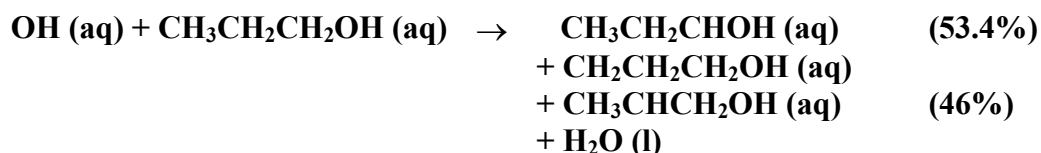


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_3

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This datasheet last evaluated: May 2017; last change in preferred values: May 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 (cf. gas phase data sheet HOx_VOC25)

Rate coefficient data

$k / \text{l mol}^{-1} \text{s}^{-1}$	T/K	$p\text{H}$	$I / \text{mol l}^{-1}$	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>					
14.7×10^8	-	7	-	Adams et al. 1965	PR/UV-vis abs. (a1)
14.8×10^8	-	10.7	-	Adams et al. 1965	PR/UV-vis abs. (a2)
1.5×10^9	-	7	-	Adams et al., 1965	PR/UV-vis abs. (b1)
1.5×10^9	-	10.7	-	Adams et al., 1965	PR/UV-vis abs. (b2)
16.5×10^8	-	9	-	Anbar et al., 1966	CW-radiolysis / UV-vis abs. (c)
2.6×10^9 2.4×10^9	-	2 5	-	Scholes and Willson, 1967	CW-radiolysis /UV-vis abs. (d)
2.7×10^9	-	-	-	Willson et al., 1971	PR/UV-vis abs. (e)
2.8×10^9	298	-	-	Buxton et al., 1988	Average value (f)
$3.2 \pm 0.2 \times 10^9$	298	6	2×10^{-5}	Ervens et al., 2003	LP-LPA (g)
$5.6 \times 10^{10} \exp[(-1000 \pm 700) / T]$ $\text{M}^{-1}\text{s}^{-1}$	288 - 328				
$2.7 \pm 0.7 \times 10^9$	298	1-2	-	Monod et al.,	ASC/

4.36×10^{10} exp [- (780 ± 200)/T]	276 - 339			2005	GC-FID (h)
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Comments

- (a) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy; Carbonate, thiocyanate or selenite were used as reference systems; (a1): 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') (a2): carbonate reference: $\cdot\text{OH} + \text{CO}_3^{2-}$; no value given for the reference rate constant. NIST lists these values as (a1) $2.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ referring to $k(\cdot\text{OH} + \text{SCN}^-) = 1.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ and (a2) $2.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ referring 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/BOA1417-1424:14>
<http://kinetics.nist.gov/solution/Detail?id=1965ADA/BOA1417-1424:13>
- (b) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy; Carbonate, thiocyanate or selenite were used as reference systems; (b1) thiocyanate reference; (b2) carbonate reference
 $k(\cdot\text{OH} + \text{CO}_3^{2-}) = 2.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$;
 $k(\cdot\text{OH} + \text{SCN}^-) = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$;
 $k(\cdot\text{OH} + \text{selenite}) = 2.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
no values given for the initial concentrations of the reactants
- (c) 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
- (d) Radicals generated by CW-irradiation, products analysed by UV-vis-spectroscopy; Reference reaction: $\cdot\text{OH} + \text{thymine}$; $k(\cdot\text{OH} + \text{thymine}) = 4.3 \pm 1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; The rate constant of the reference reaction was determined relative to benzene. The absolute rate constants in table 3 have an error of about $\pm 25\%$
Note: the literature values given for the absolute rate constants in table 3 were normalized to $k(\cdot\text{OH} + \text{ethanol}) = 1.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
- (e) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy; Reference reaction: $\cdot\text{OH} + [\text{Fe}(\text{CN})_6]^{4-}$; $k(\cdot\text{OH} + [\text{Fe}(\text{CN})_6]^{4-}) = 0.93 \pm 0.05 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; $c([\text{Fe}(\text{CN})_6]^{4-}) = 2 \times 10^{-3} \text{ mol/L}$ (no information on counterions);
Note: the reference values listed in table 1 were normalized to $k(\cdot\text{OH} + \text{ethanol}) = 1.85 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
NIST lists this value as $3.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ 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/GRE211-220:20>
- (f) Buxton et al. list that rate constant as selected value, being the average value of three recalculated rate constants originally determined by Adams et al. (1965) [$2.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ relative to $k(\cdot\text{OH} + \text{CO}_3^{2-}) = 3.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ and $2.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ relative to $k(\cdot\text{OH} + \text{SCN}^-) = 1.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$] and Willson et al. (1971) [$3.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ relative to $k(\cdot\text{OH} + [\text{Fe}(\text{CN})_6]^{4-})$ with no specific rate constant given for the reference reaction].

