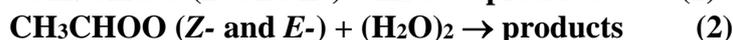
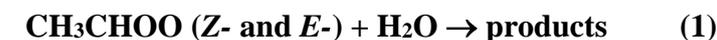


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_16

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_{1(\text{Z-})} < 4 \times 10^{-15}$	298	Taatjes et al., 2013	PLP-PIMS (a)
$k_{1(\text{E-})} = (1.0 \pm 0.4) \times 10^{-14}$	298		
$k_{1(\text{Z-})} < 2 \times 10^{-16}$	293	Sheps et al., 2014	CE-UVAS (b)
$k_{1(\text{E-})} = (2.4 \pm 0.4) \times 10^{-14}$	293		
$k_{1(\text{E-})} = (1.31 \pm 0.26) \times 10^{-14}$	298	Lin et al., 2016	PLP-UVAS (c)
$k_{1(\text{E-})} = 1.11 \times 10^{-14} \exp[(50 \pm 644)/T]$	288-328		
$k_{2(\text{E-})} = (4.40 \pm 0.29) \times 10^{-11}$	298		
$k_{2(\text{E-})} = 5.21 \times 10^{-20} \exp[(6125 \pm 332)/T]$	288-328		
<i>Relative Rate Coefficients</i>			
$k_{1(\text{E-})} = (2.0 \pm 0.6) \times 10^{-14}$	293	Berndt et al., 2014	FT/CI-API-TOF MS (d)
$k_{1(\text{E-})} = (4.9 \pm 4.3) \times 10^{-14}$	296-302	Newland et al., 2015	RR-FTIR/UVA/UV-F (e)

Comments

- (a) CH_3CHOO was produced by the reaction of $\text{CH}_3\text{CHI} + \text{O}_2$. CH_3CHI was generated by 248-nm laser photolysis of 1,1-diiodoethane, $\text{CH}_3\text{CH}_2\text{I}_2$, at 298 K and 4 torr, in a large excess of O_2 . The reacting mixture was monitored by tunable synchrotron photoionization mass spectrometry, which allowed characterisation of the PIMS. Both conformers of CH_3CHOO (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 CH_3CHOO in the presence of excess known concentrations of H_2O up to 2.4×10^{16} molecule cm^{-3} , was used to determine the rate constants. It was demonstrated that decay of Z- CH_3CHOO was independent of the presence of H_2O at this concentration, allowing only the upper limit of $k_{1(\text{Z-})}$ to be determined. On the other hand decay of E- CH_3CHOO increased monotonically with $[\text{H}_2\text{O}]$, allowing $k_{1(\text{E-})}$ to be determined with some confidence.
- (b) CH_3CHOO prepared by PLP (266 nm) of CH_3CHI_2 in O_2/Ar mixtures at 5 - 20 Torr pressure. The UV absorption spectrum of CH_3CHOO in the region 300 – 450 nm, corresponding to the $\tilde{\text{B}}(1\text{A}') \leftarrow \tilde{\text{X}}(1\text{A}')$ electronic transition was determined in this work, using time-resolved cavity enhanced absorption spectroscopy. Absorption features due to Z- and E- conformers of CH_3CHOO could be distinguished by their differing reactivities - reflected in characteristic time-dependences. IO (formed from secondary chemistry) was also detected. CH_3CHOO 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- CH_3CHOO , $160 \pm 25 \text{ s}^{-1}$, did not change as a function of $[\text{H}_2\text{O}]$, giving

the cited upper limit of $k_{1(Z-)}$. For E -CH₃CHO, the first-order decay rate increased linearly with [H₂O], and the cited value for $k_{1(E-)}$ was obtained by fitting to linear plots.

- (c) CH₃CHO prepared by PLP (266 nm) of CH₃CHI₂ in O₂/N₂ mixtures, mainly at 500 Torr pressure. The kinetics of CH₃CHO 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 ($\sigma_{(E-)} / \sigma_{(Z-)} \approx 3$), and their relative formation ($Z-/E- \approx 3$), E - and Z - CH₃CHO 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 -CH₃CHO, 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 ($E_a = -50.9 \pm 2.8$ kJ mol⁻¹), but an insignificant temperature dependence of reaction (1). Analysis of the slow component resulted in a value of $k_{1(Z-)} \approx 2.4 \times 10^{-16}$ 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 $k_{1(Z-)} < 2 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ reported by Sheps et al. (2014).
- (d) CH₃CHO 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 $k(\text{CH}_3\text{CHO} + \text{H}_2\text{O})/k(\text{CH}_3\text{CHO} + \text{SO}_2) = (8.8 \pm 0.4) \times 10^{-5}$ 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 Z - and E - conformers of different reactivity, which gave an improved fit to the [H₂SO₄] data. Assuming that Z -CH₃CHO 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 $k_{1(E-)}(\text{CH}_3\text{CHO} + \text{H}_2\text{O})/k_{(E-)}(\text{CH}_3\text{CHO} + \text{SO}_2) = 1.4 \times 10^{-4}$. The tabulated value uses $k_{(E-)}(\text{CH}_3\text{CHO} + \text{SO}_2) = 1.4 \times 10^{-10}$ cm³ molecule s⁻¹ (IUPAC, current recommendation).
- (e) 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 CH₃CHO 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 $k_{1(E-)}(\text{CH}_3\text{CHO} + \text{H}_2\text{O})/k_{(E-)}(\text{CH}_3\text{CHO} + \text{SO}_2) = (3.5 \pm 3.1) \times 10^{-4}$. The cited value uses $k_{(E-)}(\text{CH}_3\text{CHO} + \text{SO}_2) = 1.4 \times 10^{-10}$ cm³ molecule s⁻¹ (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
$k_{1(Z-)} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$< 2 \times 10^{-16}$	298
$k_{1(E-)} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.3×10^{-14}	298
$k_{2(E-)} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	4.4×10^{-11}	298
<i>Reliability</i>		
$\Delta \log k_{1(E-)}$	± 0.3	298
$\Delta \log k_{2(E-)}$	± 0.5	298

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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