### IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet CGI\_15

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**CH3CHOO (*syn and anti*) + SO2 → CH3CHO + SO3 (1)**

**Rate coefficient data**

|  |  |  |  |
| --- | --- | --- | --- |
| k/cm3 molecule-1 s-1 | Temp  /K | Reference | Technique/Comments |
| Absolute Rate Coefficients |  |  |  |
| (2.4±0.3)× 10−11  *(syn)*  (6.7±1.0)× 10−11  *(anti)* | 298 | Taatjes et al., 2013 | PLP-PIMS(a) |
|  |  |  |  |
| (2.9±0.3) x 10-11 *(syn)*  (2.2±0.2) x 10-10 *(anti)* | 295 | Sheps et al., 2014 | PLP-CEUVA (b) |
|  |  |  |  |

**Comments**

(a) CH3CHOO (acetaldehyde oxide) was produced by the reaction of CH3CHI + O2. CH3CHI was generated by 248-nm laser photolysis of 1,1-diiodoethane, CH3CH2I2, at 293 K and 4 torr, in a large excess of O2. The reacting mixture was monitored by tunable synchrotron photoionization mass spectrometry. Both conformers of CH3CHOO (*syn-* and *anti-*) are produced, which could be distinguished by the difference in their ionisation energies. It was demonstrated that *anti*-CH3CHOO is substantially more reactive toward SO2 than is *syn*-CH3CHOO. SO3 production was observed, with a rise–time correlated with the decay-time of CH3CHOO, showing it to be a primary product of the reaction. The first order decay of *syn-* and *anti-*CH3CHOO in the presence of excess SO2 was measured, linear fits to the *k*I vs [SO2] plots were used to determine the rate constants.

(b) CH3CHOO prepared by PLP (266 nm) of CH3CHI2 in O2/Ar mixtures at 5 - 20 Torr pressure. CH3CHOO kinetics observed by recording the time-resolved UV absorption spectrum in the region 300 – 450 nm, corresponding to the B̃ (1A′) ← X̃(1A′) electronic transition. IO (formed from secondary chemistry) was also detected. Absorption features due to *syn* and *anti* conformers of CH3CHOO could be distinguished by their differing reactivities - reflected in characteristic time dependencies – allowing conformer-specific rate coefficients to be determined. The pseudo first order decay plots in presence of varying excess [SO2] gave the cited values for *k*syn and *k*anti.

### Preferred Values

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | **T/K** |
|  |  |  |
| *k*syn */*cm3 molecule-1 s-1 | 2.6 x 10-11 | 298 |
| *k*anti*/*cm3 molecule-1 s-1 | 1.0 x 10-10 | 298 |
|  |  |  |
| *Reliability* |  |  |
| Δ log *k*syn | 0.1 | 298 |
| Δ log *k*anti | 0.3 | 298 |

*Comments on Preferred Values*

CH3CHOO (acetaldehyde oxide) has two possible conformers: *syn-* and *anti-*CH3CHOO, which differ in the orientation of the C-O-O group. This leads to conformer-dependent reactivity. Computational studies indicate that *syn-*CH3CHOO is significantly less reactive than *anti-*CH3CHOO towards, e.g., H2O (Anglada et al., 2011) and alkenes (Vereecken et al, 2014). Calculations place the *syn* conformer ~15 kJ mol−1 lower in energy than *anti-* CH3CHOO (Kuwata et al., 2010), reflecting the zwitterionic character of the C–O bond. The barrier to interconversion of these conformers is substantial, ~160 kJ mol−1, and consequently *syn-* and *anti-*CH3CHOO act as distinct chemical species at atmospheric temperatures.

The two studies of the reaction with SO2 both used the same source of acetaldehyde oxide, i.e. reaction of CH3CHI with O2, which produces both conformers of CH3CHOO together with iodine atoms. Different spectroscopic techniques (UVA and PIMS) were used to monitor the time dependence of reactants and products, and to determine the decay kinetics of the conformers, after extraction of their absorption components from the multiplex spectra, obtained at a similar pressure and concentration regime. The results for the rate coefficient for reaction of *syn*-CH3CHOO with SO2 are in good agreement, considering the uncertainties (quoted error limits were 1). The magnitude of the rate coefficient was similar to that for reaction of CH2OO + SO2. In the case of *anti*-CH3CHOO with SO2, the result of Sheps et al. is a factor of ~3 higher than that obtained by Taatjes et al.(2013). The difference between these rate coefficients probably reflects the sensitivity and selectivity of the detection techniques: the decay data for *anti*-CH3CHOO using the UV spectroscopy method appears superior in quality to the PIMS but there is some uncertainty in the relative UV cross sections and initial yields of the two conformers, both of which are required to extract conformer-specific rate coefficients. Nevertheless, additional weight was given to the UV data in deriving the preferred value. The observed higher reactivity of the *anti*-CH3CHOO is consistent with the theoretical predictions for the reactivity of the two conformers referred to above.

**References**

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