

Parameterisation and impact of aerosol uptake of HO₂ on a global tropospheric model

H. L. Macintyre and M. J. Evans

Institute for Climate and Atmospheric Science, School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK

Received: 18 April 2011 – Published in Atmos. Chem. Phys. Discuss.: 1 June 2011

Revised: 7 October 2011 – Accepted: 20 October 2011 – Published: 4 November 2011

Abstract. HO₂ is an important atmospheric trace gas, whose sink to aerosol is poorly understood yet significant. Previous parameterisations of the rate of uptake have been limited by the lack of laboratory studies. This paper creates a parameterisation for γ_{HO_2} based on the available laboratory studies. The calculated global mean γ_{HO_2} is 0.028, significantly lower than previous work (0.2). Modelled concentrations of HO₂ show significant regional sensitivity to the value of γ_{HO_2} (up to +106% at the surface with the parameterisation of γ_{HO_2} in this work as compared with a value of 0.2), but global sensitivity is small (+3.2%). The modelled response in O₃ is also highly regional, being up to +27% at the surface over China, and only +0.3% globally (with the parameterisation of γ_{HO_2} in this work as compared with a value of 0.2). The impact of γ_{HO_2} on sulfate is more complex, with up to +16% over China and –5% over high latitudes, resulting in a global change of +1.2% (with the parameterisation of γ_{HO_2} in this work as compared with a value of 0.2). Uncertainty in the reaction mechanism and hence products (previously assumed to be H₂O₂) impacts the processing of sulfur and hence aerosol loads. Further laboratory studies are desirable to constrain the rate of reaction and to elucidate the reaction mechanism and products.

hydroperoxyl radical (HO₂). As well as participating in gas-phase reactions, HO₂ is also taken up by aerosol particles (Jacob, 2000). The uptake of HO₂ reduces HO₂ concentrations and thus reduces OH and O₃ concentrations. HO₂ uptake has received less attention in laboratory and modelling studies than the uptake of N₂O₅, but may play a significant role in the atmospheric system (Tie et al., 2001; Martin et al., 2003; Liao et al., 2006).

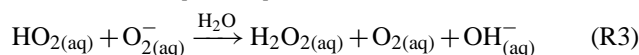
The rates of reactions on aerosol particles (“heterogeneous reactions”) are determined by the available aerosol surface area, and an uptake coefficient gamma (γ), defined as “the probability that a molecule impacting the surface of the particle undergoes irreversible reaction” (Schwartz, 1986). Determinations of the value of γ_{HO_2} from laboratory, field, and modelling studies span several orders of magnitude (~0.002 to 1.0) (Mozurkewich et al., 1987; Hanson et al., 1992; Gershenson et al., 1995; Cooper and Abbatt, 1996; Gershenson et al., 1999; Saathoff et al., 2001; Remorov et al., 2002; Thornton and Abbatt, 2005; Bedjanian et al., 2005; Taketani et al., 2008, 2009; Cantrell et al., 1996a,b; Plummer et al., 1996; Jaeglé et al., 2000; Loukhovitskaya et al., 2009). This paper reviews the laboratory studies of HO₂ uptake by tropospheric aerosol and constructs a parameterisation based on these studies. It then assesses the impact of this on tropospheric composition with a global model.

1 Introduction

Oxidants are a key component of the atmospheric system as they help control the concentrations of some pollutants and greenhouse gases. The key oxidants in the troposphere are the hydroxyl radical (OH), the nitrate radical (NO₃), ozone (O₃), and hydrogen peroxide (H₂O₂) (Logan et al., 1981). Many of these oxidants are linked by the

2 Previous studies

The uptake of HO₂ by tropospheric aerosol is thought to proceed via acid-base dissociation of HO₂ (Jacob, 2000, and references therein) followed by electron transfer to produce H₂O₂ (Reactions R1–R3):



Correspondence to: H. L. Macintyre
(h.macintyre@see.leeds.ac.uk)

A γ_{HO_2} value of 0.2 was recommended for use in models of tropospheric chemistry by Jacob (2000). This value 0.2 is based on a combination of limited laboratory data (yielding values of 0.05–0.2) (Hanson et al., 1992; Gershenson et al., 1995; Cooper and Abbatt, 1996; Gershenson et al., 1999) together with results from model-observation comparisons (giving higher values of 0.2–1.0) (Cantrell et al., 1996a,b; Plummer et al., 1996; Jaeglé et al., 2000). The very high values for γ_{HO_2} required by these modelling studies may in fact reflect the omission of halogen chemistry which cycles HO₂ to OH (Kanaya et al., 2002; Bloss et al., 2005) and hence decreases HO₂ concentrations.

A limited set of laboratory determinations of γ_{HO_2} exist for conditions relevant to the troposphere (Saathoff et al., 2001; Remorov et al., 2002; Thornton and Abbatt, 2005; Bedjanian et al., 2005; Taketani et al., 2008). Generally these studies find much lower values than the recommended value of 0.2 (Jacob, 2000). However, laboratory determinations of the rate of reaction have also found that transition metals (such as Cu(II) and to a lesser extent Fe(II)) catalyse the reaction, leading to very large γ_{HO_2} values often greater than 0.5 (Mozurkewich et al., 1987; Cooper and Abbatt, 1996; Thornton and Abbatt, 2005).

A parameterisation based on aqueous-phase reaction mechanisms has been suggested by Thornton et al. (2008). On all aerosol types other than dust, an aqueous phase recombination mechanism based on Reactions (R1) to (R3) is used to calculate uptake of HO₂ to aqueous aerosol. Uptake to dust is assumed to be uniform at 0.2 due to potential transition metal ion catalysation. They find γ_{HO_2} to be low (<0.05) in the lower troposphere especially in the tropics, but larger (0.1–0.3) in the upper troposphere. This trend is due to the temperature dependence of Reaction (R1). The calculations assume there is enough free Cu(II) in dust aerosol (and also in the continental boundary layer) to give large γ_{HO_2} values (0.2), and thus high γ_{HO_2} values are reached at the surface near dust outflow regions (e.g. the Sahara). As acknowledged in the paper, assumptions concerning aerosol pH, Cu ion speciation, and the value of the accommodation coefficient mean the parameterisation of Thornton et al. (2008) is an upper limit, in some cases leading to higher calculated γ_{HO_2} values than those found from laboratory studies.

