

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A4.13a HET_SL_13a

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This data sheet last evaluated: June 2010; last change in preferred values: June 2010.

HOCl + H₂SO₄ → products

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Solubility: H (M atm⁻¹), Diffusion: D₁ (cm² s⁻¹)</i>			
$HD_1^{1/2} = 3.4 \times 10^{-5} \exp(2640/T)$ (58.5 wt.% H ₂ SO ₄)	200-230	Hanson and Ravishankara, 1993	CWFT-CIMS (a)
$HD_1^{1/2} = 3.9 \times 10^{-5} \exp(2810/T)$ (55.6 wt.% H ₂ SO ₄)	205-250		
$HD_1^{1/2} = 1.8 \times 10^{-5} \exp(3070/T)$ (50.5 wt.% H ₂ SO ₄)	200-230		
$HD_1^{1/2} = 2.6 \times 10^{-6} \exp(3590/T)$ (46 wt.% H ₂ SO ₄)	200-230		
$HD_1^{1/2} = 41$ (57 wt.% H ₂ SO ₄)	204	Zhang et al., 1994	CWFT-MS (b)
$H = 1.4 \times 10^3$ (59.5 wt.% H ₂ SO ₄)	251	Hanson and Lovejoy, 1996	CWFT-CIMS (c)
$D_1 = (6 \pm 2) \times 10^{-7}$			
$HD_1^{1/2} = 9$ (58 wt.% H ₂ SO ₄)	220	Donaldson et al., 1997	CWFT-CIMS (d)
$HD_1^{1/2} = 7.1$ (60 wt.% H ₂ SO ₄)			
$HD_1^{1/2} = 4.6$ (63 wt.% H ₂ SO ₄)			
$HD_1^{1/2} = 2.7$ (67 wt.% H ₂ SO ₄)			
$HD_1^{1/2} = 0.9$ (75 wt.% H ₂ SO ₄)			
$H = 2.5 \times 10^3$ (52 wt.% H ₂ SO ₄)	250		
$H = 1.1 \times 10^3$ (62.5 wt.% H ₂ SO ₄)			
$H = 1.1 \times 10^3$ (65 wt.% H ₂ SO ₄)			
$H = 0.9 \times 10^3$ (67 wt.% H ₂ SO ₄)			
$H = 1.0 \times 10^3$ (70 wt.% H ₂ SO ₄)			

Comments

- (a) HOCl was made in-situ from hydrolysis of ClONO₂ in H₂SO₄ or ex-situ by the reaction of Ca(OCl)₂ with HCl. Time dependent HOCl uptake coefficients were analysed to derive values of $HD_1^{1/2}$ for 59.6, 55.6, 50.5 and 46wt.% H₂SO₄ solutions. The parameters listed in the Table were obtained by fitting to the tabulated datasets given by Hanson and Ravishankara (1993).
- (b) Time dependent HOCl uptake coefficients were analysed to derive values of $HD_1^{1/2}$. The Only a single value for $HD_1^{1/2}$ was reported. The experiment was conducted at 204 K with the H₂O vapour pressure adjusted to 3.8×10^{-4} Torr. This was converted to a H₂SO₄ concentration using the measurements of Zhang et al. (1993). Other datasets obtained were stated to be in good agreement with Hanson and Ravishankara, (1993).
- (c) Rotated CWFT. HOCl (usually present at $\sim 3 \times 10^{10}$ molecule cm⁻³) was synthesised by flowing HF over Ca(OCl)₂. The solubility was measured directly, the diffusion coefficient was derived from the dependence of the uptake coefficient on the HCl concentration in solution (i.e. measurement of $H(D_1k)^{1/2}$ where k is the first order constant for reaction of HOCl with dissolved HCl).

- (d) Rotated CWFT. The H₂SO₄ concentration (49-75 wt.%) was adjusted by variation of the H₂O partial pressure. The HOCl solubility at 250 K was measured directly. Values for $HD_1^{1/2}$ at 220 K were derived from time dependent uptake coefficients.

Preferred Values

Parameter	Value	T/K
C (cm ² cP K ⁻¹ s ⁻¹)	6.4×10^{-8}	
A	$169.5 + 5.18$ (wt%) -0.0825 (wt%) ² $+ 3.27 \times 10^{-3}$ (wt%) ³	
T_0	$144.11 + 0.166$ (wt%) $- 0.015$ (wt%) ² $+ 2.18 \times 10^{-4}$ (wt%) ³	
H^0 (M atm ⁻¹)	1.91×10^{-6}	
B (K)	5862.4	
c	0.0776	
d	59.18	

Comments on Preferred Value

The majority of the experimental data on HOCl interaction with H₂SO₄ solutions has come from one research group (Hanson and Ravishankara, 1993; Hanson and Lovejoy, 1996; Donaldson et al. 1997). Solubilities have been derived directly from stirred solutions or indirectly (via measurement of $HD_1^{1/2}$) using static solutions.

