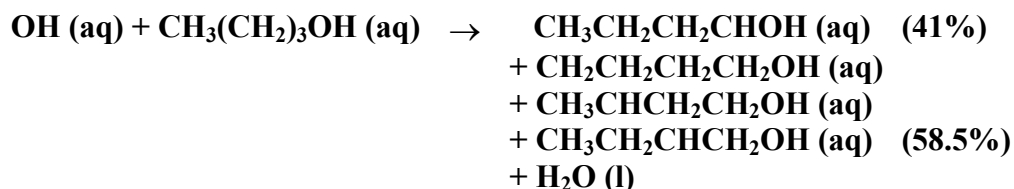


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_5

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



(Product distributions taken from Buxton et al., 1988, originally determined by Asmus et al., 1973 via PR - UV/Vis)

ΔG_R° (aq): Aqueous phase thermochemical data not available. As well, gas phase thermochemical data H_R° (g) are not available.

Rate coefficient data

$k / \text{l mol}^{-1} \text{s}^{-1}$	T / K	pH	$I / \text{mol l}^{-1}$	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>					
$(4.1 \pm 0.8) \times 10^9$	298	5.8		Hesper, 2003 Herrmann, 2003	LP/LPA (a1)
$1.0 \times 10^{11} \exp[-(1000 \pm 100)K/T]$	288 - 328				(a2)
<i>Relative Rate Coefficients</i>					
2.24×10^9		7		Adams et al. 1965	PR / UV-vis (b)
2.2×10^9		7		Adams et al., 1965	PR / UV-vis (c)
2.2×10^9		9		Anbar et al., 1966	CW-radiolysis / UV-vis (d)
3.7×10^9 3.7×10^9		2 5		Scholes and Willson, 1967	CW-radiolysis / UV-vis (e)
4.0×10^9		-	2×10^{-2}	Willson et al., 1971	CW-radiolysis / UV-vis (f)
$(4.7 \pm 0.4) \times 10^9$	291-298	6.9		Prütz and Vogel, 1976	CW-radiolysis / UV-vis (g)
4.2×10^9	298			Buxton et al., 1988	Recommended value (h1)
3.7×10^9	298				Recalculated value (h2)
4.3×10^9	298				Recalculated value (h3)

4.5×10^9	298				Recalculated value (h4)
$(4.2 \pm 0.4) \times 10^9$	298	1-2		Monod et al., 2005	ASC / GC-FID (i)

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 peroxy-radicals formed by the reaction between $\cdot\text{OH}$, 1-Butanol and O_2 ; oxygen saturated solutions (a1): determination of the temperature influence; the Arrhenius expression (a2) was calculated using these values
- (b) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy (500 nm); Carbonate, thiocyanate or selenite were used as reference systems; thiocyanate reference: $\cdot\text{OH} + \text{SCN}^-$; $k(\cdot\text{OH} + \text{SCN}^-) = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; No exact value is given for the initial concentrations of the reactants ('a few millimolar'); air or oxygen saturated solutions. [NIST](http://www.nist.gov) lists this value as $3.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, relative to $k(\cdot\text{OH} + \text{SCN}^-) = 1.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$.
<http://kinetics.nist.gov/solution/Detail?id=1965ADA/BOA131-143B:9>
- (c) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy (500 nm); reference system: $\cdot\text{OH} + \text{CO}_3^{2-}$ with $k(\cdot\text{OH} + \text{CO}_3^{2-}) = 2.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$; no values given for the initial concentrations of the reactants; oxygen saturated solutions. [NIST](http://www.nist.gov) lists this value as $4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, relative to $k(\cdot\text{OH} + \text{CO}_3^{2-}) = 3.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$.
<http://kinetics.nist.gov/solution/Detail?id=1965ADA/BOA1417-1424:6>
- (d) Radicals generated by CW-irradiation, products analysed by UV-vis-spectroscopy; Reference reaction: $\cdot\text{OH} + \text{PNDA}$ (p-nitrosodimethylaniline); no value given for the reference rate constant; no values given for the initial concentrations of the reactants; air saturated solutions; all experiments were repeated at least four times and the coefficient of variation was less than $\pm 10\%$
- (e) Radicals generated by CW-irradiation, products analysed by UV-vis-spectroscopy (264 nm); Reference reaction: $\cdot\text{OH} + \text{thymine}$; $k(\cdot\text{OH} + \text{thymine}) = 4.3 \pm 1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $c(\text{thymine}) = 8 \times 10^{-5} - 2 \times 10^{-4} \text{ mol/l}$; 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 $\pm 25\%$
Note: the reference values listed in table 1 were normalized to $k(\cdot\text{OH} + \text{ethanol}) = 1.85 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
- (f) Radicals generated by CW-irradiation, products analysed by UV-vis-spectroscopy (410 nm); Reference reaction: $\cdot\text{OH} + [\text{Fe}(\text{CN})_6]^{4-}$; $k(\cdot\text{OH} + [\text{Fe}(\text{CN})_6]^{4-}) = (0.93 \pm 0.05) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; $c([\text{Fe}(\text{CN})_6]^{4-}) = 2 \times 10^{-3} \text{ mol/l}$; The reference values listed in table 1 were recalculated using $k(\cdot\text{OH} + \text{ethanol}) = 1.85 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; in most reactions air was present or the solutions were saturated with N_2O . [NIST](http://www.nist.gov) lists the value as $4.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, referring to $k(\cdot\text{OH} + [\text{Fe}(\text{CN})_6]^{4-}) = 1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$.
<http://kinetics.nist.gov/solution/Detail?id=1971WIL/GRE211-220:11>
- (g) Radicals generated by CW-irradiation, products analysed by fluorescence measurements using Acriflavin as RCL(Radiation Induced Chemiluminescence)-dye; The absolute rate constants were obtained by comparing the slopes of the emission yields plotted against

the concentrations of the different scavengers and using $k(\cdot\text{OH} + \text{methanol}) = 8.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ as reference.

