

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A4.12 HET_SL_12

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$\text{H}_2\text{CO} + \text{H}_2\text{SO}_4 \rightarrow \text{products}$

Experimental data

Parameter	[H ₂ SO ₄] /wt%	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: γ</i>				
0.01	67	223	Tolbert et al., 1993	Kn-MS (a)
0.08	75			
$(2.7 \pm 0.4) \times 10^{-3}$	10	267	Jayne et al., 1996	DT-TDL (b)
$(6.7 \pm 0.9) \times 10^{-3}$	55	241		
$(1.14 \pm 0.09) \times 10^{-2}$	85	300		
2×10^{-3}	48-95	197-215	Iraci and Tolbert, 1997	SF-MS (c)
<i>Solubility, H^* ($M \text{ atm}^{-1}$)</i>				
2.0×10^6	48	206	Iraci and Tolbert, 1997	SF-MS (c)
4.0×10^6	64	207		
4.0×10^6	76	201		
6.3×10^6	86	209		
1.7×10^6	95	207		

Comments

- Uptake experiments of CH₂O on quiescent and stirred sulfuric acid solutions were performed in the range 60 to 75 wt% H₂SO₄ at low temperature. The concentration of CH₂O ranged from 2×10^{10} to 2×10^{11} molecule cm⁻³ and no new gas phase products were detected during uptake. Gentle stirring of the sulfuric acid solution increased the rate of uptake by CH₂O on the order of a factor of four or so owing to surface saturation at low temperatures, slow diffusion in the liquid and large gas concentrations.
- Uptake to 10-85 wt% droplets at temperatures between 241 and 300K. Time-dependent (reactive) uptake of CH₂O was observed and interpreted in terms of formation of CH₂(OH)₂ and protonated formaldehyde, CH₃O⁺, at high acidities. The formation of a chemisorbed surface complex of CH₂O at the gas-liquid interface has been invoked under mildly acidic conditions (<20 wt% acid).
- Stirred flow reactor with H₂CO partial pressures of 4×10^{-6} to 2.7×10^{-3} mbar. Thin H₂SO₄ films were made from the reaction of SO₃ with H₂O and supported on an optical window monitored by transmission FTIR spectroscopy.

Preferred Values

Parameter	Value	T/K
α_b	0.04	200-300
c	$8 \times 10^{-8} \exp(-0.0272 wt)$	200-300
$H_{\text{CH}_2\text{O}} \text{ (M atm}^{-1}\text{)}$	$\exp(-(-0.0456 + 55.5/T) \times 0.46 m_{\text{H}_2\text{SO}_4})$	200-300
$H^*_{\text{CH}_2(\text{OH})_2} \text{ (M atm}^{-1}\text{)}$	$H_{\text{CH}_2\text{O}} (1+K_2 a_{\text{H}_2\text{O}})$	200-300
$H^*_{\text{CH}_3\text{O}^+} \text{ (M atm}^{-1}\text{)}$	$H_{\text{CH}_2\text{O}} (1+K_3[\text{H}^+])$	200-300
$K_2 \text{ (M}^{-1}\text{)}$	$\exp(4020/T-5.83)$	200-300
$K_3 \text{ (M}^{-1}\text{)}$	$0.56\exp(8.84 (T-260)/T)$	200-300
$k_{\text{H}_2\text{O}} \text{ (M}^{-1} \text{ s}^{-1}\text{)}$	$7800\exp(-1910/T) (1+870[\text{H}^+])$	200-300
$\Gamma_{\text{b,poly}}$	0.001	197-215

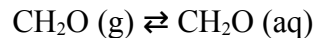
Reliability

$\Delta\log(\alpha_b)$	± 0.3	200-300
$\Delta\log(H)$	± 0.3	200-300
$\Delta\log(K)$	± 0.3	200-300
$\Delta\log(\gamma)$	± 0.7	200-300

Comments on Preferred Values

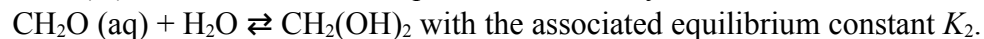
By analogy to known condensed phase kinetics CH_2O is both solvated to methyleneglycol ($\text{CH}_2(\text{OH})_2$) as well as existing in protonated form (CH_3O^+) in H_2SO_4 . The uptake of HCHO to H_2SO_4 shows a negative temperature dependence at constant $[\text{H}_2\text{SO}_4]$ and a pronounced H_2SO_4 concentration dependence: γ increases with increasing concentration starting from a concentration where formaldehyde protonation is thought to be the dominant solvation mechanism. Jayne et al. (1996) present a set of parameters that reproduced the time dependent uptake of CH_2O for the short time scale (20 ms) of their experiment, from which we adopt the value for α_b . In absence of static measurements we adopt their parameters relevant for the calculation of the solubility as a recommendation, since they appropriately link to more dilute solution as well as known hydrolysis rate constants (Jayne et al., 1992).

