

This discussion paper is/has been under review for the journal *Atmospheric Chemistry and Physics (ACP)*. Please refer to the corresponding final paper in *ACP* if available.

Validation of an experimental setup to study atmospheric heterogeneous ozonolysis of semi-volatile organic compounds

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Received: 17 September 008 – Accepted: 18 September 2008
– Published: 14 November 2008

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Published by Copernicus Publications on behalf of the European Geosciences Union.

ACPD

8, 19173–19200, 2008

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Abstract

There is currently a need of reliable experimental procedure to follow the heterogeneous processing simulating the atmospheric conditions. This work offers a new experimental approach to study the reactivity and the behaviour of SVOC associated with atmospheric particles. The heterogeneous ozonolysis of naphthalene adsorbed on silica and XAD-4 particles is investigated in specially designed flow tube reactors. The experimental procedure consists in adsorbing gaseous naphthalene on particles before exposing it to ozone. By this novel approach the kinetics is determined following the consumption of naphthalene. Using this procedure, the rate constant k_{O_3} of naphthalene is equal to $(2.26 \pm 0.09) \times 10^{-17} \text{ cm}^3 \cdot \text{molec}^{-1} \cdot \text{s}^{-1}$ and $(4.31 \pm 1.07) \times 10^{-19} \text{ cm}^3 \cdot \text{molec}^{-1} \cdot \text{s}^{-1}$ at 25°C for silica and XAD-4, respectively. The results show both that nature of the particles significantly affects the kinetics and that heterogeneous ozonolysis of naphthalene is faster than in the gaseous phase.

1 Introduction

The increasing anthropogenic activities lead to an increase in the emissions of pollutants in the atmosphere. Among these pollutants, some semi-volatile organic compounds (SVOC) such as polycyclic aromatic hydrocarbons (PAHs) (Goriaux et al., 2006; Tasdemir et al., 2007) and pesticides (Chevreuil et al., 1996; Coupe et al., 2000; Hung et al., 2005; Scheyer et al., 2005, Sauret-Szczepanski et al., 2006) are commonly measured in the atmosphere in both urban regions and remote areas.

The adsorbed organic species may react with atmospheric oxidants colliding with the aerosol solid surfaces. These heterogeneous reactions control the atmospheric fate and lifetime of organic compounds adsorbed on aerosols. By analogy with the gaseous phase, it is assumed that, in the particulate phase, reactions with OH radicals, ozone and photolysis are major chemical transformation routes (Atkinson et al., 1999). Unfortunately, the absolute and relative importance of these various reactions

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is currently not well established.

Despite the importance of the heterogeneous reactivity to understand the behaviour of SVOC in the atmosphere, most of the works have focused on the reactions in the gaseous phase (Soderquist et al., 1975; Woodrow et al., 1978; Atkinson et al., 1984; Atkinson and Aschmann, 1986; Arey et al., 1989; Kwok et al., 1995; Bunce et al., 1997; Carter et al., 1997; Le Person et al., 2007). The reviews dealing with the atmospheric chemistry of Persistent Organic Compounds (POP) such as PAHs (Calvert et al., 2002) and pesticides (Atkinson et al., 1999) underline that the heterogeneous reactions of these compounds have received less attention than those acting in the gaseous phase. Therefore, atmospheric heterogeneous reactivity is to be considered as an area of great uncertainty (Atkinson et al., 1999). The atmospheric lifetime based only on the mechanisms and the kinetic constants of the gaseous phase cannot explain the atmospheric behaviour of SVOC.

It is thus essential to investigate the heterogeneous reactivity of SVOC. To carry out such a study under controlled laboratory conditions, validated experimental procedures are required. Much of the data on heterogeneous reactions in the atmosphere, particularly the earliest work, were generated using Knudsen cells (Finlayson-Pitts and Pitts, 2000). The uptake coefficient of the gaseous reactant by the particles surfaces can be determined. However this coefficient may not represent the true trapping of the gas due to the reevaporation or the heterogeneous adsorption of organic compounds on the surface. Some other techniques permit investigation of heterogeneous reactivity by determining the quantity of unreacted SVOC. Commonly, there are static aerosol chambers for studying slow heterogeneous reactions (Bossan et al, 1994; Palm et al., 1997) or flow tubes which contain the condensed phase of interest deposited on a solid support such as the reactor's walls (Kwamena et al., 2006) or filters (Perraudin et al., 2005; Esteve et al., 2004). Whichever experimental procedure is selected, the initial step generally consists in the coating protocol of particle with SVOC. Commonly, it consists in liquid-solid equilibrium of the compounds under study. Experimentally, these compounds are dissolved in an organic solvent together with the solid particles

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in suspension (Daisey et al., 1982; Wortham et al., 1993; Palm et al., 1999; Esteve et al., 2006; Perraudin et al., 2007a). This procedure makes it possible to coat a large quantity of SVOC on the particle but it is neither representative of the atmospheric phenomenon nor of atmospheric concentrations. The work of Perraudin et al. (2007b) shows that the concentration of particulate PAH may drastically influence the kinetics. This influence of the PAH concentrations could be induced by an experimental artefact because Alebic-Juretic et al. (1990) shows that there is a significant modification of the kinetics when the particles are covered with less or more than a monolayer of PAH. Thus, it seems important to work with a sub-monolayer of SVOC. As a result, the adsorption procedure using liquid-solid equilibrium cannot be considered representative of atmospheric conditions since both the quantity of compounds adsorbed and the nature of the adsorption may be very different from those occurring in the atmosphere. In order to coat SVOC on particles under conditions simulating atmospheric conditions, we have developed a new adsorption procedure using the gas-solid equilibrium of the SVOC.

