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



This datasheet last evaluated: July 2019; last change in preferred values: July 2019

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## $CH_3CHOO$ (*Z- and E-*) + $SO_2$ → products

### Rate coefficient data

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

### Comments

(a) $CH_3CHOO$ (acetaldehyde oxide) was produced by the reaction of $CH_3CHI + O_2$. $CH_3CHI$ was generated by 248-nm laser photolysis of 1,1-diiodoethane, $CH_3CH_2I_2$, at 293 K and 4 Torr, in a large excess of $O_2$. The reacting mixture was monitored by PIMS from a synchrotron light source. Both *Z*- and *E*- conformers of $CH_3CHOO$ are produced, which could be distinguished by the difference in their ionisation energies. It was demonstrated that *E*-$CH_3CHOO$ is substantially more reactive toward $SO_2$ than is *Z*-$CH_3CHOO$. $SO_3$ production was observed, with a rise–time correlated with the decay-time of $CH_3CHOO$, showing it to be a primary product of the reaction. The first order decay of *Z*- and *E*-$CH_3CHOO$ in the presence of excess $SO_2$ was measured. Linear fits to the first order decay constants vs. [$SO_2$] plots were used to determine $k_{(Z\text{-})}$ and $k_{(E\text{-})}$ for *Z*- and *E*-$CH_3CHOO$, respectively.

(b) $CH_3CHOO$ prepared by PLP (266 nm) of $CH_3CHI_2$ in $O_2$/Ar mixtures at 5 - 20 Torr pressure. $CH_3CHOO$ kinetics observed by recording the time-resolved UV absorption spectrum in the region 300 – 450 nm, corresponding to the $\tilde{B}$ (1A′) ← $\tilde{X}$(1A′) electronic transition. IO (formed from secondary chemistry) was also detected. Absorption features due to *Z*- and *E*- conformers of $CH_3CHOO$ 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 [$SO_2$] gave the cited values of $k_{(Z\text{-})}$ and $k_{(E\text{-})}$ for *Z*- and *E*-$CH_3CHOO$.

(c) Experiments designed to determine the UV spectrum of $CH_3CHOO$ measured by wavelength-resolved transient absorption in a flow cell at 295 K and 15–100 Torr pressure ($N_2$), by following the time resolved spectra with and without $SO_2$ present. $CH_3CHOO$ prepared by PLP (266 nm) of $CH_3CHI_2$ in $O_2$/Ar mixtures. The change in absorption by $CH_3CHOO$ and other species was measured at a series of delay times (1 to 484 $\mu$s), allowing decay in the presence of known excess [$SO_2$]. $k$ was determined from plots of first order decay constant vs [$SO_2$]. 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) Kinetics of the study of $CH_3CHOO$ with $SO_2$ using 248 nm laser photolysis of $CH_3CHI_2$ in the presence of $O_2$. This gives rapid production of $CH_3CHOO$, suitable for study of the reaction kinetics. The PIMS system used in this study was unable to differentiate between the reactivity of *Z*- and *E*-conformers of $CH_3CHOO$, 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.

**Preferred Values**

| Parameter | Value | T/K |
|---|---|---|
| $k_{(Z-)}$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.2 \times 10^{-11}$ | 298 |
| $k_{(E-)}$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.4 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k_{(Z-)}$ | ± 0.1 | 298 |
| $\Delta \log k_{(E-)}$ | ± 0.3 | 298 |

*Comments on Preferred Values*

$CH_3CHOO$ (acetaldehyde oxide) has two possible conformers: *E*- and *Z*-$CH_3CHOO$, which differ in the orientation of the C-O-O group. This leads to conformer-dependent reactivity. Computational studies indicate that *Z*-$CH_3CHOO$ is significantly less reactive than *E*-$CH_3CHOO$ towards, e.g. $H_2O$ (Anglada et al., 2011). Calculations place the *Z*- conformer ~15 kJ mol$^{-1}$ lower in energy than *E*-$CH_3CHOO$ (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*-$CH_3CHOO$ act as distinct chemical species at atmospheric temperatures.

The four studies of the reaction with $SO_2$ used the same source of acetaldehyde oxide, i.e. reaction of $CH_3CHI$ with $O_2$, which produces both conformers of $CH_3CHOO$ 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 signal:noise characteristics of the spectra needed to define the resolution of 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*-$CH_3CHOO$ with $SO_2$ 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 $CH_2OO + SO_2$. 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 $k_{(Z-)}$. The difference between these rate coefficients probably reflects the sensitivity and selectivity of the detection techniques; the decay data for *E*-$CH_3CHOO$ 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. Weight was given to the UV data in deriving the preferred value. The observed higher reactivity of the *E*-$CH_3CHOO$ 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.

Quantum chemical studies predict that the reactions of the $CH_3CHOO$ conformers with $SO_2$ proceed via initial barrierless formation of chemically-activated cyclic secondary ozonides (Vereecken

et al. 2012). As discussed for the $CH_2OO + SO_2$ reaction (data sheet CGI_1), the chemically-activated $C_2$ secondary ozonides are expected to isomerise and decompose mainly to form $CH_3CHO + SO_3$, 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 $CH_3CHO$ and $SO_3$.

## References


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