

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_1

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CH₂OO + 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>			
$(3.9 \pm 0.7) \times 10^{-11}$	298	Welz et al., 2012	PLP-PIMS(a)
$(4.1 \pm 0.3) \times 10^{-11}$	295	Sheps, 2013	PLP-UVA (b)
$(3.42 \pm 0.42) \times 10^{-11}$	295	Stone et al., 2014	PLP-LIF/PIMS (c)
$(3.80 \pm 0.04) \times 10^{-11}$	293	Chhantyal-Pun et al., 2015	PLP-CRDS (d)
$(3.64 \pm 0.10) \times 10^{-11}$ (51 Torr)	295	Liu et al., 2014	PLP-LIF(e)
$(3.37 \pm 0.25) \times 10^{-11}$ (100 Torr)			
$(3.43 \pm 0.09) \times 10^{-11}$ (152 Torr)			
$(3.44 \pm 0.15) \times 10^{-11}$ (200 Torr)			
$(3.52 \pm 0.11) \times 10^{-11}$ (30.1 Torr)	298	Huang et al., 2015	PLP-UVA (f)
$(3.57 \pm 0.02) \times 10^{-11}$ (100.2 Torr)			
$(3.70 \pm 0.09) \times 10^{-11}$ (199.7 Torr)			
$(3.30 \pm 0.15) \times 10^{-11}$ (755.6 Torr)			
$(3.3 \pm 0.9) \times 10^{-11}$	295	Berndt et al., 2017	Free-Jet FR-CIMS (g)
$(3.74 \pm 0.43) \times 10^{-11}$	295	Howes et al., 2018	PLP-PIMS (h)
$(3.87 \pm 0.45) \times 10^{-11}$	295		PLP-UVA (h)
$(3.6 \pm 0.1) \times 10^{-11}$	295	Qiu and Tonokura, 2019	PLP-IR (i)

Comments

- (a) CH₂OO was produced by the reaction of CH₂I + O₂. CH₂I was generated by 248 nm laser photolysis of diiodomethane, CH₂I₂, at 298 K and 4 torr total pressure in a large excess of O₂. The reacting mixture was monitored by tunable synchrotron photoionization mass spectrometry, which allowed characterisation of the PIMS for CH₂OO and its reaction products over the region 9.5 – 11.5 eV, and time-resolved direct detection of CH₂OO at $m/z = 46$ amu. The first order decay CH₂OO in the presence of excess known concentrations of SO₂ was used to determine the rate constants. The uncertainty limits are 95 %, based on unweighted linear fit of [SO₂] dependence of decay lifetimes.
- (b) CH₂OO prepared by PLP (266 nm) of CH₂I₂ in O₂/Ar mixtures at 5.1 Torr pressure. CH₂OO kinetics observed by time-resolved UV absorption in the $\tilde{B}(1A') \leftarrow \tilde{X}(1A')$ electronic spectrum in presence of excess SO₂.
- (c) Photolysis of CH₂I₂-O₂-N₂ mixtures. in the presence of excess SO₂, under pseudo-first-order conditions. Kinetics of CH₂OO + SO₂ reaction were followed by time-resolved monitoring of HCHO products by laser-induced fluorescence (LIF) spectroscopy (pressure range: 50 – 450 Torr), and also by direct detection of CH₂OO by photo-ionisation mass spectrometry (PIMS) at 1.5 Torr pressure. Rate coefficients for CH₂OO + SO₂ were independent of pressure between 1.5 - 450 Torr, and cited values of k are average values in this range. The uncertainty limits are 1 σ errors from fitting data.

