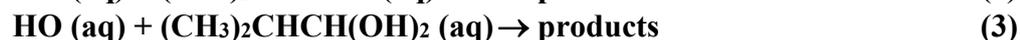
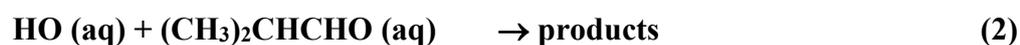
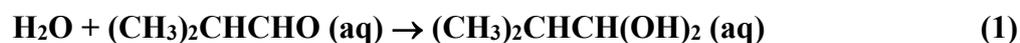


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_64

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



Rate coefficient data

$k/\text{L mol}^{-1} \text{s}^{-1}$	T/K	pH	I/ mol L ⁻¹	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>					
2.6×10^9	294	7	-	Acero et al., 2001	Competition kinetics / HPLC (a)
$(2.8 \pm 1.0) \times 10^9$	298	-	-	Gligorovski and Herrmann, 2004	LP-LPA (b)
$1.4 \times 10^{10} \exp[-(500 \pm 100)/T]$	288 - 328	-	-		LP-LPA (b)
$(2.8 \pm 1.5) \times 10^9$	298	-	-	Moise et al., 2005	LCW / photolysis (c)
2.3×10^9	298	-	-	Jürgens et al., 2007	CFSR / HRGC (d)

The equilibrium constant for the hydration (1) is recommended as $K_{298 \text{ K}} = 0.50$ by Doussin and Monod (2013).

ΔG_R° (aq): Aqueous phase thermochemical data not available. As well, gas phase thermochemical data H_R° (g) are not available.

Comments

- (a) HO radicals were generated by addition of O₃ (0.25 – 5 mg/L) to the aqueous solution; products analyzed by HPLC. Reference reaction: HO + pCBA with $k(\text{HO} + \text{pCBA}) = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (recommendation by Buxton et al., 1988); the rate coefficient has been recalculated using the recommended value for the reference reaction $k = 4.64 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; Indigo method, as described by Bader and Hoigné (1981) was used for analyzing dissolved ozone; as no exact temperature is given, T = 294 K is assumed for room temperature.
- (b) The overall reactions of the aldehyde and its hydrate were investigated; reference reaction: HO + SCN⁻ with $k(\text{HO} + \text{SCN}^-) = 1.24 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ as determined by Chin and Wine (1992); the rate coefficient has been recalculated using the recommended values for the

temperature dependent reference reaction by Zhu et al. (2003); 39% of the aldehyde is considered to be in hydrate form, with $K_H(298\text{ K}) = 0.64$, according to Pocker and Dickerson (1969).

- (c) HO radicals were generated by photolysis of H_2O_2 (aq) within a liquid core waveguide (LCW); reference reaction: $\text{HO} + \text{SCN}^-$ with $k(\text{HO} + \text{SCN}^-) = 1.24 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ as determined by Chin and Wine (1992); the rate coefficient has been recalculated using the recommended value for the reference reaction $k = 1.19 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; $c(\text{isobutyraldehyd}) = 1 \times 10^{-4} - 5 \times 10^{-4} \text{ M}$; $c(\text{SCN}^-) = 4 \times 10^{-4} \text{ M}$.
- (d) HO radicals were generated by UV irradiation of $\text{H}_2\text{O}_2(\text{aq})$ at 254 nm, reactions were performed in a continuous flow-stirred reactor (CFSR) with flow rate of 250 mL min^{-1} ; $c(\text{sample}) = 2 - 10 \text{ mg L}^{-1}$, $c(\text{H}_2\text{O}_2) = 70 - 107 \text{ mg L}^{-1}$, products were analyzed by high resolution gas chromatography (HRGC) MS and HRGC-FID; the rate coefficients represent the mean of two determinations referring to two different reference reactions (tert-butanol + HO and n-Octanol + HO) without stating the individually determined rate coefficients; no recalculation of the rate coefficient could be performed.

