influence the physicochemical properties of aerosol particles and thus their effects on atmospheric chemistry and physics, climate, and public health. Chemical reactions occurring on aerosol particles in the atmosphere can transform these components and change their physicochemical properties.

Recent results in the experimental investigation and in the mechanistic description of chemical reactions on atmospheric aerosol particles will be presented, focusing on carbonaceous particle components and on a generalized formalism for the description of reactive and non-reactive processes at the surface of atmospheric particles.

The applicability of the generalized formalism will be illustrated for the interaction of ozone, nitrogen dioxide, and water vapor with the polycyclic aromatic hydrocarbon (PAH) benzo[a]pyrene (BaP), one of the most prominent persistent organic pollutants in air particulate matter, on the surface of soot particles. The processes at work on a molecular level in this complex system have been deconvoluted by unambiguous quantification of the changing molecular composition of both the gas phase and the condensed phase. From the experimental data basic physicochemical parameters and a detailed mechanistic model for the interaction of ozone with PAHs and graphite-like soot surface structures (graphene layers) have been derived. The results indicate that the interaction of ozone with soot particles is generally dominated by reversible adsorption and irreversible surface oxidation processes rather than "catalytic ozone destruction", which had been postulated in most earlier studies but indeed appears to be insignificant (Pöschl et al., 2001).

The results indicate that BaP and other particulate air pollutants undergo efficient oxidation on a time scale of seconds to minutes at the surface of atmospheric particles. One of the implications is that the exposure of humans traveling or living along busy roadways may be significantly higher than previously estimated. Field measurements aimed at verifying these conclusions drawn from laboratory results are currently under way (Pöschl, 2002; Schauer et al., 2001; Schauer et al., 2002).

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## **Influence of Sulfate Coating on the Optical Properties of Soot Particles (HEP).**

Robert Wagner, Claudia Linke, Ottmar Möhler, Karl-Heinz Naumann, Harald Saathoff, Martin Schnaiter, Werner Schöck, and Ulrich Schurath

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The absorption of visible radiation by aerosols in the troposphere is mainly due to soot and mineral dust. The optical properties of the soot particles – and thus their influence on local and global climate – strongly depend on the mixing state of soot in the atmospheric aerosol.

Soot particles may adhere to the surface of other particulate matter due to coagulation or be encapsulated due to condensation from the gas phase. In the atmosphere, cloud processing may also lead to particle coating. Model calculations predict a significant increase in absorption of such internally mixed soot particles by a factor of about 2 compared to the isolated species (Fuller et al., 1999).

This contribution presents a selected set of first results from an intensive soot coating campaign at the AIDA aerosol chamber in Karlsruhe (see contribution by Saathoff et al.: The AIDA Soot Coating Campaign), focussing on the optical properties of soot particles coated with layers of aqueous sulfuric acid and dry ammonium sulfate. Composite particles with different radii are generated to study the influence of the layer thickness on the absorption and extinction coefficient of the aerosol. The mass concentration of the coating material is determined by ion chromatography of filter samples as well as by *in-situ* FTIR extinction spectroscopy. For the optical characterization of the aerosol the following devices are employed: (1) flow-tube extinction spectrometer in the 230 – 1000 nm region, (2) *in-situ* extinction measurements, covering the spectral range from 400 nm to 1000 nm, (3) three colour integrating nephelometer to determine scattering coefficients and backscatter ratios at 450, 550, and 700 nm.

In agreement with theory, the coating of the soot aerosol leads to a strong increase in not only the extinction but also the absorption coefficient of the particles. The dependence of this absorption enhancement on layer thickness and coating material will be thoroughly analyzed.

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## **Aerosol optical properties as a tool for studying multi-phase processes over a wide range of atmospheric conditions (HEP, Talk)**

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Recent contributions from research activities at the AIDA aerosol chamber in Karlsruhe to working Group CMD-HEP mainly focussed on the optical properties of soot particles as well as the heterogeneous interaction of soot aerosol with gas molecules like O<sub>3</sub> und NO<sub>2</sub>.

Being more than just a “soot chamber”, numerous other research projects make use of the unique features of the AIDA aerosol vessel. So the whole chamber is positioned inside a large isolating containment whose interior can be cooled to any temperature between ambient temperature and 183 K to simulate conditions prevailing in the upper troposphere and lower stratosphere.

In this talk, a selected set of results from recent AIDA measurement campaigns will be presented, focussing on an extensive Ice Nucleation/Polar Stratospheric Cloud measurement campaign (Möhler et al., 2002) to give insight into current AIDA investigations besides experiments concerning soot particles and their properties. Important issues of these studies are:

- (i) the freezing behaviour of supercooled binary H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O and ternary H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/HNO<sub>3</sub> solution droplets in the temperature range from –35 °C to –85 °C.
- (ii) the dynamical growth of ice particles upon freezing of the solution droplets.
- (iii) the optical constants of supercooled liquid aerosols.

Special attention will be drawn to results from FTIR extinction measurements as well as in-situ laser light scattering – two important optical techniques to follow phase changes during freezing of supercooled liquid aerosols.

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## Automobile emissions measured at its source in a road tunnel near Paris : Latest results (HEP).

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Our studies are dedicated to the characterisation of the physico-chemical evolution of urban air pollution. We pursue a double approach : On the one hand, field campaigns on various issues are performed continuously in order to monitor the nature of the particulate burden of the urban atmosphere. On the other hand, new laboratory experiments, including a single particle mass spectrometer, are currently being developed in our laboratory in order to study the chemical reactivity of compounds adsorbed on aerosol particles. We will present an overview of our activities with an emphasis on results obtained during recent field campaigns.

The physico-chemistry of the particulate French automotive emissions have been studied in real circulation conditions in a road tunnel (La Défense, A14). Pollutants from such a site are not photochemically processed and thus represent the original emission at its source. Furthermore, the wide distribution of car types encountered in real circulation conditions assures representativity of the actual (French) car park. The French automotive emissions are also of particular interest because the proportion of Diesel engines is bigger than in other European countries.

The aerosol was sampled in the tunnel using Dekati 13 and 4 stage cascade impactors, as well as a total collector with PM<sub>10</sub> head. A TISCH high volume biphasic collector (total filter followed by two polyurethane foam plugs) was used to sample simultaneously the gas and particle phase. The concentration of 16 (EPA recommended) PAHs was determined in each sample by using microwave-assisted solvent extraction of filters and foams followed by GC-MS analysis. Environmental conditions, such as temperature, pressure, relative humidity, wind speed as well as CO and NO<sub>x</sub> levels were monitored continuously during the campaign.

