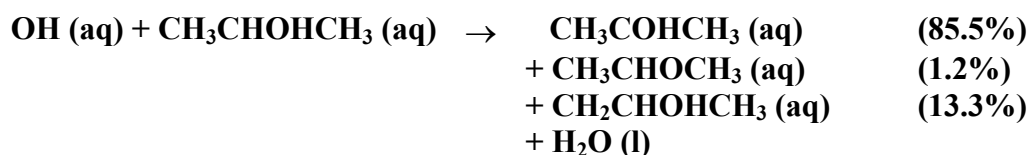


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

### – Data Sheet AQ\_OH\_4

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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)

$\Delta G_R^\circ$  (aq): Aqueous phase thermochemical data not available

For comparison:  $\Delta H_R^\circ$  (g) = -58.8 kJ·mol<sup>-1</sup> (gas phase data sheet HOx\_VOC26)

### Rate coefficient data

$k / \text{l mol}^{-1} \text{ s}^{-1}$	$T / \text{K}$	$pH$	$I / \text{mol l}^{-1}$	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>					
$2.0 \times 10^9$	-	nat. (slightly < pH 7)	No ionic additives	Janata, 2002	PR/UV-vis abs. (a)
$2.0 \times 10^9$	-	nat. (slightly < pH 7)	No ionic additives	Alam et al., 2003	PR/UV-vis abs. (b)
$(2.1 \pm 0.2) \times 10^9$ $(2.8 \pm 0.7) \times 10^9$ $(3.6 \pm 0.4) \times 10^9$ $(4.1 \pm 0.4) \times 10^9$ $(4.6 \pm 0.6) \times 10^9$ $(4.2 \pm 1.4) \times 10^9$ $(4.6 \pm 3.3) \times 10^9$	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	LP/LPA (c1)
$6.1 \times 10^{10} \exp[-(1000 \pm 300)K/T]$	288-328				(c2)
<i>Relative Rate Coefficients</i>					
only relative rate constant	295-298	9	-	Kraljic et al., 1965	CW-radiolysis /UV-vis abs. (d)
$3.9 \times 10^9$	-	7	-	Adams et al., 1965	PR/UV-vis abs. (e)
$1.6 \times 10^9$	-	-	1.0	Heckel et al., 1965	PR/UV-vis abs. (f)
$(1.2 \pm 0.1) \times 10^9$	-	2.0-2.2	-	Scholes et al., 1965	CW-radiolysis /UV-vis abs. (g)
$1.74 \times 10^9$	-	7	-	Thomas,	PR/UV-vis

				1965	abs. (h)
only relative rate constant	293	7	-	Woodward et al., 1966	CW-radiolysis (i)
$1.3 \times 10^9$	-	6	-	Anbar et al., 1966	CW-radiolysis /UV-vis abs. (j <sub>1</sub> )
$1.2 \times 10^9$	-	9	-	Anbar et al., 1966	CW-radiolysis /UV-vis abs. (j <sub>2</sub> )
$1.8 \times 10^9$ $1.8 \times 10^9$	-	2 5	-	Scholes and Willson, 1967	CW-radiolysis /UV-vis abs. (k)
$1.25 \times 10^9$	-	-	-	Greenstock et al., 1968	PR/UV-vis abs. (l)
$1.5 \times 10^9$	294	7	No ionic additives	Baxendale et al., 1969	PR/UV-vis abs. (m)
$2.01 \times 10^9$	-	-	-	Willson et al., 1971	CW-radiolysis /UV-vis abs.(n)
$(1.92 \pm 0.13) \times 10^9$	291-298	6.9	-	Prütz et al., 1976	CW-radiolysis/fluorescence detection (o1)
$(2.4 \pm 0.3) \times 10^9$	291-298	7	-	Prütz et al., 1976	CW-radiolysis/fluorescence detection (o2)
$1.7 \times 10^9$	291-298	10.4	-	Prütz et al., 1976	CW-radiolysis/fluorescence detection (o3)
$(1.9 \pm 0.1) \times 10^9$	-	6	$0.3 \times 10^{-3}$	Wolfenden and Willson, 1982	PR/UV-vis abs. (p)
$2.3 \times 10^9$	292	-	$2 \cdot 10 \times 10^{-3}$	Elliot and Simsons, 1984	PR/UV-vis abs. (q1)
$1.79 \times 10^{10} \exp[-(5000 \pm 500)/R(1/T)]$	292 - 352				(q2)
$1.9 \times 10^9$	298	-	-	Buxton et al., 1988	Recommended value (r)
$1.6 \times 10^9$		7.5	-	Motohashi and Saito, 1993	CW-irradiation /HPLC (s)
$(1.9 \pm 0.2) \times 10^9$	298	1-2	-	Monod et al., 2005	ASC/ GC-FID (t1)
$1.6 \times 10^9 \exp[-5000/R(1/T - 1/298K)]$	292 - 352				(t2)

### Comments

- (a) 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<sub>2</sub>O saturated solutions

