**IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_16**

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**CH3CHOO (*Z-* and *E-*) + H2O → products (1)**

**CH3CHOO (*Z-* and *E-*) + (H2O)2 → products (2)**

## Rate coefficient data

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *k*/cm3 molecule-1 s-1 | Temp./K | | Reference | | Technique/Comments |
| *Absolute Rate Coefficients* |  |  | | |  |
| *k*1(*Z*-) < 4 × 10−15 | 298 | Taatjes et al., 2013 | | PLP-PIMS (a) | | |
| *k*1(*E*-) = (1.0 ± 0.4) × 10−14 | 298 |  | |  | | |
| *k*1(*Z*-) < 2 × 10−16 | 293 | Sheps et al., 2014 | | CE-UVAS (b) | | |
| *k*1(*E*-) = (2.4 ± 0.4) × 10−14 | 293 |  | |  | | |
| *k*1(*E*-) = (1.31 ± 0.26) × 10−14 | 298 | Lin et al., 2016 | | PLP-UVAS (c) | | |
| *k*1(*E*-) = 1.11 × 10−14 exp[(50 ± 644)/*T*] | 288-328 |  | |  | | |
| *k*2(*E*-) = (4.40 ± 0.29) × 10−11 | 298 |  | |  | | |
| *k*2(*E*-) = 5.21 × 10−20 exp[(6125 ± 332)/*T*] | 288-328 |  | |  | | |
|  |  |  | |  | | |
| *Relative Rate Coefficients* |  |  | |  | | |
| *k*1(*E*-) = (2.0 ± 0.6) × 10−14 | 293 | Berndt et al., 2014 | | FT/CI-APi-TOF MS (d) | | |
| *k*1(*E*-) = (4.9 ± 4.3) × 10−14 | 296-302 | Newland et al., 2015 | | RR-FTIR/UVA/UV-F (e) | | |

##### Comments

1. CH3CHOO was produced by the reaction of CH3CHI + O2. CH3CHI was generated by 248-nm laser photolysis of 1,1-diiodoethane, CH3CH2I2, at 298 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 (*Z-* and *E-*) 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 *Z*-CH3CHOO was independent of the presence of H2O at this concentration, allowing only the upper limit of *k*1*(Z-*) to be determined. On the other hand decay of *E*-CH3CHOO increased monotonically with [H2O], allowing *k*1*(E-*) to be determined with some confidence.
2. 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 B̃ (1A′) ← X̃(1A′) electronic transition was determined in this work, using time-resolved cavity enhanced absorption spectroscopy. Absorption features due to *Z-* and *E-* conformers of CH3CHOO could be distinguished by their differing reactivities - reflected in characteristic time-dependences. IO (formed from secondary chemistry) was also detected. CH3CHOO kinetics were investigated by recording the time-dependence of components due to *Z-* and *E-* conformers, and fitting the observed growth and decay curves. This allowed conformer-specific rate coefficients to be determined. The first-order decay rate of *Z*-CH3CHOO, 160 ± 25 s-1, did not change as a function of [H2O], giving the cited upper limit of *k*1*(Z-*). For *E*-CH3CHOO, the first-order decay rateincreased linearly with [H2O], and the cited value for *k*1*(E-*) was obtained by fitting to linear plots.
3. CH3CHOO prepared by PLP (266 nm) of CH3CHI2 in O2/N2 mixtures, mainly at 500 Torr pressure. The kinetics of CH3CHOO removal were monitored by UV absorption at 368 nm as a function of [H2O]. Taking account of the relative cross-sections of the conformers at this wavelength ((*E*-)/(Z-) ≈ 3), and their relative formation (*Z-*/*E-* ≈ 3), *E*- and *Z*- CH3CHOO are expected to make comparable contributions to the absorption signal. Accordingly, the observed kinetics could be interpreted in terms of a combination of fast and slow decays (attributed to *E*- and *Z*-CH3CHOO, respectively). The values of *k*1*(E-*) and *k*2*(E-*) tabulated above were extracted from the pseudo-first order decay constants for the fast component and the concentrations of [H2O] and [(H2O)2], with reaction (1) dominating at low relative humidity and reaction (2) at high relative humidity. The results were consistent with a very strong negative temperature dependence of reaction (2) over the studied range (*E*a = -50.9 ± 2.8 kJ mol-1), but an insignificant temperature dependence of reaction (1). Analysis of the slow component resulted in a value of *k*1*(Z-*) ≈ 2.4 × 10-16 cm3 molecule-1 s-1 across the studied temperature range. However, this was reported to be subject to significant uncertainty, and consistent with the upper limit of *k*1*(Z-*) < 2 × 10-16 cm3 molecule-1 s-1 reported by Sheps et al. (2014).
4. CH3CHOO prepared by the 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. Propane was also present to scavenge HO radicals. The effect of [H2O] on yield of H2SO4 allowed determination of rate coefficient ratio *k*(CH3CHOO + H2O)/*k*(CH3CHOO + SO2) = (8.8 ± 0.4)  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 *Z-* and *E-* conformers of different reactivity, which gave an improved fit to the [H2SO4] data. Assuming that *Z-*CH3CHOO has negligible reactivity with H2O compared to the *E-* conformer, as indicated by theoretical calculations (e.g. Ryzhkov and Ariya, 2004; Kuwata et al., 2010), their analysis gave *k*1*(E-*)(CH3CHOO + H2O)/*k(E-*)(CH3CHOO + SO2) = 1.4  10-4. The tabulated value uses *k*(*E*-)(CH3CHOO + SO2) = 1.4 10-10 cm3 molecule s-1 (IUPAC, current recommendation).
5. The removal of SO2 in the presence of but-2-ene/ozone systems was measured as a function of humidity in EUPHORE simulation chamber, under atmospheric boundary layer conditions. Cyclohexane was also present to scavenge HO radicals. 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 *k*1*(E-*)(CH3CHOO + H2O)/*k(E-*)(CH3CHOO + SO2) = (3.5 ± 3.1)  10-4. The cited value uses *k*(*E*-)(CH3CHOO + SO2) = 1.4 10-10 cm3molecule s-1 (IUPAC, current recommendation).

