

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_15

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This datasheet last evaluated: May 2020; last change in preferred values: May 2020

CH₃CHOO (*Z*- and *E*-) + SO₂ → products

Rate coefficient data

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/Comments |
|--|---------|----------------------|--------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $k_{(Z)} = (2.4 \pm 0.3) \times 10^{-11}$ | 298 | Taatjes et al., 2013 | PLP-PIMS (a) |
| $k_{(E)} = (6.7 \pm 1.0) \times 10^{-11}$ | 298 | | |
| $k_{(Z)} = (2.9 \pm 0.3) \times 10^{-11}$ | 293 | Sheps et al., 2014 | PLP-CEUVA (b) |
| $k_{(E)} = (2.2 \pm 0.2) \times 10^{-10}$ | 293 | | |
| $(2.0 \pm 0.3) \times 10^{-11}$ | 295 | Smith et al., 2014 | PLP-CEUVA (c) |
| $(1.7 \pm 0.3) \times 10^{-11}$ | 295 | Howes et al., 2018 | PLP-PIMS (d) |
| $k_{(Z)} = (2.5 \pm 0.2) \times 10^{-11}$ | 298 | Zhou et al., 2019 | PLP-LIF (HO product) (e) |

Comments

- (a) CH₃CHOO was produced by the reaction of CH₃CHI + O₂. CH₃CHI was generated by 248-nm laser photolysis of 1,1-diiodoethane, CH₃CHI₂, at 298 K and 4 Torr, in a large excess of O₂. The reacting mixture was monitored by PIMS. Both *Z*- and *E*- conformers of CH₃CHOO are produced, which could be distinguished by the difference in their ionisation energies. It was demonstrated that *E*-CH₃CHOO is substantially more reactive toward SO₂ than is *Z*-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 *Z*- and *E*-CH₃CHOO in the presence of excess SO₂ was measured. Linear fits to the first order decay constants vs. [SO₂] plots were used to determine $k_{(Z)}$ and $k_{(E)}$ for *Z*- and *E*-CH₃CHOO, respectively.
- (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 $\tilde{B}(1A') \leftarrow \tilde{X}(1A')$ electronic transition. IO (formed from secondary chemistry) was also detected. Absorption features due to *Z*- and *E*- conformers of CH₃CHOO could be distinguished by their differing reactivities, reflected in their 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 of $k_{(Z)}$ and $k_{(E)}$ for *Z*- and *E*-CH₃CHOO.
- (c) CH₃CHOO prepared by PLP (266 nm) of CH₃CHI₂ in O₂/Ar mixtures and measured by wavelength-resolved transient absorption in a flow cell at 295 K and 15–100 Torr pressure (N₂). k was determined from plots of first order decay constant vs. [SO₂]. The absorption data quality did not allow distinction between the reactivity of *Z*- and *E*-conformers, but earlier work of Taatjes et al. (*Z*:*E* = 9:1) and Sheps et al. (*Z*:*E* = 3:1) suggests that the *Z*- conformer is dominant.
- (d) CH₃CHOO generated by 248 nm laser photolysis of CH₃CHI₂ in the presence of O₂. The PIMS system used in this study was unable to differentiate between the reactivity of *Z*- and *E*-conformers

of CH₃CHOO, but earlier work of Taatjes et al. (*Z*-:*E*- = 9:1) and Sheps et al. (*Z*-:*E*- = 3:1) suggests that the *Z*- conformer is dominant.

- (e) CH₃CHOO produced from 248 nm laser photolysis of CH₃CHI₂ in the presence of O₂, at 298 K at pressures in the range 10-100 Torr (Ar). The decay kinetics of *Z*-CH₃CHOO ($k_{(Z)}$) were monitored using HO as a marker species (LIF), making the assumption that the observed formation of HO is due to the thermal decomposition of *Z*-CH₃CHOO, with [HO] controlled by its rapid removal in the system (e.g. via reaction with CH₃CHI₂). Experiments were carried out under pseudo-first order conditions in the presence of excess [SO₂]. The tabulated value of $k_{(Z)}$ was determined from the dependence of the first-order decay constant on [SO₂].

Preferred Values

| Parameter | Value | T/K |
|--|-----------------------|-----|
| $k_{(Z)}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 2.6×10^{-11} | 298 |
| $k_{(E)}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.4×10^{-10} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k_{(Z)}$ | ± 0.1 | 298 |
| $\Delta \log k_{(E)}$ | ± 0.3 | 298 |

Comments on Preferred Values

CH₃CHOO has two possible conformers: *E*- and *Z*-CH₃CHOO, which differ in the orientation of the C-O-O group. This leads to conformer-dependent reactivity. Computational studies indicate that *Z*-CH₃CHOO is significantly less reactive than *E*-CH₃CHOO towards, e.g. H₂O (Anglada et al., 2011). Calculations place the *Z*- conformer ~15 kJ mol⁻¹ lower in energy than *E*- 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 *Z*- and *E*-CH₃CHOO act as distinct chemical species at atmospheric temperatures.

The five studies of the reaction with SO₂ used the same source of acetaldehyde oxide, i.e. reaction of CH₃CHI with O₂, which produces both conformers of CH₃CHOO together with iodine atoms. The signal:noise characteristics of the spectra needed to define conformer differences is marginal so the parameter distinction is not well defined in the case of acetaldehyde oxide. Moreover, there is uncertainty in the relative amounts of the two conformers formed in the source chemistry. Nevertheless, the results for the rate coefficient for reaction of predominantly *Z*-CH₃CHOO with SO₂ are in good agreement, considering the uncertainties (quoted error limits were 1 σ). The result of Sheps et al. (2014) for $k_{(E)}$ is a factor of ~3 higher than that obtained by Taatjes et al. (2013), and both determinations are significantly larger than their determinations of $k_{(Z)}$, and that of Zhou et al. (2019). The difference between these rate coefficients probably reflects the sensitivity and selectivity of the detection techniques; the decay data for *E*-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. The observed higher reactivity of the *E*-CH₃CHOO is consistent with theoretical predictions for the reactivity of the two conformers referred to above, and the preferred value of $k_{(E)}$ is the mean of the two reported values, which carries an uncertainty of a factor of 2. The preferred value of $k_{(Z)}$ is based on an unweighted mean of the determinations of Taatjes et al. (2013), Sheps et al. (2014) and Zhou et al. (2019), which are in good agreement.

Quantum chemical studies predict that the reactions of the CH₃CHOO conformers with SO₂ proceed via initial barrierless formation of chemically-activated cyclic secondary ozonides (Vereecken et al. 2012). As discussed for the CH₂OO + SO₂ reaction (data sheet CGI_1), the chemically-activated C₂ secondary ozonides are expected to isomerise and decompose mainly to form CH₃CHO + SO₃, and this is consistent with the results of direct kinetics studies at low pressures (Taatjes et al., 2013; Howes et al., 2018). At higher pressures, collisional stabilization of the secondary ozonides may be important (Vereecken et al. 2012), and further studies are required to characterize their onward reactions. Until additional theoretical and quantitative experimental product channel data become available, we recommend that the reaction predominantly forms CH₃CHO and SO₃.

References

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