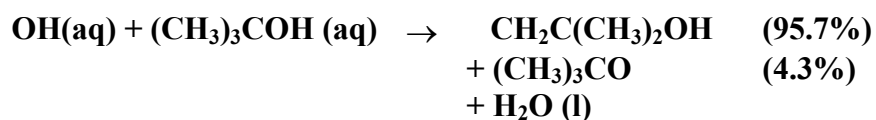


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_8

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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>					
7.55×10^8	-	7	No ionic additives	Gordon et al., 1977	PR/UV-vis abs. (a)
6.2×10^8	-	nat. (slightly < pH 7)		Janata, 2002	PR/UV-vis abs. (b)
6.2×10^8	-	nat. (slightly < pH 7)		Alam et al., 2003	PR/UV-vis abs. (c)
<i>Relative Rate Coefficients</i>					
2.5×10^8	-	7	-	Adams et al., 1965	PR/UV-vis abs. (d)
$(4.2 \pm 0.4) \times 10^8$	-	2.0 - 2.2	-	Scholes et al., 1965	CW-radiolysis /UV-vis abs. (e)
2.8×10^8	-	9	-	Anbar et al., 1966	CW-radiolysis /UV-vis abs. (f)
5.8×10^8	-	2	-	Scholes and Willson, 1967	CW-radiolysis /UV-vis abs. (g)
5.2×10^8	-	-	-	Willson et al., 1971	CW-radiolysis /UV-vis abs. (h)
$(5.4 \pm 0.4) \times 10^8$	291-298	6.9	-	Prütz and Vogel, 1976	CW-radiolysis/fluorescence detection (i1)
$(6.1 \pm 1.1) \times 10^8$	291-298	7	-		(i2)

$(6.0 \pm 0.4) \times 10^8$	-	6	0.3×10^{-3}	Wolfenden and Willson, 1982	PR/UV-vis abs. (j)
6.3×10^8	292	-	$2-10 \times 10^{-3}$	Elliot and Simons, 1984	PR/UV-vis abs. (k1)
$3.6 \times 10^{10} \exp[(-1160 \pm 120) / T]$	292 - 352				(k2)
6.0×10^8	298	-	-	Buxton et al., 1988	Selected value (l1)
4.2×10^8	298	7			Recalculated value (l2)
5.9×10^8	298	Nat.			Recalculated value (l3)
6.6×10^8	298				Recalculated value (l4)
4.8×10^8	293-298	7.5	-	Motohashi and Saito, 1993	CW-irradiation /HPLC (m)
$(5.0 \pm 0.6) \times 10^8$	298	-	2×10^{-5}	Ervens et al., 2003	LP-LPA (n)
$3.3 \times 10^{10} \exp[(-1200 \pm 360) / T]$	283 - 328				
$(7 \pm 2) \times 10^8$	298	1-2	-	Monod et al., 2005	ASC/ GC-FID (o)

Comments

- (a) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy; direct observation of OH decay (280 nm); $c(\text{t-BuOH}) = 0.5\text{-}2 \text{ M}$; the absolute rate constant has an error of $\pm 10\%$.
- (b) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy; direct observation of optical absorption of the alcohol radicals (260-290 nm); computer simulations were used to derive the rate constants; the simulations were accurate to 5%; N_2O saturated solutions
- (c) Essentially the same article as (b)
- (d) 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: $\cdot\text{OH} + \text{SCN}^-$; $k(\cdot\text{OH} + \text{SCN}^-) = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; No exact value is given for the initial concentrations of the reactants ('a few millimolar'); air or oxygen saturated solutions. NIST lists this value as $4.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, referring 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:39>
- (e) Radicals generated by cw-irradiation, products analysed by UV-vis-spectroscopy (264 nm); Reference reaction: $\cdot\text{OH} + \text{thymine}$; $k(\cdot\text{OH} + \text{thymine}) = 3.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; the reactions were carried out with thymine concentrations between $8\text{-}20 \times 10^{-5} \text{ mol/l}$; air or oxygen saturated solutions
- (f) Radicals generated by cw-irradiation, products analysed by UV-vis-spectroscopy; Reference reaction: $\cdot\text{OH} + \text{PNDA}$ (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 $\pm 10\%$

