IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

 – Data Sheet AQ\_OH\_3

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|  |  |  |
| --- | --- | --- |
| **HO (aq) + CH3CH2CH2OH (aq)** |  |  **CH3CH2CHOH (aq)**  **(53.4%)** |
|  |  | **+ CH2CH2CH2OH (aq)**  |
|  |  | **+ CH3CHCH2OH (aq)**  **(46%)****+ H2O (l)** |

(*Product distributions taken from Buxton et al., 1988, originally determined by Asmus et al., 1973 via PR - UV/Vis*)

**Rate coefficient data**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| k/ l mol-1 s-1 | T/K | pH | I/ mol l-1 | Reference | Technique/ Comments |
| *Relative Rate Coefficients* |
| 2.5  109 | 294 | 7 | - | Adams et al. 1965 | PR/UV-vis (a1) |
| 2.79  109 | 294 | 10.7 | - |  | PR/UV-vis (a2) |
| 2.5  109 | 294 | 7 | - | Adams et al., 1965 | PR/UV-vis (b1) |
| 2.8  109 | 294 | 10.7 | - |  | PR/UV-vis (b2) |
| 2.82  109 | 294 | 9 | - | Anbar et al., 1966 | CW / UV-vis (c) |
| 3.3  109 | 294 | 2 | - | Scholes and Willson, 1967 | CW /UV-vis (d1) |
| 3.0  109 | 294 | 5 | - |  | CW /UV-vis (d2) |
| 3.0  109 | 294 | - | - | Willson et al., 1971 | PR/UV-vis (e) |
| (3.1 ±0.2)  109 | 298 | 6 | 2  10-5 | Ervens et al., 2003 | LP-LPA (f) |
| 2.71  1010 exp[(-600 ±240) / T] | 288 - 328 | 6 | 2  10-5 |  |  |
| (3.8 ±0.7)  109 | 298 | 1 - 2 | - | Monod et al., 2005 | ASC / GC-FID (g1) |
| 2.85  1011 exp [- (1250 ± 220)/T] | 276 - 339 | 1 - 2 | - |  | ASC / GC-FID (g2) |

*GR* (aq): Aqueous phase thermochemical data not available. Gas phase thermochemical data *R* (g) are also not available (cf. gas phase data sheet HOx\_VOC25)

**Comments**

1. Reference systems HO + SCN- with *k*(HO + SCN-) = 6.6  109 M-1s-1 [1.10 × 1010M‑1s‑1 (Zhu et al., 2003)] (a1); HO + CO32- with *k*(HO + CO32-) = 2.0  108 M-1s-1 [3.77 × 108M‑1s‑1](a2); rate constants have been recalculated using the selected values for the reference reactions, given in brackets; no exact value is given for the initial concentrations of the reactants (‘a few millimolar’); as no exact temperature is given, for room temperature T = 294 K is assumed.
2. Reference systems:HO + SCN- with *k*(HO + SCN-) = 6.6  109 M‑1s‑1 [1.10 × 1010M‑1s‑1 (Zhu et al., 2003)](b1); HO + CO32-with *k*(HO + CO32-) = 2.0  108 M‑1s‑1 [3.77 × 108M‑1s‑1](b2); rate constants have been recalculated using the selected values for the reference reactions, given in brackets; no values given for the initial concentrations of the reactants; as no exact temperature is given, for room temperature T = 294 K is assumed.
3. Reference reaction: HO + PNDA (p-nitrosodimethylaniline), referring to HO + ethanol with *k*(HO + ethanol) = 1.10 × 109 M‑1s‑1; the rate constant has been recalculated using the selected value for the reference rate constant (1.85 × 109 M‑1s‑1); no values given for the initial concentrations of the reactants; as no exact temperature is given, for room temperature T = 294 K is assumed.
4. Reference reaction: HO + thymine; *k*(HO + thymine) = (4.3 ±1)  109 M-1s-1; the rate constant has been recalculated using the selected value for the reference rate constant (5.38 × 109 M‑1s‑1); *c*(thymine) = 8 × 10-5 - 2 × 10-4 mol/l ; The rate constant of the reference reaction was determined relative to benzene; aerated solutions; the absolute rate constants in table 3 have an error of about ± 25%; as no exact temperature is given, for room temperature T = 294 K is assumed.
5. Reference reaction: HO + [Fe(CN)6]4- ; *k*(HO + [Fe(CN)6]4-) = (9.3 ±0.5)  109 M-1s-1;rate constants have been recalculated using the selected rate constant for the reference reaction (1.03  1010 M-1s-1); *c*([Fe(CN)6]4-) = 2  10-3 mol/L (no information on counterions); the reference values listed in table 1 were normalized to *k*(·OH + ethanol) = 1.85  109 M-1s-1; as no exact temperature is given, for room temperature T = 294 K is assumed.
6. Reference reaction: HO + SCN- with *k*(T) = 7.26  1012 exp((-1900 ± 190) / T) M-1s-1 (Chin and Wine, 1992); rate constants have been recalculated using the T-dependent rate constants for reference reactions by Zhu et al., 2003.
7. Radicals generated by Fenton-reaction in a bulk reactor (an ‘aqueous phase smog chamber’ or ‘ASC’), products analysed by GC-FID; Reference reaction: HO + 2-propanol; *k*(HO + 2-propanol) = 1.9  109 M-1s-1; rate constants have been recalculated using the selected value for the reference rate constant (2.24 × 109 M‑1s‑1) (g1); For the Fenton-reaction, the initial concentrations of reactants were in the order of 10-3 M ; Arrhenius expression was calculated from the recalculated experimental data by Monod (2005) (g2), but given as: ln(*k*(T)) = 24.5 (±0.6) – 780(±200)/T in their publication, resulting from the combined data of Monod (2005) and Ervens et al. (2003); recalculation was performed using the selected T dependent rate coefficient *k*(T)(HO + 2-propanol) = 1.17 × 1011 exp(-1180/T).

**Preferred Values**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | ***T*/K** |
|  |  |  |
| *k* / l mol-1 s-1 | 3.20 × 109 | 298 |
| *k* / l mol-1 s-1 | *k*( T) = 3.2 × 1011  exp[- (1300) / *T*] | 276-339 |
|  |  |  |

*Reliability*

|  |  |  |
| --- | --- | --- |
| Δ log *k* | ± 0.10 | 298 |
| Δ EA/R | ± 280 |  |

*Comments on Preferred Values*

Buxton et al. (1988) recommended 2.8 × 109 l mol-1 s-1 in 1988 based on the averaged data from Adams et al. (1965), Anbar et al. (1966), Scholes and Willson (1967) and Willson et al. (1971). Work since then indicated a slightly higher rate coefficient. After 1988, for the first time two T-dependencies became available. As can be seen, there is considerable scatter in both T-dependent measurements and the linear regression of all data points indicates that the rate constant at T =298 K should be somewhat higher compared to the value recommend by Buxton et al. in 1988. Overall, it is suggested to use the combined result of both the recent T-dependent studies as the preferred value for this reaction.

With this, the most recent determinations are well represented in a unified way. The overall analysis shows that the rate constant at room temperature is somewhat higher than previously recommended. An error of Δ log *k* = ±0.1 or ±20% is estimated for the room temperature rate coefficient.

**References**

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 T-dependent rate constants for the reaction of 1-Propanol with HO in aqueous solution. Regression uses all data plotted in the Figure.