The object of this work is to describe this new experimental setup aimed at studying the heterogeneous reactivity of SVOC. It has been tested on the heterogeneous ozonolysis of naphthalene adsorbed both on silica and XAD-4 particles used as surrogate solid support. Naphthalene was chosen both for its high volatility for a SVOC (vapour pressure of 37 Pa at 25°C; Lei et al., 2002), and its reactivity towards ozone. Therefore, this compound was an ideal candidate to test the possible experimental volatilization artefacts. Silica particles were chosen as a model solid carrier because SiO₂ represents a significant part of tropospheric aerosol (Alebic-Juretic et al., 1990). To observe the influence of the physico-chemical properties of the particles on the heterogeneous reactivity, a second solid support, chemically different from SiO₂ was tested. The XAD-4 resin was chosen because it is frequently used to trap SVOC and heterogeneous reactions are suspected to occur during sampling (Goriaux et al., 2006).

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2 Experimental

The degradation studies were carried out in a flow reactor (30 cm long), which consists in two concentric tubes, for the larger one 5.4 cm internal diameter, and for the narrower one 4.4 cm external diameter. The two tubes were fitted inside each other leaving an annular space of 0.5 mm for the air flow (Fig. 1). The internal walls of the outer tube were fluoridric acid-etched that result in frosted-glass which facilitates the coating of particles, specifically on this part of the reactor. The outer tube was made up of a double wall which allows being thermostated. Gaseous naphthalene was gently flowed through the reactor inducing an adsorption of naphthalene on the particles. Then, the adsorbed naphthalene was exposed, in the dark to controlled ozone concentrations. The degradation kinetics were determined by analysis of the remaining quantity of naphthalene after various times of exposition.

2.1 Preliminary cleaning of the particles

Silica particles are often used to simulate the atmospheric mineral aerosol (Palm et al., 1997, 1998, 1999; Perraudin et al., 2005, 2007a, 2007b). They have the advantage to be calibrated in diameter (diameter: 6–8 nm) and to have a known specific surface ($260 \text{ m}^2 \cdot \text{g}^{-1}$). The particles were cleaned during 24 h in an oven heated to 600°C and kept in a warm (150°C) and dry atmosphere, before use.

Amberlite XAD-4 resin, a styrene-divinylbenzene polymer, is known to be an efficient sorbent trap for volatile organic compounds such as PAH (Gundel et al., 1995, Temime et al., 2004). This resin was finely crushed during 6 h in a planetary grinder (Retsch GmbH) to obtain XAD-4 particles of about $1 \mu\text{m}$ in diameter. Because of this treatment, the XAD-4 resin was contaminated by various compounds such as alkylated derivatives of benzene, styrene, naphthalene and biphenyl (Hunt and Pangaro, 1982). Therefore, several washing cycles by Soxhlet were necessary to obtain clean blanks (Temime et al., 2002). After each cycle, the liquid and solid phases were separated by ultracentrifugation during 5 min (Hettich Universal, 3200 revolutions min^{-1}). Finally, the

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XAD-4 was dried at around 100°C for 48 h.

2.2 Coating of particles on the wall of the reactor

The operating procedure to coat the walls of the reactor was first described by Gundel et al. (1995), then, adapted by Temime et al. (2002) and finally applied to the current work. To coat the frosted internal walls of the reactor with aerosols, 0.5 g of particles diluted in 50 mL of dichloromethane were ultrasonicated for 5 min (Branson 3510). The resulting slurry was applied to the walls of the reactor. Then, the excess slurry was removed and the reactor dried using a pure nitrogen flow. Several successive application/drying cycles were performed until no slurry remained. Using this procedure, the mean amount of particle losses was about 50%. Thus, the quantity of particle coated on the wall of the reactor was about 0.25 g.

2.3 Generation of a constant flux of naphthalene

The adsorption of naphthalene on the particles was performed by connecting the reactor to a permeation chamber described in detail elsewhere (Temime et al., 2002). Briefly, this device delivered a gas standard diluted in pure nitrogen that was cleared of particles and gaseous organic compounds. The permeation chamber (Fig. 2a) was a glass vessel equipped with an inlet and an outlet, allowing a flow of pure nitrogen to pass through. It was placed in an oven thermostated at 40°C and contained a permeation cell which was a glass tube sealed with a PTFE semi-porous membrane (Durieux PTFE membrane, pore: 10–15 μm, thickness: 0.0005 inches) and filled with naphthalene crystals. The membrane allowed the vapours produced by the naphthalene sublimation to flow out of the permeation cell in a steady manner. Therefore, a flow of PAH vapours diluted in pure nitrogen was obtained at the outlet of the permeation chamber. To obtain a stable concentration of PAH, two key parameters had to be accurately controlled: the flux of the carrier gas and the sublimation rate of PAH in the permeation cell.

