IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

 – Data Sheet AQ\_OH\_2

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|  |  |  |
| --- | --- | --- |
| **HO (aq) + CH3CH2OH (aq)** |  |  **CH3CHOH (aq)** **(84.3%)** |
|  |  | **+ CH3CH2O (aq) (2.5%)** |
|  |  | **+ CH2CH2OH (aq)**  **(13.2%)** |
|  |  | **+ H2O (1)**  |

(*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* |
| 2.2 × 109 | 294 | 7 | - | Alam et al., 2003 | PR-UV/Vis (a) |
| *Relative Rate Coefficients*  |
| 7.69  108 | 294 | 7 | 1  10-4 | Thomas, 1965 | PR-UV/Vis (b) |
| 1.83  109 | 294 | 10.7 | - | Adams et al., 1965 | PR-UV/Vis (c1) |
| 1.80 109 | 294 | 7 | - |  | PR-UV/Vis (c2) |
| 1.04  109 | 294 | 7 | 6.9  10-4 |  | PR-UV/Vis (c3) |
| 1.83  109 | 294 | 7 | - | Adams et al., 1965 | PR-UV/Vis (d) |
| 1.63  109 | 294 | 2 | - |  | PR-UV/Vis (d) |
| 2.26  109 | 294 | - | - | Adams et al., 1965 | PR-UV/Vis (e) |
| 1.7  109 | 291 - 298 | 10.5 – 10.8 | - | Matthews and Sangster, 1965 | cw radiolysis-Tracer (f) |
| 3.04 × 109 | 293 | 7 | - | Woodward and Sutton, 1966 | PR-UV/Vis (g) |
| 4.7  108 | 294 | - | 1 | Heckel et al., 1966 | PR-UV/Vis(h) |
| 2.0  109 | 294 | 3 | - | Scholes and Willson, 1967 | PR-UV/Vis (i) |
| 1.75  109 | 294 | 6-7 | - |  | PR-UV/Vis (i) |
| 1.81  109 | 294 | - | - | Neta P. and Dorfman L.M., 1968 | PR-UV/Vis (j1) |
| 1.83  109 | 294 | - | - |  | PR-UV/Vis (j2) |
| 1.81 109 | 294 | - | - |  | PR-UV/Vis (j3) |
| 1.6  109 | 294 | - | - | Baxendale and Khan, 1969 | PR-UV/Vis RR (k) |
| (2.1 ±0.3)  109 | 293 - 298 | 11 - 13 | - | Buxton, 1970 | PR-UV/Vis RR(l) |
| 2.04  109 | 294 | 2 | 2 × 10-2 | Willson et al., 1971 | PR-UV/Vis RR (m) |
| 1.82  109 | 294 | - | - | Matheson et al., 1973 | PR-UV/Vis RR (n) |
| (1.90 ±0.1)  109 | 294 | 6 | 3 × 10-4 | Wolfenden and Willson, 1982 | PR-UV/Vis RR (o) |
| (1.9 ±0.1)  109 | 294 | 9 | 12.5 – 25 × 10-5 | Park and Getoff, 1992 | PR-UV/Vis RR (p) |
| 2.2  109 | 294 | 7.5 | - | Motohashi and Saito, 1993 | PR-HPLC(q) |
| (2.1 ± 0.4)  109 | 293 | - | - | Monod et al., 2002 | (r) |
| (2.0 ±0.1)  109 | 298 | - | 2 × 10-5 | Ervens et al., 2003 | LP-LPA (s1) |
| 4.52 × 1010 exp[-(900 ±180) / *T*] | 283-328 | - | - |  | LP-LPA (s2) |
| (1.7±0.5) × 109 | 295 | - | - | George et al., 2003 | LCW (t) |
| (2.1 ±0.3) × 109 | 298 | 1 - 2 | - | Monod, 2005 | ASC / GC-FID (u1) |
| 2.83 × 1010 exp[-(770 ± 30) / *T*] | 276 - 328 | 2 | - |  | ASC / GC-FID (u2) |

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

For comparison: *R* (g) = -95.8 kJ mol-1 (gas phase, data sheet HOx\_VOC24)

**Comments**

1. 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; as no exact temperature is given, for room temperature T = 294 K is assumed.
2. Reference reaction HO + I-; *k*(HO + I-) = (1.02 ± 0.13)  1010 M-1s-1, *c*(I-) = 5  10-5 mol/l. This concentration is used for the calculation of I as no exact temperature is given, for room temperature T = 294 K is assumed.