- (d) Cavity ring-down spectroscopy was used to perform kinetic measurements at 293 K under low pressure (7 to 30 Torr) conditions, for reactions of CH₂OO generated by (248 nm) laser photolysis of CH₂I₂ in the presence of O₂. The cited k value for the CH₂OO + SO₂ reaction was determined from pseudo first order decay constants, obtained by fitting decay curves at different [SO₂], accounting for contribution from self-reaction of CH₂OO and unimolecular decay. k was independent of pressure up to 30 Torr. An upper limit for the unimolecular CH₂OO loss rate coefficient of $(11.6 \pm 8.0) \text{ s}^{-1}$ was deduced from the analysis. An SO₂ catalysed CH₂OO isomerization or intersystem crossing is proposed to occur with a rate coefficient of $(3.53 \pm 0.32) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (e) CH₂OO generated by 351nm laser flash photolysis of CH₂I/O₂ mixtures is accompanied by significant amounts of HO, observed by time resolved LIF. At least two different processes formed HO; a second, slower process appeared to be associated with the decay of CH₂OO. Using the HO signals as a proxy for the [CH₂OO] concentration in the presence of excess SO₂ the rate constant for the reaction of SO₂ with CH₂OO could be determined under pseudo first order conditions. k showed no pressure dependence over the range of 50–200 Torr, the average value was $(3.53 \pm 0.29) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (f) CH₂OO prepared by PLP (266 nm) of CH₂I₂ in O₂/N₂ mixtures at 30 - 755 Torr total pressure and 298 K. CH₂OO kinetics observed by time-resolved UV absorption spectrum in the $\tilde{\text{B}}(1\text{A}') \leftarrow \tilde{\text{X}}(1\text{A}')$ electronic transition in presence of excess SO₂. CH₂OO was monitored by UV absorption at 340 nm, corresponding to the maximum in the $\tilde{\text{B}}(1\text{A}') \leftarrow \tilde{\text{X}}(1\text{A}')$ electronic transition. A mean value of $k = (3.56 \pm 0.11) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, was reported, with no significant pressure dependence of k in the experimental pressure range.
- (g) CH₂OO (formaldehyde oxide) was produced by the O₃ + C₂H₄ reaction in air in a free-jet flow reactor at 1 bar and $295 \pm 2 \text{ K}$. CH₂OO was detected as CH₂OO-H⁺ using CI-API-TOF mass spectrometry. k was determined from the relative suppression of the steady state concentration of the protonated species as a function of [SO₂].
- (h) CH₂OO generated by laser flash photolysis (LF) of CH₂I₂/O₂ and its concentration monitored by photoionization mass spectrometry (PIMS). PIMS has been used to determine the rate coefficient for the reaction of CH₂OO with SO₂ at 295 K and 2 Torr (He). Additional LFP experiments were performed monitoring CH₂OO by time resolved broadband UV absorption spectroscopy (TRUVAS) at 295 K and 50 Torr (N₂). The rate coefficients determined at $295 \pm 2 \text{ K}$ in both experimental systems are in excellent agreement.
- (i) CH₂OO was produced by the 266 nm laser photolysis of CH₂I₂-O₂-N₂ mixtures at $295 \pm 3 \text{ K}$ and 7.7 Torr. The time-resolved decay kinetics of CH₂OO were followed by mid-IR continuous-wave quantum cascade laser spectroscopy in the ν_4 band at 1274 cm^{-1} , under pseudo-first order conditions in the presence of excess [SO₂]. The tabulated value of k was determined from the dependence of the first-order decay constant on [SO₂].

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	3.7×10^{-11}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.05	298

Comments on Preferred Values

The efficient and rapid production of CH₂OO in the photolysis of CH₂I₂/O₂ mixtures has been shown to be due to the reaction of the CH₂I photofragment with O₂. The results from several laboratories using different spectroscopic techniques, including use of HO-LIF as a spectroscopic marker (Liu et al., 2014), to detect and make time-resolved measurements of decay of [CH₂OO], or use of LIF (Stone et al., 2014) to follow formation of product HCHO, are in good agreement. The rate constants for CH₂OO reaction with SO₂ show no significant pressure dependence over the range 3 to 1000 mbar (Huang et al., 2015). The rate coefficient is much larger than was deduced from earlier relative rate studies (e.g. see Johnson and Marston, 2008). Although the temperature dependence has not been investigated, it is likely to be close to zero. The recommended temperature and pressure independent value of *k* is an unweighted mean of the values reported by Welz et al. (2012), Sheps (2013), Liu et al. (2014), Stone et al. (2014), Chhantyal-Pun et al. (2015) (excluding the low [SO₂] results), Huang et al. (2015), Howes et al. (2018) and Qiu and Tonokura (2019).

All these studies utilized the same photochemical source of CH₂OO. This source provides a high yield of stabilised CH₂OO and has been well characterized (Welz et al., 2012; Stone et al., 2013; Chhantyal-Pun et al., 2015). The less direct determination of Berndt et al. (2017), using the ethene + O₃ reaction as the CH₂OO source, and reported relative rate studies (Berndt et al., 2014; Newland et al., 2015), all yield results for the kinetics that are consistent with the direct laser photolysis measurements of *k*. Thus, the recommendation is valid for application in atmospheric modelling of CH₂OO reactions produced in ozone + alkene reactions.

Cox and Penkett (1972) proposed that oxidation of SO₂ to H₂SO₄ aerosols in the presence of ozone + alkene, occurred as a result of its reaction with carbonyl oxide (Criegee) intermediates to form SO₃ molecules, which then reacted with water to produce H₂SO₄ aerosol particles. Many experimental studies of ozone + alkene reactions have subsequently confirmed the importance of this process, and it is generally assumed that the CH₂OO + SO₂ reaction predominantly forms HCHO + SO₃. The theoretical investigation of Vereecken et al. (2012) re-examined the potential energy surface of the reaction, explicitly examining the open shell biradical structures than can be formed following barrierless formation of a chemically-activated secondary ozonide in the initial CH₂OO + SO₂ encounter. The subsequent mechanism involved rearrangement to a singlet biradical intermediate, HC(O)OS(O)O. Under atmospheric conditions, this was calculated to dissociate mainly to form HCHO + SO₃ (68 %), this being the dissociation channel with the lowest barrier. Alternative channels involving formation of SO₂ and a bis-oxy diradical, CH₂(O)O (17 %), and H-elimination to form the very stable formylsulfonic acid, HC(=O)OS(=O)OH (15 %), were also calculated for atmospheric conditions, using RRKM methods. The results are consistent with reported product observations, i.e. formation of HCHO and/or SO₃, (Welz et al., 2012; Stone et al., 2014), regeneration of SO₂ with an oxygen exchange between the sCI and SO₂ moieties (Hatakeyama et al., 1984, 1986), and kinetic anomalies at high [SO₂], (Chhantyal-Pun et al., 2015). Until quantitative experimental product channel data become available, we recommend that the reaction predominantly forms HCHO and SO₃.

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