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The flux of the carrier gas, set at a flow rate of $150 \text{ mL} \cdot \text{min}^{-1}$, was controlled at the inlet of the permeation chamber by a mass flow controller ($\pm 1\%$ full scale, range of the mass flow 0 to $500 \text{ mL} \cdot \text{min}^{-1}$). Under this condition, the volume of the permeation chamber was renewed every 2 min. The sublimation rate was highly sensitive to the temperature, thus the permeation chamber was thermostated at $40^\circ\text{C} \pm 1^\circ\text{C}$ and the entire experimental setup was placed in a room thermostated at $25 \pm 1^\circ\text{C}$. In addition, to avoid a temperature fluctuation induced by the carrier gas, the latter was set at the working temperature by passing it through several metres of tubing circulating in the oven prior to entering the permeation chamber. Finally, the primary flux of gaseous naphthalene was diluted in an additional flux of pure nitrogen to obtain the required concentrations of naphthalene. This dilution occurs in the thermostated oven (40°C) to avoid naphthalene condensation. Only the diluted flow of naphthalene was set at 25 ± 1 corresponding to the temperature of the thermostated room.

2.4 Adsorption of SVOC on particles

The gaseous flux of naphthalene produced by the permeation device (see Sect. 2.3) was divided into two equivalent fluxes passing through two similar reactors (Reactor A and B) set up in parallel (Fig. 2a). The connections between the permeation device and the reactors were rigorously identical and as short as possible to avoid adsorption of gaseous naphthalene on the connexion tubes. The fluxes in the reactors were set at $3 \text{ L} \cdot \text{min}^{-1}$ controlled by two mass flow controllers $\pm 1\%$ full scale, range of the mass flow 0 to $10 \text{ L} \cdot \text{min}^{-1}$ (Brooks Instrument, smart mass control) placed downstream the reactors. Under these experimental conditions and with the design of the reactors, the Reynolds number (N_{Re}) was less than 10 . Thus, the flux was laminar and by diffusion the gaseous naphthalene reached the particles coated on the walls of the reactors. Moreover, the gas flow was too weak to extract the particles from the walls (Possanzini et al., 1983). This experimental procedure permits to adsorb semi-volatile organic compounds such as PAH on particles in conformity with the gas-solid equilibrium and

to simulate realistic atmospheric conditions. For the present study, the adsorption step was carried out during 3 h to obtain a sufficient quantity of naphthalene to be readily analysed. After the adsorption step, the reactors were disconnected from the permeation device prior to starting the reactivity step.

5 A rapid calculation of the particle surface coverage allows one to demonstrate that the experiments were systematically carried out with naphthalene concentration below a monolayer. Indeed, about 0.25 g of particles was coated on reactor's walls which represents a total surface of 182 and 64 cm² for XAD-4 and silica, respectively. On the
10 other hand, knowing both the surface of the naphthalene molecule (171 Å² following the assumption of spherical geometry) and the amount of naphthalene measured on the particles after the adsorption step (an average of 4×10^{-7} mol), it is deduce that the percentage of aerosol surface coated with naphthalene was 0.3% and 0.8% for XAD-4 and silica particles, respectively.

2.5 Heterogeneous ozonolysis

15 Because of the similarity between the geometry of the reactors and the adsorption phenomenon, the two reactors were assumed equivalent. This hypothesis was verified by carrying out blank experiments (with naphthalene but without ozone) to ensure that the initial amount of naphthalene was identical in both reactors, using silica as a solid support. The results, presented on Table 1, show that the initial amount of naphthalene was almost identical in the two reactors taking into account a relative standard
20 deviation of 3% for the analytical method. Moreover, the gaseous flow passing through the reactors did not significantly influence the quantity of naphthalene adsorbed on the solid surface (Table 1). Therefore, in the present study, one of the reactors was used as a reference to determine the initial concentration of PAH adsorbed on the particles (Reactor A) while the other one was used to carry out reactivity experiments
25 (Reactor B). An ozone flux was obtained by submitting a pure dioxygen flux to an electrical discharge (Fig. 2b) and it was then diluted with a pure nitrogen flow to obtain concentrations ranging between 0.2 ppm and 4.3 ppm. The exact concentrations of

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ozone entering Reactor B were measured on line using a commercial ozone analyzer (O3 41M, Environnement S.A). The ozone concentration was kept constant throughout the experiment. Due to the applied experimental conditions (flow tube in which the gaseous phase was continuously renewed), the mean instantaneous ratio concentrations ozone/PAH corresponds to 12 and 8 for the experiments carried out with silica and XAD-4, respectively. During a test experiment, the ozone monitor was connected alternatively at the inlet and the outlet of the reactor. No significant variation of the ozone concentrations was observed. At the end of the experiments, a flux of nitrogen free of ozone was fed into Reactor B in order to eliminate the remaining ozone and stop the reaction.

