IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_29

This datasheet last evaluated: May 2020; last change in preferred values: May 2020

$(CH_3)_2COO + CH_3C(O)OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.1 \pm 0.2) \times 10^{-10}$	293	Chhantyal-Pun et al., 2018	PLP-CRDS (a)

Comments

(a) $(CH_3)_2COO$ was produced by 355 nm laser photolysis of 2,2-diiodopropane in the presence of $CH_3C(O)OH$, O_2 and N_2 at a total pressure of 13 mbar; and characterized by cavity ringdown ultraviolet absorption spectroscopy. Experiments were carried out under pseudo-first order conditions, with excess concentrations of $CH_3C(O)OH$, and k was derived from the linear dependence of the decay constant on $[CH_3C(O)OH]$.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.1×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.1	298

Comments on Preferred Values

The preferred value of k at 298 K is based on the determination reported in the sole kinetics study of Chhantyal-Pun et al. (2018). The extremely rapid rates of the reactions of sCIs with organic acids have been interpreted using a dipole-capture model, with the results for a number of sCI-acid combinations being used to formulate a structure-activity relationship, SAR (Chhantyal-Pun et al., 2018). The temperature dependence in k is expected to be weak. Based on product measurements for the $CH_2OO + CF_3C(O)OH$ reaction (using PIMS), the reactions are believed to proceed via an insertion reaction to form hydroperoxyl-esters, consistent with the results of theoretical studies (e.g. Aplincourt and Ruiz-Lopez, 2000).

References

Aplincourt, P. and Ruiz-Lopez, M. F.: J. Phys. Chem., A,104, 380, 2000.

Chhantyal-Pun, R., Rotavera, B., McGillen, M. R., Khan, M. A. H., Eskola, A. J., Caravan, R. L., Blacker, L., Tew, D. P., Osborn, D. L., Percival, C. J., Shallcross, D. E. and Orr-Ewing A. J.: ACS Earth Space Chem., 2, 833, 2018.