

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_23

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CH₂OO + CF₃C(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>			
$(3.4 \pm 0.3) \times 10^{-10}$	294	Chhantyal-Pun et al., 2017	PLP-CRDS (a)
$3.8 \times 10^{-18} T^2 \exp[(1620 \pm 180)/T] + 2.5 \times 10^{-10}$	240-340		

Comments

- (a) CH₂OO was produced by the reaction of CH₂I + O₂. CH₂I was generated by 248-nm laser photolysis of diiodomethane, CH₂I₂. Time-resolved direct detection of CH₂OO by CRDS at 355 nm in the temperature range 240 – 340 K. The measured decay constant of CH₂OO, which was linearly dependent on (excess) concentrations of trifluoroacetic acid (up to 3.6×10^{14} molecule cm⁻³), was used to determine the rate coefficient. The uncertainty limits are 95%. The rate coefficients were independent of pressure over the range 13 – 130 mbar and H/D substitution had no effect on k at all temperatures in the range studied.

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	3.3×10^{-10}	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.8 \times 10^{-18} T^2 \exp(1620/T) + 2.5 \times 10^{-10}$	240-340
<i>Reliability</i>		
$\Delta \log k$	± 0.2	298
$\Delta E/R$	± 500	240-340

Comments on Preferred Values

The reaction of CH₂OO with trifluoroacetic acid at 294 K is extremely rapid, as found for reactions with other carboxylic acids (see data sheets CGI_10 and CGI_11). The rate coefficient decreases with increasing temperature in the range 240-340 K, and exceeds the estimates for collision-limited values. This suggests rate enhancement by capture mechanisms, attributable to the large permanent dipole moments of the two reactants. However, the observed temperature dependence is steeper than predicted

by a simple dipole capture model with computed dipole moments. A different model involving competitive stabilization of a pre-reactive complex, binding the two reactants by two H-bonds, is proposed to explain the temperature dependence. This model was used in computational studies to describe the temperature dependence of the $\text{CH}_2\text{OO} + \text{HCOOH}$ reaction (Long et al., 2009), which predicts an overall T-dependence of the form,

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

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 for $\text{CH}_2\text{OO} + \text{CF}_3\text{C(O)OH}$ are based on a fit to the experimental data, as reported by Chhantyal-Pun et al. (2017) using this model.

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., Zhang, W. J.: *J. Mol. Struct. Theochem.*, 916, 159, 2009.