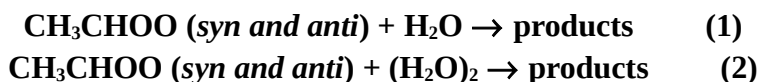


IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet CGI_16

Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. The citation for the preferred values in this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

This datasheet first evaluated: July 2015; last change in preferred values: July 2015.



Rate coefficient data

k/cm ³ molecule ⁻¹ s ⁻¹	Temp /K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_1 < 4 \times 10^{-15}$ (syn)	298	Taatjes et al., 2013	PLP-PIMS (a)
$k_1 = (1.0 \pm 0.4) \times 10^{-14}$ (anti)			
$k_1 < 2 \times 10^{-16}$ (syn)	293	Sheps et al., 2014	CE-UVAS (b)
$k_1 = (2.4 \pm 0.4) \times 10^{-14}$ (anti)			
Relative Rate Coefficients			
$k_1 = (2.1 \pm 0.6) \times 10^{-14}$ (anti)		Berndt et al., 2014	FT/CI-APi-TOF MS (c)
$k_1 = (5.2 \pm 4.9) \times 10^{-14}$ (anti)		Newland et al., 2014	RR-FTIR/UVA/ UVfluorescence (d)

Comments

- (a) CH₃CHOO (acetaldehyde oxide) was produced by the reaction of CH₃CHI + O₂. CH₃CHI was generated by 248-nm laser photolysis of 1,1-diodoethane, CH₃CH₂I₂, at 293 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 conformers of CH₃CHOO (*syn*- and *anti*-) are produced in this process, and they could be distinguished by the difference in their ionisation energies. The first order decay of CH₃CHOO in the presence of excess known concentrations of H₂O up to 2.4 × 10¹⁶ molecule cm⁻³, was used to determine the rate constants. It was demonstrated that decay of *syn*-CH₃CHOO was independent of the presence of H₂O at this concentration, allowing only the upper limit of k_{syn} to be determined. On the other hand decay of *anti*-CH₃CHOO increased monotonically with [H₂O], allowing k_{anti} to be determined with some confidence.
- (b) CH₃CHOO prepared by PLP (266 nm) of CH₃CHI₂ in O₂/Ar mixtures at 5 - 20 Torr pressure. The UV absorption spectrum of CH₃CHOO in the region 300 – 450 nm, corresponding to the $\tilde{B}(1A') \leftarrow \tilde{X}(1A')$ electronic transition was determined in this work, using time-resolved cavity enhanced absorption spectroscopy. Absorption features due to *syn* and *anti* conformers of CH₃CHOO could be distinguished by their differing reactivities - reflected in characteristic time dependencies. IO (formed from secondary chemistry) was also detected. CH₃CHOO kinetics were investigated by recording the time-dependence of components due to *syn* and *anti* conformers, and fitting the observed

growth and decay curves. This allowed conformer-specific rate coefficients to be determined. The decay rate of *syn*-CH₃CHOO) $k^l = 160 \pm 25 \text{ s}^{-1}$ did not change as a function of [H₂O], giving the cited upper limit of k_{syn} . For *anti*-CH₃CHOO, k^l increased linearly with [H₂O], and the cited value for k_{anti} was obtained by fitting to linear plots.

