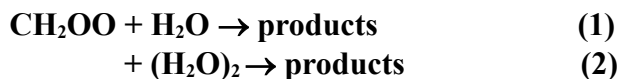


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_4

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This datasheet last evaluated: June 2015; last change in preferred values: June 2015



Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp/K	Reference	Technique/Comments
Absolute Rate Coefficients			
$< 4.0 \times 10^{-15}$	298	Weltz et al., 2012	PLP-PIMS(a)
$< 9 \times 10^{-17}$	295	Stone et al 2014	PLP-LIF/PIMS (b)
$k_2 = (6.5 \pm 0.8) \times 10^{-12}$	298	Chao et al., 2015	PLP-UVAS(c)
$k_2 = (4.2 \pm 1.2) \times 10^{-12}$	294	Lewis et al., 2015	PLP-LP-UVAS (d)
Relative Rate Coefficients			
$< 8.7 \times 10^{-15}$	298	Suto, et al., 1984	AFT-UVscat (e)
$< 1.08 \times 10^{-17}$	297	Ouyang et al., 2013	LP-UVvis (f)
$k_2 = (10.7 \pm 0.3) \times 10^{-12}$	293	Berndt et al., 2014	AFT-CIMS(ToF) (g)
$k_2 = (0.52 \pm 0.67) \times 10^{-12}$	298	Newland et al., 2015	RR-FTIR/UVAS/ UV fluorescence (h)

Comments

- (a) CH_2OO (formaldehyde oxide) was produced by the reaction of $\text{CH}_2\text{I} + \text{O}_2$. CH_2I was generated by 248-nm laser photolysis of di-iodomethane, CH_2I_2 , at 293 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 $[\text{CH}_2\text{OO}]$ decay at $m/z = 46$. The first order decay 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 $[\text{H}_2\text{O}] = 3 \times 10^{16} \text{ molecule cm}^{-3}$
- (b) Photolysis of $\text{CH}_2\text{I}_2\text{-O}_2\text{-N}_2$ mixtures. in the presence of excess SO_2 , under pseudo-first-order conditions. Kinetics of $\text{CH}_2\text{OO} + \text{H}_2\text{O}$ reaction were followed by time-resolved monitoring of HCHO product by laser-induced fluorescence (LIF) spectroscopy (pressure range: 50 – 450 Torr). Rate coefficients for $\text{CH}_2\text{OO} + \text{H}_2\text{O}$ was investigated at 200 Torr, using up to $[\text{H}_2\text{O}] = 1.7 \times 10^{17} \text{ molecule cm}^{-3}$. 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) 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 spectrum in the $\tilde{B}(1A') \leftarrow \tilde{X}(1A')$ 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 H₂O (RH = 3% to 80%). Rate constants extracted by fitting plots of k_{obs} vs RH or [(H₂O)₂], calculated using $K_p(298) = 0.0501 \text{ bar}^{-1}$ at 298K where $P_{\text{sat}} = 23.8 \text{ torr}$. Uncertainty on [dimer] was estimated to be ±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) 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 spectrum at in the $\tilde{B}(1A') \leftarrow \tilde{X}(1A')$ electronic transition between 350 – 420 nm, were first order in the presence and absence of H₂O, and independent of total pressure. However dependence of k^1 on [H₂O] on the range 0 to $25 \times 10^{16} \text{ molecule cm}^{-3}$ fitted best by a quadratic, 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 $K_p(298) = 0.0579 \text{ bar}^{-1}$ at 294K.
- (e) 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 $k_1/k(\text{SO}_2) = 2.3 \times 10^{-4}$. The cited value of k_1 is based on the assumption that $k = k_1$
- (f) 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 in a dual channel BBCEAS at 663 nm. Analysis of these data as function of [NO₂] allowed evaluation of the rate constant ratio: $(k_d(\text{CH}_2\text{OO})/k(\text{CH}_2\text{OO} + \text{NO}_2)) = (6.4 \pm 1.7) \times 10^{12} \text{ molec.cm}^{-3}$, 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 ±40%).
- (g) CH₂OO produced from O₃ + C₂H₄ reaction in atmospheric pressure FT at $293 \pm 0.5 \text{ K}$. 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, sampling the centre flow at the tube outlet. 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 of the reactions CH₂OO + (H₂O)₂ and CH₂OO + SO₂, $k_2/k(\text{SO}_2) = 0.29 \pm 0.01$, based on K_p calculated using the parameterisation of Scribano et al. (2006). Measurements at the lowest relative humidity (RH ~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 CH₂OO 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 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 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 CH₂OO 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
$k_2 / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	5.5×10^{-12}	
<i>Reliability</i>		
$\Delta \log k_2$	± 0.5	298

Comments on Preferred Values

Earlier work evaluated previously in IUPAC 2006 concluded that relative rate measurements for reactions of stabilised Criegee intermediates are the only experimental basis on which to assess the rates of these reactions, and that reaction with H₂O was an important atmospheric loss process. Recent development of novel spectroscopic techniques for direct measurements of rate coefficients for CH₂OO reactions cited above has allowed much better definition of the reaction kinetics. An important result is the discovery that the dependence of the loss of CH₂OO on water concentration is consistent with the predominant reaction is that 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.

Because of the observed quadratic dependence of the rate on [H₂O] only those experimental studies which employed conditions of high [H₂O] provide [(H₂O)₂] sufficient to compete with monomer reaction and other unimolecular loss reactions of CH₂OO such as decomposition and isomerisation. The preferred value of k_2 is the mean value from the direct kinetic studies of Chao et al., 2015 and Lewis et al., 2015. These results are in reasonably good agreement considering the experimental uncertainty, arising mainly from uncertainty in [H₂O] which propagates by a factor of 2 in calculating [(H₂O)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 $k(\text{CH}_2\text{OO} + (\text{H}_2\text{O})_2)/k(\text{CH}_2\text{OO} + \text{SO}_2)$. The reported relative rate constant ratio $k(\text{CH}_2\text{OO} + \text{H}_2\text{O})/k(\text{CH}_2\text{OO} + \text{SO}_2) = (3.3 \pm 1.1) \times 10^{-5}$ at 298K, 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 the CH₂OO Criegee intermediate 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 (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.
- 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.