This datasheet last evaluated: June 2016; last change in preferred values: June 2016

HO$_2$ + mineral oxide (dust) surfaces → products

Experimental data

Parameter	Temp./K	RH /%	p_{HO2} /mbar	Substrate	H$_2$O$_2$ yield	Reference	Technique/ Comments
Uptake coefficients: γ, γ$_0$							
$\gamma_0 = (6.7\pm0.4)\times10^{-2}$	275-320		1.5×10^{-5}-	ATD	<5%	Bedjanian et	CWFT-MS (a)
$\gamma_0 = (1.2\pm0.4)/(18.7+RH^{1.1})$	275	2-94	1.0×10^{-4}			al., 2013	
$\gamma = (4.7\pm1.1)\times10^{-2}$	291		4.0×10^{-9}	ATD		Matthews et	AFT-LIF (b)
$\gamma = (2.0\pm0.5)\times10^{-2}$			4.0×10^{-8}			al., 2014	
$\gamma = (2.2\pm0.4)\times10^{-2}$		6	4.0×10^{-9}				
$\gamma = (4.5\pm0.5)\times10^{-2}$		70					
$\gamma = (0.8\pm0.3)\times10^{-2}$		6	4.0×10^{-8}				
$\gamma = (3.0\pm0.5)\times10^{-2}$		72					
$\gamma = (4.3\pm0.4)\times10^{-3}$	294	11.6	6.5×10^{-8}	Forsterite		James et al.	AFT-LIF (c)
$\gamma = (6.9\pm1.2)\times10^{-2}$		10.0		Olivine		(2017)	
$\gamma = (7.3\pm0.4)\times10^{-2}$		9.9		Fayalite			

Comments

(a) ATD films (85 ± 10 m^2 g^{-1} surface area) were formed from a suspension in ethanol, followed by drying and baking at 100-150°C in vacuo. Samples were irradiated in the UV (315-400 nm, J_{NO2} = 0.002-0.012 s^{-1}) was . HO$_2$ $(0.3 – 3) \times 10^{12}$ molecule cm^{-3}) was produced via reaction of F or Cl atoms produced in a microwave discharge with H$_2$O$_2$ or CH$_3$OH, respectively and was was detected as HOBr or NO$_2$ following reaction with NO and scavenging OH with by Br$_2$. First order loss rates of HO$_2$ exhibited significant deactivation. Integration over long times yielded more loss than a monolayer equivalent, indicating catalytic loss. Observed first order loss rates were corrected for diffusion with D$_0$ = 430±50 Torr cm^2 s^{-1} at 298 K to obtain the geometric uptake coefficient. The mass independent range was used to report geometric uptake coefficients, correction for the specific surface area would result in about a factor of 40 lower γ_{BET} values. UV radiation had no effect on the uptake kinetics. H$_2$O$_2$ as product was below the detection limit, leading to the upper limit reported in the table.

(b) ATD aerosol (average diameter = 273 nm) was produced by aerodynamic resuspension of the powder and characterized by SMPS and APS (Aerodynamic Particle Sizer). HO$_2$ $(0.3 – 1) \times 10^{9}$ molecule cm^{-3}) was produced via photolysis of H$_2$O in humidified synthetic air and detected after conversion to OH by LIF. The laminar AFT was operated at atmospheric pressure and 291 K. Diffusion corrected uptake coefficients were determined both by varying the interaction time and by varying the aerosol surface to volume ratio at fixed injector

position to address time dependence. Initial uptake coefficients measured at the shortest reaction time dropped by about half to that at the longest interaction time of 23 s, which is reported in the table.

(c) AFT experiment as in (b), at 294 K, with the HO_2 concentration kept fixed at 1.6×10^9 molecule cm^{-3}. Amorphous powders of $Mg_xFe_{2-x}SiO_4$ (x=0: fayalite; x=1: olivine; x=2: forsterite) were produced by precipitation from aqueous precursor solutions. The lognormal size distribution of the re-suspended aerosol had a mean diameter of 368 nm. Higher initial uptake coefficients (during the first few seconds) were observed as in (b), only the uptake coefficients measured at later times are reported.

