IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_9

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

$CH_2OO + CF_3C(O)CF_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.0 \pm 0.3) \times 10^{-11}$	293	Taatjes et al., 2012	PLP-PIMS (a)
$(3.33 \pm 0.27) \times 10^{-11}$	295	Liu et al., 2014	PLP-LIF (b)

Comments

(a) CH_2OO was produced by the reaction of $CH_2I + O_2$. CH_2I was generated by 248-nm laser photolysis of diiodomethane, 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, and time-resolved direct detection of CH_2OO at m/z = 46 amu. The measured decay constant of CH_2OO, linearly dependent on known (excess) concentrations of hexafluoracetone ($0.01 – 1.0 \times 10^{14}$ molecule cm^{-3}), was used to determine the rate constant. The uncertainty limits are 95%.

(b) CH_2OO molecule generated by 351-nm laser flash photolysis of CH_2I/O_2 mixtures is accompanied by significant amounts of OH, observed by time resolved LIF. At least two different processes formed OH; a second, slower process appeared to be associated with the decay of CH_2OO. Using the OH signals as a proxy for the [CH_2OO] concentration in the presence of excess hexafluoroacetone the rate constant could be determined under pseudo first order conditions. k showed no pressure dependence over the range of 50−200 Torr, and the average value was $(3.33 \pm 0.27) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.2×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.1	298

Comments on Preferred Values

The rate constants for CH_2OO reaction with $CF_3C(O)CF_3$ appear to be accurately determined. The rate coefficient is larger than was measured for unsubstituted carbonyl compounds using a similar technique and is independent of pressure. Although the temperature dependence has not been investigated it is likely to be weak. The recommended temperature and pressure independent value is an unweighted mean of the values reported by Welz et al. (2012) and Liu et al. (2014). The products of this reaction were secondary ozonides, together with the products of ozonide decomposition.

References

Liu, Y., Bayes, K. D. and Sander, S. P.: J. Phys. Chem. A, 118, 741, 2014.

Taatjes, C. A., Welz, O, Eskola, A. J., Savee, J. D., Osborn, D. L., Lee, E. P. F., Dyke, J.M., Mok, D. W. K., Shallcross, D. E. and Percival, C. J.: Phys. Chem. Chem. Phys., 14, 10391, 2012.