IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation
– Data Sheet AQ_OH_2

This datasheet last evaluated: September 2017; last change in preferred values: September 2017

$$OH\ (aq) + CH_3CH_2OH\ (aq) \rightarrow \begin{array}{ll} CH_3CHOH\ (aq) & (84.3\%) \\ + CH_3CH_2O\ (aq) & (2.5\%) \\ + CH_2CH_2OH\ (aq) & (13.2\%) \\ + H_2O\ (1) \end{array}$$
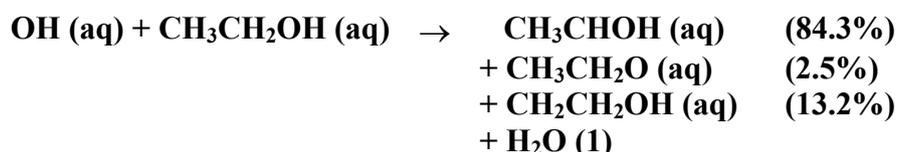
(*Product distributions taken from Buxton et al., 1988, originally determined by Asmus et al., 1973 via PR - UV/Vis*)

$\Delta G_R°$ (aq): Aqueous phase thermochemical data not available
For comparison: $\Delta H_R°$ (g) = -95.8 kJ mol^{-1} (gas phase, data sheet HOx_VOC24)

Rate coefficient data

k/ l mol^{-1} s^{-1}	T/K	pH	I/mol l^{-1}	Reference	Technique/ Comments
Relative Rate Coefficients					
7.20×10^8		7	1×10^{-4}	Thomas, 1964	PR-UV/Vis RR (a)
0.97×10^9		10.7		Adams et al., 1965	PR-UV/Vis RR (b1)
1.08×10^9		7		Adams et al., 1965	PR-UV/Vis RR (b2)
1.10×10^9		7	6.9×10^{-4}	Adams et al., 1965	PR-UV/Vis RR (b3)
11.0×10^8		7		Adams et al., 1965	PR-UV/Vis RR (c1)
9.8×10^8		2		Adams et al., 1965	PR-UV/Vis RR (c2)
1.1×10^9				Adams et al., 1965	PR-UV/Vis RR (d)
2.8×10^8	271 - 278	10.5 – 10.8		Matthews and Sangster, 1965	cw radiolysis-Tracer (e)
9.2×10^8			1	Heckel et al., 1965	PR-UV/Vis(f)
1.6×10^9 1.4×10^9		3 6-7		Scholes and Willson, 1967	PR-UV/Vis RR (g)
$(1.83 \pm 0.2) \times 10^8$				Neta P. and Dorfman L.M., 1968	PR-UV/Vis RR (h)
1.6×10^9	294			Baxendale and Khan, 1969	PR-UV/Vis RR (i)

k (M^{-1}s^{-1})	T (K)	pH	c (mol/l)	Reference	Method
$(2.2 \pm 0.3) \times 10^9$		11 - 13		Buxton, 1970	PR-UV/Vis RR(j)
1.85×10^9		2	2×10^{-2}	Willson et al., 1971	PR-UV/Vis RR (k)
1.65×10^9				Matheson et al., 1973	PR-UV/Vis RR (l)
$(1.90 \pm 0.1) \times 10^9$		6	3×10^{-4}	Wolfenden and Willson, 1982	PR-UV/Vis RR (m)
1.9×10^9	298			Buxton et al., 1988	Selected value 1988(n)
$(1.85 \pm 0.1) \times 10^9$		9	$12.5 - 25 \times 10^{-5}$	Park and Getoff, 1992	PR-UV/Vis RR (o)
2.2×10^9		7.5		Motohashi and Saito, 1993	PR-HPLC(p)
$(2.1 \pm 0.4) \times 10^9$	293			Monod et al., 2002	(q)
$(2.1 \pm 0.1) \times 10^9$	298		2×10^{-5}	Ervens et al., 2003	LP-LPA (r1)
1.0×10^{11} exp[-$(1200 \pm 600) / T$]	283-328				(r2)
$(1.9 \pm 0.5) \times 10^9$	295			George et al., 2003	LCW (s)
			Absolute Rate Coefficients		
2.2×10^9		natural		Alam et al., 2003	PR-UV/Vis (t)