The results show clearly that light PAHs, such as phenanthrene, acenaphthene or fluorene exhibit a bimodal distribution. They are found on fine particles (maximum at about 200 nm) as well as on coarse particles (maximum at about 4 micron). In contrast, heavier PAHs, like benzo(a)pyrene or benzofluoranthene, are found only on fine particles. This can be interpreted in terms of adsorption and desorption capabilities of the respective molecular species.

The measured gas/particle partitioning of the 16 PAHs is compared to measurements of urban and tunnel aerosols performed by other research groups (Wingfors et al., 2001 ; Oda et al., 2001 and some other campaigns). Considerable differences are found when comparing values encountered in a tunnel to values found at open urban sites. These differences will be discussed in terms of changing physico-chemical properties of the aerosol (Pankow, 1987).

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## Interaction of Trace Gases with Water-ice Surfaces (HEP).

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Cirrus ice in the upper troposphere can potentially play an important role in modifying photochemical cycles by providing a surface for heterogeneous processes. Reversible processes that influence the partitioning of trace gases between the gas and ice phase, and reactive processes that influence e.g. the NO<sub>x</sub> to NO<sub>y</sub> ratio are both likely to take place in cirrus clouds. Ozone production in the upper troposphere depends on levels of NO<sub>x</sub> and the NO / NO<sub>2</sub> ratio, which is strongly perturbed by the presence of peroxy radicals, e.g. HO<sub>2</sub>. As the major source of HO<sub>2</sub> in the upper troposphere is now believed to be the degradation of partially oxidised hydrocarbons (POH) [Singh *et al.*, 1995; Jaeglé *et al.*, 1998; Folkins and Chatfield, 2000], factors influencing both NO<sub>x</sub> and POH need to be understood.

In this work we present results on the interaction of various trace gases with ice surfaces at temperatures appropriate for the upper troposphere. We consider the reversible uptake of several POH (e.g. acetone, methanol and formaldehyde) on ice, and also the interaction (both reactive and reversible) of some members of the NO<sub>y</sub> family including N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub>. The experiments were carried out using a coated-wall flow tube in combination with a mass spectrometer to analyse the gas phase, with both electron impact and chemical ionisation schemes used [Adams *et al.*, 2002].

The data obtained will be presented in the form of temperature dependent uptake coefficients, and equilibrium surface coverages, that can be used to define the importance of the heterogeneous process in the upper troposphere.

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## The AIDA Soot Coating Campaign Influence of Coatings on Structure and Optics of Soot Aerosol (HEP).

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Soot is the most strongly absorbing aerosol in the atmosphere, which may have a direct climatic impact and affect photochemical reaction rates. During their atmospheric lifetime of about one week ageing processes may lead to coatings that can alter their dynamic, optical (Schnaiter et al., 2002), and hygroscopic properties significantly.

With the participation of 7 German, Swiss and Austrian institutes an intensive soot coating campaign was organised in Spring 2002 at the 84 m<sup>3</sup> large aerosol chamber AIDA of FZK. The goal of the campaign was a comprehensive investigation of the changing physical and chemical properties of spark generated (Palas) soot and soot from a commercial Diesel engine due to coating with different layers of organic material or sulphate, e.g. by *in situ* ozonolysis of  $\alpha$ -pinene, in the AIDA aerosol chamber. All experiments were carried out under atmospheric conditions (20% r.h., 296K) on time scales of 24 hours. With the instrumentation and expertise of the contributing scientists, the following aerosol parameters could be measured simultaneously: number and mass concentration, size distribution, chemical composition, particle morphology, single particle composition, spectrally resolved extinction (230-1000 nm), scattering at 450, 488, 550 and 700 nm, photoelectric charging, active surface area, hygroscopic growth, and volatility. The measured optical coefficients allow the calculation of single scattering albedo as well as absorption coefficients.

The initially fractal soot agglomerates were compacted during the coating process followed by growth upon condensation of more coating material. The coating of the soot aerosol led to a strong increase of the extinction coefficients mainly due to increased scattering but partly due to increased absorption. The scattering albedo increased and the wavelength dependence of the extinction coefficients changed.

This paper presents an overview of the campaign, and summarises first results and compares them with model calculations using the COSIMA aerosol code, describing the time evolution and optical properties of the aerosol ensembles studied. The implications of these results for the climatic impact of coated soot aerosol will be discussed.

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## Uptake Kinetics of Oxygenated Organics on Ice Surfaces (HEP).

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The kinetic and adsorption isotherms of partially oxygenated organics on ice substrates at temperatures in the range of 200 – 240 K have been investigated using the Coated Wall Flow-Tube (CWFT) technique with the detection of gaseous species by molecular beam QMS. The overall kinetics are expressed in terms of uptake coefficients ( $\gamma$ ) that represent the fraction of gas/ice collisions that has led to uptake (loss from the gas phase) and/or chemical transformation. The uptake of 1-Propanol was found to be  $\gamma = 1 \cdot 10^{-3}$  whereas the uptake of acetone and acetic acid on an ice surface is extremely slow ( $\gamma \leq 1 \cdot 10^{-5}$ ). The number of acetone molecules adsorbed on the ice increases with decreasing temperature and increasing acetone concentration in the gas phase. The adsorption enthalpy  $H_{\text{ads}}$  for acetone was calculated to be  $(50 \pm 10)$  kJ mol<sup>-1</sup> by applying adsorption isotherms to determine temperature dependent Langmuir constants,  $K(T)$  and saturation surface coverage,  $N_{\text{max}}$ .

In addition we have investigated proton exchange processes of the protic gas molecules propanol and acetic acid on D<sub>2</sub>O-ice surfaces which provide information on the degree of coverage and/or the degree of deactivation of active surface sites as well as the desorption kinetics of the isotopic product molecules. In these experiments it is found that substantial amounts of 1-propanol-d1 are released into the gas phase. Quantitative estimates indicate that the number of exchanged 1-propanol-d1 molecules is larger than the number of water molecules available on the geometrical ice surface. This indicates either substantial porosity of the ice surface or, alternatively, the access of several surface layers to the adsorbed propanol molecules. The desorption rate of 1-propanol-d1 has been measured to be  $k_{(\text{desorp})} = 3,5 \times 10^{-3}$  s<sup>-1</sup> at 220 K. The proton exchange probability of acetic acid was found to be  $\gamma_{(\text{H} \rightarrow \text{D})} = 10^{-2}$ . The residence time for those acid molecules which undergo adsorption, proton exchange and desorption increases with decreasing temperature. Measuring the temperature dependent desorption kinetic, the desorption energy was calculated to be  $(56 \pm 5)$  kJ/mol, in agreement with theoretical calculation (Giradet and Toubin, 2001).

