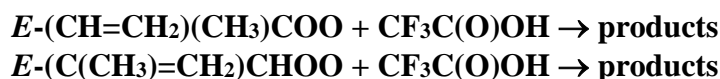


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_25

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This datasheet last evaluated: August 2017; last change in preferred values: August 2017



Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$	7.3×10^{-10}	298
$k/\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$	$4.9 \times 10^{-18} T^2 \exp(1620/T) + 6.3 \times 10^{-10}$	240-340
<i>Reliability</i>		
$\Delta \log k$	± 0.3	298
$\Delta (E/R)$	$\pm 500\text{ K}$	240-340

Comments on Preferred Values

The preferred value for the rate coefficient for reaction of both $E\text{-(CH=CH}_2\text{)(CH}_3\text{)COO}$ and $E\text{-(C(CH}_3\text{)=CH}_2\text{)CHOO}$ with $\text{CF}_3\text{C(O)OH}$ is based on the measurements and quantum calculations of Chhantyal-Pun et al. (2017) for the reaction of other Criegee intermediates with $\text{CF}_3\text{C(O)OH}$. In particular the rate coefficients for the reactions of CH_2OO and $(\text{CH}_3)_2\text{COO}$ with $\text{CF}_3\text{C(O)OH}$, and their temperature dependences, are well described by a model involving a hydrogen-bonded stabilized pre-reaction complex which is sufficiently stable to influence the temperature dependence of k (Long et al., 2009). The computational methodology used in those studies can be applied to the reactions of $\text{CF}_3\text{C(O)OH}$ with larger Criegee intermediates, such as those formed from the ozonolysis of isoprene. Rate coefficients were calculated at the DF-HF//DF-LCCSD(T)-F12a/aug-cc-pVTZ//B3LYP-6-31+G(d) level of theory by Chhantyal-Pun et al. (2017). This model predicts a T -dependence of the overall reaction of the form,

$$k = AT^2 \exp\left(\frac{\Delta H}{RT}\right) + k_d$$

(Long et al., 2009) where the first term describes the complex-forming reaction, and k_d is the rate coefficient for the direct (non complex-forming) reaction, approximated to be temperature-independent. The recommended parameters are based on the fit to the experimental data for $(\text{CH}_3)_2\text{COO}$ reported by Chhantyal-Pun et al. (2017) using this model, with the k_d term scaled upward here by about 20 % to account for the larger dipole moment and size of $E\text{-(CH=CH}_2\text{)(CH}_3\text{)COO}$ and $E\text{-(C(CH}_3\text{)=CH}_2\text{)CHOO}$, and the resultant influence on the capture limited rate constants.

References

- Chhantyal-Pun, R., McGillen, M. R., Beames, J. M., Khan, M. A. H., Percival, C. J., Shallcross, D. E., and Orr-Ewing, A. J.: *Angew. Chem. Int. Ed.*, 56, 9044, 2017.
- Long, B., Cheng, J. R., Tan, X. F. and Zhang, W. J.: *J. Mol. Struct. Theochem.*, 916, 159, 2009.