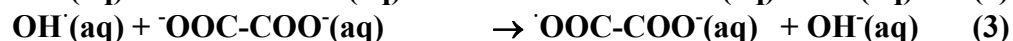
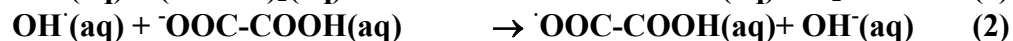
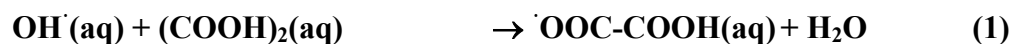


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_TH1_OH_4

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



ΔG_R° (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/K	pH	$I/ \text{mol L}^{-1}$	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>					
$k_{1/2} = 3.2 \times 10^7$		2		Scholes and Willson, 1967	PR-UV/Vis (a)
$k_1 = (1.0 \pm 0.1) \times 10^6$		0.5		Getoff et al., 1971	PR-UV/Vis (b)
$k_2 = (3.2 \pm 0.1) \times 10^7$		3			
$k_3 = (5.3 \pm 0.3) \times 10^6$		6			
$k_1 = 1.4 \times 10^6$	298	0.5		Buxton et al., 1988	Recalculated value (c)
$k_2 = 4.7 \times 10^7$	298	3			
$k_3 = 7.7 \times 10^6$	298	6			
$k_2 = (1.9 \pm 0.6) \times 10^8$	298	3		Ervens et al., 2003	LP(d)
$k_2 = 2.5 \times 10^{12}$ $\exp[(-2800 \pm 500)/T]$	288 - 328				
$k_3 = (1.6 \pm 0.6) \times 10^8$	298	8			
$k_3 = 4.6 \times 10^{14}$ $\exp[(-4300 \pm 1200)/T]$	288 - 328				
<i>Absolute Rate Coefficients</i>					
$k_2 = (5.0 \pm 0.5) \times 10^7$		2.5 – 3.5		Ershov et al., 2008	PR - UV/Vis(e)
$k_3 = (1.5 \pm 0.2) \times 10^7$		6.9 – 7.4		Ershov et al., 2008	PR-UV/Vis(f)

Comments

- (a) 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 (8×10^{-5} M) were irradiated. Reference reaction: $\cdot\text{OH} + \text{Thymine}$ with $k(\cdot\text{OH} + \text{Thymine}) = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

- (b) PR of N₂O-, or Argon-saturated solutions; [(COO⁻)₂] = (0.6 - 10) × 10⁻³ M; Reference reaction: ·OH + SCN⁻ with $k(\cdot\text{OH} + \text{SCN}^-) = 7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; pK_a values which were given in Getoff et al. (1971) and Buxton et al. (1988) are in good agreement with those from Lide (1996) (1.23, respectively 4.19).
- (c) Buxton et al. recalculated the rate constants determined by Getoff et al. (1971) relative to the selected rate constant for the reference reaction $k(\cdot\text{OH} + \text{SCN}^-) = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.
- (d) RR; hydrogen peroxide photolysis (λ = 248 nm); pH was adjusted with HClO₄; Reference reaction: ·OH + SCN⁻; Rate constant of the reference reaction is given by $k(T) = 7.26 \times 10^{12} \exp[(-1900 \pm 190) / T] \text{ M}^{-1} \text{ s}^{-1}$ referring to Chin and Wine (1992).
- (e) PR of N₂O- or Argon-saturated solutions; c(Na₂(COO)₂) = 2 × 10⁻² M; reaction was observed spectroscopically at 250 nm.
- (f) PR of N₂O- or Argon-saturated solutions; c((COO⁻)₂) = 5 × 10⁻³ M; The radical anion ·OOC-COO⁻ exhibits absorption that monotonically increases on going to 220 nm (ε_{220nm} = 1800 L mol⁻¹ cm⁻¹).

