

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_11

Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>).

This datasheet last evaluated: August 2020; last change in preferred values: August 2020

### CH<sub>2</sub>OO + HC(O)OH → products

#### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.1 \pm 0.1) \times 10^{-10}$	298	Welz et al., 2014	PLP-PIMS (a)
$(1.1 \pm 0.1) \times 10^{-10}$	298		PLP-UVA (a)
$(1.14 \pm 0.06) \times 10^{-10}$	293	Chhantyal-Pun et al., 2018	PLP-CRDS (b)
$(1.00 \pm 0.03) \times 10^{-10}$	296	Peltola et al., 2020	PLP-UVA (c)
$1.5 \times 10^{-11} \exp[(589 \pm 192)/T]$	296-458		
<i>Relative Rate Coefficients</i>			
$3.9 \times 10^{-12}$	293	Neeb et al., 1997	Static system/FTIR (d)

#### Comments

- CH<sub>2</sub>OO was produced by the reaction of CH<sub>2</sub>I + O<sub>2</sub>. CH<sub>2</sub>I was generated by 248-nm laser photolysis of diiodomethane, CH<sub>2</sub>I<sub>2</sub>, at 298 K and 4 Torr total pressure in a large excess of O<sub>2</sub>. Two complementary techniques were used for time resolved detection of CH<sub>2</sub>OO following its formation: multiplexed synchrotron photoionization mass spectrometry (MPIMS), and cavity enhanced broadband UV spectroscopy. The decay constant of CH<sub>2</sub>OO was determined by fitting a single exponential to the decay curves for each acid concentration, and a linear dependence of the decay constant on [HC(O)OH] (up to  $8 \times 10^{12}$  molecule cm<sup>-3</sup>) was observed, yielding the bimolecular rate coefficient. The uncertainty limits are 95%, based on unweighted linear fit to decay lifetime plots.
- CH<sub>2</sub>OO was produced by 355 nm laser photolysis of diiodomethane in the presence of HC(O)OH, O<sub>2</sub> and N<sub>2</sub> at a total pressure of 13 mbar; and characterized by cavity ringdown ultraviolet absorption spectroscopy. Experiments were carried out under pseudo-first order conditions, with excess concentrations of HC(O)OH, and  $k$  was derived from the linear dependence of the decay constant on [HC(O)OH].
- CH<sub>2</sub>OO produced by the 213 nm laser photolysis of CH<sub>2</sub>IBr/O<sub>2</sub>/HC(O)OH/He mixtures and the 266 nm laser photolysis of CH<sub>2</sub>I<sub>2</sub>/O<sub>2</sub>/HC(O)OH/He mixtures, with detection by time-resolved cavity-enhanced broadband UV absorption spectroscopy. Experiments were carried out under pseudo-first order conditions, with excess concentrations of HC(O)OH, and  $k$  was derived from the linear dependence of the decay constant on [HC(O)OH]. The 296 K value of  $k$  was found to be independent of pressure over the range 6 – 200 mbar He.
- The ozonolysis of ethene in the presence of H<sub>2</sub>O (up to 0.18 % v/v) in air was investigated in a static chamber experiment at 293 K and 973 mbar, with FTIR analysis. The formation and removal of HOCH<sub>2</sub>OOH and HC(O)OH was investigated. Simulations of the system yielded the reported rate coefficient ratio,  $k/k(\text{CH}_2\text{OO} + \text{H}_2\text{O}) = 14000$ . The tabulated value of  $k$  is placed on an absolute basis using this ratio and  $k(\text{CH}_2\text{OO} + \text{H}_2\text{O}) = 2.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current

recommendation). However, it is noted that the dominant competing reaction would have been with (H<sub>2</sub>O)<sub>2</sub> at the high end of the [H<sub>2</sub>O] range studied, consistent with a considerably higher value of *k*.

### Preferred Values

Parameter	Value	T/K
<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	1.1 × 10 <sup>-10</sup>	298
<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	1.52 × 10 <sup>-11</sup> exp(590/ <i>T</i> )	290-460
<i>Reliability</i>		
Δ log <i>k</i>	± 0.1	298
Δ ( <i>E</i> <sub>0</sub> / <i>R</i> )	± 300	290-460

#### Comments on Preferred Values

The values of the rate coefficients obtained by two independent direct experimental techniques by Welz et al. (2014), Chhantyal-Pun et al. (2018) and Peltola et al. (2020) give confidence that the reaction kinetics are well determined. The cited relative rate determination, using CH<sub>2</sub>OO + H<sub>2</sub>O as a reference reaction, is uncertain because of the influence of the water dimer on the kinetics. The 298 K preferred value of *k* is based on the average of the determinations in the three absolute kinetics studies, and the preferred value of *E*/*R* is based on the sole determination of Peltola et al. (2020).

The extremely rapid rates of the reactions of CH<sub>2</sub>OO with organic acids contrasts with the slower rates for reaction with aliphatic carbonyl compounds, and is orders of magnitude larger than earlier estimates based on ozonolysis experiments. These results are consistent with quantum calculations (Aplincourt and Ruiz-Lopez, 2000) which suggest that the reaction of CH<sub>2</sub>OO with acids proceeds through a barrierless association channel forming a hydroperoxymethylester of the acid, with no pre-reaction complex identified.

### References

- Aplincourt, P. and Ruiz-Lopez, M. F.: J. Phys. Chem., A, 104, 380, 2000.
- Chhantyal-Pun, R., Rotavera, B., McGillen, M. R., Khan, M. A. H., Eskola, A. J., Caravan, R. L., Blacker, L., Tew, D. P., Osborn, D. L., Percival, C. J., Shallcross, D. E. and Orr-Ewing A. J.: ACS Earth Space Chem., 2, 833, 2018.
- Neeb, P., Sauer, F., Horie, O. and Moortgat, G. K.: Atmos. Environ, 31, 1417, 1997.
- Peltola, J., Seal, P., Inkilä, A. and Eskola, A.: Phys. Chem. Chem. Phys., 22, 11797, 2020.
- Welz, O., Eskola, A. J., Sheps, L., Rotavera, B., Savee, J. D., Scheer, M., D. Osborn, D. L., Lowe, D., Booth, M., Xiao, P., Khan, M. A. H., Percival, C. J., Shallcross, D. E. and Taatjes, C. A.: Angew. Chemie Int. Ed., 53, 4347, 2014.