EXPERIMENTAL STUDIES OF THE HETEROGENEOUS KINETICS OF THE *OH* RADICAL WITH TERBUTHYLAZINE ADSORBED ON SELF-SYNTHESIZED SILICA PARTICLES

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Introduction

Atmospheric lifetimes of pesticides are limited by reactions with OH, which have been studied for a long time. Most studies were focused on the gas phase and only very few experiments on semivolatile pesticides to investigate their OH reactions with aerosol-borne compounds. In the present study we reinvestigated the reaction of gas-phase OH with aerosol-borne terbuthylazine (TBA), studied by Palm et al. (1997)[1] on Aerosil 200 (commercial SiO_2 particles with <10 nm diameter), on monodisperse, self-synthesized SiO_2 particles (diameter around 160 nm) in an aerosol smog chamber.

Materials and methods

The experiments were performed in a low temperature aerosol simulation chamber (LOTASC) at 25°C. Figure 1 shows a schematic diagram of the chamber; for a detailed description see http://www.eurochamp.org/chambers/lotasc/. Photochemical degradation of methyl nitrite by fluorescent lamps (Osram Eversun) was used to produce OH radicals in the chamber. The following hydrocarbons were used as reference compounds to calculate the OH level: n-pentane (Grüssing, 99%), n-heptane (Fluka, UV spectroscopy grade, >260 nm, >99%), 2,2-dimethylbutane (Janssen Chimica, 96%), 2,2,4-trimethylpentane (Janssen Chimica, 99+%), 2,2,3,3-tetramethylbutane (Sigma-Aldrich, ≥94%), toluene (Carl Roth, RotiSolv HPLC, ≥99.8%). Perfluorohexane (Aldrich, 99%) was present as an inert standard and to correct for dilution. The OH concentration was calculated[1] based on the known rate constants for the gas-phase reactions of the hydrocarbons with OH.

