

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A1.15 HET_H2OL_15

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This data sheet evaluated: 15th January 2009; last change in preferred values: 15th January 2009.

CINO₂ + H₂O(l) → products

Experimental data

Parameter	[X]/ M	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: $\gamma, \gamma_{ss}, \gamma_0$</i>				
$\gamma < 10^{-5}$	H ₂ O droplets	280	George et al, 1995	DT-FTIR/IC (a)
$\gamma_{ss} = 4.8 \times 10^{-6}$	H ₂ O film	291	Behnke et al., 1997	WWFT-FTIR (b)
$\gamma_0 = 3.4 \times 10^{-6}$	H ₂ O film	278	Frenzel et al., 1997	WWFT-FTIR (c)
$\gamma_0 = 9.0 \times 10^{-6}$		282		
$\gamma_0 = 4.5 \times 10^{-6}$		287		
$\gamma_0 = (4.8 \pm 0.1) \times 10^{-6}$		291		
$\gamma_{ss} = (2.6 \pm 1.8) \times 10^{-6}$	H ₂ O film	274	Fickert et al., 1998	WWFT-MS (d)
$\alpha = (9 \pm 4) \times 10^{-3}$				

Comments

- Uptake study using the droplet train technique at typically 13 to 40 mbar total pressure. The trace gas density is monitored at the entry of the flow tube by FTIR. The amounts of Cl⁻ and NO₃⁻ in the droplets measured by ion chromatography was below the detection limit, therefore only an upper limit of γ is given. The continuous flow of CINO₂ diluted in synthetic air at concentrations of up to 2500 ppm was generated by passing N₂O₅ through a 30 cm long wetted wall flow tube interacting with a 3M NaCl aqueous solution.
- Variable length (10-80 cm) wetted-wall flow tube at 1 bar of synthetic air. The liquid film thickness was between 0.8 and 1.2 mm at a surface speed of 2-10 cm s⁻¹. The gas flow rate was in the range 200-400 mL min⁻¹ at 291K resulting in an average linear flow velocity of 15-30 cm s⁻¹. The initial [CINO₂] was measured upstream, the unreacted CINO₂ was measured downstream of the WWFT using FTIR. Between pure H₂O and 1M NaCl γ decreases by more than a factor of ten.
- Experimental details as (b). The uptake coefficients were obtained by fitting the initial measured time/position-dependent concentration profiles using a complex reaction mechanism including gas and liquid phase diffusion. The formation of CINO₂ was also observed when Cl₂ interacted with the H₂O film.
- Uptake study in a wetted-wall tubular flow reactor on a falling film of pure water and aqueous alkali halide salt solutions. The CINO₂ reactant and products was monitored using a differentially-pumped MS with electron impact ionization. The value of γ_{ss} remains unchanged upon addition of 1M NaCl whereas it increased upon addition of 0.1M OH⁻. Analysis of uptake

rates measured under gas –phase diffusion controlled conditions (0.5 M KOH film) gave the cited value for the accommodation coefficient on aqueous surfaces, $\alpha = (9 \pm 4) \times 10^{-3}$.

Preferred Values

Parameter	Value	T/K
α_b	9×10^{-3}	273-298
γ_{ss}	3×10^{-6}	273-298
<i>Reliability</i>		
$\Delta \log (\alpha)$	± 0.5	298

Comments on Preferred Values

The results show consistently that ClNO₂ is non reactive towards liquid water surfaces. The recommended accommodation coefficient is based on the measurement of Fickert et.al,(1998). The reactive uptake is controlled by hydrolysis which is very slow in pure water. The products have not been definitely identified.

References

- Behnke, W., George, Ch., Scheer, V. and Zetzsch, C.: J. Geophys. Res. 102, 3795 (1997).
 Fickert, S., Helleis, F., Adams, J., Moortgat, G.K. and Crowley, J.N.: J. Phys. Chem. 102A, 10689 (1998).
 Frenzel, A., Scheer, V., Sikorski, R., George, Ch., Behnke, W., and Zetzsch, C.: J. Phys. Chem. (1997).
 George, Ch., Behnke, W., Scheer, V., Zetzsch, C., Magi, L., Ponche, J.L. and Mirabel, Ph.: Geophys. Res. Lett. 22, 1505 (1995).