IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_61

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CH_3CHO (aq) + H_2O	**→ $CH_3CH(OH)_2$ (aq)**	**(1)**
HO (aq) + CH_3CHO (aq)	**→ CH_3CO(aq) + H_2O**	**(2)**
HO (aq) + $CH_3CH(OH)_2$ (aq)	**→ $CH_3C(OH)_2$ (aq) + H_2O**	**(3)**
HO (aq) + CH_3CHO (aq)	**→ CH_2CHO(aq) + H_2O**	**(4)**
HO (aq) + $CH_3CH(OH)_2$ (aq)	**→ $CH_2CH(OH)_2$ (aq) + H_2O**	**(5)**

(Product distribution taken from Schuchmann and von Sonntag, 1988;
***(2)**: 65%; **(3)**: 26%; **(4)** and **(5)**: 5 – 10%)*

Rate coefficient data

k / L mol^{-1} s^{-1}	T/K	pH	I/ mol L^{-1}	Reference	Technique/ Comments
Relative Rate Coefficients					
9.5×10^8	291	1	-	Merz and Waters, 1949	Fenton reaction (a)
2.4×10^9	294	-	-	Schuchmann and v. Sonntag, 1988	Recommended value (b1)
$k_2 = 3.6 \times 10^9$	294	-	-		PR / UV-Vis (b2)
$k_3 = 1.2 \times 10^9$	294	-	-		(b3)
$k_4 \sim k_5 \sim 10^8$	294	-	-		(b4)
$(4.1 \pm 0.3) \times 10^9$	298	2	-	Monod et al., 2005	Fenton reaction (c)

The equilibrium constant for the hydration (1) is recommended as $K_{298\,K} = 1.2$ by Doussin and Monod (2013).

$\Delta G_R°$ (aq): Aqueous phase thermochemical data not available. As well, gas phase thermochemical data $H_R°$ (g) are not available.

Comments

(a) Merz and Waters are giving a value for $k = 2.2$, relative the reference reaction (HO + Fe^{2+}) without stating a specific rate constant; product analysis by colorimetric determination; only the overall reaction of acetaldehyde (aq) with HO radicals was considered; for the recalculation of this value, the selected rate coefficient for the reference reaction k(HO + Fe^{2+}) = 4.3×10^8 $M^{-1}s^{-1}$ has been used.

(b) N_2O saturated solutions of acetaldehyde ($4.5 \times 10^{-3} – 1.5 \times 10^{-2}$ mol L^{-1}) with c(KSCN) = $1 – 2 \times 10^{-3}$ mol L^{-1}; reference reaction: HO + SCN^- with k(HO + SCN^-) = 1.1×10^{10} $M^{-1}s^{-1}$, which agrees with the selected values for the reference reactions. Rate coefficients for all reactions of acetaldehyde in aqueous solutions [(2) – (5)] were calculated; based on the rate coefficient of $k = 2.4 \times 10^9$ $M^{-1}s^{-1}$ (b1) for the overall reaction of acetaldehyde (aq) with HO radicals, individual rate coefficients were determined according to the yields of each species: (b2): 65%; (b3): 26%; (b4): 5 – 10%; as no exact temperature is given, T = 294 K is assumed for room temperature.

(c) Radicals generated by dark Fenton reaction; Global rate coefficient for the reaction of HO radicals with acetaldehyde and its hydrate has been determined; K_{hyd}(25° C) was considered to be 1.35 (Bell and Evans, 1966). Reference reactions: HO + 1-propanol; ln k(T) = (24.5 ±0.6) – (780 ±200)/T; the rate coefficient has been recalculated using the recommended value for the reference reaction $k = 3.18 \times 10^9$ $M^{-1}s^{-1}$.

Preferred Values

Parameter	Value	*T*/K
k / L mol^{-1} s^{-1}	2.48×10^9	298
Reliability		
$\Delta \log k$	±0.15	298

Comments on Preferred Values

For the room temperature rate coefficient, only the rate coefficients referring to the overall reaction of acetaldehyde with the HO radical have been considered. The mean of the values given by Merz and Waters (1949), Schuchmann and v. Sonntag (1988), and Monod et al. (2005) is suggested. The estimated uncertainty is given as ±33% or $\Delta \log k = \pm 0.15$.

References

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