As most Aerosil materials would produce agglomerates during our experimental application, we synthesized a monodisperse SiO_2 powder by the Stöber process[2] and used it as carrier particles for our study. By adjusting the ratio of the reactants tetraethylsilicate, ammonia and water, the diameter of the SiO_2 particles was controlled[2] to obtain spherical particles with a narrow size distribution around 160 nm diameter (Figure 2). The SiO_2 powder (1 g) was mixed with TBA (47 mg) dissolved in dichloromethane and dried in a rotary evaporator (Edmund Bühler, Type RV2) to provide a stock of the aerosol material. An aqueous suspension of the coated particles (37 mg in 50 ml bidistilled water) was injected into the chamber before the hydrocarbons (10 ppb each) were injected. The suspension was treated in an ultrasonic bath for 30 minutes in order to minimize agglomeration and then introduced into the chamber by a motor-driven syringe (Perfusor Secura, Braun), atomizing it by a heated air flow through an appropriate nozzle (Schlick S6). When introduced into the chamber, a large amount of the particles remain as single particles (Figure 3). Filter samples were taken on Teflon filters (Sartorius, PTFE filter, d = 25 mm, pore size = 0.2 μm), and purified air was fed into the chamber through a bypass to keep the pressure constant. The mass of four filters samples each was determined by a microbalance (Sartorius, SC01) after charge neutralization by beta radiation from [85]Kr to determine the decrease of the aerosol density by deposition (and sampling). Another 4-6 filter samples were extracted with 1 mL of dichloromethane each, supported by an ultrasonic bath. The aerosol particles were removed by a centrifuge (Heraeus, Biofuge A), and the solution was analyzed for TBA by GC-FID, employing on-column injection (Siemens-Sichromat-1, column: CP-SIL-5CB, 1.13μm film thickness, i.d.=0.32 mm; carrier gas: nitrogen at 2 bar). The values for TBA were finally normalized for sampling volume and interpolated total aerosol mass.
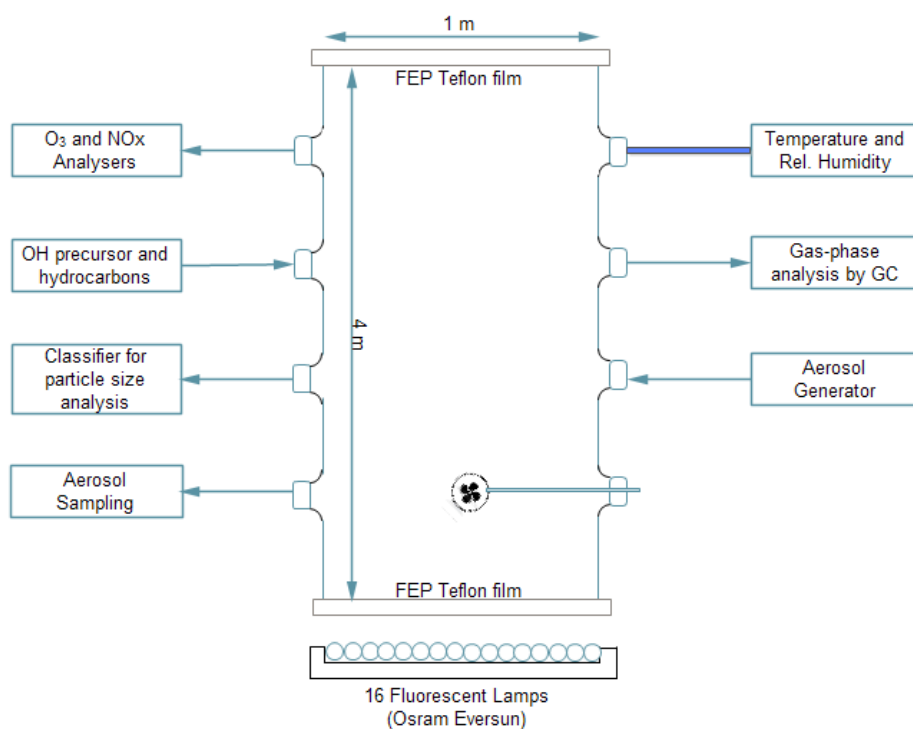
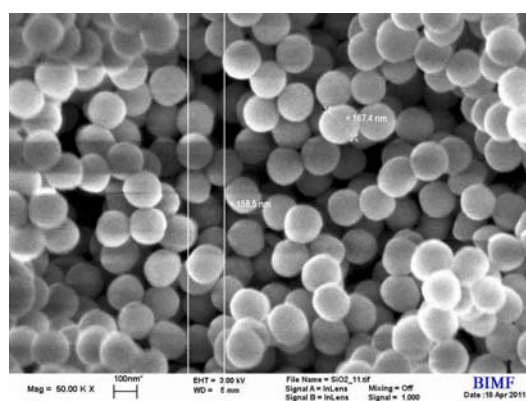Figure 1. Glass chamber LOTASC (Low Temperature Aerosol Simulation Chamber).

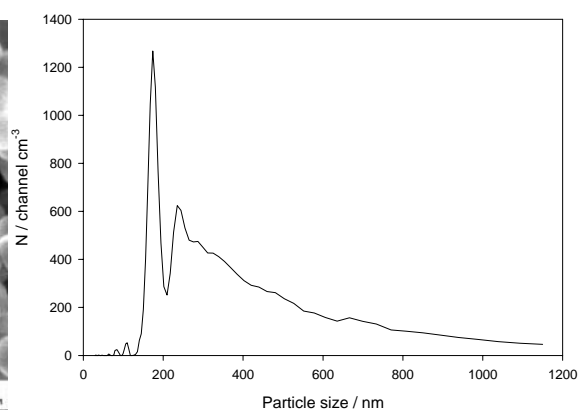Figure 2: SEM images of the self-synthesized SiO$_2$ particles

Figure 3: Size distribution of SiO$_2$ particles suspended in chamber, measured by an electrostatic classifier (TSI, model 3071)

