

Influence of an organic coating on the reactivity of aqueous aerosols probed by the heterogeneous hydrolysis of N_2O_5

M. Folkers, Th. F. Mentel, and A. Wahner

ICG II: Troposphäre, Forschungszentrum Jülich GmbH, Jülich, Germany

Received 21 February 2003; revised 28 April 2003; accepted 9 May 2003; published 26 June 2003.

[1] Surface-active organic compounds are common constituents of atmospheric aerosol particles. In this work, the effects of organic coatings on the heterogeneous hydrolysis of N_2O_5 was investigated. For this purpose aqueous NH_4HSO_4 particles were coated in situ in a large aerosol chamber. The experiments show that films composed of the ozonolysis products of α -pinene can reduce the reaction probability by more than an order of magnitude. Model calculations indicate that the main cause for the retardation of the hydrolysis is a slower uptake possibly due to a lower solubility of N_2O_5 in the organic film.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0320 Cloud physics and chemistry; 0365 Troposphere—composition and chemistry. **Citation:** Folkers, M., Th. F. Mentel, and A. Wahner, Influence of an organic coating on the reactivity of aqueous aerosols probed by the heterogeneous hydrolysis of N_2O_5 , *Geophys. Res. Lett.*, 30(12), 1644, doi:10.1029/2003GL017168, 2003.

1. Introduction

[2] An important step in the removal of nitrogen oxides from the atmosphere is the heterogeneous conversion of N_2O_5 to HNO_3 during nighttime. In the planetary boundary layer this hydrolysis occurs to a large extent on the surface of aqueous aerosol particles. The heterogeneous N_2O_5 -hydrolysis is well characterized for aqueous inorganic aerosols. The reaction probability γ , i.e. the fraction of collisions of N_2O_5 with the particle surface that lead to the formation of HNO_3 , has been determined for $(\text{NH}_4)_2\text{SO}_4$ [Hu and Abbatt, 1997], NH_4HSO_4 [Mozurkewich and Calvert, 1988], NaNO_3 , Na_2SO_4 , NaHSO_4 [Mentel et al., 1999], H_2SO_4 [Hallquist et al., 2000], and pure water [van Doren et al., 1990].

[3] In addition to the inorganic components, tropospheric aerosols contain various organic compounds which typically constitute 10–70% of the total dry mass of fine particles in the atmosphere [Turpin et al., 2000]. A large part of this organic fraction results from atmospheric oxidation of hydrocarbons of biogenic and anthropogenic origin.

[4] It has been speculated that the organic aerosol fraction must be of importance for the uptake of gases into the particle if the organic compounds act as surfactants and form organic coatings on the surface of the aerosol [Gill et al., 1983]. Field experiments indicate the presence of such organic films on the surface of particles [Pósfai et al., 1998, Tervahattu et al., 2002]. Organic films and dissolved oxidized hydrocarbons in the particu-

late phase possibly reduce the rate of evaporation of water from the droplet [Saxena et al., 1995; Xiong et al., 1998]. Furthermore, organic films may impede the transport of hydrophilic molecules from the gas phase into the droplet. Heterogeneous hydrolysis reactions would be immediately influenced by reductions of the surface reactivity or water availability. It has been demonstrated that a stearic acid coating inhibits the uptake of H_2SO_4 on $(\text{NH}_4)_2\text{SO}_4$ and NaCl particles [Jefferson et al., 1997] and that coating H_2SO_4 aerosol with straight-chain organics retards the rate of neutralization by ammonia [Däumer et al., 1992]. Fried et al. [1994] suspected that organic impurities reduced their rate of the heterogeneous N_2O_5 hydrolysis by up to a factor of 2 under certain experimental conditions.

[5] In this study, the effects of organic coatings on the heterogeneous hydrolysis of N_2O_5 were examined in relation to the film thickness. We used NH_4HSO_4 as inorganic seed aerosol and the ozonolysis products of α -pinene to produce film-forming compounds. α -pinene is the monoterpene with the highest contribution to the global emissions of monoterpenes. Extensive smog chamber studies showed that the ozonolysis of α -pinene like other monoterpenes produces oxidized species e.g. organic acids with vapor pressures that are low enough to condense on existing particles or even induce new particle formation. The main identified products of the α -pinene ozonolysis are pinonaldehyde (6–19%), norpinonic acid and its isomers (4–13%), hydroxy pinonaldehyde (2–11%), pinonic acid (2–8%), pinic acid (3–6%), hydroxy pinonic acid (1–4%), (2,2-dimethyl-3-acetyl)-cyclobutyl formate (1–4%), and norpinonaldehyde (1–3%) [Yu et al., 1999]. The dicarboxylic acids are likely to dominate in aerosol particles since their vapor pressure is lower by a factor of 100–10,000 than that of corresponding monocarboxylic acids [Ludwig and Klemm, 1988].

