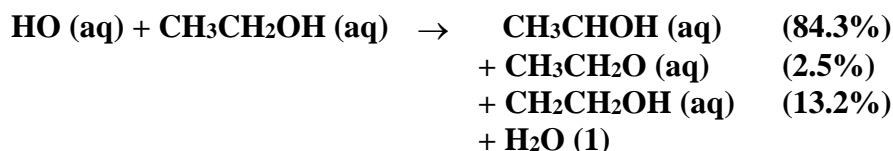


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_2

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This datasheet last evaluated: June 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	$I / \text{mol l}^{-1}$	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>					
2.2×10^9	294	7	-	Alam et al., 2003	PR-UV/Vis (a)
<i>Relative Rate Coefficients</i>					
7.69×10^8	294	7	1×10^{-4}	Thomas, 1965	PR-UV/Vis (b)
1.83×10^9	294	10.7	-	Adams et al., 1965	PR-UV/Vis (c1)
1.80×10^9	294	7	-		PR-UV/Vis (c2)
1.04×10^9	294	7	6.9×10^{-4}		PR-UV/Vis (c3)
1.83×10^9	294	7	-	Adams et al., 1965	PR-UV/Vis (d)
1.63×10^9	294	2	-		PR-UV/Vis (d)
2.26×10^9	294	-	-	Adams et al., 1965	PR-UV/Vis (e)
1.7×10^9	291 - 298	10.5 – 10.8	-	Matthews and Sangster, 1965	^{cw} radiolysis- Tracer (f)
3.04×10^9	293	7	-	Woodward and Sutton, 1966	PR-UV/Vis (g)
4.7×10^8	294	-	1	Heckel et al., 1966	PR- UV/Vis(h)
2.0×10^9	294	3	-	Scholes and Willson, 1967	PR-UV/Vis (i)
1.75×10^9	294	6-7	-		PR-UV/Vis (i)

1.81×10^9	294	-	-	Neta P. and Dorfman L.M., 1968	PR-UV/Vis (j1)
1.83×10^9	294	-	-		PR-UV/Vis (j2)
1.81×10^9	294	-	-		PR-UV/Vis (j3)
1.6×10^9	294	-	-	Baxendale and Khan, 1969	PR-UV/Vis RR (k)
$(2.1 \pm 0.3) \times 10^9$	293 - 298	11 - 13	-	Buxton, 1970	PR-UV/Vis RR(l)
2.04×10^9	294	2	2×10^{-2}	Willson et al., 1971	PR-UV/Vis RR (m)
1.82×10^9	294	-	-	Matheson et al., 1973	PR-UV/Vis RR (n)
$(1.90 \pm 0.1) \times 10^9$	294	6	3×10^{-4}	Wolfenden and Willson, 1982	PR-UV/Vis RR (o)
$(1.9 \pm 0.1) \times 10^9$	294	9	$12.5 - 25 \times 10^{-5}$	Park and Getoff, 1992	PR-UV/Vis RR (p)
2.2×10^9	294	7.5	-	Motohashi and Saito, 1993	PR-HPLC(q)
$(2.1 \pm 0.4) \times 10^9$	293	-	-	Monod et al., 2002	(r)
$(2.0 \pm 0.1) \times 10^9$	298	-	2×10^{-5}	Ervens et al., 2003	LP-LPA (s1)
$4.52 \times 10^{10} \exp[-(900 \pm 180) / T]$	283-328	-	-		LP-LPA (s2)
$(1.7 \pm 0.5) \times 10^9$	295	-	-	George et al., 2003	LCW (t)
$(2.1 \pm 0.3) \times 10^9$	298	1 - 2	-	Monod, 2005	ASC / GC-FID (u1)
$2.83 \times 10^{10} \exp[-(770 \pm 30) / T]$	276 - 328	2	-		ASC / GC-FID (u2)

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

For comparison: ΔH_R° (g) = -95.8 kJ mol⁻¹ (gas phase, data sheet HOx_VOC24)

Comments

- (a) 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%; N₂O saturated solutions; as no exact temperature is given, for room temperature T = 294 K is assumed.
- (b) Reference reaction HO + I; $k(\text{HO} + \text{I}) = (1.02 \pm 0.13) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, $c(\text{I}) = 5 \times 10^{-5} \text{ mol/l}$. This concentration is used for the calculation of I as no exact temperature is given, for room temperature T = 294 K is assumed.
- (c) Reference reactions (c1): HO + CO₃²⁻, $k(\text{HO} + \text{CO}_3^{2-}) = 2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ [$3.8 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$], no concentrations given; (c2) HO + SCN⁻, $k(\text{HO} + \text{SCN}^-) = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [$1.08 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$],

$c(\text{SCN}^-) = 8 - 400 \times 10^{-6} \text{ mol/l}$; (c3) $\text{HO} + \text{selenite} (\text{SeO}_3^{2-})$, $k(\text{HO} + \text{SeO}_3^{2-}) = 2.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [$2.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$], $c = 2.3 \times 10^{-4} \text{ mol/l}$; recalculation of the rate coefficient has been done using the selected values for the reference reaction given in brackets; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.