2.6 Extraction, filtration and analysis

After each experiment, naphthalene was extracted from the particles in 2×25 mL of dichloromethane by shaking manually the reactor during a period of 2 times 3 min. To remove the particles extracted from the walls of the reactor, 10 mL of the extract was filtered on a PTFE filtration cartridge (Iso-Disc Filters PTFE 25-4, 25 mm×0.45 μm, Supelco) previously conditioned with 5×10 mL of dichloromethane. The filtrate was immediately and quantitatively analysed using gas chromatography (Trace GC ULTRA, Thermo Electron Corporation) on a non-polar capillary column (CP-SIL8 CB; 30 m×0.32 mm df=0.25 μm; 5% diphenyle copolymere and 95% dimethylpolysiloxane; Varian). The chromatograph was equipped with a Flame Ionisation Detector (FID) and a large volume injector allowing carrying out a temperature program to evaporate the solvent (PTV-LVI). The injector contained an inert liner filled with silica wool (Silcosteel deactivated liner with deactivated silica wool; ID=2 mm; OD=2.75 mm; l=120 mm, v=0.38 mL; Thermo Electron Corporation) which retained the SVOC such as naphthalene during the evaporation process. Large volume injections in the PTV-LVI (up to 150 μL) permitted to avoid carrying out a pre-concentration step which would have decreased the precision of the analytical procedure. The volume injected was 80 μL (100 μL syringe; needle l=50 mm and gauge 23; Thermo Electron Corporation) and

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the sample quantification were carried out using external calibration. The analytic parameters are presented in Fig. 3. The performance of the analytical procedure of naphthalene using PTV-LVI-GC-FID were the following: Relative Standard Deviation (RSD)=3%, Limit of Quantification (LOQ)= $6.4 \times 10^4 \mu\text{g}$, linearity range= $[5.6 \times 10^{-2}; 6.4 \times 10^{-4}] \mu\text{g}$.

2.7 Reagents

The reagents used for the experiments were dichloromethane (>99.9%, Fluka, Sigma-Aldrich Chemical), naphthalene (Scintillation grade 99+%, Acros organics), silica particles ($\geq 99.8\%$, AEROSIL R812, specific surface: $260 \text{ m}^2 \cdot \text{g}^{-1}$, diameter: 6–8 nm), XAD-4 particles (surface area: $725 \text{ m}^2 \cdot \text{g}^{-1}$, porosity: 50 Å, diameter: 1 μm), dioxygen (99.999 %, Linde Gas, France), nitrogen (99.999 %, Linde Gas, France, and Nitrogen generator N₂LCMS, Claind).

3 Kinetics

The kinetics of heterogeneous ozonolysis of naphthalene were studied by determining the quantity of unreacted naphthalene i.e. the quantity of naphthalene remaining in Reactor B after exposure to ozone. The experimental results can be studied according to two patterns: Langmuir-Rideal and Langmuir-Hinshelwood.

3.1 Langmuir – Rideal pattern

According the Langmuir – Rideal pattern, the heterogeneous reaction between naphthalene adsorbed on particles (Nap_{ads}) and gaseous ozone (O_{3g}) passing through Reactor B is described in the following reaction:



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The kinetic of Eq. (1) is as follows:

$$\frac{d[\text{Nap}_{\text{ads}}]}{dt} = -k \times [\text{O}_{3\text{g}}] \times [\text{Nap}_{\text{ads}}] \quad (1)$$

where k is the constant rate of second order of the reaction.

Because ozone was in excess compared to the adsorbed naphthalene and continuously flowed through the reactor, we can assume a pseudo-first order kinetic. As a result, the Eq. (1) can be rewritten as follows:

$$\frac{d[\text{Nap}_{\text{ads}}]}{[\text{Nap}_{\text{ads}}]} = -k'_{\text{exp}} \times dt \text{ with } k'_{\text{exp}} = k[\text{O}_{3\text{g}}] \quad (2)$$

By integration between times 0 and t , we obtained the following equation:

$$\frac{1}{t} \times \ln \left(\frac{[\text{Nap}_{\text{ads}}]_0}{[\text{Nap}_{\text{ads}}]_t} \right) = k \times [\text{O}_{3\text{g}}] = k'_{\text{exp}} \quad (3)$$

Under these conditions, the hypothesis of pseudo-first order kinetics is verified when $k'_{\text{exp}} = f([\text{O}_{3\text{g}}])$ is a linear function, where the rate constant k is determined by the slope of the plot.

3.2 Langmuir – Hinshelwood pattern

Pöschl et al. (2001) suggested that the heterogeneous reactions between gaseous oxidant and organic compound adsorbed on solid support could be consistent with a Langmuir-Hinshelwood reaction pattern. According to this mechanism, the organic species are present on the solid support and the oxidant species is in equilibrium between the gaseous and solid surfaces. A reaction can occur only when the gaseous phase species are adsorbed on the surface. Nevertheless, only a limited number of adsorption sites are available for the oxidant gaseous species and at some gaseous phase concentration, saturation of the surface occurs (Kwamena et al., 2006). As a

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result, the rate of the reaction becomes independent of the oxidant gaseous concentration. The Langmuir-Hinshelwood reaction mechanism can be described using the following equation:

$$\frac{k''[SS]K_{O_3}[O_{3g}]}{1 + K_{O_3}[O_{3g}]} = k'_{\text{obs}} \quad (4)$$

5 where k'' is the second order surface rate coefficient, $[SS]$ is the number of adsorption sites for ozone, K_{O_3} is the ozone gas-surface equilibrium constant and $[O_{3g}]$ is the gaseous ozone concentration. By plotting k'_{obs} versus $[O_{3g}]$, the second order rate constant is observed. Moreover, k'' multiplied by $[SS]$ can be approximated as the maximum rate coefficient k'_{max} experimentally obtained at high ozone concentration
10 (Kahan et al., 2006; Kwamena et al., 2007). As a result, Eq. (4) can be modified to yield:

$$\frac{k'_{\text{max}}K_{O_3}[O_{3g}]}{1 + K_{O_3}[O_{3g}]} = k'_{\text{obs}} \quad (5)$$

According to Eq. (5), the parameters K_{O_3} can be obtained by fitting the experimental results ($k'_{\text{obs}} = f([O_{3g}])$) to a non-linear least-square.