Comments

(a) Radical generation by gamma pulse-radiolysis, competition kinetics (RR) analysis by UV/Vis spectroscopy with iodide as competitor; reference reaction $\cdot OH + I^-$; $k(OH + I^-) = (1.02 \pm 0.13) \times 10^{10}$ M^{-1}s^{-1}, $c(I^-) = 5 \times 10^{-5}$ mol/l. This concentration is used for the calculation of I.

(b) Radical generation by gamma pulse-radiolysis, competition kinetics (RR) analysis by UV/Vis spectroscopy with (b1) reference reaction $\cdot OH + CO_3^{2-}$, $k(OH + CO_3^{2-}) = 2 \times 10^8$ M^{-1}s^{-1}, no concentrations given; (b2) $\cdot OH + SCN^-$, $k(OH + SCN^-) = 6.6 \times 10^9$ M^{-1}s^{-1}, $c(SCN^-) = 8 - 400 \times 10^{-6}$ mol/l; (b3) $\cdot OH +$ selenite (SeO_3^{2-}), $k(OH + SeO_3^{2-}) = 2.7 \times 10^9$ M^{-1}s^{-1}, c = 2.3×10^{-4} mol/l; pH = 10.7, temperature not specified. NIST lists these values as (b1) 1.9×10^9 M^{-1}s^{-1}, referring to $k(OH + CO_3^{2-}) = 3.9 \times 10^8$ M^{-1}s^{-1}; (b2) 1.8×10^9 M^{-1}s^{-1}, referring to $k(OH + SCN^-) = 1.1 \times 10^{10}$ M^{-1}s^{-1}.
http://kinetics.nist.gov/solution/Detail?id=1965ADA/BOA1417-1424:8
http://kinetics.nist.gov/solution/Detail?id=1965ADA/BOA1417-1424:7

(c) Radical generation by gamma pulse-radiolysis, competition kinetics (RR) analysis by UV/Vis spectroscopy as in (b). Exp. values of (b) also listed (Table I of the reference, values given here are those of Table II of the reference). Competitor: SCN$^-$ with c = 1-50 $\times 10^{-3}$ mol/l (used to calculate the tabulated I). RR reference rate constant $k(OH + SCN^-) = 6.6 \times 10^9$ M^{-1}s^{-1}. NIST lists these values as (c1) 1.9×10^9 M^{-1}s^{-1} and (c2) 2.8×10^9 M^{-1}s^{-1} referring to $k(OH + SCN^-) = 1.1 \times 10^{10}$ M^{-1}s^{-1}.

(d) Radical generation by gamma pulse-radiolysis, competition kinetics (RR) analysis by UV/Vis spectroscopy as in (b). Competitor: $Fe(CN)_6$ with $k(OH + Fe(CN)_6) = 5.0 \times 10^9$ $M^{-1}s^{-1}$. NIST lists this value as 2.2×10^9 $M^{-1}s^{-1}$ referring to $k(OH + Fe(CN)_6) = 1.0 \times 10^{10}$ $M^{-1}s^{-1}$.

(e) Radical generation through continuous gamma-radiolysis, analysis of $^{14}CO_2$ formed from the competition reaction $\cdot OH + C_6H_5{}^{14}COO^-$ with $k(\cdot OH + benzoic\ acid) = 1.0 \times 10^9$ $M^{-1}s^{-1}$; The rate constant is calculated from the RR ratio of 0.28 from Table IV and the given reference rate constant $k(OH + benzoic\ acid)$ from Table V of the reference. The ionic strength was calculated from the given concentration of benzoic acid with $c = 8 \times 10^{-3}$ mol/l. This competition kinetics method is different from most other ones, it directly determines the yield of $^{14}CO_2$ formed by single electron transfer from the carboxylate group to OH. As OH will react by addition to the aromatic ring as well, this method should be considered with great care, however. NIST lists this value as 1.7×10^9 $M^{-1}s^{-1}$ referring to $k(\cdot OH + benzoic\ acid) = 5.9 \times 10^9$ $M^{-1}s^{-1}$.

