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Heterogeneous ozonation kinetics of 4-phenoxyphenol in presence of photosensitizer

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Heterogeneous ozonation kinetics of 4-phenoxyphenol

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Abstract

In this work we have quantitatively measured the degradation of 4-phenoxyphenol adsorbed on silica particles following oxidative processing by gas-phase ozone. This was performed under dark conditions and in presence of 4-carboxybenzophenone under simulated sunlight irradiation of the particles surface.

At mixing ratio of 60 ppb which corresponds to strongly ozone polluted areas, the first order decay of 4-phenoxyphenol is $k_1=9.95\times10^{-6}\,s^{-1}$. At very high ozone mixing ratio of 6 ppm the first order rate constants for 4-phenoxyphenol degradation were the following: $k_1=2.86\times10^{-5}\,s^{-1}$ under dark conditions and $k_1=5.58\times10^{-5}\,s^{-1}$ in presence of photosensitizer (4-carboxybenzophenone) under light illumination of the particles surface. In both cases the experimental data do follow the modified Langmuir-Hinshelwood equation for surface reactions. Langmuir-Hinshelwood and Langmuir-Rideal mechanisms are also discussed along with the experimental results.

Most importantly, the quantities of the oligomers such as 2-(4-Phenoxyphenoxy)-4-phenoxyphenol and 4-[4-(4-Phenoxyphenoxy)phenoxy]phenol formed during the heterogeneous ozonolysis of adsorbed 4-phenoxyphenol were much higher under solar light irradiation of the surface in comparison to the dark conditions.

1 Introduction

The emissions of various type of biomass combustion such as natural fires, prescribed burns and residential wood burning contribute significant amounts of aerosol particles to the troposphere (Anastasio et al., 1997).

Atmospheric organic aerosols emerged from biomass burning processes comprise large fraction of phenols and substituted phenols such as 4-phenoxyphenol (4-PP) and aromatic carbonyl compounds (e.g. 4-carboxybenzophenone (4-CB)) (Simoneit et al., 1993; Jang and McDow, 1995, 1997; Anastasio et al., 1997; Vione et al., 2006). In particular, very high concentrations of aromatic carbonyl compounds and pheno-

lic substances have been detected in aerosols and fogs in regions affected by winter residential wood burning.

In addition, phenolic substances and aromatic carbonyls can emerge as photolysis products of polycyclic aromatic hydrocarbons (PAH) which are also formed during the biomass combustion processes (Kamens et al., 1989; Vione et al., 2006). The impact of biomass burning on global tropospheric ozone concentrations was investigated due to the particular role of ozone for atmospheric chemistry and climate (e.g., Lelieveld and Dentener, 2000; Marufu et al., 2000; Galanter et al., 2000; Granier et al., 2000). All studies estimate the contribution of biomass burning to the global tropospheric ozone concentration in the order of 10%. Nevertheless, on a regional scale close to the source region, biomass burning contributes to a much larger extent to the ozone concentration (Marufu et al., 2000).

From the health point of view it is important to note that organic coated particles play an important role in the toxicity and safety assessment of nanoparticles which means there is an increased risk that people exposed to them are endangering their health (Warheit, 2004).

In the last decade, lot of interest has been drawn towards heterogeneous ozone and OH reactions on the atmospheric aerosol surfaces leading to conclusion that heterogeneous chemistry plays an important role in atmospheric organic particles (Donahue et al., 2009). On the other hand, only few studies were devoted to the light-induced heterogeneous reactions (e.g. George et al., 2005; Gomez et al., 2006)

The near-UV/vis light-absorbing organic species present on/in the condensed aerosol particles interacting with trace gases such as ozone can initiate a new and potentially important photo-induced heterogeneous chemistry.

For example, recent results from the group of George (Jammoul et al., 2008; Nieto-Gligorovski et al., 2008; Stemmler et al., 2006, 2007) and our group (Net et al., 2009; Nieto-Gligorovski et al., 2009) have shown that photosensitized and photoenhanced heterogeneous reactions can take place on the aerosol surfaces. This kind of reactions can modify the particle properties by formation of large molecular mass com-

pounds and induce the development of small volatile organics which are emitted in the atmosphere.

