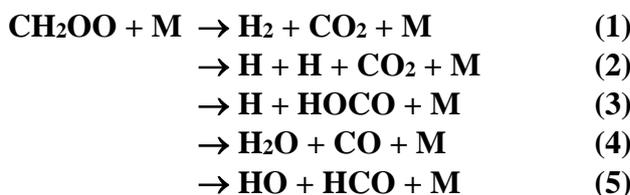


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_12

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Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

k/ s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
< 120	295	Liu et al., 2014	PLP-LIF (a)
< 11.6 ± 8.0	293	Chhantyal-Pun et al., 2015	PLP-CRDS (b)
0.19 ± 0.07 (1 bar)	297	Berndt et al., 2015	Free-Jet FR-TOF-MS (c)
$1.1^{+1.5}_{-1.1} \times 10^{-3}$ (1 bar)	298	Stone et al., 2018	PLP-UVA/LIF (d)
$k_0 = 3.2 \times 10^{-4} (T/298)^{-5.81} \exp(-12770/T)$ [M]	450-650		
$k_\infty = 1.4 \times 10^{13} (T/298)^{0.06} \exp(-10010/T)$	450-650		
$k_0 = 1.3 \times 10^{-8} \exp[-(8065 \pm 1170)/T]$ [M]	425-600	Peltola et al., 2020	PLP-UVA (e)
$k_\infty = 7.8 \times 10^{11} \exp[-(9716 \pm 1088)/T]$	425-600		
<i>Relative Rate Coefficients</i>			
< 19.2 ± 5.1	297	Ouyang et al., 2013	(f)
≤ 8.9	293	Berndt et al., 2014	(g)
0.23 ± 0.12	293	Berndt et al., 2015	APFT-ToFMS/FTIR (g),(h)

Comments

- (a) CH₂OO molecule generated by 351 nm laser flash photolysis of CH₂I/O₂ mixtures is accompanied by formation of significant amounts of HO, observed by time resolved LIF. At least two different processes formed HO; a second, slower process appeared to be associated with the decay of CH₂OO. Using the HO signals as a proxy for the [CH₂OO] concentration, in the absence of added reactant (SO₂ or CF₃C(O)CF₃) the inferred decomposition lifetime of CH₂OO was ~8 ms, corresponding to the cited upper limit for k .
- (b) Cavity ring-down spectroscopy was used to perform kinetic measurements at 293 K under low pressure (13 – 40 mbar) conditions, for reactions of CH₂OO generated by (248 nm) laser photolysis of CH₂I₂ in the presence of O₂ and SO₂. The upper limit value of k tabulated above was determined from analysis of pseudo-first order decay constants at low [SO₂], following correction for removal via self-reaction and a proposed SO₂ catalysed CH₂OO isomerization.
- (c) The rate coefficients of the unimolecular decomposition of CH₂OO, and its bimolecular reaction with the water monomer, were determined at $T = (297 \pm 1)$ K and at atmospheric pressure by using a free-jet flow system. CH₂OO was produced by the reaction of O₃ with C₂H₄, and [CH₂OO] was measured indirectly by titrating with excess SO₂ and detection of product H₂SO₄ after different reaction times in the range 1.1–7.5 s. Propane was present to scavenge HO radicals. Possible

interferences from the self-reaction of CH₂OO and its reactions with C₂H₄ and O₃ were assessed by systematic variation of experimental conditions, with removal via these reactions shown to be minor.