- (b) Essentially the same article as (a)
- (c) Radicals generated by laser photolysis, products analysed by UV-vis abs. (Long Path Absorption) (248 nm); direct observation of optical absorption of the peroxy-radicals formed by the reaction between ·OH, 2-propanol and O<sub>2</sub>; oxygen saturated solutions (c1): determination of ion strength influence; NaClO<sub>4</sub> was used to adjust the ion strength ; the numbers given in parenthesis refer to the calculated effective ion strength; (c2): determination of the temperature influence from 288-328 K; the Arrhenius expression was calculated using these values
- (d) Radicals generated by cw-irradiation, products analysed by UV-vis-spectroscopy (440 nm); Reference reaction: ·OH + PNDA (p-nitrosodimethylaniline); the absolute rate constant of the reference reaction was not determined but only roughly estimated to be in the range of  $1 \times 10^{10}$ ; the relative rate constant was determined to be 17.0 (relative to  $k(\cdot\text{OH} + \text{PNDA} = 100)$ ) ; the relative rate constant has an error of about  $\pm 5\%$
- (e) 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<sup>-</sup>;  $k(\cdot\text{OH} + \text{SCN}^-) = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ; No exact value is given for the initial concentrations of the reactants ('a few millimolar'); air or oxygen saturated solutions
- (f) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy (450 nm); Reference reaction: ·OH + HSO<sub>4</sub><sup>-</sup>;  $k(\cdot\text{OH} + \text{HSO}_4^-) = 8.0 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$  was taken from Adams et al. (1965) ; the absolute rate constant for the reaction ·OH + *i*-propanol was calculated from the relative value ( $k = 3.6$ ) listed in Table 1, which was normalized to the methanol reaction ( $k(\cdot\text{OH} + \text{methanol}) = 4.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ )
- (g) Radicals generated by cw-irradiation, products analysed by UV-vis-spectroscopy (264 nm); Reference reaction: ·OH + thymine;  $k(\cdot\text{OH} + \text{thymine}) = 3.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ; the reactions were studied with thymine concentrations between  $8 - 20 \times 10^{-5} \text{ mol/l}$  ; air or oxygen saturated solutions
- (h) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy (400 nm); Reference reaction: ·OH + I<sup>-</sup>;  $k(\cdot\text{OH} + \text{I}^-) = 1.02 \pm 0.13 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ ; no values given for concentrations. NIST lists the value as  $1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ , referring to  $k(\cdot\text{OH} + \text{I}^-) = 1.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ .  
<http://kinetics.nist.gov/solution/Detail?id=1965THO702-707:13>
- (i) Radicals generated by cw-irradiation, yields of products were determined by UV-vis abs., chromatography and other methods not described in the article; Reference reaction: ·OH + NO;  $k(\cdot\text{OH} + \text{NO}) = 6.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  ; the relative rate constant was determined to be 1.0 (relative to  $k(\cdot\text{OH} + \text{ethanol} = 1.0)$ )
- (j) Radicals generated by cw-irradiation, products analysed by UV-vis-spectroscopy; (j<sub>1</sub>): Reference reaction: ·OH + Br<sup>-</sup> ; (j<sub>2</sub>): 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  $\pm 10\%$

- (k) 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  $\pm 25\%$
- (l) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy (500 nm); Reference reaction:  $\cdot\text{OH} + \text{SCN}^-$ ;  $k(\cdot\text{OH} + \text{SCN}^-) = 7.5 \pm 0.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ;  $c(\text{KSCN}) = 2 \times 10^{-3} \text{ mol/l}$  (ionic strength might differ, as the pH is not given); aerated solutions. NIST lists the value as  $1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ , referring to  $k(\cdot\text{OH} + \text{SCN}^-) = 1.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ .  
<http://kinetics.nist.gov/solution/Detail?id=1968GRE/NG397-417:1>
- (m) Radicals generated by pulse-radiolysis, products analysed by UV-vis-spectroscopy (440 nm); Reference reaction:  $\cdot\text{OH} + \text{PNDA}$  (p-nitrosodimethylaniline);  $k(\cdot\text{OH} + \text{PNDA}) = 1.25 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ ; no values given for concentrations; aerated solutions
- (n) 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 rate constants listed in table 1 were re-calculated 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  $\text{N}_2\text{O}$ . NIST lists the value as  $2.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ , 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/GRE211-220:21>
- (o) Radicals generated by cw-irradiation, products analysed by fluorescence measurements using acriflavin ((o1) and (o2)) and Fluorescein ((o3)) 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
- (p) 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));  $k(\cdot\text{OH} + \text{ABTS}) = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ ,  $c(\text{ABTS}) = 1 \times 10^{-4} \text{ mol/l}$ ;  $\text{N}_2$  and  $\text{N}_2\text{O}$  saturated solutions
- (q) 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:  $k_{292\text{K}}(\cdot\text{OH} + \text{SCN}^-) = 11.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ;  $k_{312\text{K}}(\cdot\text{OH} + \text{SCN}^-) = 14.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ;  $k_{332\text{K}}(\cdot\text{OH} + \text{SCN}^-) = 20.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ;  $k_{352\text{K}}(\cdot\text{OH} + \text{SCN}^-) = 22.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ;  $c(\text{KSCN})$  in the range of  $2-10 \times 10^{-3} \text{ mol/l}$ ;  $\text{N}_2\text{O}$  saturated solutions. Arrhenius expression (q2) calculated using data from table 1, considering 10% error of activation energy.
- (r) Buxton et al. chose the value of  $1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  as selected value, considering the recalculated values originally determined by Thomas (1965), Scholes and Willson (1967), Greenstock et al. (1968), Willson et al. (1971), Wolffenden and Willson

(1982) and Elliot et al. (1984); for recalculation of rate constants, Buxton et al. used their selected rate constants for the reference reactions.

