**IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_4**

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This datasheet last evaluated: May 2020; last change in preferred values: February 2020

1. **CH2OO + H2O → HOCH2OOH (1a)**

 **→ HCHO + H2O2 (1b)**

 **→ HC(O)OH + H2O (1c)**

1. **CH2OO + (H2O)2 → HOCH2OOH + H2O (2a)**
2. **→ HCHO + H2O2 + H2O (2b)**
3. **→ HC(O)OH + 2H2O (2c)**
4. **Rate coefficient data**

|  |  |  |  |
| --- | --- | --- | --- |
| *k*/cm3 molecule-1 s-1 | Temp./K | Reference | Technique/Comments |
| *Absolute Rate Coefficients* |  |  |  |
| *k*1 < 4.0  10-15 | 298 | Welz et al., 2012 | PLP-PIMS(a) |
| *k*1 < 9  10-17 | 295 | Stone et al., 2014 | PLP-LIF/PIMS (b) |
| *k*1 = (3.2 ± 1.2)  10-16 | 297 | Berndt et al., 2015 | Free-Jet FR-TOF-MS (c) |
| *k*2 = (6.5 ± 0.8)  10-12 | 298 | Chao et al., 2015 | PLP-UVAS(d) |
| *k*2 = (4.2 ± 1.2)  10-12 | 294 | Lewis et al., 2015 | PLP-LP-UVAS (e) |
| *k*2 = (7.4 ± 0.6)  10-12 | 298 | Smith et al., 2015 | PLP-LP-UVAS (f) |
| *k*2 = 8.72  10-18 exp[(4076 ± 302)/*T*] | 283-324 |  |  |
| *k*1 = (2.4 ± 1.6)  10-16 | 293 | Sheps et al., 2017 | TR-BB-CEAS/PIMS (g) |
| *k*2 = (6.6 ± 0.7)  10-16 | 293 |  |  |
| *Relative Rate Coefficients* |  |  |  |
| *k*1 = (8.5 ± 3.7)  10-15  | 298 | Suto et al., 1985  | RR-AFT-UVscat (h) |
| *k*1 = (1.1 ± 0.4)  10-17  | 297 | Ouyang et al., 2013 | RR-LP-UVvis (i) |
| *k*2 = (1.07 ± 0.04)  10-11 | 293 | Berndt et al., 2014 | RR-AFT-CIMS(ToF) (j) |
| *k*1 = (9.3 ± 2.6)  10-16 | 298 | Newland et al., 2015 | RR-FTIR/UVAS/UVF (k) |
| *k*2 = (5.2 ± 6.7)  10-13 | 298 |  |  |
| *Branching ratios* |  |  |  |
| *k*1a/*k*1 = 0.73 | 295 | Nguyen et al., 2016 | (l) |
| *k*1b/*k*1 = 0.06 | 295 |  |  |
| *k*1c/*k*1 = 0.21 | 295 |  |  |
| *k*2a/*k*2 = 0.40 | 295 |  |  |
| *k*2b/*k*2 = 0.06 | 295 |  |  |
| *k*2c/*k*2 = 0.54 | 295 |  |  |
| *k*2a/*k*2 = 0.55 ± 0.15 | 293 | Sheps et al., 2017 | TR-BB-CEAS/PIMS (g) |
| *k*2b/*k*2 = 0.40 ± 0.10 | 293 |  |  |
| *k*2c/*k*2 = < 0.10 | 293 |  |  |