[6] For an easier detection of changes induced by the coating we first determined reference values for γ for non-coated sulfate and bisulfate particles in our chamber. These values were then compared to the ones obtained in experiments in which the aerosol particles were coated with the ozonolysis products of α -pinene. Finally, to estimate the effect of realistic atmospheric hydrocarbon concentrations on the heterogeneous hydrolysis of N_2O_5 , chamber experiments were performed with particle free outside air.

2. Experimental

[7] The measurements were performed in our dark Aerosol Chamber (volume: 256 m^3) at ambient pressure and temperature. The chamber is constructed as a double wall system with gas tight aluminum outside walls and chemically inert Teflon

FEP inside walls and has a surface to volume ratio of better than 1 m^{-1} (for details see *Mentel et al.* [1996]).

[8] The α -pinene experiments were conducted in synthetic air which was produced by evaporation of liquid N_2 (LIN Lipur 6.0) and liquid O_2 (LOX Lipur 6.0) with a ratio of 3.73:1. The reference experiments were performed in outside air which was purified by a particle filter stage. Prior to each experiment the Aerosol Chamber is thoroughly flushed with clean air. The outside air is dried by circulating it across a molecular sieve. In all experiments the air is humidified to the desired relative humidity with high purity water.

[9] The experiments are conducted as follows: The aerosol is generated in a small pre-chamber by spraying dilute salt solutions under deliquescent conditions and flushed into the Aerosol Chamber by the production air stream. The particle size distribution which covers a size range of approximately 20 nm–5 μm is measured with two instruments: a scanning mobility particle sizer (SMPS: TSI EC 3071, CPC 3022A) for particle diameters of 20–500 nm and an aerodynamic particle sizer (APS: TSI 3320, dilution stage: 3302A) for particle diameters larger than 700 nm. Shortly after generation the particle size distributions in the chamber are slightly distorted lognormal distributions with a count median diameter of 120–140 nm and a geometric standard deviation of 2.0–2.2. The aerosol composition is determined on-line by steam jet aerosol collection/ion chromatography (SJAC/IC) [*Slanina et al.*, 2001].

[10] N_2O_5 is formed in-situ by reaction of NO_2 and O_3 in our chamber. About one hour after aerosol production first $\approx 1.7 \text{ ppm}$ NO_2 and then $\approx 1.7 \text{ ppm}$ O_3 is added to the chamber. A sufficiently high total aerosol surface in the chamber ensures that the formation and hydrolysis of N_2O_5 is faster than the formation of oxidation products with low vapor pressure by ozonolysis of unsaturated hydrocarbons. Therefore potential impurities in our chamber air do not interfere with the correct determination of γ .

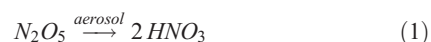
[11] In all coating experiments NH_4HSO_4 was chosen as seed aerosol. The uptake of the heterogeneously formed nitric acid into this acidic aerosol is negligible. The coating experiments were conducted at 60% relative humidity which is well above the deliquescence point of NH_4HSO_4 -aerosol (40% r.h.) to prevent recrystallization of the particles in the course of the experiment. Organic coatings on the particles were produced in-situ by reversing the order of the gas addition. After the complete ozonolysis of either pure α -pinene (1.22 ppm and 11.4 ppb, respectively) or a mix of unsaturated hydrocarbons in outside air we added NO_2 to the chamber.

[12] The gas-phase concentrations of NO_2 , N_2O_5 and HNO_3 are monitored by high resolution FTIR absorption spectroscopy (Bruker IFS 120HR), O_3 is monitored by UV absorption (Ansyc O₃ 41M). The hydrocarbon composition of the chamber is analyzed with a GC-MS-System [*Folkers*, 2002a].

