

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_80

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Rate coefficient data

k/ L mol ⁻¹ s ⁻¹	T/K	pH	I/ mol L ⁻¹	Reference	Technique/ Comments
Absolute Rate Coefficients					
$(1.3 \pm 0.1) \times 10^8$	298	5.8	-	Hesper, 2003	LP-LPA (a)
$8.4 \times 10^{10} \exp[(-1900 \pm 330)/T]$	288 - 323	6.0	-		LP-LPA (a)
Relative Rate Coefficients					
9.7×10^7	294	-	-	Adams et al., 1965	PR / UV-Vis (b)
8.2×10^7	294	-	-	Thomas, 1965	PR / UV-Vis (c)
1.3×10^8	294	-	-	Willson et al., 1971	PR / UV-Vis (d)
$(1.3 \pm 0.1) \times 10^8$	294	6	-	Wolfenden and Willson, 1982	PR / UV-Vis (e)
$(9.47 \pm 0.17) \times 10^7$	294	7	-	Williams et al., 2002	PR / UV-Vis (f)
$(2.0 \pm 0.6) \times 10^8$	298	-	-	Ervens et al., 2003	LP-LPA (g)
$9.6 \times 10^{10} \exp[(-1900 \pm 420)/T]$	283 - 318	-	-		LP-LPA (g)
$(1.1 \pm 0.5) \times 10^8$	298	2	-	Monod et al., 2005	Dark Fenton / GC-FID (h1)
$(1.2 \pm 0.6) \times 10^8$	298	-	-		CW / GC-FID (h2)
$7.17 \times 10^{10} \exp[-(1900 \pm 200)/T]$	276 - 323	-	-		CW / GC-FID (h3)
$(1.7 \pm 0.4) \times 10^8$	298	6 - 7	-	Gligorovski et al., 2009	WP / UV-Vis (i)

The equilibrium constant for the hydration (1) is recommended as $K_{298\text{ K}} = 2.0 \times 10^{-3}$ 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) Product formation observed via UV-vis abs. (Long Path Absorption) at 248 nm; direct observation of optical absorption of the peroxy-radicals formed by the reaction between HO, acetone and O₂; oxygen saturated solutions.
- (b) Reference reaction: HO + SCN⁻ with $k(\text{HO} + \text{SCN}^-) = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; recalculation has been performed using the selected value for the reference reaction ($1.10 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$); No exact value is given for the initial concentrations of the reactants. Adams et al. state, that the unexpected low figure for acetone might occur due to the effect of tautomerism in the molecule; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed.
- (c) Reference reaction: HO + I⁻ with $k(\text{HO} + \text{I}^-) = (1.02 \pm 0.13) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; relative rate coefficient given as $k(\text{HO} + \text{Aceton}) / k(\text{HO} + \text{I}^-) = (7.5 \pm 0.8) \times 10^{-3}$; recalculation has been performed using the selected value for the reference reaction ($1.09 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$); no values given for concentrations; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed..
- (d) Product formation observed via UV-vis-spectroscopy at 410 nm; Reference reaction: HO + [Fe(CN)₆]⁴⁻ with $k(\text{HO} + [\text{Fe}(\text{CN})_6]^{4-}) = (0.93 \pm 0.05) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; recalculation has been performed using the selected value for the reference reaction ($1.03 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$); $c([\text{Fe}(\text{CN})_6]^{4-}) = 2 \times 10^{-3} \text{ mol/l}$; 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 N₂O; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed..
- (e) Product formation observed via UV-vis-spectroscopy at 415 nm; Reference reaction: HO + ABTS (2,2'-Azinobis-(3-ethylbenzthiazoline-6-sulphonate)); $k(\text{HO} + \text{ABTS}) = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, $c(\text{ABTS}) = 1 \times 10^{-4} \text{ mol/l}$; N₂ and N₂O saturated solutions; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed..
- (f) Reference reaction: HO + SCN⁻ with $k(\text{HO} + \text{SCN}^-) = 1.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; $c(\text{SCN}^-) = 0.01 \text{ M}$ in N₂O saturated solution; $c(\text{acetone})$ in the range of $10^{-4} - 10^{-2} \text{ mol/l}$; as no exact temperature is given, for room temperature $T = 294 \text{ K}$ is assumed..
- (g) Reference reaction: HO + SCN⁻; $c(\text{thiocyanate}) = 2 \times 10^{-5} \text{ mol/l}$, reference reaction rate constant 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); The measured rate constants were recalculated using the new recommended temperature dependence for the reference reaction (Zhu et al., 2003).
- (h) Radicals generated by dark Fenton reaction (h1) and continuous photolysis of H₂O₂ (h2); temperature dependent rate constants (h3) were determined using both methods. Reference reaction: HO + methanol; $k(T) = 9.7 \times 10^8 \exp[-4800/R(1/T-1/298)]$ (Elliot and Simsons, 1984); recalculation has been performed using the selected temperature dependence for the reference reaction ($6.55 \times 10^{10} \exp[-(1250) / T]$); Arrhenius expression (h3) is calculated from experimental data of Monod (2005), but given as $\ln k(T) = (23.5 \pm 1.7) - [1400(\pm 500)]/T$

in their work, resulting from the combined data of Monod (2005), Ervens et al. (2003) and Buxton et al. (1988).

