IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_1

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

$$\mathbf{OH\ (aq) + CH_3OH\ (aq) \rightarrow CH_2OH\ (aq)} \quad \mathbf{(93\%)}$$
$$\mathbf{+\ CH_3O\ (aq)} \quad \mathbf{(7\%)}$$
$$\mathbf{+\ H_2O\ (l)}$$

(*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) = -95.2 kJ mol^{-1} (gas phase, data sheet HOx_VOC23)

Rate coefficient data

k/ l mol^{-1} s^{-1}	T/K	*pH*	I/mol l^{-1}	*Reference*	Technique/ Comments
Relative Rate Coefficients					
4.7×10^8		7	1.0×10^{-4}	Thomas, 1964	PR-UV/Vis RR (a)
4.6×10^8		10.7		Adams et al., 1965	PR-UV/Vis RR (b1)
4.7×10^8		7		Adams et al., 1965	PR-UV/Vis RR (b2)
5.0×10^8		7	6.9×10^{-4}	Adams et al., 1965	PR-UV/Vis RR (b3)
4.8×10^8		7		Adams et al., 1965	PR-UV/Vis RR (c1)
4.4×10^8		2		Adams et al., 1965	PR-UV/Vis RR (c2)
$(8.4 \pm 1) \times 10^8$				Neta and Dorfman, 1968	PR-UV/Vis RR (d)
9.5×10^8	294			Baxendale und Khan, 1969	PR-UV/Vis RR (e)
8.6×10^8		2		Willson et al., 1971	PR-UV/Vis RR (f)
$(0.99 \pm 0.05) \times 10^9$		6.5	3×10^{-4}	Wolfenden and Willson, 1982	PR-UV/Vis (g)
9.7×10^8	298			Buxton et al., 1988	Recalculated value-
10.1×10^8	293	7		Elliot and McCracken, 1989	PR-UV/Vis (h1)
1.05×10^{10} exp[-(685±70) / T]	293 - 353				(h2)

8.3×10^8		7.5		Motohashi and Saito, 1993	PR-HPLC (i)
$(1.3 \pm 0.4) \times 10^9$	295			George et al., 2003	LCW (j)
Absolute Rate Coefficients					
9.0×10^8		natural		Alam et al., 2003	PR-UV/Vis (k)

Comments

(a) Radical generation by gamma pulse-radiolysis, relative rate (RR) analysis by UV/Vis spectroscopy; reference reaction ·OH + I^- ; k(OH + I^-) = (1.02 ± 0.13) × 10^{10} $M^{-1}s^{-1}$, c(I^-) = 5×10^{-5} mol/l.

(b) Radical generation by gamma pulse-radiolysis, relative rate (RR) analysis by UV/Vis spectroscopy; (b1) reference reaction ·OH + CO_3^{2-} ; k(·OH + CO_3^{2-}) = 2.0×10^8 $M^{-1}s^{-1}$ (taken from previous studies) ; (b2) ·OH + SCN^- ; k(·OH + SCN^-) = 6.6×10^9 $M^{-1}s^{-1}$ (b3) ·OH + selenite (SeO_3^{2-}); k(·OH + selenite) = 2.7×10^9 $M^{-1}s^{-1}$.

(c) Radical generation by gamma pulse-radiolysis, relative rate (RR) analysis by UV/Vis-spectroscopy; not clearly specified whether carbonate, thiocyanate or selenite was used as the reference system for (c1) and (c2); k(·OH + SCN^-) = 6.6×10^9 $M^{-1}s^{-1}$ (taken from previous studies from Adams et al.).

(d) Radical generation by gamma pulse-radiolysis, relative rate (RR) analysis by UV/Vis-spectroscopy; reference reactions: ·OH + $C_6H_5CO_2^-$; k(·OH + $C_6H_5CO_2^-$) = (6.0 ± 0.7) × 10^9 $M^{-1}s^{-1}$; ·OH + $C_6H_5CH_2CO_2^-$; k(·OH + $C_6H_5CH_2CO_2^-$) = (7.9 ± 1.1) × 10^9 $M^{-1}s^{-1}$; ·OH + p-NO_2 $C_6H_4CO_2^-$; k(·OH + p-NO_2 $C_6H_4CO_2^-$) = (2.6 ± 0.4) × 10^9 $M^{-1}s^{-1}$; the tabulated value is the average of the three determinations with the different scavengers listed above. The absolute error of the mean rate constant is provided by the authors.

(e) Radical generation by gamma pulse radiolysis, relative rate (RR) analysis by UV/Vis-spectroscopy; reference reaction ·OH + 4-$Me_2NC_6H_4NO$; k(·OH + 4-$Me_2NC_6H_4NO$) = 1.25×10^{10} $M^{-1}s^{-1}$.

