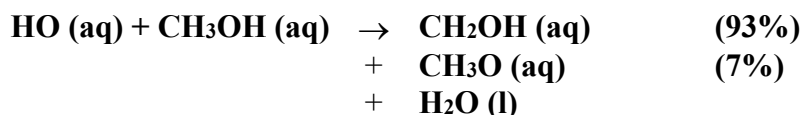


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_1

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



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

Rate coefficient data

$k / \text{l mol}^{-1} \text{s}^{-1}$	T/K	pH	I/mol l ⁻¹	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>					
9.0×10^8	294	natural	-	Alam et al., 2003	PR / UV-Vis abs. (l)
<i>Relative Rate Coefficients</i>					
5.0×10^8	294	7	1.0×10^{-4}	Thomas, 1965	PR / UV-Vis abs. (a)
8.58×10^8	294	10.7	-	Adams et al., 1965	PR / UV-Vis abs. (b1)
7.80×10^8	294	7	-		PR / UV-Vis abs. (b2)
4.68×10^8	294	7	6.9×10^{-4}		PR / UV-Vis abs. (b3)
8.7×10^8	294	10.7	-	Adams et al., 1965	PR / UV-Vis abs. (c1)
8.9×10^8	294	7	-		PR / UV-Vis abs. (c2)
9.4×10^8	294	7	-		PR / UV-Vis abs. (c2)
1.07×10^9	294	7	-	Woodward and Sutton, 1966	cw-photol. / UV-Vis abs. (d)
8.3×10^8	294	-	-	Neta and Dorfman, 1968	PR / UV-Vis abs. (e1)
8.3×10^8	294	-	-		PR / UV-Vis abs. (e2)
8.4×10^8	294	-	-		PR / UV-Vis abs. (e3)
9.5×10^8	294	-	-	Baxendale und Khan, 1969	PR / UV-Vis abs. (f)
9.5×10^8	294	2	-	Willson et al., 1971	PR / UV-Vis abs. (g)

$(1.00 \pm 0.05) \times 10^9$	294	6.5	3×10^{-4}	Wolfenden and Willson, 1982	PR / UV-Vis abs. (h)
9.74×10^8	293	7	-	Elliot and McCracken, 1989	PR / UV-Vis abs. (i1)
$3.84 \times 10^{10} \exp[-(1100 \pm 70) / T]$	293 - 353	-	-		PR / UV-Vis abs. (i2)
$8.38.4 \times 10^8$	294	7.5	-	Motohashi and Saito, 1993	PR-HPLC (j)
$(1.1 \pm 0.3) \times 10^9$	295	-	-	George et al., 2003	LCW (k)

ΔG_R° (aq): Aqueous phase thermochemical data not available

For comparison: ΔH_R° (g) = -95.2 kJ mol⁻¹ (gas phase, data sheet HOx_VOC23)