The gas-phase self-reaction of HO₂ produces H₂O₂ (Atkinson et al., 2004). It has been assumed that this is also the product of the reaction on aerosol (Mozurkewich et al., 1987), and model studies generally represent the heterogeneous reaction as HO₂ → ½ H₂O₂. However, laboratory studies tend not to monitor the composition of the products, thus the actual products of this reaction are uncertain. Many laboratory studies have observed first- rather than second-order kinetics, which suggests a mechanism other than self-reaction (Hanson et al., 1992; Gershenson et al., 1995; Cooper and Abbatt, 1996; Remorov et al., 2002). It has also been postulated that a reaction involving sulfur compounds may occur, or that a HO₂-water complex may form

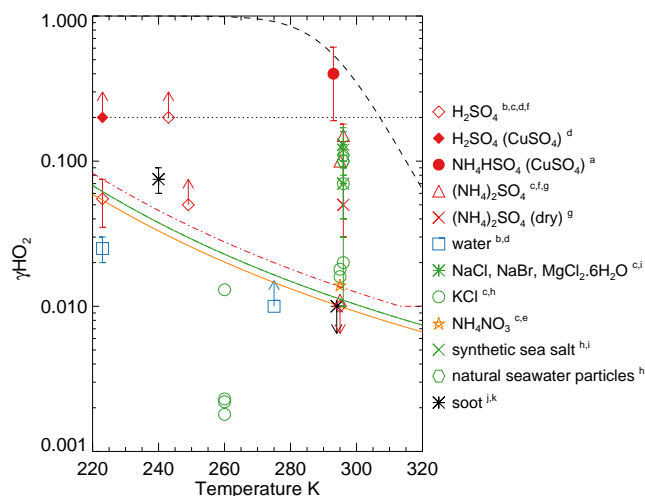


Fig. 1. Summary of laboratory data for γ_{HO_2} plotted as a function of temperature. Filled symbols denote the aerosol was doped with Cu. The colours indicate composition as follows: red is sulfurous aerosol; green is Cl (or Br) containing salts i.e. sea salt; black is soot; yellow is ammonium nitrate; blue is water. Solid lines indicate temperature dependencies on NH₄NO₃ (Gershenson et al., 1999), and on solid NaCl (Remorov et al., 2002). Error bars are given if quoted in the reference, and arrows indicate greater than/less than. The dot-dash line indicates the temperature dependence of the parameterisation in this work (assuming 50% relative humidity). The black dotted line indicates a value of 0.2, as recommended by Jacob (2000), and the dashed black line indicates the parameterisation of Thornton et al. (2008) (assuming pH = 5, $r = 100$ nm, $\alpha = 1$, [HO₂] = 10⁸ cm⁻³), used by Mao et al. (2010). Letters indicate references as follows: ^a Mozurkewich et al., 1987, ^b Hanson et al., 1992, ^c Gershenson et al., 1995, ^d Cooper and Abbatt, 1996, ^e Gershenson et al., 1999, ^f Thornton and Abbatt, 2005, ^g Taketani et al., 2008, ^h Taketani et al., 2009, ⁱ Loukhovitskaya et al., 2009, ^j Bedjanian et al., 2005, ^k Saathoff et al., 2001.

(Cooper and Abbatt, 1996; Gonzalez et al., 2010) which would not lead to H₂O₂ production. Only one laboratory study indicates that H₂O₂ is the product of the reaction (Loukhovitskaya et al., 2009). In this study H₂O₂ is observed from the reaction of HO₂ on solid (dry) sea salt particles. However, the majority of aerosol surface area in the troposphere is not dry sea salt. For other aerosol types (such as sulfate) the observed kinetics suggest other reactions may occur (Cooper and Abbatt, 1996; Gonzalez et al., 2010). Reaction with sulfur-compounds in the aerosol (forming water and sulfate) have also been suggested as alternative reaction products (Mao et al., 2010). Available laboratory studies and parameterisations of γ_{HO_2} are summarised in Fig. 1.

Thus the measured value of γ_{HO_2} varies widely (by two orders of magnitude), with the majority of laboratory studies since Jacob (2000) giving lower values than the currently accepted value of 0.2. Thornton et al. (2008) use an aqueous-phase mechanism giving a range of γ_{HO_2} values, but this is

Table 1. Uptake coefficients for HO₂.

Aerosol	Reaction probability (γ) ^a	Reference
Sulfate	$\alpha \times \beta$ where $\alpha = 5.14545 \times 10^{-4} \exp(1560/T)$ $\beta = (-26.1818 \exp(-0.078 \times \text{RH}) + 1.74545)$	Remorov et al. (2002) ^b Taketani et al. (2008) ^c
Organic carbon	0.025	Ivanov et al. (1999) ^d
Black carbon	0.01	Saathoff et al. (2001).
NaCl	$5.66 \times 10^{-5} \exp(1560/T)$ (RH < 62 %) 0.05 (RH \geq 62 %)	Remorov et al. (2002). Taketani et al. (2007).
Dust	0.1 (RH \geq 50 %); 0.05 (RH < 50 %)	Hänel (1976) reported in Dentener et al. (1996)

^a T is temperature (K), RH is relative humidity (%).

^b Temperature dependent relationship as for NaCl, as it fits data from Hanson et al. (1992), Cooper and Abbatt (1996) and Thornton and Abbatt (2005).

^c Exponential fit to available data.

^d 10^{-4} to 5×10^{-2} reported at room temperature. Mid-value of the range is used.

likely an upper-limit. There is some limited evidence to support H₂O₂ as the product of the reaction (Loukhovitskaya et al., 2009) but this is uncertain. Previous parameterisations of HO₂ uptake by aerosols have been based on gross simplifications (all aerosol types have the same value of γ_{HO_2} under all temperature and relative humidity conditions) or upon the assumption that the underlying chemistry for the uptake is based on our limited understanding of aqueous-phase chemistry. In this work we develop a new parameterisation based on the available but limited laboratory data. We then explore the impact of assumptions about the reaction products on global composition.

3 A new parameterisation

A new parameterisation is built up from available laboratory data (Table 1) in a similar manner to Evans and Jacob (2005). This includes data for different particle compositions, as well as temperature and humidity as determining factors (where data is available). A significant portion of the available laboratory measurements have been made on sea salt aerosol. A temperature dependence has been determined for the uptake onto sea salt (Remorov et al., 2002), with colder temperatures giving larger γ_{HO_2} values. The effect of temperature on uptake to sulfate aerosol has not been measured systematically. The data points that exist (for different studies at different temperatures) fit the temperature dependence found for sea salt aerosol. Thus this relationship is applied to sulfate aerosol also. Taketani et al. (2008) measure uptake of HO₂ on (NH₄)₂SO₄ at a range of relative humidities, finding an increase in γ_{HO_2} with increasing relative humidity. These data are used to incorporate humidity as a determining factor in calculating uptake of HO₂ by sulfate aerosol. This dependency on humidity is only applied above 35 % RH, as there are limited data available at humidities below this value. Below 35 % RH, γ_{HO_2} is assumed to be 0.01 (Thornton and

Abbatt, 2005). As the potential impact of transition metal catalysis is not considered in the parameterisation presented here, this likely represents a lower limit.

