

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_10

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### CH<sub>2</sub>OO + CH<sub>3</sub>C(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>			
$(1.3 \pm 0.1) \times 10^{-10}$	298	Welz et al., 2014	PLP-PIMS (a)
$(1.2 \pm 0.1) \times 10^{-10}$	298		CEA/UVS (a)
$(1.25 \pm 0.30) \times 10^{-10}$	295	Berndt et al., 2017	Free-Jet FR-CIMS (b)
$(1.47 \pm 0.09) \times 10^{-10}$	293	Chhantyal-Pun et al., 2018	PLP-CRDS (c)

#### Comments

- (a) 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>. The reacting mixture was monitored by multiplexed synchrotron photoionization mass spectrometry (MPIMS), which allowed time resolved detection CH<sub>2</sub>OO and its reaction products over the region 9.5 – 11.5 eV. Time-resolved direct detection of CH<sub>2</sub>OO at  $m/z = 46$  amu. The measured decay constant of CH<sub>2</sub>OO which was linearly dependent on (excess) concentrations of acetic acid (up to  $3.6 \times 10^{14}$  molecule cm<sup>-3</sup>) was used to determine the rate coefficient. The uncertainty limits are 95%, based on an unweighted linear fit to decay lifetime plots. No mass signal for adducts from the reaction products for CH<sub>2</sub>OO + CH<sub>3</sub>C(O)OH was identified.
- (b) CH<sub>2</sub>OO (formaldehyde oxide) was produced by the O<sub>3</sub> + C<sub>2</sub>H<sub>4</sub> reaction in air in a free-jet flow reactor at 1 bar and  $295 \pm 2$  K. CH<sub>2</sub>OO was detected as CH<sub>2</sub>OO-H<sup>+</sup> using CI-APi-TOF mass spectrometry.  $k$  was determined from the relative suppression of the steady state concentration of the protonated species as a function of [CH<sub>3</sub>C(O)OH].
- (c) CH<sub>2</sub>OO (formaldehyde oxide) was produced by 355 nm laser photolysis of diiodomethane in the presence of CH<sub>3</sub>C(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 CH<sub>3</sub>C(O)OH, and  $k$  was derived from the linear dependence of the decay constant on [CH<sub>3</sub>C(O)OH].

#### Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.3 \times 10^{-10}$	298
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.1$	298

### *Comments on Preferred Values*

The values of  $k$  obtained by Welz et al. (2014) and Chhantyal-Pun et al. (2018), using two independent experimental techniques, and with CH<sub>2</sub>OO produced from CH<sub>2</sub>I<sub>2</sub> photolysis, give confidence that the reaction is very rapid and that the kinetics are well determined. The determination of  $k$  reported by Berndt et al. (2017), with CH<sub>2</sub>OO produced from the O<sub>3</sub> + ethene reaction at atmospheric pressure, is less direct but yields a value of  $k$  that is in very good agreement with laser photolysis studies. The preferred value of  $k$  is based on the average of the determinations reported in the three studies.

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. These results are consistent with quantum calculations 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**

- Berndt, T., Herrmann, H. and Kurtén, T.: J. Am. Chem. Soc., 139, 13387, 2017.
- 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.
- 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.