

IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet CGI_4

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This datasheet last evaluated: May 2016; last change in preferred values: May 2016.

CH₂OO + H₂O → products

(1)

+ (H₂O)₂ → products

(2)

Rate coefficient data (k = k₁ + k₂)

k/cm ³ molecule ⁻¹ s ⁻¹	Temp/K	Reference	Technique/Comments
Absolute Rate Coefficients			
< 4.0 x 10 ⁻¹⁵	298	Welz et al., 2012	PLP-PIMS(a)
< 9 x 10 ⁻¹⁷	295	Stone et al 2014	PLP-LIF/PIMS (b)
k ₂ = (6.5 ± 0.8) x 10 ⁻¹²	298	Chao et al., 2015	PLP-UVAS(c)
k ₂ = (4.2 ± 1.2) x 10 ⁻¹²	294	Lewis et al., 2015	PLP-LP-UVAS (d)
k ₂ = (12.1 ± 1.7) x 10 ⁻¹²	283	Smith et al., 2016	PLP-LP-UVAS (d*)
k ₂ = (7.4 ± 0.6) x 10 ⁻¹²	298		
k ₂ = (4.8 ± 0.5) x 10 ⁻¹²	311		
k ₂ = (3.3 ± 0.7) x 10 ⁻¹²	324		
Relative Rate Coefficients			
<8.7 x 10 ⁻¹⁵	298	Suto, et al., 1984	AFT-UVscat (e)
<1.08 x 10 ⁻¹⁷	297	Ouyang et al., 2013	LP-UVvis (f)
k ₂ = (10.7 ± 0.3) x 10 ⁻¹²	293	Berndt et al., 2014	AFT-CIMS(ToF) (g)
k ₂ = (0.52 ± 0.67) x 10 ⁻¹²	298	Newland et al., 2015	RR-FTIR/UVAS/ UV fluorescence (h)

Comments

- (a) CH₂OO (formaldehyde oxide) was produced by the reaction of CH₂I + O₂. CH₂I was generated by 248-nm laser photolysis of di-iodomethane, CH₂I₂, at 293 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 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 x 10¹⁶ molecule cm⁻³
- (b) Photolysis of CH₂I₂-O₂-N₂ mixtures. in the presence of excess SO₂, 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 $[\text{H}_2\text{O}] = 1.7 \times 10^{17}$ molecule cm^{-3} . The cited value of k is an upper limit based on the lack of significant effect of $[\text{H}_2\text{O}]$ and the assumption that HCHO detected is derived solely from reaction with H_2O .