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## Application of homogeneous and heterogeneous methods in the study of the reaction of HOBr and Br<sub>2</sub> with sulphur species (APP, Talk).

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Heterogeneous (aqueous-phase) reactions of DMSO (CH<sub>3</sub>SOCH<sub>3</sub>), MSIA (CH<sub>3</sub>SO<sub>2</sub>H) and MSA (CH<sub>3</sub>SO<sub>3</sub>H) contribute to the oxidation of DMS (CH<sub>3</sub>SCH<sub>3</sub>) and decrease the yield of SO<sub>2</sub> (the relatively long-lived gaseous precursor of H<sub>2</sub>SO<sub>4</sub> in the marine boundary layer) and increase the yield of non-sea-salt sulphate. Since DMS can suppress halogen activation in aerosol smog chamber experiments, information about reactions of sulphur species with bromine compounds in aqueous phase is required to explain the role of non-sea-salt sulphate in the Arctic during ozone depletion and to elucidate multiphase processes that govern the maintenance of the tropospheric aerosol (Behnke et al., 1998, Behnke et al., 1999, Campolongo et al., 1999, Katoshevski et al., 1999, Le Bras et al., 2000, Mozurkewich, 1995). The present study investigates the kinetics between sulphur (DMS, DMSO, MSIA and MSA) and bromine species (HOBr and Br<sub>2</sub>) using homogeneous (stopped-flow – SF) and heterogeneous (wetted-wall flowtube – WWFT) methods. SF measurements (SX.18MV, Applied Photophysics) were performed at various temperatures and concentrations of HOBr and sulphur species, observing aqueous HOBr at  $\lambda = 260\text{nm}$ . The concentrations of bromine and sulphur species in aqueous phase were determined by UV-spectroscopy (Uvikon-860, Kontron). The WWFT data are obtained by observing the uptake of Br<sub>2</sub> in air (along a vertically aligned flowtube, the walls of which are conferred by a film of slowly flowing solutions of sulphur species, controlled by a peristaltic pump) at different concentrations of the sulphur species at various temperatures. The uptake rates were observed to be first order with respect to the gas phase concentration of Br<sub>2</sub>. The gas-phase inlet and outlet of the flow tube were made of PTFE tubing (outer diameter 0.6 cm, inner diameter 0.4 cm, length 140cm), the inlet being movable to vary the contact time in the Duran glass flow tube (inner diameter 0.6 cm). The uptake of Br<sub>2</sub> on each sulphur species and the rate constant measurements by both techniques are combined in a heterogeneous chemistry/transport model using numerical integration, describing the WWFT with 50 cylindrical shells of the gas and liquid phase, each (Behnke et al., 1997, Frenzel et al., 1998), by considering the radial diffusion of Br<sub>2</sub> in the aqueous phase, the Henry's law constants and gaseous and aqueous diffusion coefficients of Br<sub>2</sub> as a function of temperature.

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## Influence of pH on Kinetics of S(IV) Autoxidation in the Presence of Mn(II) (APP).

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Recent laboratory studies of chemical reactions involving S(IV) species in aqueous solution have greatly improved our understanding of the processes responsible for the oxidation of SO<sub>2</sub> in the aqueous phase (Warneck *et al.*, 1996). Since most laboratory experiments were carried out under conditions different from those in atmospheric liquid water, the laboratory data alone do not allow comparison of the individual contributions to the overall oxidation rates in the atmosphere. Anyhow, this problem may be approached by means of computer model calculations (Warneck, 1999; Herrmann *et al.*, 2000), by which it is possible to identify the leading processes involved in the oxidation of SO<sub>2</sub> under different meteorological and atmospheric conditions. However, laboratory data (i.e., kinetic measurements) in combination with field data are very important and essential parameters

Transition metal ions and their complexes either present in atmospheric liquid water or on the surface of aerosol particles at relatively high humidity are considered to be potential catalysts in the autoxidation of S(IV) oxides (Brandt and van Eldik, 1995; Grgič and Berèè, 2001). Each species (i.e., dissolved S(IV) oxides as well as transition metal ions) shows a different reactivity and it is the chemistry of these species that is the basis for understanding the complex reaction mechanisms. Catalytic activity of metal ions depends strongly on the conditions in the reaction system (e.g., oxidation state of the metal ion, the concentration of the active species, pH of the solution).

In spite of many investigations on metal ion catalysis, there are still discrepancies, particularly for manganese catalysis at pH above 4. This work presents new experimental results for aqueous S(IV) autoxidation catalyzed by Mn(II) in the pH range 3.0 – 5.0 under dark conditions and a new kinetic model based mainly on the initial step of a radical chain mechanism, that is the formation of transient metal-sulfito complexes. Experiments were carried out in a semi-batch continuous stirred tank reactor (CSTR) at constant pH provided by use of pH-controlled system. The results of kinetic model will be compared with the predictions based on simple kinetics model evaluated by standard integral approach. These results are the basis for our future experimental studies, which will evaluate the influence of some important organic constituents, present in atmospheric liquid phase, on the S(VI) autoxidation..

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## Interaction between Mineral Components of Sea Aerosols and Sulphoxy Radicals (APP, Talk).

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To shed more light on the role of atmosphere components in the autoxidation of S(IV) we extended our interests on the main electrolytes in the aqueous phase of the sea aerosol: NaCl, NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>. The autoxidation of S(IV) was carried out in a homogeneous (4 cm<sup>3</sup> in volume) or heterogeneous reactor (150 cm<sup>3</sup> in volume) under the following chemical conditions: initially 2x10<sup>-3</sup> M S(IV), 2.5x10<sup>-4</sup> M O<sub>2</sub> and 2x10<sup>-7</sup> M sobrerol or steadily 5.6x10<sup>-4</sup> M S(IV), 2.5x10<sup>-4</sup> M O<sub>2</sub> and no organic inhibitor, respectively. The experiments were conducted at pH about 7.5 and temperature 25°C, both in the absence and presence of CoSO<sub>4</sub> as a catalyst. The reaction progress was followed by measuring the decrease in oxygen concentration (Clark type electrode) or the increase in conductivity due to sulphate formation (Orion conductivity cell). The measurements were performed for reacting solutions diluted or concentrated with respect to the selected mineral components. In the first case the solution composition was near to that of coastal precipitation (Polkowska *et al.*, 2002), whereas in the second case the high concentrations of mineral components reflected the situation in evaporating sea aerosols. Comparative experiments were made for NaClO<sub>4</sub> commonly used to adjust the ionic strength (Cavalheiro *et al.*, 1987).

