IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_4

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$$CH_2OO + H_2O \rightarrow HOCH_2OOH \quad (1a)$$
$$\rightarrow HCHO + H_2O_2 \quad (1b)$$
$$\rightarrow HC(O)OH + H_2O \quad (1c)$$

$$CH_2OO + (H_2O)_2 \rightarrow HOCH_2OOH + H_2O \quad (2a)$$
$$\rightarrow HCHO + H_2O_2 + H_2O \quad (2b)$$
$$\rightarrow HC(O)OH + 2H_2O \quad (2c)$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_1 < 4.0 \times 10^{-15}$	298	Welz et al., 2012	PLP-PIMS(a)
$k_1 < 9 \times 10^{-17}$	295	Stone et al., 2014	PLP-LIF/PIMS (b)
$k_1 = (3.2 \pm 1.2) \times 10^{-16}$	297	Berndt et al., 2015	Free-Jet FR-TOF-MS (c)
$k_2 = (6.5 \pm 0.8) \times 10^{-12}$	298	Chao et al., 2015	PLP-UVAS(d)
$k_2 = (4.2 \pm 1.2) \times 10^{-12}$	294	Lewis et al., 2015	PLP-LP-UVAS (e)
$k_2 = (7.4 \pm 0.6) \times 10^{-12}$	298	Smith et al., 2015	PLP-LP-UVAS (f)
$k_2 = 8.72 \times 10^{-18} \exp[(4076 \pm 302)/T]$	283-324		
$k_1 = (2.4 \pm 1.6) \times 10^{-16}$	293	Sheps et al., 2017	TR-BB-CEAS/PIMS (g)
$k_2 = (6.6 \pm 0.7) \times 10^{-16}$	293		
Relative Rate Coefficients			
$k_1 = (8.5 \pm 3.7) \times 10^{-15}$	298	Suto et al., 1985	RR-AFT-UVscat (h)
$k_1 = (1.1 \pm 0.4) \times 10^{-17}$	297	Ouyang et al., 2013	RR-LP-UVvis (i)
$k_2 = (1.07 \pm 0.04) \times 10^{-11}$	293	Berndt et al., 2014	RR-AFT-CIMS(ToF) (j)
$k_1 = (9.3 \pm 2.6) \times 10^{-16}$	298	Newland et al., 2015	RR-FTIR/UVAS/UVF (k)
$k_2 = (5.2 \pm 6.7) \times 10^{-13}$	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		
$k_{2a}/k_2 = 0.55 \pm 0.15$	293	Sheps et al., 2017	TR-BB-CEAS/PIMS (g)
$k_{2b}/k_2 = 0.40 \pm 0.10$	293		
$k_{2c}/k_2 = < 0.10$	293		

Comments

(a) CH_2OO was produced by the reaction of $CH_2I + O_2$. CH_2I was generated by 248-nm laser photolysis of di-iodomethane, CH_2I_2, at 298 K and 4 torr, in a large excess of O_2. The reacting mixture was monitored by tunable synchrotron photoionization mass spectrometry, which allowed characterisation of the PIMS for CH_2OO and its reaction products over the region 9.5 – 11.5 eV. Time-resolved direct detection of $[CH_2OO]$ decay at m/z = 46. The first order decay of CH_2OO in the presence of excess known concentrations of H_2O 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 $[H_2O] = 3 \times 10^{16}$ molecule cm^{-3}

(b) Photolysis of CH_2I_2-O_2-N_2 mixtures in the presence of excess H_2O, under pseudo-first-order conditions. Kinetics of $CH_2OO + H_2O$ reaction were followed by time-resolved monitoring of HCHO product by laser-induced fluorescence (LIF) spectroscopy (pressure range: 50 – 450 Torr). Rate coefficients for $CH_2OO + H_2O$ was investigated at 200 Torr, using up to $[H_2O] = 1.7 \times 10^{17}$ molecule cm^{-3}. The cited value of k is an upper limit based on the lack of significant effect of $[H_2O]$ and the assumption that HCHO detected is derived solely from reaction with H_2O.