- (i) Radicals generated by flash photolysis in a Teflon AF waveguide photolysis (WP) system; products analysed by UV-Vis abs.; reference reaction: HO + SCN⁻ with $\ln k(T) = (29.614 \pm 0.636) - (1900 \pm 190)/T$ (Chin and Wine, 1992); for the recalculation, the selected T dependence by Zhu et al. (2003) has been used.

Preferred Values

Parameter	Value	T/K
$k / \text{L mol}^{-1} \text{s}^{-1}$	1.34×10^8	298
$k / \text{L mol}^{-1} \text{s}^{-1}$	$8.23 \times 10^{10} \exp[-(1900)/T]$	276 - 323
<i>Reliability</i>		
$\Delta \log k$	± 0.15	298
$\Delta E_A/R$	± 400	276 - 323

Comments on Preferred Values

All available data presented in the Table have been used for regression. The resulting rate coefficient agrees with earlier determinations within error limits as well as the recommendation by Buxton et al. (1988), of $k = 1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. From the three available T dependent determinations, the data by Ervens et al. (2003) indicates higher values for the rate coefficients, while the Arrhenius expression of Monod et al. (2005) indicates values slightly lower. The mean of them is in perfect agreement with the directly observed T dependent determination by Hesper (2003). The uncertainty of the recommended value is estimated as $\pm 33\%$ or $\Delta \log k = \pm 0.15$.

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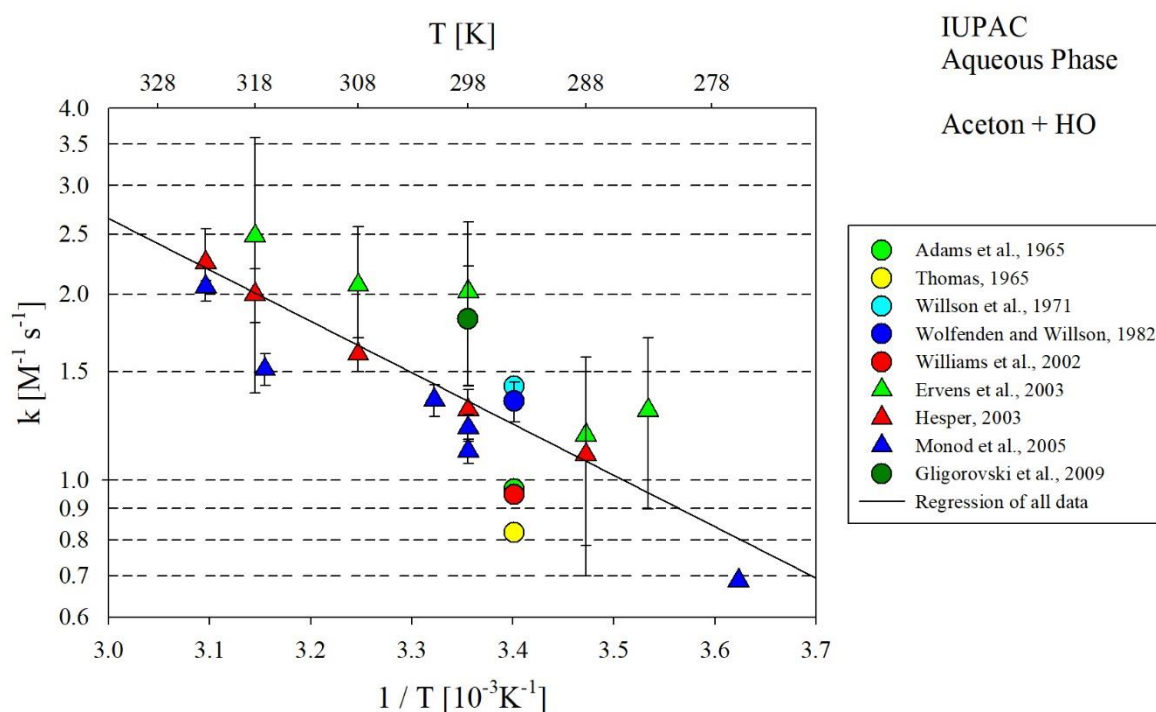
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T-dependent rate constants for the reaction of acetone with HO in aqueous solution. Regression uses all data plotted in the figure.