

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

### – Data Sheet AQ\_OH\_63

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This datasheet last evaluated: November 2019; last change in preferred values: June 2019



#### Rate coefficient data

k/ L mol <sup>-1</sup> s <sup>-1</sup>	T/K	pH	I/ mol L <sup>-1</sup>	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>					
$(3.9 \pm 0.7) \times 10^9$	298	6.2	-	Hesper, 2003	LP / LPA (a)
$8.1 \times 10^{10} \exp[-(900 \pm 300)/T]$	288 - 328	6.2	-		
<i>Relative Rate Coefficients</i>					
$3.88 \times 10^9$	294	2	-	Adams et al., 1965	PR / UV-Vis (b)
$(3.84 \pm 0.7) \times 10^9$	298	2	-	Monod et al., 2005	Fenton reaction (c)

The equilibrium constant for the hydration (1) is recommended as  $K_{298\text{ K}} = 0.60$  by Doussin and Monod (2013).

$\Delta G_R^\circ$  (aq): Aqueous phase thermochemical data not available. As well, gas phase thermochemical data  $H_R^\circ$  (g) are not available.

#### Comments

- (a) Direct observation of the peroxy-radicals at 248 nm, formed by the reaction between HO, butanal and O<sub>2</sub>. Reviewed by Herrmann (2003).
- (b) Reference reaction:  $k(\text{HO} + \text{SCN}^-) = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ; a recalculation has been performed using the selected T dependence for the reference reaction by Zhu et al. (2003); no exact value is given for the initial concentrations of the reactants; as no exact temperature is given, a room temperature of 294 K is assumed.
- (c) Radicals generated by dark Fenton reaction; Global rate constant for the reaction of HO radicals with butanal (2) and its hydrate (3) has been determined;  $K_{\text{hyd}}(25^\circ \text{C})$  was considered to be 0.42 (Bell and Evans, 1966); no specific information given on the reference reactions used for the determination; in general, multiple references were used:

HO + methanol;  $k(T) = 9.7 \times 10^8 \exp[-4800/R(1/T-1/298)]$  (Elliot and Simsons, 1984); HO + 2-propanol;  $k(T) = 1.6 \times 10^9 \exp[-5000/R(1/T-1/298)]$  (Elliot and Simsons, 1984); HO + formaldehyde;  $k(T) = \exp[(23.9 \pm 0.29) - (1020 \pm 90/T)]$  (Chin and Wine, 1994).

### Preferred Values

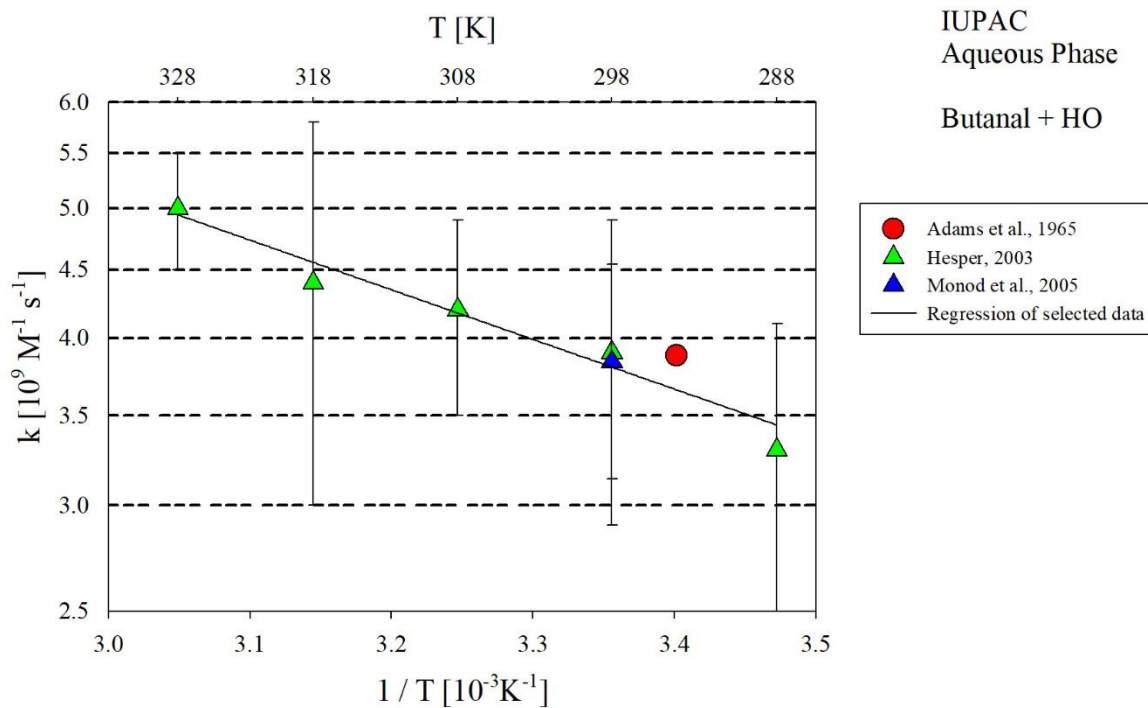
Parameter	Value	T/K
$k / \text{L mol}^{-1} \text{ s}^{-1}$	$3.79 \times 10^9$	298
$k / \text{L mol}^{-1} \text{ s}^{-1}$	$7.23 \times 10^{10} \exp[-(880)/T]$	288 - 328
<i>Reliability</i>		
$\Delta \log k$	0.09	298
$\Delta E_A/R$	$\pm 90$	288 - 328

### Comments on Preferred Values

Since the last recommendation of Buxton et al. in 1988, referring to the rate coefficient by Adams et al. (1965) a temperature dependent study by Hesper (2003) became available. The combined data of both agree well within error limits. The rate coefficient determined by Monod et al. (2005) could not be used for further evaluation, as the publication does not refer to the specific reference reactions. It is assumed, that the value given results from a mean of determinations versus several reference systems. While their determination confirms the data of Hesper (2003), it is therefore not included in the regression for the determination of the preferred value. The estimated uncertainty is given as  $\Delta \log k = \pm 0.09$  or  $\pm 20\%$ .

### References

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T-dependent rate constants for the reaction of butanal with HO in aqueous solution. Data from Adams et al. (1965) and Hesper (2003) have been used for regression.