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Atmospheric Reactions of 9,10-Anthraquinone

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Abstract

The probably carcinogenic compound 9,10-anthraquinone is mainly existing in the atmosphere in the particulate phase and is often detected and measured among other oxygenated PAHs in atmospheric samples. Its fate, once released or formed in the atmosphere, still remains unknown. In this work, heterogeneous chemical oxidation processes of 9,10-anthraquinone were investigated with ozone (O_3), nitrogen dioxide (NO_2) and hydroxyl radical (OH). The study of 9,10-anthraquinone adsorbed on silica particles showed no reactivity with O_3 and NO_2. On the other hand, the reaction with OH radicals was observed and led to the formation of 1-hydroxy-9,10-anthraquinone, another oxidation product recognized as possibly carcinogenic to humans. This study showed that reactions with ozone and nitrogen dioxide are unlikely to contribute to atmospheric degradation of 9,10-anthraquinone, whereas reactions with OH radicals could be involved in 9,10-anthraquinone degradation processes, even if such reaction is probably very slow under ambient conditions.

Keywords: 9,10-anthraquinone; Hydroxyl radical; Ozone; Nitrogen dioxide; Kinetics; 1-hydroxy-9,10-anthraquinone

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are organic compounds widely distributed in the environment. They are mainly emitted into the atmosphere as by-products of organic matter and fossil fuel incomplete combustion (domestic heating, automobile fuel combustion, wood burning…). For the most part, PAHs have an anthropogenic origin in the atmosphere and once emitted, they are present in both, gaseous form and adsorbed to particles, depending on the volatility of the PAH species. Low molecular weight compounds exist mainly in the gas phase, whereas PAHs bearing five fused rings or more are predominately adsorbed onto particulate matter (Odabasi et al., 1999; Callén et al., 2008; (Albinet et al., 2008)).

PAHs have been extensively studied in the gas phase and adsorbed to particles with atmospheric oxidants (Pitts et al., 1985; Estève et al., 2004; Perraudin et al., 2005 and 2007a; Atkinson and Arey, 2007; Gross and Bertram, 2008; Miet et al., 2009a and 2009b). Concerning oxidation products, which seem more toxic than the parent compounds ((Durant et al., 1996; Durant et al., 1998; Pedersen et al., 2004; Pedersen et al., 2005)), there is a lack of data concerning their fate. Nitrated and oxygenated PAHs are often detected in ambient air samples (Castells et al., 2003; Albinet et al., 2007; (Albinet et al., 2008; Ringuet et al., 2012a)) as compounds directly emitted during combustion processes or as oxidation products formed in the atmosphere by photolysis and reaction of PAHs with oxidants (NO_x, OH, O_3, SO_x). Among such compounds, quinones are often detected in atmospheric aerosol samples (König et al., 1983; Lewis et al., 1995; Allen et al., 1997; Cho et al., 2004; Shimmo et al.,

2004; del Rosario Sienra and Rosazza, 2006; Jakober et al., 2006; Albinet et al., 2007; Andreou et al., 2009; (Albinet et al., 2008; Ringuet et al., 2012a)) and are suspected to contribute to the toxicity of ambient particles. Their toxic effects are often attributed to their ability to form reactive oxygen species (ROS) (Lemaire and Livingstone, 1997; Kumagai and Shimojo, 2001), but also for their mutagenicity (Chesis et al., 1984; Durant et al., 1996; (Pedersen et al., 2004; Pedersen et al., 2005)). Recently, the IARC has classified 9,10-anthraquinone as a group 2B chemical, signifying its carcinogenic probability to humans ((IARC, 2012)) and highlighting the study of the fate of this compound.

The formation of quinones has been highlighted in some works as oxidation products from PAHs by photolysis or reactions with O_3, NO_3 and OH (Helmig and Harger, 1994; Dabestani et al., 1995; Barbas et al., 1996; Mallakin et al., 2000; Kwamena et al., 2006; Perraudin et al., 2007b; Wang et al., 2007; Yu, 2002; Vione et al., 2004), leading to the formation of compounds such as 9,10-phenanthrenequinone or 9,10-anthraquinone. Despite its high concentration levels observed in ambient air, very few works investigated the fate of 9,10-anthraquinone whatever the degradation pathway.