We use the GEOS-Chem global chemical-transport model version v8-02-04 (<http://acmg.seas.harvard.edu/geos/>) (Bey et al., 2001), driven by assimilated meteorological fields from the Goddard Earth Observing System (GEOS) of the NASA Global Modelling Assimilation Office (GMAO). Simulations are run at 4° latitude by 5° longitude, with 47 vertical layers. The model carries five externally-mixed aerosol types (sulfate, black carbon, organic carbon, dust, and sea-salt), with a relative-humidity-dependent size distribution based on Martin et al. (2003) and references therein. Simulations are run using γ_{HO_2} of 0.2 as recommended by Jacob (2000), and then with the parameterisation as given in Table 1. A simulation is also run with the mechanism of Thornton et al. (2008). Finally a simulation with γ_{HO_2} of zero is run to simulate no heterogeneous reaction. In order to test sensitivity to the reaction products, the simulations just outlined are repeated with H₂O₂ production shut off (i.e. HO₂ → no products, rather than HO₂ → ½ H₂O₂).

For each grid-box, γ_{HO_2} is calculated as the mean γ over all aerosol components, weighted by the relative contribution of each component to the total aerosol surface area of that grid-box (Evans and Jacob, 2005). First-order loss rate coefficients are calculated using the equation of Schwartz (1986).

$$k_{\text{het}} = \left(\frac{r}{D_g} + \frac{4}{\gamma \omega} \right)^{-1} A \quad (\text{R4})$$

where r (cm) is the aerosol particle effective radius, D_g (cm² s⁻¹) is the gas phase diffusion coefficient, γ is the reaction probability (also often referred to as the uptake parameter or uptake coefficient), ω (cm s⁻¹) is the mean molecular speed (calculated as $\omega = [8kT/\pi m]^{1/2}$), and A is the aerosol surface area concentration (cm² cm⁻³). Each simulation is run for two years. The analysis is performed on the second

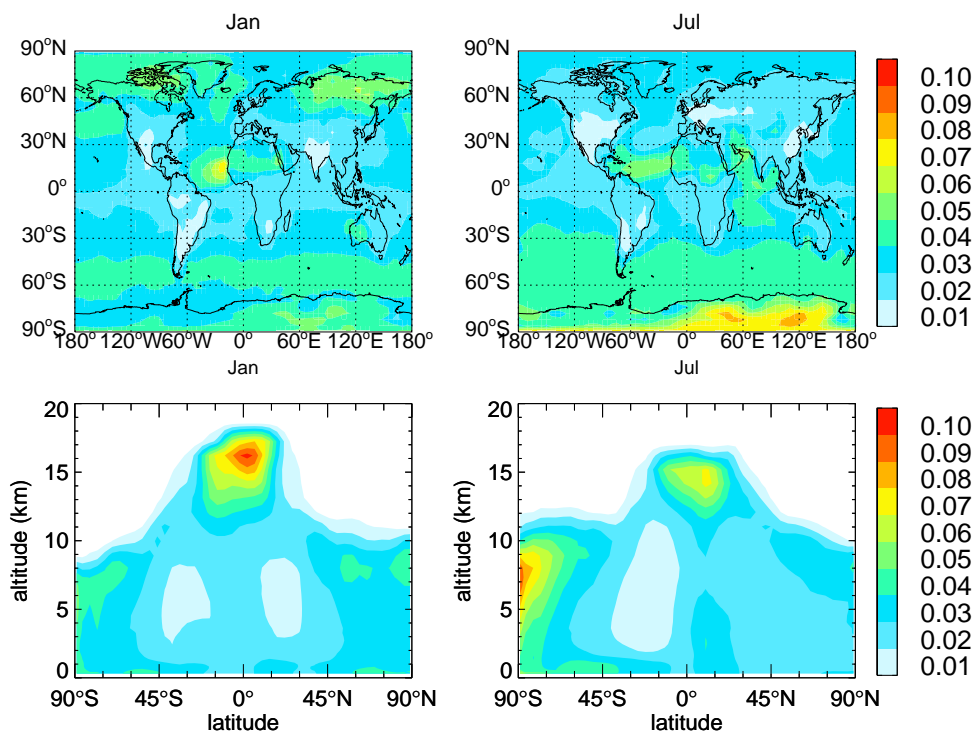


Fig. 2. Surface and zonal mean HO₂ reaction probabilities (γ_{HO_2}) for January and July as calculated in the model using the parameterisation in Table 1.

Table 2. Impact on global annual mean tropospheric burdens and concentrations of oxidants and sulfur species of different uptake schemes expressed as a fractional change as compared to γ_{HO_2} of 0.2 (Jacob, 2000). The simulation with no H₂O₂ production is run with γ_{HO_2} as in Table 1.

	Mean burdens		Fractional changes			
	$\gamma_{\text{HO}_2} =$	0.2 (Jacob, 2000)	Thornton et al. (2008)	This work	(no H ₂ O ₂ production)	0.0
HO ₂ (pptv)		5.47	+2.7 %	+3.2 %	+2.9 %	+4.0 %
OH (10 ⁶ molec cm ⁻³)		1.17	+0.8 %	+1.1 %	+0.7 %	+1.7 %
H ₂ O ₂ (ppbv)		0.85	-6.2 %	-7.3 %	-11.2 %	-9.2 %
O ₃ (Tg)		429	+0.1 %	+0.3 %	+0.3 %	+0.7 %
SO ₂ (Tg S)		3.62	+0.6 %	+0.6 %	+3.6 %	+0.9 %
SO ₄ ²⁻ (Tg S)		4.97	+1.0 %	+1.2 %	+1.4 %	+1.6 %

year of output, and the first year discarded as spin-up. The GEOS-Chem model has been extensively used and has previously been evaluated against observations for many locations (Bey et al., 2001; Martin et al., 2003; Evans and Jacob, 2005; Zhang et al., 2008; Nassar et al., 2009).

4 The value of γ_{HO_2}

Figure 2 shows the surface and zonal mean γ_{HO_2} for January and July as calculated in the model using the parameterisation in Table 1. The highest values of γ_{HO_2} (~ 0.1 in

the zonal mean) are found at high latitudes, due to the temperature and humidity dependence (γ_{HO_2} increases with decreasing temperature and increasing relative humidity). High surface values are found over Antarctica in July (Fig. 2). At this time temperatures are ~ 210 K, and relative humidity is $< 60\%$, giving a γ_{HO_2} on sea salt aerosol of ~ 0.1 . High wind speeds generate a higher sea salt flux to the atmosphere here compared to other regions. Dust outflow regions (such as to the west of the Sahara and off the tip of South America) also have high γ_{HO_2} values. Over dust emission areas themselves however, the uptake is low, as they are dry. The lowest values of γ_{HO_2} are found in the tropical regions and around