**Comments**

1. CH2OO was produced by the reaction of CH2I + O2. CH2I was generated by 248-nm laser photolysis of di-iodomethane, CH2I2, at 298 K and 4 torr, in a large excess of O2. The reacting mixture was monitored by tunable synchrotron photoionization mass spectrometry, which allowed characterisation of the PIMS for CH2OO and its reaction products over the region 9.5 – 11.5 eV. Time-resolved direct detection of [CH2OO] decay at m/z = 46. The first order decay of CH2OO in the presence of excess known concentrations of H2O was used to determine the rate constants, at a total pressure of 4.5 Torr. The upper limit determined on the basis of absence of any effect of [H2O] = 3  1016 molecule cm-3
2. Photolysis of CH2I2-O2-N2 mixtures in the presence of excess H2O, under pseudo-first-order conditions. Kinetics of CH2OO + H2O reaction were followed by time-resolved monitoring of HCHO product by laser-induced fluorescence (LIF) spectroscopy (pressure range: 50 – 450 Torr). Rate coefficients for CH2OO + H2O was investigated at 200 Torr, using up to [H2O] = 1.7  1017 molecule cm-3. The cited value of *k* is an upper limit based on the lack of significant effect of [H2O] and the assumption that HCHO detected is derived solely from reaction with H2O.
3. The rate coefficients of the bimolecular reaction of CH2OO with the water monomer have been experimentally determined at T = (297 ± 1) K and at atmospheric pressure by using a free-jet flow system. CH2OO was produced by the reaction of ozone with C2H4, and [CH2OO] was measured indirectly by titrating with excess SO2 and detection of product H2SO4 after 7.5 s reaction time. Low water concentrations of [H2O] < 1015 molecule cm-3 and, as a consequence, very low water dimer concentrations of [(H2O)2] = 2.5 × 109 molecule cm-3 (Scribano et al., 2006) permitted the separation of reaction (1) from reaction (2). The cited rate coefficient *k*1 was determined by fitting a parameterized expression for the [H2O] dependence of the ratio [H2SO4]/[C2H4], assuming *k*uni = 0.19 s-1, and appropriate uncertainty in the parameters.
4. CH2OO prepared by PLP (266 nm) of CH2I2 in O2/Ar mixtures at 5.1 Torr pressure. CH2OO kinetics observed by time-resolved UV absorption in the B̃ (1A′) ← X̃(1A′) electronic transition, measured over range 280-600 nm using a CCD or a photodiode (at 350 ± 5 nm), in the absence and presence of H2O (RH = 3 % to 80 %). Rate constants extracted by fitting plots of *k*obs vs RH or [(H2O)2], calculated using *K*p (298) = 0.0501 bar-1 at 298 K where *P*sat = 23.8 torr. Uncertainty on [(H2O)2] was estimated to be ± 12 %. Incorporation of the monomer reaction into the fit gave *k*1 < 1.5  10-15 cm3 molecule-1 s-1.
5. CH2OO prepared by PLP (266 nm) of CH2I2 in O2/Ar mixtures at 5.1 Torr pressure. CH2OO kinetics, observed by time-resolved UV absorption in the B̃ (1A′) ← X̃(1A′) electronic transition between 350 – 420 nm, were first order in the presence and absence of H2O, independent of total pressure. However, dependence of the first-order decay constant on [H2O] in the range 0 to 25  1016 molecule cm-3 was fitted best by a quadratic function, indicating that CH2OO was reacting predominantly with the water dimer. The cited rate coefficient, *k*2, was calculated using the parameterisation of Scribano et al. (2006) to calculate [(H2O)2], i.e. *K*p (298) = 0.0579 bar-1 at 294 K.
6. CH2OO prepared by PLP (248 nm) of CH2I2 in N2/O2 at 5.1 Torr pressure. CH2OO was observed by time-resolved of UV absorption at 340 nm. The kinetics of the reaction of CH2OO with water vapor was measured as a function of [H2O] at temperatures from 283 to 324 K. The observed first-order decay constant increased quadratically with [H2O], consistent with dominant reaction with the water dimer. The dimer concentrations were calculated using the T-dependent equilibrium constant for water dimerization, *Ke*q(T) of Ruscic (2013), with values of *k*2 derived from the variation of the first-order decay constant with [(H2O)2]. They report an activation energy of -(8.1 ± 0.6) kcal mol-1, from the variation of *k*2 over the studied temperature range, and this forms the basis of the Arrhenius expression tabulated above.
