**IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_6**

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**CH2OO + I → HCHO + IO**

**→ CH2I + O2**

**CH2OO + I + M → ICH2OO + M**

## Rate coefficient data

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *k*/cm3 molecule-1 s-1 | Temp./K | | Reference | | Technique/Comments |
| *Absolute Rate Coefficients* |  |  | | |  |
| (4 ± 2)  10-11 | 343 | Su et al., 2014 | | PLP-FTIR (a) | | |
| < 1  10-11 | 297 | Buras et al., 2014 | | PLP-UVA (b) | | |
| *k*1 = 9.0  10-12 | 295 | Ting et al., 2014 | | PLP-UVA (c) | | |
| < 5  10-12 | 293 | Chhantyal-Pun et al., 2015 | | PLP-CRDS (d) | | |

##### Comments

1. CH2OO (formaldehyde oxide) was produced by the reaction of CH2I + O2, following 355nm laser photolysis of CH2I2 (4  1013 cm-3) 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*(CH2OO + I) = (4 ± 2)  10-11 cm3 molecule-1s-1.
2. CH2OO was produced by the reaction of CH2I + O2 → CH2OO + I following 355 nm laser photolysis of CH2I2 (4  1013 molecule cm-3) 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 2P1/2 ← F = 4 2P3/2 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*(CH2OO + I).
3. 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 (1 ms gate width) after the probe light was dispersed using a grating monochromator 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 dependencies 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 CH2IOO\* adduct formed in the alternate channel in recombination of I atoms with CH2OO; for air at 1 atm., the yield of CH2OO was approximately 30%, which is about twice previous estimates.
4. 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 /cm3 molecule-1 s-1 | 9.0  10-12 | 298 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  log *k* | ± 0.3 | 298 |

1. *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. give a specific rate constant for the IO producing channel, which is the basis of the recommendation. The values of *k*1 appear to be independent of pressure.

**References**

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