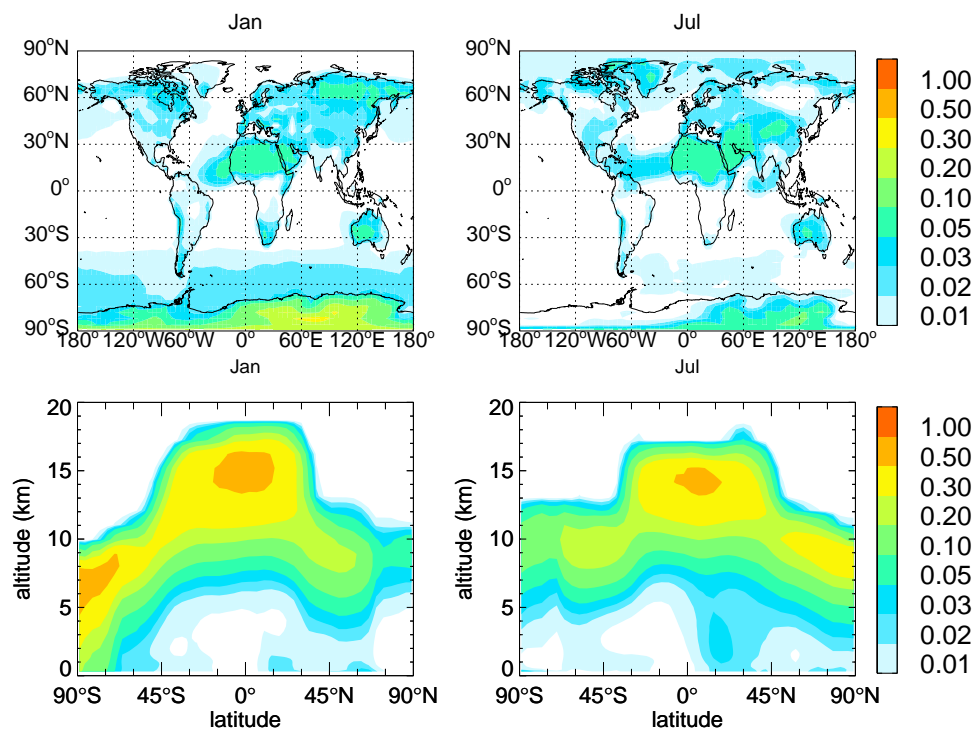


Fig. 3. Surface and zonal mean HO₂ reaction probabilities (γ_{HO_2}) for January and July as calculated in the model using the parameterisation of Thornton et al. (2008).

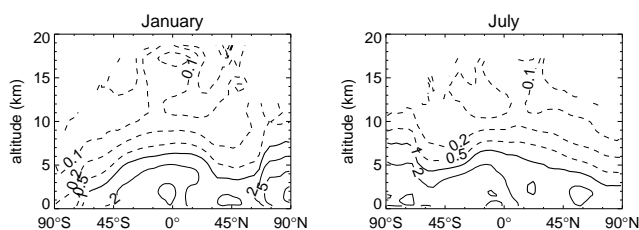


Fig. 4. Zonal mean ratio of γ_{HO_2} values calculated using the parameterisation in this work, and those using the parameterisation of Thornton et al. (2008). Using laboratory data (this work) yields lower values of γ_{HO_2} in the upper troposphere (dashed lines) and higher values nearer the surface (solid lines) than the parameterisation of Thornton et al. (2008).

30° N–50° N in the summer. Sulfate and organic aerosol dominate at this time, which combined with higher temperatures and low relative humidity, give rise to γ_{HO_2} values of ~ 0.01 . The global mass-weighted annual average γ_{HO_2} is 0.028, around an order of magnitude lower than 0.2 recommended by Jacob (2000).

The results here are in contrast to Thornton et al. (2008). Figure 3 shows the surface and zonal mean γ_{HO_2} as calculated in the model using the parameterisation of Thornton et al. (2008). The stronger dependence on temperature of Thornton et al. (2008) leads to high values in the cold

upper troposphere (0.1–0.3) and low values in the lower troposphere (< 0.01). The global mass-weighted annual average γ_{HO_2} is 0.1. Figure 4 shows the ratio of γ_{HO_2} calculated using the parameterisation in Table 1 compared to the scheme of Thornton et al. (2008). This work finds γ_{HO_2} values up to 2–5 times greater in the lower troposphere than the parameterisation in Table 1. However, in the cold upper troposphere, Thornton et al. (2008) find γ_{HO_2} an order of magnitude greater than this work. The majority of aerosol surface area above 5 km is contributed by sulfate ($\sim 2 \mu\text{m}^2 \text{cm}^{-3}$), with the next highest contribution from organic carbon ($\sim 1 \mu\text{m}^2 \text{cm}^{-3}$). The strong gradient in γ_{HO_2} with altitude seen by Thornton et al. (2008) is not simulated in this work, as the available laboratory studies suggest a weaker temperature dependence than that of Thornton et al. (2008). Laboratory studies on cold sulfuric acid measure γ_{HO_2} of around 0.05 (Hanson et al., 1992; Gershenzon et al., 1995; Cooper and Abbatt, 1996). For the same conditions, the Thornton et al. (2008) mechanism predicts higher (> 0.1) values. Laboratory studies have yet to confirm the strength of the temperature dependence for either parameterisation, the only study being on sea salt aerosol (Remorov et al., 2002), which has been adopted by this work. The discrepancy between these two approaches suggests our understanding of the appropriate γ_{HO_2} values is weak, and further laboratory studies are needed to resolve these issues.

