IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

– Data Sheet AQ\_OH\_1

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|  |  |  |
| --- | --- | --- |
| **HO (aq) + CH3OH (aq)** |  | **CH2OH (aq)**  **(93%)** |
|  | + | **CH3O (aq)**  **(7%)** |
|  | + | **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 |
| *Absolute Rate Coefficients* | | | | | | |
| 9.0 × 108 | | 294 | natural | - | Alam et al., 2003 | PR / UV-Vis abs. (l) |
| *Relative Rate Coefficients* | | | | | | |
| 5.0  108 | | 294 | 7 | 1.0  10-4 | Thomas, 1965 | PR / UV-Vis abs. (a) |
| 8.58  108 | | 294 | 10.7 | - | Adams et al., 1965 | PR / UV-Vis abs. (b1) |
| 7.80  108 | | 294 | 7 | - |  | PR / UV-Vis abs. (b2) |
| 4.68  108 | | 294 | 7 | 6.9  10-4 |  | PR / UV-Vis abs. (b3) |
| 8.7  108 | | 294 | 10.7 | - | Adams et al., 1965 | PR / UV-Vis abs. (c1) |
| 8.9  108 | | 294 | 7 | - |  | PR / UV-Vis abs. (c2) |
| 9.4  108 | | 294 | 7 | - |  | PR / UV-Vis abs. (c2) |
| 1.07 × 109 | | 294 | 7 | - | Woodward and Sutton, 1966 | cw-photol. / UV-Vis abs. (d) |
| 8.3  108 | | 294 | - | - | Neta and Dorfman, 1968 | PR / U V-Vis abs. (e1) |
| 8.3 × 108 | | 294 |  |  |  | PR / UV-Vis abs. (e2) |
| 8.4 × 108 | | 294 |  |  |  | PR / UV-Vis abs. (e3) |
| 9.5  108 | | 294 | - | - | Baxendale und Khan, 1969 | PR / UV-Vis abs. (f) |
| 9.5  108 | | 294 | 2 | - | Willson et al., 1971 | PR / UV-Vis abs. (g) |
| (1.00 ± 0.05)  109 | | 294 | 6.5 | 3  10-4 | Wolfenden and Willson, 1982 | PR / UV-Vis abs. (h) |
| 9.74  108 | | 293 | 7 | - | Elliot and McCracken, 1989 | PR / UV-Vis abs. (i1) |
| 3.84 × 1010 exp[-(1100±70) / *T*] | | 293 - 353 | - | - |  | PR / UV-Vis abs. (i2) |
| 8.38.4  108 | | 294 | 7.5 |  | Motohashi and Saito, 1993 | PR-HPLC (j) |
| (1.1±0.3) × 109 | | 295 | - | - | George et al., 2003 | LCW (k) |

*GR* (aq): Aqueous phase thermochemical data not available

For comparison: *R* (g) = -95.2 kJ mol-1 (gas phase, data sheet HOx\_VOC23)

