IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_TH1_OH_2

This datasheet last evaluated: May 2017; last change in preferred values: May 2016

$OH^{\cdot}(aq) + CH_2(OH)COOH(aq) \rightarrow {}^{\cdot}CH(OH)COOH(aq) + H_2O$ (1)

$OH^{\cdot}(aq) + CH_2(OH)COO^{-}(aq) \rightarrow {}^{\cdot}CH(OH)COO^{-}(aq) + H_2O$ (2)

$\Delta G_R°$ (aq): Aqueous phase thermochemical data not available
Gas phase data for comparison also not available.

Rate coefficient data

k/ L mol^{-1} s^{-1}	T/K	pH	I/ mol L^{-1}	*Reference*	Technique/ Comments
Relative Rate Coefficients					
$k_1 = 8.6 \times 10^8$		1		Merz and Waters, 1949	Fenton reaction(a)
$k_1 = (3.7 \pm 0.9) \times 10^8$		2.0 – 2.2		Scholes and Willson, 1967	Radiolysis-UV/Vis(b)
$k_2 = (8.6 \pm 0.7) \times 10^8$	295	5.5		Bell et al., 1975	PR-UV/Vis(c)
$k_1 = 6.6 \times 10^8$	298	1		Buxton et al., 1988	Recalculated value (d1)
$k_1 = 5.4 \times 10^8$	298	2.0 – 2.2			Recalculated value (d2)
$k_1 = 6.0 \times 10^8$	298				Average value (d3)
$k_2 = 8.6 \times 10^8$	298	5.5			PR-UV/Vis (e)
$k_2 = (8.7 \pm 0.7) \times 10^8$	293	9		Logan, 1989	FP-UV/Vis (f)
$k_2 = 9.4 \times 10^8$	295	5.5		Monod and Doussin, 2008	Recalculated value (g1)
$k_2 = 1.20 \times 10^9$	298	9			(g2)

Comments

(a) OH radicals produced by the Fenton reaction; reference reaction: $Fe^{2+} + \cdot OH$.
Reference rate constant was not mentioned in the paper (but can be found in NIST with 4.3×10^8 M^{-1} s^{-1}, http://kinetics.nist.gov/solution/Detail?id=1949MER/WAT15-25:4.

(b) The molar extinction coefficient of thymine was determined to be $\varepsilon_{264nm} = 7950 \pm 50$ over the pH range 1.2 - 7.8; Aerated solutions of thymine (8×10^{-5} M) were irradiated; Reference reaction: $\cdot OH$ + Thymine with $k(\cdot OH + \text{Thymine}) = 4.3 \times 10^9$ M^{-1} s^{-1}.

The pK_a value for Glycolic acid can be found in Lide (1996) (pKa = 3.83). The reference rate constant can be found in NIST (k(·OH + Thymine) = 6.4×10^9 M^{-1} s^{-1}, http://kinetics.nist.gov/solution/Detail?id=1967SCH/WIL2983-2993:11).

(c) Reference reaction (RR): ·OH + SCN^-; rate constant is given by $k(T) = 7.26 \times 10^{12} \exp[(-1900 \pm 190) / T]$ $M^{-1}s^{-1}$ after Chin and Wine (1992) (at pH= 6).

(d) Buxton et al. recalculated the rate constants as determined by the original authors using the selected rate constants for the reference reactions: 6.6×10^8 M^{-1} s^{-1} relative to Fe^{2+} + ·OH (no value given for Fenton reaction by Buxton et al.) (d1) and 5.4×10^8 M^{-1} s^{-1} relative to k(·OH + Thymine) = 6.4×10^9 M^{-1} s^{-1} (d2); Average of the recalculated rate constants (d3): 6.6×10^8 L mol^{-1} s^{-1} (Merz and Waters (1949)) and 5.4×10^8 L mol^{-1} s^{-1} (Scholes and Willson (1967)).

(e) Buxton et al. recalculated the rate constants as determined by Bell et al., 1975 using the selected rate constants for the reference reactions: 8.6×10^8 M^{-1} s^{-1} relative to k(·OH + SCN^-) = 1.1×10^{10} M^{-1} s^{-1}.

(f) Radicals generated by flash photolysis in N_2O saturated solutions; pH adjusted by KOH addition to a 3×10^{-2} M borax solution; reference reaction: ·OH + 4-ferrocenylbutanoate with k(·OH + 4-ferrocenylbutanoate) = 1.09×10^{10} $M^{-1}s^{-1}$; NIST lists this rate constant as 1.2×10^9 $M^{-1}s^{-1}$ relative to k(·OH + 4-ferrocenylbutanoate) = 1.6×10^{10} $M^{-1}s^{-1}$. http://kinetics.nist.gov/solution/Detail?id=1989LOG751-754:5

(g) Monod and Doussin recalculated the rate constants determined by the original authors, referring to their selected rate constants for the reference reaction; (g1): relative to k(·OH + SCN^-) = 1.2×10^{10} M^{-1} s^{-1} (Bell et al., 1975); (g2): relative to k(·OH + 4-ferrocenylbutanoate) = 1.6×10^{10} $M^{-1}s^{-1}$.

Preferred Values

Parameter	Value	*T*/K
k_1 / L mol^{-1} s^{-1}	6.0×10^8	298
k_2 / L mol^{-1} s^{-1}	8.6×10^8	295
Reliability		
$\Delta \log k_1$ $\Delta E_{A1}/R$	± 0.04	298
$\Delta \log k_2$ $\Delta E_{A1}/R$	± 0.04	295

Comments on Preferred Values

Two of the available rate constants agree, while the value of Scholes and Willson is lower by a factor of two. We are following the suggestion of Buxton et al. (1988) and recommend an average value of $k_1 = 6.0 \times 10^8$ L mol^{-1} s^{-1}. For k_2 the rate constant of Bell et al. (1975) is recommended. The error for the recommended value of k_1 is estimated the same as for k_2.

References

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