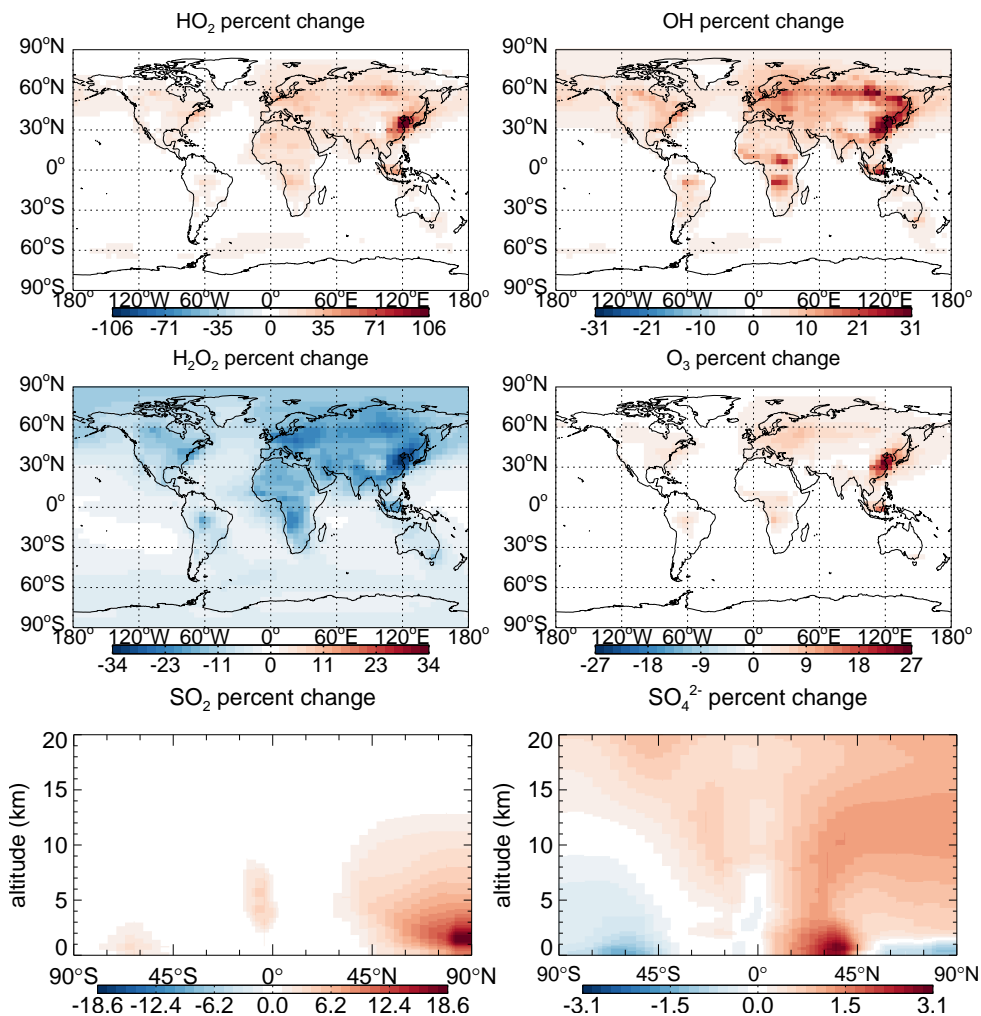


Fig. 5. Impact on annual mean concentrations of oxidants and sulfur species when moving from a γ_{HO_2} of 0.2 (Jacob, 2000) to the scheme presented in Table 1.

5 Impact on tropospheric composition

Figure 5 shows the changes in annual mean surface concentrations of HO₂, OH, H₂O₂ and O₃, and zonal mean concentrations of SO₂ and SO₄²⁻, when moving from a γ_{HO_2} of 0.2 to the parameterisation as in Table 1 (global mean γ_{HO_2} of 0.028). Regionally significant impacts are seen, notably over China, with surface concentrations of HO₂ doubling in some regions, and an increase in OH of up to 31%. O₃ is also seen to increase by up to 27% in regions where HO_x increases. However, globally the impact is small, with HO₂ and OH changing by +3.2% and +1.1%, respectively. The global impact on O₃ is even smaller (+0.3%) due to the competing effects of HO₂ + NO (which leads to NO₂ and thus O₃ production) and HO₂ + O₃ (which consumes O₃). Regions showing an increase in O₃ are those with high NO_x and/or VOC concentrations. A decrease in H₂O₂ is seen in the same regions as the HO₂ increase. Table 2 shows the

impact of different parameterisations of γ_{HO_2} on global annual mass-weighted mean burdens and concentrations of various species. While the value of γ_{HO_2} has a significant impact in regions with high aerosol loading and HO₂ concentrations (Fig. 5, e.g. S. E. Asia, surface changes of +27% to +106%), when globally integrated the impact is reduced to only a few percent. From Table 2 it is clear that at a global scale, H₂O₂ is the most significantly impacted species. Reaction of H₂O₂ with SO₂ in cloud drops is the most significant pathway by which sulfate is formed (Seinfeld and Pandis, 2006). The reduction in H₂O₂ results in less SO₂ being consumed and thus the burden of SO₂ increases (Fig. 5). This results in a reduction in sulfate at lower altitudes. The transport of SO₂ to higher altitudes (due to its longer lifetime) results in an increase in sulfate production here (Fig. 5). Thus while the global burden change of sulfate is relatively small (Table 2), the distribution of its production is impacted.

Although differing values for γ_{HO_2} are calculated using the scheme presented here compared with that of Thornton et al. (2008) (Fig. 4), the resulting changes in global burdens are rather similar (Table 2). Figure 6 shows the annual zonal mean heterogeneous reaction rates calculated using the parameterisation in this work and that used by Thornton et al. (2008). At the surface, the extra-tropics give very similar rates, with larger differences at the tropics. There are significant differences in the upper troposphere which reflect the differences in the temperature dependencies of the two parameterisations. Given much of the mass of the atmosphere lies within the lowest 5 km, the global impact of the differences between these two parameterisations in the upper troposphere is relatively small.

While at global scale the impact of a lower γ_{HO_2} has only a small effect on concentrations of oxidants and sulfur species, regionally the impact is significant.

6 Reaction mechanism

As described in Sect. 2, there is mechanistic uncertainty in the heterogeneous reaction of HO₂. In order to investigate this the simulations are repeated but with the heterogeneous reaction producing no products. Figure 7 shows the impact on oxidants and sulfur species when production of H₂O₂ is turned off (i.e. HO₂ → no products, rather than HO₂ → ½ H₂O₂). By changing the reaction products, a reduction in H₂O₂ concentrations of up to ~10% is seen in the zonal mean, with surface concentrations reduced by up to 35% in regions with high aerosol loading and HO₂ concentrations, such as S. E. Asia. The heterogeneous reaction therefore is a significant source of H₂O₂ in certain regions, even when the value of γ_{HO_2} is relatively small (as is the case with the new parameterisation). H₂O₂ can photolyse producing two OH radicals, thus the reduction in H₂O₂ concentrations leads to a reduction in OH concentrations. The largest decrease in OH is seen at high latitudes, where O₃, water vapour concentrations, and solar radiation are low, leading to H₂O₂ photolysis being a more important source of OH in these regions (Mao et al., 2010) (locally OH decreases by up to 8% at high latitudes). Changes in O₃ are very small (maximum of <0.5% at the surface). The global annual mass-weighted changes in H₂O₂, OH, O₃, and HO₂ are −4.3%, −0.4%, −0.01% and −0.3% respectively, when production of H₂O₂ by the heterogeneous reaction is shut off (while keeping γ_{HO_2} as in Table 1).

As mentioned previously, reaction of H₂O₂ with SO₂ in cloud drops is the most significant contributor to sulfate formation (Seinfeld and Pandis, 2006). The decrease in H₂O₂ from turning off its production by the heterogeneous reaction compared with H₂O₂ being produced by the heterogeneous reaction (−4.3% globally) results in slightly less sulfate, and more SO₂ (globally −0.2% and +3.0% respectively for the case where γ_{HO_2} is the new parameterisation as in Table 1).