Net et al., 2009 have shown that photo induced heterogeneous reactions of ozone with 4-PP in presence of 4-CB yield large organic molecules with molecular mass up to

5 300 Da. However, the exact role of 4-CB as photosensitizer during the heterogeneous ozonolysis remained an open issue. In the Net et al. (2009) it was suggested that presence of 4-CB does not impact the formation of the reaction products (surface bound and gas-phase products) but it can rather influence the kinetics. Therefore, in this study we focused on the kinetic measurements of heterogeneous reactions between gas-phase

10 ozone and silica particles coated with either 4-PP or with the mixture of 4-PP/4-CB. The kinetic data set was obtained by treating the reaction samples with Gas Chromatography Mass Spectrometry (GC-MS) coupled with the derivatization technique. Two kinetic data sets were obtained: i) heterogeneous reactions of ozone with silica particles coated with 4-PP, ii) light induced heterogonous reactions of ozone with silica

15 particles coated with the mixture of 4-PP/4-CB. The obtained first order rate constants were plotted as a function of the ozone concentrations. The comparison of the two data sets demonstrates an enhancement of the first order rate constants by factor of two in presence of light and photosensitizer (4-CB) and by this we revealed the importance of a photosensitizer such as 4-CB in the heterogeneous ozone reactions which occur

20 on the aerosol surfaces. A previously modified and adopted Langmuir-Hinshelwood mechanism (see e.g. Pöschl et al., 2001; Ammann et al., 2003; Mmereki et al., 2004) was applied to fit the experimental observations.

Evolving of the organics emerged from the heterogeneous ozonolysis of 4-PP in presence and in absence of photosensitizer was observed, as well.

2 Experimental

2.1 Experimental set-up

Mineral dust, of which silica is commonly a major constituent (Usher et al., 2003) adsorbs organic compounds which are (photo)oxydized during their transport (Falkovich et al., 2004).

To study the kinetic reactions of ozone with 4-PP and to evaluate the role of 4-CB at the particle surface, the organic compounds (4-PP and/or 4-CB) were coated on the silica particles (AEROSIL R812) via liquid-solid adsorption. Silica particles are characterized by a high surface-to-volume ratio that make them is ideal for investigation of surface-specific reactions. The experimental set-up has been explained in our previous paper (Net et al., 2009) so here only brief description is given.

Solution of 4-PP and/or 4-CB ($\sim$40 mg in 100 ml of dichloromethane) was mixed with 1 g of SiO_2 powder, in a pyrex bulb with a volume of 500 cm^3. This bulb was wrapped with the aluminium foil and then ultrasonicated about 30 min to obtain homogeneous particles. After that this bulb was attached to a rotary evaporator where the particles were dried during 60 min at 40°C and 850±85 mbar. The prepared particles were then additionally dried about 15 min by nitrogen gas prior proceeding with the kinetic experiments.

All experiments were performed at ambient temperature (297 K). About 300 mg of obtained particles were transferred into other pyrex bulbs with a volume of 500 cm^3. The coated silica particles were then exposed to a broad range of ozone mixing ratios between 60 ppb and 6 ppm. In other independent experiment dried coated silica particles were simultaneously exposed to ozone and transversally irradiated with simulated sunlight emitted from a broadband continuous light source such as a xenon lamp (700 W m^{-2} for 315–400 nm and 160 W m^{-2} for 400–700 nm) at distance of 10 cm from the bulb. The rotation of the bulb ensured a homogeneous irradiation of the particles during the whole experiment.

2.2 Chemicals and reagents

The standards for the identification of the following compounds: 4-carboxybenzophe-none, 4-phenoxyphenol, phenol, hydroquinone, catechol, 4-hydroxybenzoic acid, ben-zoic acid, fumaric acid, terephtalic acid, maleic acid, 1,2,4-trihydroxybenzene and 4,4′-dihydroxydiphenyl ether were provided from Sigma Aldrich, CHIMICA, TCI Europe Lab-oratory Chemicals with purity ≥98%.

The SiO_2 powder AEROSIL®R812 with purity ≥99.8%, average size of 7 nm and specific surface of $260\pm30\,m^2\,g^{-1}$ were supplied by Evonik (France).

