Uptake of HO$_2$ radicals on Arizona Test Dust

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Abstract. The interaction of HO$_2$ radicals with solid films of Arizona Test Dust (ATD) was studied using a low-pressure flow reactor (1–9 Torr) combined with a modulated molecular beam mass spectrometer for monitoring of the gaseous species involved. The reactive uptake coefficient of HO$_2$ was measured from the kinetics of HO$_2$ consumption on Pyrex rods coated with ATD as a function of HO$_2$ concentration ($(0.35$–$3.30) \times 10^{12}$ molecule cm^{-3}), relative humidity (RH $= 0.02$–94 %), temperature ($T = 275$–320 K) and UV irradiance intensity ($J_{NO_2} = 0$–0.012 s^{-1}). The initial uptake coefficient was found to be independent of concentration of HO$_2$, temperature and irradiation conditions, and to decrease with increasing relative humidity: $\gamma_0 = 1.2/(18.7 + RH^{1.1})$ (with 30 % estimated conservative uncertainty). The uptake coefficient was calculated using geometric surface area and should be considered as an upper limit of γ_0. An upper limit of 5 % was found for the gaseous H$_2$O$_2$-forming pathway of the HO$_2$ reaction with ATD surface. The results of the measurements indicate that HO$_2$ loss on dust aerosol may be a non-negligible sink for HO$_x$ species in the troposphere with the effect depending on specific local conditions.

1 Introduction

The HO$_2$ radical is an important atmospheric species, which controls the oxidative capacity of the troposphere through rapid interconversion between HO$_x$ (OH, HO$_2$) species. HO$_2$ is a precursor of the tropospheric ozone through its reaction with NO and further photodissociation of NO$_2$, resulting in production of ozone in the presence of oxygen (Finlayson-Pitts and Pitts, 2000). The HO$_2$ radical is also involved in HO$_x$- and halogen-catalysed cycles of atmospheric ozone depletion (Bedjanian and Poulet, 2003).

The atmospheric concentration of the HO$_x$ family is controlled by the production and loss rates of these species. While the chemistry of HO$_x$ in the gas phase is, in general, well understood, the lack of reliable data on heterogeneous loss of HO$_2$ and the strong need for such data are more and more frequently mentioned in the literature (Thornton et al., 2008; Mao et al., 2010; Macintyre and Evans, 2011). The information on kinetics and mechanism of the interaction of HO$_x$ with different surfaces of atmospheric relevance is essential for accurate modelling of the chemical composition and prediction of changes in the oxidative capacity of the troposphere and regional air quality. Numerous previous studies have consistently reported a discrepancy between modelled and observed concentrations of HO$_2$ in different regions. The overestimation of HO$_2$ concentrations by the models has been attributed to heterogeneous loss of these radicals on aerosol surface as a missing HO$_2$ sink, not properly accounted for in the models (Cantrell et al., 1996a, b; Jaeglé et al., 2000; Kanaya et al., 2000; Sommariva et al., 2004, 2006; de Reus et al., 2005; Mao et al., 2010). The laboratory database for uptake coefficients of HO$_2$ on different surface types is rather scarce, especially for solid surfaces. For example, only one direct study is available for HO$_2$ uptake on soot (Bedjanian et al., 2005), and no data have been reported so far for the interaction of HO$_2$ with mineral dust surfaces. In a few studies, attempts were made to summarize the available uptake data and parameterize them for further use in atmospheric modelling (Jacob, 2000; Thornton et al., 2008; Macintyre and Evans, 2011). Thus, recently, Macintyre and Evans (2011) reviewed the existing laboratory data on HO$_2$ uptake on tropospheric aerosol and derived the global mean uptake coefficient of HO$_2$, $\gamma = 0.028$, which is an order of magnitude lower than those considered in earlier works (Jacob, 2000; Thornton et al., 2008). Another critical issue concerning the heterogeneous interaction of HO$_2$ with atmospheric
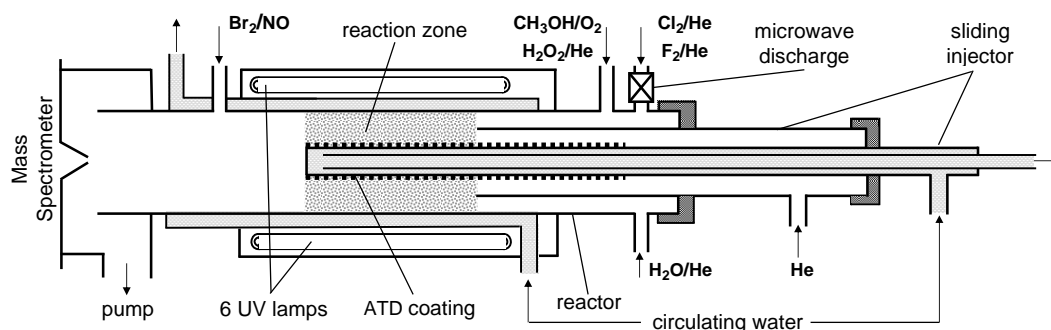
Fig. 1. Diagram of the flow photoreactor.

aerosol is the reaction mechanism, especially with regard to the formation of H$_2$O$_2$ as the reaction product. Considering that H$_2$O$_2$ in the atmosphere is produced via self-reaction of HO$_2$ radicals and H$_2$O$_2$ can photolyse to regenerate HO$_x$ species, the HO$_2$ uptake on aerosols will have different effects on the concentrations of H$_2$O$_2$ and HO$_2$, depending on whether or not H$_2$O$_2$ is formed in the heterogeneous reaction. The only product study of HO$_2$ interaction with a solid surface is that of Loukhovitskaya et al. (2009), where H$_2$O$_2$ was identified as the main product of the HO$_2$ reaction with a solid salt surface.