(c) The rate coefficients of the bimolecular reaction of CH_2OO with the water monomer have been experimentally determined at T = (297 ± 1) K and at atmospheric pressure by using a free-jet flow system. CH_2OO was produced by the reaction of ozone with C_2H_4, and $[CH_2OO]$ was measured indirectly by titrating with excess SO_2 and detection of product H_2SO_4 after 7.5 s reaction time. Low water concentrations of $[H_2O] < 10^{15}$ molecule cm^{-3} and, as a consequence, very low water dimer concentrations of $[(H_2O)_2] = 2.5 \times 10^9$ 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 $[H_2O]$ dependence of the ratio $[H_2SO_4]/[C_2H_4]$, assuming k_{uni} = 0.19 s^{-1}, and appropriate uncertainty in the parameters.

(d) CH_2OO prepared by PLP (266 nm) of CH_2I_2 in O_2/Ar mixtures at 5.1 Torr pressure. CH_2OO kinetics observed by time-resolved UV absorption in the $\tilde{B}$ (1A′) ← $\tilde{X}$(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 H_2O (RH = 3 % to 80 %). Rate constants extracted by fitting plots of k_{obs} vs RH or $[(H_2O)_2]$, calculated using K_p (298) = 0.0501 bar^{-1} at 298 K where P_{sat} = 23.8 torr. Uncertainty on $[(H_2O)_2]$ was estimated to be ± 12 %. Incorporation of the monomer reaction into the fit gave $k_1 < 1.5 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}.

(e) CH_2OO prepared by PLP (266 nm) of CH_2I_2 in O_2/Ar mixtures at 5.1 Torr pressure. CH_2OO kinetics, observed by time-resolved UV absorption in the $\tilde{B}$ (1A′) ← $\tilde{X}$(1A′) electronic transition between 350 – 420 nm, were first order in the presence and absence of H_2O, independent of total pressure. However, dependence of the first-order decay constant on $[H_2O]$ in the range 0 to 25 × 10^{16} molecule cm^{-3} was fitted best by a quadratic function, indicating that CH_2OO 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 $[(H_2O)_2]$, i.e. K_p (298) = 0.0579 bar^{-1} at 294 K.

(f) CH_2OO prepared by PLP (248 nm) of CH_2I_2 in N_2/O_2 at 5.1 Torr pressure. CH_2OO was observed by time-resolved of UV absorption at 340 nm. The kinetics of the reaction of CH_2OO with water vapor was measured as a function of $[H_2O]$ at temperatures from 283 to 324 K. The observed first-order decay constant increased quadratically with $[H_2O]$, consistent with dominant reaction with the water dimer. The dimer concentrations were calculated using the T-dependent equilibrium constant for water dimerization, K_{eq}(T) of Ruscic (2013), with values of k_2 derived from the variation of the first-order decay constant with $[(H_2O)_2]$. 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.

(g) CH_2OO prepared by PLP (248, 266 or 351nm) of CH_2I_2 in O_2/He or O_2/N_2 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 [H_2O], using a simplified mechanism in which CH_2OO 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).

(h) Flow system involving C_2H_4-O_3-SO_2-H_2O mixtures in which H_2SO_4 aerosol concentrations were monitored by scattered UV light. Relative rate coefficients obtained from the dependencies of the aerosol formation on the concentrations of O_3, SO_2, and H_2O. The relative rate constant reported was $k_1/k(CH_2OO + SO_2) = (2.3 \pm 1.0) \times 10^{-4}$. The value of k_1 tabulated above is based on $k(CH_2OO + SO_2) = 3.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(i) Photolysis of CH_2I_2-O_2-N_2-NO_2 mixtures at 348 nm in continuous flow conditions at 760 Torr pressure. CH_2OO produced in this system was allowed to react with NO_2. Simultaneous measurement of products NO_3 and [N_2O_5+NO_2] was made at 663 nm. Analysis of these data as function of [NO_2] allowed evaluation of the rate constant ratio: $k_d(CH_2OO)/k(CH_2OO + NO_2) = (6.4 \pm 1.7) \times 10^{12}$ 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: $k(CH_2OO + H_2O)/k(CH_2OO + NO_2) = 3.6 \times 10^{-6}$ (error ± 40 %). The value of k_1 tabulated above is based on $k(CH_2OO + NO_2) = 3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(j) CH_2OO produced from $O_3 + C_2H_4$ reaction in atmospheric pressure flow tube at 293 ± 0.5 K. H_2SO_4 formation from the reaction $CH_2OO + SO_2$ as a function of RH (= 2% to 50%) for close to atmospheric conditions, was measured using NO_3^--CI-APi-TOF-MS. The uncertainty in the [H_2SO_4] estimated to be ± 45%. Second-order kinetics with regard to water vapour concentration indicates a preferred reaction of CH_2OO with the water dimer. The relative rate coefficient $k_2/k(CH_2OO + SO_2) = 0.29 \pm 0.01$, 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 $k_{uni}/k(CH_2OO + SO_2) = 2.4 \times 10^{11}$ molecule cm^{-3}, where k_{uni} is the total first order loss coefficient for CH_2OO in the absence of water dimer. Combining $k_2/k(CH_2OO + SO_2) = 0.29 \pm 0.01$ with $k(CH_2OO + SO_2) = 3.7 \times 10^{-11}$ (IUPAC, current recommendation) gives the tabulated value of k_2 above.