Preferred Values

Parameter	Value	T/K
$k / \text{L mol}^{-1} \text{ s}^{-1}$	2.75×10^9	298
$k / \text{L mol}^{-1} \text{ s}^{-1}$	$1.58 \times 10^{10} \exp[-(520)/T]$	288 - 328
<i>Reliability</i>		
$\Delta \log k$	± 0.09	298
$\Delta E_A/R$	± 80	288 - 328

Comments on Preferred Values

For the recommendation, the determinations by Acero et al. (2001), Gligorovski and Herrmann (2004) and Moise et al. (2005) have been used for the regression of the Arrhenius expression. The rate coefficient by Jürgens et al. (2007) is given as the mean value of two individual determinations. As the single determinations are not given in their work, the data could not be used for the evaluation and therefore has not been considered for the regression, even though the rate coefficient is in agreement with all other determinations within error limits. The estimated uncertainty is given as $\Delta \log k = \pm 0.09$ or $\pm 20\%$.

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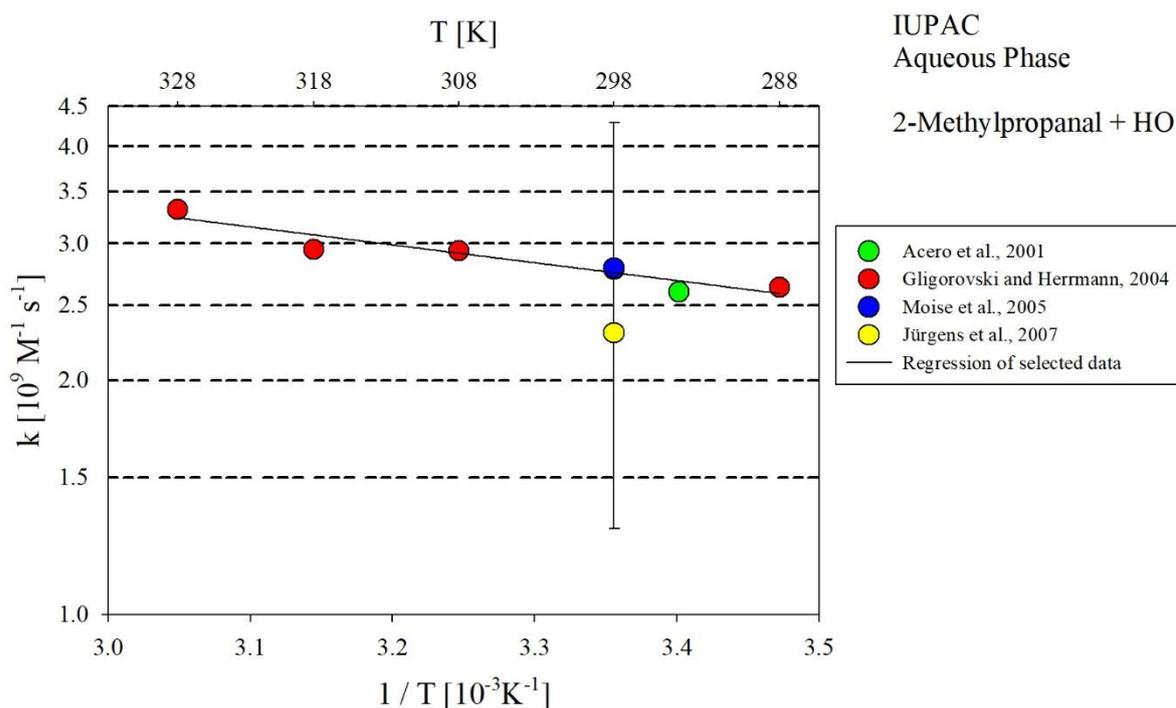
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T-dependent rate constants for the reaction of 2-methylpropanal with HO in aqueous solution. The rate coefficient determined by Jürgens et al. (2007) have not been included in the regression.