In this work, the heterogeneous reactivity of 9,10-anthraquinone was investigated with three oxidants of tropospheric interest (O_3, NO_2 and OH). 9,10-Anthraquinone was coated on silica particles as a model for mineral particles. Atmospheric particulate matter constitutes a complex medium and silica, which constitutes an important fraction of mineral particles, allows to simplify the solid substrate (Harrison and Yin, 2000; Rodriguez et al., 2008) in order to obtain better reproductility in kinetic measurements. This kind of particle has been used in previous studies (Behymer and Hites, 1985; Alebic-Juretic et al., 1990; Barbas et al., 1996; Wang et al., 1999; Perraudin et al., 2005 and 2007a; Miet et al., 2009a and 2009b), showing that such particles constitute a good model in order to investigate heterogeneous reaction processes.

2. Experimental

2.1. Preparation of the particles

Silica particles IT70-5 were supplied by Interchim. According to their certificate of analysis, the silica particles have an average particle diameter of 5 µm and an average pore diameter of 70 Å. Their specific surface area is about 500 m^2 g^{-1}. The diameter of these particles is situated in the coarse particle mode. These particles have well-defined properties already detailed in a previous work by Perraudin et al. (2005).

Silica particles were first cleaned by ultrasonication using dichloromethane (HPLC grade, Acros Organics). After drying, the particles were introduced in a solution of dichloromethane containing 9,10-anthraquinone (97 %, Aldrich). The solvent was then evaporated using a rotary evaporator (at atmospheric pressure and T = 35 °C). Coated particles were finally stored in amber glass flasks at ambient temperature until reactivity experiments.

2.2. Analytical procedures

After the addition of a surrogate standard (fluoranthene-d10, 99.2 %, MSD isotopes), coated particles were extracted using pressurized fluid extraction (ASE® 200, Dionex) with dichloromethane (P = 100 bars, T = 100 °C, heat time of 5 min and 2 static extraction cycles of 8 min). Extracts were then evaporated in the ASE extract-collecting flask and changed to isooctane (HPLC Grade, Scharlau) using a vacuum evaporation system (Rapidvap, Labconco), with the following parameters: 70 %, 900 mbar, 50 °C during 20 min.

After the addition of a internal standard (pyrene-d10, 98%, MSD isotopes) (used to quantify surrogate standard), samples were analysed by gas chromatography (HP model series 6890 Gas Chromatograph, Agilent Technologies) coupled to mass spectrometry (HP model 5973 mass selective detector, Agilent Technologies), using a HP-5MS capillary column (30 m × 0.25 mm ID × 0.25 µm film thickness, Hewlett Packard). The temperature program was 70 °C during 2 min up to 300 °C at a rate of 10 °C min^{-1} and held at 300 °C during 5 min. The carrier gas was helium (He 99.9999+ % purity, Linde Gas) at a constant flow rate of 1 mL min^{-1}. The interface temperature was kept at 280°C during analysis. The mass spectrometer was operating under electron impact ionisation (70 eV) and mass detection was carried out in selected ion monitoring (SIM) mode (dwell time = 100 ms, number of cycles per second = 1.16 and electron multiplier voltage = (2400 ± 50) V).

The analysis performed by GC-MS allowed to evaluate the initial 9,10-anthraquinone particulate concentration: (592 ± 27) µg g^{-1} of silica (n = 22). Extraction efficiencies were also determined using the surrogate standard recovery yield, obtained from its quantification related to pyrene-d10 : (98 ± 3) % (n = 22). This value, close to 100 %, shows that 9,10-anthraquinone extraction from silica particles is very efficient.

2.3. Experimental reaction setups

All experiments were performed in a total darkness to avoid any photodegradation and to only account for the 9,10-anthraquinone degradation in the reactors. 9,10-Anthraquinone oxidation was followed by measuring the remaining concentration present on silica particles versus oxidant exposure time.