- (d) Experimental conditions see (c); exp. values of (c) also listed (Table I of the reference, values given here are those of Table II of the reference). reference reaction: $\text{HO} + \text{SCN}^-$ with $k(\text{HO} + \text{SCN}^-) = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $c(\text{SCN}^-) = 1-50 \times 10^{-3} \text{ mol/l}$; rate coefficient recalculated using the selected value $k = 1.10 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (e) Experimental conditions see (c); Reference reaction: $\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}$ with $k(\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}) = 5.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; recalculations performed, using the selected rate coefficient $k(\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}) = 1.03 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (f) Analysis of $^{14}\text{CO}_2$ formed from the competition reaction $\text{HO} + \text{C}_6\text{H}_5^{14}\text{COO}^-$ with $k(\text{HO} + \text{benzoate}) = 1.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; relative rate coefficient given as 0.28; recalculated using the selected rate coefficient $k(\text{HO} + \text{benzoate}) = 5.88 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; The ionic strength was calculated from the given concentration of benzoic acid with $c = 8 \times 10^{-3} \text{ mol/l}$. This competition kinetics method is different from most other ones, it directly determines the yield of $^{14}\text{CO}_2$ formed by single electron transfer from the carboxylate group to HO. As HO will react by addition to the aromatic ring as well, this method should be considered with great care, however; for evaluation, the mean of the given temperature range was used.
- (g) Reference reaction: $\text{HO} + \text{NO}$; $k(\text{HO} + \text{NO}) = 6.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; a relative rate constant of $k_{(\text{HO} + \text{NO})} / k_{(\text{HO} + \text{EtOH})}$ is given as (4.8 ± 0.6) ; rate coefficient has been recalculated using the selected value $k(\text{HO} + \text{NO}) = 1.46 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$.
- (h) Reference reaction $\text{HO} + \text{HSO}_4^-$; $k(\text{HO} + \text{HSO}_4^-) = 8 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ is calculated based on data by Adams et al.; a separate determination of this reference rate constant lead to $k(\text{HO} + \text{HSO}_4^-) = 6.9 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$, the authors decide to use the above value by Adams as the reference rate constant. Table 1 of the reference gives ratios $k_{\text{Substance}} / k_{(\text{HO} + \text{HSO}_4^-)}$ and, specifically, $k_{\text{Ethanol}} / k_{(\text{HO} + \text{HSO}_4^-)} = 5.5 \times 10^2$, leading to the tabulated absolute rate constant; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (i) Reference reaction: $\text{HO} + \text{thymine}$; $k(\text{HO} + \text{thymine}) = 4.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, $c(\text{thymine}) = 0.8 - 2 \times 10^{-4} \text{ mol/l}$; recalculations performed using the selected rate coefficient $k(\text{HO} + \text{thymine}) = 5.38 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (j) Reference reactions: $\text{C}_6\text{H}_5\text{CO}_2^- + \text{HO}$ with $k(\text{C}_6\text{H}_5\text{CO}_2^- + \text{HO}) = (6.0 \pm 0.7) \times 10^{-9} \text{ M}^{-1}\text{s}^{-1}$ (j1); $\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2^- + \text{HO}$ with $k(\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2^- + \text{HO}) = (7.9 \pm 1.1) \times 10^{-9} \text{ M}^{-1}\text{s}^{-1}$ (j2); $p\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2^- + \text{HO}$ with $k(p\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2^- + \text{HO}) = (2.6 \pm 0.4) \times 10^{-9} \text{ M}^{-1}\text{s}^{-1}$ (j3); the authors recommend the mean of the three determinations with the above different scavengers, given as $(1.83 \pm 2) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; the rate coefficient of (i1) has been recalculated using the selected rate coefficient for the reference reaction $k(\text{HO} + \text{C}_6\text{H}_5\text{CO}_2^-) = 5.88 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (k) Reference reaction $\text{HO} + p\text{-nitrosodimethylanilin} (4\text{-Me}_2\text{NC}_6\text{H}_4\text{NO})$; $k(\text{HO} + 4\text{-Me}_2\text{NC}_6\text{H}_4\text{NO}) = (1.25 \pm 0.2) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, $c = 9.4 \times 10^{-6} \text{ mol/l}$, The concentration of $p\text{-nitrosodimethylanilin}$ used for the ethanol measurement was taken from Figure 5 of the reference.