Comments

- (a) Reference reaction: HO + I⁻ with $k(\text{HO} + \text{I}^-) = (1.2 \pm 0.13) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; relative rate coefficient given as $k(\text{HO} + \text{methanol}) / k(\text{HO} + \text{I}^-) = (4.6 \pm 0.4) \times 10^{-2}$; the rate constant was recalculated using the selected value for the reference reaction $k(\text{HO} + \text{I}^-) = 1.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; as no exact temperature is given, for room temperature T = 294 K is assumed.
- (b) Reference reaction HO + CO₃²⁻ with $k(\text{HO} + \text{CO}_3^{2-}) = 2.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ [$3.77 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$] (b1); HO + SCN⁻ with $k(\text{HO} + \text{SCN}^-) = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [$1.08 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$] (b2); HO + selenite (SeO₃²⁻) with $k(\text{HO} + \text{selenite}) = 2.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [$2.60 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$] (b3); recalculations of the rate constants were done using the selected values for the reference reactions (given in brackets); as no exact temperature is given, for room temperature T = 294 K is assumed.
- (c) Reference reaction: HO + CO₃²⁻ with $k(\text{HO} + \text{CO}_3^{2-}) = 2.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (taken from previous studies by Adams et al.), recalculations of the rate constants were done using the selected value for the reference reaction $k(\text{HO} + \text{CO}_3^{2-}) = 3.8 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, determinations differ from pH = 10.7 (c1) and 7 (c2); as no exact temperature is given, for room temperature T = 294 K is assumed.
- (d) Reference reaction: HO + NO; $k(\text{HO} + \text{NO}) = 6.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; a relative rate constant of $k_{(\text{HO} + \text{NO})} / k_{(\text{HO} + \text{EtOH})}$ is given as (4.8 ± 0.6); determined rate constants were then referenced to $k_{(\text{HO} + \text{EtOH})}$, defined as 1, with $k_{(\text{HO} + \text{MeOH})}$ being 0.35.
- (e) Reference reactions: HO + C₆H₅CO₂⁻; $k(\text{HO} + \text{C}_6\text{H}_5\text{CO}_2^-) = (6.0 \pm 0.7) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (e1); HO + C₆H₅CH₂CO₂⁻; $k(\text{HO} + \text{C}_6\text{H}_5\text{CH}_2\text{CO}_2^-) = (7.9 \pm 1.1) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (e2); HO + *p*-NO₂ C₆H₄CO₂⁻; $k(\text{HO} + \textit{p}\text{-NO}_2 \text{C}_6\text{H}_4\text{CO}_2^-) = (2.6 \pm 0.4) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (e3); rate constant (e1) was recalculated using the selected value for the reference reaction ($5.97 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$); the authors recommend the average of the three determinations with the different scavengers listed above, given as $(8.4 \pm 1) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$; the absolute error of the mean rate constant is provided by the authors; as no exact temperature is given, for room temperature T = 294 K is assumed.
- (f) Reference reaction HO + PNDA; $k(\text{HO} + \text{PNDA}) = 1.25 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$.

- (g) Reference reaction $\text{HO} + \text{Fe}(\text{CN})_6^{4-}$; $k(\text{HO} + \text{Fe}(\text{CN})_6^{4-}) = (0.93 \pm 0.05) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; rate constant has been recalculated using the selected value for the reference reaction ($1.03 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$); $c([\text{Fe}(\text{CN})_6]^{4-}) = 2 \times 10^{-3} \text{ mol/l}$; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (h) Reference reaction $\text{HO} + \text{ABTS}^{2-}$ (ABTS = 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)); $k(\text{HO} + \text{ABTS}^{2-}) = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; $c(\text{ABTS}) = 1 \times 10^{-4} \text{ mol/l}$; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (i) Reference reaction (i1) $\text{HO} + \text{SCN}^-$ Arrhenius expression (i2) has been calculated using the given T-dependent data referring to $\text{HO} + \text{SCN}^-$; as reference rate coefficients, it is suggested to refer to Elliot and Simsons, 1984, as no specific reference is mentioned.
- (j) Reference reaction: $\text{HO} + \text{benzoate}$; $k(\text{HO} + \text{benzoate}) = 5.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; rate constant was recalculated using the selected value for the reference reaction ($5.97 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$); as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (k) Radicals generated by photolysis of H_2O_2 in a liquid core waveguide (LCW) at $\leq 366 \text{ nm}$; reference reaction: $\text{HO} + \text{SCN}^-$ with $k(\text{HO} + \text{SCN}^-) = 1.29 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ referring to Chin and Wine (1992); $c(\text{H}_2\text{O}_2) = 10^{-3} \text{ M}$, $c(\text{SCN}^-) = 2 \times 10^{-4} \text{ M}$, $c(\text{methanol}) = 10^{-3} \text{ M}$.
- (l) Products analysed by UV-vis-spectroscopy; direct observation of optical absorption of the alcohol radicals (260-290 nm); computer simulations were used to derive the rate constants; the simulations were accurate to 5%; N_2O saturated solutions.