- (c) 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 spectrum in the $\tilde{\text{B}}(1\text{A}') \leftarrow \tilde{\text{X}}(1\text{A}')$ electronic transition, measured over range 280-600 nm using a CCD at various delay times; and by continuous time-resolved measurements using a photodiode (at 350 ± 5 nm), at in absence and presence of H_2O (RH = 3% to 80%). Rate constants extracted by fitting plots of k_{obs} vs RH or $[(\text{H}_2\text{O})_2]$, calculated using $K_{\text{p}}(298) = 0.0501 \text{ bar}^{-1}$ at 298K where $P_{\text{sat}} = 23.8 \text{ torr}$. Uncertainty on [dimer] was estimated to be $\pm 12\%$. Incorporation of the monomer reaction into the fit gave $k_1 < 1.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (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 spectrum at in the $\tilde{\text{B}}(1\text{A}') \leftarrow \tilde{\text{X}}(1\text{A}')$ electronic transition between 350 – 420 nm, were first order in the presence and absence of H_2O , and independent of total pressure. However dependence of k^{I} on $[\text{H}_2\text{O}]$ on the range 0 to 25×10^{16} molecule cm^{-3} fitted best by a quadratic, 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 $[(\text{H}_2\text{O})_2]$, i.e $K_{\text{p}}(298) = 0.0579 \text{ bar}^{-1}$ at 294K.
- (d*) 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 $[\text{H}_2\text{O}]$ at temperatures from 283 to 324 K. The decay constant k^{I} increased exponentially with $[\text{H}_2\text{O}]$, consistent with reaction dominated by reaction with the water dimer. The dimer concentration was calculated using the T-dependent equilibrium constant for water dimerization, $K_{\text{eq}}(\text{T})$ of Ruscic (2013). The Arrhenius expression: $k_2 = 3.65 \times 10^{-18} \exp((4328 \pm 302)/\text{T})$ is obtained by linear regression from the data cited.
- (e) Flow system involving $\text{C}_2\text{H}_4\text{-O}_3\text{-SO}_2\text{-H}_2\text{O}$ 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 $k_1/k(\text{SO}_2) = 2.3 \times 10^{-4}$. The cited values of k_2 is based on the assumption that $k = k_1$
- (f) Photolysis of $\text{CH}_2\text{I}_2 - \text{O}_2 - \text{N}_2 - \text{NO}_2$ 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 $[\text{N}_2\text{O}_5 + \text{NO}_2]$ was made in a dual channel BBCEAS at 663 nm. Analysis of these data as function of $[\text{NO}_2]$ allowed evaluation of the rate constant ratio: $(k_{\text{d}}(\text{CH}_2\text{OO})/k(\text{CH}_2\text{OO} + \text{NO}_2)) = (6.4 \pm 1.7) \times 10^{12} \text{ molec.cm}^{-3}$, where k_{d} is the total loss rate constant for competing first order processes. Assuming the competing kinetics is dominated by the reaction of Creigee radicals with water gave the rate constant ratio: $(k(\text{CH}_2\text{OO} + \text{H}_2\text{O})/k(\text{CH}_2\text{OO} + \text{NO}_2)) = 3 \times 10^{-6}$ (error $\pm 40\%$).
- (g) CH_2OO produced from $\text{O}_3 + \text{C}_2\text{H}_4$ reaction in atmospheric pressure FT at $293 \pm 0.5 \text{ K}$. H_2SO_4 formation from the reaction $\text{CH}_2\text{OO} + \text{SO}_2$ as a function of RH (= 2% to 50%) for close to atmospheric conditions, was measured using NO_3^- -CI-API-TOF MS, sampling

the centre flow at the tube outlet. The uncertainty in the $[\text{H}_2\text{SO}_4]$ estimated to be $\pm 45\%$. Second-order kinetics with regard to water vapour concentration indicates a preferred reaction of CH_2OO with the water dimer. The relative rate coefficient of the reactions $\text{CH}_2\text{OO} + (\text{H}_2\text{O})_2$ and $\text{CH}_2\text{OO} + \text{SO}_2$, $k_2/k(\text{SO}_2) = 0.29 \pm 0.01$, based on K_p calculated using the parameterisation of Scribano et al. (2006). Measurements at the lowest relative humidity (RH $\sim 2\%$) yield an upper limit of the rate coefficient ratio $k_{\text{uni}}/k(\text{SO}_2) = 2.4 \times 10^{11} \text{ molecule cm}^{-3}$, where k_{uni} is the total first order loss coefficient for CH_2OO in the absence of water dimer. Combining $k_2/k(\text{SO}_2) = 0.29 \pm 0.01$ with $k(\text{SO}_2) = 3.7 \times 10^{-11}$ (IUPAC, 2015) gives the tabulated value of k_2 above.

- (h) 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 relative rate constants, $k(\text{CH}_2\text{OO} + \text{H}_2\text{O})/k(\text{CH}_2\text{OO} + \text{SO}_2) = (3.3 \pm 1.1) \times 10^{-5}$. The reaction of the water dimer with CH_2OO is also considered, with a derived value for $k(\text{CH}_2\text{OO} + (\text{H}_2\text{O})_2)/k(\text{CH}_2\text{OO} + \text{SO}_2)$ of $(1.4 \pm 1.8) \times 10^{-2}$.