Considering the limited kinetic and mechanistic data on HO$_2$–aerosol interaction and that heterogeneous reactions of HO$_2$ still remain a significant source of uncertainty in atmospheric modelling of the HO$_x$ budget, it is clear that additional laboratory studies of HO$_2$ uptake, including product study as well as temperature and relative humidity dependence, on various aerosol types are strongly required. In the present study we report the measurements of the uptake coefficient of HO$_2$ radicals on Arizona Test Dust (ATD) under dark and UV irradiation conditions as a function of relative humidity and temperature. The possible formation of H$_2$O$_2$ as a reaction product is also examined. Arizona Test Dust is a mixture of metal oxides which are generally present in atmospheric mineral aerosols in various proportions (Karagulian et al., 2006). Analysis of the experimental data available for the uptake of atmospheric trace gases on different mineral surfaces reveals that ADT mimics quite well the reactivity of authentic dust samples. Indeed, for the uptake to the ATD surface, uptake coefficients identical to those on Saharan dust for NO$_2$ and NO$_3$ and somewhat lower uptake coefficients (by a factor of 1.5–2) for N$_2$O$_5$ and HNO$_3$ were reported (Crowley et al., 2010).

2 Experimental

2.1 Preparation of ATD films

Solid films of ATD were deposited on the outer surface of a Pyrex tube (0.9 cm o.d.) using suspension of ATD (Powder

Technology Inc., nominal 0–3 µm ATD) in ethanol. Prior to film deposition, the Pyrex tube was treated with hydrofluoric acid and washed with distilled water and ethanol. Then the tube was immersed into the suspension, withdrawn and dried with a fan heater. As a result, rather homogeneous (to the eye) solid films were formed at the Pyrex surface. In order to eliminate the possible residual traces of ethanol, prior to uptake experiments, the freshly prepared ATD samples were heated at 100–150 °C for 20–30 min under pumping. In order to measure the mass of the sample on the Pyrex tube, the deposited solid film was mechanically removed at the end of the kinetic experiments. BET surface area of the ATD powder was determined using a Quantachrome Autosorb-1-MP-6 apparatus, and nitrogen as adsorbate gas and was found to be $85 \pm 10 \, \mathrm{m^2 \, g^{-1}}$.

2.2 Flow reactor

The interaction of HO$_2$ with solid ATD films was studied at 1–9 Torr total pressure of He (used as a carrier gas) in a discharge flow reactor with mass spectrometric detection of the gaseous species involved. The experimental equipment and approach used for the kinetic measurements have been described in previous papers from this group (Bedjanian et al., 2005; Loukhovitskaya et al., 2009; El Zein and Bedjanian, 2012). The main reactor (Fig. 1) consisted of a Pyrex tube (40 cm length and 2.4 cm i.d.) with a jacket for the thermostatted liquid circulation. Experiments were carried out using a coaxial configuration of the flow reactor with movable central injector: the Pyrex tube with deposited sample was introduced into the main reactor along its axis. The coated tube could be moved relative to the outer tube of the injector that allowed the variation of the solid film length exposed to gas phase reactant and consequently of the reaction time. The walls of the main reactor as well as of the outer tube of the movable injector (in contact with HO$_2$) were coated with halocarbon wax in order to minimize the heterogeneous loss of HO$_2$ outside the reaction zone.

Externally, the reactor was surrounded by 6 UV lamps (Sylvania BL350, 8 W) with a broad UV emission spectrum between 315 and 400 nm. The UV lamps were installed into
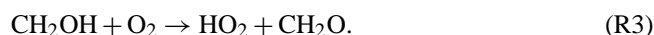
an aluminum light-tight box covering the main reactor tube. Therefore, by switching on or off the lamps, the kinetic measurements could be realized under UV irradiation or dark conditions, respectively. The irradiance intensity in the reactor was characterized by direct measurements of the NO$_2$ photolysis frequency, J_{NO_2}, as a function of the number of lamps switched on. The values of J_{NO_2} were found to be between 0.002 and 0.012 s^{-1}, corresponding to 1 to 6 lamps being switched on (El Zein and Bedjanian, 2012).

2.3 Generation of HO$_2$ radicals and measurement of absolute concentrations

Two methods were used to produce HO$_2$ radicals. In the first one, HO$_2$ radicals were formed in the fast reaction of fluorine atoms, produced in the microwave discharge of F$_2$/He mixture, with excess H$_2$O$_2$:

$$F + H_2O_2 \rightarrow HO_2 + HF. \tag{R1}$$

It was verified by mass spectrometry that more than 90 % of F$_2$ was dissociated in the microwave discharge. The initial concentrations of F$_2$ and H$_2$O$_2$ were $\sim 10^{12}$ and $\sim 10^{14}$ molecule cm^{-3}, respectively. To reduce F atom reactions with the glass surface inside the microwave cavity, a ceramic (Al$_2$O$_3$) tube was inserted in this part of the discharge tube. The second source of HO$_2$ used in this study was the reaction of Cl atoms with an excess of CH$_3$OH in the presence of O$_2$:

$$Cl + CH_3OH \rightarrow CH_2OH + HCl \tag{R2}$$

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O. \tag{R3}$$

Chlorine atoms were generated by microwave discharge in Cl$_2$ diluted with He. The initial concentration of Cl$_2$ was in the range $(1–3) \times 10^{12}$ molecule cm^{-3}, and the fraction of dissociated Cl$_2$ was around 20–30 %. Methanol was introduced into the reactor from a bubbler containing thermostatted ($T = 298$ K) liquid methanol. The concentrations of methanol and oxygen in the reactor were generally in the range $(1–3) \times 10^{14}$ and $(3–10) \times 10^{14}$ molecule cm^{-3}, respectively. Under these experimental conditions Reactions (2) and (3) were rapidly completed, ensuring that chlorine atoms and CH$_2$OH radicals did not reach the reaction zone (in contact with dust sample).