(k) The removal of SO_2 in the presence of ethene-ozone systems was measured as a function of humidity in EUPHORE simulation chamber, under atmospheric boundary layer conditions. SO_2 and O_3 abundance were measured using conventional fluorescence and UV absorption monitors, respectively; alkene abundance was determined via FTIR spectroscopy. SO_2 removal decreased with increasing relative humidity (1.5 – 21%) confirming a significant reaction for CH_2OO with H_2O. The observed SO_2 removal kinetics are consistent with the relative rate constant, $k_1/k(CH_2OO + SO_2) = (3.3 \pm 1.1) \times 10^{-5}$, if removal is due solely to reaction (1). An expanded analysis considering removal by both reactions (1) and (2) yielded $k_1/k(CH_2OO + SO_2) = (2.5 \pm 0.7) \times 10^{-5}$ and $k_2/k(CH_2OO + SO_2) = (1.4 \pm 1.8) \times 10^{-2}$. The values of k_1 and k_2 tabulated above are based on $k(CH_2OO + SO_2) = 3.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(l) Products formed from the ozonolysis of isoprene investigated in the multi-instrumented Caltech dual 24m^3 teflon chamber at atmospheric pressure. CH_2OO reported to dominate the population of stabilized Criegee intermediates formed, and their bimolecular reactivity. $HOCH_2OOH$, HC(O)OH and H_2O_2 were quantified with a triple-quadrupole chemical ionization mass spectrometer (CIMS) using CF_3O^- 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 [H_2O], by

simulations of the system using a detailed chemical mechanism, with $k_1 = 9.0 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} and $k_2 = 8.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k_1 /cm^3 molecule^{-1} s^{-1}	2.8×10^{-16}	298
k_2 /cm^3 molecule^{-1} s^{-1}	6.4×10^{-12}	298
k_2 /cm^3 molecule^{-1} s^{-1}	$7.35 \times 10^{-18} \exp(4076/T)$	280-325
Reliability		
$\Delta \log k_1$	± 0.3	298
$\Delta \log k_2$	± 0.2	298
$\Delta (E_2/R)$	± 500 K	280-325

Comments on Preferred Values

An important discovery arising from the direct studies of CH_2OO reaction with water vapour was the quadratic dependence of the pseudo-first order rate constant for loss of CH_2OO on $[H_2O]$. 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 CH_2OO 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 $[H_2O]$ only those experimental studies which employed conditions of high enough $[H_2O]$ provide $[(H_2O)_2]$ sufficient to compete with monomer reaction and other loss reactions of CH_2OO. 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 $[H_2O]$ which propagates by a factor of two in calculating $[(H_2O)_2]$. 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 $k_2/k(CH_2OO + SO_2)$. The reported relative rate constant ratio $k_1/k(CH_2OO + SO_2) = (2.5 \pm 0.7) \times 10^{-5}$ at 298 K in their expanded analysis, implies the contribution of k_1 to the overall rate of CH_2OO loss too small to detect at $[H_2O]$ used in the experiments of Welz et al. (2012).

Work of Neeb et al. (1997) shows that the reaction of CH_2OO with H_2O leads initially to hydroxymethyl hydroperoxide ($HOCH_2OOH$). Estimates using quantum chemistry calculations of the rate coefficient for reaction of CH_2OO with water vapour dimer forming $HOCH_2OOH$ product (Ryzhkov and Ariya, 2004), are of a similar order of magnitude to the experimental values. $HOCH_2OOH$ is expected to be formed chemically activated, and is either subsequently thermalized or decomposes to form HCHO and H_2O_2 or HC(O)OH and H_2O. In their study of the ozonolysis of isoprene, from which CH_2OO 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 CH_2OO was produced by photolysis of CH_2I_2/O_2. Although both studies report an important contribution from channel (2a), forming $HOCH_2OOH$, 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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