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

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$CH_2OO + SO_2 \rightarrow HCHO + SO_3$ (1)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp /K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.9\pm0.7) \times 10^{-11}$	298	Welz et al., 2012	PLP-PIMS(a)
$(4.1\pm0.3) \times 10^{-11}$	295	Sheps, 2013	PLP-UVA (b)
$(3.42\pm0.42) \times 10^{-11}$	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) $(3.37 \pm 0.25) \times 10^{-11}$ (100 Torr) $(3.43 \pm 0.09) \times 10^{-11}$ (152 Torr) $(3.44 \pm 0.15) \times 10^{-11}$ (200 Torr)	295	Lui et al., 2014	PLP-LIF(e)

Comments

(a) CH_2OO (formaldehyde oxide) was produced by the reaction of $CH_2I + O_2$. CH_2I was generated by 248-nm laser photolysis of diiodomethane, CH_2I_2, at 293 K and 4 torr total pressure in a large excess of O_2. The reacting mixture was monitored by tunable synchrotron photoionization mass spectrometry, which allowed characterisation of the PIMS for CH_2OO and its reaction products over the region 9.5 – 11.5 eV, Time-resolved direct detection of CH_2OO at m/z = 46 amu. The first order decay CH_2OO in the presence of excess known concentrations of SO_2 was used to determine the rate constants. The uncertainty limits are 95% , based on unweighted linear fit of $[SO_2]$ dependence of decay lifetimes.

(b) CH_2OO prepared by PLP (266 nm) of CH_2I_2 in O_2/Ar mixtures at 5.1 Torr pressure. CH_2OO kinetics observed by time-resolved UV absorption spectrum at in the $\tilde{B}$ (1A′) ← $\tilde{X}$(1A′) electronic transition in presence of excess SO_2.

(c) Photolysis of CH_2I_2-O_2-N_2 mixtures. in the presence of excess SO_2, under pseudo-first-order conditions. Kinetics of $CH_2OO + SO_2$ 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 CH_2OO by photo-ionisation mass

spectrometry (PIMS) at 1.5 Torr pressure. Rate coefficients for CH_2OO + SO_2 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.

(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 CH_2OO generated by (248-nm) laser photolysis of CH_2I_2 in the presence of O_2. The cited *k* value for the CH_2OO + SO_2 reaction was determined from pseudo first order decay constants, obtained by fitting decay curves at different [SO_2], accounting for contribution from self-reaction of CH_2OO and unimolecular decay. *k* was independent of pressure up to 30 Torr. An upper limit for the unimolecular CH_2OO loss rate coefficient of (11.6 ± 8.0) s^{-1} was deduced from the analysis. An SO_2 catalysed CH_2OO isomerization or intersystem crossing is proposed to occur with a rate coefficient of (3.53 ± 0.32) x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.

(f) CH_2OO molecule generated by 351-nm laser flash photolysis of CH_2I/O_2 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 CH_2OO. Using the OH signals as a proxy for the [CH_2OO] concentration in the presence of excess SO_2 the rate constant for the reaction of SO_2 with CH_2OO 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 ± 0.29) x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 $molecule^{-1}$ s^{-1}	3.7 x 10^{-11}	298
Reliability		
Δ log *k*	0.1	298

Comments on Preferred Values

The recent direct photoionization mass spectrometric detection of formaldehyde oxide (CH_2OO) as a product of the photolysis of CH_2I_2 in the presence of O_2 provides a novel source of Criegee intermediates. The efficient and rapid production of CH_2OO has been shown to be due to the reaction of CH_2I photofragment with O_2. This has enabled direct laboratory determinations of CH_2OO kinetics, including the reaction: $CH_2OO + SO_2 \rightarrow CH_2O + SO_3$ (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 [CH_2OO], or use of LIF (Stone et al, 2014) to follow formation of product HCHO, are in good agreement. The rate constants for CH_2OO reaction with SO_2 appear to be accurately determined and show no significant pressure dependence over the range 3 to 1000 mbar. 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).

All these studies utilized the same photochemical source of CH_2OO (formaldehyde oxide). This source provides a high yield of stablised CH_2OO 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 SO_2 oxidation in ethene + O_3 reaction (Berndt et al., 2014; Newland et al., 2015) produced results for kinetics consistent with the direct measurements of $k(CH_2OO + SO_2)$. Thus the *k* values are valid for application in atmospheric modeling of CH_2OO reactions produced in ozone + alkene reactions.

Cox and Penkett (1972) proposed that oxidation of SO_2 to H_2SO_4 aerosols in the presence of ozone + alkene, occurred as a result of its reaction with carbonyl oxide (Criegee) intermediates to form SO_3 molecules, which then reacted with water to produce H_2SO_4 aerosol particles. Many experimental studies of ozone + alkene reactions have subsequently confirmed the importance of this process, and it is generally assumed that SO_3 is the predominant product of the $CH_2OO + SO_2$ 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 $CH_2OO + SO_2$ encounter. The subsequent route involved a singlet biradical intermediate, $^{\cdot}OCH_2OS(O)O$, from which the lowest barrier channel is dissociation to SO_3 + carbonyl. Alternate channels involving SO_2-catalyzed isomerization to a bis-oxy diradical form of $CH_2(O^{\cdot})O^{\cdot}$ 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 + SO_3, (Welz et al., 2012), regeneration of SO_2 with an oxygen exchange between the stablised Criegee and SO_2 moieties (Hatakeyama, et al., 1984, 1986), and kinetic anomalies at high $[SO_2]$, (Chhantyal-Pun, et al., 2015). Until experimental data become available we assume the products to be SO_3 and HCHO.

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