Combination of the chemical conversion method with mass spectrometry provides a few possibilities for HO$_2$ detection (Bedjanian et al., 2001). HO$_2$ radicals may be detected at their parent peak at $m/z = 33$ (HO$_2^+$). This signal should be corrected for the contribution of H$_2$O$_2$ due to its fragmentation in the ion source, which was operating at 25–30 eV. These corrections could be easily done by simultaneous detection of the signals from H$_2$O$_2$ at $m/e = 33$ and 34. The contribution of H$_2$O$_2$ at $m/z = 33$ was on the order of 3 % of the intensity of H$_2$O$_2$ peak at $m/z = 34$. HO$_2$ may

also be detected by chemical conversion to NO$_2$ ($m/z = 46$) through reaction with NO:

$$HO_2 + NO \rightarrow OH + NO_2. \tag{R4}$$

Reaction (4) leads to simultaneous production of OH radicals, which may be rapidly scavenged by Br$_2$ (when added simultaneously with NO) through Reaction (5), forming HOBr (Bedjanian et al., 1999b):
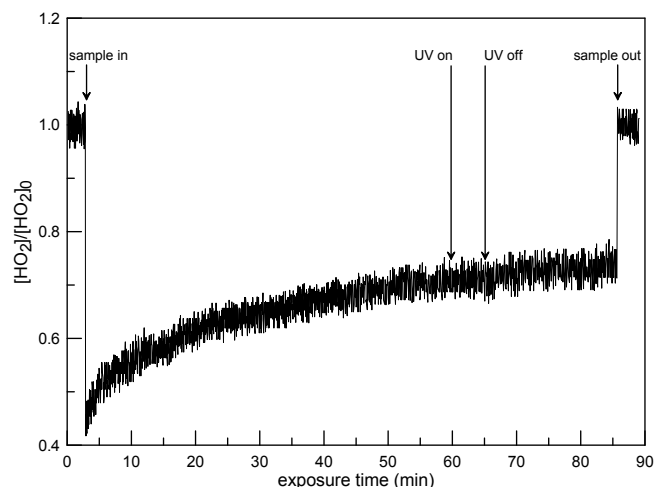
$$OH + Br_2 \rightarrow Br + HOBr. \tag{R5}$$

Assuming a stoichiometric conversion of HO$_2$ to NO$_2$ and OH to HOBr, one has [HO$_2$] = [NO$_2$] = [HOBr]. Thus, in addition, HO$_2$ may be detected at $m/e = 96/98$ as HOBr$^+$. In the present study, the HO$_2$ detection at $m/z = 46$ (NO$_2^+$) and $m/z = 96/98$ (HOBr$^+$) was preferred to the detection at its parent peak ($m/z = 33$, HO$_2^+$), since the sensitivity of the mass spectrometer at these masses was higher and corresponding MS signals were free of contributions of other species and, consequently, did not require any corrections. It should be mentioned that the concentrations of HO$_2$ determined through [NO$_2$] and [HOBr] measurements were found to be in agreement within 10 %. NO and Br$_2$, involved in titration Reactions (4) and (5), were introduced at relatively high concentrations ($\sim 5 \times 10^{13}$ molecule cm^{-3}) at the end of the reactor through an inlet located upstream of the sampling cone (Fig. 1).

Similar reactive configuration, consisting of conversion of HO$_2$ to NO$_2$ and HOBr, was also used for the determination of the absolute concentrations of HO$_2$ radicals. The absolute concentrations of HOBr were measured using the reaction of OH radicals with excess Br$_2$ (Reaction 5). In the calibration experiments OH radicals were formed through the fast reaction of H atoms with excess NO$_2$:

$$H + NO_2 \rightarrow OH + NO. \tag{R6}$$

Thus, HOBr concentrations were determined from the consumed concentration of Br$_2$: [OH] = [HOBr] = Δ[Br$_2$]. The possible influence of secondary chemistry on the procedure used for the absolute calibration of HOBr signals has been discussed in detail in previous papers (Bedjanian et al., 1999a, 2001) and shown to be negligible.

The concentrations of the stable gas phase species (NO, NO$_2$, Br$_2$) in the reactor were calculated from their volumetric flow rates obtained from the measurements of pressure drop of mixtures of the species with helium in calibrated volume flasks. The absolute calibration of H$_2$O$_2$ has been performed by injecting (using graduated syringes) known amounts (0.5–10 µL) of the 60 wt % solution inside the flow tube reactor and recording the parent mass peak intensity of H$_2$O$_2$ at $m/z = 34$. The integrated area of the mass spectrometric signals corresponding to the known total number of H$_2$O$_2$ molecules injected into the reactor allowed the determination of the calibration factor. The concentrations of water vapour were determined by calculating the H$_2$O flow rate

Fig. 2. Typical uptake profile of HO$_2$ on ATD surface: $T = 300$ K, $P = 1$ Torr, dry conditions (RH ≈ 0.02 %), [HO$_2$]$_0 = 1.3 \times 10^{12}$ molecule cm^{-3}, sample mass = 0.47 mg cm^{-1}. HO$_2$ is monitored as HOBr$^+$ at $m/z = 98$ (see text).
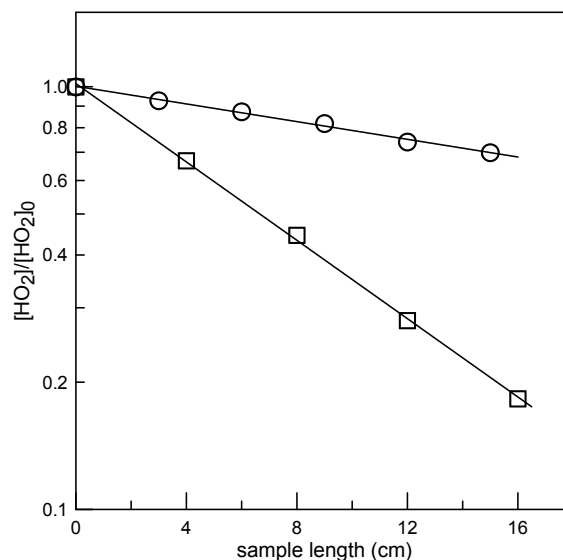
from the total (H$_2$O + He) and H$_2$O vapour pressures in the bubbler and the measured flow rate of He through the bubbler.

