IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_5

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$$\mathbf{HO\ (aq) + CH_3(CH_2)_3OH\ (aq) \rightarrow \begin{array}{l} CH_3CH_2CH_2CHOH\ (aq)\quad (41\%) \\ + CH_2CH_2CH_2CH_2OH\ (aq) \\ + CH_3CHCH_2CH_2OH\ (aq) \\ + CH_3CH_2CHCH_2OH\ (aq)\quad (58.5\%) \\ + H_2O\ (l) \end{array}}$$

(*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
Absolute Rate Coefficients					
$(4.1 \pm 0.8) \times 10^9$	298	5.8	-	Hesper, 2003 Herrmann, 2003	LP/LPA (a1)
1.0×10^{11} exp[-(1000 ± 100)K/T]	288 - 328	5.8	-		LP/LPA (a2)
Relative Rate Coefficients					
3.73×10^9	294	7	-	Adams et al. 1965	PR / UV-vis (b)
4.2×10^9	294	7	-	Adams et al., 1965	PR / UV-vis (c)
3.8×10^9	294	9	-	Anbar et al., 1966	CW-radiolysis / UV-vis (d)
4.6×10^9	294	2	-	Scholes and Willson, 1967	CW-radiolysis / UV-vis (e)
4.6×10^9	294	5	-		CW-radiolysis / UV-vis (e1)
4.4×10^9	294	-	2×10^{-2}	Willson et al., 1971	CW-radiolysis / UV-vis (f)
$(5.1 \pm 0.4) \times 10^9$	291-298	6.9	-	Prütz and Vogel, 1976	CW-radiolysis / UV-vis (g)
$(4.2 \pm 0.4) \times 10^9$	298	1-2	-	Monod et al., 2005	ASC / GC-FID (h)

$\Delta G_R°$ (aq): Aqueous phase thermochemical data not available. As well, gas phase thermochemical data $H_R°$ (g) are not available.

Comments

(a) Product formation observed at 260 nm; direct observation of optical absorption of the peroxyl-radicals formed by the reaction between HO, 1-Butanol and O_2; oxygen saturated solutions (a1): determination of the temperature influence; the Arrhenius expression (a2) was calculated using these values

(b) Product formation observed at 500 nm; Reference reaction: HO + SCN^-; k(HO + SCN^-) = 6.6×10^9 $M^{-1}s^{-1}$; the rate coefficient has been recalculated using the selected rate coefficient for the reference reaction (1.10×10^{10} $M^{-1}s^{-1}$; 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.

(c) Product formation observed at 500 nm; reference system: HO + CO_3^{2-} with k(HO + CO_3^{2-}) = 2.0×10^8 $M^{-1}s^{-1}$; the rate coefficient has been recalculated using the selected rate coefficient for the reference reaction (3.77×10^8 $M^{-1}s^{-1}$); no values given for the initial concentrations of the reactants; oxygen saturated solutions; as no exact temperature is given, for room temperature T = 294 K is assumed.

(d) Reference reaction: HO + PNDA (p-nitrosodimethylaniline); rate coefficients of the reference reactions were determined versus ethanol with k(HO + ethanol) = 1.10×10^9 $M^{-1}s^{-1}$; recalculation was performed using the selected rate coefficient (1.88×10^9 $M^{-1}s^{-1}$); no values given for the initial concentrations of the reactants; air saturated solutions; all experiments were repeated at least four times and the coefficient of variation was less than ± 10%; as no exact temperature is given, for room temperature T = 294 K is assumed.

(e) Product formation observed at 264 nm; Reference reaction: HO + thymine; k(HO + thymine) = $(4.3 \pm 1) \times 10^9$ $M^{-1}s^{-1}$; rate coefficient was recalculated using the selected value for the reference reaction (5.38×10^9 $M^{-1}s^{-1}$); c(thymine) = 8×10^{-5} - 2×10^{-4} mol/l; The rate coefficient of the reference reaction was determined relative to benzene ; aerated solutions; The absolute rate coefficients have an error of about ±25%; as no exact temperature is given, for room temperature T = 294 K is assumed.
Note: the reference values listed in table 1 were normalized to k(HO + ethanol) = 1.85×10^9 $M^{-1}s^{-1}$

(f) Product formation observed at 410 nm; Reference reaction: HO + $[Fe(CN)_6]^{4-}$ with k(HO + $[Fe(CN)_6]^{4-}$) = $(0.93 \pm 0.05) \times 10^{10}$ $M^{-1}s^{-1}$; rate coefficients have been recalculated using the selected rate coefficient for reference reactions (1.03×10^{10} $M^{-1}s^{-1}$); c($[Fe(CN)_6]^{4-}$) = 2×10^{-3} mol/l; in most reactions air was present or the solutions were saturated with N_2O; as no exact temperature is given, for room temperature T = 294 K is assumed.

