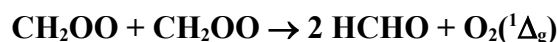


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_5

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The citation for the preferred values in this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

This datasheet last evaluated: June 2015; last change in preferred values: June 2015.



Rate coefficient data (*k*)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp/K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4 \pm 2) \times 10^{-10}$	343	Su et al., 2014	PLP-FTIR (a)
$(6.0 \pm 2.1) \times 10^{-11}$	297	Buras et al, 2014	PLP-UVA (b)
$(7.35 \pm 0.63) \times 10^{-11}$	295	Chhantyal-Pun, et al., 2015	PLP-CRDS (c)
$(8.2 \pm 1.4) \times 10^{-11}$	295	Ting et al, 2014	PLP-UVA (d)

Comments

- (a) CH_2OO (formaldehyde oxide) was produced by the reaction of $\text{CH}_2\text{I} + \text{O}_2$, following 355nm 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). The overall second order rate coefficient ($(3.1 \pm 0.1) \times 10^{-10}$ and $(4.5 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively) was determined from plots of $1/[\text{CH}_2\text{OO}]$ vs t 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 \pm 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 355nm laser photolysis of CH_2I_2 ($4 \times 10^{13} \text{ cm}^{-3}$) 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 $\text{F} = 3 \text{ } ^2\text{P}_{1/2} \leftarrow \text{F} = 4 \text{ } ^2\text{P}_{3/2}$ 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 (2014)b which form the basis of the IUPAC recommended value (see data sheet P33).
- (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. $[\text{CH}_2\text{OO}]_0 \sim 2.5 - 5.0 \times 10^{12} \text{ molecule cm}^{-3}$ decay was second order. Extraction of the rate coefficient for the reaction $\text{CH}_2\text{OO} + \text{CH}_2\text{OO}$ was performed by $k = (7.35 \pm 0.63) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived from the measured CH_2OO decay rates, using an absorption cross-section value reported previously.

- (d) CH₂OO was prepared by pulsed 248 nm photolysis of CH₂I₂/O₂ mixtures in the pressure range 7.6–779 Torr. 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 CH₂ + I, contributed to decay. The rate coefficients were determined with a detailed mechanism to model the observed temporal dependencies of observed species. The fitted value for the self-reaction ranged from (8.2 to 12.0) × 10⁻¹¹ cm³ molecule⁻¹s⁻¹, with the cited value an average of N₂ and O₂ bath-gas results. The error limits are 1 σ in averaging. The yield of CH₂OO from CH₂I + O₂ was found to have a pressure dependence; for air at 1 atm., the yield of approx. 30% is about twice previous estimates.

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	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, Chhantyal-Pun, et al., 2015, and Ting et al, 2014, 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

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