

**IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation
Data Sheet MD14**

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This datasheet last evaluated: June 2017; last change in preferred values: June 2017

OH + mineral oxide (dust) surfaces → products

Experimental data

<i>Parameter</i>	Substrate	pOH /mbar	Temp. /K	RH	H ₂ O ₂ yield	H ₂ O yield	Reference	Technique/ Comments
<i>Uptake</i>								
<i>coefficients: γ, γ_0</i>								
$(6.3 \pm 2) \times 10^{-3}$	SiO ₂	10 ⁻⁷	253-				Gershenzon et al., 1986	FT-EPR(a)
0.12 ± 0.08	FeO _x		348					
0.04 ± 0.02	AlO _x							
$(2 \pm 1) \times 10^{-3}$	SiO ₂	10 ⁻⁴	308				Suh et al., 2000	PBFT-LIF (b)
$(5 \pm 2) \times 10^{-3}$	Al ₂ O ₃							
$(2 \pm 1) \times 10^{-4}$	TiO ₂							
0.11-0.44	Al ₂ O ₃	10 ⁻⁷	298				Bertram et al., 2001	CWFT-CIMS (c)
$(3.2 \pm 0.7) \times 10^{-2}$	SiO ₂	10 ⁻⁷	298	0			Park et al., 2008	PBFT-CIMS (d)
$(8.4 \pm 1.7) \times 10^{-2}$				20				
$(9.8 \pm 2.2) \times 10^{-2}$				33				
$(4.5 \pm 0.5) \times 10^{-2}$	Al ₂ O ₃			0				
$(7.2 \pm 0.8) \times 10^{-2}$				20				
$(8.4 \pm 1.2) \times 10^{-2}$				38				
0.19	ATD	1.7 × 10 ⁻⁵	300		10	98	Bedjanian et al., 2012	CWFT-MS (e)
0.074		2.2 × 10 ⁻⁴			10	98		
$\gamma_0 = 0.2 \pm 0.02$								
$(0.18 \pm 0.5) / (1 + \text{RH}^{0.36})$		4.1 × 10 ⁻⁵	275-	<26				
			320					

Comments

- (a) Substrate material coated onto movable rod. Iron and aluminium were used with their native oxide layers. SiO₂ was pre-treated with either chromic acid or hydrochloric acid. The uptake coefficients do not show a significant temperature dependence and average values are listed in the table.
- (b) Small pieces of SiO₂ or α -Al₂O₃ and powders of anatase and rutile TiO₂ (8.7 and 4.8 m² g⁻¹, respectively) were deposited on a frit and exposed to OH at a total pressure of a few mbar

- (c) Coated wall flow tube operated at 1 mbar and CIMS using SF_6^- for detection of OH which was produced by microwave discharge of H_2 followed by reaction of H with O_2 or NO_2 . The diffusion coefficient derived from pressure dependent loss rate measurements was $665 \pm 35 \text{ Torr cm}^2 \text{ s}^{-1}$.
- (d) Al_2O_3 and SiO_2 powder mixed with halocarbon wax and coated onto glass beads. Total pressure 133 mbar. OH loss rates derived from measured OH loss and comparison to a reference with halocarbon wax only. Uptake coefficients derived using the virtual cylindrical flow tube approximation (tube with equal surface area to gas volume ratio) and assuming that the fraction of reactive surface area corresponds to the volume fraction of the component in the coating mixture. OH produced by microwave discharge of H_2 and reaction of H with O_2 , leading to OH via $\text{H} + \text{HO}_2$. OH detection with SF_6^- as reagent ion.
- (e) ATD films ($85 \pm 10 \text{ m}^2 \text{ g}^{-1}$ surface area) formed from a suspension in ethanol, followed by drying and baking at 100-150°C in vacuo. UV irradiation (315-400 nm, $J_{\text{NO}_2} = 0.002\text{-}0.012 \text{ s}^{-1}$). OH ($(0.4 - 5.2) \times 10^{12} \text{ molecule cm}^{-3}$) was produced via reaction of H atoms with NO_2 or of F atoms with H_2O and was detected as HOBr following reaction with Br_2 . Observed first order loss rates were corrected for diffusion with $D_0 = 640 \times (T/298)^{1.85} \text{ Torr cm}^2 \text{ s}^{-1}$ to obtain the geometric uptake coefficient, which did not depend on coating mass, and thus the true surface explored is not exactly known. First-order loss rates exhibited significant deactivation with integration over long times resulting in more loss than a monolayer equivalent, indicating catalytic loss. Due to the uncertainties related to the surface area and to the extent products diffusing into the interior of the films, only initial uptake coefficients were reported. UV radiation had no effect on the uptake kinetics.

Preferred Values

Parameter	Value	T/K
γ	0.2	280-320
<i>Reliability</i>		
$\Delta \log (\gamma)$	± 0.7	280-320

Comments on Preferred Values

The recommendation is based on the initial uptake coefficient obtained for ATD (though this is not an authentic airborne dust) and for experiments at the lowest partial pressures of OH and the lowest total pressure in the flow tube (data by Bedjanian et al. (2012) and Bertram et al. (2001)). Experiments at higher partial pressures of OH indicate saturation or deactivation above 10^{-5} mbar. Experiments at higher total pressures in the reactor are likely affected by diffusion that is in addition difficult to be taken into account for the configurations of experiments by Park et al. (2008) and Suh et al. (2000). No temperature dependence of the uptake coefficient was observed.