- (g) Radicals generated by laser photolysis, products analysed by UV-vis abs. (long path absorption); reference reaction: $\cdot\text{OH} + \text{SCN}^-$; 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)
- (h) Radicals generated by Fenton-reaction in a bulk reactor (an 'aqueous phase smog chamber' or 'ASC'), products analysed by GC-FID; Reference reaction: $\cdot\text{OH} + 2\text{-propanol}$; $k(\cdot\text{OH} + 2\text{-propanol}) = 1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; For the Fenton-reaction, the initial concentrations of reactants were in the order of $10 \times 10^{-3} \text{ M}$; Arrhenius expression for $\cdot\text{OH} + 1\text{-propanol}$ was given as: $\ln(k(T)) = 24.5 (\pm 0.6) - 780(\pm 200)/T$

Preferred Values

Parameter	Value	T/K
$k / \text{l mol}^{-1} \text{ s}^{-1}$	3.35×10^9	298
$k / \text{l mol}^{-1} \text{ s}^{-1}$	$k(T) = 4.2 \times 10^{10} \exp[-(760) / T]$	293-353
<i>Reliability</i>		
$\Delta \log k$	± 0.10	298
$\Delta E_A/R$	± 200	

Comments on Preferred Values

Buxton et al. (1988) recommended $2.8 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in 1988. Work since then in one study (Ervens et al., 2003) indicated a slightly higher rate constant while another study (Monod et al., 2005) essentially confirms the former recommended value. For the first time after 1988 two-T-dependences became available. As can be seen, there is considerable scatter in both T-dependent measurements and the linear regression of all data points indicates that the rate constant at $T = 298 \text{ K}$ should be somewhat higher compared to the value recommended by Buxton et al. in 1988. Overall, it is suggested to use the combined result of both the recent T-dependent studies as the preferred value for this reaction.

With this, the most recent determinations are well represented in a unified way. The overall analysis shows that the rate constant at room temperature is somewhat higher than previously recommended.

References

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

Ervens, B., Gligorovski, S., and Herrmann, H.: Phys. Chem. Chem. Phys., 5(9), 1811-1824, 2003.

Monod, A., Poulain, L., Grubert, S., Voisin, D., and Wortham, H.: Atmos. Environ., 39(40), 7667-7688, 2005.

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.

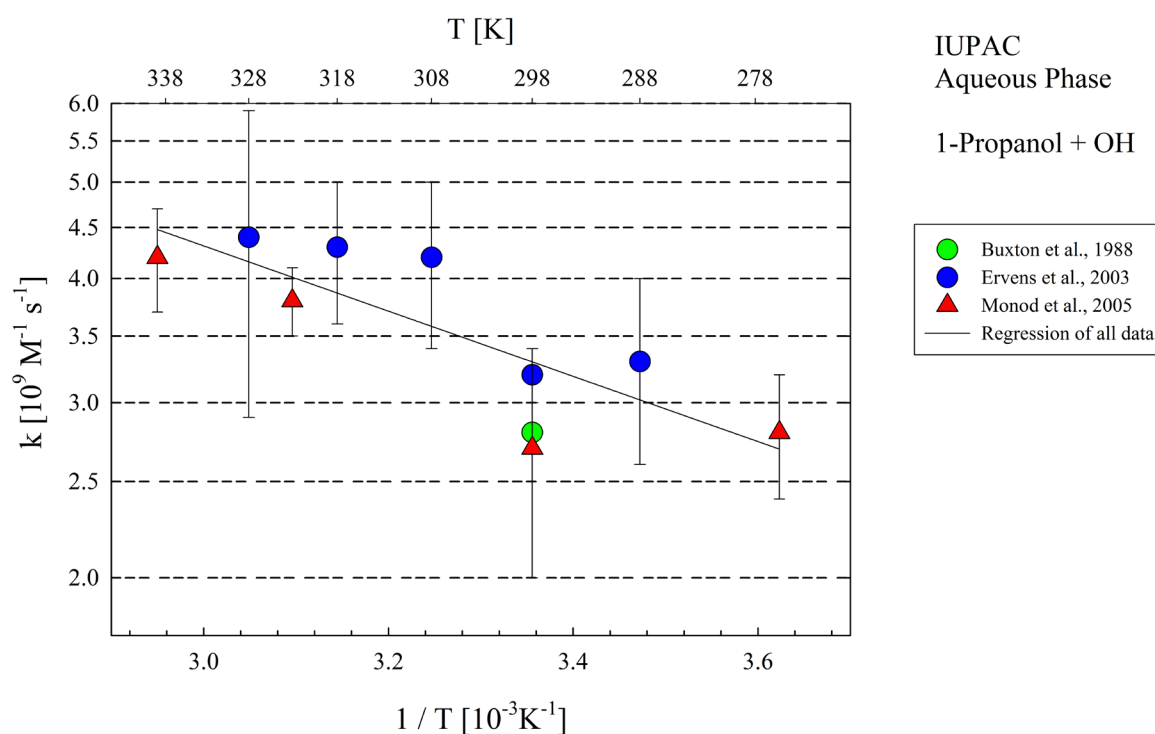


Figure 1: T-dependent rate constants for the reaction of 1-Propanol with OH in aqueous solution. Data from Buxton et al. (1988), Ervens et al. (2003) and Monod et al. (2005).