Preferred Values

Parameter	Value	T/K
γ	3×10^{-2}	280-320
Reliability		
$\Delta \log (\gamma)$	± 1.0	280-320

Comments on Preferred Values

The preferred value is based on the range of uptake coefficients determined in the aerosol flow tube study performed by Matthews et al. (2014), because it mimics reasonably well the physical representation of mineral dust aerosol, in spite of ATD not being an authentic airborne dust material, and because it has been performed at low HO_2 partial pressures. The difference to the somewhat larger initial uptake coefficient observed by Bedjanian et al. (2013) at much higher HO_2 partial pressures may be due to uncertainties in the relevant dust surface area, since uptake could not be measured in the linear mass dependent regime by Bedjanian et al.

The weak HO_2 pressure dependence observed by Matthews et al. may be due to adsorption saturation (and thus the uptake switching from initial to steady state mode) or due to the consumption of redox active surface sites. The former would have led to pressure independent uptake at the larger HO_2 pressures of the Bedjanian et al. study, and the second would explain the slow deactivation over time. Formation of H_2O_2 as a product of the HO_2 self-reaction was not observed by Bedjanian et al., possibly a result of the involvement of the basic metal or transition metal oxides in the dust for direct reaction or reaction with H_2O_2. Support from this comes also from the James et al. (2017) study showing that the two iron containing minerals fayalite and olivine have significantly higher uptake coefficients than forsterite (a Mg silicate), which is supported by theoretical calculations.

Matthews et al. suggest that the slight, positive humidity dependence they observed was a result of larger wall losses and concomitantly decreasing HO_2 pressure with time, and thus from an indirect pressure dependence. In turn, we caution that at high relative humidity, ATD takes up significant amounts of water and may undergo restructuring due to capillary condensation in its interstitial space (Vlasenko et al., 2005) that could result in a reduction of the available surface area for the coatings used in the Bedjanian et al. study and thus be the origin of the decrease in the uptake coefficient. The preferred value is thus independent of humidity but has expanded error limits.

In view of the uncertainties with respect to the detailed chemical loss process and the limited parameter range available, no detailed parameterization is given for γ. More studies with authentic dusts and at higher RH are needed.

References

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Vlasenko, A., Sjogren, S., Weingartner, E., Gäggeler, H. W., and Ammann, M.: Aerosol Sci. Technol., 39, 452-460, 2005.
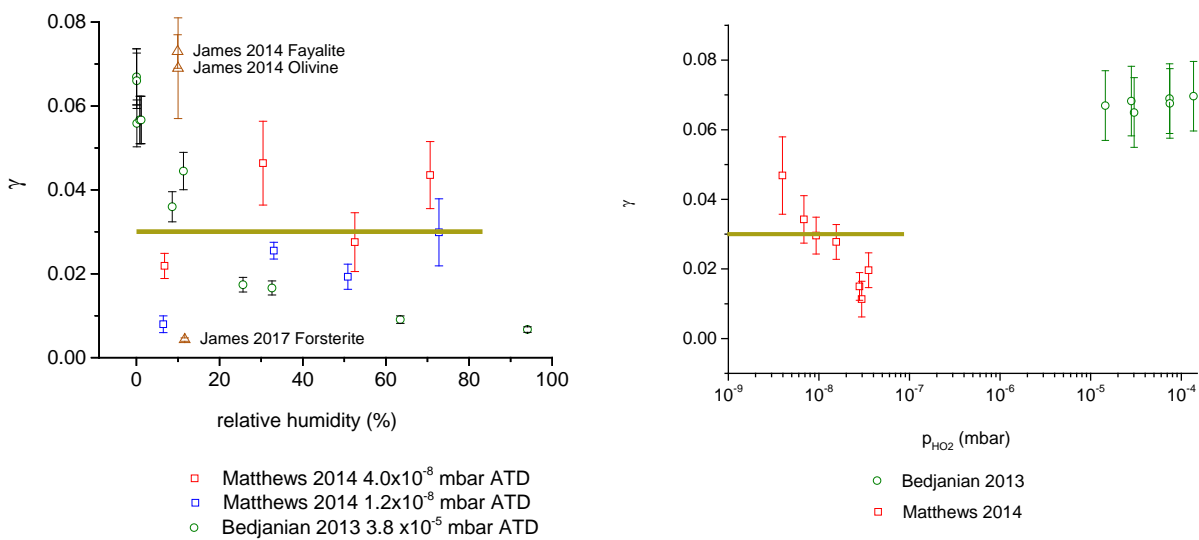
Figure 1: Left: uptake coefficient of HO_2 on mineral dust as a function of relative humidity (left), HO_2 partial pressure (right), and temperature (below). Experimental data: symbols; olive line: preferred value