1. Reference reactions (c1): HO + CO32-, *k*(HO + CO32-) = 2  108 M-1s-1 [3.8  108 M‑1s‑1], no concentrations given; (c2) HO + SCN-, *k*(HO + SCN-) = 6.6  109 M‑1s‑1 [1.08  108 M‑1s‑1], *c*(SCN-) = 8 - 400  10-6 mol/l; (c3) HO + selenite (SeO32-), *k*(HO + SeO32-) = 2.7  109 M-1s-1 [2.6  108 M‑1s‑1], c = 2.3  10-4 mol/l; recalculation of the rate coefficient has been done using the selected values for the reference reaction given in brackets; as no exact temperature is given, for room temperature T = 294 K is assumed.
2. Experimental conditions see (c); exp. values of (c) also listed (Table I of the reference, values given here are those of Table II of the reference). reference reaction: HO + SCN- with *k*(HO + SCN-) = 6.6  109 M-1s-1; *c*(SCN‑) = 1-50  10-3 mol/l; rate coefficient recalculated using the selected value *k* = 1.10 × 1010 M‑1s‑1; as no exact temperature is given, for room temperature T = 294 K is assumed.
3. Experimental conditions see (c); Reference reaction: HO + [Fe(CN)6]4- with *k*(HO + [Fe(CN)6]4-) = 5.0  109 M‑1s‑1; recalculations performed, using the selected rate coefficient *k*(HO + [Fe(CN)6]4-) = 1.03 × 1010 M‑1s-1; as no exact temperature is given, for room temperature T = 294 K is assumed.
4. Analysis of 14CO2 formed from the competition reaction HO + C6H514COO- with *k*(HO + benzoate) = 1.0  109 M-1s-1; relative rate coefficient given as 0.28; recalculated using the selected rate coefficient *k*(HO + benzoate) = 5.88  109 M-1s-1; The ionic strength was calculated from the given concentration of benzoic acid with c = 8  10-3 mol/l. This competition kinetics method is different from most other ones, it directly determines the yield of 14CO2 formed by single electron transfer from the carboxylate group to HO. As HO will react by addition to the aromatic ring as well, this method should be considered with great care, however; for evaluation, the mean of the given temperature range was used.
5. 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); rate coefficient has been recalculated using the selected value *k*(HO + NO) = 1.46 × 1010 M‑1s‑1.
6. Reference reaction HO + HSO4-; *k*(HO + HSO4-) = 8  105 M-1s-1 is calculated based on data by Adams et al.; a separate determination of this reference rate constant lead to *k*(HO + HSO4-) = 6.9  105 M-1s-1, the authors decide to use the above value by Adams as the reference rate constant. Table 1 of the reference gives ratios *k*Substance / *k*(HO + HSO4-) and , specifically, *k*Ethanol/*k*(HO + HSO4-) = 5.5  102, leading to the tabulated absolute rate constant; as no exact temperature is given, for room temperature T = 294 K is assumed.
7. Reference reaction: HO + thymine; *k*(HO + thymine) = 4.3  109 M-1s-1, *c*(thymine) = 0.8 - 2  10-4 mol/l; recalculations performed using the selected rate coefficient *k*(HO + thymine) = 5.38  109 M-1s-1; as no exact temperature is given, for room temperature T = 294 K is assumed.
8. Reference reactions: C6H5CO2- + HO with *k*(C6H5CO2- + HO) = (6.0 ± 0.7) × 10-9 M-1s-1 (j1); C6H5CH2CO2- + HO with *k*(C6H5CH2CO2- + HO) = (7.9 ± 1.1) × 10-9 M-1s-1 (j2); *p*-NO2 C6H4CO2- + HO with *k*(*p*-NO2 C6H4CO2- + HO) = (2.6 ± 0.4) × 10-9 M-1s-1 (j3); the authors recommend the mean of the three determinations with the above different scavengers, given as (1.83 ±2) × 109 M‑1s‑1; the rate coefficient of (i1) has been recalculated using the selected rate coefficient for the reference reaction *k*(HO + C6H5CO2-) = 5.88 × 10-9 M-1s-1; as no exact temperature is given, for room temperature T = 294 K is assumed.
9. Reference reaction HO + p-nitrosodimethylanilin (4-Me2NC6H4NO); *k*(HO + 4-Me2NC6H4NO) = (1.25 ± 0.2)  1010 M-1s-1, c = 9.4  10-6 mol/l, The concentration of *p*-nitrosodimethylanilin used for the ethanol measurement was taken from Figure 5 of the reference.
10. Reference reaction HO + CO32- , *k*(HO + CO32-) = 4.0  108 M-1s-1, recalculation of the rate coefficient has been done using the selected values for the reference reaction (3.8  108 M‑1s‑1); measurements at pH 11 (0.01mol l-1 CO32- + 2.3  10-2 HCO3-) and pH 13 (0.1M CO32-).
11. Reference reaction HO + [Fe(CN)6]4-; *k*(HO + [Fe(CN)6]4-) = 0.93±0.05  1010 M-1s-1, recalculations performed, using the selected rate coefficient *k*(HO + [Fe(CN)6]4-) = 1.03 × 1010 M‑1s-1; *c*([Fe(CN)6]4-) = 2  10-3 mol/l – used for calculating I; as no exact temperature is given, for room temperature T = 294 K is assumed.
12. Reference reaction HO + [Fe(CN)6]4- ; *k*(HO + [Fe(CN)6]4-) = 0.93  1010 M‑1s‑1; recalculations performed, using the selected rate coefficient *k*(HO + [Fe(CN)6]4-) = 1.03 × 1010 M‑1s-1; as no exact temperature is given, for room temperature T = 294 K is assumed.
13. Reference reaction ABTS2- + HO, *k*(HO + ABTS2-) = 1.2  1010 M-1s-1, *c*(ABTS2-) = 10-4 mol/l; as no exact temperature is given, for room temperature T = 294 K is assumed.
14. Reference reaction HO + [Fe(CN)6]4- ; *k*(HO + [Fe(CN)6]4-) = 1  1010 M-1s-1 taken from Elliot and Simsons (1984); recalculations performed, using the selected rate coefficient *k*(HO + [Fe(CN)6]4-) = 1.03 × 1010 M‑1s-1; *c*([Fe(CN)6]4-) = 2.5 – 5.0  10-5 mol/l, used to calculate I; as no exact temperature is given, for room temperature T = 294 K is assumed.
15. Reference reaction C6H5CO2- + HO, *k*(HO + C6H5CO2-) = 5.9  109 M-1s-1, *c*(C6H5CO2‑) = 2  10-4 mol/l; as no exact temperature is given, for room temperature T = 294 K is assumed.
16. cw-photolysis of H2O2 with a Xe-lamp solar simulator. Product analysis by GC, HPLC and IC; proof of concept study with no reference given for the competition kinetics; no further evaluation of this rate coefficient can be done.
17. Reference reaction HO + SCN‑; *k*(HO + SCN-) = 7.26  1012 exp(-1900±190/T) M-1s-1, *c*(SCN-) = 2  10-5mol/l, *c*(H2O2) = 5  10-4 mol/l; the Arrhenius expression (s2) is resulting from the determined temperature dependent data; rate coefficients have been recalculated using the selected T dependent values for the reference reaction (Zhu et al., 2003).
18. 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); rate coefficient recalculated using the selected value *k* = 1.10 × 1010 M‑1s‑1; *c*(H2O2) = 10-3 M, *c*(SCN‑) = 2 × 10‑4 M, *c*(ethanol) = ~10‑3 M.
19. (u1) Radicals generated by Photo-Fenton-reaction in a bulk reactor (an ‘aqueous phase smog chamber’ or ‘ASC’), products analysed by GC-FID; Reference reaction: HO + methanol; *k*(HO + methanol) = 9.8 × 108 M-1s-1