15 4 Results and discussion

Twelve experiments of heterogeneous ozonolysis of naphthalene were carried out: i) 8 with a solid support of silica (Experiments Silica 1 to Silica 8), ii) 4 with solid support of XAD-4 (Experiments Resin 1 to Resin 4). The results (Table 2) show that the amounts of naphthalene adsorbed on the reference reactor (Reactor A) were equivalent in the various experiments carried out using the same solid support independently of the
20 duration of the experiments. These results clearly demonstrate both that the adsorption

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procedure was reproducible and the volatilization phenomenon was negligible under the experimental conditions (in absence of oxidant) applied in this study.

4.1 Treatment of the experimental data with Langmuir-Rideal pattern

Langmuir-Rideal mechanism involves only one reactant adsorbed on the surface prior to the reaction. The atmospheric oxidant such as ozone then collides with the surface adsorbed species (in this case naphthalene) and further reacts.

For each experiment, the remaining concentration of naphthalene, $[\text{Nap}_{\text{ads}}]_t$, following the exposure to ozone was compared to the concentration, $[\text{Nap}_{\text{ads}}]_0$, in the reference reactor (R_A). The value of k'_{exp} was determined according to Eq. (3) where t is the time of ozone exposure (Table 2).

The experiments were carried out at median ozone concentrations ranging between 0.2 ppm and 4.3 ppm. These concentrations were higher than those usually observed in the atmosphere but were essential to obtain a significant degradation of naphthalene during an experiment of 12 to 204 min (Table 2).

Due to the instability of the ozone generator, the concentrations of ozone fluctuated during a few minutes. However, the instantaneous concentrations of ozone were not the relevant for the kinetic experiments. Nevertheless, because the ozone concentrations were not well described by a Gaussian, the median ozone concentrations were used instead of the usual mean ozone concentrations. The uncertainty of the median concentration is given by the ozone analyser (5%).

A linear regression was observed on the plots presenting k'_{exp} versus ozone concentrations for the two solid supports on which naphthalene was adsorbed (Fig. 4a and b). The regression lines of plots show regression coefficients (R^2) of 0.99 and 0.89. According to Eq. (3), the linear regressions lead to the rate constants $k=(2.26\pm 0.09)\cdot 10^{-17}\text{ cm}^3\cdot\text{molec}^{-1}\cdot\text{s}^{-1}$ (at 25°C) and $k=(4.31\pm 1.07)\cdot 10^{-19}\text{ cm}^3\cdot\text{molec}^{-1}\cdot\text{s}^{-1}$ (at 25°C) for solid supports of silica and XAD-4, respectively.

The experiments performed by Michel et al. (2003) and Usher et al. (2003) have

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shown that ozone reacts with solid surfaces such as silica or kaolinite. Thus, we could assume that these reactions may modify the physico-chemical properties of the solid surface and change the gas/solid equilibrium of the organic compounds. The latter implies that the interactions between ozone and the silica support can arguably induce the volatilization of organic compounds (naphthalene) in Reactor B. The latter behaviour could possibly explain why the regression lines in Fig. 4a and b do not pass through the origin.

4.2 Treatment of the experimental data with Langmuir-Hinshelwood pattern

The solid lines in Fig. 4a and b display fits of Eq. (5) to the experimental kinetic data. The k'_{\max} obtained were $5.42 \cdot 10^{-5} \text{ s}^{-1}$ and $2.52 \cdot 10^{-3} \text{ s}^{-1}$ for XAD-4 and silica particles, respectively and K_{O_3} resulting from fitting Eq. (5) are summarized in Table 3.

The two substrates under study affect the reactions of naphthalene with ozone. On the silica particles, as was underlined, above the reaction of ozone with naphthalene follows pseudo first order kinetics (Fig. 4a and b). When XAD-4 was used as a medium, the fit looks much better compared to the regression line indicating that kinetics rather follows the Langmuir-Hinshelwood mechanism. In this case the reactivity occurs between adsorbed naphthalene and adsorbed ozone at the aerosol surface and when all surface sites are occupied the reaction rate becomes independent of the gas concentration.

In the recent study by Kwamena et al., 2004 it was suggested that higher values of K_{O_3} lead to the smaller values of k'_{\max} and therefore less ozone was available for the reaction with the adsorbed naphthalene, due to the reduced mobility. It has been shown (Kwamena et al., 2004) by comparison of K_{O_3} values for different substrates that adsorption of ozone is favoured by non polar surfaces.

Since XAD-4 is hydrophobic polyaromatic compound with dipole moment of 0.3 D and silica particles are even less polar (0 D), it is difficult to apply above mentioned rules in order to distinguish between the two reaction mechanisms.

Indeed, applying an extended range of ozone concentrations, the solid surface will

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get saturated and the rate constants in Fig. 4a and b could presumably reach the plateau. In this case, the heterogeneous reactivity could be ascribed to Langmuir-Hinshelwood mechanism.