2.3 Gas Chromatography-Mass Spectrometry (GC-MS) analysis

Following the reaction times of 1, 2, 4, 6 and 8 h the adsorbed organic material of the silica particles was extracted in DCM by ultrasonication (Branson 3510, USA) for a time period of about 30 min. The obtained suspension of coated particles was further cen-trifuged 6000 r/min (Sorvall LEGEND MICRO17, Electron Corp., TermoFisher). The obtained clear solutions were then analyzed by GC-MS using electron impact ionisa-tion (70 eV) according to the following parameters: column THERMO TR-5MS (inter-nal diameter 0.25 mm, length 30 m, film thickness 0.25 µm), injection volume: 1 µl, inlet temperature: 250°C, interface temperature: 330°C, with the following temperature pro-gram: hold 1 min at 80°C ; increase temperature to 220 at a rate 15°C/min; increase temperature to 300 at 25°C/min; hold 15 min at 300°C. A Combi PAL autosampler was used to allow automated analysis. For reagent analysis, the samples were injected in the split (1/100) injection mode. For products analysis, the samples were injected in the splitless injection mode. The injector was switched to split mode 1 min after an injection was made.

Spectra were taken before and after ozonolysis or simultaneous ozone and light exposure of the organic coated silica particles. These spectra were obtained using GC-MS coupled to a derivatization analytical technique as reported in a previous paper (Net et al., 2009).

2.4 Calibration and method validation

2.4.1 Selectivity

The selectivity was assessed by comparing the chromatograms of 5 blanks of pure silica particles and 5 blank samples (silica particles coated with 4-PP and 4-CB before the exposure) with the corresponding sample after the simultaneous ozone and light exposure. Each blank sample was tested using the proposed coating preparation, experimental procedure and GC-MS conditions to ensure no interference peak of organic compounds in the sample.

2.4.2 Homogenization of the adsorption test

Ten points of coated particles extracted from different sides of the bulb were analysed. Peak area ratios of the analyte to the internal standard were used to calculate the percent relative standard deviations (RSD%). RSD% values of 4 and 4.5% were estimated for 4-PP and 4-CB, respectively. Internal standard used in this study was O-toluic acid and its stability in the sample was tested. The RSD% value of 15 injections of O-toluic acid within 1 h interval was 4.5%.

2.4.3 Linearity of calibration curves and limit of quantification

Peak area ratios of the analytes to the internal standard were used to draw the calibration curves. Regression analysis was used to assess the linearity of the analytical method. Six point calibration curves were obtained with correlation coefficients R^2>0.99. Daily calibration curves were constructed during sample analysis. Limit of detection (LOD) (defined as a peak giving a response equal to a blank signal plus three times the standard deviation of the noise) of reagents and reaction products were calculated with a derivatization technique (for details see Net et al., 2009). Limits of quantification (LOQ) were calculated for full scan or SIM of signal of the MS and are as follows: 0.01 mg/L for 4-PP, 0.005 mg/L for 4-CB, 0.3 mg/L for phenol, 0.08 mg/L

for benzoic acid, 0.5 mg/L for maleic acid, 0.01 mg/L for catechol, 0.007 mg/L for fumaric acid, 0.05 mg/L for hydroquinone, 0.06 mg/L for 1,2,3-trihydroxybenzoic acid, 0.08 mg/L for 4-hydroxybenzoic acid, 0.8 mg/L for terephtalic acid and 0.08 mg/L for 4,4′-dihydroxydiphenyl ether. These LOQ were confirmed by experimental analysis.

3 Results

3.1 Kinetics of heterogeneous reactions

Following the heterogeneous reactions between gas-phase ozone and 4-PP adsorbed on the surface of silica particles the disappearance of 4-PP was followed by monitoring the intensity of GC-MS signals. The latter was done i) in absence of light and ii) in presence of photosensitizer (4-CB) under solar light irradiation. In both cases, an irreversible loss of 4-PP was observed.

The 4-PP loss is illustrated in Fig. 1 by typical profiles of its reactive normalized concentrations versus exposure time for the ozone concentrations ranging between 60 ppb and 6 ppm.

The growth of the organics formed during the heterogeneous reactions was quantitatively determined. The presence of photosensitizer (4-CB) under solar light irradiation can significantly influence the evolution of products formation. Figure 2 shows the difference in phenol l's evolving during ozonolysis of 4-PP under dark conditions (Fig. 2a) and under solar light illumination of the silica surface in presence of 4-CB (Fig. 2b).

