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

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$CH_2OO + CF_3C(O)CF_3$ (HFA) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp /K	Reference	Technique/Comments
Absolute Rate Coefficients			
(3.0±0.3) x 10^{-11}	293	Taatjes et al., 2012	PLP-PIMS(a)
(3.33 ± 0.27) x 10^{-11} (51torr)	295	Lui et al., 2014	PLP-LIF(b)

Comments

(a) CH_2OO (formaldehyde oxide) 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 was linearly dependent on known (excess) concentrations of hexafluoracetone (0.01 – 1.0 x 10^{14} cm^{-3}) was used to determine the rate constants. The uncertainty limits are 95% , based on unweighted linear fit to decay lifetime plots.

(f) 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 SO_2 the rate constant for the reaction of SO_2 with CH_2OO could be determined under pseudo first order conditions. *k* showed no pressure dependence over the range of 50−200 torr, the average value was (3.33 ± 0.27) x 10^{-11} cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.16 x 10^{-11}	298

Reliability

$\Delta \log k$	± 0.1	298

Comments on Preferred Values

The rate constants for CH_2OO reaction with $CF_3C(O)CF_3$ (HFA) 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 close to zero. The recommended temperature and pressure independent value is a simple 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, 741−747, 2014.

Taatjes, C.A., Welz, O., Eskola, A.K., 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.