(f) Radical generation by gamma pulse-radiolysis, competition kinetics (RR) analysis by UV/Vis spectroscopy, reference reaction $\cdot OH + HSO_4^-$. $k(OH + HSO_4^-) = 8 \times 10^5$ $M^{-1}s^{-1}$ is calculated based on data by Adams et al.; a separate determination of this reference rate constant lead to $k(OH + HSO_4^-) = 6.9 \times 10^5$ $M^{-1}s^{-1}$, the authors decide to use the above value by Adams as the reference rate constant. Table 1 of the reference gives ratios $k_{Substance} / k_{(OH + HSO4\text{-})}$ and , specifically, $k_{Ethanol}/k_{(OH + HSO4\text{-})} = 5.5 \times 10^2$, leading to a the tabulated absolute rate constant. NIST lists this value as 2.0×10^9 $M^{-1}s^{-1}$ referring to $k(\cdot OH + HSO_4^-) = 9.7 \times 10^8$ $M^{-1}s^{-1}$.

(g) Radical generation by gamma pulse-radiolysis, competition kinetics (RR) analysis by UV/Vis spectroscopy; reference reaction $\cdot OH + thymine\ anion\ (Ty)$; $k(OH + Thy^-) = 4.3 \times 10^9$ $M^{-1}s^{-1}$, thymine concentration $c = 8 \times 10^{-5}\text{- }2 \times 10^{-4}$ mol/l.

(h) Radical generation by gamma pulse-radiolysis, competition kinetics analysis by UV/Vis-spectroscopy; (h1) reference reaction $C_6H_5CO_2^- + \cdot OH$; $k(C_6H_5CO_2^- + \cdot OH) = (6.0 \pm 0.7) \times 10^{-9}$ $M^{-1}s^{-1}$, (h2) $C_6H_5CH_2CO_2^- + \cdot OH$; $k(C_6H_5CH_2CO_2^- + \cdot OH) = (7.9 \pm 1.1) \times 10^{-9}$ $M^{-1}s^{-1}$, (h3) $p\text{-}NO_2\ C_6H_4CO_2^- + \cdot OH$; $k(p\text{-}NO_2\ C_6H_4CO_2^- + \cdot OH) = (2.6 \pm 0.4) \times 10^{-9}$ $M^{-1}s^{-1}$. The tabulated value is the mean of the three determinations with the above different scavengers. The absolute error of the mean rate constant is provided by the authors.

(i) Radical generation by gamma pulse-radiolysis, competition kinetics analysis by UV/Vis-spectroscopy; reference reaction $\cdot OH + p\text{-nitrosodimethylanilin}\ (4\text{-}Me_2NC_6H_4NO)$; $k(OH + 4\text{-}Me_2NC_6H_4NO) = (1.25 \pm 0.2) \times 10^{10}$ $M^{-1}s^{-1}$, $c = 9.4 \times 10^{-6}$ mol/l, The concentration of p-nitrosodimethylanilin used for the ethanol measurement was taken from Figure 5 of the reference.

(j) Radical generation by gamma pulse-radiolysis, competition kinetics analysis by UV/Vis-spectroscopy, reference reaction $\cdot OH + CO_3^{2-}$, $k(OH + CO_3^{2-}) = 4.0 \times 10^8$ $M^{-1}s^{-1}$, measurements at pH 11 (0.01 mol l^{-1} CO_3^{2-} + 2.3×10^{-2} HCO_3^-) and pH 13 (0.1 M CO_3^{2-}).