Typical experimental results showed the non-monotonous dependence of the S(IV) autoxidation rate on the mineral component concentration. This effect was discussed taking into account the SO<sub>x</sub><sup>•-</sup> scavenging, metal cation complexing, additional initiation by newly generated inorganic radicals and influence of the ionic strength on component rate constants.

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## Laser-based Studies of OH with Oxygenated Organics in Aqueous Solutions (APP).

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Free radicals play an important role in the chemistry of the tropospheric aqueous phase. The OH radical is the most important oxidant both in the tropospheric gas and aqueous phase. Organic solvents are used in a large number of industrial processes including cleaning and degreasing applications, paints, pharmaceutical process synthesis, polymer disposal agents and adhesives. Due to their volatility, in many of these processes they are emitted either directly or indirectly into the atmosphere. A number of organic compounds employed as solvents at the present time have been shown to have adverse health effects i.e., carcinogenic, mutagenic and reprotoxic properties.

In the present study the rate constants of the OH radical reactions with such organic compounds have been investigated at different conditions for T and I i.e. temperatures and ionic strengths. These investigations were performed using a laser photolysis long path absorption apparatus (LFP-LPLA) and applying competition kinetics (reference substance: SCN<sup>-</sup>). For the reactions of OH with (1) acetone, (2) methyl ethyl ketone, (3) acetylacetone, (4) isobutyraldehyde, (5) ethyl formate, the following Arrhenius expressions were obtained:

- (1)  $k(T) = (2.8 \pm 0.4) \cdot 10^{11} \exp((-2200 \pm 1300)/T) \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $E_a = (18 \pm 11) \text{ kJ/mol}$
- (2)  $k(T) = (1.2 \pm 0.1) \cdot 10^{13} \exp((-3000 \pm 1100)/T) \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $E_a = (23 \pm 9) \text{ kJ/mol}$
- (3)  $k(T) = (5.1 \pm 0.1) \cdot 10^{11} \exp((-1900 \pm 1000)/T) \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $E_a = (16 \pm 8) \text{ kJ/mol}$
- (4)  $k(T) = (3.0 \pm 0.2) \cdot 10^{10} \exp((-720 \pm 360)/T) \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $E_a = (6 \pm 3) \text{ kJ/mol}$
- (5)  $k(T) = (1.8 \pm 0.1) \cdot 10^{10} \exp((-1200 \pm 500)/T) \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $E_a = (10 \pm 4) \text{ kJ/mol}$

No T-dependent data are currently available in the literature.

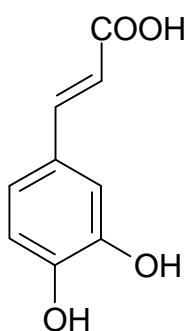
The kinetic investigations contribute to fill the existing gaps with regard to OH radical reaction kinetics in aqueous solution and will be implemented into the chemical aqueous phase mechanism CAPRAM 2.4 (MODAC mechanism) in an extended version..

## Kinetics of the Mn-Catalysed Autoxidation of S(IV) Inhibited by Caffeic Acid as a Representative of Polyphenols (APP).

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In this work the term 'polyphenol' is understood as a substance which possesses an aromatic ring bearing more than one hydroxy substituents and, moreover, functional derivatives such as esters, methyl ethers etc. These compounds, the main source of which are plants, can contribute to organic aerosols (Hoffmann, 2001). Caffeic acid (3-(3,4-dihydroxyphenyl)-2-propenoic acid), chosen as a model inhibitor of S(IV) autoxidation, represents not only polyphenols but also carboxylic acids, compounds detected among secondary products of atmospheric degradation of biogenic and anthropogenic hydrocarbons (Chien *et al.*, 1998).

As shown in our previous communications, caffeic acid may decrease the formation of S(VI) by scavenging sulphydryl radicals and by chelating and reducing transition metal ions (Pasiuk-Bronikowska *et al.*, 2001, Krajewska *et al.*, 2002). Now, we try to derive the rate law governing the S(IV) autoxidation at caffeic acid inhibition. For this purpose we performed a number of laboratory experiments to determine the overall reaction orders with respect to oxygen, hydrogen sulphite, caffeic acid and manganese sulphate, the latter applied as a catalyst. The experiments were carried out in a gradientless reactor (4 ml volume) at 25°C and pH ≤ 5. The extent of reaction was determined from the decrease in O<sub>2</sub> concentration measured with the Clark-type electrode. The experimental results are discussed with the view to bind them with the chain mechanism of the studied reaction. They are also compared to the kinetics of the uninhibited autoxidation of S(IV).

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## **Aqueous phase reactivity of acetone and its parent compounds in the troposphere (APP).**

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Acetone is both an intermediate and final product of OH-oxidation of VOCs. Because of its long atmospheric lifetime towards gas phase photolysis and OH-oxidation, acetone is one of the main radical precursors in the upper troposphere. Although its water solubility is low, acetone was identified in clouds and rain samples, indicating that this compound can be either formed within the aqueous phase or directly transferred from the gas phase. The present study is aimed at exploring acetone's chemical behaviour in the aqueous phase of the troposphere. Aqueous phase OH-oxidation of acetone and its parent compounds under simulated tropospheric conditions were performed.

The experiments took place in a static photoreactor, equipped with a continuous UV-visible irradiation. Different OH sources, and initial reagent concentrations have been tested. To obtain the time profiles of the stable reactants and products, analysis were performed periodically using gas chromatography, mass spectrometry, HPLC and ionic chromatography.

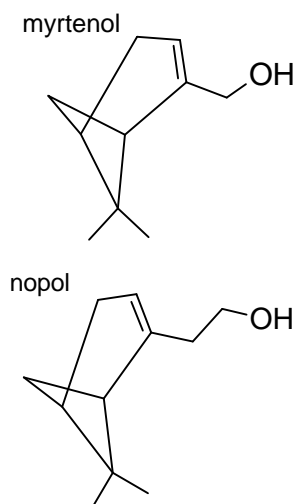
Mechanistic and kinetic studies of OH-oxidation of methyltetriobutylether (MTBE) in the aqueous phase have shown that together with formaldehyde, acetone is the main reaction product under atmospheric conditions.