The diffusion of HOCl in H₂SO₄ has not been investigated directly. Klassen et al (1998) have parameterised the diffusion coefficient for HOCl in H₂SO₄ as:

$$D_1 = CT / \eta$$

where C is a constant (cm² cP K⁻¹ s⁻¹) and η is the viscosity of H₂SO₄ at a given wt.% and temperature. Shi et al., have taken viscosity data from Williams and long (1995) and for pure water to derive an extended formulation to cover H₂SO₄ viscosities from 0 to 80 wt%., which can be used with the C constant above to derive D_1 over the same concentration range using:

$$\eta = AT^{-1.43} \exp(448/(T-T_0))$$

This parameterisation results in values of η which agree to better than 10 % (for 40 – 70 wt.% H₂SO₄ solutions) with those of Klassen et al. (1998). Solubilities derived from measurements of $HD_1^{1/2}$ and values of D_1 calculated as described above are in good agreement.

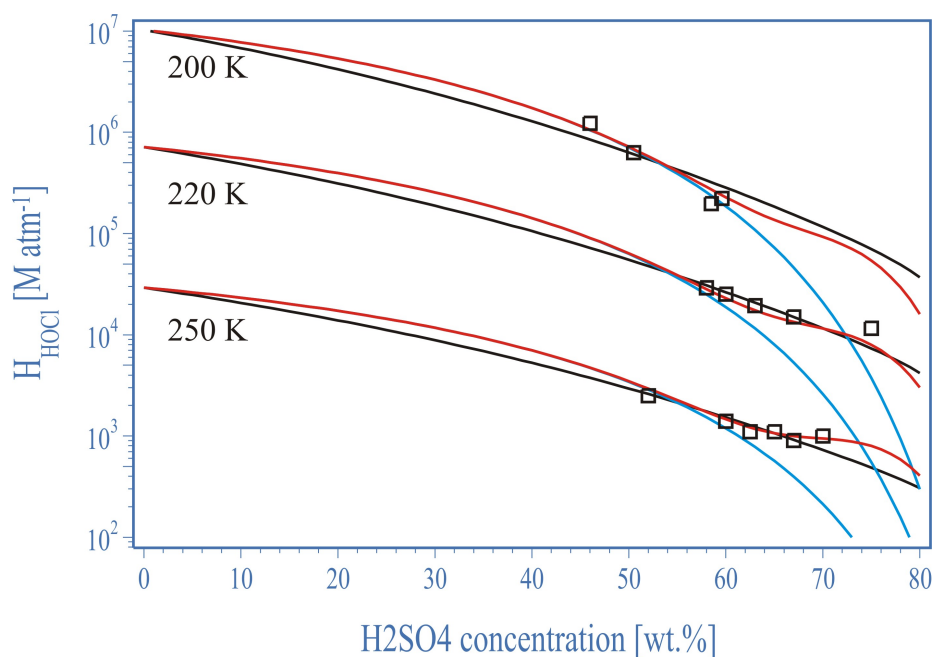
Based on the experimental data of Hanson and Ravishankara (1993) and solubility data for pure H₂O, Huthwelker et al (1995) developed a semi-empirical expression for the solubility of HOCl in H₂SO₄ solutions. Experimental data which appeared later (Donaldson et al., 1996) indicates an HOCl solubility which is substantially larger than that calculated at high H₂SO₄ concentrations (> 65 wt.%). Donaldson et al (1996) suggested application of a temperature independent, empirical correction factor (f) to the calculated solubilities of Huthwelker et al.: $f = 1 + 1.052 \exp(0.273 \times \text{wt.\%} - 65.66)$. Use of this factor and the diffusion coefficients of Huthwelker et al. also aligns the direct measurements of $HD_1^{1/2}$ presented in Donaldson et al. In addition, Shi et al. (2001) have reanalysed the available data for HOCl solubility in H₂SO₄ and H₂O and derived a further expression, which reproduces the data well. We adopt their formulation, which can be used for a wide range of temperatures (190-250 K) and H₂SO₄ concentrations (0-75 wt%):

$$H = H^0 \exp(B / T) \exp (-SM_{\text{H}_2\text{SO}_4})$$

where S is the Setchenow coefficient ($S = c + d / T$) and $M_{\text{H}_2\text{SO}_4}$ is the molarity of the H_2SO_4 solution, which can be calculated from temperature and concentration dependent H_2SO_4 densities.

References

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HOCl solubility. Data points at 250 K are directly obtained solubilities (Donaldson et al., 1997). Data points at 200 and 250 K were derived from measurements of $HD_1^{1/2}$ (Hanson and Ravishankara, 1993, Hanson and Lovejoy, 1996). The blue, red and black curves are parameterisations by Huthwelker et al (1995), Donaldson et al, (1997) and Shi et al, (2001), respectively.