##### Preferred Values

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | **T/K** |
|  |  |  |
| *k*1(*Z*-) /cm3 molecule-1 s-1 | < 2  10-16 | 298 |
| *k*1(*E*-) /cm3 molecule-1 s-1 | 1.3  10-14 | 298 |
| *k*2(*E*-) /cm3 molecule-1 s-1 | 4.4  10-11 | 298 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  log *k*1(*E*-) | ± 0.3 | 298 |
|  log *k*2(*E*-) | ± 0.5 | 298 |

1. *Comments on Preferred Values*

The results of the direct studies of conformer-specific kinetics show that the *Z*-conformer is substantially less reactive than the *E*- conformer. This is consistent with the theoretical calculations of Anglada et.al. (2011), which predicted a lower reaction barrier for the *E-* form. The relative rate constants for the *E-* conformer reaction with H2O relative to SO2 were determined in two studies for CH3CHOO produced by ozonolysis of *cis*- and/or *trans*-2-butene at 1 bar pressure. The results are consistent with the direct studies at both low pressure (4 to 20 Torr) and high pressure (500 Torr), where CH3CHOO was produced from the reaction of CH3CHI with O2. Overall the results for *k*1(*E*-) 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*1(*Z*-) is that determined in the study of Sheps et al. (2014), which was based on a well-defined absence of [H2O] dependence of *k*1(*Z*-). The preferred values for *k*1(*E*-) and *k*2(*E*-) at 298 K are adopted from the direct UVA study of Lin et al. (2016), with that for *k*2(*E*-) being the only reported laboratory determination. However, the preferred value for *k*1(*E*-) is also consistent with those reported in the direct PIMS and UVA studies of Taatjes et al. (2013) and Sheps et al. (2014) (which are encompassed by the assigned uncertainty range), and comparable to the mean of the three direct determinations. Lin et al. (2016) also reported a very strong negative temperature dependence for *k*2(*E*-), based on measurements over a 40 K temperature range. Although this is in qualitative agreement with theoretical calculations (e.g. Vereecken et al., 2017), the value of the temperature coefficient is substantially higher than predicted. At present, we make no recommendation for the temperature dependence, and await the results of confirmatory studies.

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