

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

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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp /K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7^{+3}_{-2}) \times 10^{-12}$	298	Weltz et al., 2012	PLP-PIMS(a)
$(1.5 \pm 0.5) \times 10^{-12}$	295	Stone et al., 2014	PLP-LIF/PIMS (b)
Relative Rate Coefficients			
$k_1/k_{\text{ref}} = (1.4 \pm 0.4) \times 10^{-2} (\text{NO}_2/\text{SO}_2)$	298	Manzanares, Suto and Leifert 1987 <sup>4</sup>	(c)
$k_1/k_{\text{ref}} = 2.8 \times 10^5 (\text{NO}_2/\text{H}_2\text{O})$	297	Ouyang et al., 2013	LP-UVvis (d)

### 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  $\text{O}_2$ . 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 first order decay  $\text{CH}_2\text{OO}$  in the presence of excess known concentrations of  $\text{NO}_2$  was used to determine the rate constants. The asymmetrical uncertainty limits are 95%, based on un-weighted linear fit of  $[\text{NO}_2]$  dependence of decay lifetimes.
- (b) Laser photolysis at 248 nm of  $\text{CH}_2\text{I}_2\text{-O}_2\text{-N}_2$  mixtures was used to produce  $\text{CH}_2\text{OO}$ . in the presence of excess  $\text{NO}_2$ . Kinetics of  $\text{CH}_2\text{OO}$  were followed by time-resolved monitoring of HCHO reaction products by laser-induced fluorescence (LIF), under pseudo-first-order conditions.  $k_1$  was determined as a function of pressure at 295 K. Rate coefficients for  $\text{CH}_2\text{OO} + \text{NO}_2$  were independent of pressure over range: 25 – 300 Torr, and cited value of  $k$  is an average values in this range. The uncertainty limits are  $1\sigma$  errors from fitting kinetic data. Yield of HCHO is 100% of  $\text{CH}_2\text{OO}$  reacted.
- (c) Flow system involving  $\text{C}_2\text{H}_4\text{-O}_3\text{-SO}_2\text{-H}_2\text{O}$  mixtures in which  $\text{H}_2\text{SO}_4$  aerosol concentrations were monitored by scattered UV light. Relative rate coefficients obtained from the dependencies of the aerosol formation on the concentrations of  $\text{O}_3$ ,  $\text{SO}_2$ , and

H<sub>2</sub>O, and the inclusion of the effect of added NO<sub>2</sub> on the formation of the H<sub>2</sub>SO<sub>4</sub> aerosol:  $k_1/k_{\text{ref}}(\text{NO}_2/\text{SO}_2) = (1.4 \pm 0.4) \times 10^{-2}$ .

- (d) Photolysis of CH<sub>2</sub>I<sub>2</sub> – O<sub>2</sub> – N<sub>2</sub>– NO<sub>2</sub> mixtures at 348 nm in continuous flow conditions at 760 Torr pressure. CH<sub>2</sub>OO produced in this system was allowed to react with NO<sub>2</sub>. Simultaneous measurement of products NO<sub>3</sub> and [N<sub>2</sub>O<sub>5</sub>+NO<sub>2</sub>] was made in a dual channel BBCEAS at 663 nm. Analysis of these data as function of [NO<sub>2</sub>] allowed evaluation of the rate constant ratio:  $(k_d(\text{CH}_2\text{OO})/k(\text{CH}_2\text{OO} + \text{NO}_2)) = (6.4 \pm 1.7) \times 10^{12} \text{ molec.cm}^{-3}$ , where  $k_d$  is the total loss rate constant for competing first order processes. Assuming the competing kinetics is dominated by the reaction of Criegee radicals with water gave the rate constant ratio:  $(k(\text{CH}_2\text{OO} + \text{H}_2\text{O})/k(\text{CH}_2\text{OO} + \text{NO}_2)) = 3 \times 10^{-6}$  (error  $\pm 40\%$ ).

### 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

The recent direct photoionization mass spectrometric detection of formaldehyde oxide (CH<sub>2</sub>OO) as a product of the photolysis of CH<sub>2</sub>I<sub>2</sub> in the presence of O<sub>2</sub>, has enabled direct laboratory determinations of CH<sub>2</sub>OO kinetics (Welz et al., 2012). For the reaction: CH<sub>2</sub>OO + NO<sub>2</sub> → CH<sub>2</sub>O + NO<sub>3</sub> the only direct studies of the reaction kinetics are those of Welz et al., 2012 and of Stone et al. (2014) who used LIF to follow formation of product HCHO. These results are not in good agreement, and both studies have significant uncertainty limits. The preferred value is a weighted mean of the reported rate constants from the two direct studies. Neither of the relative rate studies have a well defined reference reaction and were not taken into account.

A recent theoretical investigation of the reaction mechanism by Vereecken et al. (2012) re-examined the PES, explicitly examining the open shell bi-radical structures than can be formed following barrier-less formation of a cyclic ozonide in the initial CH<sub>2</sub>OO + NO<sub>2</sub> encounter. Decomposition of the cyclic ozonide to HCHO + NO<sub>3</sub> is likely to be the major product-forming channel, as indicated by the experiments of Stone et al.(2014), and Ouang et al., (2013).

### References

- Ouang, B., McLeod, M.W., Jones, R.L., and Bloss, W.J., Phys.Chem.Chem.Phys., **15**, 17070, 2013.  
 Stone, D.; Blitz, M.; Daubney, L.; Howes, N. U. M.; Seakins, P., Phys.Chem.Chem.Phys., **16**, 1139-1149, 2014.  
 M. Suto, E. R. Manzanares, and L. C. Lee, Environ. Sci. Technol. **19**, 815 (1985); E.R. Manzanares, M. Suto, and L. C. Lee (unpublished data).

Welz, O, Savee, J. D. Osborn, D. L., Vasu, S. S., Percival, C. J., Shallcross, D. E., Taatjes, C. A. *Science*, **335**, 204, 2012