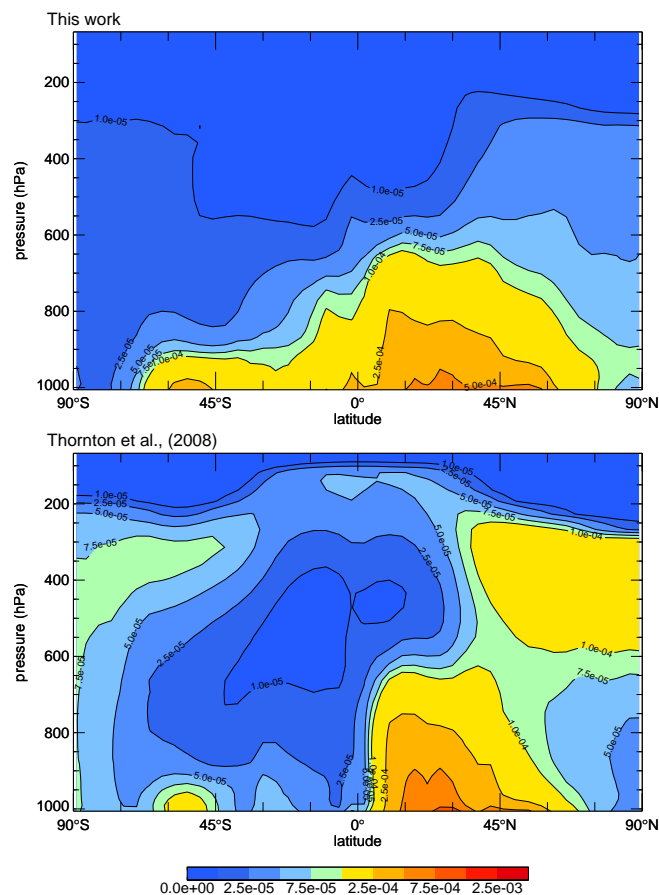


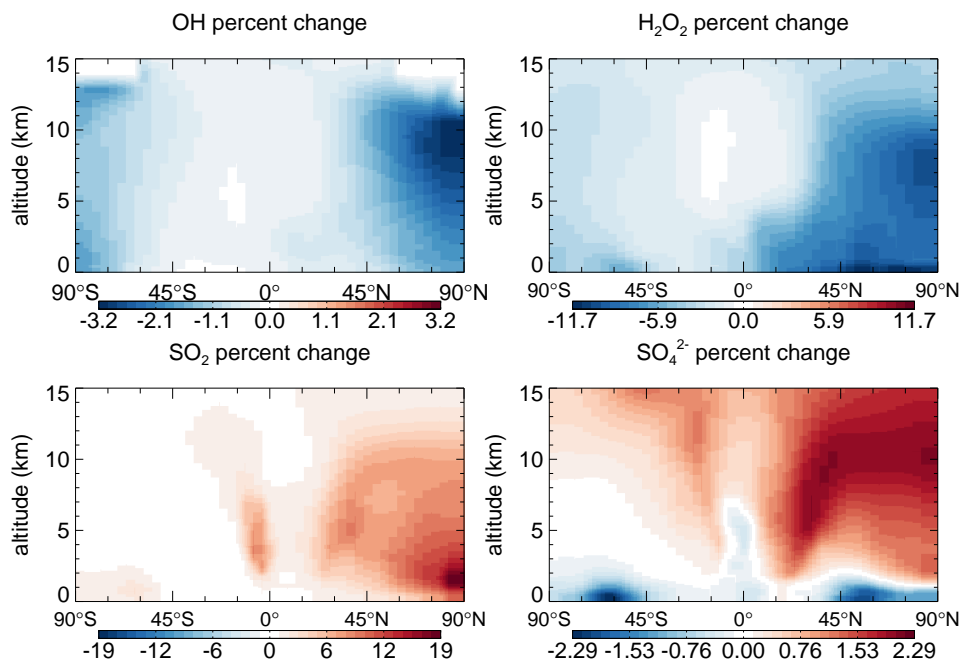
Fig. 6. Zonal annual mean heterogeneous reaction rates as calculated in the model using the parameterisation presented in this work (top panel) and the scheme of Thornton et al. (2008) (bottom).

There is a drop in SO₄^{2−} at low altitudes, and an increase at higher altitudes (Fig. 5). The reduction in H₂O₂ increases the SO₂ lifetime, thus more SO₂ escapes to the free troposphere where it is oxidised there. The overall change in sulfate is smaller than the change in SO₂ as the production is just shifted to the upper troposphere. The penultimate column in Table 2 shows the impact of simultaneously using the lower γ_{HO_2} value from the parameterisation in Table 1 and also shutting off production of H₂O₂, as compared to using the recommendation as in Jacob (2000) (i.e. a γ_{HO_2} value of 0.2 and with H₂O₂ produced). The most significant impact is on H₂O₂ (−11.2%), as the rate of reaction has been reduced, as well as the production of H₂O₂ being shut off. The impact on SO₂ (+3.6%) is mainly due to shutting off H₂O₂ production (as the change is only +0.6% if only γ_{HO_2} is changed). The overall burden of sulfate is changed by just over 1%, but as seen in Fig. 7 the main impact is on its distribution.

The modelled impacts due to different parameterisations of γ_{HO_2} are highly regional. For most regions the variations are small and of the order of a few percent.

Table 3. As Table 2 but with the analysis restricted to below 5 km over China (bounded by 97.5° E to 127.5° E longitude and 20° S to 44° N latitude.).

	Mean burdens		Fractional changes			
	$\gamma_{\text{HO}_2} =$	0.2 (Jacob, 2000)	Thornton et al. (2008)	This work	(no H ₂ O ₂ production)	0.0
HO ₂ (pptv)		7.41	+17.3 %	+17.8 %	+16.7 %	+23.4 %
OH (10 ⁶ molec cm ⁻³)		1.69	+6.7 %	+7.2 %	+6.4 %	+9.3 %
H ₂ O ₂ (ppbv)		1.99	-15.7 %	-16.9 %	-27.5 %	-21.5 %
O ₃ (Tg)		2.73	+3.4 %	+3.9 %	+3.8 %	+5.1 %
SO ₂ (Tg S)		4.1 × 10 ⁻²	-0.9 %	-1.3 %	+4.2 %	-1.1 %
SO ₄ ²⁻ (Tg S)		2.4 × 10 ⁻²	+6.3 %	+7.4 %	+5.6 %	+9.4 %

**Fig. 7.** Impact of not producing H₂O₂ from the heterogeneous reaction of HO₂, using γ_{HO_2} as in Table 1.

Thus comparisons between available observations (e.g. the TRACE-P campaign conducted off the coast of S. E. Asia, data composites from Emmons et al., 2000) does not show a systematic improvement in model performance with any of the different simulations performed here.

Many tropospheric chemistry models do not currently include uptake of HO₂. The results of this study suggest that models that do not include uptake of HO₂ will slightly over-predict sulfate formation in the lowest part of the atmosphere, and underestimate it in the upper troposphere. This implies a greater role of sulfur oxidation and sulfate aerosol formation in the free troposphere than models which do not include uptake of HO₂ suggest, with implications for global aerosol nucleation rates.

In contrast to the uptake of N₂O₅ which shows both regional and global impacts (Macintyre and Evans, 2010), the

impact of uptake of HO₂ is far more significant regionally than globally. Table 3 shows the same impacts as in Table 2, but with the analysis restricted to altitudes below 5 km over China. It is clear that regionally the impacts are far more significant, with HO₂ showing ~17 % increase (compared to ~3 % globally), and H₂O₂ decreasing by around 16–28 % (compared to ~7–11 % globally).

