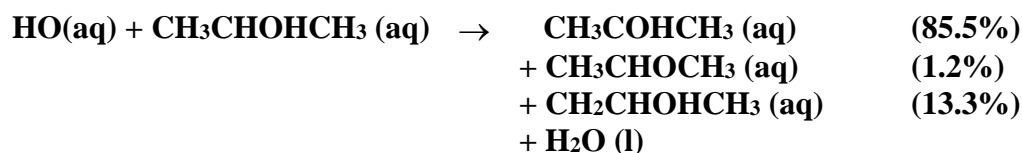


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_4

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This datasheet last evaluated: June 2019; last change in preferred values: March 2019



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

Rate coefficient data

k/ l mol ⁻¹ s ⁻¹	T/K	pH	I/ mol l ⁻¹	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>					
2.0 × 10 ⁹	-	slightly <pH 7	-	Janata, 2002	PR/UV-vis abs. (a)
2.0 × 10 ⁹	-	slightly <pH 7	-	Alam et al., 2003	PR/UV-vis abs. (b)
(2.1 ± 0.2) × 10 ⁹			0		
(2.8 ± 0.7) × 10 ⁹			0.5 (0.46)		
(3.6 ± 0.4) × 10 ⁹			1.0 (0.85)		
(4.1 ± 0.4) × 10 ⁹	298	5.8	1.5 (1.21)	Hesper, 2003	LP/LPA (c1)
(4.6 ± 0.6) × 10 ⁹			2.0 (1.53)		
(4.2 ± 1.4) × 10 ⁹			2.5 (1.83)		
(4.6 ± 3.3) × 10 ⁹			3.0 (2.11)		
6.1 × 10 ¹⁰ exp[- (1000 ± 300)K/T]	288-328	-	-		LP/LPA (c2)
<i>Relative Rate Coefficients</i>					
2.13 × 10 ⁹	295-298	9	-	Kraljic et al., 1965	CW-radiolysis /UV-vis abs. (d)
6.5 × 10 ⁹	294	7	-	Adams et al., 1965	PR/UV-vis abs. (e)
1.6 × 10 ⁹	294	-	1.0	Heckel et al., 1965	PR/UV-vis abs. (f)

$(2.08 \pm 0.2) \times 10^9$	294	2.0-2.2	-	Scholes et al., 1965	CW-radiolysis /UV-vis abs. (g)
1.86×10^9	294	7	-	Thomas, 1965	PR/UV-vis abs. (h)
3.04×10^9	293	7	-	Woodward and Sutton, 1966	CW-radiolysis (i)
2.22×10^9	294	6	-	Anbar et al., 1966	CW-radiolysis /UV-vis abs. (j1)
2.05×10^9	294	9	-		CW-radiolysis /UV-vis abs. (j2)
2.25×10^9	294	2	-	Scholes and Willson, 1967	CW-radiolysis /UV-vis abs. (k1)
2.25×10^9	294	5	-		(k2)
1.83×10^9	294	-	-	Greenstock et al., 1968	PR/UV-vis abs. (l)
1.5×10^9	294	7	-	Baxendale and Khan, 1969	PR/UV-vis abs. (m)
2.22×10^9	294	-	-	Willson et al., 1971	CW-radiolysis /UV-vis abs.(n)
$(2.08 \pm 0.14) \times 10^9$	291-298	6.9	-	Prütz et al., 1976	CW-radiolysis / fluorescence detection (o1)
$(2.6 \pm 0.3) \times 10^9$	291-298	7	-		CW-radiolysis / fluorescence detection (o2)
1.8×10^9	291-298	10.4	-		CW-radiolysis / fluorescence detection (o3)
$(2.0 \pm 0.1) \times 10^9$	294	6	0.3×10^{-3}	Wolfenden and Willson, 1982	PR/UV-vis abs. (p)
2.2×10^9	292	-	$2-10 \times 10^{-3}$	Elliot and Simsons, 1984	PR/UV-vis abs. (q1)
$7.41 \times 10^{10} \exp[-(1000 \pm 70)/T]$	292 - 352	-	-		(q2)

