IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_TH1_OH_3

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

$$OH^{\cdot}(aq) + CH(OH)_2COOH(aq) \rightarrow {}^{\cdot}C(OH)_2COOH + H_2O \quad (1)$$

$$OH^{\cdot}(aq) + CH(OH)_2COO^{-}(aq) \rightarrow {}^{\cdot}C(OH)_2COO^{-} + H_2O \quad (2)$$

$\Delta G_R°$ (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
Relative Rate Coefficients					
$k_1 = (3.6 \pm 0.2) \times 10^8$	298	1		Ervens et al. 2003	LP(a)
$k_1 = 8.1 \times 10^9$ exp[-(1000 ± 400) / T]	288 - 328				
$k_2 = (2.6 \pm 0.9) \times 10^8$	298	8			
$k_2 = 6.0 \times 10^{15}$ exp[-(4500 ± 800) / T]	288 - 328				

Glyoxylic acid is hydrated in water, as shown in the following equation:

CHOCOOH + H_2O (1) → $CH(OH)_2COOH$(aq) with K = 5.4 M^{-1}, (Sørensen et al., 1974)

pKa value for glyoxylic acid can be found in Lide (1996) (pK_a = 3.18).

Comments

(a) Laser photolysis of H_2O_2 (c = 5 × 10^{-4} M, λ = 248 nm); pH adjusted to pH = 1 by $HClO_4$. Analysis light at λ = 436 nm; Reference reaction (RR): ·OH + SCN^-; rate constant is given by k(T) = 7.26 × 10^{12} exp[(-1900 ± 190) / T] M^{-1}s^{-1} after Chin and Wine (1992) (at pH = 6).

Preferred Values

Parameter	Value	*T*/K
k_1 / l mol^{-1} s^{-1}	3.6×10^8	298
k_1 / l mol^{-1} s^{-1}	8.1×10^9 exp[- (1000) / *T*]	293-353
k_2 / l mol^{-1} s^{-1}	2.6×10^8	298
k_2 / l mol^{-1} s^{-1}	6.0×10^{15} exp[- (4500) / *T*]	293-353

Reliability

$\Delta \log k_1$	± 0.02	298
$\Delta E_{A1}/R$	± 400	293-353
$\Delta \log k_2$	± 0.16	298
$\Delta E_{A2}/R$	± 800	293-353

Comments on Preferred Values

These are the only available kinetic data on these reactions.

References

Chin, M., and Wine, P. H: J. Photochem. Photobiol., A, 69(1), 17-25, 1992.

Ervens, B., Gligorovski, S. and Herrmann, H.: Phys. Chem. Chem. Phys., 5(9), 1811-1824, 2003.

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

Sørensen, P. E.; Bruhn, K. and Lindelov, F.: Acta Chem. Scand., 28(2), 162 - 168 , 1974.

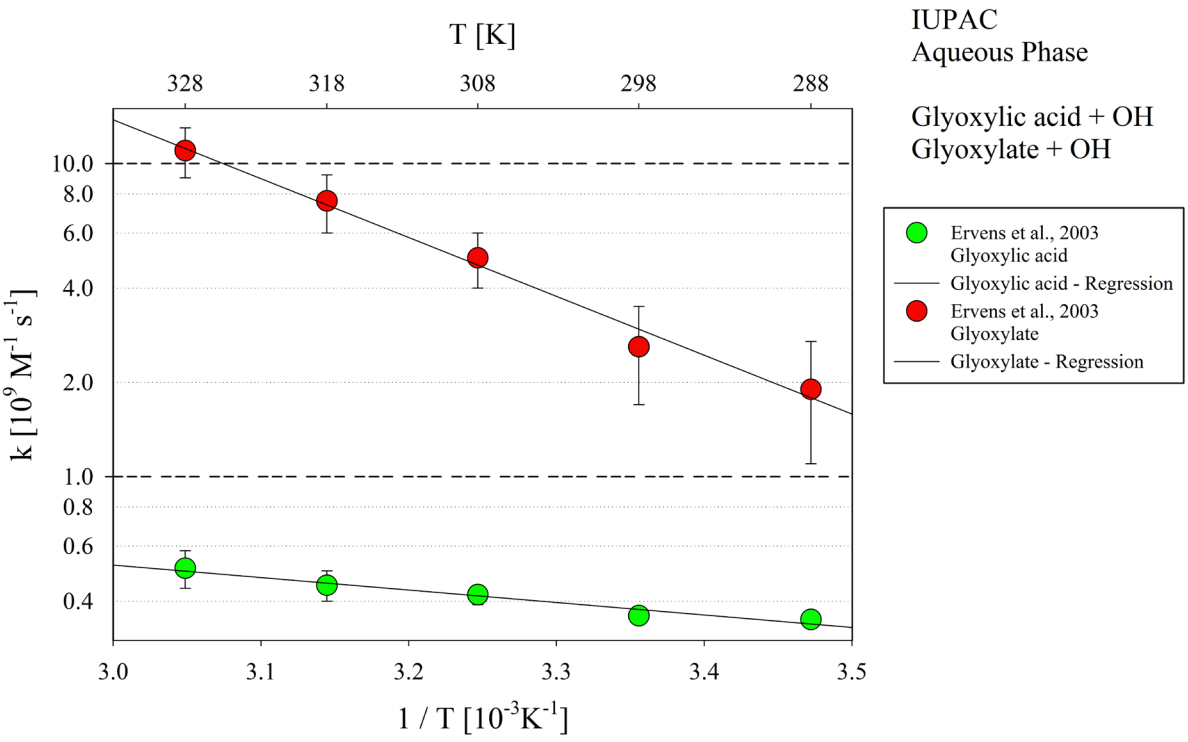

Figure 1: T-dependent rate constants for the reaction of glyoxylic acid and glyoxylate with OH in aqueous solution. Data from Ervens et al. (2003).