3 Results

3.1 Kinetics of HO$_2$ loss

Figure 2 displays a typical behaviour of the concentration of HO$_2$ radicals upon introduction of the ATD-coated tube into the reaction zone (sample in). Fast initial consumption of HO$_2$, followed by surface deactivation resulting in a decrease of HO$_2$ loss rate, was observed. When the mineral sample was withdrawn from the reaction zone after exposure to HO$_2$ (sample out, $t \approx 86$ min) – that is, when HO$_2$ was no longer in contact with the sample surface – the concentration of HO$_2$ recovered rapidly to its initial value. One may note that irradiation of the ATD surface with 6 UV lamps (UV on) had no impact on the kinetics of HO$_2$ loss. For the data presented in Fig. 2, the total number of HO$_2$ radicals lost on the surface is 8×10^{15} molecule cm^{-2} (lower limit, as calculated using total BET surface area), i.e. much higher than a monolayer coverage ($< 10^{15}$ molecule cm^{-2}). This observation seems to clearly indicate that HO$_2$ loss on ATD has a catalytic nature; i.e. it is not limited by site-filling.

In the present study we have measured the initial uptake coefficient of HO$_2$ (γ_0), because the "quasi" steady-state uptake of HO$_2$ was found to slowly decrease with exposure time (Fig. 2). The slow rise in HO$_2$ signal with time is a result of the surface deactivation, which may be due to its progressive saturation with the products of the heterogeneous reaction, H$_2$O being the most probable final reaction product partly remaining on the surface. The prolonged exposure to

Fig. 3. Example of kinetics of HO$_2$ consumption in reaction with ATD surface: $T = 300$ K, $P = 1$ Torr, dry conditions, [HO$_2$]$_0 = 2.0 \times 10^{12}$ molecule cm^{-3}. Circles and squares correspond to the results obtained using F + H$_2$O$_2$ and Cl + CH$_3$OH + O$_2$ systems to produce HO$_2$ and with samples of 2.5 and 2.8 mg cm^{-1} after 75 and 20 min of exposure, respectively. HO$_2$ is monitored as NO$_2^+$ at $m/z = 46$ (see text).

the compounds coming from HO$_2$ sources used in the study (CH$_3$OH, HCl, Cl$_2$, H$_2$O$_2$, HF) can also lead to modification of the surface reactivity with time, although no impact of these species on the initial uptake was observed (see below). The uptake coefficient was determined as the probability of irreversible loss of the radicals per collision with dust surface:

$$\gamma = \frac{4k'}{\omega} \times \frac{V}{S}, \tag{1}$$

where k' is the first-order rate coefficient of HO$_2$ loss (s^{-1}), ω the average molecular speed (cm s^{-1}), V the volume of the reaction zone (cm^3) and S the surface area of the solid sample involved in the heterogeneous reaction (cm^2).

Figure 3 displays examples of HO$_2$ loss kinetics in heterogeneous reaction with the surface of ATD. Each of the kinetics shown in Fig. 3 was obtained with one mineral film in a single experiment by varying the length of the mineral film in contact with HONO. The kinetic runs were measured under quasi steady-state uptake conditions on a partly deactivated surface, where decrease of the uptake with time is rather slow and could be considered as negligible during the few minutes of the acquisition time. The decays of HO$_2$ were found to be exponential (solid lines in Fig. 3) and were treated with the first-order kinetics formalism, the rate constant being determined as
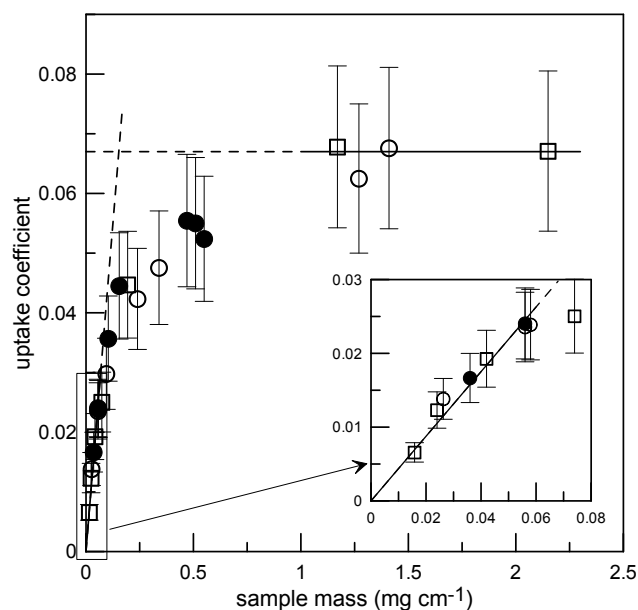
$$k'_{\text{obs}} = -\frac{d \ln([HO_2])}{dt}, \tag{2}$$

where t is the reaction time defined by the sample length to flow velocity ratio. The values of the observed first-order rate constants, k'_{obs}, determined from the decays of HO$_2$ should be corrected for the diffusion limitation in the HO$_2$ radial transport from the volume to the reactive surface. The radial diffusion problem for the coaxial configuration of the reactor used in the present study was solved by Gershenzon and co-workers (Gershenzon et al., 1994, 1995):

$$\frac{1}{k'_{obs}} = \frac{1}{k'} + \frac{R^2}{K^d(q)D_0} \times P, \qquad (3)$$

where k' is a true rate constant, D_0 is the diffusion coefficient of HO$_2$ at 1 Torr pressure (Torr cm^2 s^{-1}), P is the total pressure in the reactor and $K^d(q)$ is a dimensionless rate constant of radial diffusion, which is a function of sample tube radius (r) to main reactor radius (R) ratio, $q = r/R = 0.375$ (for the configuration used in the present study). Diffusion corrections on k'_{obs} were calculated using Eq. (3) with $D_0 = 430$ Torr cm^2 s^{-1} (Bedjanian et al., 2005; Ivanov et al., 2007) at $T = 298$ K and assuming $T^{1.75}$ dependence of the diffusion coefficient on temperature and $K^d(q) = 4.4$ (Gershenzon et al., 1995). In order to reduce rather elevated diffusion corrections on k'_{obs} due to high uptake of HO$_2$ on the ATD surface, most of experiments were carried out at relatively low pressure of 1 Torr. The diffusion corrections applied to k'_{obs} were generally between 10 and 30 %; however, for a few points measured at elevated pressures (up to 9 Torr) they reached a factor as high as 1.5.
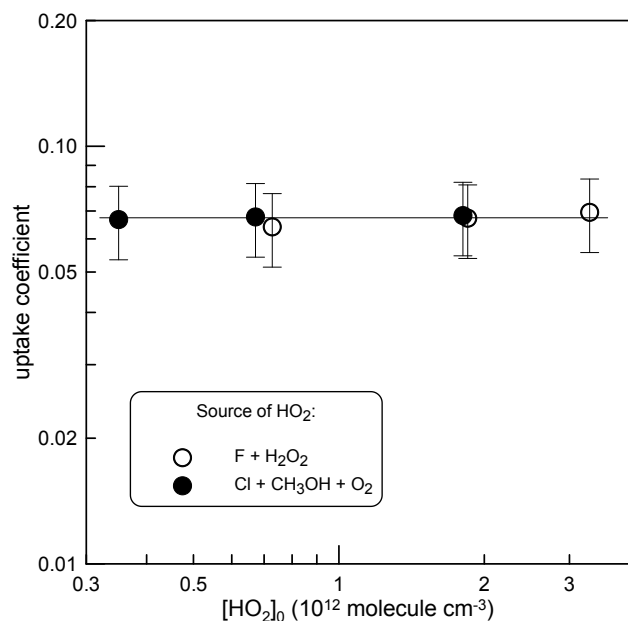
3.2 Dependence on sample mass

