IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet AQ_OH_9

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OH(aq) + $CH_3(CH_2)_4OH$ (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
Relative Rate Coefficients					
2.8×10^9		9		Anbar et al., 1966	CW-radiolysis /UV-vis (a)
4.1×10^9 4.4×10^9		2 5		Scholes and Willson, 1967	CW-radiolysis /UV-vis (b)
3.5×10^9				Reuvers et al., 1973	PR/UV-vis (c1)
3.7×10^9					PR/UV-vis (c2)
3.9×10^9	298			Buxton et al., 1988	Average value (d1)
4.0×10^9	298				Recalculated value (d2)
$(5.0 \pm 0.2) \times 10^9$	298			Stemmler and von Gunten, 2000	CW-radiolysis /GC-FID (e)

Comments

(a) 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%.

(b) Radicals generated by cw-irradiation, products analysed by UV-vis-spectroscopy (264 nm); Reference reaction: ·OH + thymine; k(·OH + thymine) = $(4.3\pm1) \times 10^9$ 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 have an error of about ± 25%.

(c) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy; ferrocyanide (c1) and thiocyanate (c2) were used as reference systems; ferrocyanide

reference: $\cdot$OH + $[Fe(CN)_6]^{4-}$; $k(\cdot OH + [Fe(CN)_6]^{4-}) = 0.93 \times 10^{10}$ $M^{-1}s^{-1}$; thiocyanate reference: $\cdot$OH + SCN^-; $k(\cdot OH + SCN^-) = 1.1 \times 10^{10}$ $M^{-1}s^{-1}$. NIST lists the value for (c1) as 4.0×10^9 $M^{-1}s^{-1}$, referring to $k(\cdot OH + [Fe(CN)_6]^{4-}) = 1.0 \times 10^{10}$ $M^{-1}s^{-1}$.
http://kinetics.nist.gov/solution/Detail?id=1973REU/GRE533-536:11

(d) Buxton et al. calculated the average value of two rate constants determined by Reuvers et al. (1973)(d1) [3.7×10^9 $M^{-1}s^{-1}$ relative to $k(\cdot OH + SCN^-) = 1.1 \times 10^{10}$ $M^{-1}s^{-1}$ and 4.0×10^9 $M^{-1}s^{-1}$ relative to $k(\cdot OH + [Fe(CN)_6]^{4-}) = 1.05 \times 10^{10}$ $M^{--1}s^{-1}$]; the rate constant (d2) has been recalculated, using the selected value for reference reactions.

(e) Radicals generated by cw-irradiation, products analysed by GC-FID; Reference reaction: $\cdot$OH + n-butanol; $k(\cdot OH$ + n-butanol$) = 4.2 \times 10^9$ $M^{-1}s^{-1}$; the rate constant of the reference reaction was taken from Buxton et al. (1988).

Preferred Values

Parameter	Value	*T*/K
k /L mol^{-1} s^{-1}	4.5×10^9	298
Reliability		
$\Delta \log k$	± 0.06	298

Comments on Preferred Values

The one most recent re-determination indicates that the rate constant might be somewhat higher than the value recommended by Buxton et al. (1988). Hence, the average of this recent determination and the value by Buxton is recommended. The recommened value is in agreement with both Buxton et al. (1988) as well as Stemmler and von Gunten (2000) within its error limits.

References

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Reuvers, A. P., Greenstock, C. L., Borsa, J. and Chapman, J. D.: Int. J. Rad. Biol., 24(5), 533-536, 1973.

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

Stemmler, K. and von Gunten, U.: Atmos. Environ., 34(25), 4241-4252, 2000.