IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_40

This datasheet last evaluated: June 2019; last change in preferred values: June 2019

$HO(aq) + HO(CH_2)_2OH(aq) \rightarrow HOCHCH_2OH + H_2O$

(product distribution suggested by Buxton et al., 1988)

Rate coefficient data

k/ L mol^{-1} s^{-1}	T/K	pH	I/ mol L^{-1}	Reference	Technique/ Comments
Relative Rate Coefficients					
1.6×10^9	294	~7	-	Adams et al., 1965	PR / UV-Vis (a1)
1.4×10^9	294	~7	-		(a2)
1.5×10^9	294	9	-	Anbar et al., 1966	PR / UV-Vis (b)
1.8×10^9	294	2.0-2.2	-	Scholes and Willson, 1967	PR / UV-Vis (c)
1.62×10^9	294	-	-	Willson et al., 1971	PR / UV-Vis (d)
2.30×10^9 2.61×10^9 2.84×10^9 2.72×10^9	298 ±2	-	-	Matheson et al., 1973	PR / UV-Vis (e)
$(1.6 \pm 0.03) \times 10^9$	298	7	-	Hoffmann et al., 2009	LFP-LPA (f)
$3.53 \times 10^{10} \exp[-(900 \pm 110)/T]$	288 – 328	7	-		(f1)

$\Delta G_R°$ (aq): Aqueous phase thermochemical data not available. As well, gas phase thermochemical data $H_R°$ (g) are not available.

Comments

(a) Reference reactions: HO + CO_3^{2-} with k(HO + CO_3^{2-}) = 2.0×10^8 M^{-1}s^{-1} [3.77×10^8 M^{-1}s^{-1}] (a1); HO + SCN^- with k(HO + SCN^-) = 6.6×10^9 M^{-1}s^{-1} [1.10×10^{10} M^{-1}s^{-1}, Zhu et al., 2003] (a2); no values given for the initial concentrations of the reactants; pH is given as natural; as no exact temperature is given, a room temperature of 294 K is assumed.

(b) Reference reaction: HO + PNDA (p-nitrosodimethylaniline); reference rate constant was determined versus ethanol with k(HO + ethanol) = 1.10×10^9 M^{-1}s^{-1}; rate coefficients have

been recalculated using the selected value for the reference reaction 1.88×10^9 $M^{-1}s^{-1}$; no values given for initial concentrations; air saturated solutions; all experiments were repeated at least four times and the coefficient of variation was less than ±10%; as no exact temperature is given, a room temperature of 294 K is assumed.

(c) Aerated solutions of thymine (c(thymine) = 8×10^{-5} M) were irradiated (pH range: 1.5 – 9); rate constant was determined relative to thymine reference with k(HO + thymine) = 4.3×10^9 M^{-1} s^{-1}; rate constants have been recalculated using the selected value for the reference reaction (5.38×10^9 $M^{-1}s^{-1}$); as no exact temperature is given, a room temperature of 294 K is assumed.

(d) Reference reaction: HO + $[Fe(CN)_6]^{4-}$; k(HO + $[Fe(CN)_6]^{4-}$) = $(9.3 \pm 0.05) \times 10^9$ M^{-1} s^{-1}; rate constants have been recalculated using the selected values for the reference reactions (1.03×10^{10} $M^{-1}s^{-1}$); c($[Fe(CN)_6]^{4-}$) = 2×10^{-3} mol/L (no information on counterions); reference values were normalized to k(HO + ethanol) = 1.85×10^9 $M^{-1}s^{-1}$; as no exact temperature is given, a room temperature of 294 K is assumed.

(e) Rate constants were determined relative to the reference reaction with k(HO + $[Fe(CN)_6]^{4-}$) = 0.93×10^{-10} M^{-1} s^{-1}; rate constants have been recalculated using the selected value for the reference reaction (1.10×10^{10} $M^{-1}s^{-1}$); Depending on four different concentrations of ethylene glycol (2×10^{-3} M, 4×10^{-3} M, 8×10^{-3} M and 1×10^{-2} M), rate constants were measured as listed.

(f) Radicals generated by laser flash photolysis of H_2O_2 (c(H_2O_2) = 1×10^{-4} M) at 248 nm (LP-LPA); Reference reaction: HO + SCN^- with k(HO + SCN^-) = 1.24×10^{10} M^{-1} s^{-1} as reported by Chin and Wine (1992); rate constants have been recalculated using the selected values for reference reactions (Zhu et al., 2003); c(KSCN) = 1.59×10^{-5} M. Arrhenius expression (f1) was calculated using the recalculated experimental data from Hoffmann et al. (2009).

