IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_27

This datasheet last evaluated: May 2020; last change in preferred values: May 2020

CH_3CHOO (*Z*- and *E*-) + $CH_3C(O)OH$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_{(Z\text{-})} = (1.7 \pm 0.5) \times 10^{-10}$	298	Welz et al., 2014	PLP-PIMS (a)
$k_{(E\text{-})} = (2.5 \pm 0.6) \times 10^{-10}$	298		

Comments

(a) CH_3CHOO was produced by the reaction of O_2 with CH_3CHI, generated by 248-nm laser photolysis of $CH_3CH_2I_2$ in a large excess of O_2 at 298 K and 4 Torr. Time-resolved detection of CH_3CHOO was carried out using multiplexed synchrotron photoionization mass spectrometry (MPIMS). The decay constant of each of *Z*- and *E*-CH_3CHOO was determined by fitting a single exponential to the decay curves for each acid concentration, and a linear dependence of the decay constant on [CH_3COOH] was observed, yielding the bimolecular rate coefficient. The uncertainty limits are 95%, based on unweighted linear fit to decay lifetime plots.

Preferred Values

Parameter	Value	T/K
$k_{(Z\text{-})}$/cm^3 molecule^{-1} s^{-1}	1.7×10^{-10}	298
$k_{(E\text{-})}$/cm^3 molecule^{-1} s^{-1}	2.5×10^{-10}	298
Reliability		
$\Delta \log k_{(Z\text{-})}$	± 0.15	298
$\Delta \log k_{(E\text{-})}$	± 0.15	298

Comments on Preferred Values

The results of the direct studies of conformer-specific kinetics show that the *Z*- conformer of CH_3CHOO is less reactive than the *E*- conformer. This is consistent with the theoretical calculations, which generally predict a lower reaction barrier for the *E*- form. The preferred values of $k_{(Z\text{-})}$ and $k_{(E\text{-})}$ are based on the determinations reported in the sole kinetics study of Welz et al. (2014), and are consistent with the rapid reaction of the CH_3CHOO conformers with HC(O)OH, as also observed by Welz et al. (2014).

The extremely rapid rates of the reactions of sCIs with organic acids have been interpreted using a dipole-capture model, with the results for a number of sCI-acid combinations being used to formulate a structure-activity relationship, SAR (Chhantyal-Pun et al., 2018). *k* is expected to be only very weakly dependent on temperature. Based on product measurements for the CH_2OO + $CF_3C(O)OH$ reaction (using PIMS), the reactions are believed to proceed via an insertion reaction to form hydroperoxyl-esters, consistent with the results of theoretical studies (e.g. Aplincourt and Ruiz-Lopez, 2000).

References

Aplincourt, P. and Ruiz-Lopez, M. F.: J. Phys. Chem., A,104, 380, 2000.

Chhantyal-Pun, R., Rotavera, B., McGillen, M. R., Khan, M. A. H., Eskola, A. J., Caravan, R. L., Blacker, L., Tew, D. P., Osborn, D. L., Percival, C. J., Shallcross, D. E. and Orr-Ewing A. J.: ACS Earth Space Chem., 2, 833, 2018.

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. and Taatjes, C. A.: Angew. Chemie Int. Ed., 53, 4347, 2014.