Surface area involved in the heterogeneous reaction is an important parameter which is required for calculation of the uptake coefficient. In order to determine the surface area of ATD accessible to HO$_2$, the uptake of HO$_2$ was measured as a function of the thickness of ATD sample. The experiments were performed at $T = 300$ K under dry conditions. The obtained results are presented in Fig. 4, where the uptake coefficient of HO$_2$, calculated applying the geometric (projected) surface area of ATD sample, is shown as a function of the ATD mass deposited per unity length of the support tube. One may note that three different regimes were observed: the first one, where the geometric uptake coefficient linearly increases upon increase of the sample mass (up to nearly 0.06 mg cm^{-1}); the second one (transition region, between 0.06 and nearly 1 mg cm^{-1}), where γ continues to increase slowly; and, finally, the saturation region, where the uptake coefficient is mass-independent (> 1 mg cm^{-1}). The linear dependence of γ_{geom} on mass (thickness) of the reactive film is generally considered as an indication that the entire surface area of the solid sample is accessible to the gaseous reactant (Underwood et al., 2000), which implies the use of the BET surface area in the calculations of the true uptake coefficient. In the present study the linear regime of the uptake coefficient was observed at relatively low masses

Fig. 4. Dependence of the uptake coefficients of HO$_2$ (calculated using geometric surface area) on mass of ATD samples (per 1 cm length of the support tube): $T = 300$ K, $P = 1$ Torr, dry conditions, $[\text{HO}_2]_0 \approx 10^{12}$ molecule cm^{-3}. Circles and squares correspond to the results obtained using F + H$_2$O$_2$ and Cl + CH$_3$OH + O$_2$ systems to produce HO$_2$; filled and open symbols represent the data observed with HO$_2$ detection at $m/z = 96$ (HOBr$^+$) and 46 (NO$_2^+$), respectively.

of the ATD coating. Working with such low masses of solid samples was associated with some experimental difficulties. Firstly, by the method that we used, the measurement of the total dust masses of a few tenths of mg was problematic and associated with high uncertainties. Secondly, the reproducibility of the kinetic data observed with dust samples of low masses was rather poor. In addition, the reason for the initial linear mass dependence of γ at very low masses could also be the incomplete coverage of the support tube by dust aggregates. It is not certain that for sample mass lower than 0.06 mg cm^{-1} a coherent dust coating is provided, although no uncovered area on the support tube was observed by visual inspection. For all these reasons we have chosen a compromise solution. Uptake experiments were carried out with masses of ATD higher than 1 mg cm^{-1} (where geometric uptake is independent of the sample mass), and the uptake coefficient of HO$_2$ was calculated with geometric (projected) surface area. Therefore, the uptake coefficient of HO$_2$ from the present study should be considered as an upper limit. On the other hand, the lower limit of the uptake coefficient may be also estimated. So applying the BET surface area to the experimental data observed for geometric uptake coefficient at low masses (in linear regime), it turns out that the uptake coefficient calculated with total specific surface area is a factor of 40 lower than that with the geometric one.

Fig. 5. Uptake coefficients as function of the initial concentration of HO$_2$: $T = 300$ K, $P = 1$ Torr, dry conditions, sample mass = (1.2–1.4) mg cm^{-1}.

3.3 Dependence on initial concentration of HO$_2$

The dependence of γ on the initial concentration of HO$_2$ radicals, varying in the range (0.35–3.3) $\times$ 10^{12} molecule cm^{-3}, was measured at $T = 300$ K under dry conditions (RH = 0.03 %). The observed results are displayed in Fig. 5. The initial uptake coefficient of HO$_2$, γ ($\pm 2\sigma$) = (6.7 $\pm$ 0.4) $\times$ 10^{-2}, was found to be independent of the initial radical concentration in the range of [HO$_2$]$_0$ used. The concentrations of HO$_2$ used in these experiments are rather high, especially if compared with those in the atmosphere. The question arises if different uptake rates may be observed with lower, more atmospherically relevant concentrations of HO$_2$. Although no dependence of the initial uptake on HO$_2$ concentration was observed within the range studied, it may nevertheless be the case that the surface was saturated under these conditions. In the example presented in Fig. 2, the total number of HO$_2$ radicals taken up by the surface during the first 30 s of exposure is $\sim$ 10^{16} molecules per cm^2 of geometric surface area ($\approx$ 7 $\times$ 10^{13} molecules cm^{-2}, if calculated with BET surface area). The number of HO$_2$ radicals lost on the surface, calculated with geometric surface area (which seems to be more relevant for rapid initial uptake), is much higher than a monolayer coverage ($<$ 10^{15} molecule cm^{-2}); nevertheless these data do not suggest the saturation of the reactive surface, considering that HO$_2$ uptake is not limited by site-filling. Therefore, on the basis of the present data, it is difficult to make definite conclusions about HO$_2$ uptake at lower concentrations. However, we believe that the experimental observations of

the independence of γ_0 of the initial concentration of HO$_2$ and catalytic nature of HO$_2$ uptake suggest that similar values of the initial uptake coefficient may be expected at lower concentrations of HO$_2$.