- (d) Decomposition kinetics of CH₂OO and CD₂OO investigated as a function of temperature (450–650 K) and pressure 2.6 – 395 mbar, using 266 nm photolysis of CH₂I₂/O₂/He or CD₂I₂/O₂/He mixtures, coupled with time-resolved cavity-enhanced broadband UV absorption spectroscopy. Direct production of HO radicals in the $v = 0$ and $v = 1$ states in low yields was observed (LIF), and CH₂OO decay kinetics were also measured using time-resolved measurements of HO ($v = 1$). The kinetics required correction for a background loss process, attributed to the reaction of CH₂OO with CH₂I₂, which was dominant at temperatures below 500 K. Master equation calculations enabled fitting of barriers for decomposition of CH₂OO and CD₂OO to the experimental data. The low- and high-pressure limiting rate coefficients for CH₂OO are as tabulated above, with $F_c = 0.447$, based on fitting to the extended Troe expression for broad fall-off curves. Extrapolation to atmospheric conditions yields $k = 1.1^{+1.5}_{-1.1} \times 10^{-3} \text{ s}^{-1}$ at 298 K and 1.013 bar. The master equation calculations for CH₂OO provide $k_1/k = 0.637$, $k_4/k = 0.360$ and $k_5/k = 0.003$, with no significant dependence on temperature (400 – 1200 K) or pressure (1.3 – 4000 mbar). For CD₂OO, the corresponding rate coefficients are $k_0 = 5.2 \times 10^{-5} (T/298)^{-5.28} \exp(-11610/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_\infty = 1.2 \times 10^{13} (T/298)^{0.06} \exp(-9800/T) \text{ s}^{-1}$. Decomposition of CD₂OO observed to be faster than CH₂OO under equivalent conditions, with the extrapolated $k = 5.5^{+9}_{-5.5} \times 10^{-3} \text{ s}^{-1}$ at 298 K and 1.013 bar.
- (e) Decomposition kinetics of CH₂OO investigated as a function of temperature (296 – 600 K) and pressure (6.7 – 530 mbar), with measurable rate coefficients at $T \geq 425$ K. CH₂OO produced mainly by the 213 nm laser photolysis of CH₂I₂/O₂/He mixtures, with detection by time-resolved cavity-enhanced broadband UV absorption spectroscopy. Confirmatory measurements also made using 266 nm photolysis of CH₂I₂/O₂/He mixtures. Corrections for background processes (see comment (d)) were found to be lower using the CH₂I₂ system, owing to the reaction of CH₂OO with CH₂I₂ being uncompetitive under the experimental conditions. The low- and high-pressure limiting rate coefficients tabulated above, were based on a standard Troe fit to all data at $T \geq 425$ K, using $F_c = 0.6$ (and $N = 1.0$). Master equation simulations agreed well with the observed data, and provide a value of $k_1/k = 0.61$ for the dominant product channel forming H₂ + CO₂.
- (f) Photolysis of CH₂I₂/O₂/N₂/NO₂ mixtures at 348 nm in continuous flow conditions at 1.013 mbar pressure. Simultaneous measurement of products NO₃ and [N₂O₅+NO₂] was made in a dual channel BB-CEAS at 663 nm. Analysis of these data as function of [NO₂] allowed evaluation of the rate constant ratio: $k_1/k(\text{CH}_2\text{OO} + \text{NO}_2) = (6.4 \pm 1.7) \times 10^{12} \text{ molecule cm}^{-3}$, where k_1 is the total loss rate constant for competing first order processes. Using $k(\text{CH}_2\text{OO} + \text{NO}_2) = 3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation) gives the tabulated value of k_1 above, as an upper limit of k for thermal decomposition.
- (g) CH₂OO produced from O₃ + C₂H₄ reaction at atmospheric pressure 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 $\pm 45\%$. Measurements at the lowest relative humidity (RH ~2%) yield the rate coefficient ratio $k_1/k(\text{CH}_2\text{OO} + \text{SO}_2) \leq 2.4 \times 10^{11} \text{ molecule cm}^{-3}$, where k_1 is the total first order loss coefficient for CH₂OO in the absence of water. Combining this ratio with $k(\text{CH}_2\text{OO} + \text{SO}_2) = 3.7 \times 10^{-11}$ (IUPAC, current recommendation) gives the upper limit value of k tabulated above.
- (h) Analysis of data for steady state conditions from atmospheric pressure flow tube (IfT-LFT) at (293 ± 0.5) K with residence time = 39.5 s. The tabulated value of k includes a correction for wall loss, $k_{\text{wall}} = 0.034 \text{ s}^{-1}$.