(k) Radical generation by gamma pulse-radiolysis, competition kinetics analysis by UV/Vis-spectroscopy, reference reaction $\cdot OH + Fe(CN)_6{}^{4-}$; $k(OH + [Fe(CN)_6]^{3-}) = 0.93\pm0.05 \times 10^{10}$ $M^{-1}s^{-1}$, $c([Fe(CN)_6]^{4-}) = 2 \times 10^{-3}$ mol/l – used for calculating I. NIST lists this value as 2.1×10^9 $M^{-1}s^{-1}$ referring to $k(\cdot OH + Fe(CN)_6{}^{4-}) = 1.0 \times 10^{10}$ $M^{-1}s^{-1}$.
http://kinetics.nist.gov/solution/Detail?id=1971WIL/GRE211-220:12

(l) Radical generation by gamma pulse-radiolysis, competition kinetics analysis by UV/Vis-spectroscopy, reference reaction $\cdot OH + [Fe(CN)_6]^{3-}$; $k(OH + [Fe(CN)_6]^{3-}) = 0.93 \times 10^{10}$ $M^{-1}s^{-1}$. The listed rate constant is given at the end of the introduction and compared to the one by Willson et al.1971. NIST lists this value as 1.9×10^9 $M^{-1}s^{-1}$ referring to $k(\cdot OH + Fe(CN)_6{}^{4-}) = 1.0 \times 10^{10}$ $M^{-1}s^{-1}$.
http://kinetics.nist.gov/solution/Detail?id=1973MAT/MAM2420-2424:1

(m) Radical generation by gamma pulse-radiolysis, competition kinetics analysis by UV/Vis-spectroscopy, reference reaction $ABTS^{2-} + \cdot OH$, $k(OH + ABTS^{2-}) = 1.2 \times 10^{10}$ $M^{-1}s^{-1}$, $c(ABTS^{2-}) = 10^{-4}$ mol/l.

(n) Buxton et al. in 1988 recommended this value.

(o) Radical generation by gamma pulse-radiolysis, competition kinetics analysis by UV/Vis-spectroscopy, reference reaction $\cdot OH + [Fe(CN)_6]^{4-}$; $k(OH + [Fe(CN)_6]^{4-}) = 1 \times 10^{10}$ $M^{-1}s^{-1}$ taken from Elliot and Simsons (1984); $c([Fe(CN)_6]^{4-}) = 2.5 - 5.0 \times 10^{-5}$ mol/l, used to calculate I.

(p) Radical generation by gamma pulse-radiolysis and cw-radiolysis, competition kinetics by HPLC product analysis, reference reaction $C_6H_5CO_2{}^- + \cdot OH$, $k(OH + C_6H_5CO_2{}^-) = 5.9 \times 10^9$ $M^{-1}s^{-1}$, $c(C_6H_5CO_2{}^-) = 2 \times 10^{-4}$ mol/l

(q) cw-photolysis of H_2O_2 with a Xe-lamp solar simulator. Product analysis by GC, HPLC and IC. Proof of concept study.

(r) Laser-photolysis long-path absorption, competition kinetics, reference reaction $\cdot OH + SCN^-$; $k(OH + SCN^-) = 7.26 \times 10^{12}$ $\exp(-1900\pm190/T)$ $M^{-1}s^{-1}$, $c(SCN^-) = 2 \times 10^{-5}$ mol/l, $c(H_2O_2) = 5 \times 10^{-4}$ mol/l; temperature dependent data delivering Arrhenius expression (r2).

(s) Radicals generated by photolysis of H_2O_2 in a liquid core waveguide (LCW) at ≤366 nm; reference reaction: $\cdot OH + SCN^-$ with $k(\cdot OH + SCN^-) = 1.29 \times 10^{10}$ $M^{-1}s^{-1}$ referring to Chin and Wine (1992); $c(H_2O_2) = 10^{-3}$ M, $c(SCN^-) = 2 \times 10^{-4}$ M, $c(ethanol) = \sim10^{-3}$ M.

