IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_3

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

HO (aq) + $CH_3CH_2CH_2OH$ (aq) → CH_3CH_2CHOH (aq) (53.4%) + $CH_2CH_2CH_2OH$ (aq) + CH_3CHCH_2OH (aq) (46%) + H_2O (l)

(*Product distributions taken from Buxton et al., 1988, originally determined by Asmus et al., 1973 via PR - UV/Vis*)

Rate coefficient data

k/ l mol^{-1} s^{-1}	T/K	pH	I/ mol l^{-1}	Reference	Technique/ Comments
Relative Rate Coefficients					
2.5×10^9	294	7	-	Adams et al. 1965	PR/UV-vis (a1)
2.79×10^9	294	10.7	-		PR/UV-vis (a2)
2.5×10^9	294	7	-	Adams et al., 1965	PR/UV-vis (b1)
2.8×10^9	294	10.7	-		PR/UV-vis (b2)
2.82×10^9	294	9	-	Anbar et al., 1966	CW / UV-vis (c)
3.3×10^9	294	2	-	Scholes and Willson, 1967	CW /UV-vis (d1)
3.0×10^9	294	5	-		CW /UV-vis (d2)
3.0×10^9	294	-	-	Willson et al., 1971	PR/UV-vis (e)
$(3.1 \pm 0.2) \times 10^9$	298	6	2×10^{-5}	Ervens et al., 2003	LP-LPA (f)
2.71×10^{10} exp[(-600 ±240) / T]	288 - 328	6	2×10^{-5}		
$(3.8 \pm 0.7) \times 10^9$	298	1 - 2	-	Monod et al., 2005	ASC / GC-FID (g1)
2.85×10^{11} exp [-(1250 ± 220)/T]	276 - 339	1 - 2	-		ASC / GC-FID (g2)

$\Delta G_R°$ (aq): Aqueous phase thermochemical data not available. Gas phase thermochemical data $H_R°$ (g) are also not available (cf. gas phase data sheet HOx_VOC25)

Comments

(a) Reference systems HO + SCN^- with $k(HO + SCN^-) = 6.6 \times 10^9\ M^{-1}s^{-1}$ [$1.10 \times 10^{10} M^{-1}s^{-1}$ (Zhu et al., 2003)] (a1); HO + CO_3^{2-} with $k(HO + CO_3^{2-}) = 2.0 \times 10^8\ M^{-1}s^{-1}$ [$3.77 \times 10^8 M^{-1}s^{-1}$](a2); rate constants have been recalculated using the selected values for the reference reactions, given in brackets; no exact value is given for the initial concentrations of the reactants ('a few millimolar'); as no exact temperature is given, for room temperature T = 294 K is assumed.

(b) Reference systems: HO + SCN^- with $k(HO + SCN^-) = 6.6 \times 10^9\ M^{-1}s^{-1}$ [$1.10 \times 10^{10} M^{-1}s^{-1}$ (Zhu et al., 2003)](b1); HO + CO_3^{2-} with $k(HO + CO_3^{2-}) = 2.0 \times 10^8\ M^{-1}s^{-1}$ [$3.77 \times 10^8 M^{-1}s^{-1}$](b2); rate constants have been recalculated using the selected values for the reference reactions, given in brackets; no values given for the initial concentrations of the reactants; as no exact temperature is given, for room temperature T = 294 K is assumed.

(c) Reference reaction: HO + PNDA (p-nitrosodimethylaniline), referring to HO + ethanol with $k(HO + ethanol) = 1.10 \times 10^9\ M^{-1}s^{-1}$; the rate constant has been recalculated using the selected value for the reference rate constant ($1.85 \times 10^9\ M^{-1}s^{-1}$); no values given for the initial concentrations of the reactants; as no exact temperature is given, for room temperature T = 294 K is assumed.

(d) Reference reaction: HO + thymine; $k(HO + thymine) = (4.3 \pm 1) \times 10^9\ M^{-1}s^{-1}$; the rate constant has been recalculated using the selected value for the reference rate constant ($5.38 \times 10^9\ M^{-1}s^{-1}$); $c(thymine) = 8 \times 10^{-5} - 2 \times 10^{-4}$ mol/l ; The rate constant of the reference reaction was determined relative to benzene; aerated solutions; the absolute rate constants in table 3 have an error of about ± 25%; as no exact temperature is given, for room temperature T = 294 K is assumed.

(e) Reference reaction: HO + $[Fe(CN)_6]^{4-}$; $k(HO + [Fe(CN)_6]^{4-}) = (9.3 \pm 0.5) \times 10^9\ M^{-1}s^{-1}$;rate constants have been recalculated using the selected rate constant for the reference reaction ($1.03 \times 10^{10}\ M^{-1}s^{-1}$); $c([Fe(CN)_6]^{4-}) = 2 \times 10^{-3}$ mol/L (no information on counterions); the reference values listed in table 1 were normalized to $k(\cdot OH + ethanol) = 1.85 \times 10^9\ M^{-1}s^{-1}$; as no exact temperature is given, for room temperature T = 294 K is assumed.

(f) Reference reaction: HO + SCN^- with $k(T) = 7.26 \times 10^{12} \exp((-1900 \pm 190) / T)\ M^{-1}s^{-1}$ (Chin and Wine, 1992); rate constants have been recalculated using the T-dependent rate constants for reference reactions by Zhu et al., 2003.

