

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_2

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### CH<sub>2</sub>OO + NO<sub>2</sub> → products

#### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(7^{+3.2}) \times 10^{-12}$	298	Welz et al., 2012	PLP-PIMS (a)
$(1.5 \pm 0.5) \times 10^{-12}$	295	Stone et al., 2014	PLP-LIF/PIMS (b)
$(4.4 \pm 0.2) \times 10^{-12}$	295	Qiu and Tonokura, 2019	PLP-IR (c)
$(1.0 \pm 0.2) \times 10^{-12}$	298	Luo et al., 2019	PLP-IR (d)
<i>Relative Rate Coefficients</i>			
$(5.2 \pm 1.5) \times 10^{-13}$	298	Manzanares et al., 1987	RR-AFT-UVscat (e)
$\sim 7.8 \times 10^{-11}$	297	Ouyang et al., 2013	RR-LP-UVvis (f)

#### 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 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 NO<sub>2</sub> was used to determine the rate constants. The asymmetrical uncertainty limits are 95 %, based on un-weighted linear fit of [NO<sub>2</sub>] dependence of decay lifetimes.
- (b) Laser photolysis at 248 nm of CH<sub>2</sub>I<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures was used to produce CH<sub>2</sub>OO in the presence of excess NO<sub>2</sub> at 295 K. Kinetics of CH<sub>2</sub>OO were followed by time-resolved monitoring of HCHO reaction products by laser-induced fluorescence (LIF), under pseudo-first-order conditions.  $k$  was found to be independent of pressure over range 25 – 300 Torr, and the cited value is an average of the values in this range. The uncertainty limits are 1 $\sigma$  errors from fitting kinetic data. Yield of HCHO is 100 % of CH<sub>2</sub>OO reacted.
- (c) CH<sub>2</sub>OO was produced by the 266 nm laser photolysis of CH<sub>2</sub>I<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures at 295  $\pm$  3 K and 10.6 Torr. The time-resolved decay kinetics of CH<sub>2</sub>OO were followed by mid-IR continuous-wave quantum cascade laser spectroscopy in the  $\nu_4$  band at 1274 cm<sup>-1</sup>, under pseudo-first order conditions in the presence of excess [NO<sub>2</sub>]. The tabulated value of  $k$  was determined from the dependence of the first-order decay constant on [NO<sub>2</sub>].
- (d) CH<sub>2</sub>OO was produced by the 248 nm laser photolysis of CH<sub>2</sub>I<sub>2</sub>-O<sub>2</sub> mixtures at 298 K and 5.9 – 9.7 Torr. The time-resolved decay kinetics of CH<sub>2</sub>OO were followed by mid-IR continuous-wave quantum cascade laser spectroscopy using high-resolution features in the 880-932 cm<sup>-1</sup> region, corresponding to the O-O stretching band. Experiments were carried out under pseudo-first order

conditions in the presence of excess  $[\text{NO}_2]$ , measured by UV absorption at 340 nm. The tabulated value of  $k$  was determined from the dependence of the first-order decay constant on  $[\text{NO}_2]$ .

- (e) Flow system involving  $\text{C}_2\text{H}_4\text{-O}_3\text{-SO}_2\text{-H}_2\text{O}$  mixtures in which  $\text{H}_2\text{SO}_4$  particle concentrations were monitored by scattered UV light, as described by Suto et al. (1985). Relative rate coefficients obtained from the dependencies of the aerosol formation on the concentrations of  $\text{O}_3$ ,  $\text{SO}_2$ , and  $\text{H}_2\text{O}$ , and the inclusion of the effect of added  $\text{NO}_2$  on the formation of the  $\text{H}_2\text{SO}_4$  aerosol. The resultant measured value of  $k(\text{CH}_2\text{OO} + \text{NO}_2)/k(\text{CH}_2\text{OO} + \text{SO}_2) = (1.4 \pm 0.4) \times 10^{-2}$  is placed on an absolute basis using  $k(\text{CH}_2\text{OO} + \text{SO}_2) = 3.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).
- (f) Photolysis of  $\text{CH}_2\text{I}_2\text{-O}_2\text{-N}_2\text{-NO}_2$  mixtures at 348 nm in continuous flow conditions at 760 Torr pressure. Simultaneous measurement of products  $\text{NO}_3$  and  $[\text{N}_2\text{O}_5 + \text{NO}_2]$  was made using cavity-enhanced absorption spectroscopy at 663 nm. Analysis of these data as function of  $[\text{NO}_2]$  allowed evaluation of the rate constant ratio:  $k_d(\text{CH}_2\text{OO})/k(\text{CH}_2\text{OO} + \text{NO}_2) = (6.4 \pm 1.7) \times 10^{12} \text{ molecule cm}^{-3}$ , where  $k_d$  is the total loss rate constant for competing first order processes. Assuming the competing kinetics is dominated by the reaction of  $\text{CH}_2\text{OO}$  with water gave the rate constant ratio:  $k(\text{CH}_2\text{OO} + \text{H}_2\text{O})/k(\text{CH}_2\text{OO} + \text{NO}_2) = 3.6 \times 10^{-6}$  (error  $\pm 40\%$ ). The tabulated approximate value of  $k(\text{CH}_2\text{OO} + \text{NO}_2)$  is based on using  $k(\text{CH}_2\text{OO} + \text{H}_2\text{O}) = 2.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3 \times 10^{-12}$	298
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.5$	298

### Comments on Preferred Values

There are four absolute studies of the  $\text{CH}_2\text{OO} + \text{NO}_2$  reaction kinetics, three based on the removal kinetics of  $\text{CH}_2\text{OO}$  (Welz et al., 2012; Qiu and Tonokura, 2019; Luo et al., 2019), and one less direct study, based the formation kinetics of the product,  $\text{HCHO}$  (Stone et al., 2014). The results of these studies are not in good agreement, with the reported values of  $k$  covering a range of a factor of seven. The preferred value of  $k$  is the geometric mean of the three values based on observation of  $\text{CH}_2\text{OO}$  removal, with wide uncertainty limits that encompass the reported range. Given that the three studies employ the same chemical system, and two the same method of detection, the origin of the large disagreement is unclear, and further studies are therefore required to allow the uncertainty limits to be reduced. The absolute rate coefficient reported by Stone et al. (2014) lies within the recommended range, although the interpretation of their results may be complicated by  $\text{HCHO}$  not being a direct product of the reaction. Neither of the relative rate studies has a well-defined reference reaction and they are not taken into account.

Decomposition of the cyclic ozonide formed in the initial  $\text{CH}_2\text{OO} + \text{NO}_2$  encounter, to  $\text{HCHO} + \text{NO}_3$ , was proposed to be the major product-forming channel, as indicated by the experiments of Stone et al. (2014) and Ouyang et al., (2013). However, the experimental work reported by Taatjes et al. (2013) and Caravan et al. (2017) did not detect  $\text{NO}_3$  in low-pressure photo-ionization experiments, placing an upper limit of 30 % on the  $\text{NO}_3$  yield. Their observation of a product mass equivalent to the  $\text{sCI} + \text{NO}_2$  adduct suggests that addition is the main product pathway. A multi-reference theoretical study by Vereecken and Nguyen (2017) predicted formation of the nitromethyl-peroxy radical adduct, in agreement with these latter experimental studies, with  $\text{HCHO}$  formed from its subsequent chemistry.

## References

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