**IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_1**

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**CH2OO + SO2 → products**

## Rate coefficient data

|  |  |  |  |
| --- | --- | --- | --- |
| *k*/cm3 molecule-1 s-1 | Temp./K | Reference | Technique/Comments |
| *Absolute Rate Coefficients* |  |  |  |
| (3.9 ± 0.7)  10-11 | 298 | Welz et al., 2012 | PLP-PIMS(a) |
| (4.1 ± 0.3)  10-11 | 295 | Sheps, 2013 | PLP-UVA (b) |
| (3.42 ± 0.42)  10-11 | 295 | Stone et al., 2014 | PLP-LIF/PIMS (c) |
| (3.80 ± 0.04)  10-11 | 293 | Chhantyal-Pun et al., 2015 | PLP-CRDS (d) |
| (3.64 ± 0.10)  10-11  (51 Torr) | 295 | Liu et al., 2014 | PLP-LIF(e) |
| (3.37 ± 0.25)  10-11  (100 Torr) |  |  |  |
| (3.43 ± 0.09)  10-11  (152 Torr) |  |  |  |
| (3.44 ± 0.15)  10-11  (200 Torr) |  |  |  |
| (3.52 ± 0.11)  10-11  (30.1 Torr) | 298 | Huang et al., 2015 | PLP-UVA (f) |
| (3.57 ± 0.02)  10-11  (100.2 Torr) |  |  |  |
| (3.70 ± 0.09)  10-11  (199.7 Torr) |  |  |  |
| (3.30 ± 0.15)  10-11  (755.6 Torr) |  |  |  |
| (3.3 ± 0.9)  10-11 | 295 | Berndt et al., 2017 | Free-Jet FR-CIMS (g) |
| (3.74 ± 0.43)  10-11 | 295 | Howes et al., 2018 | PLP-PIMS (h) |
| (3.87 ± 0.45)  10-11 | 295 |  | PLP-UVA (h) |
| (3.6 ± 0.1)  10-11 | 295 | Qiu and Tonokura, 2019 | PLP-IR (i) |

##### Comments

1. 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.
2. 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 B̃ (1A′) ← X̃(1A′) electronic spectrum in presence of excess SO2.
3. 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** errors from fitting data.
4. 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 ± 8.0) 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 ± 0.32)  10-11 cm3 molecule-1 s-1.
5. 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 ± 0.29)  10-11 cm3 molecule-1 s-1.
6. 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 B̃ (1A′) ← X̃(1A′) electronic transition in presence of excess SO2. CH2OO was monitored by UV absorption at 340 nm, corresponding to the maximum in the B̃ (1A′) ← X̃(1A′) electronic transition. A mean value of *k* = (3.56 ± 0.11)  10-11 cm3 molecule-1 s-1, was reported, with no significant pressure dependence of *k* in the experimental pressure range.
7. CH2OO (formaldehyde oxide) was produced by the O3 + C2H4 reaction in air in a free-jet flow reactor at 1 bar and 295 ± 2 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].
8. 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 ± 2 K in both experimental systems are in excellent agreement.
9. CH2OO was produced by the 266 nm laser photolysis of CH2I2-O2-N2 mixtures at 295 ± 3 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 ν4 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* /cm3 molecule-1 s-1 | 3.7  10-11 | 298 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  log *k* | ± 0.05 | 298 |

1. *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 formylsulfinic 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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