**IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_17**

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**CH3CHOO (*Z-* and *E-*) + NO2 → products**

## Rate coefficient data

|  |  |  |  |
| --- | --- | --- | --- |
| *k*/cm3 molecule-1 s-1 | Temp./K | Reference | Technique/Comments |
| *Absolute Rate Coefficients* |  |  |  |
| (2 ± 1)  10-12 | 298 | Taatjes et al., 2013 | PLP-PIMS (a) |
| *k*(*Z*-) = (2.0 ± 0.3)  10-12 | 298 |  |  |
| *k*(*E*-) = (3.1 ± 1.1)  10-12 | 298 |  |  |
| *k*(*Z*-) = (1.7 ± 0.3)  10-12 (20 Torr) | 300 | Caravan et al., 2017 | PLP-PIMS (b) |
| *k*(*Z*-) = (2.0 ± 0.3)  10-12 (40 Torr) | 300 |  |  |

##### Comments

1. CH3CHOO was produced by the reaction of CH3CHI + O2. CH3CHI was generated by 248 nm laser photolysis of 1,1-diiodoethane, CH3CH2I2, at 298 K and 4 Torr, in a large excess of O2. The reacting mixture was monitored by tunable synchrotron photoionization mass spectrometry, which allowed characterisation of the PIMS. Both *Z-* and *E-*CH3CHOO are produced, which could be distinguished by the difference in the ionisation energy of the two conformers. The first order decay plots of *Z-* and *E-*CH3CHOO in the presence of excess known concentrations of NO2 were used to determine the rate constants. The cited values were given by unweighted fits of the data, with uncertainty limits of 95%; returns from weighted fits gave *k* values lower by 30% but also indicated a slightly larger value for *E-* conformer. Although a small (statistically significant at 1 level) conformer dependence was reported, their preferred recommendation is *k* = (2 ± 1) × 10-12 cm3 molecule-1 s-1, for both conformers.
2. CH3CHOO was produced by the reaction of CH3CHI + O2. CH3CHI was generated by 248-nm pulsed laser photolysis of 1,1-diiodoethane, CH3CH2I2, at 300 K and pressures of 20 and 40 Torr, in a large excess of O2. The reacting mixture was monitored by PIMS at 10.5 eV, which allowed kinetic decay attributed to the *Z-* conformer of CH3CHOO to be monitored. The first order decay plots in the presence of excess NO2 (0 – 6.5 moleculecm-3) were used to determine the rate constants. Products were investigated using multiplexed photoionization mass spectrometry.

##### Preferred Values

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | **T/K** |
|  |  |  |
| *k*(*Z*-)/cm3 molecule-1 s-1 | 2.0  10-12 | 298 |
| *k*(*E*-)/cm3 molecule-1 s-1 | 2.0  10-12 | 298 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  log *k*(*Z*-) | ± 0.15 | 298 |
|  log *k*(*E*-) | ± 0.3 | 298 |

1. *Comments on Preferred Values*
2. The reported measurements on the overall rate coefficient for the reaction of *Z-* and *E-*CH3CHOO with NO2 from the two studies show good agreement. In the study of Taatjes et al. (2013) a slightly faster reaction with the *E*- conformer (statistically significant at 1 confidence interval) was reported. However, the experiments suffered from low signal quality, and the conformer dependence was not well defined. The Caravan et al. (2017) kinetic measurements were confined predominantly to the *Z*- conformer of CH3CHOO, and reported a barely significant pressure dependence over the range 2040 Torr.
3. Earlier efforts to characterize the yield of NO3 from this and other sCI + NO2 reactions have been inconclusive. Many studies have failed to detect NO3, including Caravan et al. (2017) over a pressure range of 440 Torr. However, a temporally resolved and [NO2]-dependent signal was observed at the mass of the Criegee-NO2 adduct for both the CH2OO and CH3CHOO systems, and the structure of this adduct was explored through *ab initio* calculations. Its origin from a direct CI reaction was demonstrated by observation of its efficient scavenging by SO2. It is postulated that this adduct is the major reaction product and, based on the acetaldehyde signal, an upper limit of < 30 % is placed on the NO3 + acetaldehyde yield. The fate of these Criegee-NO2 adducts requires further investigation to fully understand the impact of this reaction on tropospheric NOx.

**References**

Caravan, R. L., Khan, M. A. H., Rotavera, B., Papajak, E., Antonov, I. O., Chen, M.-W., Au, K., Chao, W., Osborn, D. L., Lin, J. J.-M., Percival, C. J., Shallcross, D. E., and C. A. Taatjes: Faraday Discuss., 200, 313, 2017.

Taatjes, C. A., Welz, O.; Eskola, A. J., Savee, J. D., Scheer, A. M., Shallcross, D. E., Rotavera, B., Lee, E. P. F., Dyke, J. M., Mok, D. K. W., Osborn, D. L., and Percival, C. J.: Science, 340, 171, 2013.