Preferred Values

Parameter	Value	T/K
$k / \text{l mol}^{-1} \text{ s}^{-1}$	9.7×10^8	298
$k / \text{l mol}^{-1} \text{ s}^{-1}$	$6.55 \times 10^{10} \exp[-(1250) / T]$	293-353
<i>Reliability</i>		
$\Delta \log k$	± 0.09	298
$\Delta E_A/R$	± 100	293-353

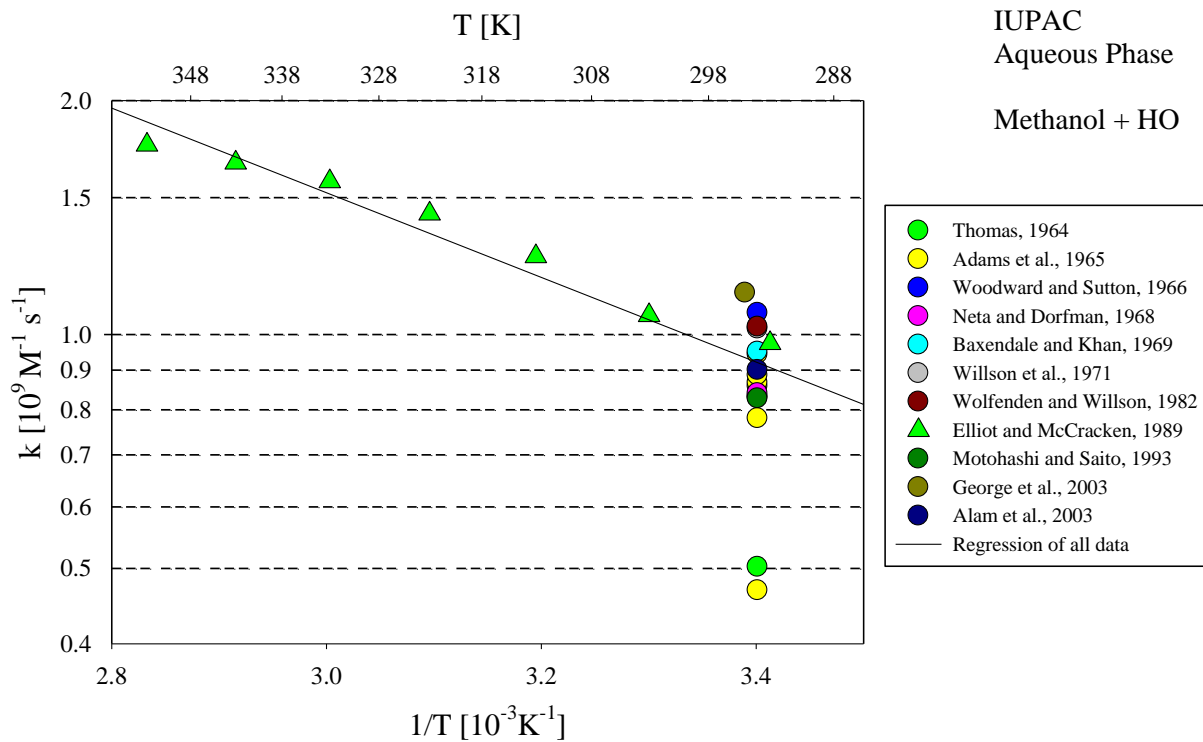
Comments on Preferred Values

Buxton et al. recommended $9.7 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ in 1988 based on the standardization study of Willson et al. The carefully performed and only available T-dependent study by Elliot and McCracken leads to $k = 1.03 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ for $T = 298 \text{ K}$ by applying the provided Arrhenius expression as no direct measurement has been performed by these authors at $T = 298 \text{ K}$. The most recent determination of this rate constant by George et al. (2003) is in agreement with the others within error limits and is included in the calculation of the recommended value of $9.7 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$. The rate coefficients determined by Thomas (1964) and Adams et al. (1965) [$5.02 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ and $4.68 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$] have not been considered for the evaluation of the recommendations because the rate constants from these studies are too small even after their re-evaluation with new competition kinetics reference data.

The reliability of the preferred value is estimated to be $\pm 20\%$ or $\Delta \log k = 0.09$.

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T-dependent rate coefficients for the reaction of Methanol with HO in aqueous solution. Data determined by Thomas (1964) and Adams et al. (1965) were not included in the regression.