2.3.1. Ozone setup

The ozone setup used in this study was developed in our laboratory by Perraudin et al. (2007a). It consists of a photolysis cell in which a mixture of nitrogen and oxygen is introduced and photolysed at 185 nm by a low pressure mercury lamp (NIQ 120/80, Heraeus SAS). The ozone concentration was controlled by varying the oxygen ratio (total flow constant at 3 L min^{-1}), and the distance between the photolysis cell and the lamp. The $N_2/O_2/O_3$ flow was then directed to the reactor in which a filter, with the coated particles, was placed. The output of the reaction cell was directed to the O_3 measurement cell (41.5 cm long), in which O_3 concentration was measured by its well-known absorption at 254 nm, the irradiation being emitted from a deuterium lamp (L7296, Hamamatsu Photonics). The monochromator (Jobin Yvon) wavelength was regularly calibrated using a low-pressure mercury lamp.

2.3.2. OH and NO_2 setup

The OH and NO_2 experimental setup was similar to that previously used in our laboratory to study heterogeneous reactivity (Estève et al., 2003 and 2004; Miet et al., 2009c, (Ringuet et al., 2012b)). It consists of a fast flow-tube reactor (2.4 cm inside diameter / 48 cm long Pyrex tube) in which a movable injector (1 cm inside diameter, 60 cm long quartz tube) slides. Gases were introduced in the main reactor through the injector, which was wall-coated inside with halocarbon wax (Halocarbon Products Corporation, series 1500) in order to minimize heterogeneous recombination on the walls. The reactor pressure was regulated by a two-stage primary pump (Alcatel T2060) and monitored with a capacitance gauge (Edwards Barocel 600, 0 - 10 Torr). Total pressure was held at (1.8 ± 0.1) Torr during all experiments. Total

flow in the reactor was approximately 1 L min^{-1} and was laminar in all experiments based on the Reynolds number.

NO_2 concentration was controlled by dilution of NO_2 (5% NO_2 in Helium 99.995% purity, Alphagaz, Air liquide) in helium (Alphagaz 1, Air liquide) using calibrated mass flow controllers (FC260 and FC2900 Mykrolis).

OH radicals were generated *in situ* at the upstream of the movable injector by the fast reaction between nitrogen dioxide and a hydrogen atom, produced by hydrogen impurities from helium (Alphagaz 1, Air liquide), the main carrier gas, passing through an 80 W microwave discharge (Raitek LRE 300, 2450 MHz). NO_2 concentration was used in excess and held at 2.7×10^{13} molecules cm^{-3} during experiments, in order to convert stoichiometrically all H atoms into OH radicals.

OH formation was controlled by light induced fluorescence (LIF) using the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition. The radical excitation, by a dye laser (Quantel TLV IV) pumped by a Nd:YAG laser (Quantel YG 481C) system, was performed at 282 nm. The resulting fluorescence, at 314 and 309 nm was focused with a biconvex lens on a photomultiplier after being filtered with an interferential filter (Oriel 5703: (310 ± 10) nm). The signal was monitored using an oscilloscope (Tektronix 2439).

2.3.3. Experimental procedures

About 5 mg of coated particles were placed with a sieve (45 mm diameter, 100 μm, Sigma-Aldrich) on a glass fibre filter (QF/F, 47 mm diameter, Whatman) previously cleaned by ultrasonication in dichloromethane and heated at 723 K. Particles were weighted before and after reaction (TR-64, Denver Instrument Company, 0.01 mg precision).

For each experiment, the kinetic information was obtained by monitoring the remaining concentration of 9,10-anthraquinone versus exposure time to oxidant. Concentrations vs. time were normalised, i.e. the PAH concentration measured in μg g^{-1} of particles after an exposure time *t* was divided by the corresponding initial particulate-PAH concentration (measured at *t = 0*), leading to a normalised particulate concentration of compound in %.

2.4. Uncertainties

Errors on internal and syringe standards weighting, on silica particles weighting, on chromatographic peak integration and on GC/MS measurements were considered as random errors. Total random error was estimated by the standard deviation on the exponential coefficients obtained from the non-linear least square fit of the experimental points, and was less than 25% for all experiments. Systematic errors (oxidant concentration, pressure, temperature, and calibration of mass flow controllers) were also taken into account. Finally, global uncertainties (random + systematic) on pseudo-first order rate constants were evaluated around 35%.