1.6×10^9	294	7.5	-	Motohashi and Saito, 1993	CW-irradiation /HPLC (r)
$(2.2 \pm 0.2) \times 10^9$	298	1-2	-	Monod et al., 2005	ASC/ GC-FID (s)

ΔG_R° (aq): Aqueous phase thermochemical data not available

For comparison: ΔH_R° (g) = -58.8 kJ·mol⁻¹ (gas phase data sheet HOx_VOC26)

Comments

- (a) Direct observation of the alcohol radicals (260-290 nm); computer simulations were used to derive the rate coefficients; the simulations were accurate to 5%; N₂O saturated solutions.
- (b) Essentially the same article as (a)
- (c) Product formation observed at 248 nm; direct observation of optical absorption of the peroxy-radicals formed by the reaction between HO, 2-propanol and O₂; oxygen saturated solutions (c1): determination of ion strength influence; NaClO₄ 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) Product formation observed at (440 nm); Reference reaction: HO + PNDA (p-nitrosodimethylaniline); rate coefficient of the reference reaction was estimated to $\sim 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; the relative rate coefficient was determined to be 17.0 (relative to $k(\text{HO} + \text{PNDA} = 100)$); the relative rate coefficient has an error of about $\pm 5\%$
- (e) Product formation observed at 500 nm; reference reaction: HO + SCN⁻ with $k(\text{HO} + \text{SCN}^-) = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; the rate coefficient was recalculated using the selected rate coefficient for the reference reaction ($1.08 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; Zhu et al., 2003); No exact value is given for the initial concentrations of the reactants ('a few millimolar'); air or oxygen saturated solutions; as no exact temperature is given, for room temperature T = 294 K is assumed.
- (f) Reference reaction: HO + HSO₄⁻; $k(\text{HO} + \text{HSO}_4^-) = 8.0 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ was taken from Adams et al. (1965); the absolute rate coefficient for the reaction HO + *i*-propanol was calculated from the relative value ($k = 3.6$) listed in Table 1 of the reference, which was normalized to the methanol reaction ($k(\cdot\text{OH} + \text{methanol}) = 4.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$); as no exact temperature is given, for room temperature T = 294 K is assumed.
- (g) Product formation observed at 264 nm; reference reaction: HO + thymine with $k(\text{HO} + \text{thymine}) = 3.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; rate coefficient was recalculated using the selected rate coefficient for reference reactions ($5.38 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$); $c(\text{thymine}) = 8 - 20 \times 10^{-5} \text{ mol/l}$; air or oxygen saturated solutions; as no exact temperature is given, for room temperature T = 294 K is assumed.
- (h) Product formation observed at 400 nm; reference reaction: HO + I⁻; $k(\text{HO} + \text{I}^-) = (1.02 \pm 0.13) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; rate coefficient was recalculated using the selected rate coefficient for reference reactions ($1.09 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$); no values given for concentrations; as no exact temperature is given, for room temperature T = 294 K is assumed.