However, an extended range of ozone concentrations would not represent the realistic atmospheric conditions. Note, that in the work of Goriaux, 2006 has been demonstrated that at much lower ozone concentrations the rate constants for the same heterogeneous reaction (ozone with naphthalene on XAD-4) exhibit pseudo first order kinetics. In addition, the pseudo first order rate constant from this study agrees very well with the one emerged from the study of Goriaux, 2006 (Table 3).

4.3 Atmospheric implications

The rate constants as emerged from this study were used to calculate the atmospheric lifetimes (τ) of naphthalene according to the following equation (Finlayson-Pitts and Pitts, 2000): $\tau=1/(k[\text{O}_3])$ (adapted for the Langmuir-Hinshelwood pattern: $\tau=1/k_{\text{obs}}^I$), assuming, (i) that the heterogeneous reactions of naphthalene with ozone are the only degradation process occurring in the atmosphere, (ii) and ozone concentration was 28.6 ppb. The above mentioned concentration allows comparison of the lifetimes with the published data (Table 3).

Atmospheric lifetime of naphthalene due to the reaction with ozone in the gas phase has been calculated to be >80 days (Zielinska, 2005). In comparison, based on our results, the heterogeneous lifetime of naphthalene, is much smaller independently of both the solid substrate (XAD-4 or silica) and the reaction mechanism (Table 3). These results corroborate a previous study carried out on 13 PAH adsorbed on silica and graphite (Perraudin et al., 2007b).

Perraudin et al., 2005 and Perraudin et al., 2007b have studied the ozonolysis of PAHs (excluding naphthalene) adsorbed on graphite and silica. They observed different reactivities depending on the substrate. The same phenomenon was monitored in the current study. The authors suggested a possible influence of both the chemical composition of the aerosols and their physical structure (specific surface, pore size).

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They assumed that these physical parameters could modify the surface rate coverage and thus the quantity available for reaction (Perraudin et al., 2007b; Alebic-Juretic et al., 1990). Using our experimental protocol, the amount of PAH initially adsorbed on the solid support was controlled, thus, it was possible to assert that both the amount of naphthalene was similar on the two solid surfaces and the experiments were carried out with naphthalene concentrations far below a monolayer. As a result, the amount of naphthalene available for reaction was similar for the two solid supports under study (Table 2) which invalidates their hypothesis. Two other hypotheses could be put forward to explain this phenomenon:

1. The difference in the chemical composition of the solid support could modify the nature of the Van der Waals bonds occurring between naphthalene and the solid surface which in turn could modify the activation energy of the PAH under study.
2. The difference in the pores size of the solid supports under study could more or less efficiently protect the PAH depending on the ability of ozone to penetrate into the pores.

Unfortunately, the current study does not permit validation and credibility of these hypotheses.

5 Conclusions

An experimental setup was developed to study the heterogeneous reactivity of SVOC with ozone. It consisted in generating a constant gaseous flow of SVOC which was split between two reactors. The internal walls of each reactor were covered with a homogeneous surface of particles. Thus, according to the solid-gas equilibrium, a part of the gaseous SVOC was adsorbed on the solid surface simulating the adsorption-desorption phenomenon occurring in the atmosphere. The compounds adsorbed on particles were exposed to ozone and the kinetics of ozonolysis were calculated by comparing adsorbed SVOC concentrations exposed to an O₃/N₂ flow to adsorbed SVOC

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concentrations exposed to a N₂ flow. Naphthalene was chosen as the surrogate compound to simulate atmospheric PAH because of its high reactivity with ozone and its high volatility which facilitated its production into the gaseous phase and allowed us to test the experimental artefacts of volatilization under the worst conditions.

5 The results obtained in this study were treated with the two reaction mechanisms i.e. (1) Langmuir-Rideal and (2) Langmuir-Hinshelwood. It seems that at lower ozone concentrations, which in turn are more realistic, the reaction of ozone with naphthalene proceeds through mechanism (1) while at much higher ozone concentrations the solid surface get saturated and the reaction follows mechanism (2). Much effort must be
10 put forward in order to comprehensively understand heterogeneous kinetics under real atmospheric conditions.

The heterogeneous reactivity of naphthalene adsorbed on two different kinds of particles (silica and XAD-4) shown that the degradation rate was significantly influenced by the particles (chemical and/or physical composition). Moreover, our results demonstrated that the heterogeneous kinetics are faster to those found in the gaseous phase
15 (Atkinson et al., 1984, 1986). Hence, it can be concluded that degradation of naphthalene adsorbed on solid carriers under ozone processing could be an important sink for this compound in the atmosphere.

Because of the important degradation rate of PAH adsorbed on particles, a realistic estimation of their atmospheric lifetime must take into account both the homogeneous and heterogeneous reactivities. In the absence of satisfying estimates of these lifetimes, it is impossible to understand the atmospheric behaviour of these compounds.
20

Acknowledgements. This work is financed by the French Environmental Ministry (Primequal program) and ADEME (Agence de l'Environnement et de la Maîtrise de l'Energie).

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Table 1. Ratio of the amount of naphthalene adsorbed on silica particles coated on the internal surface of the two reactors.

Experiment name	Reactor _A	Reactor _B	Exposition time to N ₂ at 3 L.min ⁻¹
Blank 1	1.04		0
Blank 2	1.09		0
Blank 3	0.99		20 min
RSD of the concentration ratio:	5%		

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Table 2. Results of the heterogeneous ozonolysis of naphthalene (Nap) adsorbed on silica and XAD-4 particles.

