

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

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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp /K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.4 \pm 0.3) \times 10^{-11}$ (syn) $(6.7 \pm 1.0) \times 10^{-11}$ (anti)	298	Taatjes et al., 2013	PLP-PIMS(a)
$(2.9 \pm 0.3) \times 10^{-11}$ (syn) $(2.2 \pm 0.2) \times 10^{-10}$ (anti)	295	Sheps et al., <a href="#">2014</a>	PLP-CEUVA (b)

### Comments

- (a)  $\text{CH}_3\text{CHOO}$  (acetaldehyde oxide) was produced by the reaction of  $\text{CH}_3\text{CHI} + \text{O}_2$ .  $\text{CH}_3\text{CHI}$  was generated by 248-nm laser photolysis of 1,1-diiodoethane,  $\text{CH}_3\text{CH}_2\text{I}_2$ , at 293 K and 4 torr, in a large excess of  $\text{O}_2$ . The reacting mixture was monitored by tunable synchrotron photoionization mass spectrometry. Both conformers of  $\text{CH}_3\text{CHOO}$  (*syn*- and *anti*-) are produced, which could be distinguished by the difference in [their ionisation energies](#). It was demonstrated that *anti*- $\text{CH}_3\text{CHOO}$  is substantially more reactive toward  $\text{SO}_2$  than is *syn*- $\text{CH}_3\text{CHOO}$ .  $\text{SO}_3$  production was observed, with a rise-time correlated with the decay-time of  $\text{CH}_3\text{CHOO}$ , showing it to be a primary product of the reaction. The first order decay of *syn*- and *anti*- $\text{CH}_3\text{CHOO}$  in the presence of excess  $\text{SO}_2$  was measured, linear fits to the  $k^l$  vs  $[\text{SO}_2]$  plots [were](#) used to determine the rate constants.
- (b)  $\text{CH}_3\text{CHOO}$  prepared by PLP (266 nm) of  $\text{CH}_3\text{CHI}_2$  in  $\text{O}_2/\text{Ar}$  mixtures at 5 - 20 Torr pressure.  $\text{CH}_3\text{CHOO}$  kinetics observed by recording the time-resolved UV absorption spectrum in the region 300 – 450 nm, corresponding to the  $\tilde{\text{B}}(1\text{A}') \leftarrow \tilde{\text{X}}(1\text{A}')$  electronic transition. IO ([formed from secondary chemistry](#)) was also detected. Absorption features due to *syn* and *anti* conformers of  $\text{CH}_3\text{CHOO}$  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  $[\text{SO}_2]$  gave the cited values for  $k_{\text{syn}}$  and  $k_{\text{anti}}$ .

### Preferred Values

Parameter	Value	T/K
$k_{\text{syn}}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.6 \times 10^{-11}$	298
$k_{\text{anti}}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.0 \times 10^{-10}$	298

#### Reliability

$\Delta \log k_{\text{syn}}$	0.1	298
$\Delta \log k_{\text{anti}}$	0.3	298

#### Comments on Preferred Values

CH<sub>3</sub>CHOO (acetaldehyde oxide) has two possible conformers: *syn*- and *anti*-CH<sub>3</sub>CHOO, which differ in the orientation of the C-O-O group. This leads to conformer-dependent reactivity. Computational studies indicate that *syn*-CH<sub>3</sub>CHOO is significantly less reactive than *anti*-CH<sub>3</sub>CHOO towards, e.g., H<sub>2</sub>O (Anglada et al., 2011) and alkenes (Vereecken et al., 2014). Calculations place the *syn* conformer ~15 kJ mol<sup>-1</sup> lower in energy than *anti*-CH<sub>3</sub>CHOO (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<sup>-1</sup>, and consequently *syn*- and *anti*-CH<sub>3</sub>CHOO act as distinct chemical species at atmospheric temperatures.

The two studies of the reaction with SO<sub>2</sub> both used the same source of acetaldehyde oxide, i.e. reaction of CH<sub>3</sub>CHI with O<sub>2</sub>, which produces both conformers of CH<sub>3</sub>CHOO [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*-CH<sub>3</sub>CHOO with SO<sub>2</sub> are in good agreement, considering the uncertainties (quoted error limits were 1σ). The magnitude of the rate coefficient was similar to that for reaction of CH<sub>2</sub>OO + SO<sub>2</sub>. In the case of *anti*-CH<sub>3</sub>CHOO with SO<sub>2</sub>, 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*-CH<sub>3</sub>CHOO 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*-CH<sub>3</sub>CHOO is consistent with [the](#) theoretical predictions for the reactivity of the two conformers referred to above.

### References

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