Preferred Values

Parameter	Value	*T*/K
k / L mol^{-1} s^{-1}	1.65×10^9	298
k / L mol^{-1} s^{-1}	2.82×10^{10} exp[-(850)/T]	288 - 328
Reliability		
Δ log k	±0.09	298
Δ E_A/R	±150	288 – 328

Comments on Preferred Values

For the Arrhenius equation regression, the temperature dependent data by Hoffmann et al. (2009), as well as the recalculated rate coefficients by Adams et al. (1965), Anbar et al. (1966), Scholes and Willson (1967) and Willson et al. (1971) have been considered. Due to the hugely different determinations by Matheson et al. (1973) to, their data is not included in the regression. The recommended rate constant is in good agreement with the temperature dependent data of Hoffmann et al. (2009). The estimated uncertainty is given as Δ log k = 0.09 or ±20%.

References

Adams, G. E., Boag, J. W. and Michael, B. D.: Trans. Faraday Soc., 61, 1417-1424, 1965.

Adams, G.E., Boag, J.W., Currant, J. and Michael, B.D., Pulse Radiolysis, Ebert, M., Keene, J.P., Swallow, A.J. and Baxendale, J.H. (eds.): Academic Press, New York, 131-143, 1965.

Anbar, M., Meyerstein, D. and Neta, P.: J. Chem. Soc. B, 742-747, 1966.

Buxton, G. V., Greenstock, C. L., Helman, W. P. and Ross, A. B.: J. Phys. Chem. Ref. Data, 12(2), 513 – 886, 1988.

Chin, M., and Wine, P. H: J. Photochem. Photobiol., A, 69(1), 17-25, 1992.

Hoffmann, D., Weigert, B., Barzaghi, P. and Herrmann, H.: Phys. Chem. Chem. Phys., 11, 9351-9363, 2009

Kraljić, I. and Trumbore, C. N.: J. Am. Chem. Soc. 87(12), 2547-2550, 1965.

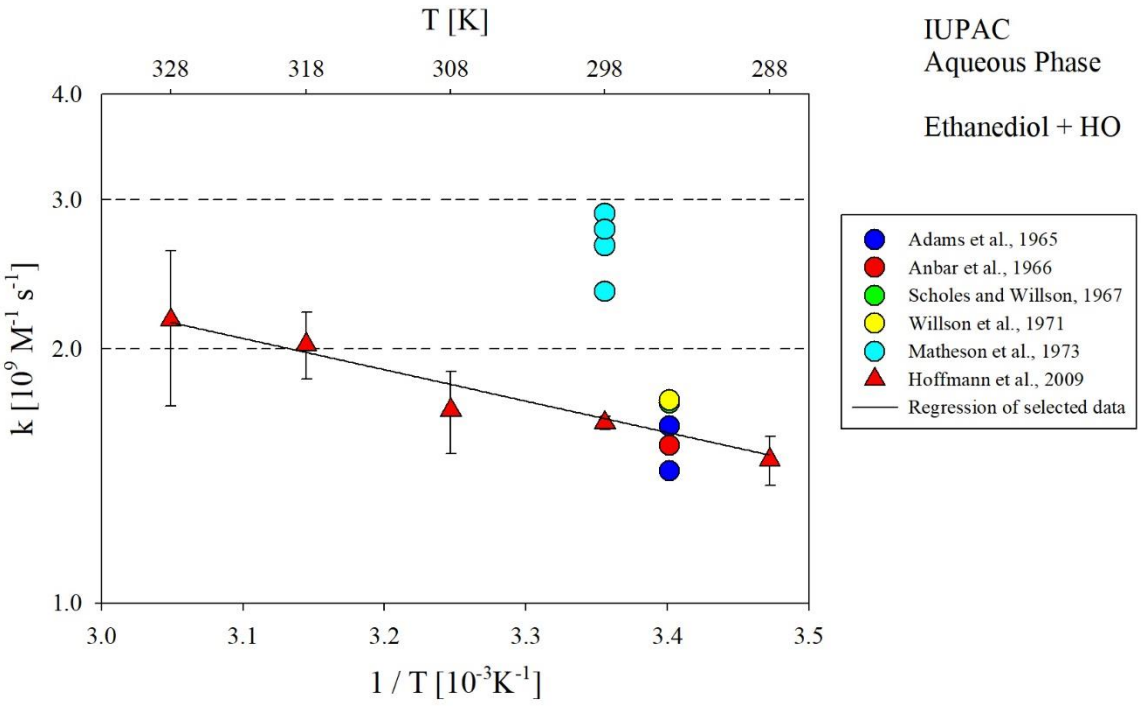
Matheson, M. S., Mamou, A., Silverman, J. and Rabani, J.: J. Phys. Chem., 77(20), 2420-2424, 1973.

Monod, A. and Doussin, J. F.: Atmos. Environ., 42, 7611- 7622, 2008.

Scholes, G. and Willson, R.L.: Trans. Faraday Soc., 63, 2983-2993, 1967.

Willson, R. L., Greenstock, C. L., Adams, G. E., Wageman, R. and Dorfman, L. M.: Int. J. Radiat. Phys. Chem., 3(3), 211-220, 1971.

Zhu, L., Nicovich, J. M. and Wine, P. H.: Aquat. Sci., 65(4), 425-435, 2003.



T-dependent rate coefficients for the reaction of ethanediol with HO radical in aqueous solution. The data of Matheson et al. (1973) is excluded from the evaluation.