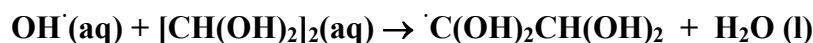


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_TH1_OH_1

Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. The citation for this datasheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

This datasheet last evaluated: May 2017; last change in preferred values: May 2016



Aqueous phase thermochemical data not available. Thermochemical gas phase data for comparison also not available because of the hydration of glyoxal in aqueous solution.

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>					
6.6×10^7	298	1.3		Buxton et al., 1988	(a)
$(1.10 \pm 0.04) \times 10^9$	293	2.0 – 6.0		Buxton et al., 1997	PR-UV/Vis (b1)
$(1.10 \pm 0.1) \times 10^9$	293	4			PR-UV/Vis (b2)
$1.9 \times 10^{11} \exp[(-1516 \pm 30)/T]$	279 - 319	4			
$(9.4 \pm 0.4) \times 10^8$	298	2.0		Schaefer et al., 2015	LFP (c)
$(9.2 \pm 0.5) \times 10^8$	298	6.0			
$(1.1 \pm 0.1) \times 10^9$	298	9.0			
$5.8 \times 10^{10} \exp[(-1200 \pm 120)/T]$	278 - 318	6.0			

Comments

(a) Buxton et al. refers to a value determined by Draganic and Marcovic (1968, unpublished work) in their review, relative to $\cdot\text{OH} + \text{oxalic acid}$; for the rate constant of oxalic acid, Buxton et al. recommends $k(\cdot\text{OH} + \text{oxalic acid}) = 1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; these values are also given in the NIST database.

<http://kinetics.nist.gov/solution/Detail?id=1968DRA/MARB:1>

(b) Measured in N_2O -saturated solution; competition kinetics; reference reaction: $\cdot\text{OH} + \text{Fe}(\text{CN})_6^{4-}$ with $k(\cdot\text{OH} + \text{Fe}(\text{CN})_6^{4-}) = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988); measured at $\lambda = 420 \text{ nm}$; the rate constant has been confirmed by direct observation; temperature dependent data was gathered via direct observation with no specific values for $k(T)$

given; activation energy is given as $E_A = (12.6 \pm 0.9) \text{ kJ mol}^{-1}$; Arrhenius expression was calculated using the given data; reviewed by Schaefer et al. (2015).

- (c) Reference reaction (RR): $\cdot\text{OH} + \text{SCN}^-$; rate constant is given by $k(T) = 7.26 \times 10^{12} \exp[-(1900 \pm 190) / T] \text{ M}^{-1}\text{s}^{-1}$ according to Chin and Wine (1992) (at pH = 6). An activation energy E_A of $(12.6 \pm 0.9) \text{ kJ mol}^{-1}$ was obtained from direct measurements of k .

Preferred Values

Parameter	Value	T/K
$k / \text{l mol}^{-1} \text{ s}^{-1}$	9.2×10^8	298
$k / \text{l mol}^{-1} \text{ s}^{-1}$	$5.8 \times 10^{10} \cdot \exp[-(1200)/T]$	278 - 318
<i>Reliability</i>		
$\Delta \log k$	± 0.390	298
$\Delta E_A/R$	± 120	278 - 318

Comments on Preferred Values

The recent T-dependent determination by Schaefer et al. (2015) leads to a slightly lower rate constant than suggested by Buxton et al. in the first determination of this rate constant when the data for pH 6 are compared. The value previously recommended by Buxton et al. (1988) as determined by Draganic and Marcovic (1968, unpublished) is not confirmed by the later determinations.

References

- Adams, G. E., and R. L. Willson: *Trans. Faraday Soc.*, 65, 2981-2987, 1969.
- Buxton, George V., Malone, T. N. and Salmon, G. Arthur: *J. Chem. Soc., Faraday Trans.*, 93, 2889-2891, 1997.
- Chin, M., and Wine, P. H: *J. Photochem. Photobiol.*, A, 69(1), 17-25, 1992.
- Ervens, B., and Volkamer, R.: *Atmos. Chem. Phys.*, 10 (17), 8219 – 8244, 2010.
- Schaefer, T., van Pinxteren, D., and Herrmann, H.: *Environ. Sci. Technol.*, 49, 343 – 350, 2015.

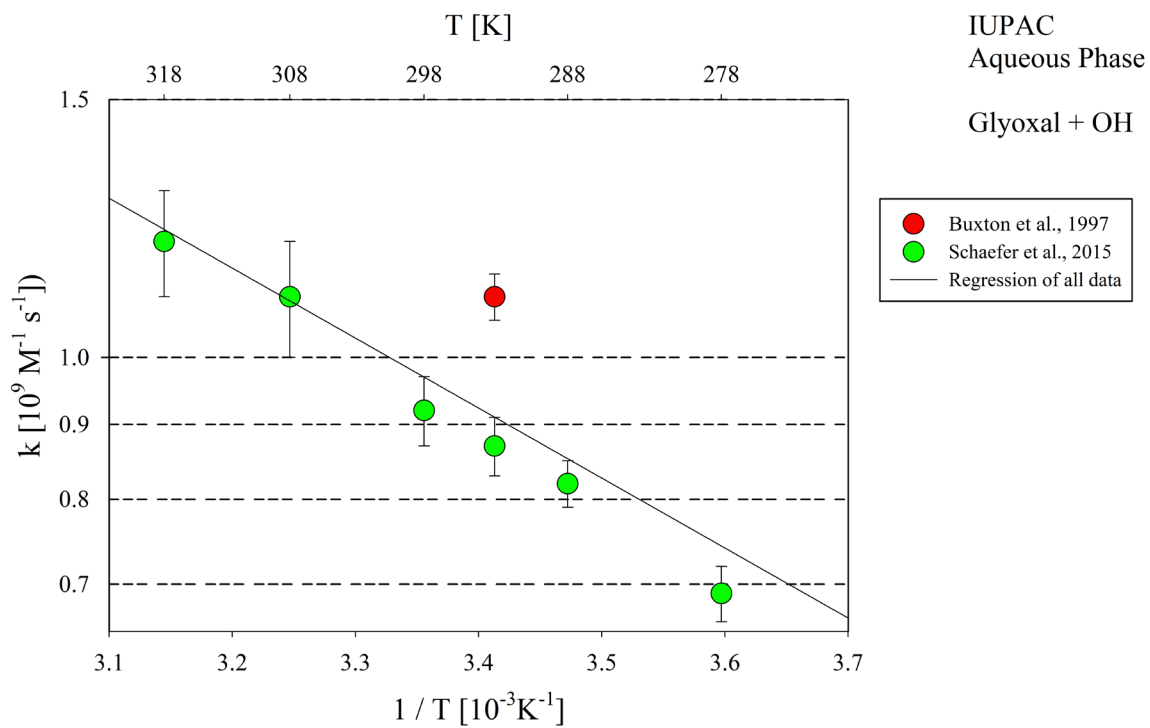


Figure 1: T-dependent rate constants for the reaction of glyoxal with OH in aqueous solution. Data from Buxton et al. (1997) and Schaefer et al. (2015).