$H_{\text{CH}_2\text{O}}$ describes the physical Henry's Law for formaldehyde:

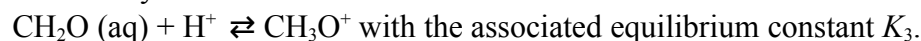


It includes a Setchenow coefficient referenced to that for HOCl .

$H^*_{\text{CH}_2(\text{OH})_2}$ includes the further equilibrium due to hydration to the more soluble *gem*-diol form:



$H^*_{\text{CH}_3\text{O}^+} \text{ (M atm}^{-1}\text{)}$ can be used to describe the partitioning into the protonated form of formaldehyde:



We suggest using the parameterisation of Shi et al. (2001) for the proton concentration and the water activity:

$$[\text{H}^+] = \exp [60.51 - 0.095wt + 0.0077wt^2 - 1.61 \times 10^{-5}wt^3 - (1.76 + 2.52 \times 10^{-4} wt^2)T^{0.5} + (-805.89 + 253.05wt^{0.076})/T^{0.5}]$$

$$a_w = \exp [(-69.775 X - 18253.7 X^2 + 31072.2 X^3 - 25668.8 X^4)(1/T - 26.9033/T^2)]$$

where the mole fractions can be calculated from weight percent concentration by: $X = wt/(wt + (100-wt)98/18)$

The three Henry's Law constants can be used to calculate the overall equilibrium uptake and partitioning into CH_2O (aq), $\text{CH}_2(\text{OH})_2$, and CH_3O^+ . Jayne et al. also invoked a surface process, parameterized by a time dependent direct gas – surface reaction probability to fully explain the observed uptake coefficient at short gas-droplet interaction times. Since the surface density of the corresponding surface complex remains low it does not affect the overall equilibrium of the other species. Iraci and Tolbert (1997) did not see evidence for the presence of $\text{CH}_2(\text{OH})_2$ in IR spectra taken after long exposure time at 210 K and 80 wt% H_2SO_4 , but rather suspected formation of a polymer, e.g., through dehydration of $\text{CH}_2(\text{OH})_2$, which would lead to an apparently higher effective solubility than predicted from the equilibria above alone. The absence of $\text{CH}_2(\text{OH})_2$ may have been due to the fall off of K_2 at high H_2SO_4 concentration. Since the long term kinetics has not been measured at higher T and lower $[\text{H}_2\text{SO}_4]$, where $\text{CH}_2(\text{OH})_2$ concentrations would be higher, we refrain from giving detailed kinetic parameters for this potential sink of formaldehyde, but simply recommend a constant value of 10^{-3} for $\Gamma_{b,\text{poly}}$ with large error limits, so that the overall γ becomes consistent with the steady state uptake observed by Iraci and Tolbert after long exposure times.

The overall uptake coefficient is given by the expression:

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_{sol,HCHO} + \frac{1}{\frac{1}{\Gamma_{sol,CH_2(OH)_2}} + \frac{1}{\Gamma_{b,CH_2(OH)_2}}} + \Gamma_{sol,CH_3O^+} + \Gamma_{b,poly}}$$

The time dependent solubility limited uptake terms are given by:

$$\Gamma_{sol,X} = \frac{4H_X RT \sqrt{\frac{4D_l}{\pi t}}}{\bar{c}_{HCHO}}$$

The hydration reaction is parameterized by:

$$\frac{1}{\Gamma_{b,CH_2(OH)_2}} = \frac{4H_{HCHO} RT \sqrt{D_l a_w k_{H_2O}}}{\bar{c}_{HCHO}}$$

For the hydration rate constant k_{H_2O} we adopt the expression provided by Jayne et al. that is consistent with more dilute aqueous solutions.

For the diffusion coefficient, we suggest using the expression for the c parameter given above, based on Jayne et al. (1996), via $D_l = cT/\eta$. For the viscosity, we suggest using the parameterization presented by Shi et al. (2001), which fits well to data by Williams and Long (1995) but extends into the troposphericly more relevant dilute solutions at high T:

$$\eta = aT^{-1.43} \exp(448K/(T-T_0)), \quad (2)$$

$$\text{with } a = 169.5 + 5.18 \text{ wt} - 0.0825 \text{ wt}^2 + 3.27 \times 10^{-3} \text{ wt}^3,$$

$$\text{and } T_0 = 144.11 + 0.166 \text{ wt} - 0.015 \text{ wt}^2 + 2.18 \times 10^{-4} \text{ wt}^3$$

The combination of all three experiments shows that the rate of uptake of CH_2O by H_2SO_4 solutions increases with acidity of H_2SO_4 at 228K for $[\text{H}_2\text{SO}_4] \geq 70$ wt% to values close to $\gamma = 0.10$. At higher temperatures in the range of 241-300K the solubility of dissolved CH_2O and methyleneglycol ($\text{CH}_2(\text{OH})_2$) increases with increasing temperature and decreases with increasing acid activity. For protonated formaldehyde (CH_3O^+) the solubility increases with increasing acid activity as well as decreasing temperature.

References

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