$(CH_3)_2COO + CF_3C(O)OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.1 \pm 0.2) \times 10^{-10}$	294	Chhantyal-Pun et al., 2017	PLP-PIMS (c)
$4.9 \times 10^{-18} \, T^2 \exp[(1620 \pm 230)/T] + 5.2 \times 10^{-10}$	259-313		

Comments

(a) $(CH_3)_2COO$ was produced by the reaction of $(CH_3)_2CI + O_2$. $(CH_3)_2CI$ was generated by 248-nm laser photolysis of $(CH_3)_2CI_2$. Time-resolved direct detection of $(CH_3)_2COO$ by cavity ring-down spectroscopy at 355nm. $(CH_3)_2COO$ concentrations were $\sim 2 \times 10^{12}$ molecule cm^{-3}, deduced using previously published absorption cross sections. The measured decay constant of $(CH_3)_2COO$, which was linearly dependent on (excess) concentrations of $CF_3C(O)OH$ (up to 3.6×10^{14} molecule cm^{-3}), was used to determine the rate coefficient. 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. The expression for the temperature dependence is based on a model involving competitive stabilization of a pre-reactive complex.

Preferred Values

Parameter	Value	T/K
k/ cm^3 molecule^{-1} s^{-1}	6.2×10^{-10}	298
k/ cm^3 molecule^{-1} s^{-1}	$4.9 \times 10^{-18} \, T^2 \exp(1620/T) + 5.2 \times 10^{-10}$	260-315
Reliability		
$\Delta \log k$	± 0.2	298
$\Delta (E/R)$	± 500 K	260-315

Comments on Preferred Values

There has only been one study of the reaction of $(CH_3)_2COO$ with trifluoroacetic acid (Chhantyal-Pun et al., 2017). The reaction is extremely rapid at 294 K, as found for reaction of CH_2OO with carboxylic acids (see IUPAC data sheets CGI_10, CGI_11 and CGI_23). The rate coefficient is independent of pressure 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. The observed temperature dependence was best represented by a model involving competitive

stabilization of a pre-reactive complex (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 are based on a fit of the experimental data using this model, as reported by Chhantyal-Pun et al. (2017).

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.