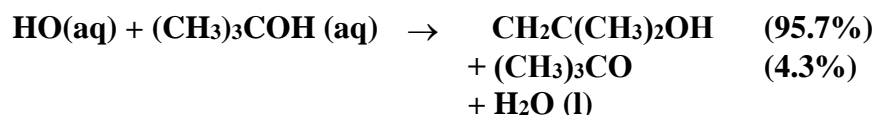


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_8

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This datasheet last evaluated: November 2019; last change in preferred values: March 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>					
7.55×10^8	294	7	-	Gordon et al., 1977	PR/UV-vis abs. (a)
6.2×10^8	294	slightly <pH 7	-	Janata, 2002	PR/UV-vis abs. (b)
6.2×10^8	294	slightly <pH 7	-	Alam et al., 2003	PR/UV-vis abs. (c)
<i>Relative Rate Coefficients</i>					
4.2×10^8	294	7	-	Adams et al., 1965	PR/UV-vis (d)
$(7.3 \pm 0.7) \times 10^8$	294	2.0 - 2.2	-	Scholes et al., 1965	CW-radiolysis /UV-vis (e)
4.8×10^8	294	9	-	Anbar et al., 1966	CW-radiolysis /UV-vis (f)
7.3×10^8	294	2	-	Scholes and Willson, 1967	CW-radiolysis /UV-vis (g)
5.7×10^8	294	-	-	Willson et al., 1971	CW-radiolysis /UV-vis (h)
$(5.9 \pm 0.4) \times 10^8$	291 - 298	6.9	-	Prütz and Vogel, 1976	CW-radiolysis/ UV-vis (i1)
$(6.6 \pm 1.2) \times 10^8$	291 - 298	7	-		CW-radiolysis/ UV-vis (i2)
$(6.2 \pm 0.4) \times 10^8$	294	6	0.3×10^{-3}	Wolfenden and Willson, 1982	PR/UV-vis abs. (j)
6.2×10^8	292	-	$2-10 \times 10^{-3}$	Elliot and Simsons, 1984	PR/UV-vis (k1)
$3.2 \times 10^{10} \exp\left[\frac{-1120 \pm 180}{T}\right]$	292 - 352	-	$2-10 \times 10^{-3}$		PR/UV-vis (k2)

4.8×10^8	293 - 298	7.5	-	Motohashi and Saito, 1993	CW-irradiation /HPLC (l)
$(4.8 \pm 0.6) \times 10^8$	298	-	2×10^{-5}	Ervens et al., 2003	LP-LPA (m)
$9.20 \times 10^{10} \exp[(-890 \pm 120) / T]$	288 - 308	-	2×10^{-5}		
$(8 \pm 2) \times 10^8$	298	1-2	-	Monod et al., 2005	ASC/ GC-FID (n)

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

Comments

- (a) Direct observation of HO decay (280 nm); $c(\text{t-BuOH}) = 0.5\text{-}2 \text{ M}$; the absolute rate coefficient has an error of $\pm 10\%$.
- (b) Direct observation of optical absorption of the alcohol radicals (260-290 nm); computer simulations were used to derive the rate coefficients; the simulations were accurate to 5%; N_2O saturated solutions
- (c) Essentially the same article as (b)
- (d) Product formation observed at 500 nm; reference reaction: $\text{HO} + \text{SCN}^-$ with $k(\text{HO} + \text{SCN}^-) = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; rate coefficients have been recalculated using the selected value for the reference reactions ($1.10 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, Zhu et al., 2003); No exact value is given for the initial concentrations of the reactants ('a few millimolar'); air or oxygen saturated solutions; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (e) Product formation observed at 264 nm; Reference reaction: $\text{HO} + \text{thymine}$; $k(\text{HO} + \text{thymine}) = 3.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; rate coefficients have been recalculated using the selected value for the reference reaction ($5.38 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$); $c(\text{thymine}) = 8\text{-}20 \times 10^{-5} \text{ mol/l}$; air or oxygen saturated solutions; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (f) Reference reaction: $\text{HO} + \text{PNDA}$ (p-nitrosodimethylaniline); the rate coefficient for the reference reaction was determined versus ethanol with $k(\text{HO} + \text{ethanol}) = 1.88 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; no values given for initial concentrations; air saturated solutions; all experiments were repeated at least four times and the coefficient of variation was less than $\pm 10\%$; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (g) Product formation observed at 264 nm; Reference reaction: $\text{HO} + \text{thymine}$; $k(\text{HO} + \text{thymine}) = (4.3 \pm 1) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; rate coefficients have been recalculated using the selected value for reference reactions ($5.38 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$); $c(\text{thymine}) = 8 \times 10^{-5} - 2 \times 10^{-4} \text{ mol/l}$; The rate coefficient of the reference reaction was determined relative to benzene; aerated solutions; The absolute rate coefficients have an error of about $\pm 25\%$; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (h) Product formation observed at 410 nm; 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 coefficients have been recalculated using the selected values for the reference reactions ($1.03 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$); $c([\text{Fe}(\text{CN})_6]^{4-}) = 2 \times 10^{-3} \text{ mol/l}$; The reference values listed in table 1 were recalculated using $k(\text{HO} + \text{ethanol}) = 1.85$