7 Conclusions

There are clearly large uncertainties in the heterogeneous reaction of HO₂, not only in terms of the rate of reaction (as manifest by γ_{HO_2}), but also the reaction mechanism. Laboratory determinations of γ_{HO_2} suggest that the value of 0.2, recommended previously, is too large. This work uses available laboratory data to construct a new parameterisation for

the uptake of HO₂, finding a global mean value of 0.028, roughly an order of magnitude lower than the 0.2 recommended by Jacob (2000). The parameterisation in this work also finds lower values than recent work by Thornton et al. (2008) (global mean $\gamma_{\text{HO}_2} \sim 0.1$). The recent parameterisation of Thornton et al. (2008) yields γ_{HO_2} values higher than those suggested by laboratory studies, due to the strong temperature dependence and assumptions on aerosol pH and Cu ion speciation. This work uses measured rates from available laboratory studies to avoid the overestimates that may have been made previously, thus the parameterisation likely represents a lower limit as we neglect the potential impact of transition metal catalysis. Laboratory studies of the temperature and relative humidity dependence of γ_{HO_2} on various aerosol types should now be undertaken, together with an assessment of the role of transition metals.

Our study also suggests that models of tropospheric chemistry that do not currently include uptake of HO₂ will slightly over-predict sulfate formation in the lowest part of the atmosphere, and underestimate it in the upper troposphere, potentially influencing transport and distribution of sulfur in the atmosphere.

Acknowledgements. The authors wish to acknowledge funding from NERC studentship NER/S/C/2006/14266 as well as support from the UK Met Office and the GEOS-Chem team at Harvard.

Edited by: C. H. Song

References

- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of O_x, HO_x, NO_x and SO_x species, *Atmos. Chem. Phys.*, 4, 1461–1738, doi:10.5194/acp-4-1461-2004, 2004.
- Bedjanian, Y., Lelièvre, S., and Le Bras, G.: Experimental study of the interaction of HO₂ radicals with soot surface, *Phys. Chem. Chem. Phys.*, 7, 334–341, doi:10.1039/b414217a, 2005.
- Bey, I., Jacob, D. J., Yantosca, R. M., Logan, J. A., Field, B. D., Fiore, A. M., Li, Q., Liu, H. Y., Mickley, L. J., and Schultz, M. G.: Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, *J. Geophys. Res.*, 106, 23073–23095, 2001.
- Bloss, W. J., Lee, J. D., Johnson, G. P., Sommariva, R., Heard, D. E., Sais-Lopez, A., Plane, J. M. C., McFiggans, G., Coe, H., Flynn, M., Williams, P., Rickard, A. R., and Fleming, Z. L.: Impact of halogen monoxide chemistry upon boundary layer OH and HO₂ concentrations at a coastal site, *Geophys. Res. Lett.*, 32, L06814, doi:10.1029/2004GL022084, 2005.
- Cantrell, C. A., Shetter, R. E., Gilpin, T. M., and Calvert, J. G.: Peroxy radicals measured during Mauna Loa Observatory Photochemistry Experiment 2: The data and first analysis, *J. Geophys. Res.*, 101, 14643–14652, doi:10.1029/95JD01698, 1996a.
- Cantrell, C. A., Shetter, R. E., Gilpin, T. M., Calvert, J. G., Eisele, F. L., and Tanner, D. J.: Peroxy radical concentrations measured and calculated from trace gas measurements in the Mauna Loa Observatory Photochemistry Experiment 2, *J. Geophys. Res.*, 101, 14653–14664, doi:10.1029/95JD03613, 1996b.
- Cooper, P. L. and Abbatt, J. P. D.: Heterogeneous Interactions of OH and HO₂ Radicals with Surfaces Characteristic of Atmospheric Particulate Matter, *J. Phys. Chem.*, 100, 2249–2254, 1996.
- Dentener, F. J., Carmichael, G. R., Zhang, Y., Lelieveld, J., and Crutzen, P. J.: Role of mineral aerosol as a reactive surface in the global troposphere, *J. Geophys. Res.*, 101, 22869–22889, doi:10.1029/96JD01818, 1996.
- Emmons, L. K., Hauglustaine, D. A., Müller, J.-F., Carroll, M. A., Brasseur, G. P., Brunner, D., Staehelin, J., Thouret, V., and Marengo, A.: Data composites of airborne observations of tropospheric ozone and its precursors, *J. Geophys. Res.*, 105, 20497–20538, doi:10.1029/2000JD900232, 2000.
- Evans, M. J. and Jacob, D. J.: Impact of new laboratory studies of N₂O₅ hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH, *Geophys. Res. Lett.*, 32, D00F10, doi:10.1029/2005GL022469, 2005.
- Gershenson, Y. M., Grigorieva, V. M., Ivanov, A. V., and G., R. R.: O₃ and OH sensitivity to heterogeneous sinks of HO_x and CH₃O₂ on aerosol particles, *Faraday Discussions*, 100, 83–100, doi:10.1039/FD9950000083, 1995.
- Gershenson, Y. M., Grigorieva, V. M., Zasytkin, A. Y., Ivanov, A. V., G., R. R., and Aptekar, E. L.: Capture of HO₂ radicals by an NH₄NO₃ surface at low temperatures, *Chemical Physics Reports*, 18, 79–90, 1999.
- Gonzalez, J., Torrent-Sucarrat, M., and Anglada, J. M.: The reactions of SO₃ with HO₂ radical and H₂O...HO₂ radical complex. Theoretical study on the atmospheric formation of HSO₅ and H₂SO₄, *Phys. Chem. Chem. Phys.*, 12, 2116–2125, doi:10.1039/B916659A, 2010.
- Hänel, G.: The Properties of Atmospheric Aerosol Particles as Functions of the Relative Humidity at Thermodynamic Equilibrium with the Surrounding Moist Air, in: *Advances in Geophysics*, edited by: Landsberg, H. E. and Van Mieghem, J., Elsevier, 19, 73–188, doi:10.1016/S0065-2687(08)60142-9, 1976.
- Hanson, D. R., Burkholder, J. B., Howard, C. J., and Ravishankara, A. R.: Measurement of OH and HO₂ Radical Uptake Coefficients on Water and Sulfuric Acid Surfaces, *J. Phys. Chem.*, 96, 4979–4985, 1992.
- Ivanov, A. V., Trakhtenberg, S., Bertram, A. K., Molina, L. T., and Molina, M. J.: HO₂ Uptake by Organic Surfaces, Department of Earth, Atmospheric and Planetary Sciences and of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, 1999.
- Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, *Atmos. Environ.*, 34, 2131–2159, doi:10.1016/S1352-2310(99)00462-8, 2000.
- Jaeglé, L., Jacob, D. J., Brune, W. H., Faloon, I., Tan, D., Heikes, B. G., Kondo, Y., Sachse, G. W., Anderson, B., Gregory, G. L., Singh, H. B., Poeschel, R., Ferry, G., Blake, D. R., and Shetter, R.: Photochemistry of HO_x in the upper troposphere at northern midlatitudes, *J. Geophys. Res.*, 105, 3877–3892, doi:10.1029/1999JD901016, 2000.
- Kanaya, Y., Yokouchi, Y., Matsumoto, J., Nakamura, K., Kato, S., Tanimoto, H., Furutani, H., Toyota, K., and Akiyama, H.: Implications of iodine chemistry for daytime