Experiment name	Quantity of Nap (μg) in Reactor A ^a	O ₃ exposition time <i>t</i> (min)	[O ₃] _{median} ^b (ppm)	Reactor _A /Reactor _B	<i>k'</i> _{exp} (s ⁻¹)
Silica 1	44.9	12	3.44±0.17	5.1	2.3 (±0.2)×10 ⁻³
Silica 2	46.7	12.25	3.32±0.17	5.0	2.2 (±0.2)×10 ⁻³
Silica 3	46.5	17	2.40±0.12	5.0	1.6 (±0.1)×10 ⁻³
Silica 4	46.0	17	1.80±0.09	3.6	1.2 (±0.1)×10 ⁻³
Silica 5	46.7	22.5	0.95±0.05	3.0	8.2 (±0.5)×10 ⁻⁴
Silica 6	47.1	17.25	0.61±0.03	1.9	6.4 (±0.7)×10 ⁻⁴
Silica 7	47.8	32	0.84±0.04	3.5	6.5 (±0.4)×10 ⁻⁴
Silica 8	50.3	15.75	4.27±0.21	10.8	2.5 (±0.3)×10 ⁻³
Resin 1	54.5	193	2.41±0.12	1.4	2.7 (±0.4)×10 ⁻⁵
Resin 2	59.2	204	4.08±0.20	1.9	5.4 (±0.5)×10 ⁻⁵
Resin 3	56.2	187	0.97±0.05	1.3	2.6 (±0.4)×10 ⁻⁵
Resin 4	53.2	193	0.22±0.01	1.1	8.0 (±0.4)×10 ⁻⁵

^a Reactor A=reference reactor

^b Median ozone concentration of ozone measured during the ozonolysis experiments

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Table 3. Kinetic constants of ozonolysis of naphthalene and there resulting lifetimes in both the gaseous and particulate (silica and XAD-4) phases according to both the Langmuir-Rideal (LR) and Langmuir-Hinshelwood models (LH).

Reactions	Lifetimes [O ₃] _g = 28.6 ppb	k (10 ⁻¹⁹ cm ³ .molec ⁻¹ .s ⁻¹)	k'_{obs} (s ⁻¹) (298 K)	K_{O_3} (10 ⁻¹⁵ cm ³) (298 K)	References
Nap _g + O _{3g} → P Gas	> 80 days ^a > 82 days ^a > 55 days ^a	– <2.01 <3.01	–	–	Zielinska, 2005 Atkinson et al., 1984 Atkinson et al., 1986
Nap _{ads} + O _{3g} → P XAD-4 LR	16 days ^b 35 days ^b	10±2 (298 K) 4.29±1.06 (298 K)	– –	– –	Goriaux, 2006 This work
Nap _{ads} +O _{3s} → P XAD-4 LH	11 days ^b	–	1.05 10 ⁻⁶	28	This work
Nap _{ads} + O _{3g} → P Silica LR	17 h	225±9 (298 K)	–	–	This work
Nap _{ads} + O _{3s} → P Silica LH	5 h	–	5.43 10 ⁻⁵	31	This work

^a Lifetimes reported by Zielinska (2005) and calculated according to the rate constants determined by Atkinson et al. (1984, 1986), respectively.

^b The lifetime of heterogeneous ozonolysis of naphthalene adsorbed on XAD-4 has no atmospheric implication (XAD-4 do not represent atmospheric particles), however, the obtained values demonstrate a possible artefact reaction during sampling.

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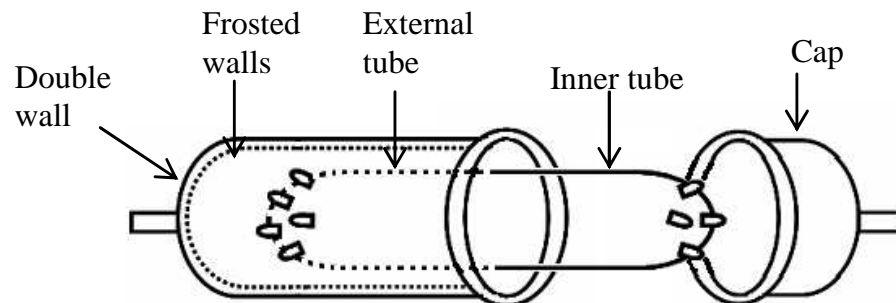


Fig. 1. The flow reactor.