$\times 10^9 \text{ M}^{-1}\text{s}^{-1}$; in most reactions air was present or the solutions were saturated with N_2O ; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.

- (i) Products analysed by fluorescence measurements using Acriflavin ((i1) and (i2)) as RCL (Radiation Induced Chemiluminescence)-dye; (i1): buffered solution; (i2): unbuffered neutral solution; The absolute rate coefficients were obtained by comparing the slopes of the emission yields plotted against the concentrations of the different scavengers and using $k(\text{HO} + \text{methanol}) = 8.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ as reference; recalculation was performed using the selected value for the reference reaction ($9.22 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$).
- (j) Product formation observed at 415 nm; Reference reaction: $\text{HO} + \text{ABTS}$ (2,2'-Azinobis-(3-ethylbenzthiazoline-6-sulphonate)); $k(\text{HO} + \text{ABTS}) = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; $c(\text{ABTS}) = 1 \times 10^{-4} \text{ mol/l}$; N_2 and N_2O saturated solutions; the rate coefficient was recalculated using the selected value for the reference reaction ($1.24 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$); as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (k) Product formation observed at 420 nm; Reference reaction: $\text{HO} + \text{Fe}[(\text{CN})_6]^{4-}$ with T-dependent rate coefficients given as $k_{292\text{K}}(\text{HO} + \text{Fe}[(\text{CN})_6]^{4-}) = 10.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $k_{312\text{K}}(\text{HO} + \text{Fe}[(\text{CN})_6]^{4-}) = 14.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $k_{332\text{K}}(\text{HO} + \text{Fe}[(\text{CN})_6]^{4-}) = 19.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $k_{352\text{K}}(\text{HO} + \text{Fe}[(\text{CN})_6]^{4-}) = 24.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $c(\text{K}_4\text{Fe}[(\text{CN})_6])$ in the range of $2\text{-}10 \times 10^{-3} \text{ mol/l}$; N_2O saturated solutions. Arrhenius expression (k2) calculated using data from table 1, considering 10% error of activation energy; rate coefficients have been recalculated using the selected temperature dependence for the reference reaction rate coefficients ($1.81 \times 10^{12} \exp[-(1500/T)]$).
- (l) Products analysed by HPLC (abs. 240-300 nm) and fluorescence measurements (irradiation at 305 nm); Reference reaction: $\text{HO} + \text{benzoate}$; $k(\text{HO} + \text{benzoate}) = 5.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; rate coefficients have been recalculated using the selected value for reference reactions ($5.88 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$); $c(\text{benzoate}) = 2 \times 10^{-4} \text{ mol/l}$; deviations of less than $\pm 5\%$ for the determined rate coefficients; N_2O saturated solutions
- (m) Reference reaction: $\text{HO} + \text{SCN}^-$; $c(\text{thiocyanate}) = 2 \times 10^{-5} \text{ mol/l}$, reference reaction rate coefficient given by: $k(T) = 7.26 \times 10^{12} \exp((-1900 \pm 190) / T) \text{ M}^{-1}\text{s}^{-1}$ by Chin and Wine (1992); rate coefficients have been recalculated using the selected T-dependent rate coefficients for the reference reaction by Zhu et al., 2003.
- (n) Radicals generated by Photo-Fenton-reaction in a bulk reactor (an 'aqueous phase smog chamber' or 'ASC'), products analysed by GC-FID; Reference reaction: $\text{HO} + 2\text{-propanol}$; $k(\text{HO} + 2\text{-propanol}) = 1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; recalculation of the rate coefficient was performed using the selected value for the reference reaction ($2.27 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$).

