

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ_OH_90

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(primary radical products (2) determined by Kumar et al., 1990; a more detailed discussion of product distribution can be found in Zhang et al., 2010 and Schoene et al., 2014)

Rate coefficient data

k/ L mol ⁻¹ s ⁻¹	T/K	pH	I/ mol L ⁻¹	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>					
7 × 10 ⁸	294	6.8	-	Kumar et al., 1990	PR-UV/Vis (a)
<i>Relative Rate Coefficients</i>					
8.5 × 10 ⁹	294	-	-	Lilie and Henglein, 1970	PR / UV-Vis (b)
8.5 × 10 ⁸	294	6.8	-	Kumar et al., 1990	PR / UV-Vis (c)
7.1 × 10 ⁹	298	7	-	Szeremeta et al., 2009	LP-LPA (d)
1.6 × 10 ¹⁰	298	7	-		Corrected value (d1)
4.54 × 10 ¹¹ exp[- (1200 ± 70)/T]	278 - 318	7	-		LP-LPA (d2)
(7.1 ± 0.5) × 10 ⁹	298	-	-	Schoene et al., 2014	LP-LPA (e)
4.37 × 10 ¹¹ exp[- (1200 ± 60)/T]	278 - 308	-	-		LP-LPA (e1)

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

As observed by Zhang et al. (2010), methyl vinyl ketone (MVK) in aqueous systems tends to isomerize to crotonaldehyde (1) by rearrangement (approx. 14% of dissolved MVK, independent of H₂O₂ or H₂SO₄ addition; studies performed at pH = 4, 283 K; exact mechanism is still to be determined).

Comments

- (a) Kumar et al. verified their determined rate coefficient (c) by observing the build up of the transient species (T_2) of MVK at 310 nm under the same conditions as (c); as no exact temperature is given, $T = 294$ K is assumed as room temperature.
- (b) HO radicals were generated by irradiation of N_2O saturated solutions; $c(N_2O) = 2.5 \times 10^{-2}$ M, concentration of the carbonyl compounds was given as “some 10^{-4} molar”, concentration of the compound radicals was calculated to be around 10^{-5} M; reference reaction: $HO + SCN^-$ with $k(HO + SCN^-) = 6.6 \times 10^9$ $M^{-1} s^{-1}$; rate coefficients have been recalculated using the selected temperature dependence for the reference reaction by Zhu et al.(2003); analysis was performed within a buffered pH range from 5 to 9; Lilie and Henglein determined, that 30% of the nonhydrated compound radical disproportioned to yield the enol and β -alcohol while the rest forms a dimer; as no exact temperature is given, $T = 294$ K is assumed for room temperature.
- (c) Radicals generated by pulse radiolysis of N_2O saturated solutions, formation of $(SCN)_2^-$ species observed at 500 nm; reference reaction: $HO + SCN^-$ with no rate coefficient given for reference; $c(\text{methyl vinyl ketone}) = 4 \times 10^{-3}$ M; rate coefficient was confirmed by direct observation of transient species at 310 nm (see (a), $k = 7.0 \times 10^8$ $M^{-1} s^{-1}$); as no exact temperature is given, $T = 294$ K is assumed for room temperature.
- (d) Radicals generated by photolysis of H_2O_2 solution at 248 nm, product detection at 436 nm; reference reaction: $HO + SCN^-$ with $\ln k(T) = (29.614 \pm 0.636) - (1900 \pm 190)/T$ $M^{-1} s^{-1}$ (according to Chin and Wine (1992)); rate coefficients were recalculated using the selected temperature dependent rate coefficients by Zhu et al., 2003; $c(H_2O_2) = 2 \times 10^{-5}$ M, $c(KSCN) = 1 \times 10^{-4}$ M, $c(\text{methyl vinyl ketone})$ ranging from 5×10^{-6} to 1×10^{-4} M; the rate coefficients at 298 K were determined from plotted data, as no specific temperature dependent value was given in the publication; (d1): corrected rate coefficient, calculated by considering simultaneous diffusion and first order chemical reaction, referring to the recalculated $k(298$ K) value; (d2): Arrhenius expression derives from regression of the corrected recalculated data; activation parameters given in the original publication: $A = (8.96 \pm 2.35) \times 10^{11}$, $E_A = (11.90 \pm 0.64)$ $kJ mol^{-1}$; all experiments were repeated eight times for reproducibility.
- (e) Radicals generated by photolysis of H_2O_2 solution at 248 nm, for detection, a cw laser was used at 407 nm (laser flash photolysis long-path absorption setup (LP-LPA)); for detection of the carbonyl products formed, derivatization with 2,4-dinitrophenylhydrazine was performed; reference reaction: $HO + SCN^-$ with $\ln k(T) = (29.614 \pm 0.636) - (1900 \pm 190)/T$ $M^{-1} s^{-1}$ (according to Chin and Wine (1992)); rate coefficients were recalculated using the selected temperature dependence for the reference reaction (Zhu et al., 2003); $c(KSCN) = 1.59 \times 10^{-5}$ M, $c(H_2O_2) = 1 \times 10^{-4}$ M; (e1): Arrhenius expression derives from regression of the corrected recalculated data; activation parameters given in the original publication: $A = (9.0 \pm 0.4) \times 10^{11}$, $E_A = (12 \pm 3)$ $kJ mol^{-1}$; rate coefficients for k_{313 K and k_{318 K were measured, but have not been used to calculate activation parameters.