- HO₂ levels at Rishiri Island, *Geophys. Res. Lett.*, 29, 1212, doi:10.1029/2001GL014061, 2002.
- Liao, H., Chen, W.-T., and Seinfeld, J. H.: Role of climate change in global predictions of future tropospheric ozone and aerosols, *J. Geophys. Res.*, 111, D12304, doi:10.1029/2005JD006852, 2006.
- Logan, J. A., Prather, M. J., Wofsy, S. C., and McElroy, M. B.: Tropospheric Chemistry: A Global Perspective, *J. Geophys. Res.*, 86, 7210–7254, doi:10.1029/JC086iC08p07210, 1981.
- Loukhovitskaya, E., Bedjanian, Y., Morozov, I., and Le Bras, G.: Laboratory study of the interaction of HO₂ radicals with the NaCl, NaBr, MgCl₂·6H₂O and sea salt surfaces, *Phys. Chem. Chem. Phys.*, 11, 7896–7905, doi:10.1039/b906300e, 2009.
- Macintyre, H. L. and Evans, M. J.: Sensitivity of a global model to the uptake of N₂O₅ by tropospheric aerosol, *Atmos. Chem. Phys.*, 10, 7409–7414, doi:10.5194/acp-10-7409-2010, 2010.
- Mao, J., Jacob, D. J., Evans, M. J., Olson, J. R., Ren, X., Brune, W. H., Clair, J. M. S., Crouse, J. D., Spencer, K. M., Beaver, M. R., Wennberg, P. O., Cubison, M. J., Jimenez, J. L., Fried, A., Weibring, P., Walega, J. G., Hall, S. R., Weinheimer, A. J., Cohen, R. C., Chen, G., Crawford, J. H., McNaughton, C., Clarke, A. D., Jaeglé, L., Fisher, J. A., Yantosca, R. M., Le Sager, P., and Carouge, C.: Chemistry of hydrogen oxide radicals (HO_x) in the Arctic troposphere in spring, *Atmos. Chem. Phys.*, 10, 5823–5838, doi:10.5194/acp-10-5823-2010, 2010.
- Martin, R. V., Jacob, D. J., and Yantosca, R. M.: Global and regional decreases in tropospheric oxidants from photochemical effects of aerosols, *J. Geophys. Res.*, 108, 4097, doi:10.1029/2002JD002622, 2003.
- Mozurkewich, M., McMurry, P. H., Gupta, A., and Calvert, J. G.: Mass Accommodation Coefficient for HO₂ Radicals on Aqueous Particles, *J. Geophys. Res.*, 92, 4163–4170, doi:10.1029/JD092iD04p04163, 1987.
- Nassar, R., Logan, J. A., Megretskaya, I. A., Murray, L. T., Zhang, L., and Jones, D. B. A.: Analysis of tropical tropospheric ozone, carbon monoxide, and water vapour during the 2006 El Niño using TES observations and the GEOS-Chem model, *J. Geophys. Res.*, 114, D17304, doi:10.1029/2009JD011760, 2009.
- Plummer, D. A., McConnel, J. C., Shepson, P. B., Hastie, D. R., and Niki, H.: Modeling of ozone formation at a rural site in Southern Ontario, *Atmos. Environ.*, 30, 2195–2217, doi:10.1016/1352-2310(95)00086-0, 1996.
- Remorov, R. G., Gershenzon, Y. M., Molina, L. T., and Molina, M. J.: Kinetics and Mechanism of HO₂ Uptake on Solid NaCl, *J. Phys. Chem. A.*, 106, 4558–4565, doi:10.1021/jp013179o, 2002.
- Saathoff, H., Naumann, K.-H., Riener, N., Kamm, S., Möhler, O., Schurath, U., Vogel, H., and Vogel, B.: The loss of NO₂, HNO₃, NO₃/N₂O₅, and HO₂/HOONO₂ on soot aerosol: A chamber and modeling study, *Geophys. Res. Lett.*, 28, 1957–1960, doi:10.1029/2000GL012619, 2001.
- Schwartz, S.: Mass-transport considerations pertinent to aqueous phase reactions of gases in liquid-water clouds, in: *Chemistry of Multiphase Atmospheric Systems*, edited by: Jaeschke, J., NATO ASI Series, Springer, Berlin, vol. G6, 415–471, 1986.
- Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, Wiley, Hoboken, New Jersey, 2nd Edn., 2006.
- Taketani, F., Kanaya, Y., and Akimoto, H.: Heterogeneous reaction of HO₂ radical: HO₂ uptake to aqueous and crystalline aerosols for NaCl and (NH₄)₂SO₄, available at: <http://earth2007.jtbcom.co.jp/session/pdf/F118/F118-016.e.pdf> (last access: August 2007), 2007.
- Taketani, F., Kanaya, Y., and Akimoto, H.: Kinetics of Heterogeneous Reaction of HO₂ Radical at Ambient Concentration Levels with (NH₄)₂SO₄ and NaCl Aerosol Particles, *J. Phys. Chem. A.*, 112, 2370–2377, doi:10.1021/jp0769936, 2008.
- Taketani, F., Kanaya, Y., and Akimoto, H.: Heterogeneous loss of HO₂ by KCl, synthetic sea salt, and natural seawater aerosol particles, *Atmos. Environ.*, 43, 1660–1665, doi:10.1016/j.atmosenv.2008.12.010, 2009.
- Thornton, J. A. and Abbatt, J. P. D.: Measurements of HO₂ uptake to aqueous aerosol: Mass accommodation coefficients and net reactive loss, *J. Geophys. Res.*, 110, D08309, doi:10.1029/2004JD005402, 2005.
- Thornton, J. A., Jaeglé, L., and McNeill, V. F.: Assessing known pathways for HO₂ loss in aqueous atmospheric aerosols: Regional and global impacts on tropospheric oxidants, *J. Geophys. Res.*, 113, D05303, doi:10.1029/2007JD009236, 2008.
- Tie, X., Brasseur, G., Emmons, L., Horowitz, L., and Kinison, D.: Effects of aerosols on tropospheric oxidants: A global model study, *J. Geophys. Res.*, 106, 22931–22964, doi:10.1029/2001JD900206, 2001.
- Zhang, Y., Jacob, D. J., Boersma, K. F., Jaffe, D. A., Olson, J. R., Bowman, K. W., Worden, J. R., Thompson, A. M., Avery, M. A., Cohen, R. C., Dibb, J. E., Flock, F. M., Fuelberg, H. E., Huey, L. G., McMillan, W. W., Singh, H. B., and Weinheimer, A. J.: Transpacific transport of ozone pollution and the effect of recent Asian emission increases on air quality in North America: an integrated analysis using satellite, aircraft, ozonesonde, and surface observations, *Atmos. Chem. Phys.*, 8, 6117–6136, doi:10.5194/acp-8-6117-2008, 2008.