IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_13

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

CH_3CHOO (*Z*- and *E*-) + M → products

Rate coefficient data

k/ s^{-1}	P/mbar	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients				
$k_{(Z\text{-})}$, $k_{(E\text{-})} < 250$	5.3	298	Taatjes et al., 2013	PLP-PIMS (a)
$k_{(Z\text{-})} < 160 \pm 25$	6.7-27	298	Sheps et al., 2014	CE-UVA (b)
$k_{(E\text{-})} < 240$	6.7-27	298		
$3 < k_{(Z\text{-})} < 30$	133	293	Novelli et al., 2014	LIF (HO product) (c)
$k_{(Z\text{-})}$, $k_{(E\text{-})} < 150$	2.7 (He)	295	Howes et al., 2018	PLP-PIMS (d)
$k_{(Z\text{-})} = (182 \pm 66)$	33-133	298	Zhou et al., 2019	PLP-LIF (HO product) (e)
$k_{(Z\text{-})} = (67 \pm 15)$	400	278	Li et al., 2020	PLP-UVA (f)
$k_{(Z\text{-})} = (146 \pm 31)$	400	298		
$k_{(Z\text{-})} = (288 \pm 81)$	400	318		
Relative Rate Coefficients				
$76\ ^{+150}_{-50}$	1000*	298*	Fenske et al., 2000	(g)
$k_{(Z\text{-})} = 86 \pm 13$	1000*	293	Berndt et al., 2014	(h)
$k_{(E\text{-})} = 38 \pm 24$				
$k_{(Z\text{-})} = 310 \pm 290$	1000*	296-302	Newland et al., 2015	(i)

Comments

(a) CH_3CHOO was produced by the reaction of $CH_3CHI + O_2$. CH_3CHI was generated by 248-nm laser photolysis of 1,1-diiodoethane, CH_3CHI_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. The upper limit for k is assumed to be represented by the decay in the absence of added reagents to the gas mixtures, and was approximately the same for both conformers.

(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 dependences, allowing conformer-specific rate coefficients to be determined. The pseudo-first order decay plots in the absence of added H_2O gave the cited upper limit values of $k_{(Z\text{-})}$ and $k_{(E\text{-})}$ for *Z*- and *E*-CH_3CHOO.

(c) Observation of the time dependence of HO formation and removal (LIF) during the ozonolysis of propene or *cis*-but-2-ene in flow-tube experiments at 100 Torr pressure. k was calculated by assuming that the observed formation of HO, over timescales of up to about 30 ms, is due to the thermal decomposition of *Z*-CH_3CHOO. The analysis required simulations using a detailed chemical

mechanism which also took account of HO removal reactions, primarily reaction with the precursor alkene.

(d) CH_3CHOO produced from 248 nm laser photolysis of CH_3CHI_2 in the presence of O_2, at 295 K at 2 Torr (He). 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. (2013) and Sheps et al. (2014) suggests that the *Z*- conformer is dominant. The reported upper limit for *k* was expected to include losses due to wall removal and self-reaction.

(e) CH_3CHOO produced from 248 nm laser photolysis of CH_3CHI_2 in the presence of O_2, at 298 K at pressures in the range 10-100 Torr (Ar). The decay kinetics of *Z*-CH_3CHOO ($k_{(Z-)}$) 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*-CH_3CHOO, with [HO] controlled by its rapid removal in the system (e.g. via reaction with CH_3CHI_2). Corrections for other loss processes for *Z*-CH_3CHOO under the experimental conditions (e.g. reaction with I atoms) were also made. The value of $k_{(Z-)}$ was reported to be insensitive to variation of pressure above 25 Torr, but was observed to decrease at lower pressure with a value of about 70 s^{-1} determined at 10 Torr.

(f) CH_3CHOO produced from 248 nm laser photolysis of CH_3CHI_2 in the presence of 10 Torr O_2, at 298 K. Measurements were made at pressures in the range 100-700 Torr (balance N_2 and H_2O). H_2O was present at concentrations of about 2×10^{17} molecule cm^{-3} or higher to remove *E*-CH_3CHOO via its rapid reactions with H_2O and (H_2O). *Z*-CH_3CHOO was monitored at 340 nm, and the observed decay constant, k_{obs}, was obtained as a function of the initial concentration, $[Z\text{-}CH_3CHOO]_0$. Values of $k_{(Z-)}$ were determined from the intercepts of k_{obs} vs. $[Z\text{-}CH_3CHOO]_0$ plots, following correction for the slow reaction of *Z*-CH_3CHOO with H_2O. Most experiments were carried out at 300 Torr total pressure, leading to the reported rate coefficients tabulated above. A weak dependence of $k_{(Z-)}$ on pressure was observed over the range 100-700 Torr at 298 K.