Preferred Values

Parameter	Value	T/K
$k_1 / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$< 4.0 \times 10^{-16}$	298
$k_2 / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.40 \times 10^{-18} \exp(4328/T)$	280-325
<i>Reliability</i>		
$\Delta \log k_2$	± 0.2	298
$\Delta (E/R)$	± 500	283-323

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 $[\text{H}_2\text{O}]$. This is consistent with the predominant reaction is with the water dimer (k_2). The reaction with monomeric water molecules (k_1) is very slow, and probably unimportant 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., (2016) reports a strong negative temperature dependence for the bimolecular reaction of CH_2OO with the water dimer, also consistent with dimer reaction.

Because of the observed quadratic dependence of the rate on $[\text{H}_2\text{O}]$ only those experimental studies which employed conditions of high $[\text{H}_2\text{O}]$ provide $[(\text{H}_2\text{O})_2]$ sufficient to compete with monomer reaction and other unimolecular loss reactions of CH_2OO such as decomposition and isomerisation. The preferred value of k_2 at 298 K is the mean value from the direct kinetic studies of Chao et al., 2015, Lewis et al., 2015, and Smith et al (2016). 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 2 in calculating $[(H_2O)_2]$. Support for these high values of k_2 comes from the relative rate study of Berndt et al., 2014. 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) suggests a significant reaction with water dimer, but only provides an indeterminate value for $k(CH_2OO + (H_2O)_2)/k(CH_2OO + SO_2)$. The reported relative rate constant ratio $k(CH_2OO + H_2O)/k(CH_2OO + SO_2) = (3.3 \pm 1.1) \times 10^{-5}$ at 298K, 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). The recommended upper limit suggested for k_1 is based on these results and those of Stone et al. (2014).

Work of Neeb et al.(1997) shows that the reaction of the CH_2OO Criegee intermediate 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 (Ryzhov and Ariya, 2004), are of similar order of magnitude to the experimental values.

Reference

- Berndt, T., Voigtlander, J., Stratmann, F., Junninen, H., Mauldin III, R.L., Sipila, M., Kulmala, M., and Herrmann, H., *Phys.Chem.Chem.Phys.*, **16**, 19130, 2014.
- Chao, W., Hsieh, J-T., Chang, C-H., Lin, Jim Jr-M., *Science*, **347**, 751-754, 2015.
- Lewis, T.R., Blitz, M.A., Heard, D.E., and Seakins, P.W., *Phys.Chem.Chem.Phys.*, **17** 4859, 2015.
- Neeb, P., Sauer, F., Horie, O. and Moortgat, G. K., *Atmos. Environ.* **31**, 1417,1997.
- Newland, M.J., Rickard, A.R., Alam, M.S., Vereecken, L., Munoz, A., Rodenas, M., and Bloss, W.J., *Phys.Chem.Chem.Phys.*, **17**, 4076, 2015.
- Ouang, B., McLeod, M.W., Jones, R.L., and Bloss, W.J., *Phys.Chem.Chem.Phys.*, **15**, 17070, 2013.
- Ryzhkov, A.B., and Ariya, P.A., *Phys.Chem.Chem.Phys.*, **6**, 5042, 2004.
- Scribano, Y., Goldman, N., Saykally, and Leforestier, C., *J. Phys. Chem. A*, **110**, 5411–5419, 2006.
- Smith, M.C., Chang, C-H.,Chao, Wen., Lin, L-C., Takahashi, K., Boering, K.A. and Lin, Jim Jr-M., *J Phys. Chem. Lett.*, **6**, 2708, 2015.
- Stone, D.; Blitz, M.; Daubney, L.; Howes, N. U. M.; Seakins, P., *Phys.Chem.Chem.Phys.*, **16**, 1139-1149, 2014.
- M. Suto, E. R. Manzanares, and L. C. Lee, *Environ. Sci. Technol.* **19**, 815 (1985); E.R. Manzanares, M. Suto, and L. C. Lee (unpublished data).
- Welz, O, Savee, J. D. Osborn, D. L., Vasu, S. S., Percival, C. J., Shallcross, D. E., Taatjes, C. A. *Science*, **335**, 204, 2012.