IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

 – Data Sheet AQ\_TH1\_NO3\_4

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**NO3·(aq) + (COOH)2(aq) → ·OOC-COOH(aq) + HNO3 (1)**

**NO3·(aq) + -OOC-COOH(aq) → ·OOC-COOH(aq) + NO3-(aq) (2)**

**NO3·(aq) + -OOC-COO- (aq) → ·OOC-COO-(aq) + NO3-(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 |
| *Absolute Rate Coefficients* |
| *k*2 = 8.4 × 109 exp[-(2180 ± 660)/T] | 278 - 298 | 1 |  | Zellner et al., 1996Raabe, 1996 | LFP- LPLA (a) |
| *k*2 = (6.1 ± 1.5) × 106 | 298 | 1 |  |
|  |  |  |  |
| *k*3 = 3.2 × 1011 exp[(-2526 ± 1680)/T] | 278 - 298 | 9 |  |
| *k*3 = (2.1 ± 0.6) × 108 | 298 | 9 |  |
|  |  |  |  |
| (1.4 ± 0.4) × 108 | 298 |  | I → 0 | Herrmann et al., 2003 | LFP- LPLA (b) |
| (2.0 ± 0.4) × 108 |  | I → ∞ |
| *k*1 = (2.4 ± 0.2) × 104 | 298 | <0 |  | Yang et al., 2004 | PR(c) |
| *k*2 = (7.8 ± 0.7) × 107 | 3 |  |
| *k*3 = (2.2 ± 0.1) × 108 | 7 |  |
| *k*1 < 5 × 104 | 298 |  |  | G. de Semainville et al., 2010 | LFP - Teflon Waveguide/ S2O82-(d) |
| *k*2 = (4.4 ± 0.2) × 107 |
| *k*3 = (2.2 ± 0.8) × 108 | 2.7 |  |
| *k*3 = 2.2 × 1012 exp[(-2766 ± 720)/T] | 278 - 298 | 8 |  |

**Comments**

(a) Project report with strongly summarized results from the Ph.D. thesis of Raabe (1996). Measurements at pH = 1 (cf. pKa values from Lide (1996) of 1.23 and 4.19, respectively) have been corrected to obtain the given Arrhenius expression and room temperature rate constant for the reaction of NO3 with the oxalate mono-anion (*k*2). In the cited project report an additional rate constant of *k*obs = (1.7 ± 0.5) × 108 l mol-1 s-1 for pH = 4 is given. It is important to note that this value is an uncorrected observed rate constant representing a mixture of *k*2 and *k*3.

(b) The I –effect was studied at pH = 4 and T =298 K (Dissertation G. Raabe, 1996). Reviewed data from Zellner et al. (1996) and Herrmann et al. (1998).

(c) Direct measurement; NO3 radicals generated by pulse radiolysis of N2O saturated HNO3 solution (2.0 M) and Ar saturated NaNO3 solution (1.0 M); analyzing light: 630 nm; reactions were carried out at ambient temperature.

(d) NO3 radicals were produced through laser flash photolysis of peroxodisulfate in presence of nitrate anion at 355 nm; He-Ne laser was used as the analyzing light (output wavelength of 633 nm); Liquid core waveguide (LCW) setup (made of Teflon AF 2400) was used. (length of 50 cm / inner volume of 0.25 mL); temperature dependent data for rate constants were used from plotted expression.

**Preferred Values**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | ***T*/K** |
|  |  |  |
| *k1* / l mol-1 s-1 | 2.4 × 104 | 298 |
|  |  |  |
| *k2* / l mol-1 s-1 | 6.1 × 106 | 298 |
|  | 8.4 × 109 exp[-(2180)/T] | 278 – 298 K |
|  |  |  |
| *k3* / l mol-1 s-1 | 1.7 × 107 | 298 |
|  | 1.3 × 1012 exp[(-2650)/T] | 278 – 298 K |

*Reliability*

|  |  |  |
| --- | --- | --- |
| Δ log *k1* | ± 0.03  | 298 |
|  |  |  |
| Δ log *k2* | ± 0.11 | 298 |
| Δ EA2/R | ± 660 | 278 – 298 |
|  |  |  |
| Δ log *k3* | ± 0.08 | 298 |
| Δ EA3/R | ± 1200 | 278 - 298 |
|  |  |  |

*Comments on Preferred Values*

For the reaction with the undissociated acid the rate constant *k*1 by Yang et al. (2004) is recommended. For the reaction with the mono-anion (*k*2) the rate constant from the determinations of Zellner et al. (1996) and Raabe (1996) is recommended. Possibly, the higher Yang et al. (2004) and Semainville et al (2010) rate constants might be due to contributions of the faster di-anion reactions. Then, for the reaction with the di-anion (*k*3), data of all the three mentioned studies are averaged.

T-dependent data: For the reaction with the mono-anion (*k*2) the Arrhenius expression by Zellner et al. (1996) is recommended. For the reaction with the di-anion (*k*3), the average T-dependence of Zellner et al. (1996) with Raabe (1996) and de Semainville et al. (2010) is recommended.

**References**

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Yang, X. K., Wang, J. Q. and Wang, T. D.: Chin. Chem. Lett., 15, 583 ‑ 586, 2004.

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Figure 1: T-dependent rate constants for the reaction of oxalic acid with NO3 in aqueous solution. Data from Zellner et al. (1996), Herrmann et al. (2003), Yang et al. (2004) and de Semainville et al. (2010). ); the regression for the dianion refers to data by Raabe (1996) and de Semainville et al. (2010); the regression for the monoanion refers to data from Zellner et al. (1996) and Raabe (1996); as the rate constant for oxalic acid by Yang et al. (2004) was the only available value, it was not considered in the Arrhenius plot.