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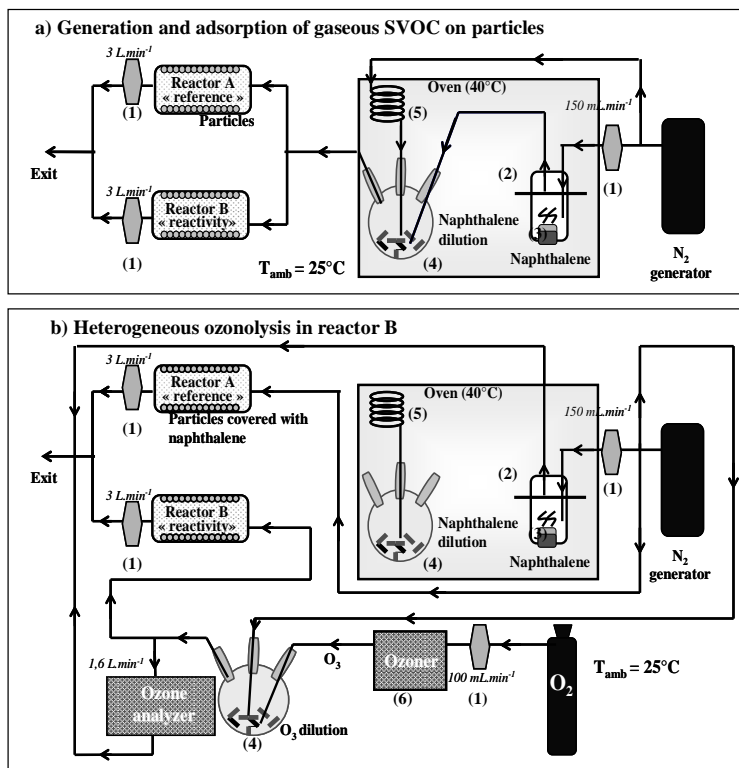


Fig. 2. Experimental set-up to study the heterogeneous ozonolysis of SVOC : **(a)** generation and adsorption of gaseous SVOC on particles, **(b)** heterogeneous ozonolysis in Reactor B.

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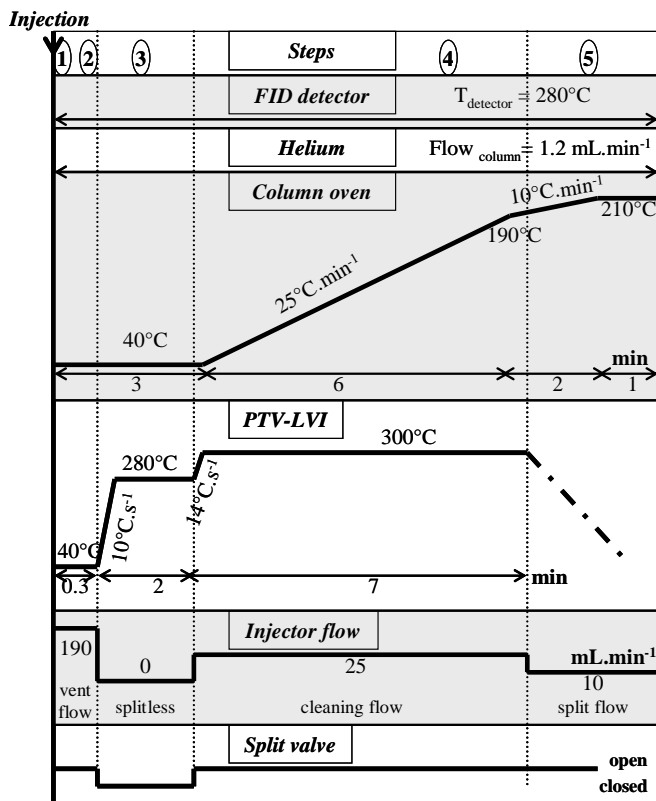


Fig. 3. Parameters of the analysis line.

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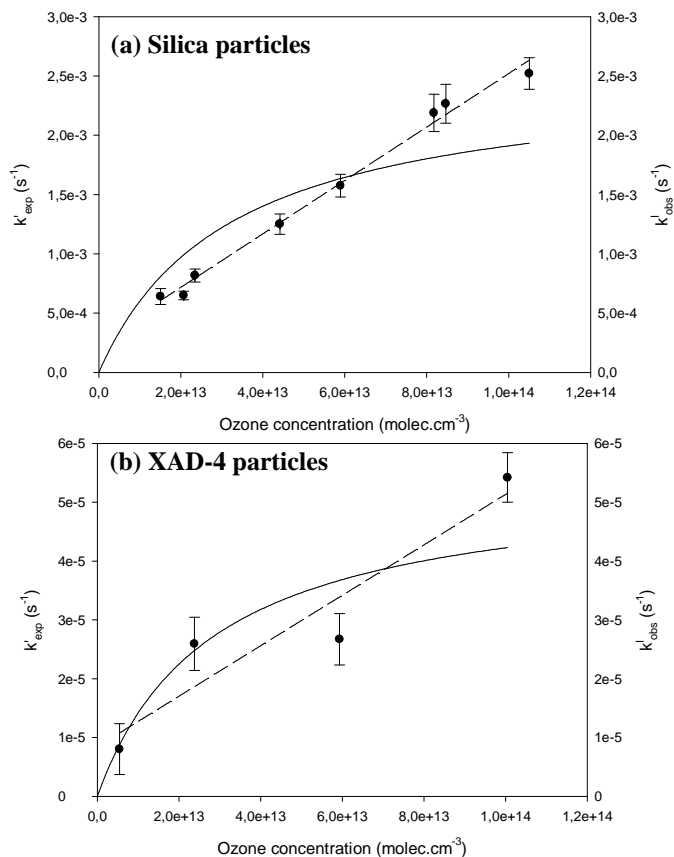


Fig. 4. Graph of the experimental apparent rate constant k'_{exp} (s^{-1}) and k'_{obs} (s^{-1}) versus ozone concentration (molec.cm^{-3})¹ of naphthalene adsorbed **(a)** on silica particles, and **(b)** on XAD-4 particles.

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