(g) Products analysed by fluorescence measurements using Acriflavin 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(HO + methanol) = 8.5×10^8 $M^{-1}s^{-1}$ as reference; rate coefficient was recalculated using the selected value for the reference reaction (9.22×10^8 $M^{-1}s^{-1}$).

(h) Radicals generated by Photo-Fenton-reaction in a bulk reactor (an 'aqueous phase smog chamber' or 'ASC'), products analysed by GC-FID; Reference reactions: HO + 1-propanol; k(HO + 1-propanol) = 2.8×10^9 $M^{-1}s^{-1}$ and HO + 2-propanol; k(HO + 2-

propanol) = 1.9×10^9 $M^{-1}s^{-1}$ with no values given for the rate coefficients of the individual determinations.

Preferred Values

Parameter	Value	*T*/K
k / l mol^{-1} s^{-1}	4.30×10^9	298
k / l mol^{-1} s^{-1}	5.16×10^{10} exp[-(750)/T]	288 - 328
Reliability		
Δ log k	± 0.04	298
Δ E_A/R	± 220	288 – 328

Comments on Preferred Values

A rate coefficient of $k = 4.2 \times 10^9$ l mol^{-1} s^{-1} was recommended by Buxton et al. in 1988. To obtain the overall recommended T-dependent data, all available rate coefficients were used for regression. The obtained room temperature rate coefficient is slightly higher, then suggested, but can be explained well by the recalculated data of the determinations. The rate coefficient determined by Monod et al. (2005) is published as the mean of two determinations without stating the values of the single determinations. Therefore, a further evaluation of this rate coefficient cannot be undertaken, but it has to stated, that the recommended mean value of their work agrees well within error limits.
The uncertainty for the recommended rate coefficient is estimated and determined to be Δ log k = ±0.04 or ±10%.

References

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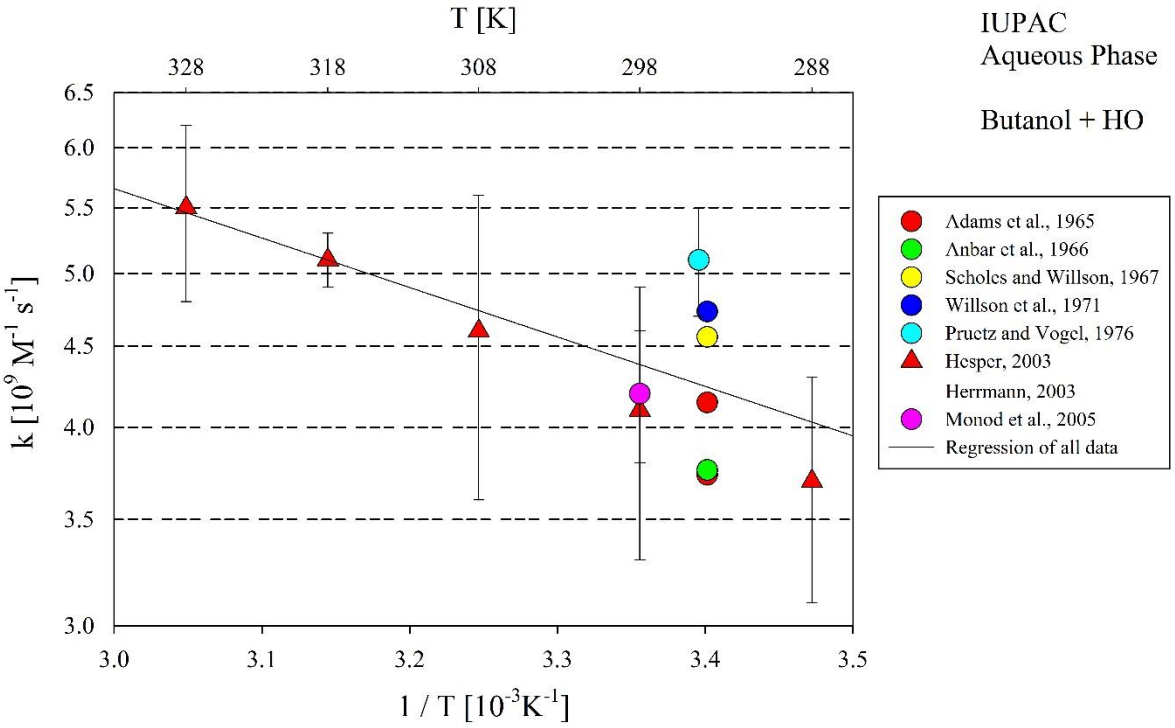

T-dependent rate coefficients for the reaction of 1-Butanol with HO in aqueous solution. The rate coefficient by Monod et al. (2005) is excluded from the regression.