One may note that good agreement exists between the results obtained for the uptake coefficient using two different methods to generate HO$_2$ radicals (Fig. 5). This observation seems to indicate that the presence of H$_2$O$_2$ (when the F + H$_2$O$_2$ reaction is used for generation of HO$_2$) in the reactive system has a negligible impact, at least, on the initial uptake of HO$_2$ radicals on the ATD surface. This was verified in additional experiments where the uptake coefficient of HO$_2$ was measured with concentration of H$_2$O$_2$ varied between 2 $\times$ 10^{13} and 2.6 $\times$ 10^{14} molecule cm^{-3}. The values of γ measured in the presence of different concentrations of H$_2$O$_2$ in the reactor were found to be similar within uncertainty of the measurements. Similar invariance of the initial uptake coefficient was observed using the Cl + CH$_3$OH +O$_2$ system as a source of HO$_2$ and with concentration of methanol varying in the range 3.5 $\times$ 10^{13}–3.0 $\times$ 10^{14} molecule cm^{-3}.

3.4 Dependence on RH, temperature and UV irradiation intensity

RH dependence of the uptake coefficient was studied at $T = 275$ K, with relative humidity in the reactor being varied in the range (0.02–94) %. Rather low temperature was chosen for these experiments in order to provide reasonably high RH in the reactor with relatively low total pressures used. The results obtained for initial uptake coefficients of HO$_2$ on the ATD surface are displayed in Fig. 6. One may note again that the uptake data obtained using different chemical systems for generation of HO$_2$ radicals (filled and open symbols in Fig. 6) are in agreement within the experimental uncertainty on the determination of γ (estimated to be 20–30 %).
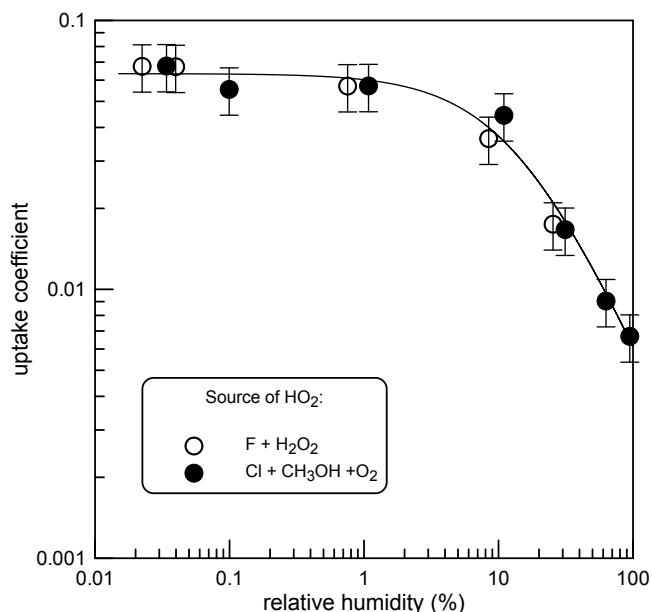
As it may be seen in Fig. 6, the values of the uptake coefficient can be considered as RH independent under dry conditions (up to RH $\sim$ 2 %). However, significant decrease of γ is observed when RH is further increased. The solid line in Fig. 6 represents a fit to the experimental data according to the following expression:

$$\gamma_0 = 1.2/(18.7 + RH^{1.1}).$$

This empirical equation allows describing our results in the whole RH range used with the estimated conservative uncertainty of 30 %.

Temperature dependence of the uptake coefficient was measured in the temperature range 275–320 K at a fixed relative humidity of 0.04 %. The results are presented in Fig. 7. As one may note, the initial uptake coefficient was found to be independent of temperature.

Considering that ATD contains photo-active components, such as Fe$_2$O$_3$ (2–5 %) and TiO$_2$ (0.5–1 %) and in order to check for the possible impact of UV irradiation on the uptake of HO$_2$, a series of experiments has been carried out
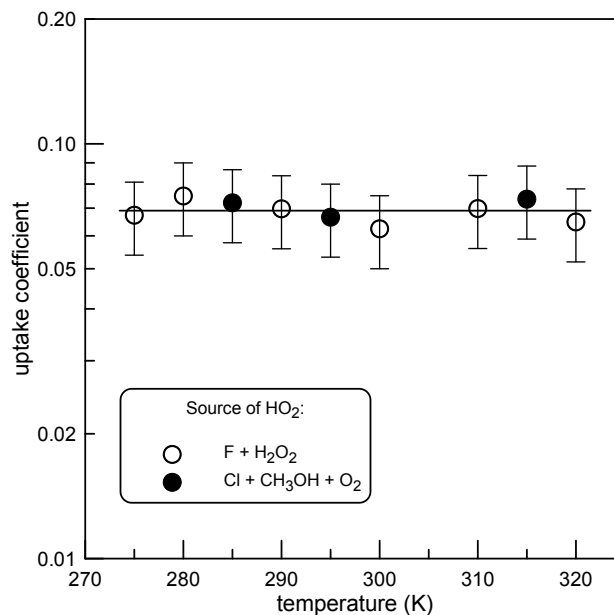
Fig. 6. Initial uptake coefficients of HO_2 on ATD as a function of relative humidity: $T = 275 \, K$, $P = 1.0$–$9.0 \, Torr$, $[HO_2]_0 \approx 10^{12} \, molecule \, cm^{-3}$, sample mass = $(1.2$–$1.5) \, mg \, cm^{-1}$. The data were obtained with two sources of HO_2 radicals: reactions $F + H_2O_2$ (open symbols) and $Cl + CH_3OH + O_2$ (filled symbols).