3. Determination of γ

[13] The reaction probability γ is determined through box model calculations (for details see [*Folkers*, 2002b]). The box model consists of a gas phase mechanism for the $\text{NO}_x/\text{O}_3/\text{NO}_y$ chemistry, experimentally determined chamber specific loss terms [*Mentel et al.*, 1996], and a linear

source term to simulate the trace gas addition. The heterogeneous hydrolysis of N_2O_5 is included by the reaction



The rate of the heterogeneous reaction is derived from the kinetic theory of gases and is given by

$$k_1(t) = \frac{1}{4} \cdot \bar{c}_{\text{N}_2\text{O}_5} \cdot \gamma \cdot S_{\text{tot}}(t) \quad (2)$$

where $\bar{c}_{\text{N}_2\text{O}_5}$ is the mean molecular velocity of N_2O_5 and $S_{\text{tot}}(t)$ is the aerosol surface density as a function of time. The experimental boundary conditions (temperature, pressure, relative humidity) and $S_{\text{tot}}(t)$ (see below) are constrained to the experimental data in the model calculations. The reaction probability is determined by least squares fitting the model to the observed values of $[\text{N}_2\text{O}_5](t)$, $[\text{NO}_2](t)$, and $[\text{O}_3](t)$ with γ as free parameter (FACSIMILE for Windows, Version 2.0.98).

[14] Since the reaction rate of the heterogeneous hydrolysis is determined by the product $\gamma \cdot S_{\text{tot}}$ an accurate determination of S_{tot} is of central importance for a precise determination of γ . To derive S_{tot} from the measured particle size distributions the combined data from the SMPS and APS are fitted by a modified log-normal function and integrated over the whole size range to yield S_{tot} as a function of time (for details see [*Folkers*, 2002b]).

[15] The goodness of the determination of S_{tot} was indirectly evaluated by determining both N_{tot} and V_{tot} through independent methods. The total particle number density N_{tot} was determined with an additional CPC. Linear regression of N_{tot} determined by the CPC and N_{tot} as derived from the particle size measurements yields a non significant intercept and a slope of 1.04 ± 0.004 . The total volume density V_{tot} was converted into the total anion density in the chamber and compared with SJAC/IC measurements. The deviation between the two values is less than 6%. Therefore it is assumed that the aerosol surface density can be determined with an accuracy better than 10% from the measured size distributions. Thus, an accurate determination of γ is possible.

4. Results and Discussion

[16] In a first step we determined reference values for non-coated sulfate and bisulfate particles in our chamber. Our experiments show that for metastable and deliquescent particles $\gamma \approx 0.02$ (see Table 1) which is at the lower range of the literature data but similar to γ for the respective sodium salts that were determined in the Aerosol Chamber [*Mentel et al.*, 1999]. The reaction probability is fairly independent of the aerosol substrate and the relative humidity as expected from the ionic mechanism proposed by *Mozurkewich and Calvert* [1988].

[17] In the first coating experiment we ozonolysed 1.22 ppm α -pinene. The results of the trace gas and particle measurements of this experiment are shown in Figure 1. Despite the large number of seed particles in the chamber ($17,000 \text{ cm}^{-3}$) ozonolysis of 1.22 ppm α -pinene induced new particle formation (lower panel in Figure 1). The growth of the particles reveals that approximately 50% of the ozonolysed α -pinene is converted into particulate matter. As a result, the fraction of the inorganic aerosol constitutes

Table 1. Reaction Probabilities for Purely Inorganic and Organically Coated Aerosols

Aerosol	[α -pinene]	r.h./%	$\gamma/10^{-2}$
NH ₄ HSO ₄ ^a		45–76	5
(NH ₄) ₂ SO ₄ ^b		50–93	2–5
(NH ₄) ₂ SO ₄		62.1	1.82 + 0.34/–0.30
NH ₄ HSO ₄		60.1	1.87 + 0.34/–0.24
NH ₄ HSO ₄		79.7	1.86 + 0.43/–0.35
Na ₂ SO ₄		82.5	1.87 + 0.32/–0.28
NH ₄ HSO ₄	1.22 ppm	57.6	0.054 + 0.017/–0.012
–	1.22 ppm	58.1	0.045 + 0.015/–0.009
NH ₄ HSO ₄	11.4 ppb	60.3	0.34 + 0.15/–0.12
NH ₄ HSO ₄ , (NH ₄) ₂ SO ₄	particle free ambient air	55–83	0.25–0.63

The last row summarizes the results from multiple experiments that were performed in particle free outside air (atmospheric concentrations of unsaturated hydrocarbons, see text). All of the experiments were conducted at room temperature ($T = 293\text{ K} - 297\text{ K}$).

