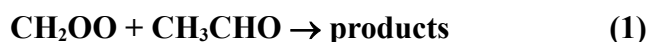


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_7

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



### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp /K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.5 \pm 0.7) \times 10^{-13}$ (4 Torr)	293	Taatjes et al., 2012	PLP-PIMS(a)
$(1.48 \pm 0.04) \times 10^{-12}$ (25 Torr) $2.2 \times 10^{-12}$ (50 Torr)	xxx	Stone et al., 2014	PLP-LIF/PIMS (b)
<i>Relative Rate Coefficients</i>			
$(2.5 \pm 0.06) \times 10^{-12}$ (730 Torr)	xxx	Horie et al., 1999	Static system/FTIR (c)

### Comments

- (a)  $\text{CH}_2\text{OO}$  (formaldehyde oxide) was produced by the reaction of  $\text{CH}_2\text{I} + \text{O}_2$ .  $\text{CH}_2\text{I}$  was generated by 248-nm laser photolysis of di-iodomethane,  $\text{CH}_2\text{I}_2$ , at 293 K and 4 Torr total pressure in a large excess of  $\text{O}_2$ . The reacting mixture was monitored by tunable synchrotron photoionization mass spectrometry, which allowed characterisation of the PIMS for  $\text{CH}_2\text{OO}$  and its reaction products over the region 9.5 – 11.5 eV. Time-resolved direct detection of  $\text{CH}_2\text{OO}$  at  $m/z = 46$  amu. The measured decay constant of  $\text{CH}_2\text{OO}$ , which was linearly dependent on (excess) concentrations of acetaldehyde (up to  $3.6 \times 10^{14}$  molecule  $\text{cm}^{-3}$ ), was used to determine the rate coefficient. The uncertainty limits are 95%, based on unweighted linear fit to decay lifetime plots. No secondary ozonide was observed in the reaction products for  $\text{CH}_2\text{OO} + \text{CH}_3\text{CHO}$  under reaction conditions but  $\text{CH}_3\text{C}(\text{O})\text{OH}$  was identified as a product, probably formed by decomposition of secondary ozonide.
- (b) Photolysis of  $\text{CH}_2\text{I}_2\text{-O}_2\text{-N}_2$  mixtures. in the presence of excess acetaldehyde ( $0.2$  to  $1.0 \times 10^{15}$  molecule  $\text{cm}^{-3}$ ), under pseudo-first-order conditions. Kinetics of  $\text{CH}_2\text{OO} + \text{CH}_3\text{CHO}$  reaction were followed by time-resolved monitoring of HCHO product by laser-induced fluorescence (LIF) spectroscopy.  $\text{CH}_2\text{OO} + \text{CH}_3\text{CHO}$  reaction rates were determined by fitting the single exponential growth of the fluorescence signal for different  $[\text{CH}_3\text{CHO}]$ , and rate coefficients derived from a bimolecular plot at each total pressure (range: 25 – 300 Torr). The HCHO yields decreased with pressure indicating stabilisation of the initially formed ozonide.
- (c) Ozonolysis of ethene studied in presence of  $\text{CH}_3\text{CHO}$ . The relative rates of  $\text{CH}_2\text{OO}$  reaction with  $\text{CH}_3\text{CHO}$  and  $\text{CF}_3\text{COCF}_3$  determined at 730 Torr in synthetic air using FT-IR spectroscopy to monitor the decay of  $\text{CF}_3\text{COCF}_3$  and the production of the secondary ozonide

(methyl-1,2,4-trioxolane) from the reaction with CH<sub>3</sub>CHO. Reaction with  $k(\text{CH}_2\text{OO}+\text{CF}_3\text{COCF}_3)/k(\text{CH}_2\text{OO}+\text{CH}_3\text{CHO}) = 13$ . The cited value of  $k$  calculated using the pressure independent IUPAC recommended value for  $k(\text{CF}_3\text{COCF}_3) = (3.16 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

### Preferred Values

Parameter	Value	T/K
$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.7 \times 10^{-12}$	298
$k_0 / \text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	$1.6 \times 10^{-29}$	
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.1$	298

### Comments on Preferred Values

The three cited determinations of the rate coefficient for this reaction indicate that the rate reaction of CH<sub>2</sub>COO with CH<sub>3</sub>CHO is pressure dependent. This is assigned to pressure quenching ( $k_q$ ) of the initially formed ozonide, which otherwise decomposes to HCHO ( $k_d$ ). Stone et al (2014) presented a Stern-Volmer analysis of the pressure dependence of the HCHO yields, corrected for any HCHO production from CH<sub>2</sub>IO<sub>2</sub> in the source chemistry. The Stern–Volmer plot gave an intercept of  $1.19 \pm 0.39$  and slope ( $k_q/k_d$ ) of  $(1.09 \pm 0.08) \times 10^{-18} \text{ cm}^3$ . Assuming an intercept of 1, the estimated yield of HCHO of 88% at 4 Torr, and a yield of 4% at 730 Torr, reconciling the results of Taatjes et al. (2012) and Horie et al.(1999). Taatjes et al. also observed acetic acid as a product at low pressure.

Stone et al. (2014) used the results of Taatjes et al. at 4 Torr ( $k = 9.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ ) with their own results cited here at 25 Torr and at 50 Torr, together the determination of  $k_q/k_d$  from the Stern–Volmer plot ( $(1.09 \pm 0.08) \times 10^{-18} \text{ cm}^3$ ), to obtain estimates for the low and high pressure limits defining the pressure dependence of  $k$  over the atmospheric range.

### References

- Horie, O., Schafer, C., and G. K. Moortgat, *Int. J. Chem. Kinet.*, **31**, 261–269 1999.
- Stone, D.; Blitz, M.; Daubney, L.; Howes, N. U. M.; Seakins, P., *Phys.Chem.Chem.Phys.*, **16**, 1139-1149, 2014.
- 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., Percival, C. J., *Phys.Chem.Chem.Phys.*, **14**, 10391, 2012