Preferred Values

Parameter	Value	T/K
k / s^{-1}	≤ 0.2 (1 bar)	298

Comments on Preferred Values

The values of k derived from most of the experiments carried out at ambient temperature are upper limits because they relate to the total first order loss process, including thermal decomposition. The lowest value from direct studies at room temperature, using the $\text{CH}_2\text{I} + \text{O}_2$ reaction as a source of CH_2OO , is that reported by Chhantyal-Pun et al. (2015), who presented evidence for an SO_2 catalysed CH_2OO isomerization, which gives rise to non-linear dependence of the decay constant of CH_2OO with $[\text{SO}_2]$. The occurrence of this process, together with the non-linearity due to presence of the self-reaction at high $[\text{CH}_2\text{OO}]$, leads to systematic inaccuracies in the measurement and assignment of the first order loss by slow thermal decomposition. However, Berndt et al. (2015) reported the lowest absolute determination of k , obtained from experiments using ozonolysis of ethene as a source of CH_2OO . That value of k agrees with that obtained in the same study relative to the $\text{CH}_2\text{OO} + \text{SO}_2$ reaction, also using ozonolysis of ethene as the CH_2OO source (Berndt et al., 2015).

The more recent measurements of Stone et al. (2018) and Peltola et al. (2020) provide direct measurements of k at higher temperatures (450-650 K and 425-600 K respectively) and indicate that the reaction exhibits the pressure dependence typical of classic unimolecular decomposition of small molecules, i.e. fall-off behaviour which can be fitted with the Troe formulism, modified to account for background losses. Although the rate coefficients reported in the two studies are comparable over similar temperature and pressure ranges, the rate coefficients reported by Peltola et al. (2020) are consistently between a factor of two and five greater than those reported by Stone et al. (2018), on average by a factor of four. The rate coefficients measured in both studies required correction for background losses. These were substantial in the CH_2I_2 photolysis system of Stone et al. (2018), and were attributed to the reaction of CH_2OO with CH_2I_2 . In conjunction with master equation calculations, Stone et al. (2018) reported an extrapolation to atmospheric conditions (see comment (d)). This predicted the reaction to be in the fall-off regime, with $k = 1.1^{+1.5}_{-1.1} \times 10^{-3} \text{ s}^{-1}$ at 1 bar and 298 K (and more than an order of magnitude lower than the extrapolated high-pressure limit). This is substantially lower than suggested from all room temperature experiments carried out previously. Although this may reflect that the reported experimental room temperature rate coefficients have contributions from first-order loss processes other than decomposition, it is also clear that there are substantial uncertainties associated with the extrapolation procedure, particularly in view of the very large background corrections applied to the experimental data.

A number of theoretical studies report the high-pressure limiting value of k to be about 0.3 s^{-1} at 298 K (Olzmann et al., 1997; Long et al., 2016; Vereecken et al., 2017), with k calculated to be 0.072 s^{-1} at 1 bar and 298 K (Long et al., 2016). Although in some conflict with the much lower value of k obtained by extrapolation of the high temperature results of Stone et al. (2018), this nonetheless confirms that the reaction is in the fall-off regime under lower tropospheric conditions. The calculated value of Long et al. (2016) is lower than all reported room temperature measurements, although only just outside the uncertainty limits of the lowest measurement, reported by Berndt et al. (2015). On this basis, the preferred value of k at 298 K and 1 bar is an upper limit based on the absolute determination of Berndt et al. (2015). This indicates that unimolecular decomposition of CH_2OO is unimportant under atmospheric conditions, compared with removal by bimolecular reactions, particularly the reactions with H_2O and $(\text{H}_2\text{O})_2$.

Many experimental product studies have reported evidence for unimolecular decomposition of CH_2OO , formed from alkene ozonolysis, including formation of HO radicals and other products identified in channels (1)-(5) listed above (e.g. see data sheet Ox_VOC5). However, the thermal

stability of stabilized CH₂OO discussed above indicates that this is likely a result of prompt unimolecular decomposition of the chemically activated Criegee intermediate, [CH₂OO]*.

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