3. Results and discussion

3.1. Desorption

The desorption study is very important to ensure that 9,10-anthraquinone losses are only due to reactions with oxidants. Experiments were performed in the same conditions than those used to oxidation reactions but without O_3 for the ozone setup and without NO_2 and OH for the fast flow tube. The 9,10-anthraquinone desorption curves for both reactors are presented

in Fig. 1. Each point represents the average of 3 replicates and the error bars correspond to ± 1 standard deviation. As losses due to desorption were not significantly different from zero, they were considered as negligible.

3.2. Heterogeneous ozone reaction

Heterogeneous reactions of ozone with 9,10-anthraquinone were carried out with a high O_3 concentration (5.4×10^{14} molecule cm^{-3}) for two exposure times: 1800 and 3600 s. As presented on Fig. 1, the loss of 9,10-anthraquinone with O_3 could not be separated from that obtained for desorption experiments within uncertainties, whatever the exposure time. The ozone concentration used in this work is very higher than the mean values encountered in the troposphere: 0.5 to 1×10^{12} molecule cm^{-3} in the northern hemisphere (Vingarzan, 2004), even in high polluted locations with concentrations reaching 4.5×10^{12} molecule cm^{-3} (European Environment Agency, 2006). The high stability of 9,10-anthraquinone adsorbed on silica particles with ozone shows that this way cannot be involved in 9,10-anthraquinone atmospheric degradation processes.

These results confirm those of Grosjean et al. (1987), which were unable to detect any loss of 9,10-anthraquinone coated on Teflon, cellulose or silica gel exposed to ozone (about 2.5×10^{14} molecule cm^{-3}) during 18 to 80 hours in the absence of light. Perraudin et al. (2007b) observed that the reaction between anthracene adsorbed on silica particles with ozone led to the formation of 9,10-anthraquinone. Once it was formed, 9,10-anthraquinone seemed to reach a plateau and thus not react with ozone, showing that this compound was stable to ozone exposure. Only Ringuet et al. (2012b) observed a slight degradation of 9,10-anthraquinone associated to natural ambient aerosol and exposed to high concentrations of ozone (about 1×10^{14} molecule cm^{-3}). As showed by different authors ((Nguyen et al., 2009;

Bedjanian et al., 2010; Ringuet et al., 2012b)), the particle substrate (silica vs "real" particle) could play a role in the degradation processes.

3.3. Heterogeneous NO_2 reaction

The exposure of 9,10-anthraquinone adsorbed on silica particles to NO_2 showed the absence of reactivity, as presented on Fig. 1, despite the NO_2 concentration used in this work: 2.7×10^{14} molecule cm^{-3}. This concentration is much higher than those measured in polluted areas such as Mexico City with concentrations reaching 3×10^{12} molecule cm^{-3} (Dunlea et al., 2007) demonstrates that 9,10-anthraquinone will not react in the atmosphere with NO_2, and thus that NO_2 reactions are not involved in 9,10-anthraquinone degradation in the atmosphere. These results are in total agreement with the observations made recently by Ringuet et al. (2012b) for 9,10-anthraquinone (and other quinones) associated to natural ambient particles exposed to O_3 and NO_2 in similar conditions than ours (O_3 and NO_2 concentrations about 1×10^{14} molecule cm^{-3}).

3.4. Heterogeneous OH reaction

Contrary to heterogeneous O_3 and NO_2 reactions, 9,10-anthraquinone was degraded by OH reactions in the presence of NO_2 (2.7×10^{13} molecule cm^{-3}). These results are also in agreement with those reported for 9,10-anthraquinone associated to "real" ambient particle (Ringuet et al., 2012b). If here, the degradation of 9,10-anthraquinone was total, in the case of the study of Ringuet et al. (2012b), only about 30 % was degraded after 60 minutes of exposure to similar OH concentration levels. The influence of the nature of the substrate and compound accessibility could explain the differences observed between these studies.