Acetone slowly reacts towards OH radicals in the aqueous phase, leading to the formation of methylglyoxal, which is also an ubiquitous compound in tropospheric water droplets. The influence of different parameters (pH, temperature, OH sources) on the kinetics and the mechanisms will be presented.

## Fe-Catalysed Autoxidation of S(IV) Inhibited by Aliphatic Alcohols, Nonterpenic and Substituted with $\alpha$ -Pinene Skeletal Structure (APP).

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Alcohols are common VOCs both in urban and in rural atmosphere ( Isidorov, 2001 ). Since they belong to the group of organics rather well water soluble, the reactivity of alcohols with respect to intermediates in S(IV) autoxidation may have a bearing on acidity formation in clouds. The aim of this work is to elucidate the monoterpene alcohol inhibition of the S(IV) autoxidation by comparing the behaviour of myrtenol ( $C_{10}H_{15}OH$ ) and nopol ( $C_{11}H_{17}OH$ ) with that of ethanol ( $C_2H_5OH$ ) and 2-propanol ( $C_3H_7OH$ ). Results of laboratory experiments on the rate of S(IV) autoxidation in the presence of these alcohols are interpreted using the equation derived by Alyea and Bäckström, 1929, brought into relationship with the actual mechanistic knowledge on the reactivity of the inhibitors with respect to sulphate radicals (Clifton and Huie, 1989).

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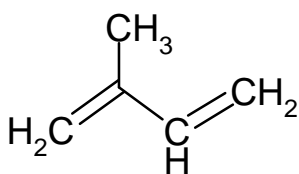
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## Degradation of Isoprene during Aqueous Autoxidation of SO<sub>2</sub> under Various Conditions of Initiation (APP).

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Isoprene, a major organic pollutant of biogenic and anthropogenic origin, was shown to slow down the aqueous-phase autoxidation of SO<sub>2</sub> [Rudzinski *et al.*, 2000, 2002a] at the cost of undergoing degradation [Rudzinski *et al.*, 2002b]. In the latter work a chemical mechanism of degradation was proposed, assuming the chain oxidation of isoprene initiated by the sulphony radicals generated within the autoxidation of SO<sub>2</sub>.



In this work we aim to refine the proposed mechanism, attempting to discriminate the shares of sulphite and sulphate radicals in the oxidation of isoprene. Therefore, we compare experimentally the influence of the initiation mode of SO<sub>2</sub> autoxidation on the rate of isoprene degradation, namely the initiation by manganese ions (generation of sulphite radicals) and by thermal decomposition of peroxydisulphate (generation of sulphate radicals) in the absence of metal ions. The experiments are performed in a perfectly stirred reactor (25 °C, pH 8÷9), by measuring electrochemically the concentration of dissolved oxygen and spectrophotometrically (uv) the concentration of isoprene and sulphite. The results are analysed with the aid of chemical kinetic modelling.

The possible participation of the aqueous phase oxidation of isoprene within the overall transformation of isoprene in the troposphere is also discussed.

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## Experimental Simulation of Iron Cycling (APP).

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Iron is one of the most abundant trace metals found in atmospheric water. Its redox partition results from photochemical processes. Transition metals are thought to play a major role in the redox cycle of sulphur and organic compounds in the troposphere, as well as controlling free radical production in cloud. The photolysis of Fe(III) species as well as the Fenton reaction with Fe(II) are a significant source of OH radicals in rains, fogs and clouds. Iron participate in redox and photochemical reactions with H<sub>2</sub>O<sub>2</sub> But only a few studies have investigated the iron speciation or reactivity of trace metals in cloud water or in ambient aerosol. Dissolution of aerosol in cloud droplets is the major source of trace metal. Interaction aerosol/water is an important point to understand iron redox state in aqueous phase.

This speciation, which is dependent on the chemical composition of the droplets (pH, organic and inorganic ligands...) and on the photochemistry within cloud, is still poorly documented because of severe analytical conditions : risk of contamination during the sampling and the analyse of trace metals at the nmole/L level. The redox cycle Fe(II)/Fe(III) strongly differs from other catalytic cycles (Cu, Mn) because the reduced form is much more stable for iron than for other metals and this stability increases with the acidity. This particularity explains the opportunity of the analytical determination of the ratio between the two oxidation states. To control this iron cycle, we have adapted an analytical protocol already used for the separation of Fe(II) and Fe(III) in the seawater

We will present results of crustal origin particles dissolution experiment where kinetic parameters are determined, including iron speciation. Major function of variation are pH and photochemistry in the aqueous weathering solution.

## **Aerosol dissolution enhancement by light irradiation (APP).**

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Trace metals and especially transition metals strongly affect chemistry inside a cloud drop. Because of their availability through aerosol dissolution, we have investigated the effect of light irradiation on the dissolution rate of elements, including transition metals, from particulate matter in water. The first step of this work is to build and validate a device which can simulate in a laboratory the process occurring in a cloud. We have developed an open-flow reactor where a weathering solution flows continuously through a small Teflon cell (50 mL). This cell previously loaded with a small amount of particulate material and closed with a filter membrane (Sartorius<sup>TM</sup> cellulose-acetate, 0.45 $\mu$  porosity) which prevent particle to flow out of the device. A silica window allows light to enter the system. Light is provided by a high pressure xenon discharge lamp and guided to the silica window by a liquid optical fibre.

The lamp spectra is quite continuous and close to sun spectra, but stronger in the blue and UV region. To calibrate the light intensity in the cell, we have made chemical actinometrical measurements on H<sub>2</sub>O<sub>2</sub> photochemical decay. We have measured that for H<sub>2</sub>O<sub>2</sub> photo-dissociation with the full power of the lamp, the light intensity is 50 times greater than we can expect in a summer clear sky.

Comparisons of dissolution measurements with and without light clearly indicates a large influence of irradiation for iron and manganese dissolution rate, but no influence for sodium, calcium, potassium, and so on.... Two hypotheses are emitted concerning this dissolution rate enhancement:

- 1/ Irradiation acts directly on the surface of particles and help to extract the metals from its mineral lattice, probably by changing its redox state.
- 2/ Irradiation acts on the soluble species, creates radicals who react themselves on the surface of the particles, helping transition metal extraction.

