IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet AQ_TH1_NO3_4

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

$$NO_3^{\cdot}(aq) + (COOH)_2(aq) \rightarrow {}^{\cdot}OOC\text{-}COOH(aq) + HNO_3 \quad (1)$$
$$NO_3^{\cdot}(aq) + {}^{-}OOC\text{-}COOH(aq) \rightarrow {}^{\cdot}OOC\text{-}COOH(aq) + NO_3^{-}(aq) \quad (2)$$
$$NO_3^{\cdot}(aq) + {}^{-}OOC\text{-}COO^{-}(aq) \rightarrow {}^{\cdot}OOC\text{-}COO^{-}(aq) + NO_3^{-}(aq) \quad (3)$$

$\Delta G_R°$ (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
Absolute Rate Coefficients					
$k_2 = 8.4 \times 10^9 \exp[-(2180 \pm 660)/T]$	278 - 298	1		Zellner et al., 1996 Raabe, 1996	LFP- LPLA (a)
$k_2 = (6.1 \pm 1.5) \times 10^6$	298	1			
$k_3 = 3.2 \times 10^{11} \exp[(-2526 \pm 1680)/T]$	278 - 298	9			
$k_3 = (2.1 \pm 0.6) \times 10^8$	298	9			
$(1.4 \pm 0.4) \times 10^8$	298		$I \rightarrow 0$	Herrmann et al., 2003	LFP- LPLA (b)
$(2.0 \pm 0.4) \times 10^8$			$I \rightarrow \infty$		
$k_1 = (2.4 \pm 0.2) \times 10^4$	298	<0		Yang et al., 2004	PR(c)
$k_2 = (7.8 \pm 0.7) \times 10^7$		3			
$k_3 = (2.2 \pm 0.1) \times 10^8$		7			
$k_1 < 5 \times 10^4$	298			G. de Semainville et al., 2010	LFP - Teflon Waveguide/ $S_2O_8^{2-}$(d)
$k_2 = (4.4 \pm 0.2) \times 10^7$					
$k_3 = (2.2 \pm 0.8) \times 10^8$		2.7			
$k_3 = 2.2 \times 10^{12} \exp[(-2766 \pm 720)/T]$	278 - 298	8			

Comments

(a) Project report with strongly summarized results from the Ph.D. thesis of Raabe (1996). Measurements at pH = 1 (cf. pK_a 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 NO_3 with the oxalate mono-anion (k_2). In the cited project report an additional rate constant of $k_{obs} = (1.7 \pm 0.5) \times 10^8$ 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; NO_3 radicals generated by pulse radiolysis of N_2O saturated HNO_3 solution (2.0 M) and Ar saturated $NaNO_3$ solution (1.0 M); analyzing light: 630 nm; reactions were carried out at ambient temperature.

(d) NO_3 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
k_1 / l mol^{-1} s^{-1}		2.4×10^4	298
k_2 / l mol^{-1} s^{-1}		6.1×10^6	298
		8.4×10^9 exp[-(2180)/T]	278 – 298 K
k_3 / l mol^{-1} s^{-1}		1.7×10^7	298
		1.3×10^{12} exp[(-2650)/T]	278 – 298 K
Reliability			
$\Delta \log k_1$	± 0.03		298
$\Delta \log k_2$	± 0.11		298
$\Delta E_{A2}/R$	± 660		278 – 298
$\Delta \log k_3$	± 0.08		298
$\Delta E_{A3}/R$	± 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

Herrmann, H.; Zellner, R. In "N-Centered Radicals". Alfassi, Z. B., Ed.; John Wiley and Sons: New York; pp. 291; 1998.

Herrmann, H.: Chem. Rev., 103 (12), 4691–4716, 2003.

Lide, D.R.: "CRC Handbook of Chemistry and Physics", 76th Ed., CRC Press, Boca Raton, 1996.

Raabe, G., Dissertation, Essen 1996.

Semainville, Ph. G. de., D'Anna, B. and George, Ch.: Z. Phys. Chem., 224(7-8), 1247 - 1260, 2010.

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

Zellner, R., Herrmann, H., Exner, M., Jacobi, H.-W., Raabe, G. and Reese, A. In "Heterogeneous and Liquid-Phase Processes". Warneck, P., Ed.; Springer: Berlin, pp. 146, 1996.

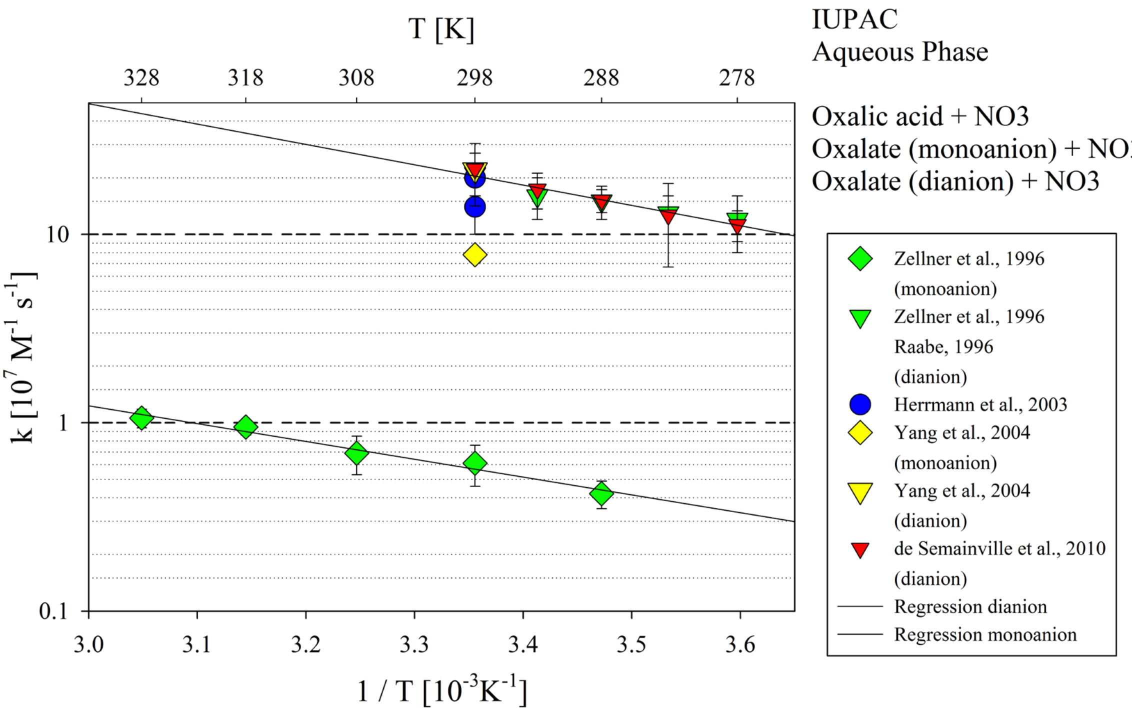

Figure 1: T-dependent rate constants for the reaction of oxalic acid with NO_3 in aqueous solution. Data from Zellner et al. (1996), Herrmann et al. (2003), Yang et al. (2004) and de Semainville et al. (2010).); the regression for the dianion refers to data by Raabe (1996) and de Semainville et al. (2010); 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.