(t) 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.

Preferred Values

Parameter	Value	T/K
k / l mol^{-1} s^{-1}	1.9×10^9	298
k / l mol^{-1} s^{-1}	6.84×10^{10} $\exp[-(1756) / T]$	293-353

Reliability

$\Delta \log k$	$\pm$ 0.36	298
$\Delta E_A/R$	$\pm$ 250	293 - 353

Comments on Preferred Values

Buxton et al. recommended 1.9×10^9 l mol^{-1} s^{-1} in 1988. Even though work since then in four out of five studies indicates that the rate constant may be slightly higher, calculations of the recommended value confirm the rate constant as determined by Buxton et al.. The most recent determination of this rate constant by George et al. (2003) is in agreement with this value within error limits as well. The uncertainty of the preferred value is twice the one given by Ervens et al. thus including the recommended value by Buxton et al. (1988). The recommended Arrhenius expression uses all plotted data points except Matthews and Sangster (1965).

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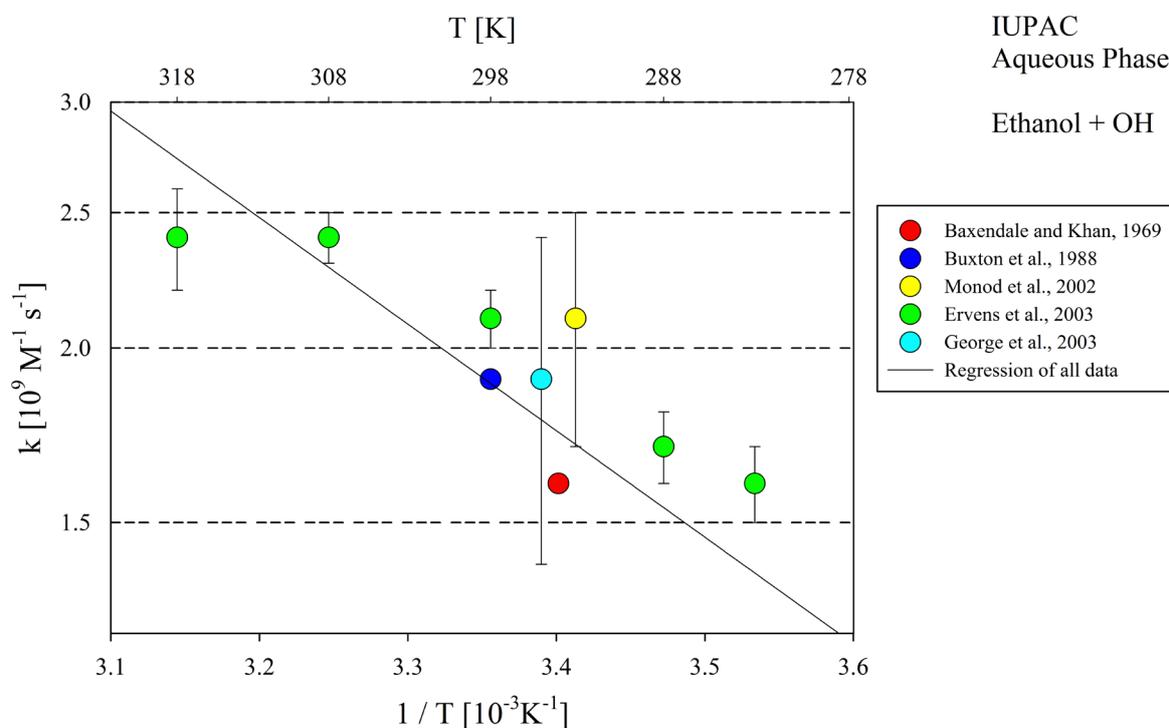
Figure 1: T-dependent rate constants for the reaction of Ethanol with OH in aqueous solution. Data from Baxendale and Kahn (1969), Buxton et al. (1988), Monod et al. (2002), Ervens et al. (2003) and George et al. (2003).