IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_7

$CH_2OO + CH_3CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.5 \pm 0.7) \times 10^{-13}$ (4 Torr)	293	Taatjes et al., 2012	PLP-PIMS (a)
$(1.48 \pm 0.04) \times 10^{-12}$ (25 Torr)	295	Stone et al., 2014	PLP-LIF/PIMS (b)
$\sim 2.2 \times 10^{-12}$ (50 Torr)			
$(1.7 \pm 0.5) \times 10^{-12}$ (760 Torr)	297	Berndt et al., 2015	Free-Jet FR-TOF-MS (c)
Relative Rate Coefficients			
$\sim 2.5 \times 10^{-12}$ (730 Torr)	295	Horie et al., 1999	Static system/FTIR (d)

Comments

(a) CH_2OO was produced by the reaction of $CH_2I + O_2$. CH_2I was generated by 248-nm laser photolysis of di-iodomethane, CH_2I_2, at 293 K and 4 Torr total pressure in a large excess of O_2. The reacting mixture was monitored by tunable synchrotron photoionization mass spectrometry, which allowed characterisation of the PIMS for CH_2OO and its reaction products over the region 9.5 – 11.5 eV. Time-resolved direct detection of CH_2OO at m/z = 46 amu. The measured decay constant of CH_2OO, which was linearly dependent on (excess) concentrations of acetaldehyde (up to 3.6×10^{14} molecule cm^{-3}), was used to determine the rate coefficient. The uncertainty limits are 95 %. No secondary ozonide was observed in the reaction products for $CH_2OO + CH_3CHO$ under reaction conditions but $CH_3C(O)OH$ was identified as a product, probably formed by decomposition of secondary ozonide.

(b) Photolysis of CH_2I_2-O_2-N_2 mixtures in the presence of excess acetaldehyde (0.2 to 1.0×10^{15} molecule cm^{-3}), under pseudo-first-order conditions. Kinetics of $CH_2OO + CH_3CHO$ reaction were followed by time-resolved monitoring of HCHO product by laser-induced fluorescence (LIF) spectroscopy. $CH_2OO + CH_3CHO$ reaction rates were determined by fitting the single exponential growth of the fluorescence signal for different [CH_3CHO], and rate coefficients derived from a bimolecular plot at each total pressure (range: 25 – 300 Torr). The HCHO yields decreased with pressure indicating stabilisation of the initially formed ozonide.

(c) Rate coefficients for the bimolecular reaction of CH_2OO with acetaldehyde have been experimentally determined at 1 bar and (297 ± 1) K by using a free-jet flow system. CH_2OO was produced by the $O_3 + C_2H_4$ reaction and [CH_2OO] was measured indirectly by titrating with excess SO_2 and measurement of product H_2SO_4 by ToF-CIMS. k was determined by non-linear regression fitting a parameterized expression for the [CH_3CHO] dependence of the ratio [H_2SO_4]/[C_2H_4], assuming $k_{uni} = 0.19$ s^{-1}, and appropriate uncertainty in the parameters. The value cited is close to the high-pressure limit calculated by Stone et al. (2014) from their direct measurements.

(d) Ozonolysis of ethene studied in the presence of CH_3CHO. The relative rates of CH_2OO reaction with CH_3CHO and CF_3COCF_3 determined at 730 Torr in synthetic air using FT-IR spectroscopy to monitor the decay of CF_3COCF_3 and production of the secondary ozonide (methyl-1,2,4-trioxolane) from the reaction with CH_3CHO, leading to $k(CH_2OO+CF_3COCF_3)/k(CH_2OO+CH_3CHO) \approx 13$. The cited value of k is calculated using the pressure independent value for $k(CH_2OO+CF_3COCF_3) = 3.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
k_0 / cm^3 molecule^{-1} s^{-1}	1.6×10^{-29} [M]	298
k_∞ /cm^3 molecule^{-1} s^{-1}	1.7×10^{-12}	298
Reliability		
$\Delta \log k_0$	± 0.2	298
$\Delta \log k_\infty$	± 0.2	298

Comments on Preferred Values

The determinations of the rate coefficient for this reaction indicate that the reaction of CH_2OO with CH_3CHO is pressure dependent. This is assigned to pressure quenching (k_q) of the initially formed ozonide, which otherwise decomposes to HCHO (k_d). Stone et al. (2014) presented a Stern-Volmer analysis of the pressure dependence of the HCHO yields, corrected for any HCHO production from CH_2IO_2 in the source chemistry. The Stern–Volmer plot gave an intercept of 1.19 ± 0.39 and slope (k_q/k_d) of $(1.09 \pm 0.08) \times 10^{-18}$ cm^3. Assuming an intercept of 1, the estimated yield of HCHO of 88 % at 4 Torr, and a yield of 4 % at 730 Torr, reconciling the results of Taatjes et al. (2012) and Horie et al. (1999). Taatjes et al. also observed acetic acid as a product at low pressure.

Stone et al. (2014) used the results of Taatjes et al. at 4 Torr ($k = 9.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}) with their own results at 25 Torr and at 50 Torr, together with the determination of k_q/k_d from the Stern–Volmer plot ($(1.09 \pm 0.08) \times 10^{-18}$ cm^3), to obtain estimates for the low and high pressure limits defining the pressure dependence of k over the atmospheric range, using a simple Lindemann-Hinshelwood mechanism for chemical activation. These form the basis of our 298 K preferred values, with k_∞ applying at pressures above about 100 Torr. The preferred value of k_∞ is also supported by the atmospheric pressure rate coefficient reported subsequently by Berndt et al. (2015).

References

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