In both cases (Fig. 2a and b) the mass of phenol increases linearly with the reaction time and with ozone concentrations. Nevertheless, the mass of phenol expressed in mg was higher in the experiment under dark condition than under solar light illumination of the surface. The quantities of the oligomers such as 2-(4-Phenoxyphenoxy)-4-phenoxyphenol and 4-[4-(4-Phenoxyphenoxy)phenoxy]phenol (Fig. 8s and Fig. 9s, respectively in the supplemental electronic material http://www.atmos-chem-phys-discuss.net/9/21647/2009/

acpd-9-21647-2009-supplement.pdf) also increase linearly in function of time and in function of ozone concentration. It is more important that both oligomers exhibited higher masses in the experiment under solar light illumination of the silica surface in presence of 4-CB in comparison to the experiment under dark conditions. The quantities of both oligomers increased rapidly in the first 4 h of the experiment but then their masses slightly diminished especially at high ozone concentrations. The evolution of masses of the other products (already identified and with standards confirmed, see Net et al., 2009) formed during the ozonolysis of 4-PP under dark conditions and in presence of 4-CB are presented in the supplemental electronic material http://www.atmos-chem-phys-discuss.net/9/21647/2009/acpd-9-21647-2009-supplement.pdf.

3.2 Reaction pathway

Independently of 4-PP degradation experiments we checked the GC-MS intensity signals of the photosensitizer (4-CB) during the simultaneous ozonolysis and light illumination of the coated particles. At different ozone concentrations ranging from 60 ppb to 6 ppm and for the reaction time between 0 and 8 h, the initial concentration of 4-CB remained practically unchanged.

The later implies that the reaction pathway (note that term reaction pathway is different than Langmuir-Hinshelwood mechanism and Langmuir-Rideal mechanism described in the next section) is such that is able to restore the original sensitizer molecule (4-CB), in which case the process is photocatalytic. Typically, a photosensitized process requires absorption of light by the photosensitizer, followed by energy transfer or charge transfer between the excited triplet of the photosensitizer and its neighbouring molecules (in this case 4-PP). In Net et al., 2009 it was shown by ab-initio calculations that energy transfer is not possible between the excited triplet of 4-CB and 4-PP but it is rather electron transfer or hydrogen abstraction (Canonica et al., 1995, 2000).

Recently, George et al., 2005 have reported that the excited triplet of 4-CB may initiate further photochemistry. Type II photoinitiators represent compounds which triplet excited states such as ^{3}4-CB* readily react with hydrogen donors, thereby producing
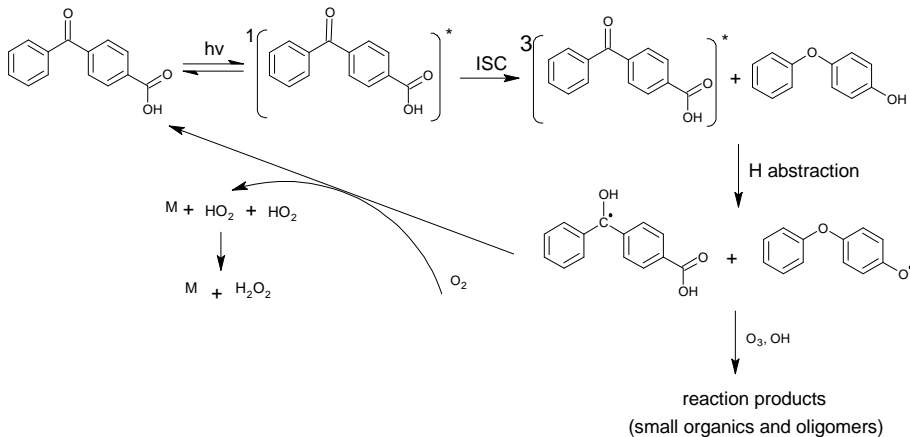
Scheme 1

an initiating radical (Davidson, 1983). Hence, in our system ^{3}4-CB* can react with 4-PP, thus producing an initiating radical that can further induce formation of small volatile organics and oligomers in presence of atmospheric oxidants (OH, O$_3$) (Net et al., 2009). It is noteworthy that formed radical in presence of electron acceptors e.g. O$_2$ can lead to the formation of hydrogen peroxide and then falls to its initial state (ground state of 4-PP) (Scheme 1).