Arrhenius expression (u2) is calculated from the experimental data of Monod (2005), but given as ln *k*(T) = (24.2 ±0.4) – [(830 ±140)/T] in their publication, resulting from the combined data of Monod (2005) and Ervens et al. (2003); reference systems used for recalculations: HO + 1‑propanol, with *k*(T) = 7.0 × 1010 exp(-900 ±250/T) and HO + methanol with *k*(T) = 6.7 × 1010 exp(-1200. ±120).

**Preferred Values**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | ***T*/K** |
|  |  |  |
| *k* / l mol-1 s-1 | 1.99  109  | 298 |
|  |  |  |
| *k* / l mol-1 s-1 | 3.45 × 1010 exp[-(860) / *T*] | 293-353 |
|  |  |  |

*Reliability*

|  |  |  |
| --- | --- | --- |
| Δ log *k* | ± 0.3 | 298 |
|  |  |  |
| Δ EA/R | ± 250 | 293 - 353 |
|  |  |  |

*Comments on Preferred Values*

Buxton et al. recommended 1.9  109 l mol-1 s-1 in 1988. Work since then in four out of five studies indicates that the rate constant may be slightly higher, calculations of the recommended value confirm the rate constant to be 2.0 × 109 l mol-1s-1. The most recent determination of this rate constant by George et al. (2003) is in agreement with this value within error limits as well. The uncertainty of the preferred value is twice the one given by Ervens et al. thus including the recommended value by Buxton et al. (1988). The recommended Arrhenius expression is based on the regression of the available data, excluding the determinations by Thomas (1965) and Woodward and Sutton (1966) due to their values exceeding the accepted range for the rate constants, as well as Heckel et al. (1966) and Monod et al. (2002). Even though the rate coefficient determined by Monod et al. (2002) agrees with the recommended value within an error limit of 10%, it is not considered for the final regression. Lack of information concerning the reference rate constants used for the competition kinetics method do not allow for proper evaluation. As Heckel et al. (1966) use H2SO4 as reference, it is advised to not consider this rate constant, as the rate coefficient exceeds the referencing rate coefficient by a factor of 103.

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T-dependent rate constants for the reaction of Ethanol with HO in aqueous solution. Data from Thomas (1965), Heckel et al. (1965), Woodward and Sutton (1966) and Monod et al. (2002) were excluded from regression.