IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet CG1-24
Website: http://iupac.pole-ether.fr. See website for latest evaluated data.
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$(CH_3)_2COO$ + $CF_3C(O)OH$ → products

(1)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp /K	Reference	Technique/Comments
Absolute Rate Coefficients			
(6.1±0.2) x 10^{-10}	294	Chhantyal-Pun et al.,	PLP-(CRDS)
(4.9±4.1) x 10^{-18} T^2exp (1620 ± 230)/T) + 5.2 x 10^{-10}	240-340	2017	

Comments

(a) $(CH_3)_2COO$ (acetone oxide) was produced by the reaction of $(CH_3)_2CI$ + O_2. $(CH_3)_2CI$ was generated by 248-nm laser photolysis of diiodomethane, $(CH_3)_2CI_2$. Time-resolved direct detection of $(CH_3)_2COO$ by cavity ring-down spectroscopy at 355nm. $(CH_3)_2COO$ concentrations were ~2 × 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 TFA acetic acid (up to 3.6 x 10^{14} molecule cm^{-3}) was used to determine the rate coefficient. The uncertainty limits are 2σ, based on 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. 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}	4.9 x 10^{-18} T^2 exp(1620/T) + 5.2 x 10^{-10}	298

Reliability

Δ log k	± 0.2	298

Comments on Preferred Values

The reaction of $(CH_3)_2COO$ with trifluoroacetic acid (TFA) at 294 K is extremely rapid, as found for reaction of CH_2COO with carboxylic acids (see IUPAC data sheet CGI_10, CGI_11 and CGI_23). The rate coefficient is independent of pressure, is a factor of 2 larger than for CH_2COO with TFA, has a similar temperature dependence in the range 260-310 K, and exceeds the estimates for collision-limited values, again 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 a T-dependence of the form:

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

The recommended parameters 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.