Results and discussion

The OH-radical exposure was calculated as time integral of concentration[1] from the fairly exponential (except for a more rapid, initial consumption) loss of the hydrocarbons, measured by GC-FID (Figure 4), using

well-known OH reaction rate constants. A second order rate constant for the reaction of gaseous OH with the adsorbed TBA can be obtained from the slope of ln [TBA] versus the OH exposure of the coated particles (Figure 5).
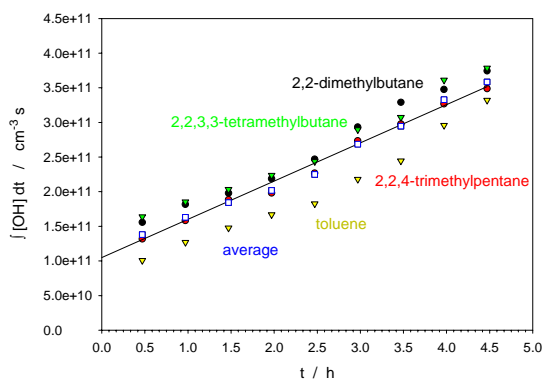

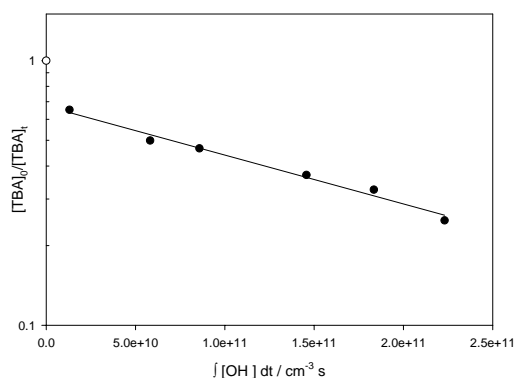Figure 4: Integral OH concentration (exposure) derived from different hydrocarbons versus time

Figure 5: Semilogarithmic plot of relative ratios of TBA on the aerosol versus OH exposure

Figure 6 shows the observed dependence of k^I_{obs} on the OH radical concentration as blue diamonds. Instead of the linear dependence of the previous study[1] on Aerosil 200 (corresponding to a direct reaction of OH with the adsorbed TBA according to an Eley-Rideal mechanism), k^I_{obs} approaches a limiting value, k^I_{max}, at high [OH]. This behavior corresponds to the Langmuir- Hinshelwood mechanism, governed by a reversible adsorption of OH and leading to equation 1.

$$k^I_{obs} = \frac{k^I_{max} \cdot K_{OH} \cdot [\text{OH}]}{(1 + K_{OH} \cdot [\text{OH}])} = k_{OH} \cdot [\text{OH}]$$ (1)

where k^I_{max} is the maximum rate constant that would be observed at high OH radical concentrations, k^I_{obs} is the experimental pseudo-first-order rate constant, K_{OH} the OH radical gas-to-surface adsorption equilibrium constant and [OH] is the gas-phase OH radical concentration. Such a mechanism has been applied before by Ammann et al.[3] to explain the kinetics of surface reactions of ozone with semivolatile compounds.

We conclude that both terbuthylazine and gaseous OH radicals have to become adsorbed to the SiO_2-particle surface before reaction. The experimental results for the rate constant of the reaction of aerosol-borne terbuthylazine with OH radicals according to the Langmuir-Hinshelwood mechanism can be summarized as $k_{obs}=1.4 \cdot 10^{-11}$ [OH]/ $(1+1.5 \cdot 10^{-7}$ [OH])), where the limiting slope for [OH]=>0 according to an Eley-Rideal mechanism leads to $k_{Eley-Rideal} = 1.4 \times 10^{-11}$ $cm^3 s^{-1}$.