Preferred Values

Parameter	Value	T/K
$k_1 / \text{L mol}^{-1} \text{ s}^{-1}$	$k_1 = 1.4 \times 10^6$	298
$k_2 / \text{L mol}^{-1} \text{ s}^{-1}$	$k_2 = 1.0 \times 10^8$	298
$k_3 / \text{L mol}^{-1} \text{ s}^{-1}$	$k_3 = 6 \times 10^7$	298
<i>Reliability</i>		
Δ log k_1	± 0.11	298
Δ log k_2	± 0.30	298
Δ log k_3	± 0.20	298

Comments on Preferred Values

Available rate constants are largely scattered. Therefore, only room temperature rate constants are recommended as follows: For k_1 (the undissociated oxalic acid reaction) the recommendation is the value of Buxton et al. (1988). For k_2 (oxalate mono-anion) the recommended value is the average of the room temperature rate constants given by Buxton et al. (1988) and Ervens et al. (2003). For the oxalate dianion reaction (k_3), the recommended value is the average of the data by Buxton et al. (1988), Ervens et al. (2003) and Ershov et al (2007). The relative errors of the average recommended rate constants is estimated to ± 20 %, ± 50 % and ± 30 % for k_1 , k_2 and k_3 , respectively. No T-dependence is currently recommended. Overall, based on the currently existing kinetic data for this set of OH reactions further measurements appear to be required to better resolve the existing discrepancies.

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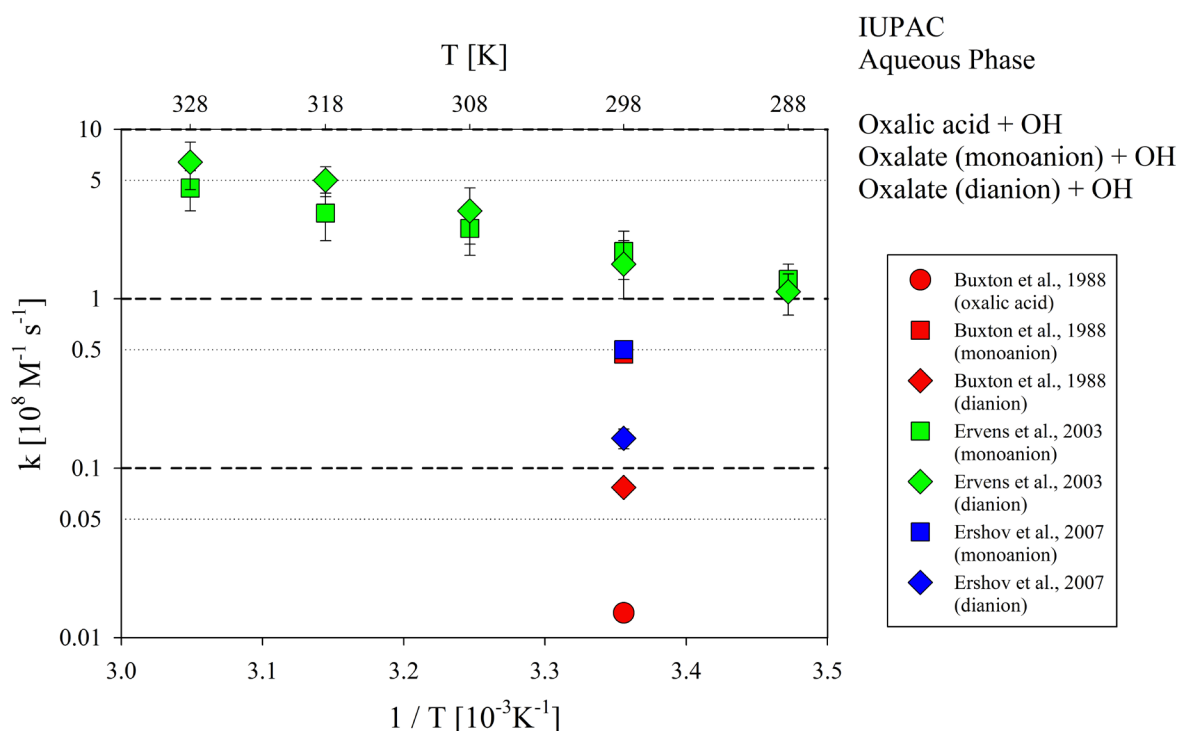


Figure 1: T-dependent rate constants for the reaction of Oxalic acid (monoanion and dianion, respectively) with OH in aqueous solution. Data taken from Buxton et al. (1988), Ervens et al. (2003) and Ershov et al (2007).