IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet CG1-24

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This datasheet created: June 2017; last evaluated; July 2017.

 **(CH3)2COO + CF3C(O)OH  products (1)**

 **Rate coefficient data**

|  |  |  |  |
| --- | --- | --- | --- |
| k/cm3 molecule-1 s-1 | Temp/K | Reference | Technique/Comments |
| *Absolute Rate Coefficients* |  |  |  |
|  (6.1±0.2) x 10-10 (4.9±4.1) x 10-18 *T*2exp(1620 ± 230)/*T*) + 5.2 x 10-10 | 294240-340 | Chhantyal-Pun et al., 2017 | PLP-(CRDS)  |
|  |  |  |  |

**Comments**

(a) (CH3)2COO (acetone oxide) was produced by the reaction of (CH3)2CI + O2. (CH3)2CI was generated by 248-nm laser photolysis of diiodomethane, (CH3)2CI2. Time-resolved direct detection of (CH3)2COO by cavity ring-down spectroscopy at 355nm. (CH3)2COO concentrations were ~2 × 1012 molecule cm-3, deduced using previously published absorption cross sections. The measured decay constant of (CH3)2COO which was linearly dependent on (excess) concentrations of TFA acetic acid (up to 3.6 x 1014 molecule cm-3) was used to determine the rate coefficient. The uncertainty limits are 2, 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* */*cm3 molecule-1 s-1 | 4.9 x 10-18 *T*2 exp(1620/*T*) + 5.2 x 10-10 | 298 |
| *Reliability* |  |  |
|  log *k* | ± 0.2 | 298 |

*Comments on Preferred Values*

The reaction of (CH3)2COO with trifluoroacetic acid (TFA) at 294 K is extremely rapid, as found for reaction of CH2COO 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 CH2COO 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:



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.