3.3 Treatment of the kinetic data with the modified Langmuir-Hinshelwood mechanism

The unimolecular reactions on the surface can be described with Langmuir-Hinshelwood rate law by the following equation:

$$\text{rate} = \frac{k_1 K_X[X]}{1 + K_X[X]} \tag{1}$$

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Where K_X is the equilibrium constant of the X species and $[X]$ is the concentration of X and k_1 is the first order rate constant.

This equation has been modified and adopted for the bimolecular surface reaction assuming that organic compound was previously adsorbed on the surface and that the concentration of the gas-phase oxidant is in excess compared to the concentration of the adsorbed organic (see for instance Mmereki et al., 2004; Kahan et al., 2006; Kwamena et al., 2007).

Consequently, the observed rate constant (k_{1obs}) of the 4-PP degradation can be expressed as:

$$\frac{k_{2nd}[SS]K_{O_3}[O_{3g}]}{1 + K_{O_3}[O_{3g}]} = k_{1obs} \tag{2}$$

where k_{2nd} is the second order rate constant, $[SS]$ is the number of adsorption sites available for ozone, K_{O_3} is the ozone gas-surface equilibrium constant and $[O_{3g}]$ is the gas-phase ozone concentration. The second order rate constant k_{2nd} can be obtained by plotting k_{1obs} versus $[O_{3g}]$. k_{2nd} multiplied by $[SS]$ gives the maximum rate constant k_{1max} which is experimentally obtained at very high ozone concentrations (Kahan et al., 2006; Kwamena et al., 2007).

Equation (2) can be rewritten as:

$$\frac{k_{1max}K_{O_3}[O_{3g}]}{1 + K_{O_3}[O_{3g}]} = k_{1obs} \tag{3}$$

It can be seen that Eq. (3) is very similar to Eq. (1) with one difference that is k_1 is replaced with k_{1max}. In Eq. (3) it is assumed that the organic compound has a very long residence time on the surface which means that it represents a part of the surface.

According to Eq. (3), K_{O_3} can be obtained by fitting the experimental results, obtained from the plot of k_{1obs} versus $[O_{3g}]$, to a non-linear least-square.

By fitting the observed kinetic data for the ozonolysis of 4-PP to Eq. (2) the obtained values of K_{O_3} are $(5\pm1)\times10^{-14}$ cm^3 and $(9\pm3)\times10^{-14}$ cm^3 on a 4-PP/4-CB and on a 4-PP silica surface, respectively. These two values are very similar which implies that

low concentrations of adsorbed organics do not significantly affect ozone's surface partitioning coefficient. Moreover, these values fall in the range of the observed literature data for various solid substrates (Kwamena et al., 2004; 2006, Poeschl et al., 2001).

Figure 4 illustrates non-linear dependence of the first-order rate constants on ozone concentrations.

This result is obtained under simulated sunlight irradiation (full line) and in absence of light and photosensitizer (4-CB) (dash line) (Fig. 4).

A clear change is observed in the kinetics of the heterogeneous reaction between gas phase ozone and 4-PP at the particle surface when the surface is illuminated in the presence of 4-CB. This observation extends the number and type of system in which a photoenhancement in heterogeneous chemical reactions has been reported.

3.4 Bimolecular surface reactions

In the past studies (e.g. Kwamena et al., 2006; Clifford et al., 2008; Pflieger et al., 2009a) including this work the experimental results of heterogeneous bimolecular reactions on the surface (liquid and solid) were fitted with Eq. (3). However, this equation does not reflect the Langmuir-Hinschelwood mechanism for bimolecular surface reactions (see e.g. Adamson and Gast, 1997; Finlayson-Pitts and Pitts, 1983).

It is known that in the case of bimolecular reactions both reactant species diffuse around until a reaction occurs. For a bimolecular process the reaction rate is taken to be proportional to the product of the two surface concentrations (see later section, Eq. 4).

Moreover, in the past studies (e.g. Miet et al., 2009; Pflieger et al., 2009a,b; Cabe and Abbatt, 2009) such bimolecular surface reactions were discussed in term of Langmuir-Rideal mechanism known also as Eley-Rideal mechanism.

Langmuir-Rideal mechanism was presented as a simple linear regression describing a bimolecular collision between the gas phase molecule and adsorbed organics. The accurate description of L-H and L-R mechanism for bimolecular surface reaction is given bellow.

