

IUPAC Task Group on Atmospheric Chemical Kinetic data Evaluation – Data Sheet VIA4.19 HET_SL_19

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

Acetone + H₂SO₄ → products

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: γ</i>			
$\gamma_0 = 0.7$ (85 wt. % H ₂ SO ₄)	200	Duncan et al., 1998	(a)
$\gamma_{ss} = 0.4$ (85 wt. % H ₂ SO ₄)	200		
$\gamma_{ss} = 0.25$ (75 wt. % H ₂ SO ₄)	201	Duncan et al., 1999	(a)
$\gamma_{ss} = 0.48$ (85 wt. % H ₂ SO ₄)	221		
$\gamma_{ss} = 0.57$ (85 wt. % H ₂ SO ₄)	221		
$\gamma_{ss} = 5.2 \times 10^{-5}$ (89.4 wt. % H ₂ SO ₄)	298	Esteve and Noziere, 2005	(b)
$\gamma_{ss} = 5.6 \times 10^{-6}$ (85.0 wt. % H ₂ SO ₄)			
$\gamma_{ss} = 4.7 \times 10^{-6}$ (80.8 wt. % H ₂ SO ₄)			
$\gamma_{ss} = 1.6 \times 10^{-6}$ (73.9 wt. % H ₂ SO ₄)			
<i>Solubility: H^* (M atm⁻¹)</i>			
$H^* = 7.1 \times 10^7$ (70 wt. % H ₂ SO ₄)	180	Duncan et al., 1999	(a)
$H^* = 1.2 \times 10^7$ (70 wt. % H ₂ SO ₄)	187		
$H^* = 2.4 \times 10^6$ (70 wt. % H ₂ SO ₄)	195		
$\log H^* = -7.50 + 2920/T$ (67.7 wt. % H ₂ SO ₄)	220-239	Klassen et al., 1999	Knud-MS (c)
$\log H^* = -7.43 + 2750/T$ (60.7 wt. % H ₂ SO ₄)	223-234		
$\log H^* = -7.39 + 2650/T$ (54.4 wt. % H ₂ SO ₄)	213-226		
$\log H^* = -7.35 + 2580/T$ (48.3 wt. % H ₂ SO ₄)	212-222		
$\ln H^* = 3.0 - [H_2SO_4]f - 4850 (1/298.15 - 1/T)$ (40-75 WT. %)	198-292	Kane et al., 1999	WWFT-MS (d)
$H^* = 2.1 \times 10^4$ (50 wt. % H ₂ SO ₄)	230	Imamura and Akiyoshi, 2000	WWFT-PIMS (e)
$H^* = 1.3 \times 10^3$ (50 wt. % H ₂ SO ₄)	250		
$H^* = 8.2 \times 10^4$ (60 wt. % H ₂ SO ₄)	230		
$H^* = 4.4 \times 10^3$ (60 wt. % H ₂ SO ₄)	250		
$H^* = 2.5 \times 10^4$ (69 wt. % H ₂ SO ₄)	250		
$H^* = 2.2 \times 10^5$ (76 wt. % H ₂ SO ₄)	250		
$H^* = 2.2 \times 10^4$ (76 wt. % H ₂ SO ₄)	270		
$H^* = 9.5 \times 10^4$ (79 wt. % H ₂ SO ₄)	270		

Comments

- (a) Low pressure, molecular flow reactor with FTIR and MS. Reflection-Absorption infrared spectroscopic analysis of H₂SO₄ films (0.05-0.1 μm thick, 180-260 K, 35 – 96 wt. % H₂SO₄) exposed to acetone (10⁻⁷ – 10⁻⁴ mbar) reveal presence of mesityl oxide and trimethylbenzene. The reaction proceeds via formation of protonated acetone, which, in H₂SO₄ solutions of > 70 wt. %, can undergo self-dehydration to form mesityl oxide. Trimethylbenzene is formed from mesityl oxide in solutions of > 85 wt. %. At concentrations lower than 70wt. % acetone uptake is reversible and the effective solubility, H^* , was determined by integrating the uptake until the thin film was saturated. Errors on H^* are estimated as 25 %. Uptake coefficients obtained by gas-analysis using MS. The enthalpy and entropy of solution were determined as –66 kJ mol⁻¹ and –249 J mol⁻¹ K⁻¹, respectively. The solubility data (180-195 K) can be described by: $H^* = \exp\{(T*216.7 - 66000)/ 8.314 * T)\}$ for 70 wt. % H₂SO₄.
- (b) Rotated WWFT generally at ≈ 100 mbar with MS detection of acetone at high concentrations (1-5 x10⁻⁵ atm). The experimental uptake coefficient, γ_{ss} , was observed to increase with [acetone]. Reactive uptake observed at [H₂SO₄] > 70 wt. % and reversible uptake at lower concentrations. Uptake coefficients were corrected for gas diffusion.
- (c) Knudsen reactor using 48-68 wt. % H₂SO₄ at 210 – 240 K. Solubility determined by measuring the time dependence of the acetone uptake and using liquid-phase diffusion coefficients calculated from viscosity data. Uncertainty estimated as ± 33 %. Addition of ammonium sulphate reduced the solubility slightly.
- (d) WWFT reactor using 40-87 wt. % H₂SO₄ at 198 – 300 K. Uptake in dilute solutions (< 75 wt. %) was found to be reversible. Solubility determined by measuring the time dependence of the acetone uptake and using liquid-phase diffusion coefficients calculated from viscosity data. The dependence of the solubility on the H₂SO₄ concentration and temperature is given by the equation in the table where $f = 0.23 + 5/T$ and [H₂SO₄] is the molality of the H₂SO₄ solution. Note that the original expression given by the authors contains a typographical error, which has been subsequently corrected (Leu, 2003). The error limits on H^* are reported to be 50%. In H₂SO₄ solutions of greater than 80 wt. %, both mesityl oxide and trimethylbenzene were observed by MS when liquid acetone was mixed with H₂SO₄.
- (e) WWFT with PIMS detection of reversible acetone uptake to thin H₂SO₄ films (50-79 wt. %) at 230-270 K. Solubility determined by integrating the acetone uptake until the film was saturated. Uncertainties in H^* reported to be ± 30 %.

Preferred Values

Parameter	Value	T/K
$\ln H^*$	$3.0 - [H_2SO_4]f - 4850 (1/298.15 - 1/T)$ (40-75 wt. % H ₂ SO ₄ ,	195 – 295 K
<i>Reliability</i>		
$\Delta \log H$	± 0.5	

Comments on Preferred Values

The experimental data show that acetone is protonated to some extent in H₂SO₄ solutions and, at H₂SO₄ concentrations greater than 75 wt. %, dehydration reactions result in the formation of mesityl oxide and trimethylbenzene. At concentrations lower than 70 wt. % acetone uptake is reversible and solubility controls the amount taken up to the solution. The preferred values for the effective Henry's law solubility are taken from the most extensive study by Kane et al. (1999), which covered the largest temperature and H₂SO₄ concentration range. Where comparison is possible (overlap in T and H₂SO₄ wt. %) the agreement between the studies is

generally within a factor of 2-4. For this reason we present errors limits significantly greater than the 25 –50 % uncertainties reported by the various authors. The uptake coefficients presented by Duncan et al. (1998, 1999) and Esteve and Noziere (2005) diverge by several orders of magnitude, most likely due to the different temperature regimes investigated, and no recommendation is given.

References

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Kane, S. M., Timonen, R. S. and Leu, M. T.: *J. Phys. Chem. A* 103, 9259-9265, 1999.
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