

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_26

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CH₃CHOO (*Z*- and *E*-) + HC(O)OH → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_{(Z-)} = (2.5 \pm 0.3) \times 10^{-10}$	298	Welz et al., 2014	PLP-PIMS (a)
$k_{(E-)} = (5 \pm 3) \times 10^{-10}$	298		

Comments

- (a) CH₃CHOO was produced by the reaction of O₂ with CH₃CHI, generated by 248-nm laser photolysis of CH₃CH₂I₂ in a large excess of O₂ at 298 K and 4 Torr. Time-resolved detection of CH₃CHOO was carried out using multiplexed synchrotron photoionization mass spectrometry (MPIMS). The decay constant of each of *Z*- and *E*-CH₃CHOO was determined by fitting a single exponential to the decay curves for each acid concentration, and a linear dependence of the decay constant on [HCOOH] 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
$k_{(Z-)}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.5×10^{-10}	298
$k_{(E-)}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	5.0×10^{-10}	298
<i>Reliability</i>		
$\Delta \log k_{(Z-)}$	± 0.1	298
$\Delta \log k_{(E-)}$	± 0.3	298

Comments on Preferred Values

The results of the direct studies of conformer-specific kinetics show that the *Z*- conformer of CH₃CHOO 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 $k_{(Z-)}$ and $k_{(E-)}$ are based on the determinations reported in the sole kinetics study of Welz et al. (2014), and are consistent with the rapid reaction of CH₂OO with HC(O)OH, as also observed by Welz et al. (2014) and by Chhantyal-Pun et al. (2018).

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 $\text{CH}_2\text{OO} + \text{CF}_3\text{C}(\text{O})\text{OH}$ 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.