- (h) Buxton et al. list the average value of three rate constants (h1), determined by the original authors that were recalculated, using the selected rate constants for reference reactions; Adams et al. (1965) ($3.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, relative to $k(\cdot\text{OH} + \text{SCN}^-) = 1.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ (h2)); $4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, relative to $k(\cdot\text{OH} + \text{CO}_3^{2-}) = 3.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (h3)) and Willson et al. (1971) ($4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, relative to $k(\cdot\text{OH} + [\text{Fe}(\text{CN})_6]^{4-}) = 1.05 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ (h4)).
- (i) Radicals generated by Photo-Fenton-reaction in a bulk reactor (an 'aqueous phase smog chamber' or 'ASC'), products analysed by GC-FID; Reference reaction: $\cdot\text{OH} + 1$ -propanol; $k(\cdot\text{OH} + 1\text{-propanol}) = 2.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $\cdot\text{OH} + 2$ -propanol; $k(\cdot\text{OH} + 2\text{-propanol}) = 1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$

Preferred Values

Parameter	Value	T/K
$k / \text{l mol}^{-1} \text{ s}^{-1}$	4.15×10^9	298
$k / \text{l mol}^{-1} \text{ s}^{-1}$	$9.43 \times 10^{10} \exp[-(930)/T]$	288 - 328
<i>Reliability</i>		
$\Delta \log k$	± 0.02	298
$\Delta E_A/R$	± 10	288 - 328

Comments on Preferred Values

T-dependent data from Hesper (2003) and Monod et al. (2005) have been used for regression together with the value of $k = 4.2 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ recommended by Buxton et al. (1988) to obtain the overall recommended T-dependent data. Accordingly, at room temperature, the average value between Hesper (2003) and Monod et al. (2003) and Buxton et al. (1988) is recommended.

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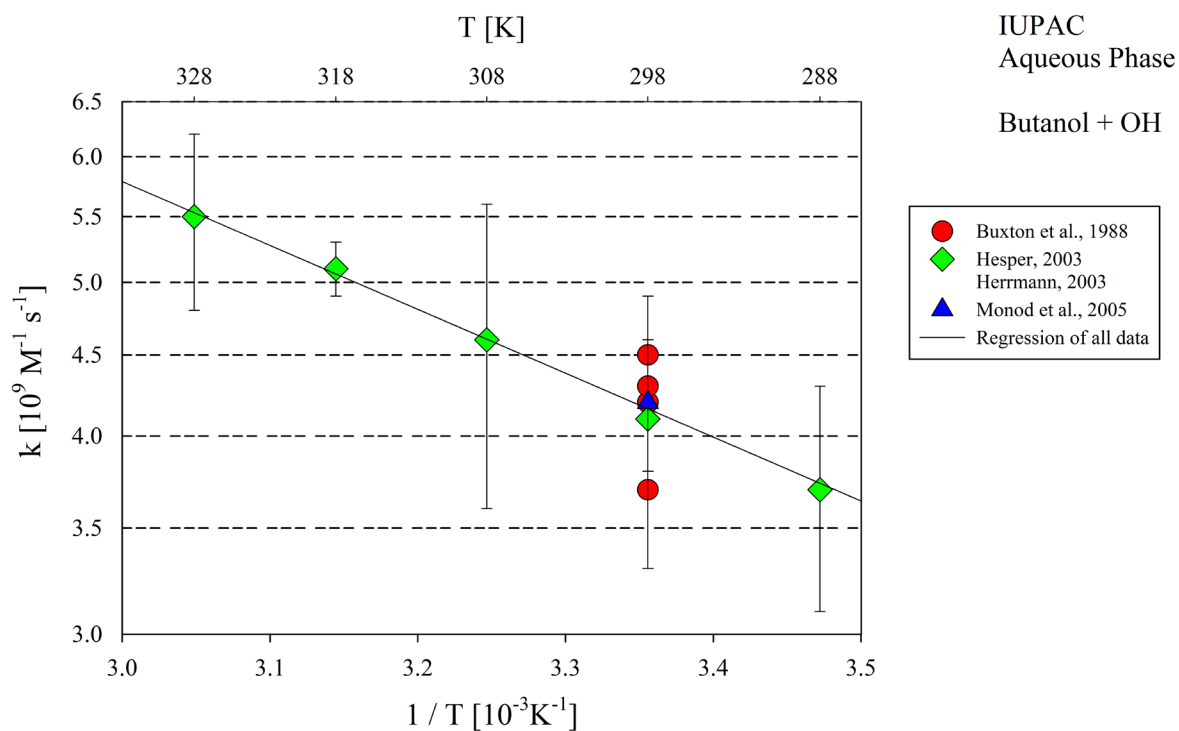


Figure 1: T-dependent rate constants for the reaction of 1-Butanol with OH in aqueous solution. Data from Buxton et al. (1988), Hesper (2003) and Herrmann (2003) and Monod et al. (2005).