



# Heterogeneous Interaction of Ozone, NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> with Soot Aerosol

A contribution to subproject CMD

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## Introduction

Atmospheric soot concentrations range from 0.002  $\mu\text{g}/\text{m}^3$  in the stratosphere up to 40  $\mu\text{g}/\text{m}^3$  in the polluted urban troposphere. Due to its irregular agglomerate structure soot aerosol offers a large surface for interactions with reactive trace gases like ozone. Recent laboratory studies and model results indicated a possible effect of soot surface reactions on the nitrogen partitioning in the troposphere (Kalberer *et al.*, 1996; Hauglustaine *et al.*, 1997; Rogaski *et al.*, 1997) and on the stratospheric (Lary *et al.*, 1997) and tropospheric ozone concentrations (Bekki *et al.*, 1997).

However, the model predictions are still speculative because the required soot surface reaction probabilities are either unknown or uncertain. Furthermore, most previous laboratory measurements of heterogeneous reaction rates have been carried out on short time scales using bulk samples and high surface to trace gas concentration ratios compared with atmospheric situations. We report reaction probabilities of ozone and nitrogen oxides on airborne soot particles determined from aerosol chamber experiments lasting up to several days.

## Experimental and modelling

To investigate the kinetics and mechanisms of the soot - trace gas interactions we use an evacuable aerosol chamber of about 80 m<sup>3</sup> volume which can be thermostated in the temperature range from 183 to 333 K. In this aerosol chamber AIDA (Bunz *et al.*, 1996) experiments can be carried out close to atmospheric conditions on time scales of several days, thus comparable to tropospheric aerosol lifetimes.

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Soot particles were generated using a graphite spark generator (GfG 1000, Pallas). The initial mass concentrations typically amounted to about  $200 \mu\text{g}/\text{m}^3$  corresponding to roughly  $2.7 \text{ m}^2$  of accessible soot surface area inside the reaction chamber. Ozone was generated with silent discharge generators (Witte, Sorbios) using  $\text{O}_2$  (5.0).  $\text{NO}_2$  was introduced from a 0.1 % mixture in synthetic air (99.5 % purity).  $\text{N}_2\text{O}_5$  was synthesised by oxidation of NO with  $\text{O}_3$  and used as a 0.4 % mixture in nitrogen. Aerosol characterisation included number concentration (CNC, TSI), mass concentration (filter samples and coulometric analysis), size distribution (SMPS, TSI), and particle shape (electron microscopy). Trace gas concentrations were monitored *in-situ* employing a long path absorption system (112 m, White type) equipped with a FT-IR/visible spectrometer (IFS 66v, Bruker) as well as *ex-situ* with  $\text{O}_3$  and  $\text{NO}/\text{NO}_x$  monitors. To obtain mechanistic information on soot surface processes, we systematically varied experimental parameters: soot mass concentrations between 50 and  $200 \mu\text{g}/\text{m}^3$ , initial trace gas concentrations between 100 ppb and 10 ppm, and the temperature between 238 and 330 K. The dew point in all experiments was below 213 K.

The aerosol and trace gas measurement data were analysed theoretically by comparing them to the results of model calculations with an improved version of the aerosol physico-chemical simulation code COSIMA. This programme simultaneously accounts for the dynamics of fractal particles, particle sources and sampling losses, gas to surface transport, and homogeneous as well as heterogeneous chemistry. Fitting the model results to the experimental observations, an effective minimal set of pseudo-elementary reactions and the corresponding reaction probabilities could be established.

## Results

The ozone depletion rate depends significantly on temperature (see Fig. 1) as well as on the initial  $[\text{O}_3]/[\text{surface}]$  concentration ratio and on time. Three different regimes can be distinguished. On fresh soot a fast surface coverage process (1) takes place, which cannot be time-resolved in the AIDA chamber. However, the amount of ozone consumed by this process is equivalent to one monolayer as can be estimated from the difference between the concentration expected after introduction of a known amount of ozone and the concentration measured after mixing. For this process an uptake coefficient  $\alpha \approx 3 \times 10^{-3}$  has previously been measured (Stephens *et al.*, 1986; Fendel *et al.*, 1995; Rogaski *et al.*, 1997). Following the rapid surface saturation a much slower  $\text{O}_3$  depletion (2) was observed. The upper limit of the reaction probability is given by  $\gamma = 2 \times 10^{-6}$  at 296 K and 100 ppb initial ozone concentration.  $\gamma$  decreases with temperature and with increasing initial ozone concentration, the latter

indicating an effective reaction order of less than one in [O<sub>3</sub>]. Therefore, a minimum of two independent pseudo elementary reactions, one of first order in [O<sub>3</sub>] and one of zeroth order, are required to model the observed recoverage rate for reactive surface sites.