3.5 Langmuir-Hinshelwood mechanism

In the Langmuir-Hinshelwood mechanism (L-H) mechanism the two gas-phase species of interest are first adsorbed on the surface and then they react which means L-H describes a bimolecular surface reaction between two adsorbed reactant species (see e.g. Adamson and Gast, 1997; Finlayson-Pitts and Pitts, 1983). In case of surface reaction between adsorbed ozone and adsorbed organic compound the pseudo-first-order rate coefficient can be interpreted as follows (Finlayson-Pitts and Pitts, 1983):

$$k_1 = \frac{k_2 K_{O_3} K_{OC}[O_3][OC]}{(1 + K_{O_3}[O_3] + K_{OC}[OC])^2} \tag{4}$$

where K_{O_3} is the adsorption equilibrium constant of ozone, K_{OC} is the adsorption equilibrium constant of the organic compound, $[O_3]$ is the gas-phase concentration of ozone and $[OC]$ is the gas-phase concentration of the organic compound.

Equation (4) shows that if $[OC]$ is held constant and $[O_3]$ is varied, the reaction rate (k_1) first increases with $[O_3]$ and then at high ozone concentrations, k_1 decreases. A falls of k_1 arises because very high ozone concentrations yield large amounts of adsorbed ozone on the surface and correspondingly there is less quantity of organic compound.

3.6 Langmuir-Rideal mechanism

Langmuir-Rideal (L-R) mechanism also known as Eley-Rideal (E-R) mechanism describes the heterogeneous reaction between the gas-phase ozone and adsorbed organic compound on the surface and can be interpreted as follows (Finlayson-Pitts and Pitts, 1983):

$$k_1 = \frac{k_2 K_{OC}[O_3][OC]}{1 + K_{O_3}[O_3] + K_{OC}[OC]} \tag{5}$$

In this mechanism only one of the molecules (organic compound) adsorbs on the surface and the other one (in this case ozone) reacts with it directly from the gas phase, without adsorbing. According to (Eq. 5) the reaction rate (k_1) is proportional to the ozone concentrations at low [O_3] and it goes to a plateau at high [O_3].

4 Conclusions and outlook

At atmospherically relevant ozone mixing ratio of about 60 ppb the first order rate constant of 4-PP degradation at the silica surface is 9.95×10^{-6} s^{-1}. At extremely high ozone concentrations (see the plateau in Fig. 4) the degradation of 4-PP is enhanced by factor of 2 in presence of 4-CB under simulated solar irradiation compared to the dark conditions.

The evolution of the products that were already identified in Net et al., 2009 was followed under different conditions. Evolution of small organics e.g. phenol was more pronounced under dark conditions compared to the experiment were the surface was illuminated with the simulated solar light. On the other hand, the two oligomers i.e. 2-(4-Phenoxyphenoxy)-4-phenoxyphenol and 4-[4-(4-Phenoxyphenoxy)phenoxy]phenol exhibited higher masses under solar light illumination of the silica surface in presence of 4-CB.

The first order rate constants of heterogeneous reactions between gas-phase ozone and adsorbed 4-PP on the silica surface do follow the behaviour of modified Langmuir-Hinshelwood mechanism (Eq. 3) which is originally valid for unimolecular surface reactions.

However, in a very recent paper by Finlayson-Pitts, 2009 it was highlighted one of the current problems in atmospheric chemistry that is the Langmuir–Hinshelwood kinetics apply to different kind of solid and liquid substrates whose interactions with gas-phase ozone is not expected to be much alike. Arguably, one of the reasons for such behaviour could be that the modified Langmuir–Hinshelwood mechanism described by Eq. (3) is not properly applied for the bimolecular surface reactions (liquid or solid sur-

face) as we highlighted in this article.

In this work we have shown that 4-CB can play an important role in enhancing the degradation of particle-adsorbed aromatic compounds such as phenols and substituted phenols in presence of ozone. It would therefore be very important to determine if the described process of enhanced heterogeneous reactivity upon sunlight irradiation is associated only to benzophenone and its derivatives (4-CB) as photosensitisers, or if it represents a more general phenomenon.

Keeping in mind that atmospheric aerosols contain an important fraction of photo-sensitizers, such as quinones and aromatic carbonyls, and knowing the potential of the photosensitizers (Anastasio et al., 1997; George et al., 2005; Vione et al., 2006) to induce phototransformation and to enhance the loss of organic molecules, further studies are recommended which include photosensitizers during the heterogeneous reactions. Although is out of scope of this paper it is noteworthy that photosensitized degradation of organic compounds represents an important source of hydrogen peroxide and thus OH radical.