7. CH2OO prepared by PLP (248, 266 or 351nm) of CH2I2 in O2/He or O2/N2 at 30-100 Torr pressure. The experiments were probed using either time-resolved broadband cavity-enhanced absorption spectroscopy (TR-BB-CEAS) or photoionization mass spectrometry (PIMS). Values of *k*1 and *k*2 obtained from variation of observed first-order decay constants in experiments performed over a range of [H2O], using a simplified mechanism in which CH2OO was removed by reactions (1), (2) and background loss process. Product identification and quantification using PIMS allowed channel contributions to be determined for reaction (2).
8. Flow system involving C2H4-O3-SO2-H2O mixtures in which H2SO4 aerosol concentrations were monitored by scattered UV light. Relative rate coefficients obtained from the dependencies of the aerosol formation on the concentrations of O3, SO2, and H2O. The relative rate constant reported was *k*1/*k*(CH2OO + SO2) = (2.3 ± 1.0)  10-4. The value of *k*1 tabulated above is based on *k*(CH2OO + SO2) = 3.7  10-11 cm3 molecule-1 s-1 (IUPAC, current recommendation).
9. Photolysis of CH2I2-O2-N2-NO2 mixtures at 348 nm in continuous flow conditions at 760 Torr pressure. CH2OO produced in this system was allowed to react with NO2. Simultaneous measurement of products NO3 and [N2O5+NO2] was made at 663 nm. Analysis of these data as function of [NO2] allowed evaluation of the rate constant ratio: *k*d(CH2OO)/*k*(CH2OO + NO2) = (6.4 ± 1.7)  1012 molecule cm-3, where *k*d is the total loss rate constant for competing first order processes. Assuming the competing kinetics is dominated by the reaction of Criegee intermediates with water gave the rate constant ratio: *k*(CH2OO + H2O)/*k*(CH2OO + NO2) = 3.6  10-6 (error ± 40 %). The value of *k*1 tabulated above is based on *k*(CH2OO + NO2) = 3  10-12 cm3 molecule-1 s-1 (IUPAC, current recommendation).
10. CH2OO produced from O3 + C2H4 reaction in atmospheric pressure flow tube at 293 ± 0.5 K. H2SO4 formation from the reaction CH2OO + SO2 as a function of RH (= 2% to 50%) for close to atmospheric conditions, was measured using NO3--CI-APi-TOF-MS. The uncertainty in the [H2SO4] estimated to be ± 45%. Second-order kinetics with regard to water vapour concentration indicates a preferred reaction of CH2OO with the water dimer. The relative rate coefficient *k*2/*k*(CH2OO + SO2) = 0.29 ± 0.01, based on *K*p calculated using the parameterisation of Scribano et al. (2006). Measurements at the lowest relative humidity (RH ~2%) yield an upper limit of the rate coefficient ratio *k*uni/*k*(CH2OO + SO2) = 2.4  1011 molecule cm-3, where *k*uni is the total first order loss coefficient for CH2OO in the absence of water dimer. Combining *k*2/*k*(CH2OO + SO2) = 0.29 ± 0.01 with *k*(CH2OO + SO2) = 3.7  10-11 (IUPAC, current recommendation) gives the tabulated value of *k*2 above.
11. The removal of SO2 in the presence of ethene-ozone systems was measured as a function of humidity in EUPHORE simulation chamber, under atmospheric boundary layer conditions. SO2 and O3 abundance were measured using conventional fluorescence and UV absorption monitors, respectively; alkene abundance was determined via FTIR spectroscopy. SO2 removal decreased with increasing relative humidity (1.5 – 21%) confirming a significant reaction for CH2OO with H2O. The observed SO2 removal kinetics are consistent with the relative rate constant, *k*1/*k*(CH2OO + SO2) = (3.3 ± 1.1)  10-5, if removal is due solely to reaction (1). An expanded analysis considering removal by both reactions (1) and (2) yielded *k*1/*k*(CH2OO + SO2) = (2.5 ± 0.7)  10-5 and *k*2/*k*(CH2OO + SO2) = (1.4 ± 1.8)  10-2. The values of *k*1 and *k*2 tabulated above are based on *k*(CH2OO + SO2) = 3.7  10-11 cm3 molecule-1 s-1 (IUPAC, current recommendation).
12. Products formed from the ozonolysis of isoprene investigated in the multi-instrumented Caltech dual 24m3 teflon chamber at atmospheric pressure. CH2OO reported to dominate the population of stabilized Criegee intermediates formed, and their bimolecular reactivity. HOCH2OOH, HC(O)OH and H2O2 were quantified with a triple-quadrupole chemical ionization mass spectrometer (CIMS) using CF3O- as an ionization reagent. The product channel contributions for reactions (1) and (2) were determined from from the observed product distribution, and its dependence on [H2O], by simulations of the system using a detailed chemical mechanism, with *k*1 = 9.0 × 10-16 cm3 molecule-1 s-1 and *k*2 = 8.0 × 10-13 cm3 molecule-1 s-1.

