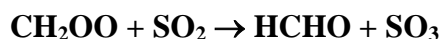


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_1

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This datasheet last evaluated: January 2016; last change in preferred values: January 2016



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)
$(3.80 \pm 0.04) \times 10^{-11}$	295	Chhantyal-Pun et al., 2015	PLP-CRDS (d)
$(3.64 \pm 0.10) \times 10^{-11}$ (51 Torr)	295	Lui 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)			

Comments

- CH₂OO (formaldehyde oxide) was produced by the reaction of CH₂I + O₂. CH₂I was generated by 248-nm laser photolysis of diiodomethane, CH₂I₂, at 293 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, 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.
- 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 spectrum at in the $\tilde{\text{B}}(1\text{A}') \leftarrow \tilde{\text{X}}(1\text{A}')$ electronic transition in presence of excess SO₂.
- 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 1σ errors from fitting data.
- 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 molecule generated by 351-nm laser flash photolysis of CH₂I/O₂ mixtures is accompanied by significant amounts of OH, observed by time resolved LIF. At least two different processes formed OH; a second, slower process appeared to be associated with the decay of CH₂OO. Using the OH 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 at 30 - 755 Torr total pressure and 298 K. CH₂OO kinetics observed by time-resolved UV absorption spectrum at in the $\tilde{B}(1A') \leftarrow \tilde{X}(1A')$ electronic transition in presence of excess SO₂. CH₂COO was monitored by UV absorption in the region 340 nm, corresponding to the maximum in the $\tilde{B}(1A') \leftarrow \tilde{X}(1A')$ electronic transition. The 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.

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 recent direct photoionization mass spectrometric detection of formaldehyde oxide (CH₂OO) as a product of the photolysis of CH₂I₂ in the presence of O₂ provides a novel source of Criegee intermediates. The efficient and rapid production of CH₂OO has been shown to be due to the reaction of CH₂I photofragment with O₂. This has enabled direct laboratory determinations of CH₂OO kinetics, including the reaction: CH₂OO + SO₂ → CH₂O + SO₃ (Welz et al., 2012). The results from several laboratories using different spectroscopic techniques, including use of OH-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 appear to be accurately determined and show no significant pressure dependence over the range 3 to 1000 mbar, confirmed recently in the study of Huang et al (2015). The rate coefficient is much larger than was deduced from earlier *relative rate* studies (see IUPAC 2002) and is close to the collision rate for simple bimolecular radical-molecule reactions. 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 a simple 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); and Huang et al (2015).

All these studies utilized the same photochemical source of CH₂OO (formaldehyde oxide). This source provides a high yield of stabilised CH₂OO and has been well characterized (see Welz, et al.(2012), Stone, et al.(2013), Chhantyal-Pun, et al.(2015)). Two recent relative rate studies of SO₂ oxidation in ethene + O₃ reaction (Berndt et al., 2014; Newland et al., 2015) produced results for kinetics consistent with the direct measurements of $k(\text{CH}_2\text{OO} + \text{SO}_2)$. Thus the k values are valid for application in atmospheric modeling 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 SO₃ is the predominant product of the CH₂OO + SO₂ reaction. A recent theoretical investigation of the reaction mechanism by Vereecken et al. (2012) re-examined the PES, explicitly examining the open shell bi-radical structures than can be formed following barrier-less formation of a cyclic ozonide in the initial CH₂OO + SO₂ encounter. The subsequent route involved a singlet biradical intermediate, $\cdot\text{OCH}_2\text{OS}(\text{O})\text{O}$, from which the lowest barrier channel is dissociation to SO₃ + carbonyl. Alternate channels involving SO₂-catalyzed isomerization to a bis-oxy diradical form of CH₂(O)O \cdot and H-elimination to form a very stable formylsulfinic acid: HC(=O)OS(=O)OH were investigated and the branching ratios for specified conditions were calculated by RRKM methods. The results are consistent with the product observations i.e. formation of a carbonyl compound + SO₃, (Welz et al., 2012), regeneration of SO₂ with an oxygen exchange between the stabilised Criegee and SO₂ moieties (Hatakeyama, et al., 1984, 1986), and kinetic anomalies at high [SO₂], (Chhantyal-Pun, et al., 2015). Until experimental data become available we assume the products to be SO₃ and HCHO.

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