IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet CGI_6

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

(1) $CH_2OO + I \rightarrow HCHO + IO$

(2) $CH_2OO + I \rightarrow CH_2I + O_2$

(3) $CH_2OO + I + M \rightarrow ICH_2OO + M$

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

k/cm^3 molecule^{-1} s^{-1}	Temp/K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4 \pm 2) \times 10^{-11}$	343	Su et al., 2014	PLP-FTIR (a)
$<1.0 \times 10^{-11}$	297	Buras et al, 2014	PLP-UVA (b)
$<0.5 \times 10^{-11}$	295	Chhantyal-Pun, et al., 2015	PLP-CRDS (c)
$k_2 = 9.0 \times 10^{-12}$	295	Ting et al, 2014	PLP-UVA (d)

Comments

(a) CH_2OO (formaldehyde oxide) was produced by the reaction of $CH_2I + O_2$, following 355nm laser photolysis of CH_2I_2 (4×10^{13} 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). Kinetic modelling to fit the experimental decay profiles yielded a value of $k(CH_2OO + I) = (4 \pm 2) \times 10^{-11}$ cm^3 molecule^{-1}s^{-1}.

(b) CH_2OO was produced by the reaction of $CH_2I + O_2 \rightarrow CH_2OO + I$ following 355nm laser photolysis of CH_2I_2 (4×10^{13} cm^{-3}) in a large excess of O_2. CH_2OO 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. $[CH_2OO]_0$ determined by fitting simultaneous decay of [I] and $[CH_2OO]$, allowing a determination of the self-reaction rate coefficient, k_{self} with an uncertainty of ±35%, and an upper limit for $k(CH_2OO + I)$.

(c) 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 CH_2I_2 in the presence of O_2, and monitored by a probe laser at 355 nm. $[CH_2OO]_0 \sim 2.5 – 5.0 \times 10^{12}$ molecule cm^{-3}. Decay was essentially second order and dominated by the self-reaction of CH_2OO. Estimation of the upper limit of rate coefficient for the reaction $CH_2OO + I$ was obtained by numerical simulation of decay traces at lowest pressure, where there was minimal contribution from pressure dependent reactions,

e.g. CH_2OO + I (+ M) → ICH_2OO. The upper limit values cited are based on the value where the goodness of fit to experimental data starts to deteriorate.

(d) CH_2OO was prepared by pulsed 248 nm photolysis of CH_2I_2/O_2 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 CH_2I_2 , CH_2OO, CH_2I, and IO in the reaction system. The decay of CH_2OO was second order and various channels, including the self-reaction and the reaction of CH_2OO + 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 CH_2OO from $CH_2I + O_2$ was found to have a pressure dependence due to pressure stablisation of CH_2IOO^* adduct formed in the alternate channel in recombination of I atoms with CH_2OO; for air at 1 atm., the yield of CH_2OO was approx. 30%, which is about twice previous estimates.

Preferred Values

Parameter	Value	T/K
k_2 /cm^3 molecule^{-1} s^{-1}	9 x 10^{-12}	298
Reliability		
$\Delta \log k$	± 0.3	298

Comments on Preferred Values

When the reaction of CH_2I with O_2 is used as a source of CH_2OO, 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 CH_2OO kinetics, are consistent within the error limits. The value reported by Su et al. (2104) using the less sensitive IR detection to monitor CH_2OO 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_2 appear to be independent of pressure.

References

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