

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

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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp /K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.1 \pm 0.1) \times 10^{-10}$ (MPIMS)	293	Welz et al., 2014	PLP-MPIMS/
$(1.1 \pm 0.1) \times 10^{-10}$ (UV)			CEA-UVS (a)
<i>Relative Rate Coefficients</i>			
$< 5.6 \times 10^{-12}$		Neeb et al. 1997	FTIR/Static ozonolysis

## 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 diiodomethane,  $\text{CH}_2\text{I}_2$ , at 293 K and 4 torr total pressure in a large excess of  $\text{O}_2$ . Two complementary techniques were used for time resolved detection of  $\text{CH}_2\text{OO}$  following its formation: multiplexed synchrotron photoionization mass spectrometry (MPIMS), and cavity enhanced broadband UV spectroscopy. The decay constant of  $\text{CH}_2\text{OO}$  was determined by fitting a single exponential to the decay curves for each acid concentration, and a linear dependence of  $k^1$  on  $[\text{HCOOH}]$  (up to  $8 \times 10^{12}$  molecule  $\text{cm}^{-3}$ ) was observed, yielding the bimolecular rate coefficient. The uncertainty limits are 95% , based on unweighted linear fit to decay lifetime plots.
- (b) Static chamber experiment; FTIR. Upper limit based on  $k_1/k(\text{CH}_2\text{OO} + \text{H}_2\text{O}) = 14000$  at 293 K and 730 Torr from ozonolysis of ethane in the presence of water vapour. Cited value uses IUPAC upper limit for  $k(\text{H}_2\text{O}) < 4 \times 10^{-16}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

## Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.1 \times 10^{-10}$	298
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.1$	298

*Comments on Preferred Values*

The values of the rate coefficients obtained in two independent direct experimental techniques in the cited study give confidence that the reaction kinetics are well determined. The cited relative rate study using  $\text{CH}_2\text{OO} + \text{H}_2\text{O}$  as a reference reaction is uncertain because of the influence of the water dimer on the kinetics. The extremely rapid rates of the reactions of  $\text{CH}_2\text{OO}$  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, et al. 2014) which suggest that the reaction of  $\text{CH}_2\text{OO}$  with acids proceeds through a barrierless association channel forming a hydroperoxymethylester of the acid, with no pre-reaction complex identified.

### References

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Neeb, P., Sauer, F., Horie, O. Moortgat, G.K., *Atm. Environ*, 31, 1417, 1997.

Vereecken, L., Harder, H. and Novelli, A., *Phys. Chem. Chem. Phys.*, 14, 14682–14695, 2012.

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