**IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_23**

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This datasheet last evaluated: July 2017; last change in preferred values: July 2017

**CH2OO + CF3C(O)OH → products**

1. **Rate coefficient data**

|  |  |  |  |
| --- | --- | --- | --- |
| *k*/cm3 molecule-1 s-1 | Temp./K | Reference | Technique/Comments |
| *Absolute Rate Coefficients* |  |  |  |
| (3.4 ± 0.3)  10-10 | 294 | Chhantyal-Pun et al., 2017 | PLP-CRDS (a) |
| 3.8  10-18 *T*2 exp[(1620 ± 180)/*T*] + 2.5  10-10 | 240-340 |  |  |

##### Comments

1. CH2OO was produced by the reaction of CH2I + O2. CH2I was generated by 248-nm laser photolysis of diiodomethane, CH2I2. Time-resolved direct detection of CH2OO by CRDS at 355 nm in the temperature range 240 – 340 K. The measured decay constant of CH2OO, which was linearly dependent on (excess) concentrations of trifluoroacetic acid (up to 3.6  1014 molecule
cm-3), was used to determine the rate coefficient. The uncertainty limits are 95%. 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* /cm3 molecule-1 s-1 | 3.3  10-10 | 298 |
| *k* /cm3 molecule-1 s-1 | 3.8  10-18 *T*2 exp(1620/*T*) + 2.5  10-10 | 240-340 |
|  |  |  |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  log *k* | ± 0.2 | 298 |
|  *E*/*R* | ± 500 | 240-340 |

1. *Comments on Preferred Values*
2. The reaction of CH2OO with trifluoroacetic acid at 294 K is extremely rapid, as found for reactions with other carboxylic acids (see data sheets CGI\_10 and CGI\_11). The rate coefficient decreases with increasing temperature in the range 240-340 K, and exceeds the estimates for collision-limited values. This suggests 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 the CH2OO + HCOOH reaction (Long et al., 2009), which predicts an overall T-dependence of the form,

1. 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 for CH2OO + CF3C(O)OH are based on a fit to the experimental data, as 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.