We will present in the poster the photochemical design, its validation, and the first experimental results obtained until today.



## **Aqueous Phase Radical Chemistry of new oxygenated solvents (APP, Talk).**

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The chemical reactions occurring in aqueous particles have important drawbacks to the water cycle and global atmospheric chemistry. Multiphase chemistry becomes especially important for soluble compounds which are not reactive in the gas phase. This becomes especially true for a full range of new oxygenated solvents for which our current understanding is poor. We therefore undertook to study their aqueous phase chemistry.

i.e, Two set-up have been developed, based on time resolved concentration monitoring (ie, laser flash photolysis) or a steady state approach (flow tube technique). Teflon AF 2400 tubing was used as the photolysis cell in these set-ups, taking benefit of its particular properties enabling light conduction, to increase the detection sensitivity.

Teflon AF2400 tubing is a great alternative to classical "White" configuration. In fact this material has a lower refraction index ( 1,29) than water and is chemically and physically inert, transparent to UV light, and has a large flexibility which could be largely used as a waveguide photolysis cell.

Current results of the reactivity of some oxygenated compounds toward the hydroxyl radical will be presented and discussed.

# Mass Spectrometric Studies Related to In-situ Measurements and Chemical Processes of Oxygenated Volatile Organic Compounds in the UT-LS.

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The upper troposphere–lower troposphere (UT-LS) has attracted recently increasing attention because of persistent disagreement between the measurements and modeling of OH and NO<sub>x</sub>/NO<sub>y</sub> ratio concentrations (Wennberg et al., 1998; Jaeglé et al., 1998). The formation and destruction of ozone depends on the concentrations of these species, and must be better understood as this gas plays a particularly important chemical and radiative role in this region. The emissions of particles, H<sub>2</sub>O and NO<sub>x</sub> from commercial aircraft, the transport of oxygenated volatile organic compounds (OVOC) and NO<sub>x</sub> from the lower troposphere, and the presence of cirrus clouds are among the factors that influence the OH, NO<sub>x</sub> and NO<sub>y</sub> concentrations in the UT-LS.

In-situ measurements of OVOC using the chemical ionization mass spectrometry (CIMS) technique are based on reactions of proton hydrates:



with  $0 \leq m \leq n \leq 5$  (Arnold et al., 1997; Pöschl et al., 2001). The OVOC concentration is derived from the knowledge of the rate constants and product ions of the reactions involved. Some rate constants and product ions have been already determined in laboratory studies performed at room temperature and low pressure (< 1 mbar; see, for example, Spanel et al., 1997). However, these data need to be measured at the lower temperatures and higher pressures of the UT-LS, since different mechanisms may occur, as it is the case for formaldehyde (Midey et al., 2000). An existing ion flow tube coupled to a quadrupole mass spectrometer (Catoire et al., 2001) has been modified, enabling studies under these conditions. The validation of this apparatus by the study of the reactions of  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  with acetone has been undertaken.

In parallel to the in-situ measurements, the interactions (diffusion, adsorption, and heterogeneous reactions) of OVOC with the ice of cirrus clouds must be studied, in order to better assess the role of ice in the heterogeneous chemistry of the UT-LS. A time-of-flight secondary ion mass spectrometer (TOF-SIMS) has been adapted for the laboratory analysis of OVOC doped ice under very low pressure (< 10<sup>-7</sup> mbar) without ice sublimation. The TOF-SIMS capabilities are known to be excellent for analysis of solid material at room temperature, but have not been tested for ice, except in one recent study (Donsig et al., 1999). A preliminary study validating the method by the measurement of HCl diffusion coefficients in ice is under progress.

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## **A New Chemical Module for Tropospheric Isoprene Degradation Applied to the RACM Mechanism (MPM, Talk).**

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### **Abstract**

A highly condensed reaction scheme for the tropospheric oxidation of isoprene is presented. The mechanism has been implemented into the Regional Atmospheric Chemistry Mechanism (RACM), which is an established chemical module for regional air quality modelling but contains an isoprene chemistry which is no longer state-of-the-art. The reaction scheme developed here is based on the recently published MIM ("Mainz Isoprene Mechanism") that was constructed for application in global chemistry transport models. The MIM scheme has been reduced to a size suitable for use in regional atmospheric chemistry models. Redundant reactions have been identified and removed from the reaction scheme by means of sensitivity analyses. A model intercomparison between both the original and the updated RACM mechanism has been performed for a number of well-defined scenarios employing conditions ranging from very clean to highly polluted air masses. The calculations revealed large deviations in the concentration-time profiles of important reactants for isoprene degradation, particularly under "low-NO<sub>x</sub>" conditions. The new isoprene chemistry requires only a few additional reactants (7) and chemical reactions (7) and, therefore, offers the possibility for the successful application of the revised reaction scheme in chemistry-transport models (CTM) without an excessive increase in computational efforts.

## Sensitivity study of the influence of new kinetic data and of species lumping on the simulation results (MPM).

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We applied the programme CHEMATA (which generates explicit or lumped chemical gas phase mechanisms by using experimental data, structure-reactivity relationships and lumping group prescriptions as input) in order to contribute to the CMD targets of:

- simplifying the schemes of gas phase reactions by means of scenario-dependent modelling-based sensitivity analyses.
- developing application-oriented chemical codes which meet the criteria of cost-effectiveness as well as scientific correctness, to provide a basis for modelling-guided abatement strategies.

### Results

New kinetic data were included to the mechanism and the influence of uncertainties in kinetic data or degradation schemes on the simulation results was determined. Higher rate constants for the decomposition reaction of RO (as measured by Zabel et al.) lead to higher aldehyde concentrations which increase the ozone production in the case of VOC sensitive conditions. Updated alkene + NO<sub>3</sub> kinetic (based on the results of Martinez et al.) reduces the night and daytime concentrations of terminal alkenes whereas the ozone reduction is very small. Updating the HO<sub>2</sub> + NO rate constant according to the measurements of Zetzsch et al. influences the ozone values for NO<sub>x</sub> sensitive conditions (increase of ozone). A sensitivity study for the decay of aromatic compounds shows that the degradation channel has a high influence on the ozone production as well as on other product yields. CHEMATA can now be used for modelling and interpreting experimental studies of the aromatic decay.