- (i) Product yields determined by UV-vis abs., chromatography and other methods not described in the article; Reference reaction: HO + NO; $k(\text{HO} + \text{NO}) = 6.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; a relative rate coefficient of $k_{(\text{HO} + \text{NO})} / k_{(\text{HO} + \text{iPrOH})}$ is given as (4.8 ± 0.6) ; determined rate coefficients were than referenced to $k_{(\text{HO} + \text{EtOH})}$, defined as 1; recalculation of was performed using the selected value for the reference rate coefficient $k(\text{HO} + \text{NO}) = 1.46 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$.
- (j) Reference reactions: HO + Br⁻ (j1); HO + PNDA (p-nitrosodimethylaniline) (j2); no values given for initial concentrations; rate coefficients of the reference reactions were determined versus ethanol with $k(\text{HO} + \text{ethanol}) = 1.88 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; air saturated solutions; all experiments were repeated at least four times and the coefficient of variation was less than $\pm 10\%$; as no exact temperature is given, for room temperature T = 294 K is assumed.
- (k) Product formation observed at 264 nm; reference reaction: HO + thymine with $k(\text{HO} + \text{thymine}) = 4.3 \pm 1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; rate coefficient was recalculated using the selected rate coefficient for the reference reaction ($5.38 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$); $c(\text{thymine}) = 8 \times 10^{-5} - 2 \times 10^{-4} \text{ mol/l}$; rate coefficient of reference reaction determined relative to benzene; aerated solutions; absolute rate coefficients given have an error of about $\pm 25\%$; as no exact temperature is given, for room temperature T = 294 K is assumed.
- (l) Product formation observed at 500 nm; reference reaction: HO + SCN⁻ with $k(\text{HO} + \text{SCN}^-) = (7.5 \pm 0.5) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $c(\text{KSCN}) = 2 \times 10^{-3} \text{ mol/l}$; aerated solutions; recalculation was performed using the selected rate coefficient for the reference reaction ($1.10 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) as no exact temperature is given, for room temperature T = 294 K is assumed.
- (m) Product formation observed at 440 nm; reference reaction: HO + PNDA (p-nitrosodimethylaniline); $k(\text{HO} + \text{PNDA}) = 1.25 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; no values given for concentrations; aerated solutions
- (n) Product formation observed at 410 nm; reference reaction: HO + [Fe(CN)₆]⁴⁻ with $k(\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}) = (0.93 \pm 0.05) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; rate coefficient has been recalculated using the selected value for the reference reaction ($1.03 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$) $c([\text{Fe}(\text{CN})_6]^{4-}) = 2 \times 10^{-3} \text{ mol/l}$; in most reactions air was present or the solutions were saturated with N₂O; as no exact temperature is given, for room temperature T = 294 K is assumed.
- (o) Products analysed by fluorescence measurements using acriflavin ((o1) and (o2)) and Fluorescein (o3) as RCL (Radiation Induced Chemiluminescence)-dye; The absolute rate coefficients were obtained by comparing the slopes of the emission yields plotted against the concentrations of the different scavengers and using $k(\text{HO} + \text{methanol}) = 8.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ as reference; recalculation was performed using the selected value for the rate coefficient of the reference reaction ($9.22 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$).
- (p) Product formation observed at 415 nm; reference reaction: HO + ABTS (2,2'-Azinobis-(3-ethylbenzthiazoline-6-sulphonate)); $k(\text{HO} + \text{ABTS}) = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, $c(\text{ABTS}) = 1 \times 10^{-4} \text{ mol/l}$; N₂ and N₂O saturated solutions; as no exact temperature is given, for room temperature T = 294 K is assumed.
- (q) Product formation observed at 420 nm; reference reaction: HO + SCN⁻; relative rate coefficients given as k_S/k_R ; $c(\text{KSCN})$ in the range of $2-10 \times 10^{-3} \text{ mol/l}$; N₂O saturated solutions. Arrhenius expression (q2) calculated using the relative data k_S/k_R from table 1, relative to the selected T-dependent rate coefficients (Zhu et al., 2003) considering 10% error of activation energy.

(r) Products analysed by HPLC (abs. 240-300 nm) and fluorescence measurements (irradiation at 305 nm); Reference reaction: HO + benzoate ; $k(\text{HO} + \text{benzoate}) = 5.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $c(\text{benzoate}) = 2 \times 10^{-4} \text{ mol/l}$; deviations of less than $\pm 5\%$ for the determined rate coefficients; N_2O saturated solutions; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.

(s) Radicals generated by Photo-Fenton-reaction in a bulk reactor (an 'aqueous phase smog chamber' or 'ASC'), products analysed by GC-FID; Reference reaction: HO + 1-propanol with $k(\text{HO} + 1\text{-propanol}) = 2.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; recalculation performed using the selected value for the reference reaction ($3.18 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$).