- (g) 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 $\pm 25\%$
- (h) Radicals generated by CW-irradiation, products analysed by UV-vis-spectroscopy (410 nm); Reference reaction: $\text{OH} + [\text{Fe}(\text{CN})_6]^{4-}$; $k(\cdot\text{OH} + [\text{Fe}(\text{CN})_6]^{4-}) = 0.93 \pm 0.05 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; $c([\text{Fe}(\text{CN})_6]^{4-}) = 2 \times 10^{-3} \text{ mol/l}$; 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 lists this value as $5.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, 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/GRE211-220:17>
- (i) Radicals generated by CW-irradiation, products analysed by fluorescence measurements using Acriflavin ((i1) and (i2)) as RCL(Radiation Induced Chemiluminescence)-dye; (i1): buffered solution; (i2): unbuffered neutral solution; The absolute rate constants were obtained by comparing the slopes of the emission yields plotted against the concentrations of the different scavengers and using $k(\text{OH} + \text{methanol}) = 8.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ as reference
- (j) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy (415 nm); Reference reaction: $\cdot\text{OH} + \text{ABTS}$ (2,2'-Azinobis(3-ethylbenzthiazoline-6-sulphonate)); $k(\cdot\text{OH} + \text{ABTS}) = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, $c(\text{ABTS}) = 1 \times 10^{-4} \text{ mol/l}$; N_2 and N_2O saturated solutions
- (k) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy (420 nm); Reference reaction: $\cdot\text{OH} + \text{SCN}^-$; Rate constants for reference reactions calculated from table 1: $k_{292\text{K}}(\cdot\text{OH} + \text{SCN}^-) = 10.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $k_{312\text{K}}(\cdot\text{OH} + \text{SCN}^-) = 14.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $k_{332\text{K}}(\cdot\text{OH} + \text{SCN}^-) = 19.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $k_{352\text{K}}(\cdot\text{OH} + \text{SCN}^-) = 24.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $c(\text{KSCN})$ in the range of $2-10 \times 10^{-3} \text{ mol/l}$; N_2O saturated solutions. Arrhenius expression (k2) calculated using data from table 1, considering 10% error of activation energy.
- (l) Buxton et al. recommends a value of $6.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, which is also given as the selected rate constant for reference reactions; rate constants from original authors have been recalculated, using the selected rate constants for reference reactions; (l2): $4.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, relative to $k(\cdot\text{OH} + \text{SCN}^-) = 1.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ (Adams et al., 1965), (l3): $5.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, relative to $k(\cdot\text{OH} + [\text{Fe}(\text{CN})_6]^{4-}) = 1.05 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ (Willson et al., 1971), (l4): $6.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, relative to $k(\cdot\text{OH} + [\text{Fe}(\text{CN})_6]^{4-}) = 1.05 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ (Elliot et al., 1984).
- (m) Radicals generated by cw-irradiation, products analysed by HPLC (abs. 240-300 nm) and fluorescence measurements (irradiation at 305 nm); Reference reaction: $\cdot\text{OH} + \text{benzoate}$; $k(\cdot\text{OH} + \text{benzoate}) = 5.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $c(\text{benzoate}) = 2 \times 10^{-4} \text{ mol/l}$; deviations of less than $\pm 5\%$ for the determined rate constants; N_2O saturated solutions
- (n) Radicals generated by laser photolysis, products analysed by UV-vis abs. (long path absorption); reference reaction: $\cdot\text{OH} + \text{SCN}^-$; $c(\text{thiocyanate}) = 2 \times 10^{-5} \text{ mol/l}$, reference

reaction rate constant given by: $k(T) = 7.26 \times 10^{12} \exp((-1900 \pm 190) / T) \text{ M}^{-1}\text{s}^{-1}$ by Chin and Wine (1992)

- (o) Radicals generated by Photo-Fenton-reaction in a bulk reactor (an 'aqueous phase smog chamber' or 'ASC'), products analysed by GC-FID; Reference reaction: $\cdot\text{OH} + 2\text{-propanol}$; $k(\cdot\text{OH} + 2\text{-propanol}) = 1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$

Preferred Values

Parameter	Value	T/K
$k / \text{L mol}^{-1} \text{ s}^{-1}$	6.0×10^8	298
$k / \text{L mol}^{-1} \text{ s}^{-1}$	$8.71 \times 10^{10} \exp[-(1475)/T]$	288 - 352
<i>Reliability</i>		
$\Delta \log k$	± 0.145	298
$\Delta E_A/R$	± 100	288 - 352

Comments on Preferred Values

Data from Elliot et al. (1984), Buxton et al. (1988), Ervens et al. (2003) and Monod et al. (2005) have been used for regression and to obtain the average recommended room temperature rate coefficient.

