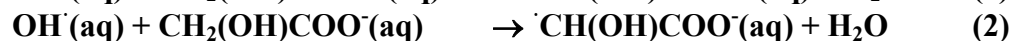
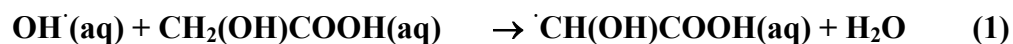


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

### – Data Sheet AQ\_TH1\_OH\_2

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



$\Delta G_R^{\circ}$  (aq): Aqueous phase thermochemical data not available

Gas phase data for comparison also not available.

#### Rate coefficient data

$k / \text{L mol}^{-1} \text{s}^{-1}$	$T/\text{K}$	$pH$	$I / \text{mol L}^{-1}$	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>					
$k_1 = 8.6 \times 10^8$		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:  $\text{Fe}^{2+} + \cdot\text{OH}$ . Reference rate constant was not mentioned in the paper (but can be found in NIST with  $4.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , <http://kinetics.nist.gov/solution/Detail?id=1949MER/WAT15-25:4>).
- (b) The molar extinction coefficient of thymine was determined to be  $\epsilon_{264\text{nm}} = 7950 \pm 50$  over the pH range 1.2 - 7.8; Aerated solutions of thymine ( $8 \times 10^{-5} \text{ M}$ ) were irradiated; Reference reaction:  $\cdot\text{OH} + \text{Thymine}$  with  $k(\cdot\text{OH} + \text{Thymine}) = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

The pK<sub>a</sub> value for Glycolic acid can be found in Lide (1996) (pK<sub>a</sub> = 3.83). The reference rate constant can be found in NIST ( $k(\cdot\text{OH} + \text{Thymine}) = 6.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , <http://kinetics.nist.gov/solution/Detail?id=1967SCH/WIL2983-2993:11>).

- (c) Reference reaction (RR):  $\cdot\text{OH} + \text{SCN}^-$ ; rate constant is given by  $k(T) = 7.26 \times 10^{12} \exp[(-1900 \pm 190) / T] \text{ M}^{-1} \text{ s}^{-1}$  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:  $6.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  relative to  $\text{Fe}^{2+} + \cdot\text{OH}$  (no value given for Fenton reaction by Buxton et al.) (d1) and  $5.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  relative to  $k(\cdot\text{OH} + \text{Thymine}) = 6.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (d2); Average of the recalculated rate constants (d3):  $6.6 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$  (Merz and Waters (1949)) and  $5.4 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$  (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:  $8.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  relative to  $k(\cdot\text{OH} + \text{SCN}^-) = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .
- (f) Radicals generated by flash photolysis in N<sub>2</sub>O saturated solutions; pH adjusted by KOH addition to a  $3 \times 10^{-2} \text{ M}$  borax solution; reference reaction:  $\cdot\text{OH} + 4\text{-ferrocenylbutanoate}$  with  $k(\cdot\text{OH} + 4\text{-ferrocenylbutanoate}) = 1.09 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ; NIST lists this rate constant as  $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  relative to  $k(\cdot\text{OH} + 4\text{-ferrocenylbutanoate}) = 1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .  
<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  $k(\cdot\text{OH} + \text{SCN}^-) = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (Bell et al., 1975); (g2): relative to  $k(\cdot\text{OH} + 4\text{-ferrocenylbutanoate}) = 1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .

#### Preferred Values

Parameter	Value	T/K
$k_1 / \text{L mol}^{-1} \text{ s}^{-1}$	$6.0 \times 10^8$	298
$k_2 / \text{L mol}^{-1} \text{ s}^{-1}$	$8.6 \times 10^8$	295
<i>Reliability</i>		
$\Delta \log k_1$	$\pm 0.04$	298
$\Delta E_{A1}/R$		
$\Delta \log k_2$	$\pm 0.04$	295
$\Delta E_{A1}/R$		

#### 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  $k_1 = 6.0 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ . 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  $k_2$ .

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