- (s) 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;  $\text{N}_2\text{O}$  saturated solutions
- (t) (t1): Radicals generated by Photo-Fenton-reaction in a bulk reactor (an 'aqueous phase smog chamber' or 'ASC'), products analysed by GC-FID; Reference reaction:  $\cdot\text{OH} + 1\text{-propanol}$ ;  $k(\cdot\text{OH} + 1\text{-propanol}) = 2.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$   
 (t2): Arrhenius expression for  $\cdot\text{OH} + 2\text{-propanol}$ , given as :  $k(T) = 1.6 \times 10^9 \exp(-5000/R(1/T-1/298\text{K}))$ , was calculated using values determined by Elliot et al. (1984)

### Preferred Values

Parameter	Value	T/K
$k / \text{l mol}^{-1} \text{ s}^{-1}$	$2.06 \times 10^9$	298
$k / \text{l mol}^{-1} \text{ s}^{-1}$	$8.98 \times 10^{10} \exp[-(1130) / T]$	288 - 352

#### Reliability

$\Delta \log k$	$\pm 0.091$
$\Delta E_A/R$	$\pm 130$

#### Comments on Preferred Values

Data of Buxton et al. (1988), Hesper (2003) and Monod et al. (2005) have been used for regression to obtain the recommended Arrhenius expression. The error of the recommended room temperature rate constant is estimated.

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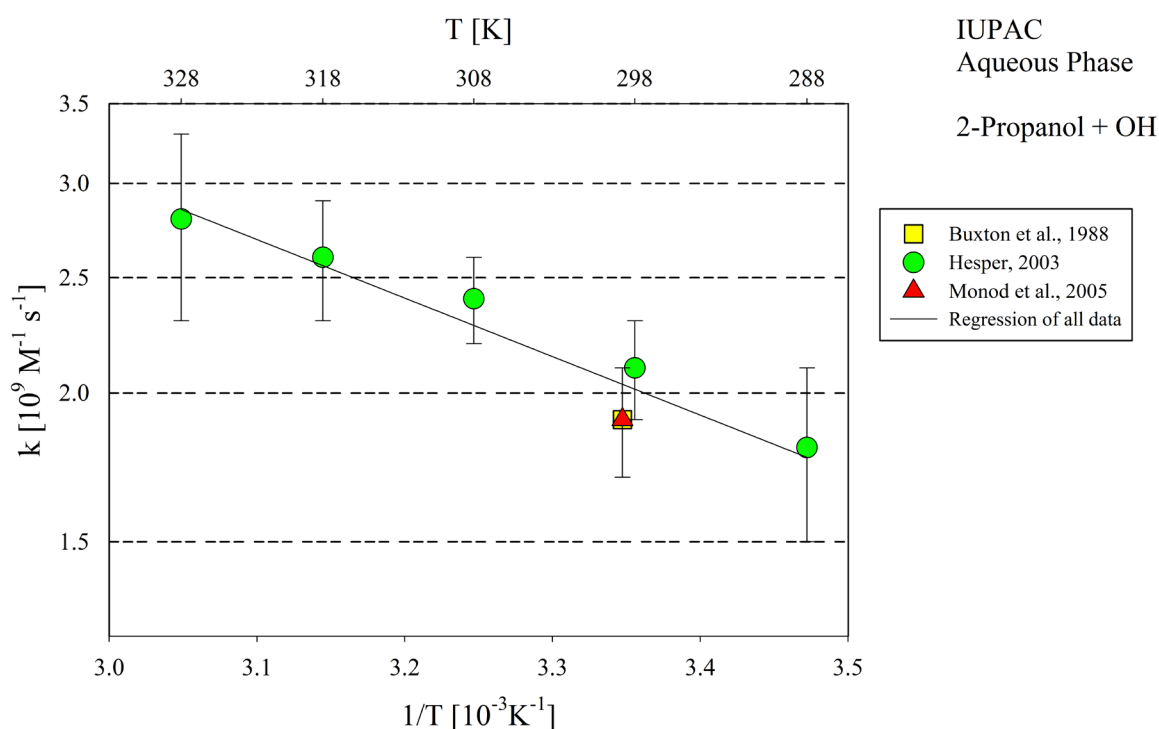


Figure 1: T-dependent rate constants for the reaction of 2-Propanol with OH in aqueous solution. Data from Buxton et al. (1988), Hesper (2003) and Monod et al. (2005).