(f) Radical generation by gamma pulse-radiolysis, relative rate (RR) analysis by UV/Vis-spectroscopy; reference reaction ·OH + $Fe(CN)_6^{4-}$; k(·OH + $Fe(CN)_6^{4-}$) = (0.93 ± 0.05) × 10^{10} $M^{-1}s^{-1}$; c($[Fe(CN)_6]^{4-}$) = 2×10^{-3} mol/l. NIST lists the rate constant as 9.7×10^8 $M^{-1}s^{-1}$ referring to k(OH + $Fe(CN)_6^{4-}$) = 1.0×10^{10} $M^{-1}s^{-1}$.
http://kinetics.nist.gov/solution/Detail?id=1971WIL/GRE211-220:16

(g) Radical generation by gamma pulse-radiolysis, relative rate (RR) analysis by UV/Vis-spectroscopy; reference reaction ·OH + $ABTS^{2-}$ (ABTS = 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid); k(·OH + $ABTS^{2-}$) = 1.2×10^{10} $M^{-1}s^{-1}$; c(ABTS) = 1×10^{-4} mol/l. NIST lists the rate constant as 1.09×10^9 $M^{-1}s^{-1}$ referring to k($ABTS^{2-}$ + OH) = 1.2×10^{10} $M^{-1}s^{-1}$.
http://kinetics.nist.gov/solution/Detail?id=1982WOL/WIL805-812:12

(h) Radical generation by gamma pulse-radiolysis, relative rate (RR) analysis by UV/Vis-spectroscopy; (h1) reference reaction ·OH + SCN^-; no value given for the reference rate constant; (h2) Arrhenius expression has been calculated using the given T-dependent data.

(i) Radical generation by gamma pulse-radiolysis, analysis by HPLC, reference reaction: OH + benzoate; k(·OH + benzoate) = 5.9×10^9 $M^{-1}s^{-1}$.

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

(k) 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}	1.1×10^9	298
k / l mol^{-1} s^{-1}	$8.68 \times 10^9 \exp[-(620) / T)]$	293-353
Reliability		
$\Delta \log k$	± 0.1	298
$\Delta E_A/R$	± 100	293-353

Comments on Preferred Values

Buxton et al. recommended 9.7×10^8 l mol^{-1} s^{-1} in 1988 based on the standardization study of Willson et al.. The carefully performed and only available T-dependent study by Elliot and McCracken leads to k = 1.03×10^9 l mol^{-1} s^{-1} for T = 298 K by applying the provided Arrhenius expression as no direct measurement has been performed by these authors at T = 298 K. The most recent determination of this rate constant by George et al. (2003) is in agreement with the others within error limits and is included in the calculation of the recommended value of 1.1×10^9 l mol^{-1} s^{-1}.

The reliability of the preferred value is estimated.

References

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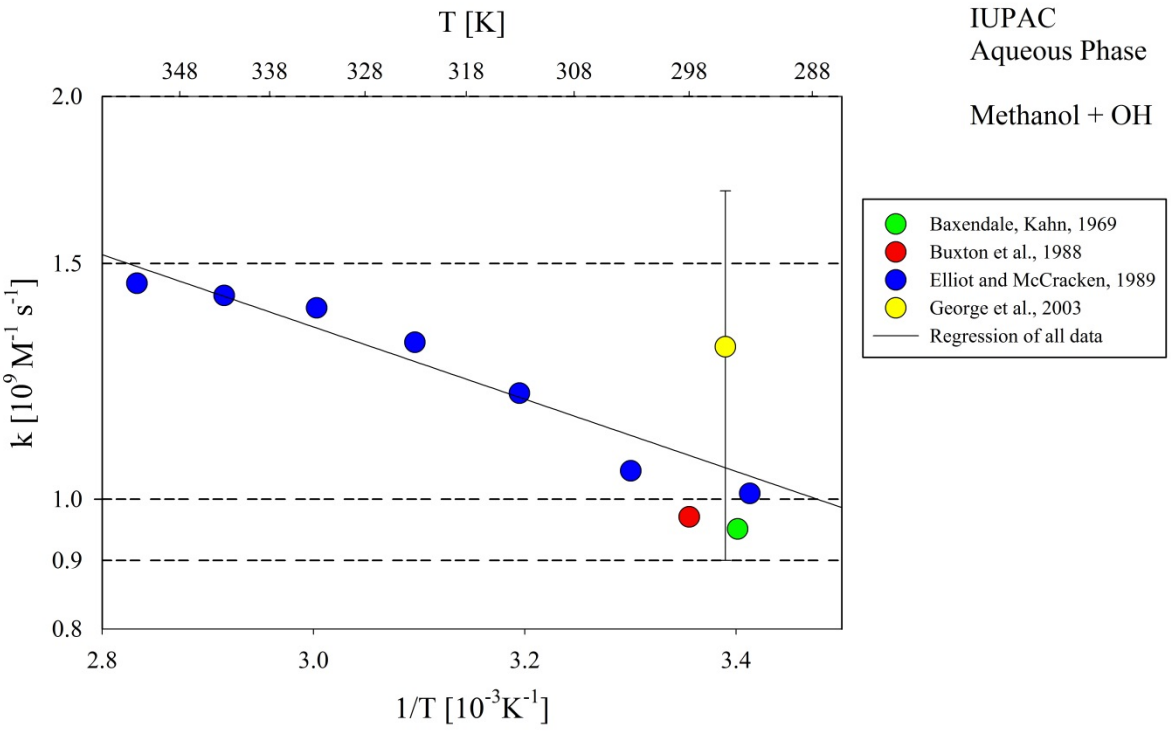

Figure 1: T-dependent rate constants for the reaction of Methanol with OH in aqueous solution. Data from Baxendale and Kahn (1969), Buxton et al. (1988), Elliot et al. (1989) and George et al. (2003).