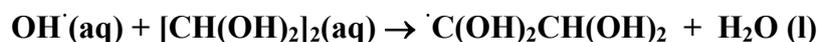


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

### – Data Sheet AQ\_TH1\_OH\_1

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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

$k/\text{L mol}^{-1} \text{s}^{-1}$	$T/\text{K}$	$pH$	$I/\text{mol L}^{-1}$	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>					
$6.6 \times 10^7$	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 refers to a value determined by Draganic and Marcovic (1968, unpublished work) in their review, relative to  $\cdot\text{OH} + \text{oxalic acid}$ ; for the rate constant of oxalic acid, Buxton et al.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  $\text{N}_2\text{O}$ -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
$k / \text{l mol}^{-1} \text{ s}^{-1}$	$9.2 \times 10^8$	298
$k / \text{l mol}^{-1} \text{ s}^{-1}$	$5.8 \times 10^{10} \cdot \exp[-(1200)/T]$	278 - 318
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.390$	298
$\Delta E_A/R$	$\pm 120$	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

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- Ervens, B., and Volkamer, R.: *Atmos. Chem. Phys.*, 10 (17), 8219 – 8244, 2010.
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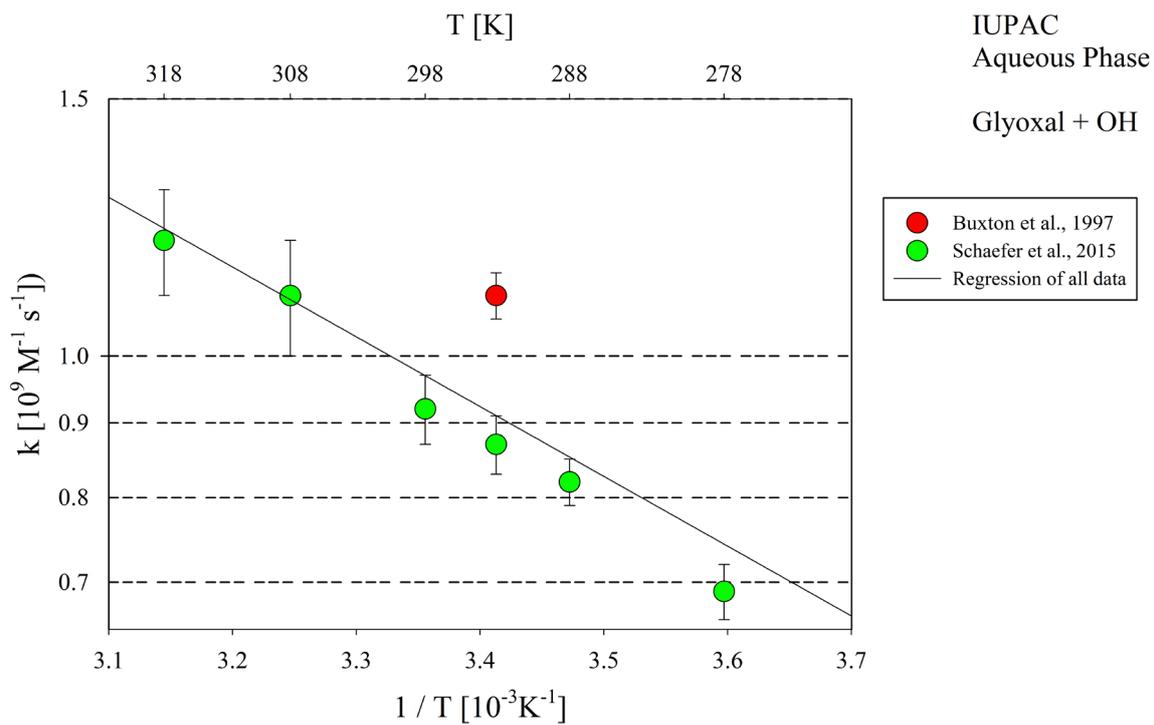


Figure 1: T-dependent rate constants for the reaction of glyoxal with OH in aqueous solution. Data from Buxton et al. (1997) and Schaefer et al. (2015).