(g) Reaction studied in an atmospheric pressure flow-tube at room temperature, with CH_3CHOO produced from the ozonolysis of *trans*-but-2-ene. Excess acetaldehyde was added to the reaction mixture to allow thermalised CH_3CHOO to be converted to the corresponding secondary ozonide (SOZ). The SOZ was detected using FTIR. Numerical analysis of the observed SOZ formation at various time points along the tube allowed determination of $k/k(CH_3CHOO + \text{acetaldehyde})$ and an estimate of $k(CH_3CHOO + \text{acetaldehyde}) = 1.0 \times 10^{-12}$ cm^3molecule $^{-1}s^{-1}$; allowing the tabulated value of *k* to be reported. The *E*- and *Z*- conformers could not be resolved by the method, so that the reported parameters are bulk observations for their combined population.

(h) *Z*- and *E*-CH_3CHOO prepared by the O_3 + *trans*-2-butene reaction in the presence of SO_2 in an atmospheric pressure flow system, equipped with CIMS for detection of H_2SO_4, using NO_3^- as the reagent ion. Experiments performed as a function of [SO_2] allowed decomposition rates to be determined relative to the rate of reaction with SO_2. An expanded analysis using a two sCI model yielded the rate coefficient ratios $k_{(E-)}/k(E\text{-}CH_3CHOO + SO_2) = (2.7 \pm 1.7) \times 10^{11}$ molecule cm^{-3} and $k_{(Z-)}/k(Z\text{-}CH_3CHOO + SO_2) = (3.3 \pm 0.5) \times 10^{12}$ molecule cm^{-3}, where the former value also required correction for a pseudo-first order contribution to *E*-CH_3CHOO removal resulting from reaction with H_2O. The values of $k_{(E-)}$ and $k_{(Z-)}$ are placed on an absolute basis using $k(E\text{-}CH_3CHOO + SO_2) = 1.4 \times 10^{-10}$ cm^{-3} $molecule^{-1}$ s^{-1} and $k(Z\text{-}CH_3CHOO + SO_2) = 2.6 \times 10^{-11}$ cm^{-3} $molecule^{-1}$ s^{-1} (IUPAC current recommendations).

(i) The removal of SO_2 in the presence of O_3 and either *cis*- or *trans*-but-2-ene was studied as a function of humidity, under atmospheric conditions in the EUPHORE chamber. The relative rate constants for the major competitive reactions, $k_{(Z-)}/k(Z\text{-}CH_3CHOO + SO_2) = (1.2 \pm 1.1) \times 10^{13}$ molecule cm^{-3} and $k(E\text{-}CH_3CHOO + H_2O)/k(E\text{-}CH_3CHOO + SO_2) = (3.5 \pm 3.1) \times 10^{-4}$, were determined from experiments performed over a range of [H_2O], allowing explicitly for the differing reactivity for the *Z*- and *E*- conformers. The decomposition rate constant, $k_{(Z-)}$, is placed on an absolute basis here using $k(Z\text{-}CH_3CHOO + SO_2) = 2.6 \times 10^{-11}$ cm^{-3} $molecule^{-1}$ s^{-1} (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
$k_{(Z\text{-})}$/ s^{-1}	150	298
$k_{(Z\text{-})}$/ s^{-1}	7.4×10^{6} exp(-3220/T)	275-320
$k_{(E\text{-})}$/ s^{-1}	60	298
Reliability		
$\Delta \log k_{(Z\text{-})}$	± 0.3	298
$\Delta \log k_{(E\text{-})}$	± 0.5	298
$\Delta (E_{(Z\text{-})}/R)$	± 700	275-320

Comments on Preferred Values

Measurements of the unimolecular decay rate coefficient for thermal decomposition of CH_3CHOO have been reported in five direct studies, using pulsed photolysis of CH_3CHI_2 as the source, and detection methods which provided a distinction between the *Z*- an *E*- conformers in four of these studies. The studies of Taatjes et al. (2013), Sheps et al. (2013) and Howes et al. (2018), performed at pressures below 30 mbar, provide only upper limit estimates because the observed decay rates are reported to include contributions from other processes, e.g. diffusive loss from the analyzing probe area, wall loss or self-reaction. The more recent studies of Zhou et al. (2019) and Li et al. (2020), performed at higher pressures over the range 33-930 mbar, provide firm measurements of $k_{(Z\text{-})}$, and suggest that the high-pressure limit is reached over this range. However, correction for a number of other loss processes for *Z*-CH_3CHOO were required, introducing a level of uncertainty into the determinations. It is also noted that the measurements of Zhou et al. (2019), using HO as a marker for *Z*-CH_3CHOO (see comment (e)), may also be complicated by other sources of HO in the system, e.g. from decomposition of the vinoxy radical co-product, which has been observed at pressures below about 270 mbar (see data sheet RO_22). The preferred values of $k_{(Z\text{-})}$ are therefore based on those reported as a function of temperature by Li et al. (2020), but with the assigned uncertainty at 298 K encompassing the determination of Zhou et al. (2019).