The kinetics of this reaction was investigated by monitoring normalised concentrations of 9,10-anthraquinone as a function of He/OH/NO_2/NO exposure time. A complete degradation was observed after a sufficient exposure time to (OH + NO_2) (no more 9,10-anthraquinone was detected), meaning that the reaction between the oxidants and 9,10-anthraquinone was total. Experimental data points, presented in Fig. 1, were fitted by a simple mono-exponential function using non linear least square fitting, allowing to determine a pseudo-first-order rate constant: $(2.8 \pm 0.7) \times 10^{-3}$ s^{-1} for the (OH + NO_2) reaction with 9,10-anthraquinone adsorbed on silica particles. Previous experiments performed in this work showed that heterogeneous NO_2 reactivity with 9,10-anthraquinone was negligible. Thus, the pseudo-first order rate constant determined for (OH + NO_2) reactivity can be attributed to that of OH alone.

It is important to note that the pseudo-first order rate constant for the (OH + 9,10-anthraquinone) reaction was derived at a higher OH concentration than the typical ambient concentrations (~ 10^5 - 10^6 molecule cm^{-3}) and therefore would not be logically applicable to the atmospheric conditions. Although the OH radical concentrations could not be measured in this study, a rough estimation of the OH radical concentrations may provide some atmospherically relevant information. In a previous work carried out by our group (Estève et al., 2003), the OH radical concentration measured in the same conditions was [OH] = 3.4×10^{10} molecule cm^{-3}. Considering that this concentration is similar to that obtained in this work, the second-order rate constant for the OH + 9,10-anthraquinone reaction would be 8.2×10^{-14} cm^3 $molecule^{-1}$ s^{-1}. With typical OH concentrations in ambient air, the lifetime of 9,10-anthraquinone by the heterogeneous reaction with OH radicals would be 140 - 1400 days. This lifetime seems to be relatively long, but its determination has to be taken with caution. The OH concentration used to calculate the lifetime is a possible value measured previously with the same experimental setup, but with a another helium bottle. Due to the way of OH production (fast reaction between NO_2 and a H atom, produced by hydrogen impurities from a

helium bottle), it is possible that the bottle used in this work contained less (or more) hydrogen impurities than that used by Estève et al. (2003). Thus the real OH concentration available to 9,10-anthraquinone adsorbed to particles could be smaller (or more important) and the lifetime shorter (or longer). However this work shows for the first time that OH radicals can react with 9,10-anthraquinone in the particulate-phase, showing that OH can be involved in 9,10-anthraquinone degradation processes.

3.5. Oxidation product study

The investigation of oxidation products was carried out by GC-MS in the scan mode (mass/charge ratio ranging from 50 to 550 and number of scans per second = 1.53). The chromatograms showed only one peak from the oxidation 9,10-anthraquinone adsorbed on silica particles with (OH + NO_2). Its mass spectrum (Fig. 2) was compared to that obtained from the library mass spectra (NIST 98, HP Mass Spectral Libraries, 1998), allowing to identify 1-hydroxy-9,10-anthraquinone. The comparison of its retention time with that of a standard confirmed that this oxidation product was 1-hydroxy-9,10-anthraquinone. This compound was the only product identified, and thus neither a nitrated nor another hydroxylated oxidation product was identified in the extract. The formation of 1-hydroxy-9,10-anthraquinone is also important because it confirms that OH radicals have reacted with 9,10-anthraquinone adsorbed on silica particles (addition of OH to 9,10-anthraquinone).

To our knowledge, 1-hydroxy-9,10-anthraquinone has never been identified as an oxidation product from (9,10-anthraquinone + OH) of atmospheric interest. However, the formation of this compound was observed by several studies. Lehto et al. (2003) observed the formation of 1-hydroxy-9,10-anthraquinone after UV-irradiation in the presence of oxygen during 51 h of a saturated solution of 9,10-anthraquinone, probably implying the formation of

hydroxyl radical. 1,4-Dihydroxy-9,10-anthraquinone was also characterized as a product from 1-hydroxy-9,10-anthraquinone. These oxidation products were also observed by Mallakin et al. (2000) with the formation of other oxidation products. Fox and Olive (1979) reported also the formation of 1-hydroxy-9,10-anthraquinone during the photooxidation of anthracene associated to atmospheric particulate matter (which led also to the formation of 9,10-anthraquinone).