- (c) CH₃CHOO prepared by O₃ + *trans*-2-butene reaction in the presence of SO₂ in a flow system, equipped with CIMS for detection of H₂SO₄ using NO₃⁻ as reagent ion. Total pressure = 1 bar. The effect of [H₂O] on yield of H₂SO₄ allowed determination of rate coefficient ratio $k(\text{CH}_3\text{CHOO} + \text{H}_2\text{O})/k(\text{CH}_3\text{CHOO} + \text{SO}_2) = (8.8 \pm 0.4) \times 10^{-5}$ where k refers to the effective value for both conformers reacting. A refined analysis was conducted using a ‘two conformer’ model where distinction is made between *syn* and *anti* conformers of different reactivity, which gave an improved fit to the [H₂SO₄] data. Assuming that *syn*-CH₃CHOO had negligible reactivity with H₂O compared to the *anti*-conformer, as indicated by theoretical calculations (Ryzhkov and Ariya, 2004; Kuwata et al., 2010), their analysis gave the $k_{\text{anti}}(\text{H}_2\text{O})/k_{\text{anti}}(\text{SO}_2) = 1.4 \times 10^{-4}$. The cited value uses the IUPAC recommendation for $k(\text{anti-CH}_3\text{CHOO} + \text{SO}_2)$, i.e. $1.5 \times 10^{-10} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$.
- (d) The removal of SO₂ in the presence of 2-butene–ozone systems was measured as a function of humidity in EUPHORE simulation chamber, under atmospheric boundary layer conditions. SO₂ and O₃ abundance were measured using conventional fluorescence and UV absorption monitors, respectively; alkene abundance was determined via FTIR spectroscopy. SO₂ removal decreased with relative humidity (1.5 – 21%) confirming a significant reaction for CH₃CHOO with H₂O. The best fit to the data was obtained using a two conformer model applied to data from both *cis*- and *trans*-2-butene isomers. The observed SO₂ removal kinetics are consistent with the rate constant ratio: $k_{\text{anti}}(\text{H}_2\text{O})/k_{\text{anti}}(\text{SO}_2) = (3.5 \pm 3.1) \times 10^{-4}$. The cited value uses the IUPAC recommendation for $k(\text{anti-CH}_3\text{CHOO} + \text{SO}_2)$, i.e. $1.5 \times 10^{-10} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$.

Preferred Values

Parameter	Value	T/K
$k_{\text{syn}}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$<2 \times 10^{-16}$	298
$k_{\text{anti}}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.1×10^{-14}	298
<i>Reliability</i>		
$\Delta \log k_{\text{anti}}$	0.3	298

Comments on Preferred Values

The results of the direct studies of conformer-specific kinetics show that the *syn*-conformer is substantially less reactive than the *anti*-conformer. This is consistent with the theoretical calculations of Anglada et.al. (2011), which predicted a lower reaction barrier for the *anti*-form. The relative rate constants for the *anti*-conformer reaction with H₂O relative to SO₂ were determined in two studies for CH₃CHOO produced by ozonolysis of 2-butene at 1 bar pressure. The results are consistent with the direct studies at low pressure (4 to 10 Torr),

where CH_3CHOO was produced from the reaction of CH_3CHI with O_2 . Overall the results for k_{anti} are consistent but the uncertainties of the relative rate studies are much larger due to possible systematic errors deriving from the analytical procedures. The preferred upper limit value for k_{syn} is that determined in the study of Sheps et al. (2014), which was based on well defined absence of $[\text{H}_2\text{O}]$ -dependence of k . The preferred value for k_{anti} is a weighted mean of the results of the direct PIMS and UVA studies of Taatjes et al.,(2013) and Sheps et al. (2014), with emphasis in favour of the less scattered data of the UV study.

References

- Anglada, J.M., Gonzalez, J. and Torrent-Sucarrat, M.: *Phys.Chem.Chem.Phys.*, **13**, 13034, 2011.
- Berndt, T., Voigtlander, J., Stratmann, F., Junninen, H., Mauldin III, R.L., Sipila, M., Kulmala, M., and Herrmann, H.: *Phys. Chem. Chem. Phys.*, **16**, 19130, 2014.
- Newland, M.J., Rickard, A.R., Alam, M.S., Vereecken, L., Munoz, A., Rodenas, M., and Bloss, W.J., *Phys. Chem. Chem. Phys.*, **17**, 4076, 2015.
- Sheps, L., Scully, A.M. and Au, K.: *Phys. Chem. Chem. Phys.*, **16**, 26701, 2014.
- Taatjes, C. A. , Welz, C. A.; 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.