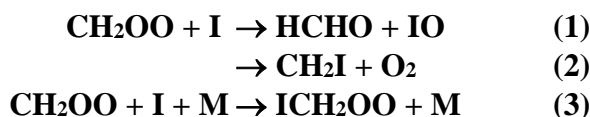


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_6

Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>).

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.
 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., L, Lin, H-Y., Putikam, R., Matsui, H., Lin, M.C., and Lee, Y-P.: Nature Chem., 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, 2014.