Preferred Values

Parameter	Value	T/K
$k / \text{l mol}^{-1} \text{ s}^{-1}$	2.27×10^9	298
$k / \text{l mol}^{-1} \text{ s}^{-1}$	$1.17 \times 10^{11} \exp[-(1180 / T)]$	288 - 352

Reliability

$\Delta \log k$	± 0.15
$\Delta E_A/R$	± 200

Comments on Preferred Values

Buxton et al. (1988) recommended a rate coefficient of $1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. Considering the only temperature dependent kinetic data from Elliot and Simsons (1984) as well as the remaining averaged data available, a slightly higher rate coefficient is suggested. The latest determination by Monod (2005) also agrees with the preferred value. Data determined by Adams et al. (1965) and Heckel et al. (1965) have not been considered for the evaluation. For the method of Heckel et al. it must be considered that the rate coefficient is exceeding its reference rate constant by a factor of 10^3 requiring very high reference reactant concentrations and leading to high uncertainties. The error of the recommended room temperature rate coefficient is estimated to be $\Delta \log k = \pm 0.15$ or $\pm 33\%$.

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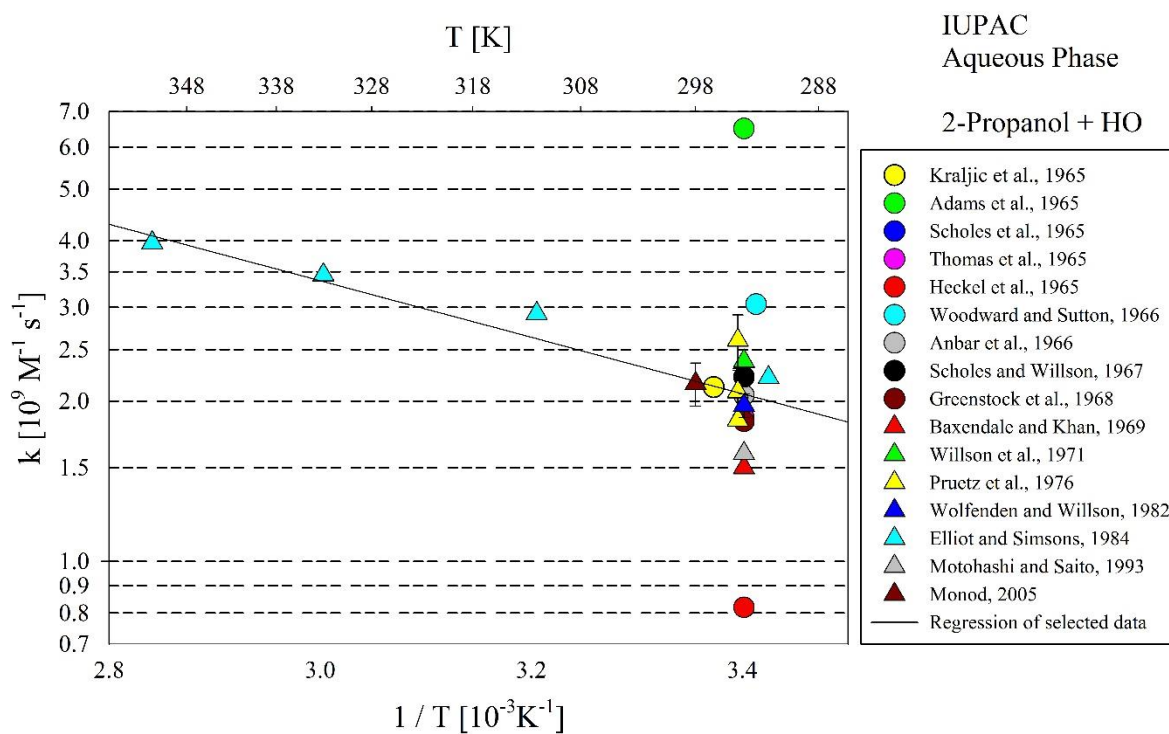
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T-dependent rate coefficients for the reaction of 2-Propanol with OH in aqueous solution. Rate coefficients determined by Adams et al. (1965) and Heckel et al. (1966) were excluded from the regression.