^a[Mozurkewich and Calvert, 1988]. ^b[Hu and Abbatt, 1997].

only about 3% to the total particle surface and about 7% to the particle volume. The hydrolysis on this almost purely organic aerosol is much slower than on aqueous inorganic aerosols. The reaction probability is reduced by a factor of 35 compared to pure NH₄HSO₄-aerosol at the same relative humidity (compare Table 1). This value for γ represents an average $\bar{\gamma}$ for the pure organic and coated inorganic particles since we can not differentiate between them:

$$\bar{\gamma} = \gamma_{\text{coated}} \cdot \frac{S_{\text{coated}}}{S_{\text{tot}}} + \gamma_{\text{organic}} \cdot \frac{S_{\text{organic}}}{S_{\text{tot}}} \quad (3)$$

In an experiment with pure organic particles (no seed aerosol) we determined the maximum possible reduction of γ in the presence of α -pinene oxidation products. In this experiment the hydrolysis is even slower than in the experiment with inorganic seed particles: $\gamma = 4.5 \cdot 10^{-4}$, it is reduced by a factor of 42 compared to the reference value. Thus, it can be concluded that the large reduction of γ in the first experiment is due to the deactivation of the particle surface by the organic film. If the ozonolysis of α -pinene had produced an externally mixed aerosol with a hydrolysis inert organic aerosol fraction the reaction rate would have been faster than observed in the experiment. Virkkula *et al.* [1999] showed that pure organic particles formed by ozonolysis of α -pinene are only slightly hygroscopic with a hygroscopic growth factor of 1.07. The low value for γ is therefore an indication that the organic particles do not contain enough water to allow for the dissociation of N₂O₅. Thus, the hydrolysis is inhibited.

[18] In a third experiment only 11.4 ppb α -pinene (i.e. 5% of the particle volume at the time of the ozonolysis) were added to the chamber air. We did not observe new particle formation. Due to the high ionic strengths of the aerosol particles, the solubility of the organic compounds in the aqueous solution is low (salting-out-effect). E.g. Shulman *et al.* [1996] showed that cis-pinonic acid is only slightly soluble in concentrated solutions of (NH₄)₂SO₄ and NH₄HSO₄. The oxidation products of α -pinene therefore mostly remain on the surface forming an organic film with a thickness of $\approx 15\text{ nm}$ on the aqueous droplets. It is not possible to determine the thickness of the organic layer on the particles in our chamber through particle size measurements because the temporal evolution of the particle size distribution is a convolution of several processes like

sedimentation, coagulation, condensation, and evaporation. The reaction probability on this organically coated aerosol was reduced by a factor of 5 compared to the reference value of 0.02 for the sulfate aerosols (compare Table 1).

[19] To demonstrate the importance of this process under atmospheric conditions we conducted experiments in particle free outside air. The hydrocarbon content of the air was characterized with a GC-MS system [Folkers, 2002a] which is able to detect both oxidized organic compounds and monoterpenes. E.g. the monoterpene concentrations in the air were in the order of 30 ppt. In these experiments with ambient concentrations of unsaturated hydrocarbons we observed a reduction of γ by a factor of 3–7 compared to the reference value (see last row in Table 1). This value is comparable to the value obtained in the 11 ppb α -pinene experiment.

[20] To clarify the cause for the observed large retardation of the hydrolysis we performed model calculations. Coating an aqueous particle with a nonpolar organic film could have two consequences for the reaction which involves the uptake and subsequent solvation of a hydrophilic molecule in a liquid droplet as well as reactions in the liquid phase: 1. The initial solvation of a polar gas is slowed down in the presence of a nonpolar coating. The rate of this initial solvation depends on both the mass accommodation coefficient α and the Henry's law constant K_H . 2. The coating represents a diffusion barrier for the mass transfer of N₂O₅ if a reaction does not occur in the organic phase. The rate of the hydrolysis then decreases with increasing film thickness.