The relative rate determinations from ozonolysis of *cis*- and/or *trans*-but-2-ene, using reaction of CH_3CHOO with SO_2 as a reference, provide approximate indirect estimates of $k_{(Z\text{-})}$ and $k_{(E\text{-})}$, although the results are all consistent within the reported error limits. The preferred value of $k_{(E\text{-})}$ is based on that reported by Berndt et al. (2014), following correction to 298 K using the temperature dependence of the likely dominant decomposition reaction (see below) calculated by Vereecken et al. (2017). It is noted value of $k_{(Z\text{-})}$ reported by Berndt et al. (2014) lies well within the uncertainty bounds on preferred value at 293 K. Further studies are required to allow the rates of unimolecular decomposition to be defined with more certainty.

Theoretical studies predict the dominant decomposition reactions to be 1,4-H atom migration to a vinyl hydroperoxide intermediate for *Z*-CH_3CHOO, and 1,3-cyclisation to a dioxirane intermediate for *E*-CH_3CHOO; and the 298 K rates calculated by Vereecken et al. (2017), $k_{(Z\text{-})}$ = 136 and $k_{(E\text{-})}$ = 53, agree well with the preferred values. Although decomposition of *E*-CH_3CHOO is unlikely to compete with removal by bimolecular reactions under atmospheric conditions, the 1,4-H atom migration of *Z*-CH_3CHOO is estimated to be its major fate. The resultant vinyl hydroperoxide intermediate decomposes to produce HO and the vinoxy radical, and this mechanism more generally is believed to be the most important route to HO radical formation from the ozonolysis of alkenes.

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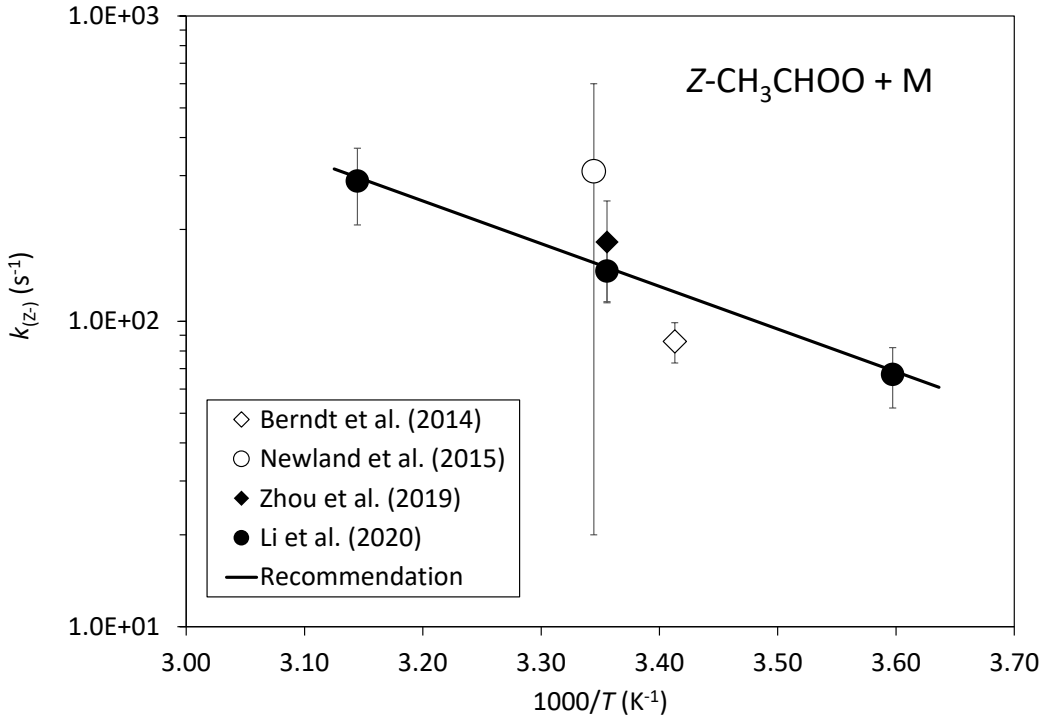

Arrhenius plot of $k_{(Z\text{-})}$. Direct determinations are shown as filled points; relative rate determinations are shown as open points. The displayed errors are the experimental limits cited by the authors (but do not include uncertainty in the reference reaction for the relative rate studies). The line is the IUPAC recommendation, $k_{(Z\text{-})} = 7.4 \times 10^6 \exp(-3220/T)$ s^{-1}.