In this work, only 1-hydroxy-9,10-anthraquinone was determined but this oxidation product could have a health impact and account for global 9,10-anthraquinone toxicity, since it is also recognized as possibly carcinogenic to humans (Group 2B) (IARC, 2002),. 1-Hydroxy-9,10-anthraquinone disappearance after all 9,10-anthraquinone degradation demonstrates that other oxidation products must be formed. More investigations will be performed to improve the analytical procedure in order to complete oxidation products determination, and thus better understand oxidation mechanisms involved in this reaction.

4. Conclusions

In this work, the heterogeneous chemical oxidation of the carcinogenic 9,10-anthraquinone has been investigated in order to evaluate its atmospheric fate in the particulate-phase. 9,10-Anthraquinone adsorbed on silica particles was exposed to ozone, nitrogen dioxide and hydroxyl radical in the darkness. Such experiments highlight the high stability of 9,10-Anthraquinone to O_3 and NO_2 exposures, when OH radicals seems to account as a possible 9,10-Anthraquinone degradation process in the atmosphere. 1-Hydroxy-9,10-anthraquinone, another compound possibly carcinogen to humans, has been detected as an oxidation product from the heterogeneous OH reaction, demonstrating that (9,10-anthraquinone + OH) reaction could have an atmospheric health impact.

This work shows for the first time that O_3 and NO_2 are not involved in 9,10-anthraquinone degradation, when OH may play an important role. However, other oxidation processes are probably involved in 9,10-anthraquinone degradation. Thus, more investigations need to be performed in order to complete and better understand 9,10-anthraquinone fate in the atmosphere. For example, it could be interesting to better document 9,10-anthraquinone photodegradation. A previous study performed by Kamens et al. (1989) observed that 9,10-anthraquinone adsorbed on soot particles was stable to midday sunlight exposure, but other works showed that 9,10-anthraquinone could be degraded by UV-irradiation (Fox and Olive, 1979; Mallakin et al., 2000; Lehto et al., 2003). These observations highlight that photooxidation could be an important degradation process for 9,10-anthraquinone degradation in the atmosphere.

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Figure captions

Fig. 1. Experimental decay corresponding to the normalised concentration of 9,10-anthraquinone adsorbed on silica particles as a function of exposure time to O_3 (white circles: loss by desorption; black circles: loss by O_3 reaction for $[O_3] = 5.4 \times 10^{14}$ molecule cm^{-3}), NO_2 (white triangles: loss by desorption; white circles: loss by NO_2 reaction for $[NO_2] = 2.7 \times 10^{14}$ molecule cm^{-3}) and to OH (inversed black triangles: loss by OH reaction). Error bars represent 1 standard deviation (n = 3).

Fig. 2. Mass spectrum of 1-hydroxy-9,10-anthraquinone as a product from the heterogeneous reaction of ($OH + NO_2$) with 9,10-anthraquinone adsorbed on silica particles.