Preferred Values

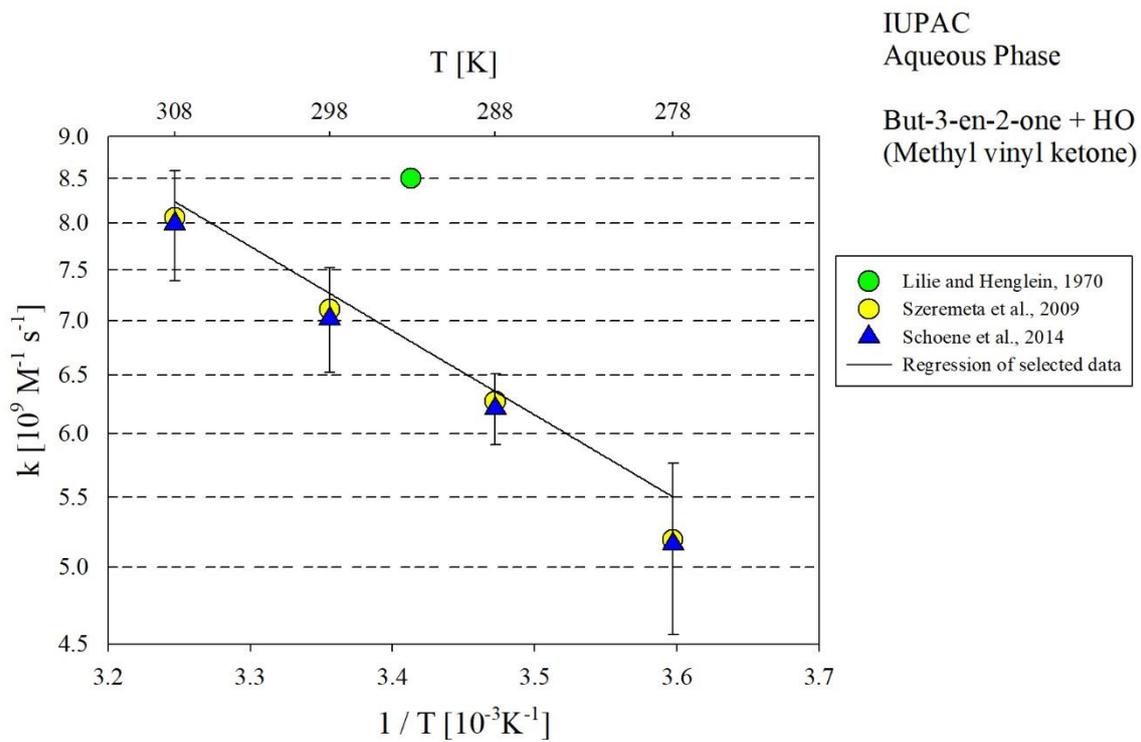
Parameter	Value	T/K
$k / \text{L mol}^{-1} \text{ s}^{-1}$	7.27×10^9	298
$k / \text{L mol}^{-1} \text{ s}^{-1}$	$4.72 \times 10^{11} \exp[-(1250)/T]$	278 - 308
<i>Reliability</i>		
$\Delta \log k$	± 0.24	298
$\Delta E_A/R$	± 250	278 – 308

Comments on Preferred Values

Data from Lilie and Henglein (1970), Szeremeta et al. (2009) and Schoene et al. (2014) have been used for regression ($r^2 = 0.94$). As the rate coefficients determined by Kumar et al. (1990) differ by a factor of 10 from all other determinations, they have not been considered for the evaluation. While both Szeremeta et al. (2009) and Schoene et al. (2014) determined values in perfect agreement, the rate coefficient of Lilie and Henglein from 1970 implies a higher value. From the regression of the considered data, a rate coefficient of $k(298 \text{ K}) = 7.26 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ is suggested, which is still in perfect agreement with both T dependent determinations within the error limits. The recommendation of $k = 8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ from 1988 by Buxton et al. (without recalculations) considers only the determination by Lilie and Henglein, which explains the deviation to the newly evaluated recommendation. The estimated uncertainty is given as $\Delta \log k = \pm 0.24$ or $\pm 50\%$.

References

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T-dependent rate coefficients for the reaction of methyl vinyl ketone with HO in aqueous solution. Data from Lilie and Henglein (1970), Szeremeta et al. (2009) and Schoene et al. (2014) have been considered for regression. Due to the high deviation, data from Kumar et al. (1990) is not shown.