Fig. 7. Temperature dependence of the uptake coefficient of HO_2 on ATD: $P = 1 \, Torr$, $T = 275$–$320 \, K$, $RH = 0.04 \, \%$, $[HO_2]_0 \approx 10^{12} \, molecule \, cm^{-3}$. The data were obtained with two sources of HO_2 radicals: reactions $F + H_2O_2$ (open symbols) and $Cl + CH_3OH + O_2$ (filled symbols).

with irradiated ATD surface. Dependence of the uptake coefficient on the irradiation intensity was studied by switching on the different number of lamps in the reactor, from 1 to 6. This corresponds to the variation of the NO_2 photolysis frequency from 0.002 to $0.012 \, s^{-1}$. Under these irradiance conditions we have not observed any effect of the UV irradiation on the kinetics of HO_2 loss (see Fig. 2, for example) on the ATD samples in the whole range of RH used. The measured values of γ were similar (within a few %) to those under dark conditions.

3.5 Estimation of H_2O_2 yield

In a previous study from this group, H_2O_2 was detected as a product of the HO_2 uptake on a salt surface (Loukhovitskaya et al., 2009). In this work, we have examined the possible H_2O_2 formation in the gas phase (H_2O_{2gas}) upon interaction of HO_2 radicals with ATD surface. Experiments were carried out at $P = 1 \, Torr$ total pressure, $T = 300 \, K$ and under dry conditions. A reaction of Cl atoms with a large excess of CH_3OH/O_2 mixture was used as a source of HO_2 radicals. The experiment consisted in the introduction of an ATD sample in the reaction zone (in contact with HO_2) and monitoring of the consumed HO_2 concentration and possibly formed H_2O_{2gas} concentration. No changes in the relatively high (due to contribution of molecular oxygen) background signal at $m/z = 34$ (parent peak of H_2O_2) were observed upon heterogeneous consumption of $2.1 \times 10^{12} \, molecule \, cm^{-3}$ of

HO_2. This non-observation of H_2O_2 in the gas phase allowed setting an upper limit of 5 % for its yield in reaction of HO_2 with ATD surface. This upper limit of H_2O_{2gas} yield was determined as a ratio of the concentration of H_2O_{2gas} formed ($< 9.7 \times 10^{10} \, molecule \, cm^{-3}$) to the concentration of HO_2 consumed.

4 Discussion

This work reports the first measurement of the HO_2 radical uptake on mineral dust. The uptake coefficient of HO_2 on Arizona Test Dust measured in the present study decreases with relative humidity being nearly 2.6×10^{-2} and 8.4×10^{-3} at RH = 20 and 80 %, respectively. The negative dependence of HO_2 uptake on the ATD surface on RH may be compared with the effect of humidity on the rate of the heterogeneous loss of HO_2 on salt surfaces, for which a number of studies are available. For dry aerosol particles of NaCl, Taketani et al. (2008) observed an enhancement of the HO_2 uptake in the presence of water vapor; however, Remorov et al. (2002) reported a decrease in the probability of HO_2 uptake on NaCl upon addition of water in the reactor. In a previous work from this group (Loukhovitskaya et al., 2009), no impact of water was observed for the uptake of HO_2 on solid NaCl and NaBr; however, an inhibiting effect of water was observed for the uptake of HO_2 on $MgCl_2 \times 6H_2O$, which is a more hygroscopic salt (Bedjanian and Loukhovitskaya, 2011). Much

higher values of the uptake coefficient compared to dry salt were systematically observed for wet particles (Taketani et al., 2008, 2009), suggesting that heterogeneous loss of HO$_2$ is enhanced by particles containing water. One may note that even for salt surfaces the available information on RH dependence of HO$_2$ uptake is controversial. The RH dependence of γ observed in the present study (decrease of the uptake coefficient upon increase of RH) points to the role of water rather as blocking the available active sites on the surface. It may be noted that the γ values measured in the present study for RH between 20 and 80 % are close to that measured for the uptake coefficient of HO$_2$ on water, $\gamma \geq 0.01$ (Hanson et al., 1992). This fact seems to correlate, at least qualitatively, with the available data for the adsorption of water on mineral oxides (Goodman et al., 2001; Ma et al., 2010). Indeed, it was reported that water adsorption to SiO$_2$, Al$_2$O$_3$, MgO, Fe$_2$O$_3$, and TiO$_2$ (which are components of ATD) could be well described with the Brunauer–Emmett–Teller (BET) type isotherm, with the monolayer coverage occurring between 20 and 30 % relative humidity (Goodman et al., 2001; Ma et al., 2010).

In only one previous product study of HO$_2$ interaction with solid surface (Loukhovitskaya et al., 2009) H$_2$O$_2$ was identified as the main gaseous product of the HO$_2$ reaction with the surface of NaBr. Considering the measured H$_2$O$_{2\,gas}$ yield of nearly 0.5, Loukhovitskaya et al. (2009) proposed a two-step reaction mechanism resulting in the HO$_2$ recombination on the surface. The upper limit of 5 %, determined in the present study for the gaseous H$_2$O$_2$-forming channel of the HO$_2$ + ATD reaction, points to a different mechanism of the reactive uptake of HO$_2$ on mineral oxides. For example, HO$_2$ may react with OH groups present on the surfaces of mineral oxides, leading to formation of H$_2$O and O$_2$ as final reaction products (Lin and Gurol, 1998). Another point which should be mentioned is the rather high reactive uptake of H$_2$O$_2$ on mineral surfaces which has recently been reported in a number of studies (Pradhan et al., 2010a, b; Wang et al., 2011; Romanias et al., 2012). Concerning the interaction of H$_2$O$_2$ with ATD surface, we have found (unpublished data) that the uptake of H$_2$O$_2$ to ATD is rather rapid ($\gamma_0 \sim 0.001$ under dry conditions, decreasing upon increase of RH) and mainly reactive, i.e. practically irreversible. The products of this heterogeneous reaction are not known; however they are expected to be O$_2$ and H$_2$O. Thus, H$_2$O$_2$ (if formed in primary reaction of HO$_2$) may be partially processed in the heterogeneous reaction on the ATD surface. However, in our opinion, the transformation of H$_2$O$_2$ on the ATD surface is not the main reason for the absence of H$_2$O$_2$ in gaseous products of the HO$_2$ + ATD reaction. Thus in a recent study from our group H$_2$O$_2$ was distinctly observed as a gaseous product of the interaction of the OH radical with the same ATD surface, although with a relatively low yield of 10 % (Bedjanian et al., 2013). The present results seem to indicate that HO$_2$ uptake by atmospheric aerosols does not necessarily produce H$_2$O$_{2\,gas}$. In this context, in a recent paper by Mao
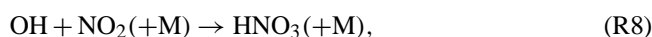
et al. (2013), a catalytic mechanism was proposed which involves a coupling of the transition metal ions Cu(I)/Cu(II) and Fe(II)/Fe(III) to rapidly convert HO$_2$ to H$_2$O in aqueous aerosols.