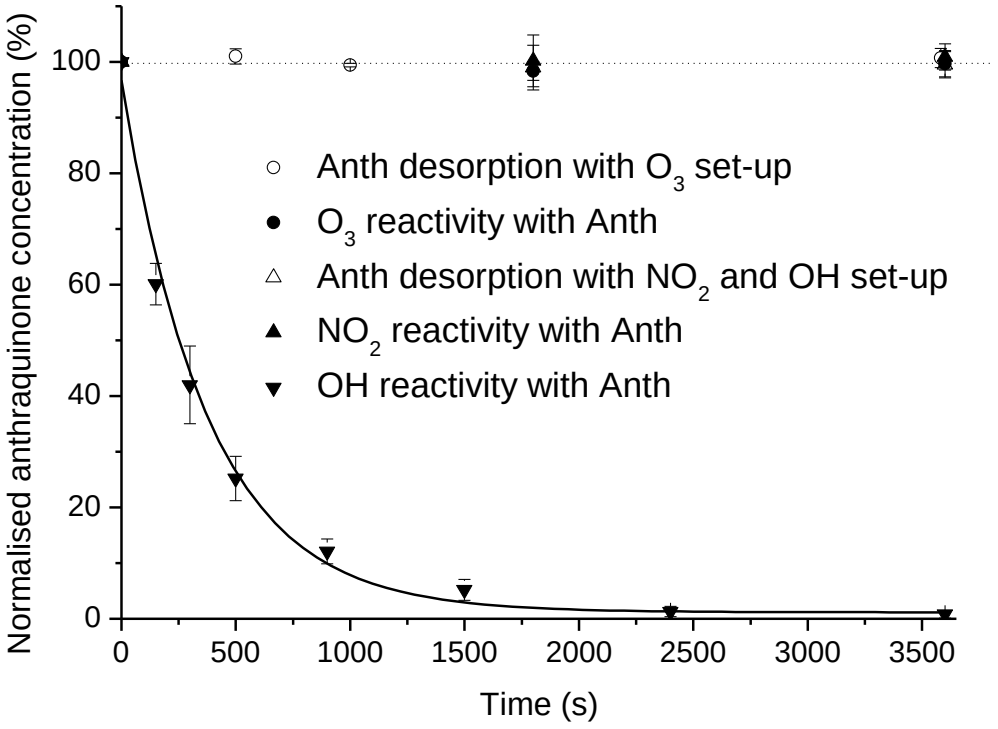

Fig. 1. Experimental decay corresponding to the normalised concentration of 9,10-anthraquinone (Anth) adsorbed on silica particles as a function of exposure time to O_3 (white circles: loss by desorption; black circles: loss by O_3 reaction for $[O_3] = 5.4 \times 10^{14}$ molecule cm^{-3}), NO_2 (white triangles: loss by desorption; white circles: loss by NO_2 reaction for $[NO_2] = 2.7 \times 10^{14}$ molecule cm^{-3}) and to OH (inversed black triangles: loss by OH reaction). Error bars represent 1 standard deviation (n = 3).

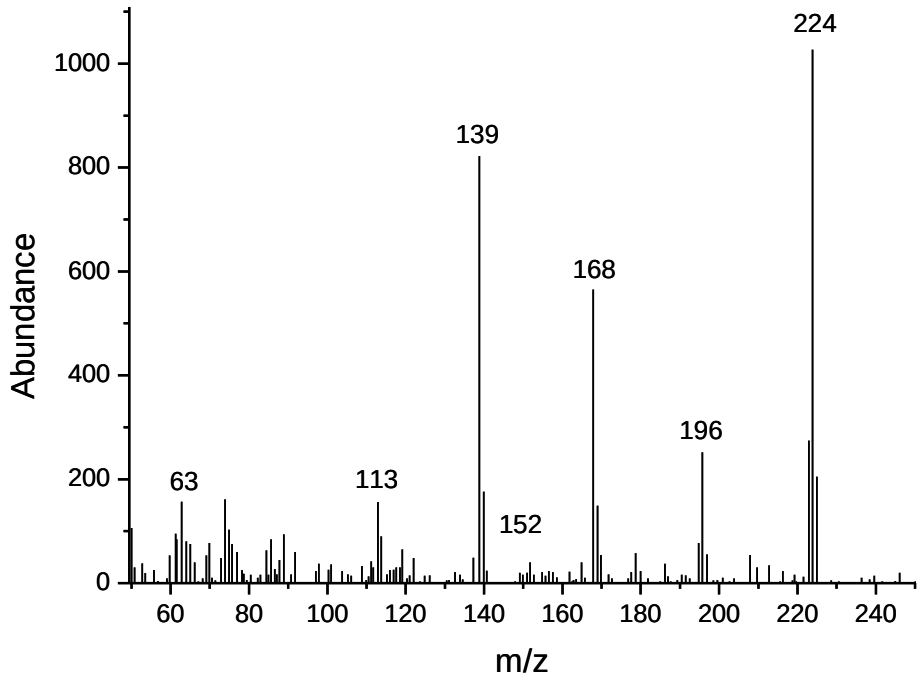

Fig. 2. Mass spectrum of 1-hydroxy-9,10-anthraquinone as a product from the heterogeneous reaction of OH with 9,10-anthraquinone adsorbed on silica particles.