[21] We extended our previously described box model to include the chemical reactions in the particles assuming the ionic mechanism for the hydrolysis, aqueous phase diffusion and N₂O₅, HNO₃ transfer at the gas/liquid interface. The solubility of N₂O₅ in the organic phase is given by the partition coefficient K_P between the organic and aqueous phase:

$$K_P = \frac{K_{H,o}}{K_{H,aq}} \quad (4)$$

The reaction constants of the liquid phase reactions, the Henry's law constant and the liquid phase diffusion coefficients were taken as discussed by Mentel *et al.* [1999]. The

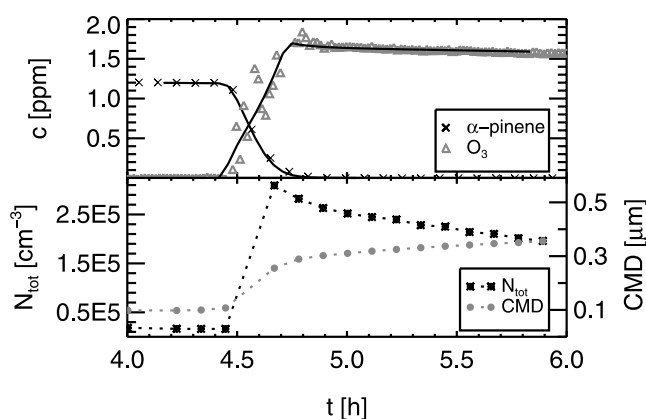


Figure 1. Time evolution of trace gas concentrations and particle size distribution. The experimental data for α -pinene and O₃ (symbols) are in good agreement with box model calculations (solid lines) that take into account the HO_x/O₃/ α -pinene-chemistry and an OH-yield of 76% from the α -pinene ozonolysis [Chew and Atkinson, 1996].

data of the experiments without organic coatings was used to determine the rate constant for the dissociation of N_2O_5 into NO_2^+ and NO_3^- ($k \approx 2.5 \cdot 10^{-5} \text{ s}^{-1}$). The particle size distribution was approximated with 20 size classes to match the experimental data. Each particle size class was subdivided into 25 cells of equal volume. In the model calculations it is assumed that organic coatings behave like a separate bulk phase through which the gases must diffuse before they reach the aqueous core where the reaction occurs.

[22] We alternatively modified α , the organic volume fraction (i.e. the film thickness), and K_P assuming a volume fraction of the organic film of 10%. To simulate both a more solid-like and a liquid film the organic phase diffusion coefficient was varied from $1 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ to $1 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The results demonstrate that only a minor fraction of the observed reduction of γ can be attributed to the coating acting as a diffusion barrier for the mass transfer of gaseous N_2O_5 . A volume fraction of the organic component of $\approx 60\text{--}75\%$ (solid-like/liquid film) is required to reduce γ by a factor of 3. On the other hand, such a reduction would also be observed if α was a factor of 8 smaller. For an organic volume fraction of 10% γ is reduced by a factor of 3 if $K_P = (0.5\text{--}3) \cdot 10^{-2}$ which is comparable to the partitioning of e.g. ethanol between hexane and water. From these results it is concluded that the main cause for the retardation of the hydrolysis in the presence of organic films is a smaller Henry's law constant or mass accommodation coefficient for the films, thus a slower initial solvation of N_2O_5 in the droplets.

5. Conclusion for the Atmosphere

[23] Organic coatings on atmospheric particles can significantly retard the heterogeneous N_2O_5 hydrolysis. Another process which can markedly retard this reaction is the nitrate effect [Mentel *et al.*, 1999]. As a consequence the removal of nitrogen oxides from the boundary layer to which the heterogeneous hydrolysis of N_2O_5 contributes an estimated 30–50% may be significantly slower than previously believed and considered up to now in atmospheric models. An overestimation of one of the main removal mechanisms for nitrogen oxides from the atmosphere raises the question about unknown or underestimated loss paths especially during nighttime.

[24] In addition to water insoluble organic compounds like the investigated organic films, atmospheric particles contain various water soluble organic compounds. Thus, further research is necessary to fully evaluate the importance of organic aerosol components on the reactivity of atmospheric aerosols.

[25] **Acknowledgments.** We thank A. Folkers and S. Rodríguez Bares for analyzing the hydrocarbon composition of the chamber air. We also thank H. Henk for analyzing the aerosol composition. This work was supported by an EC grant (EVK2-CT-2001-00124).

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M. Folkers, Th. F. Mentel, and A. Wahner, ICG II: Troposphäre, Forschungszentrum Jülich, Leo-Brandt-Str., 52425 Jülich, Germany. (m.folkers@fz-juelich.de)