IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

 – Data Sheet AQ\_TH1\_OH\_4

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**OH·(aq) + (COOH)2(aq) → ·OOC-COOH(aq) + H2O (1)**

**OH·(aq) + -OOC-COOH(aq) → ·OOC-COOH(aq)+ OH-(aq) (2)**

**OH·(aq) + -OOC-COO-(aq) → ·OOC-COO-(aq) + OH-(aq) (3)**

*GR*° (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*1/2 =  3.2 × 107 |  | 2 |  | Scholes and Willson, 1967 | PR-UV/Vis (a) |
| *k*1 = (1.0 ± 0.1) × 106 |  | 0.5 |  | Getoff et al., 1971 | PR-UV/Vis (b) |
| *k*2 =  (3.2 ± 0.1) × 107 |  | 3 |  |
| *k*3 =  (5.3 ± 0.3) × 106 |  | 6 |  |
| *k*1 = 1.4 × 106 | 298 | 0.5 |  | Buxton et al., 1988 | Recalculated value (c) |
| *k*2 = 4.7 × 107 | 298 | 3 |  |
| *k*3 = 7.7 × 106 | 298 | 6 |  |
| *k*2 =  (1.9 ± 0.6) × 108 | 298 | 3 |  | Ervens et al., 2003 | LP(d) |
| *k*2 = 2.5 × 1012 exp[(‑2800 ± 500)/T] | 288 - 328 |  |
| *k*3 =  (1.6 ± 0.6) × 108 | 298 | 8 |  |
| *k*3 = 4.6 × 1014 exp[(‑4300 ± 1200)/T] | 288 - 328 |  |
| *Absolute Rate Coefficients* |
| *k*2 =  (5.0 ± 0.5) × 107 |  | 2.5 – 3.5 |  | Ershov et al., 2008 | PR - UV/Vis(e) |
| *k*3 =  (1.5 ± 0.2) × 107 |  | 6.9 – 7.4 |  | Ershov et al., 2008 | PR-UV/Vis(f) |

**Comments**

(a) The molar extinction coefficient of thymine was determined to be ε 264nm = 7950 ± 50 over the pH range 1.2 - 7.8. Aerated solutions of thymine (8 × 10‑5 M) were irradiated. Reference reaction: ·OH + Thymine with *k*(·OH + Thymine) = 4.3 × 109 M-1 s-1.

(b) PR of N2O-, or Argon-saturated solutions; [(COO‑)2] = (0.6 ‑ 10) × 10‑3 M; Reference reaction: [·OH](http://webbook.nist.gov/cgi/cbook.cgi?ID=3352576&Units=SI) + SCN- with *k*([·OH](http://webbook.nist.gov/cgi/cbook.cgi?ID=3352576&Units=SI) + SCN-) = 7.5 × 109 M-1 s-1; pKa 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*([·OH](http://webbook.nist.gov/cgi/cbook.cgi?ID=3352576&Units=SI) + SCN-) = 1.1 × 1010 M-1 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 × 1012 exp[(-1900 ± 190) / T] M-1s-1 referring to Chin and Wine (1992).

(e) PR of N2O- or Argon-saturated solutions; *c*(Na2(COO)2) = 2 x 10-2 M; reaction was observed spectroscopically at 250 nm.

(f) PR of N2O- or Argon-saturated solutions; *c*((COO-)2) = 5 x 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** |
|  |  |  |
| *k1* /L mol-1 s-1 | *k*1 = 1.4 × 106 | 298 |
|  |  |  |
| *k2* / L mol-1 s-1 | *k*2 = 1.0× 108 | 298 |
|  |  |  |
| *k3* / L mol-1 s-1 | *k*3 = 6 × 107 | 298 |
|  |  |  |

*Reliability*

|  |  |  |
| --- | --- | --- |
| Δ log *k1* | ± 0.11 | 298 |
|  |  |  |
| Δ log *k2* | ± 0.30 | 298 |
|  |  |  |
| Δ log *k3* | ± 0.20 | 298 |
|  |  |  |

*Comments on Preferred Values*

Available rate constants are largely scattered. Therefore, only room temperature rate constants are recommended as follows: For k1 (the undissociated oxalic acid reaction) the recommendation is the value of Buxton et al. (1988). For k2 (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 (k3), 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.

**References**

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