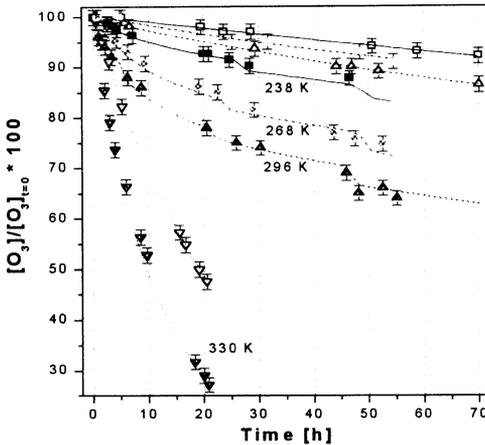


Fig.1: Temperature dependence of the ozone ([O<sub>3</sub>]<sub>t=0</sub> = 100–120 ppb) decay on soot particles (C<sub>t=0</sub> ≈ 200 μg/m<sup>3</sup>). The measurements have been made without soot (open symbols, lines are single exponential fits to the data, 1<sup>st</sup> order wall loss) and with soot (closed symbols, lines depict the COSIMA model results). The steps are due to dilution during filter sampling.

Parallel to recoverage steps a passivation (3) of reaction sites occurred with a characteristic time  $\tau = 1/k_3 = 12$  h. No significant dependence on the initial ozone concentration or on temperature could be detected for  $\tau$ .

The whole set of experimental data can be described with COSIMA model calculations assuming a minimal set of pseudo elementary reactions (Table 1).

Based on this reaction scheme, we deduced an analytical expression which allows us to calculate effective reaction probabilities ( $\gamma_{\text{eff}}$ ) for the ozone depletion on soot:

$$\gamma_{\text{eff}} = \left[ 2 \cdot (\gamma_{2a} + \gamma_{2b}) + \frac{2,6 \cdot 10^{15} \cdot k_{2c}}{[\text{O}_3] \cdot \langle c \rangle} \right] \cdot e^{-k_3 t}$$

[ $\langle c \rangle$ ]: mean molecular velocity (cm/s),  $t$ : reaction time (s), [O<sub>3</sub>]: ozone concentration (cm<sup>-3</sup>)

Table 1: Minimum set of reactions necessary to describe the experimental observations.

No	Reaction	Rate at 296 K	Comments	Ref.
1	$\text{SS} + \text{O}_3 \rightarrow \text{SSO} + \text{O}_2$	$\alpha_1 = 3.3 \times 10^{-3}$	fast	Fendel <i>et al.</i>
2a	$\text{SSO} + \text{O}_3 \rightarrow \text{SS} + 2 \text{O}_2$	$\gamma_{2a} + \gamma_{2b} = (1.0 \pm 0.3) \times 10^{-7}$	slow	this work
2b	$\text{SSO} + \text{O}_3 \rightarrow \text{SS}' + \text{CO}_2 + \text{O}_2$			
2c	$\text{SSO} \rightarrow \text{SS}' + \text{CO}$	$k_{2c} = (4.5 \pm 1.0) \times 10^{-5}$ [s <sup>-1</sup> ]	slow	this work
3	$\text{SSO} \rightarrow \text{SS}_p$	$k_3 = (2.3 \pm 1.0) \times 10^{-5}$ [s <sup>-1</sup> ]	slow passivation	this work
4	$\text{O}_3 \rightarrow \text{products}$	$k_4 = (6.8 \pm 2.0) \times 10^{-7}$ [s <sup>-1</sup> ]	wall loss	this work

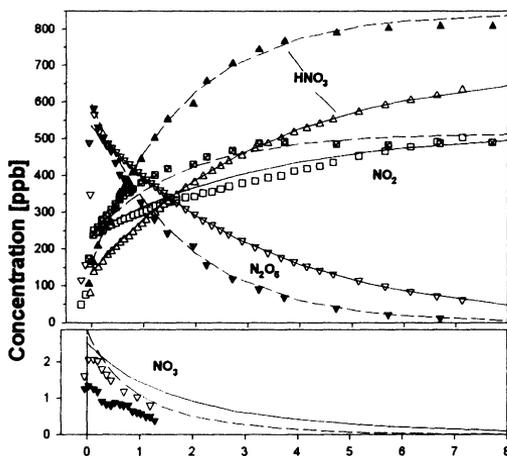


Fig.2: Measured behaviour of trace gases (initial: N<sub>2</sub>O<sub>5</sub>) at 296 K in the presence (filled symbols) and absence (open symbols) of soot aerosol. The lines represent results from COSIMA calculations.