- (l) Reference reaction $\text{HO} + \text{CO}_3^{2-}$, $k(\text{HO} + \text{CO}_3^{2-}) = 4.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, recalculation of the rate coefficient has been done using the selected values for the reference reaction ($3.8 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$); measurements at pH 11 ($0.01 \text{ mol l}^{-1} \text{ CO}_3^{2-} + 2.3 \times 10^{-2} \text{ HCO}_3^-$) and pH 13 (0.1 M CO_3^{2-}).
- (m) Reference reaction $\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}$; $k(\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}) = 0.93 \pm 0.05 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, recalculations performed, using the selected rate coefficient $k(\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}) = 1.03 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; $c([\text{Fe}(\text{CN})_6]^{4-}) = 2 \times 10^{-3} \text{ mol/l}$ – used for calculating I; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (n) Reference reaction $\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}$; $k(\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}) = 0.93 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; recalculations performed, using the selected rate coefficient $k(\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}) = 1.03 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (o) Reference reaction $\text{ABTS}^{2-} + \text{HO}$, $k(\text{HO} + \text{ABTS}^{2-}) = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, $c(\text{ABTS}^{2-}) = 10^{-4} \text{ mol/l}$; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (p) Reference reaction $\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}$; $k(\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}) = 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ taken from Elliot and Simons (1984); recalculations performed, using the selected rate coefficient $k(\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}) = 1.03 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; $c([\text{Fe}(\text{CN})_6]^{4-}) = 2.5 - 5.0 \times 10^{-5} \text{ mol/l}$, used to calculate I; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (q) Reference reaction $\text{C}_6\text{H}_5\text{CO}_2^- + \text{HO}$, $k(\text{HO} + \text{C}_6\text{H}_5\text{CO}_2^-) = 5.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, $c(\text{C}_6\text{H}_5\text{CO}_2^-) = 2 \times 10^{-4} \text{ mol/l}$; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (r) cw-photolysis of H_2O_2 with a Xe-lamp solar simulator. Product analysis by GC, HPLC and IC; proof of concept study with no reference given for the competition kinetics; no further evaluation of this rate coefficient can be done.
- (s) Reference reaction $\text{HO} + \text{SCN}^-$; $k(\text{HO} + \text{SCN}^-) = 7.26 \times 10^{12} \exp(-1900 \pm 190/T) \text{ M}^{-1}\text{s}^{-1}$, $c(\text{SCN}^-) = 2 \times 10^{-5} \text{ mol/l}$, $c(\text{H}_2\text{O}_2) = 5 \times 10^{-4} \text{ mol/l}$; the Arrhenius expression (s2) is resulting from the determined temperature dependent data; rate coefficients have been recalculated using the selected T dependent values for the reference reaction (Zhu et al., 2003).
- (t) 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); rate coefficient recalculated using the selected value $k = 1.10 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; $c(\text{H}_2\text{O}_2) = 10^{-3} \text{ M}$, $c(\text{SCN}^-) = 2 \times 10^{-4} \text{ M}$, $c(\text{ethanol}) = \sim 10^{-3} \text{ M}$.
- (u) (u1) Radicals generated by Photo-Fenton-reaction in a bulk reactor (an ‘aqueous phase smog chamber’ or ‘ASC’), products analysed by GC-FID; Reference reaction: $\text{HO} + \text{methanol}$; $k(\text{HO} + \text{methanol}) = 9.8 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$
Arrhenius expression (u2) is calculated from the experimental data of Monod (2005), but given as $\ln k(T) = (24.2 \pm 0.4) - [(830 \pm 140)/T]$ in their publication, resulting from the combined data of Monod (2005) and Ervens et al. (2003); reference systems used for recalculations: $\text{HO} + 1\text{-propanol}$, with $k(T) = 7.0 \times 10^{10} \exp(-900 \pm 250/T)$ and $\text{HO} + \text{methanol}$ with $k(T) = 6.7 \times 10^{10} \exp(-1200 \pm 120)$.

