

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_8

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### CH<sub>2</sub>OO + CH<sub>3</sub>C(O)CH<sub>3</sub> → products

#### Rate coefficient data

<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
(2.3 ± 0.3) × 10 <sup>-13</sup> (4 Torr)	293	Taatjes et al., 2012	PLP-PIMS (a)
(3.4 ± 0.9) × 10 <sup>-13</sup> (760 Torr)	297	Berndt et al., 2015	Free-Jet FR-TOF-MS (b)

#### 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 293 K and 4 Torr total pressure in a large excess of O<sub>2</sub>. The reacting mixture was monitored by tunable synchrotron photoionization mass spectrometry, which allowed characterisation of the PIMS for CH<sub>2</sub>OO and its reaction products over the region 9.5 – 11.5 eV, and time-resolved direct detection of CH<sub>2</sub>OO at *m/z* = 46 amu. The first order decay CH<sub>2</sub>OO in the presence of excess known concentrations of acetone was used to determine the rate constants. The uncertainty limits are 95%. The secondary ozonide (3,3-dimethyl-1,2,4-trioxalane) was identified as a reaction product from its PIMS aided by quantum chemical calculations.
- (b) Rate coefficients for the bimolecular reaction of CH<sub>2</sub>OO with acetone have been experimentally determined at 1 bar and (297±1) K by using a free-jet flow system. CH<sub>2</sub>OO was produced by the O<sub>3</sub> + C<sub>2</sub>H<sub>4</sub> reaction and [CH<sub>2</sub>OO] was measured indirectly by titrating with excess SO<sub>2</sub> and measurement of product H<sub>2</sub>SO<sub>4</sub> by ToF-CIMS. *k* was determined by non-linear regression fitting a parameterized expression for the [CH<sub>3</sub>C(O)CH<sub>3</sub>] dependence of the ratio [H<sub>2</sub>SO<sub>4</sub>]/[C<sub>2</sub>H<sub>4</sub>], assuming *k*<sub>uni</sub> = 0.19 s<sup>-1</sup>, and appropriate uncertainty in the parameters.

#### Preferred Values

Parameter	Value	T/K
<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	3.4 × 10 <sup>-13</sup>	298
<i>Reliability</i> Δ log <i>k</i>	± 0.3	298

### *Comments on Preferred Values*

The value of  $k$  reported by Berndt et al. (2015) at 1 bar is somewhat higher than that reported by Taatjes et al. (2012) at 4 Torr pressure, which was probably influenced by fall-off behaviour, as demonstrated for the  $\text{CH}_2\text{OO} + \text{CH}_3\text{CHO}$  reaction by Stone et al. (2014). The rate measurements appear to be precise and consistent with the emerging reactivity pattern for  $\text{CH}_2\text{OO}$  reactivity. The recommendation applies to 1 bar pressure and probably corresponds to the high-pressure limit.

### **References**

- Berndt, T., Kaethner, R., Voigtlander, J., Stratmann, F., Pfeifler, M, Reichler, P., Sipila, M., Kulmala, M., and Olzmann, M.: *Phys. Chem. Chem. Phys.*, 17, 19862, 2015.
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- Taatjes, C. A., Welz, O, Eskola, A. J., Savee, J. D., Osborn, D. L., Lee, E. P. F., Dyke, J.M., Mok, D. W. K., Shallcross, D. E. and Percival, C. J.: *Phys. Chem. Chem. Phys.*, 14, 10391, 2012.