Temperature dependence of the uptake coefficient measured on ATD surfaces is also quite different from those on salt surfaces. All temperature dependence studies of HO$_2$ uptake on solid salt particles report a rather strong negative temperature dependence of the uptake coefficient (Antsupov, 1988; Gratpanche et al., 1996; Remorov et al., 2002; Loukhovitskaya et al., 2009), while in the present study we have not observed any effect of temperature (for $T = 275$–320 K) on the HO$_2$ uptake on ATD. This seems to indicate once again the difference in the uptake mechanism on these surfaces. Let us note that the temperature-independent value of γ was also reported for the uptake of HO$_2$ on a soot surface (Bedjanian et al., 2005).

The importance of HO$_2$ loss in the heterogeneous reaction with atmospheric dust aerosol,

$$HO_2 + dust \rightarrow products, \tag{R7}$$

may be briefly discussed. First, it should be noted that the range of γ reported in the present study is close to the global mean value of 0.028 based on recent parameterization of the available laboratory data by Macintyre and Evans (2011), but this value is significantly lower than those adopted in earlier modelling studies. The potential atmospheric impact of Reaction (7) may be roughly estimated by comparing its rate with that of the known loss processes of HO$_x$ in the atmosphere. In the high-NO$_x$ regime (polluted urban troposphere) a major gas phase sink for the HO$_x$ species is Reaction (8) of OH radicals with NO$_2$,

$$OH + NO_2(+M) \rightarrow HNO_3(+M), \tag{R8}$$

combined with the heterogeneous removal of HNO$_3$. For the ratio of the rates of the Reactions (7) and (8), one has

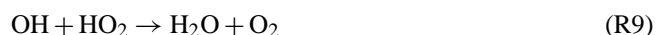$$\frac{R_7}{R_8} = \frac{k_7'[HO_2]}{k_8[OH][NO_2]}.$$

In accordance with

$$k_7' = \frac{\omega \gamma}{4} \frac{S}{V}$$

and using $\gamma = 0.02$, the upper limit of the uptake coefficient measured in the present study for RH = 30 %, dust surface loading of $\sim 10^{-6}$ cm^2 cm^{-3} (Zhang and Carmichael, 1999; de Reus et al., 2005), the calculated value is $k_7' \approx 2.2 \times 10^{-4}$ s^{-1} (for $T = 300$ K). Further, using the value $k_8 \sim 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Sander et al., 2011) and a typical ratio [HO$_2$]/[OH] ~ 100, we obtain $R_7/R_8 = 2.2 \times 10^9/[NO_2]$. This ratio indicates that for concentrations of NO$_2$ of a few ppbv heterogeneous loss of HO$_2$ does not represent a significant sink for HO$_x$ compared with Reaction (8). However, under specific conditions, for example, of severe

dust storm, when aerosol surface loading can be as high as 2×10^{-5} cm^2 cm^{-3} (Zhang and Carmichael, 1999), the rate of Reaction (7) may be comparable with that of the OH + NO$_2$ reaction.

Under low-NO$_x$ conditions (free troposphere) the loss of atmospheric HO$_x$ is mainly due to reactions between HO$_x$ radicals:

$$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \qquad \text{(R9)}$$

$$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2. \qquad \text{(R10)}$$

The rate of HO$_2$ loss in heterogeneous Reaction (7) may be compared with that of self-reaction of HO$_2$ radicals:

$$\frac{R_7}{R_{10}} = \frac{k_7'[\text{HO}_2]}{2k_{10}[\text{HO}_2]^2} = \frac{k_7'}{2k_{10}[\text{HO}_2]}.$$

One may note that the relative contribution of Reaction (7) in this case depends on the absolute concentration of HO$_2$, because the rate of the self-reaction of HO$_2$ is proportional to the square of the concentration of the radicals and heterogeneous reaction is first order in [HO$_2$]. With $k_7' = (0.22\text{–}4.4) \times 10^{-3}$ s^{-1} (calculated for aerosol surface in the range $(0.1\text{–}2) \times 10^{-5}$ cm^2 cm^{-3}), $k_{10} \cong 2.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Sander et al., 2011) and typical HO$_2$ concentration of $\sim 10^8$ molecule cm^{-3}, we obtain $R_7/R_{10} = 0.44\text{–}8.8$. These calculations show that the heterogeneous sink for HO$_2$ on aerosol surface may be comparable and even higher, during severe dust storm events, than HO$_2$ loss through self-reaction. This point is of importance not only for HO$_x$ but also for the H$_2$O$_2$ budget, considering the absence of H$_2$O$_2$ in the gas phase products of HO$_2$ interaction with dust aerosol shown in the present study. The conclusion of these rough estimations is that HO$_2$ loss on dust aerosol may be a non-negligible sink for HO$_x$ species in the troposphere with an effect depending on specific conditions such as aerosol loading, relative humidity, and concentrations of HO$_x$. It should be emphasized, however, that all the considerations above should be regarded as nothing more than a rough estimate. We recall that the upper limit of the uptake coefficient (initial one and calculated with geometric surface area), which can greatly differ from the true value, was used in the estimation of the possible atmospheric impact. Another point is that in the present study the uptake data were measured on fresh dust samples, whereas real atmospheric dust is chemically aged during transport and can be coated with organic and inorganic species. This can lead to significant changes in dust reactivity, which are difficult to predict a priori. This remark is not specific for the present data on HO$_2$ uptake, but concerns the studies of heterogeneous reactions on atmospheric aerosol in general. Finally, it is clear that additional measurements of the HO$_2$ interaction (preferably with lower radical concentrations) with aged (or coated prior to experiments, or/and in the presence of other atmospheric trace gases) dust samples, preferably authentic ones from different locations, are needed.

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