(g) Radicals generated by Fenton-reaction in a bulk reactor (an 'aqueous phase smog chamber' or 'ASC'), products analysed by GC-FID; Reference reaction: HO + 2-propanol; $k(HO + 2\text{-propanol}) = 1.9 \times 10^9\ M^{-1}s^{-1}$; rate constants have been recalculated using the selected value for the reference rate constant ($2.24 \times 10^9\ M^{-1}s^{-1}$) (g1); For the Fenton-reaction, the initial concentrations of reactants were in the order of 10^{-3} M ; Arrhenius expression was calculated from the recalculated experimental data by Monod (2005) (g2), but given as: $\ln(k(T)) = 24.5 (\pm 0.6) - 780(\pm 200)/T$ in their publication, resulting from the combined data of Monod (2005) and Ervens et al. (2003); recalculation was performed using the selected T dependent rate coefficient $k(T)(HO + 2\text{-propanol}) = 1.17 \times 10^{11} \exp(-1180/T)$.

Preferred Values

Parameter	Value	*T*/K
k / l mol^{-1} s^{-1}	3.20×10^9	298
k / l mol^{-1} s^{-1}	$k(\mathrm{T}) = 3.2 \times 10^{11} \exp[-(1300)/T]$	276-339

Reliability

$\Delta \log k$	$\pm$ 0.10	298
$\Delta E_A/R$	$\pm$ 280	

Comments on Preferred Values

Buxton et al. (1988) recommended 2.8×10^9 l mol^{-1} s^{-1} in 1988 based on the averaged data from Adams et al. (1965), Anbar et al. (1966), Scholes and Willson (1967) and Willson et al. (1971). Work since then indicated a slightly higher rate coefficient. After 1988, for the first time two T-dependencies became available. As can be seen, there is considerable scatter in both T-dependent measurements and the linear regression of all data points indicates that the rate constant at T =298 K should be somewhat higher compared to the value recommend by Buxton et al. in 1988. Overall, it is suggested to use the combined result of both the recent T-dependent studies as the preferred value for this reaction.
With this, the most recent determinations are well represented in a unified way. The overall analysis shows that the rate constant at room temperature is somewhat higher than previously recommended. An error of $\Delta \log k = \pm 0.1$ or $\pm 20\%$ is estimated for the room temperature rate coefficient.

References

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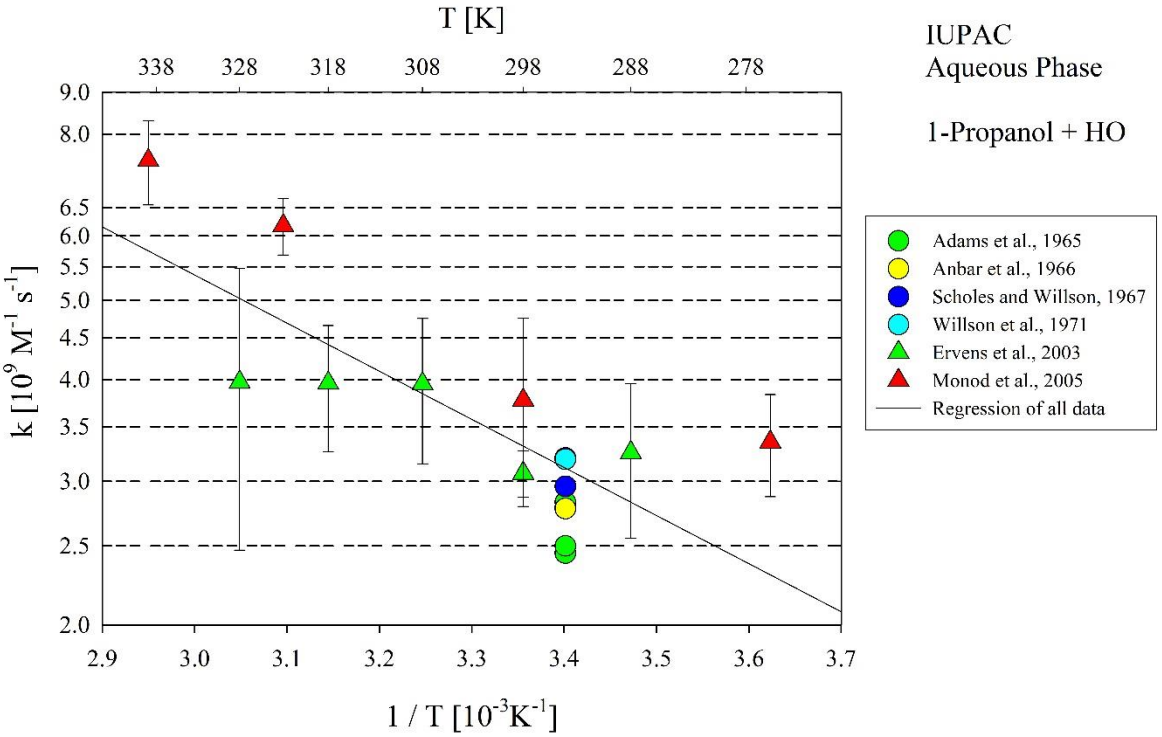

T-dependent rate constants for the reaction of 1-Propanol with HO in aqueous solution. Regression uses all data plotted in the Figure.