Preferred Values

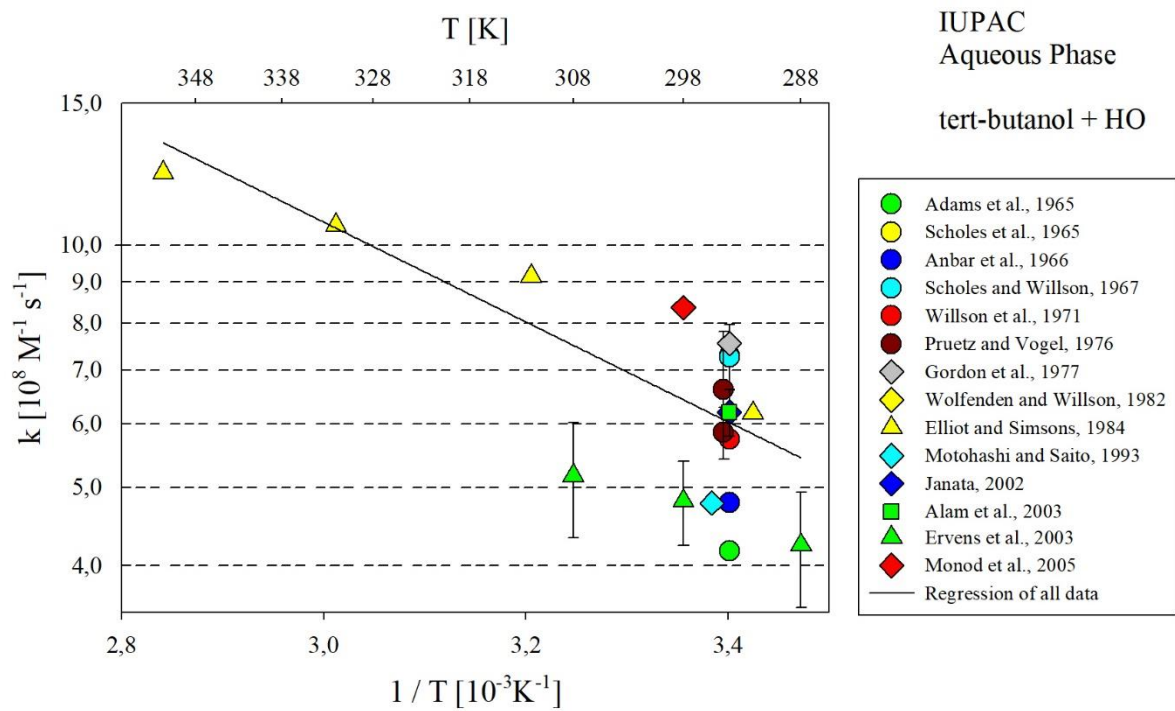
Parameter	Value	T/K
$k / \text{L mol}^{-1} \text{ s}^{-1}$	6.29×10^8	298
$k / \text{L mol}^{-1} \text{ s}^{-1}$	$9.15 \times 10^{10} \exp[-(1500)/T]$	288 - 352
<i>Reliability</i>		
$\Delta \log k$	± 0.15	298
$\Delta E_A/R$	± 310	288 - 352

Comments on Preferred Values

The rate constants available for room temperature show scatter within about a factor of two ranging from 4.2 to $7.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (Adams et al., 1965 and Gordon et al., 1977). Considering the two available temperature dependent determinations by Elliot and Simsons (1984) and Ervens et al. (2003), the regression is leading to a mean of $6.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, which is confirmed by other determinations within error limits. The uncertainty is estimated to be $\pm 33\%$ or $\Delta \log k = 0.15$.

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T-dependent rate coefficients for the reaction of *tert*-butanol with HO in aqueous solution. All data sets shown in the Figure were considered for regression.