For simplifying chemical mechanisms the influence of the species lumping on the simulation results was investigated. Using the RACM mechanism (Stockwell et al., 1997) as starting point we extended and reduced the number of lumping groups and evaluated the sensitivity of the model results to each variation in the mechanism. The tests were done in a boxmodel as well as a 3D model which was used for simulating an ozone episode from spring 1998 in the region of Milan (Martilli et al., 2002):

- The treatment of secondary VOC species: Many mechanisms have very simple approaches of representing secondary VOC, e.g. treating all higher aldehydes as CH<sub>3</sub>CHO. Our simulations show that this is justified for simulating ozone episodes ≤ 2 days.
- The reducing the mechanism by parameterising of the RO<sub>2</sub> reaction and by lowering the number of the VOC lumping groups. The results show that further mechanism reduction is possible by changing the parameterising of the RO<sub>2</sub> reactions. Reducing the VOC groups can affect the results especially in the case of very polluted air.

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## Development of an Automatic Generator of Explicit Chemical Schemes for tropospheric VOC Oxidation (Guest, Talk).

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VOCs emitted into the atmosphere are oxidized in complex reaction sequences that produce a much larger number of intermediates (e.g. oxy, peroxy, and Criegee radicals; ketones, aldehydes, alcohols, nitrates, peroxides, carboxylic acids and peracids – often multifunctional). These intermediates play a key role in the formation of tropospheric ozone (O<sub>3</sub>), in the budgets of odd hydrogen (HO<sub>x</sub>) and odd nitrogen (NO<sub>x</sub>) on regional and global scales, and probably in the formation of organic aerosols. Although their cumulative importance is widely acknowledged, the estimated number of intermediates far exceeds that for which direct laboratory measurements are available. However, reasonable estimates for their reaction kinetics and pathways can be made by analogy to known reactions, with the aid of several structure-activity relations (SARs). We have codified the various estimation methods to generate explicit reaction pathways, and the associated kinetics, for the oxidation of specified VOCs down to one carbon species (for which direct laboratory data are then available). The SARs are based on evaluated laboratory data (e.g. the OH abstraction and addition reactions given by Kwok and Atkinson 1995), analogies to similar known reactions, thermodynamic estimates (Benson 1976 and updates), and for photolysis constants assuming additivity of spectra from 51 species. Peroxy radical permutation reactions are treated explicitly with 10 different reactivity classes. Numerical simulations were performed using a resulting explicit chemical scheme to study how the multifunctional organics evolve during the oxidation of a given VOC. First results will be presented.

# Concentration Profiles Using a Lognormal Distribution Regarding Aerosols with CAPRAM 2.4 (MODAC Mechanism) (MPM).

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In this study a detailed chemical mechanism (147 species and 438 reactions) describing tropospheric aqueous phase chemistry by CAPRAM2.4 (Chemical Aqueous Phase Radical Mechanism) (Herrmann et al., 2002) was used in order to understand different chemical reaction systems and to determine diurnal concentration profiles for different species in the troposphere (Table 1). The aqueous chemistry is coupled to the gas phase mechanism RACM (Stockwell et al., 1997) and the phase exchange is accounted by using a resistance model (Schwartz, 1986).

The latest development is the application of a size-resolved model system. In the present work different size bins (1, 2, 3, 4, 5, 10, 20, 30, 50) are considered in order to evaluate the effect of the size resolution on the diurnal concentration profiles.

The mechanism was applied for three different scenarios: (i) urban, (ii) remote and (iii) marine varying the atmospheric initial conditions. The obtained results show for all of the considered species in this study an agreement in the diurnal trend but was observed a relevant effect on the daily maximal concentration due to size resolution of the system. In the aqueous phase a lower OH concentration ( $6 \cdot 10^{-14}$  M) compared to the non size-resolved system ( $1 \cdot 10^{-13}$  M) for the urban scenario was found.

**Table 1:** List of the species of interest included in the present work.

Species	
Gas phase	Aqueous phase
O <sub>3</sub>	OH
NO <sub>2</sub>	NO <sub>2</sub>
NO	Fe <sup>2+</sup> /Fe <sup>3+</sup>
NO <sub>3</sub>	Cu <sup>2+</sup> /Cu <sup>+</sup>
OH	HO <sub>2</sub> /O <sub>2</sub> <sup>-</sup>
HONO	O <sub>3</sub>
N <sub>2</sub> O <sub>5</sub>	HONO/NO <sub>2</sub> <sup>-</sup>
HO <sub>2</sub> NO <sub>2</sub>	HO <sub>2</sub> NO <sub>2</sub>
	Oxalate
	HSO <sub>3</sub> <sup>-</sup> /SO <sub>3</sub> <sup>2-</sup>
	S(IV)

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## Numerical Simulations of Nitrous Acid in the Planetary Boundary Layer – Rate Constants and Unknown Sources (MPM, Talk).

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There is a general agreement that the photolysis of nitrous acid is an important source of OH radicals shortly after sunrise whereas the relative importance of HONO on photochemistry during the rest of the day is still an open question. This study is an application of recent observational findings on the HONO formation (Kurtenbach et al., 2001) using the comprehensive numerical simulation model KAMM/DRAIS (Vogel et al., 1995) and addresses the following questions: 1. What is the relative importance of a) the direct HONO emissions, b) the heterogeneous reactions at aerosol surfaces, and c) heterogeneous reactions at the ground itself for the diurnal cycle of HONO? 2. What is the relative importance of HONO as a source for the OH radical?

The results of the model simulations (Vogel et al., 2002) are compared to observational data of Kleffmann et al. (2002). The measurements were carried out during October 18-19, 2001. When all processes mentioned above were taken into account the simulated HONO concentrations during night are in agreement with observations. However, during daytime HONO is underestimated by the model during daytime by a factor of two.

We checked the rate constant of the reaction of  $\text{NO} + \text{OH} \rightarrow \text{HONO}$  which is the main HONO gas phase source during day and found differences by a factor of two between the values currently used in chemical transport models and recent data published by IUPAC. Using the new kinetic data we reduced the difference between the observed and the simulated HONO concentration by 50 %. However, the daytime HONO concentrations are still underestimated by the model. This implies that there is an additional source of HONO during the day.

We introduced an artificial HONO source which is proportional to the daily cycle of photolysis rate constant of  $\text{NO}_2$ . With this parameterisation we were able to reproduce the observed HONO concentrations during daytime. At least for the day in October, when low ozone concentrations were present HONO was the main source of OH. However, additional simulations show that HONO seems to be a minor source of OH during typical summer smog episodes.

