# IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet VI.A4.2 HET_SL_2



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**$HO_2 + H_2SO_4 \rightarrow$ products**

## Experimental data

| *Parameter* | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Uptake coefficients: γ* | | | |
| > 0.05 | 249.5 | Hanson et al, 1992 | WWFT-LIF (a) |
| > 0.1 | 243 | Gershenzon et al., 1995 | CRFT-EPR (b) |
| 0.055 ± 0.02 | 223 | Cooper and Abbatt, 1996 | CWFT-RF (c) |
| < 0.01 | 295 | Thornton et al, 2005 | AFT-CIMS (d) |
| *Accommodation coefficients*: $\alpha_b$ | | | |
| > 0.2 | 223 | Cooper and Abbatt, 1996 | CWFT-RF (c) |
| 0.8 ± 0.3 | 295 | Thornton et al, 2005 | AFT-CIMS (d) |

## Comments

(a) Uptake of $HO_2$ (5-30 × $10^{10}$ molecule $cm^{-3}$) to 28 wt. % $H_2SO_4$ films ≈ 0.3 mm thick. $HO_2$ was formed in the reaction of F with $H_2O_2$ and detected as OH after reaction with NO. $HO_2$ uptake was limited by diffusion through the 1 Torr of He bath gas.

(b) $HO_2$ was detected either directly ([$HO_2$] = 3-5 × $10^9$ molecule $cm^{-3}$) or as OH following reaction with NO ([$HO_2$] = 1-3 × $10^{11}$ molecule $cm^{-3}$). $H_2SO_4$ films were either 80 or 96 wt. %.

(c) Uptake of $HO_2$ to 55 wt % $H_2SO_4$ to determine γ. α was determined by doping the $H_2SO_4$ with with 0.1 M $CuSO_4$. $HO_2$ was formed in the reaction of F with $H_2O_2$ and detected as OH after reaction with NO.

(d) $H_2SO_4$ aerosol (diameter ≈ 100 nm) at 35 – 40 % RH. α was determined by doping the $H_2SO_4$ aerosol (made from 0.0005 – 0.005 M aqueous solutions) with 0.1 M $CuSO_4$. No dependence on RH was observed over the small range covered. $HO_2$ (at concentrations of ≈ 4 × $10^{10}$ molecule $cm^{-3}$) was formed in the reaction of H with $O_2$ and detected as $O_2^-$ using $F^-$ as chemi-ion or as $HSO_4^-$ following conversion to $H_2SO_4$ (addition of NO and $SO_2$) and ionisation with $I^-$. Loss of $HO_2$ to 55 wt. % $H_2SO_4$ was indistinguishable from loss due to the reactor walls, hence the upper limit to γ.

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $\alpha_b$ | 0.8 | 220 – 300 |

*Reliability*

| | | |
|---|---|---|
| $\Delta \alpha$ | $^{+0.2}_{-0.4}$ | |

*Comments on Preferred Value*

Two studies (Cooper and Abbatt, 1996; Thornton and Abbatt, 2005) show that mass accomodation of $HO_2$ to sulphate aerosol is very efficient with values of $\alpha_b$ consistent with unity. The results from the four studies of the net uptake coefficient are however rather divergent, with values of $\gamma$ obtained that vary from > 0.1 to < 0.01. A probable explanation is related to the different experimental temperatures, with low temperatures favouring large uptake coefficients. Thornton and Abbatt (2005) suggest that the results from these studies are internally consistent and the increase in uptake coefficient at low tempertaure is due to enhanced solubility of $HO_2$. Moreover, Thornton and Abbatt (2005) suggest that the net uptake depends on the gas-phase $HO_2$ concentration which impacts strongly on aqueous phase loss rates (due to self-reaction) of $HO_2$. As all experiments were carried out using $HO_2$ concentations orders of magnitude greater than found in the atmosphere, no expression for $\gamma$ is given.

## References


Cooper, P. L. and Abbatt, J. P. D.: J. Phys. Chem. 100, 2249-2254, 1996.

Gershenzon, Y. M., Grigorieva, V. M., Ivanov, A. V. and Remorov, R. G.: Faraday Disc., 83-100, 1995.

Hanson, D. R., Burkholder, J. B., Howard, C. J. and Ravishankara, A. R.: J. Phys. Chem. 96, 4979-4985, 1992.

Thornton, J. and Abbatt, J. P. D.: J. Geophys. Res. 110, 2005.