

IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet VI.A4.1 HET_SL_1

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Experimental data

Parameter	[H ₂ SO ₄] /wt %	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: γ</i>				
$\gamma_{\text{ss}} = (4.5 \pm 0.5) \times 10^{-4}$	>96	298	Baldwin and Golden, 1980	Kn-MS (a)
1	96	298	Gershenzon et al., 1986	(b)
$\gamma_{\text{ss}} > 8 \times 10^{-2}$	28	249	Hanson et al., 1992	WWFT-LIF(c)
<i>Accommodation coefficients: α_b</i>				
> 0.2	45-96	220-298	Cooper and Abbatt, 1996	CWFT-RF (d)

Comments

- (a) Hydroxyl radicals were generated by reaction of hydrogen atoms from microwave discharge of hydrogen with excess NO₂. The uptake coefficient as listed in the table was not found to depend on OH pressure. The sulfuric acid solution was >95 wt %
- (b) Hydroxyl radicals were generated by reaction of hydrogen atoms from microwave discharge of hydrogen with NO₂, leading to OH concentrations of 2×10^{12} molecule cm⁻³ and lower. OH was detected by EPR. H₂SO₄ was coated onto a quartz rod that was inserted into a Teflon coated quartz flow tube at about 6 mbar. No error is given to account for uncertainty due to the effects of gas phase diffusion.
- (c) OH [$(0.5-3) \times 10^{11}$ molecule cm⁻³] was generated through the reaction H + NO₂ and was monitored using LIF. A fluid 28% H₂SO₄-H₂O mixture was used at 249.5 K (2.1 mbar total pressure). The value listed in the table was corrected for gas phase diffusion. The diffusion coefficient for OH in H₂O vapor was taken to be the value of the self-diffusion coefficient for H₂O, 116 ± 20 Torr cm² s⁻¹.
- (d) Coated-wall flow tube with resonance fluorescence detection of OH. First-order loss rate of OH measured in the presence of various types of surfaces. OH ($< 5 \times 10^{10}$ molecule cm⁻³) was generated using both F + H₂O and H + NO₂. Total pressure in the flow tube was 1.33 mbar. Measured uptake was corrected for gas phase diffusion; the following binary diffusion coefficients were used: $0.035T^{1.75}$ Torr cm²/s for OH in He, $0.0063T^{1.75}$ Torr cm²/s for OH in H₂O.

Preferred Values

Parameter	Value	T/K
α_b	1	220 - 298
Reliability		
$\Delta \log (\alpha_b)$	0.7	220 - 298

Comments on Preferred Values

The experiment by Hanson et al. (1992) was close to the diffusion limit, and the corrected uptake coefficient was still roughly consistent with bulk reaction limited uptake due to OH reacting with HSO_4^- (Buxton et al., 1988), indicating that the bulk accommodation coefficient is significantly larger than this. The very high H_2SO_4 concentration (due to pumping on it) and thus lower HSO_4^- concentration may have led to the lower uptake coefficient reported by Baldwin and Golden (1980). Gershenzon et al. (1986) estimated the uptake coefficient to be 1, also at room temperature, for 96% sulfuric acid not further concentrated. The experiment by Cooper and Abbatt (1996) was performed at a lower total pressure in the flow tube to reduce gas phase diffusion limitation and at high enough H_2SO_4 concentration to provide a strong enough bulk liquid sink for OH, leading to 0.2 as lower limit, without indication of temperature dependence. We provide relatively large error limits to the recommended value for α_b to take into account the uncertainty associated with diffusion limitations in Gershenzon's experiment.

References

- Baldwin, A. C., and Golden, D. M.: *J. Geophys. Res.*, 85, 2888-2889, 1980.
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Gershenzon, Y. M., Ivanov, A. V., Kucheryavyi, S. I., and Rozenshtein, V. B.: *Kin. Catal.*, 27, 923-927, 1986.
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