IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_10

This datasheet updated: May 2015;

$CH_2OO + CH_3C(O)OH \rightarrow$ products (1)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp /K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.3\pm0.1) \times 10^{-10}$ (MPIMS) $(1.2\pm0.1) \times 10^{-10}$ (UV)	293	Welz et al., 2014	PLP-MPIMS/ CEA-UVS (a)

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 multiplexed synchrotron photoionization mass spectrometry (MPIMS), which allowed time resolved detection 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 acetic acid (up to 3.6×10^{14} molecule cm^{-3}) was used to determine the rate coefficient. The uncertainty limits are 95% , based on unweighted linear fit to decay lifetime plots. No mass signal for adducts from the reaction products for $CH_2OO + CH_3C(O)OH$ was identified.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.2×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.1	298

Comments on Preferred Values

The values of the rate coefficients obtained by Welz et al (2014), using two independent experimental techniques in the cited study, give confidence that the reaction is very rapid and kinetics are well determined. The extremely rapid rates of the reactions of CH_2COO with organic acids contrasts with the slower rates for reaction with aliphatic carbonyl compounds. These results are consistent with quantum calculations which suggest that the reaction of CH_2OO with acids proceeds through a barrierless association channel forming a hydroperoxymethylester of the acid, with no pre-reaction complex identified.

References

Welz, O, Eskola, A. J., Sheps, L., Rotavera, B., Savee, J.D., Scheer, M., D. Osborn, D. L., Lowe, D., Booth, M., Xiao, P., Khan, M.A.H., Percival, C. J., Shallcross, D. E., Taatjes, C. A.,Angew,Chemie Int.Ed., **53**, 4347, 2014.