Preferred Values

Parameter	Value	T/K
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$k / 1 \text{ mol}^{-1} \text{ s}^{-1}$	1.99×10^9	298
$k / 1 \text{ mol}^{-1} \text{ s}^{-1}$	$3.45 \times 10^{10} \exp[-(860) / T]$	293-353
<i>Reliability</i>		
$\Delta \log k$	± 0.3	298
$\Delta E_A/R$	± 250	293 - 353

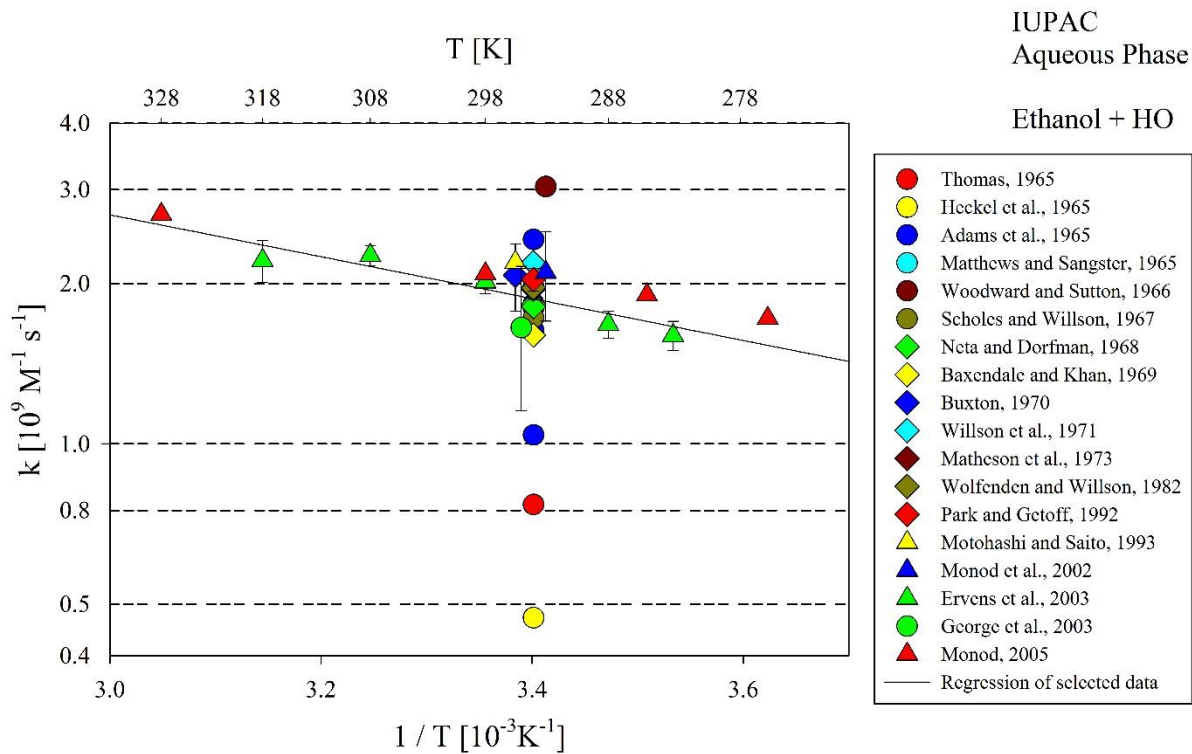
Comments on Preferred Values

Buxton et al. recommended $1.9 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in 1988. Work since then in four out of five studies indicates that the rate constant may be slightly higher, calculations of the recommended value confirm the rate constant to be $2.0 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. The most recent determination of this rate constant by George et al. (2003) is in agreement with this value within error limits as well. The uncertainty of the preferred value is twice the one given by Ervens et al. thus including the recommended value by Buxton et al. (1988). The recommended Arrhenius expression is based on the regression of the available data, excluding the determinations by Thomas (1965) and Woodward and Sutton (1966) due to their values exceeding the accepted range for the rate constants, as well as Heckel et al. (1966) and Monod et al. (2002). Even though the rate coefficient determined by Monod et al. (2002) agrees with the recommended value within an error limit of 10%, it is not considered for the final regression. Lack of information concerning the reference rate constants used for the competition kinetics method do not allow for proper evaluation. As Heckel et al. (1966) use H_2SO_4 as reference, it is advised to not consider this rate constant, as the rate coefficient exceeds the referencing rate coefficient by a factor of 10^3 .

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T-dependent rate constants for the reaction of Ethanol with HO in aqueous solution. Data from Thomas (1965), Heckel et al. (1965), Woodward and Sutton (1966) and Monod et al. (2002) were excluded from regression.