IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet CG1-23
Website: http://iupac.pole-ether.fr. See website for latest evaluated data.
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$CH_2OO + CF_3C(O)OH \rightarrow$ products

(1)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp /K	Reference	Technique/Comments
Absolute Rate Coefficients			
(3.4±0.3) x 10^{-10}	294	Chhantyal-Pun et al.,	PLP-(CRDS)
(3.8±2.6) x 10^{-18} T^2exp (1620 ± 180)/T) + 2.5 x 10^{-10}	240-340	2017	

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. Time-resolved direct detection of CH_2OO by CRDS at 355 nm in the temperature range 240 – 340 K. The measured decay constant of CH_2OO which was linearly dependent on (excess) concentrations of TFA acetic acid (up to 3.6 x 10^{14} molecule cm^{-3}) was used to determine the rate coefficient. The uncertainty limits are 95% from an unweighted linear fit to decay lifetime plots. 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 /cm^3 molecule^{-1} s^{-1}	3.8 x 10^{-18} T^2 exp(1620/T) + 2.5 x 10^{-10}	298

Reliability

Δ log k	± 0.2	298

Comments on Preferred Values

The reaction of CH_2OO with trifluoroacetic acid (TFA) at 294 K is extremely rapid, as found for reaction with carboxylic acids (see IUPAC data sheet CGI_10 and CGI_11). The rate coefficient decreases with increasing temp. in the range 240-340 K, and exceeds the estimates for collision-limited values, suggesting 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 CH_2OO + HCOOH reaction (Long et al., 2009), which predicts a T-dependence of the form:

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

The recommended parameters for CH_2OO + CF_3COOH are based on a fit of the experimental data 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.