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.
- Alam, M. S., Rao, B. S. M., and Janata, E.: *Radiat. Phys. Chem.*, 67(6), 723-728, 2003.
- Anbar, M., Meyerstein, D., and Neta, P.: *J. Chem. Soc. B*, 742-747, 1966.
- Asmus, K. D., Möckel, H. and Henglein, A.: *J. Phys. Chem.*, 77(10), 1218-1221, 1973.
- Buxton, G. V., Greenstock, C. L., Helman, W. P., and Ross, A. B.: *J. Phys. Chem Ref. Data*, 17(2), 513-886, 1988.
- Chin, M., and Wine, P. H: *J. Photochem. Photobiol., A*, 69(1), 17-25, 1992.
- Elliot, A. J. and Simons, A. S.: *Radiat. Phys. Chem.*, 24(2), 229-231, 1984.
- Ervens, B., Gligorovski, S., and Herrmann, H.: *Phys. Chem. Chem. Phys.*, 5(9), 1811-1824, 2003.
- Gordon, S., Schmidt, K. H., and Hart, E. J.: *J. Phys. Chem.*, 81(2), 104-109, 1977.
- Janata, E.: *J. Chem. Sci.*, 114(6), 731-737, 2002.
- Monod, A., Poulain, L., Grubert, S., Voisin, D., and Wortham, H.: *Atmos. Environ.*, 39(40), 7667-7688, 2005.

Motohashi, N., and Saito, Y.: Chem. Pharm Bull., 41(10), 1842-1845, 1993.

Pruetz, W. A. and Vogel, S.: Z. Naturforsch., B: Chem. Sci., 31(11), 1501-1510, 1976.

Scholes, G., Shaw, P., and Willson, R.L.: Pulse Radiolysis, academic press, 61, 1965

Scholes, G., and Willson, R. L.: Trans. Far. 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.

Wolfenden, B. S., and Willson, R. L.: J. Chem. Soc. Perkin Trans. II, 7, 805-812, 1982.

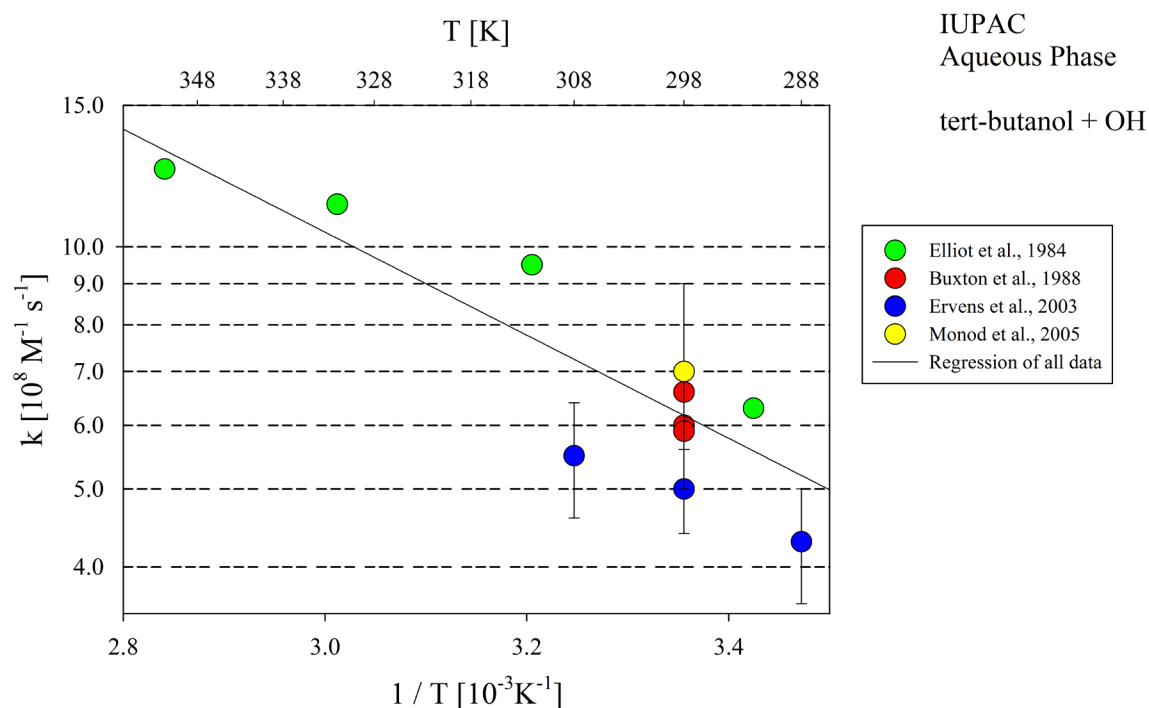


Figure 1: T-dependent rate constants for the reaction of 2-Methyl-2-propanol with OH in aqueous solution. Data from Elliot and Simsons. (1984), Buxton et al. (1988), Ervens et al. (2003) and Monod et al. (2005).