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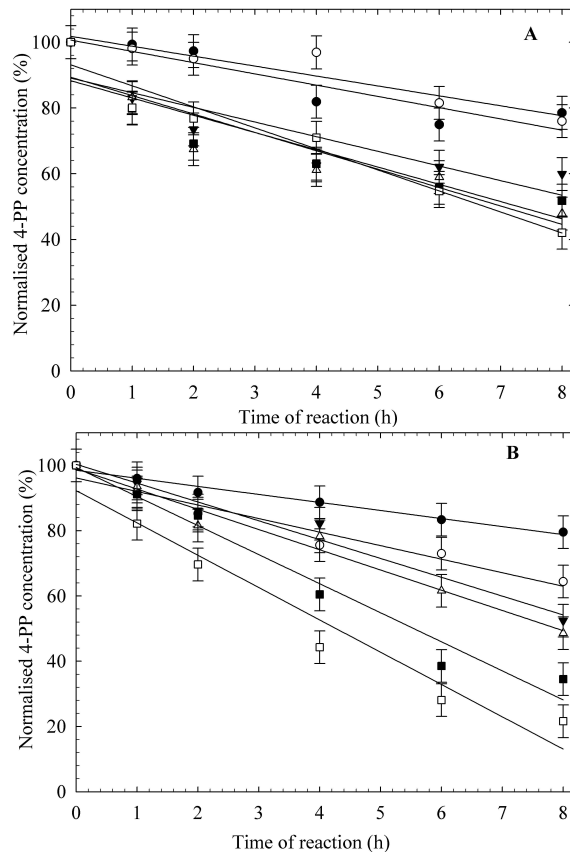Printer-friendly Version