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## Simulation of Atmospheric Photochemistry In a large Reaction Chamber (SAPHIR)

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SAPHIR is an experimental tool that allows to study tropospheric gas-phase chemistry under natural burdens of trace gases ranging from low concentrations in the background atmosphere to polluted conditions of the boundary layer in industrialized areas. Compared to investigations in the real atmosphere chamber studies have a series of advantages:

- reproducibility of experiments,
- independent variation of the concentration of individual source gases to explore their contributions to the radical budget i.e. the cleaning capability of the atmosphere and the formation of ozone,
- Perturbative experiments as they are frequently used in lab kinetics to study transient chemical processes on the time scale of minutes.

The sensitivity of a predicted trace gas concentration to small changes of a selected rate constant inside a photochemical box model is a measure for the relative significance of the observed reaction. In chemical models the differential change of the species concentrations related to the change of one input parameter, e.g. the rate constant is defined as the sensitivity coefficient. An indirect method is chosen that calculates normalised sensitivity coefficients from simulation runs changing only one rate constant of a photochemical box model for each investigated scenario.

Sensitivity studies of the concentrations of the short lived compounds OH and HO<sub>2</sub> are used to design experiments that allow to validate the HO<sub>x</sub> chemistry in the reaction system OH/CO/CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> within currently used photochemical models. There are five main pathways which characterize the OH/HO<sub>2</sub> system: 1) primary production of OH, 2) conversion of OH to HO<sub>2</sub>, 3) conversion of HO<sub>2</sub> to OH, 4) depletion of OH, 5) depletion of HO<sub>2</sub>. From these five pathways one or two reactions might be selected for sensitivity analysis. The concentrations of the precursors of OH and HO<sub>2</sub> have to be varied over a large scale in this study.

If a constellation is found where high values of the sensitivity coefficient are yielded, a closer look will be necessary to derive an experimental design, since there might be interferences between several reactions for one condition. For a successful experimental design the change in the species concentrations due to a change of a rate constant should be larger than the precision of the measuring instrument. Careful investigation of the discovered constellations will result in practical experiments which enable to validate individual rate constants.

SAPHIR webpage: (<http://www.fz-juelich.de/icg/icg-ii>)



## FTIR study of the ozonolysis of Isoprene and methylbutenol under simulated atmospheric conditions

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Biogenic volatile organic compounds (BVOCs) account for around 90% of hydrocarbon emissions into the Earth's atmosphere ([1], [2]). Several thousand different BVOCs have been identified, the most well known being unsaturated hydrocarbons such as ethene, isoprene, monoterpenes and sesquiterpenes. However, over the last ten years an increasing number of oxygenated BVOCs, such as the methyl-butanol (MBO) have also been detected in field measurement campaigns and plant emission studies ([3], [4]).

In order to determine the environmental impact of biogenic VOCs, a thorough knowledge of the rates and mechanisms for their atmospheric degradation is required. The major atmospheric degradation processes for biogenic VOCs are gas-phase reaction with hydroxyl (OH) radicals, nitrate (NO<sub>3</sub>) radicals and ozone (O<sub>3</sub>). These reactions produce oxidised hydrocarbons, ozone and secondary organic aerosol and, as a result, exert a strong influence on the chemical composition of the atmosphere.

Although a number of studies have been made on the kinetics of the degradation of isoprene, very few studies are available concerning the reactivity of MBO. Furthermore, the mechanism of the atmospheric degradation of isoprene and the speciation of their products are still subject to controversy and very little is known about the reaction products and chemical mechanisms of the reactions with MBO.

To extend the available database on the atmospheric chemistry of biogenic compounds, the reactions of O<sub>3</sub> with isoprene and MBO at 296(±2)K have been investigated in reaction chamber using long-path FTIR spectroscopy. The rate constant for these reactions was determined using an absolute rate technique, yielding a value of  $(1.19 \pm 0.08) \times 10^{17}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> for isoprene and  $(7.5 \pm 0.8) \times 10^{18}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> for MBO. The production yield for formaldehyde (0.69±0.01), methacrolein (0.42±0.02) and methy-vinyl ketone (0.18±0.01) have been found for the ozonolysis of isoprene. For the ozonolysis of MBO, Formaldehyde yield (0.40±0.03) and acetone yield (0.27±0.02) have been determined.

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## Chemical composition of aerosol particles from the oxidation of $\alpha$ -pinene by ozone and OH-radicals (GPP)

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Secondary organic aerosol (SOA) formed by the oxidation of biogenically emitted compounds appears to give a relevant contribution to the global aerosol burden, but the magnitude of this contribution is uncertain (Andreae and Crutzen, 1997). Monoterpenes, such as  $\alpha$ -pinene, have been found to be the main biogenic precursors of SOA. Chemical analysis of the aerosol formed by the oxidation of monoterpenes in chamber experiments, simulating atmospheric reactions, can serve to identify compounds that are characteristic products and thus may be used as 'tracers' of such reactions in the environment. Further, the chemical analysis can give information about which reactions are forming the condensable products.

In the present study, the time dependent chemical composition of aerosol particles, formed by the oxidation of  $\alpha$ -pinene has been investigated by liquid chromatography/mass spectrometry (LC-MSn) using negative and positive ionisation methods (ESI(-) and APCI(+)) (Larsen et al, 2001). The experiments were performed at the EUHORE facility in Valencia (Spain) under various experimental conditions, including dark ozone reactions, photo-smog experiments with low NO<sub>x</sub> mixing ratios and reaction with OH radicals in the absence of NO<sub>x</sub> (H<sub>2</sub>O<sub>2</sub>-photolysis). Particles were sampled on PTFE filters at different stages of the reaction and extracted with methanol. The predominant identified products from  $\alpha$ -pinene in the particulate phase are cis-pinonic acid, cis-pinonic acid and hydroxy-pinonic acid isomers. Another major compound with molecular weight 172 was detected, possibly a hydroxy-carboxylic acid. Besides these major compounds, accounting for 30% to 70% of the identified aerosol products depending on the time of sampling and type of experiment, more than 20 different products have been detected and tentatively assigned based on their molecular weight and responses to the different ionisation modes. The different experiments performed showed that the aerosol formation is mainly caused by the ozonolysis reaction. The highest aerosol yields were observed in the dark ozone experiments and also the highest ratio of mass of identified products to the formed aerosol mass. In this case, assuming a density of 1 g.cm<sup>-3</sup>, the identified chemical components accounted for 30 to 50% of the aerosol mass.

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