IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_6

This datasheet last evaluated: May 2017; last change in preferred values: January 2016

OH (aq) + $CH_3CH_2CH(OH)CH_3$ (aq) → Products

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

Rate coefficient data

k/ l mol^{-1} s^{-1}	T/K	pH	I/ mol l^{-1}	*Reference*	Technique/ Comments
Absolute Rate Coefficients					
$3.5 \pm 0.4 \times 10^9$ $4.7 \pm 0.8 \times 10^9$ $6.3 \pm 0.5 \times 10^9$ $6.8 \pm 1.4 \times 10^9$ $6.3 \pm 1.2 \times 10^9$ $7.3 \pm 2.5 \times 10^9$ $5.4 \pm 3.0 \times 10^9$	298	5.8	0 0.5 (0.46) 1.0 (0.85) 1.5 (1.21) 2.0 (1.53) 2.5 (1.83) 3.0 (2.11)	Hesper, 2003, Herrmann, 2003	LP/LPA (a1)
7.4×10^{10} exp[-(910 ± 330)K/T]	288-328				(a2)
Relative Rate Coefficients					
1.86×10^9	-	7	-	Adams et al., 1965	PR/UV-vis abs. (b)
1.4×10^9	-	9	-	Anbar and Neta, 1966	CW-radiolysis /UV-vis abs. (c)
2.2×10^9	-	2	-	Scholes and Willson, 1967	CW-radiolysis /UV-vis abs. (d)
3.1×10^9	298	7		Buxton et al., 1988	Recalculated value (e)

Comments

(a) Radicals generated by laser photolysis, products analysed by UV-vis abs. (Long Path Absorption) (260 nm); direct observation of optical absorption of the peroxyl-radicals formed by the reaction between ·OH, 2-Butanol and O_2; oxygen saturated solutions (a1): determination of ion strength influence; $NaClO_4$ was used to adjust the ion strength ; the numbers given in parenthesis refer to the calculated effective ion strength; (a2): determination of the temperature influence from 288-328 K; the Arrhenius expression was calculated using these values. Reviewed by Herrmann (2003).

(b) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy (500 nm); Carbonate, thiocyanate or selenite were used as reference systems; here: thiocyanate reference: ·OH + SCN^-; k(·OH + SCN^-) = 6.6×10^9 $M^{-1}s^{-1}$; No exact value is given for the initial concentrations of the reactants ('a few millimolar') ; air or oxygen saturated solutions. NIST lists this value as 3.1×10^9 $M^{-1}s^{-1}$, referring to k(·OH + SCN^-) = 1.1×10^{10} $M^{-1}s^{-1}$.
http://kinetics.nist.gov/solution/Detail?id=1965ADA/BOA131-143B:10

(c) Radicals generated by CW-irradiation, products analysed by UV-vis-spectroscopy; Reference reaction: ·OH + PNDA (p-nitrosodimethylaniline); no values given for initial concentrations; no values given for the reference rate constants; air saturated solutions; all experiments were repeated at least four times and the coefficient of variation was less than ± 10%

(d) Radicals generated by CW-irradiation, products analysed by UV-vis-spectroscopy (264 nm); Reference reaction: ·OH + thymine; k(·OH + thymine) = $4.3 \pm 1 \times 10^9$ $M^{-1}s^{-1}$; c(thymine) = 8×10^{-5} - 2×10^{-4} mol/l ; The rate constant of the reference reaction was determined relative to benzene ; aerated solutions ; The absolute rate constants in table 3 have an error of about ± 25%

(e) Buxton et al. recalculated the rate constant, determined by Adams et al. (1965) as 3.1×10^9 $M^{-1}s^{-1}$, using the selected rate constant for the reference reaction k(·OH + SCN^-) = 1.1×10^{10} $M^{-1}s^{-1}$.

Preferred Values

Parameter	Value	*T*/K
k / l mol^{-1} s^{-1}	3.4×10^9	298
k / l mol^{-1} s^{-1}	9.86×10^{10} exp[-(1002) / T]	288 – 328
Reliability		
Δ log k	± 0.26	298
Δ E_A/R	± 180	

Comments on Preferred Values
The recommended value is a combination of the more recent determination by Hesper et al. (2003) and the older recommendation by Buxton et al. (1988). The error of the room temperature rate constant is estimated to be ± 10 %. The data by Hesper essentially confirm the older value by an independent measurement.

References

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.

Herrmann, H.: Chem. Rev., 103(12), 4691-4716, 2003.

Hesper, J.: Ph.D. Dissertation, University of Leipzig, Leipzig, Germany, 2003.

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

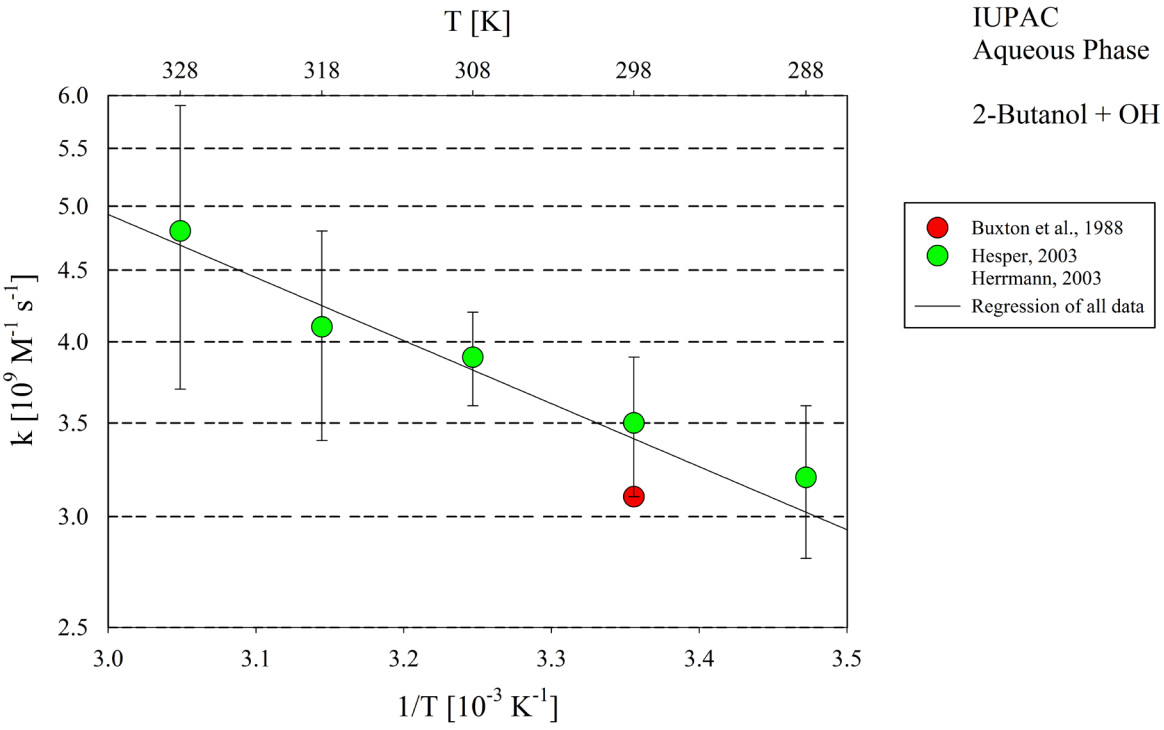

Figure 1: T-dependent rate constants for the reaction of 2-Butanol with OH radicals in aqueous solution. Data from Buxton et al. (1988) and Hesper (2003) and Herrmann (2003).