In view of the inconsistent relative dependence of the uptake coefficient on relative humidity for the Bedjanian et al. and Park et al. data sets, we prefer a humidity independent uptake coefficient with large error bounds.

Various mechanisms have been suggested by which OH is transformed into H_2O and H_2O_2 (Suh et al., 2000; Bogart et al., 1997; Fisher et al., 1993; Gershenson et al., 1986). In view of secondary chemistry involving both secondary sources (including gas phase) and sinks (on mineral oxides) for H_2O_2 it is difficult to determine the H_2O_2 yield unambiguously.

References

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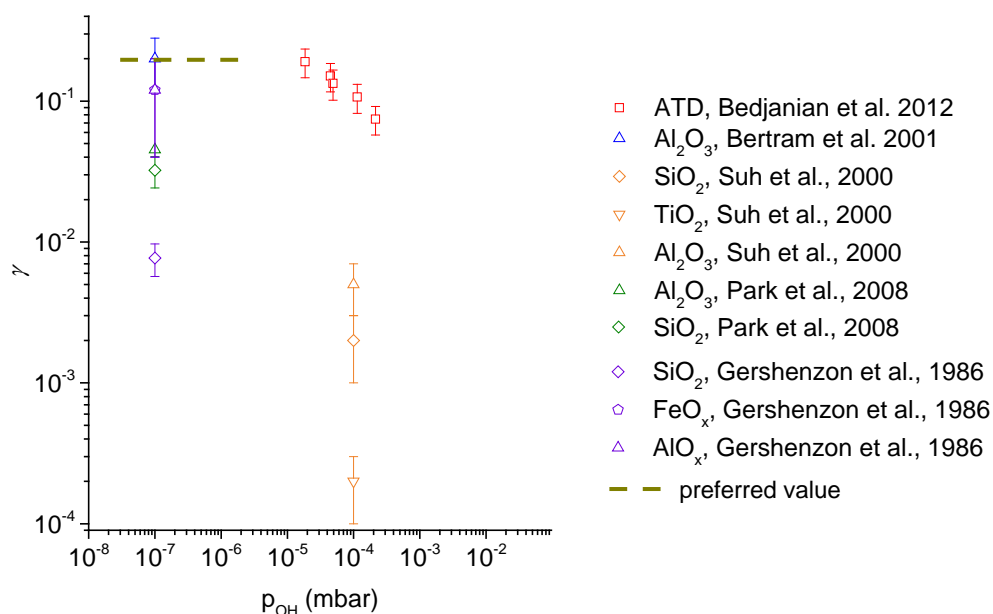


Figure 1: Dependence of uptake coefficient of OH on mineral dust on OH partial pressure.

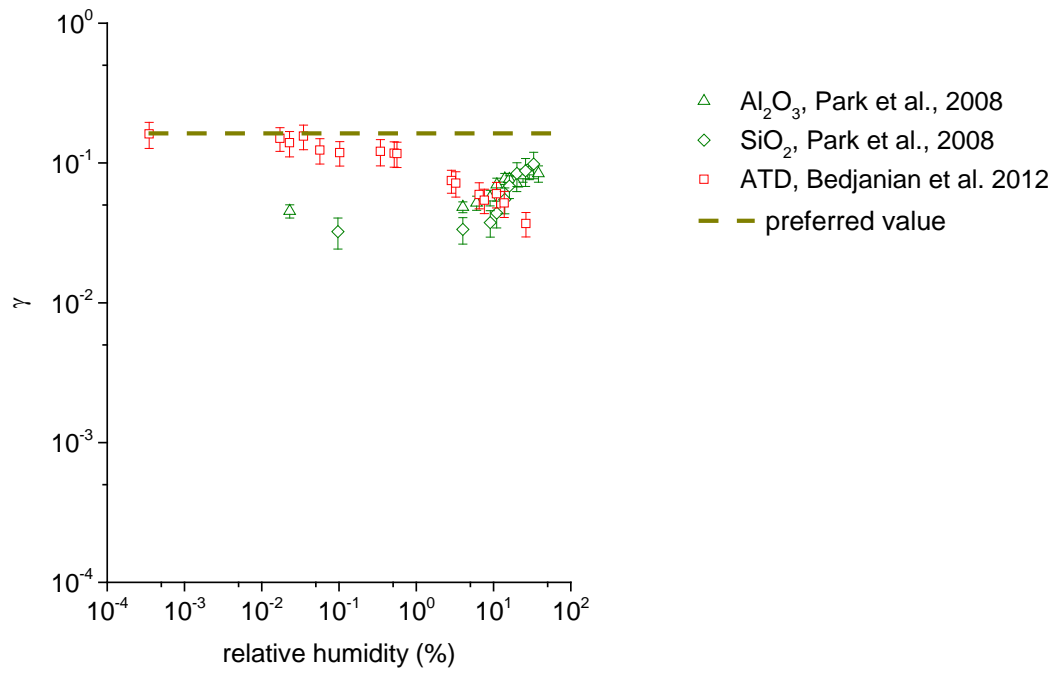


Figure 2: Dependence of uptake coefficient of OH on mineral dust on relative humidity