Repetitive experiments were also performed using Aerosil 200 as carrier particles. The results of Aerosil 200 in this study (black points in figure 6) show reasonable agreement with the previous results from Palm et al. (1997)[1] of $k_{OH}=(1.1\pm0.2) \times 10^{-11}$ $cm^3 s^{-1}$ (yellow points in figure 6). The Eley-Rideal regression from the combined data on Aerosil 200 lead to the dotted line, $k_{Eley-Rideal} =(1.4\pm0.35) \times 10^{-11}$ $cm^3 s^{-1}$. Although the results on Aerosil 200 appear to follow a linear regression, which would indicate an Eley-Rideal regression where the OH radicals can freely access the terbuthylazine adsorbed on the aerosol surface, one may fit a Langmuir-Hinshelwood regression to the combined data points of Aerosil 200 to obtain the expression $k_{obs}=2 \cdot 10^{-11}$ [OH]/ $(1+8 \cdot 10^{-8}$ [OH] with a quite large statistical error of the parameters (dashed curve, Aerosil 200).
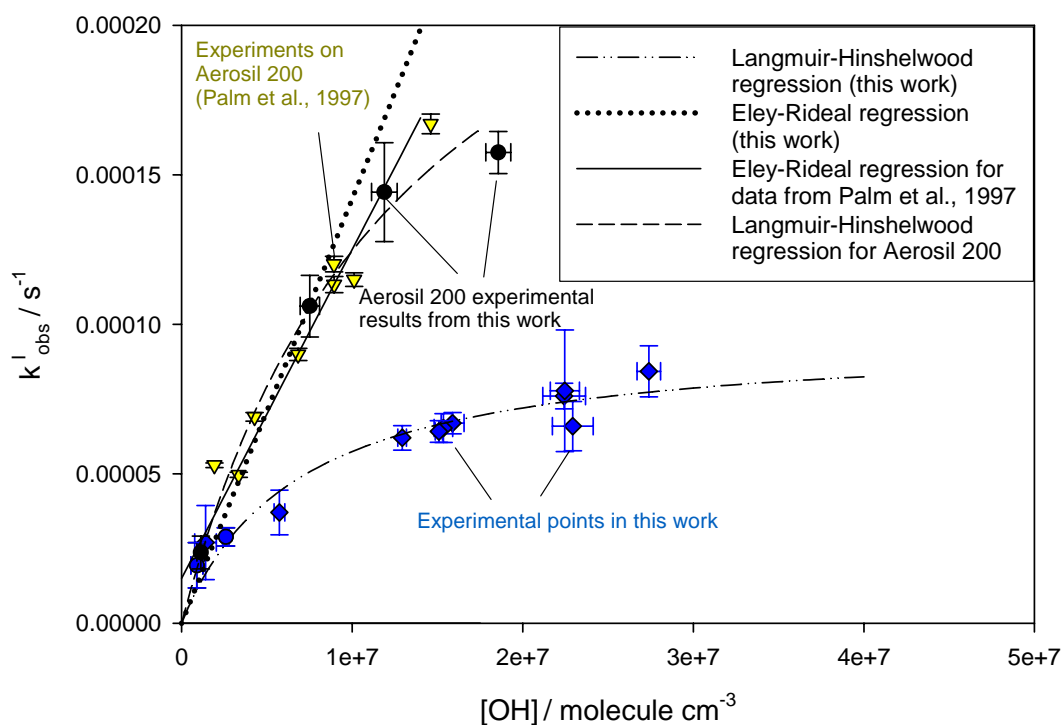
Figure 6: Experimental pseudo-first-order rate constant, k^I_{obs}, for the loss of aerosol-borne TBA versus the OH radical concentration in comparison with experiments on Aerosil 200 as carrier particles.

The consequences of this behavior for semivolatile environmental aerosol-borne pesticides are not clear at the present time, since environmental aerosols cannot be considered to be inert against OH radicals. On the other hand, the Eley-Rideal values may still be taken as a model for the gas-phase rate constant.

References
1. Palm W-U, Elend M, Krüger H-U, Zetzsch C. (1997); *Environ Sci Technol*. 31: 3389–3396
2. Stöber W, Fink A, Bohn E. (1968); *J Colloid Interface Sci*. 26: 62-69
2. Ammann M, Pöschl U, Rudich Y. (2003); *Phys Chem Chem Phys*. 5: 351–356