

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_5

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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>			
$(4 \pm 2) \times 10^{-10}$	343	Su et al., 2014	PLP-FTIR (a)
$(6.0 \pm 2.1) \times 10^{-11}$	297	Buras et al., 2014	PLP-UVA (b)
$(8 \pm 4) \times 10^{-11}$	295	Ting et al., 2014a	PLP-UVA (c)
$(7.35 \pm 0.63) \times 10^{-11}$	293	Chhantyal-Pun et al., 2015	PLP-CRDS (d)

Comments

- (a) CH_2OO was produced by the reaction of $\text{CH}_2\text{I} + \text{O}_2$, following 355 nm laser photolysis of CH_2I_2 ($4 \times 10^{13} \text{ cm}^{-3}$) in a large excess of O_2 . CH_2OO was detected by time-resolved step scan FTIR spectroscopy using absorption coefficients determined in their investigation of the IR spectrum of CH_2OO (Su et al., 2013). Rate coefficients ($(3.1 \pm 0.1) \times 10^{-10}$ and $(4.5 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively) were determined at pressures of 10 and 90 Torr. Kinetic modelling of experimental decay profiles yielded the cited value of k_1 , which has an estimated uncertainty of a factor of 2. Fitting also yielded a value of $k(\text{CH}_2\text{OO} + \text{I}) = (4 \pm 2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (b) CH_2OO was produced by the reaction of $\text{CH}_2\text{I} + \text{O}_2 \rightarrow \text{CH}_2\text{OO} + \text{I}$ following 355 nm laser photolysis of CH_2I_2 in a large excess of O_2 . CH_2OO kinetics was followed by time resolved absorption at 375 nm in the $\text{B} \leftarrow \text{X}$ transition and the atomic I co-product followed by probing the 1315.246 nm $\text{F} = 3 \ ^2\text{P}_{1/2} \leftarrow \text{F} = 4 \ ^2\text{P}_{3/2}$ atomic transition. $[\text{CH}_2\text{OO}]_0$ determined by fitting simultaneous decay of $[\text{I}]$ and $[\text{CH}_2\text{OO}]$, allowing a determination of the self-reaction rate coefficient, k_{self} with an uncertainty of $\pm 35\%$. The absorption cross section of CH_2OO at the UV probe wavelength ($\lambda = 375 \text{ nm}$) was derived as $(6.2 \pm 2.2) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$, which is consistent with the results of Ting et al (2014b) which form the basis of the IUPAC recommended value (see data sheet P33).
- (c) CH_2OO was prepared by pulsed 248 nm photolysis of $\text{CH}_2\text{I}_2/\text{O}_2$ mixtures in the pressure range 7.6–779 Torr. Transient absorption spectra were recorded using a gated intensified CCD camera (1 ms gate width) to monitor simultaneously CH_2I_2 , CH_2OO , CH_2I , and IO . The decay of CH_2OO was second order and various reactions, including the self-reaction and the reaction of $\text{CH}_2\text{OO} + \text{I}$, contributed to decay. The rate coefficients were determined with a detailed mechanism to model the observed temporal dependences of observed species. The fitted value of k ranged from $(8.2 - 12.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with the cited value an average of N_2 and O_2 bath-gas results. The error limits are 1σ . The yield of CH_2OO from $\text{CH}_2\text{I} + \text{O}_2$ was found to have a pressure dependence; for air at 1 atm., the yield of approximately 30 % is about twice previous estimates.
- (d) Cavity ring-down spectroscopy was used to perform kinetic measurements at 293 K under low pressure (7 to 30 Torr) conditions, for reactions of CH_2OO generated by (248 nm) laser photolysis

of CH₂I₂ in the presence of O₂, and monitored by a probe laser at 355 nm. Decay of [CH₂OO], from initial concentrations in the range 2.5 – 5.0 × 10¹² molecule cm⁻³, was second order. The rate coefficient, $k = (7.35 \pm 0.63) \times 10^{-11}$ cm³ molecule⁻¹s⁻¹, was derived from the measured CH₂OO decay rates, using an absorption cross-section reported previously.

Preferred Values

Parameter	Value	T/K
k /cm ³ molecule ⁻¹ s ⁻¹	7.4×10^{-11}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.1	298

Comments on Preferred Values

The occurrence of a rapid self-reaction of CH₂OO was discovered during the search for infrared spectroscopic features of CH₂OO, using the reaction of CH₂I with O₂ as a source (Su et al., 2013), when high concentrations of CH₂OO were required to observe the weak IR absorptions. However, the results of Su et al. (2014) are a factor of 10 higher, than the subsequent studies using UV detection. The reported rate coefficient values of Buras et al. (2014), Ting et al. (2014a) and Chhantyal-Pun et al. (2015), who all used time resolved UV absorption spectroscopy to determine CH₂OO kinetics, are in agreement within the error limits. These are quite significant in the former two studies, which used simulations with a complex kinetic scheme to extract the rate coefficient of interest. The data quality and analysis methods in the CRDS experiments provided more precise measurements of the kinetics and are the basis of our recommendation. The values of k appear to be independent of pressure.

References

- Buras, Z. J., Elsamra, R. M. and Green, W. H.: J. Phys. Chem. Lett., 5, 2224, 2014.
- Chhantyal-Pun, R., Davey, A., Shallcross, D.E., Percival, C.J. and Orr-Ewing, A.J.: Phys. Chem. Chem. Phys., 17, 3617, 2015.
- Su, Y-T., Huang, Y-H., Witek, H. and Lee, Y-P.: Science, 340, 174, 2013.
- Su, Y-T., Lin, H-Y., Putikam, R., Matsui, H., Lin, M.C., and Lee, Y-P.: Nature Chemistry, 6, 477, 2014.
- Ting, W-L, Chen, Y-H., Lee, Y-F, Matsui, H., Lee, Y-P. and Lin, J Jr -M.: J. Chem. Phys., 141, 104308, 2014a.
- Ting, W-L, Chen, Y-H., Chao, W., Smith, M.C. and Lin, J Jr -M.: Phys. Chem. Chem. Phys., 16, 10438, 2014b.