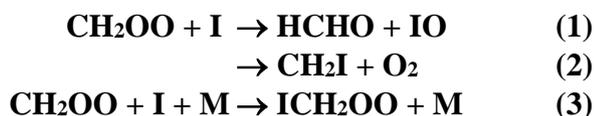


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_6

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This datasheet last evaluated: November 2016; last change in preferred values: November 2016



Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4 \pm 2) \times 10^{-11}$	343	Su et al., 2014	PLP-FTIR (a)
$< 1 \times 10^{-11}$	297	Buras et al., 2014	PLP-UVA (b)
$k_1 = 9.0 \times 10^{-12}$	295	Ting et al., 2014	PLP-UVA (c)
$< 5 \times 10^{-12}$	293	Chhantyal-Pun et al., 2015	PLP-CRDS (d)

Comments

- CH₂OO was produced by the reaction of CH₂I + O₂, following 355nm laser photolysis of CH₂I₂ in a large excess of O₂. CH₂OO was detected by time-resolved step scan FTIR spectroscopy using absorption coefficients determined in their investigation of the IR spectrum of CH₂OO (Su et al., 2013). Kinetic modelling to fit the experimental decay profiles yielded a value of $k(\text{CH}_2\text{OO} + \text{I}) = (4 \pm 2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- CH₂OO was produced by the reaction of CH₂I + O₂ → CH₂OO + I following 355 nm laser photolysis of CH₂I₂ in a large excess of O₂. CH₂OO kinetics was followed by time resolved absorption at 375 nm in the B ← X transition and the atomic I co-product followed by probing the 1315.246 nm F = 3 ²P_{1/2} ← F = 4 ²P_{3/2} atomic transition. [CH₂OO]₀ determined by fitting simultaneous decay of [I] and [CH₂OO], allowing a determination of the self-reaction rate coefficient, k_{self} with an uncertainty of ± 35%, and an upper limit for $k(\text{CH}_2\text{OO} + \text{I})$.
- CH₂OO was prepared by pulsed 248 nm photolysis of CH₂I₂/O₂ mixtures in the pressure range 10–798 mbar. Transient absorption spectra were recorded using a gated intensified CCD camera to monitor simultaneously CH₂I₂, CH₂OO, CH₂I, and IO in the reaction system. The decay of CH₂OO was second order and various channels, including the self-reaction and the reaction of CH₂OO + I, contributing to decay. The rate coefficients were determined with a detailed mechanism to model the observed temporal dependences of observed species. The fitted value for formation of IO was independent of pressure. The yield of CH₂OO from CH₂I + O₂ was found to have a pressure dependence due to pressure stabilisation of ICH₂OO* adduct formed in the alternative channel (3); for air at 1 atm., the yield of CH₂OO was approximately 30 %, which is about twice previous estimates.
- Cavity ring-down spectroscopy was used to perform kinetic measurements at 293 K under low pressure (7 to 30 Torr) conditions, for reactions of CH₂OO generated by (248-nm) laser photolysis of CH₂I₂ in the presence of O₂, and monitored by a probe laser at 355 nm. [CH₂OO]₀ ~ 2.5 – 5.0 × 10¹² molecule cm⁻³. Decay was essentially second order and dominated by the self-reaction of

CH₂OO. Estimation of the upper limit of rate coefficient for the reaction CH₂OO + I was obtained by numerical simulation of decay traces at lowest pressure, where there was minimal contribution from pressure dependent reactions, e.g. CH₂OO + I (+ M) → ICH₂OO (+ M). The upper limit values cited are based on the value where the goodness of fit to experimental data starts to deteriorate.

Preferred Values

Parameter	Value	T/K
$k_1 / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	9.0×10^{-12}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.3	298

Comments on Preferred Values

When the reaction of CH₂I with O₂ is used as a source of CH₂OO, secondary chemistry results, requiring simulations with a complex kinetic scheme to extract the rate coefficients of interest. The reported upper limit values of k reported by Buras et al. (2014) and Chhantyal-Pun, et al. (2015) and the value of Ting et al. (2014), who all used time-resolved UV absorption spectroscopy to determine CH₂OO kinetics, are consistent within the error limits. The value reported by Su et al. (2014) using the less sensitive IR detection to monitor CH₂OO kinetics is higher and has substantial error limits. The results of Ting et al. (2014) give a specific rate constant for the IO producing channel (k_1), which is the basis of the recommendation. The value of k_1 appears to be independent of pressure.

References

- Buras, Z. J., Elsamra, R. M. and Green, W. H.: J. Phys. Chem. Lett., 5, 2224, 2014.
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 Su, Y-T., Huang, Y-H., Witek, H. and Lee, Y-P.: Science, 340, 174, 2013.
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 Ting, W-L, Chen, Y-H., Lee, Y-F, Matsui, H., Lee, Y-P. and Lin, J Jr -M.: J. Chem. Phys., 141, 104308, 2014.