IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_3

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.

$CH_2OO + NO \rightarrow$ products (1)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp /K	Reference	Technique/Comments
Absolute Rate Coefficients			
< 6 x 10^{-14}	298	Weltz et al., 2012	PLP-PIMS(a)
< 2 x 10^{-13}	295	Stone et al., 2014	PLP-LIF/PIMS (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 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 photo-ionization 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 first order decay CH_2OO in the presence of 5 x 10^{15} molec.cm^{-3} NO was unaffected leading to the cited upper limit for *k,* based on the assumption that a 25% increase on the decay constant could be detected.

(b) Laser photolysis at 248 nm of CH_2I_2-O_2-N_2 mixtures was used to produce CH_2OO in the presence of excess NO (0.36 - 1.7) x 10^{15} molec.cm^{-3}. Kinetics of CH_2OO followed by time-resolved monitoring of HCHO reaction products by laser-induced fluorescence (LIF), which exhibited exponential growth (1st order kinetics) on two timescales. The fast HCHO production is assigned to the reaction of CH_2IO_2 with NO and the slower growth due to CH_2OO reactions. The upper limit for k_1 was based on the observation of no effect of [NO] on the slow growth curves, assuming the HCHO production was due to the reaction with NO.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	<6 x 10^{-14}	298

Comments on Preferred Values

The use of direct photoionization mass spectrometric detection of CH_2OO and of LIF to follow formation of product HCHO, was used to follow CH_2OO kinetics produced by the photolysis of CH_2I_2 in the presence of O_2, (Welz et al., 2012). For the reaction: $CH_2OO + NO \rightarrow CH_2O + NO_2$ the only studies of the reaction kinetics are those of Welz et al., 2012 and of Stone et al. (2014), who both reported only upper limits for *k*. These results are consistent but the preferred upper limit is the lower one from Welz et al. as their monitoring of [CH_2OO] is more direct and the possible interferences are less. Since no clear reaction has been observed, the products under atmospheric conditions are not known. Theoretical calculations (Vereeken et al., 2012) using DFT methods found the H_2COO + NO reaction show a barrier at all levels of theory employed. The lowest entrance transition state was found for the formation of a cyclic adduct with a nitrogen-centered radical, with a barrier calculated at 5.8 kcal mol^{-1}. The estimated rate coefficient was 1.7 x 10^{-18} $cm^3 molecule^{-1}s^{-1}$ is well below the experimental value of Welz et al. (2012).

References

Stone, D.; Blitz, M.; Daubney, L.; Howes, N. U. M.; Seakins, P., Phys.Chem.Chem.Phys., **16**, 1139-1149, 2014.

Welz, O, Savee, J. D. Osborn, D. L., Vasu, S. S., Percival, C. J., Shallcross, D. E., Taatjes, C. A. Science, **335**, 204, 2012

Vereeken, L., Harder, H. amd Novelli, A. Phys Chem Chem. Phys., 14, 14682, 2012.