**Comments**

1. Reference reaction: HO + I- with *k*(HO + I-) = (1.2±0.13)  1010 M‑1s‑1; relative rate coefficient given as *k*(HO + methanol) / *k*(HO + I-) = (4.6±0.4)  10-2; the rate constant was recalculated using the selected value for the reference reaction *k*(HO + I-) = 1.1  1010 M‑1s‑1; as no exact temperature is given, for room temperature T = 294 K is assumed.
2. Reference reaction HO + CO32- with *k*(HO + CO32-) = 2.0  108 M-1s-1 [3.77  108M‑1s‑1] (b1); HO + SCN- with *k*(HO + SCN-) = 6.6  109 M-1s-1 [1.08  1010 M-1s-1 ] (b2); HO + selenite (SeO32-) with *k*(HO + selenite) = 2.7  109 M-1s-1 [2.60  109 M-1s-1 ] (b3); recalculations of the rate constants were done using the selected values for the reference reactions (given in brackets); as no exact temperature is given, for room temperature T = 294 K is assumed.
3. Reference reaction: HO + CO32- with *k*(HO + CO32-) = 2.0  108 M-1s-1 (taken from previous studies by Adams et al.), recalculation of the rate constants were done using the selected value for the reference reaction *k*(HO + CO32-) = 3.8  108 M-1s-1, determinations differ from pH = 10.7 (c1) and 7 (c2); as no exact temperature is given, for room temperature T = 294 K is assumed.
4. Reference reaction: HO + NO; *k*(HO + NO) = 6.0 × 109 M-1s-1; a relative rate constant of *k*(HO + NO) / *k*(HO + EtOH) is given as (4.8 ±0.6); determined rate constants were than referenced to *k*(HO + EtOH), defined as 1, with *k*(HO + MeOH) being 0.35.
5. Reference reactions: HO + C6H5CO2-; *k*(HO + C6H5CO2-) = (6.0 ± 0.7)  109 M-1s-1 (e1); HO + C6H5CH2CO2-; *k*(HO + C6H5CH2CO2-) = (7.9 ± 1.1)  109 M-1s-1 (e2); HO + *p*-NO2 C6H4CO2-; *k*(HO + *p*-NO2 C6H4CO2-) = (2.6 ± 0.4)  109 M-1s-1 (e3); rate constant (e1) was recalculated using the selected value for the reference reaction (5.97  109 M-1s-1); the authors recommend the average of the three determinations with the different scavengers listed above, given as(8.4 ±1) × 108 M‑1s‑1; the absolute error of the mean rate constant is provided by the authors; as no exact temperature is given, for room temperature T = 294 K is assumed.
6. Reference reaction HO + PNDA; *k*(HO + PNDA) = 1.25  1010 M-1s-1.
7. Reference reaction HO + Fe(CN)64-; *k*(HO + Fe(CN)64-) = (0.93 ± 0.05)  1010 M-1s-1; rate constant has been recalculated using the selected value for the reference reaction (1.03  1010 M-1s-1); *c*([Fe(CN)6]4-) = 2  10-3 mol/l; as no exact temperature is given, for room temperature T = 294 K is assumed.

1. Reference reaction HO + ABTS2- (ABTS = 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid); *k*(HO + ABTS2-) = 1.2  1010 M-1s-1; *c*(ABTS) = 1  10-4 mol/l; as no exact temperature is given, for room temperature T = 294 K is assumed.
2. Reference reaction (i1) HO + SCN- Arrhenius expression (i2) has been calculated using the given T-dependent data referring to HO + SCN-; as reference rate coefficients, it is suggested to refer to Elliot and Simsons, 1984, as no specific reference is mentioned.
3. Reference reaction: HO + benzoate; *k*(HO + benzoate) = 5.9  109 M-1s-1; rate constant was recalculated using the selected value for the reference reaction (5.97  109 M-1s-1; as no exact temperature is given, for room temperature T = 294 K is assumed.
4. Radicals generated by photolysis of H2O2 in a liquid core waveguide (LCW) at ≤366 nm; reference reaction: HO + SCN- with *k*(HO + SCN-) = 1.29 × 1010M‑1s‑1 referring to Chin and Wine (1992); *c*(H2O2) = 10-3 M, *c*(SCN‑) = 2 × 10‑4 M, *c*(methanol) = 10‑3 M.
5. Products analysed by UV-vis-spectroscopy; 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.

**Preferred Values**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | ***T*/K** |
|  |  |  |
| *k* / l mol-1 s-1 | 9.7 × 108 | 298 |
|  |  |  |
| *k* / l mol-1 s-1 | 6.55 × 1010 exp[-(1250) / *T*)] | 293-353 |
|  |  |  |

*Reliability*

|  |  |  |
| --- | --- | --- |
| Δ log *k* | ± 0.09 | 298 |
| Δ EA/R | ± 100 | 293-353 |
|  |  |  |

*Comments on Preferred Values*

Buxton et al. recommended 9.7  108 l mol-1 s-1 in 1988 based on the standardization study of Willson et al.. The carefully performed and only available T-dependent study by Elliot and McCracken leads to *k* = 1.03  109 l mol-1 s-1 for T = 298 K by applying the provided Arrhenius expression as no direct measurement has been performed by these authors at T = 298 K. The most recent determination of this rate constant by George et al. (2003) is in agreement with the others within error limits and is included in the calculation of the recommended value of 9.7  108 l mol-1 s-1. The rate coefficients determined by Thomas (1964) and Adams et al. (1965) [5.02 × 108 l mol-1 s-1 and 4.68 × 108 l mol-1 s-1] have not been considered for the evaluation of the recommendations because the rate constants from these studies are too small even after their re-evaluation with new competition kinetics reference data.

The reliability of the preferred value is estimated to be ±20% or Δ log *k* = 0.09.

**References**

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T-dependent rate coefficients for the reaction of Methanol with HO in aqueous solution. Data determined by Thomas (1964) and Adams et al. (1965) were not included in the regression.