For  $\text{NO}_2$  the initial uptake coefficient on fresh airborne soot samples is only about  $4 \times 10^{-4}$  (Kalberer *et al.*, 1996) and thus an order of magnitude smaller than for ozone. The following decomposition process (formation of NO) is very slow under dry conditions, probably due to rapid passivation of reactive surface sites. In fact, starting with an initial  $\text{NO}_2$  concentration of about 100 ppb, we were not able to detect any significant loss at all within the precision of our measurement ( $\pm 2$  ppb) nor did we observe any significant formation of NO within 6 days.

With a dew point below 213 K during our experiments homogeneous gas phase hydrolysis of  $\text{N}_2\text{O}_5$  is completely negligible. In the absence of aerosol particles the removal rate is controlled by wall losses, where the molecules are converted to  $\text{HNO}_3$ . In the presence of soot agglomerates the  $\text{N}_2\text{O}_5$  life time roughly halves while the rate of  $\text{HNO}_3$  formation doubles (Figs. 2 and 3). Furthermore,  $\text{NO}_3$  is much more rapidly depleted. In experiments starting with  $\text{N}_2\text{O}_5$  and without  $\text{O}_3$  (Fig. 2), also an increase of  $\text{NO}_2$  formation results from the addition of soot.

Fig. 3 presents a typical result for the interaction of soot particles with a mixture of  $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$  under dry conditions.

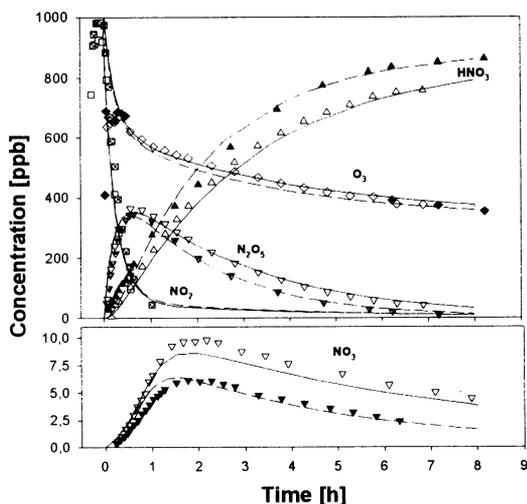
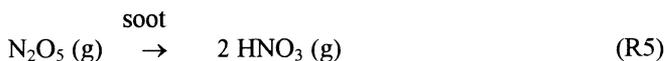


Fig. 3: Measured behaviour of trace gases (initial:  $\text{NO}_2$  and  $\text{O}_3$ ) at 296 K in the presence (filled symbols) and absence (open symbols) of soot aerosol. The lines represent results from COSIMA calculations.

Here the nitrogen chemistry was initiated by introducing about 1 ppm NO<sub>2</sub> and 1 ppm ozone into the chamber. Practically no additional ozone is destroyed in the presence of soot. Our experiments performed so far may be consistently interpreted by supplementing the homogeneous gas phase reaction scheme with the two heterogeneous processes:



The respective reaction probabilities were estimated to  $\gamma(\text{R5}) = (2.5 \pm 1.5) \times 10^{-5}$  and  $\gamma(\text{R6}) = (3 \pm 1) \cdot 10^{-6}$ . Still further studies are necessary to rule out definitely the possibility of direct NO<sub>3</sub> loss processes like: NO<sub>3</sub> + soot → NO + products or NO<sub>3</sub> + soot → NO<sub>2</sub> + products.

## Conclusions

Under dry conditions spark generated soot depletes ozone with an initial reaction probability  $\gamma = 2 \times 10^{-6}$  at 296 K but the soot is largely passivated by ozone within one day and the reaction is much slower at lower temperatures. The simultaneous presence of NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and HNO<sub>3</sub> suppresses the ozone loss on soot particles much faster than observed for the isolated process. These results suggest that atmospheric ozone loss on soot surfaces has been overestimated in recent model studies by (Lary *et al.*, 1997) and (Bekki *et al.*, 1997). Further investigations including soot particles from combustion sources as well as experiments at higher humidities are under way to substantiate this conclusion. Similarly, the reduction of NO<sub>2</sub> on soot as an isolated process is negligible in dry air. In contrast to NO<sub>2</sub> the atmospheric lifetime of higher oxides of nitrogen can be significantly reduced by soot particles. Furthermore N<sub>2</sub>O<sub>5</sub> is efficiently converted to HNO<sub>3</sub> on the soot surface, even if only trace amounts of water are present. Both effects could be relevant with respect to night-time atmospheric chemistry.

Complementary to short time laboratory experiments studies on airborne material conducted over several days are indispensable to assess realistically the possible impact of soot particles on atmospheric chemistry. Due to the existence of saturation and passivation processes the extrapolation of results from investigations covering only short time scales to atmospheric conditions can be severely misleading.



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