**Preferred Values**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | **T/K** |
|  |  |  |
| *k*1 /cm3 molecule-1 s-1 | 2.8  10-16 | 298 |
| *k*2 /cm3 molecule-1 s-1 | 6.4  10-12 | 298 |
| *k*2 /cm3 molecule-1 s-1 | 7.35  10-18 exp(4076/*T*) | 280-325 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  log *k*1 | ± 0.3 | 298 |
|  log *k*2 | ± 0.2 | 298 |
|  (*E*2/*R*) | ± 500 K | 280-325 |

1. *Comments on Preferred Values*

An important discovery arising from the direct studies of CH2OO reaction with water vapour was the quadratic dependence of the pseudo-first order rate constant for loss of CH2OO on [H2O]. This is consistent with the predominant reaction being with the water dimer (*k*2). The reaction with monomeric water molecules (*k*1) is slow, and probably less important under atmospheric conditions. This conclusion is supported by recent relative rate studies, although there remain inconsistencies in results obtained in different laboratories. The most recent study of Smith et al. (2015) reports a strong negative temperature dependence for the reaction of CH2OO with the water dimer, also consistent with dimer reaction. Their reported (negative) activation energy forms the basis of the preferred value of *E*2/R.

Because of the observed quadratic dependence of the rate on [H2O] only those experimental studies which employed conditions of high enough [H2O] provide [(H2O)2] sufficient to compete with monomer reaction and other loss reactions of CH2OO. The preferred value of *k*2 at 298 K is the mean of the values from the direct kinetic studies of Chao et al. (2015), Smith et al (2015) and Sheps et al. (2017) (corrected to 298 K using the preferred value of *E*2/R); and is also consistent with the direct kinetic determination of Lewis et al. (2015) within the assigned uncertainty. These results at room temperature are in very good agreement, considering the experimental uncertainty arising mainly from uncertainty in [H2O] which propagates by a factor of two in calculating [(H2O)2]. Support for these high values of *k*2 comes from the relative rate study of Berndt et al. (2014). The preferred value of *k*1 at 298 K is the mean of the absolute values reported by Berndt et al. (2015) and Sheps et al. (2017), which are in good agreement. Most other kinetic studies take no account of the dimer reaction and only provide upper limits pertaining to *k*1. The relative rate study of Newland et al. (2015) considers the possibility of a significant reaction with water dimer, but only provides an indeterminate value for *k*2/*k*(CH2OO + SO2). The reported relative rate constant ratio *k*1/*k*(CH2OO + SO2) = (2.5 ± 0.7) × 10-5 at 298 K in their expanded analysis, implies the contribution of *k*1 to the overall rate of CH2OO loss too small to detect at [H2O] used in the experiments of Welz et al. (2012).

Work of Neeb et al. (1997) shows that the reaction of CH2OO with H2O leads initially to hydroxymethyl hydroperoxide (HOCH2OOH). Estimates using quantum chemistry calculations of the rate coefficient for reaction of CH2OO with water vapour dimer forming HOCH2OOH product (Ryzhkov and Ariya, 2004), are of a similar order of magnitude to the experimental values. HOCH2OOH is expected to be formed chemically activated, and is either subsequently thermalized or decomposes to form HCHO and H2O2 or HC(O)OH and H2O. In their study of the ozonolysis of isoprene, from which CH2OO is believed to be the dominant sCI formed, Nguyen et al. (2016) were able to derive the product channel contributions tabulated above for reactions (1) and (2). However, there is some disagreement with those subsequently reported for reaction (2) by Sheps et al. (2017), in which CH2OO was produced by photolysis of CH2I2/O2. Although both studies report an important contribution from channel (2a), forming HOCH2OOH, they provide contradictory conclusions for the contributions of the HCHO and HC(O)OH forming channels (2b) and (2c). Further studies are required before firm recommendations can be made.

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