Interactive Discussion

Fig. 1. Normalized concentrations of 4-PP degradation in function of time. **(A)** ozonolysis under dark conditions **(B)** ozonolysis under solar light illumination of the silica surface in presence of 4-CB.
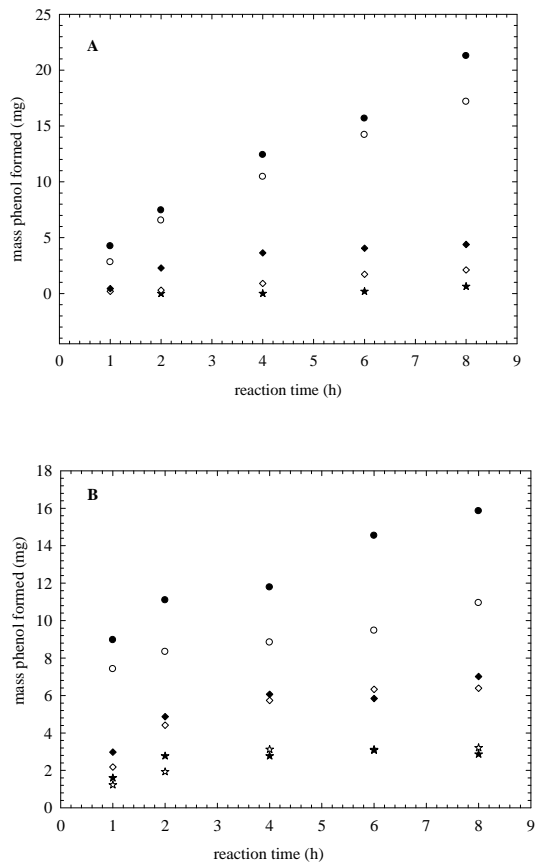
Fig. 2. Representative phenol formed during ozonolysis of 4-PP. **(A)** under dark condition in function of time at ozone concentration ★): 250 ppb, ◇): 500 ppb, ◆): 1 ppm, ○): 3 ppm and ●): 6 ppm and **(B)**: under solar light illumination of the silica surface in presence of 4-CB in function of time at ozone concentrations ☆): 60 ppm, ★): 250 ppb, ◇): 500 ppb, ◆): 1 ppm, ○): 3 ppm and ●): 6 ppm.
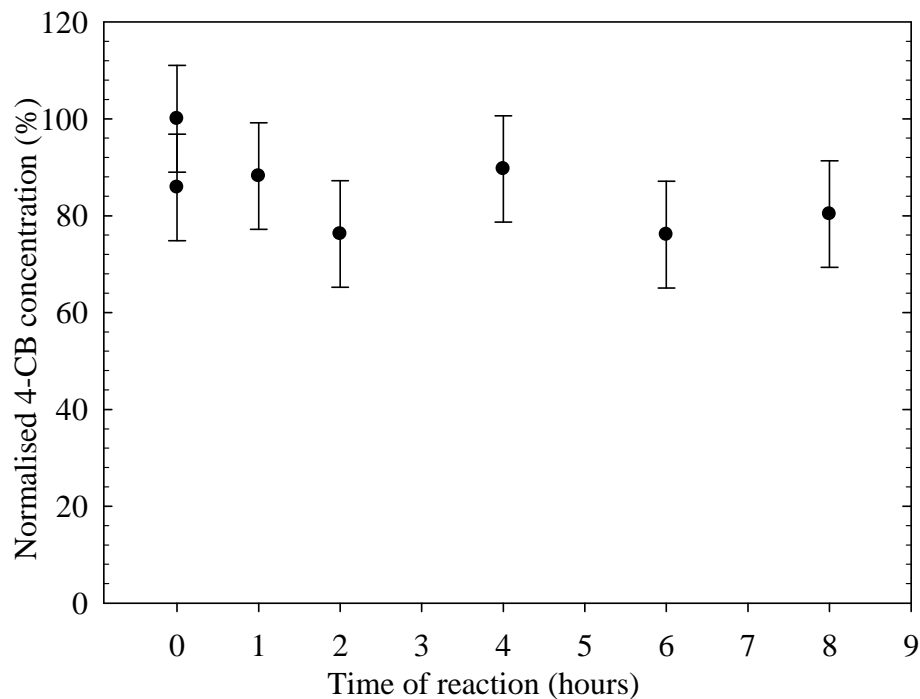
Fig. 3. Normalized concentrations of 4-CB degradation in function of time. The applied ozone mixing ratio is 6 ppb.
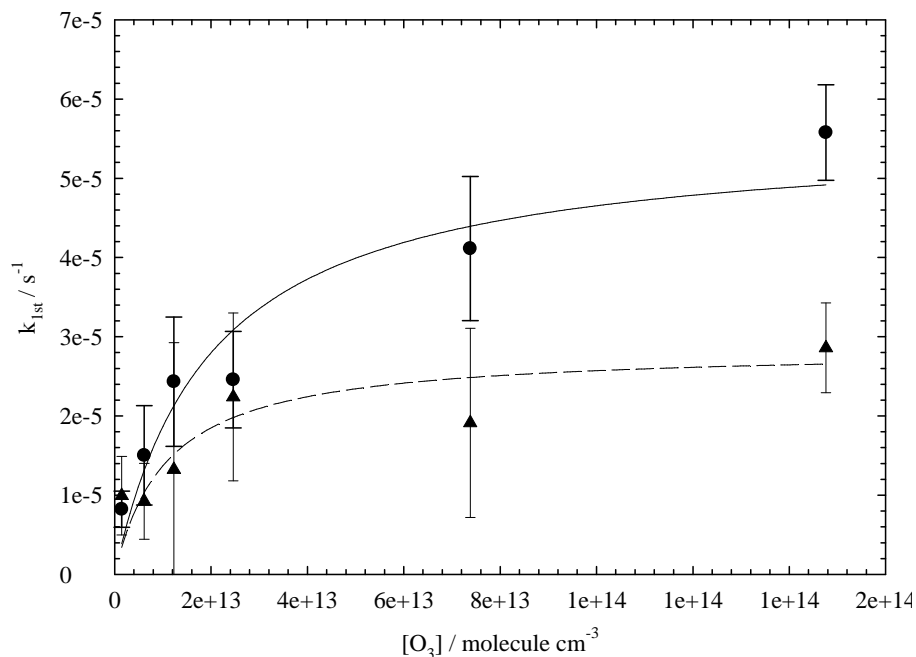
Fig. 4. First order rate constants of 4-PP degradation (derived from the slopes of the plots in Fig. 1) as a function of gas-phase ozone concentration. ▲) under dark conditions, ●) under solar light irradiation of the surface in presence of 4-CB. The dashed line and solid line represent the fit of the experimental observations to the modified Langmuir-Hinshelwood mechanism (Eq. 3).