### IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet CGI\_12

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**CH2OO (+ M) → H2 + CO2 (1)**

**CO2 + 2H (2)**

**H + HOCO (3)**

**CO + H2O (4)**

**OH + HCO (5)**

**Rate coefficient data (k = k1 + k2 + k3 + k4 + k5)**

|  |  |  |  |
| --- | --- | --- | --- |
| *k*/ s-1 | Temp./K | Reference | Technique/Comments |
| ***Absolute Rate Coefficients*** |  |  |  |
|  |  |  |  |
| <500 | 298 | Weltz et al., 2012 | PLP-PIMS(a) |
| <100 | 298 |  |  |
| <73 | 298 | Tatjes et al., 2012 | PLP-PIMS(a) |
| <300 | 295 | Stone et al., 2014 | LIF (HCHO product)(b) |
| <120 | 295 | Lui.Sander, et al., 2014 | LIF (OH product)(c) |
| <155 ± 20 | 298 | Sheps et al., 2014 | CE-UVA(d) |
| <11.6 ± 8.0 | 295 | Chhantyal-Pun, et  al., 2015 | PLP-CRDS (e) |
| 0.1 (1 bar) | 298 | Stone et al 2016 | PLP-UVA (f) |
| 12483±3572 (200 mbar) | 650 |  | PLP-UVA |
| 3720±2344 (200 mbar) | 600 |  | PLP-UVA |
| 1130±35 (26 mbar) | 600 |  | LIF(OH v=1) |
| 2233±711 (200 mbar) | 550 |  | PLP-UVA |
| 1278±9.9 (200 mbar) | 525 |  | PLP-UVA |
| 440±5 (6.5 mbar) | 525 |  | LIF(OH v=0) |
| 973±389 (200 mbar) | 500 |  | PLP-UVA |
| 521±6 (200 mbar) | 475 - |  | PLP-UVA |
| 448±5 (200 mbar) | 450 - |  | PLP-UVA |
| ***Relative Rate Coefficients*** |  |  |  |
|  |  |  |  |
| <19.2±5 . | 297 | Ouyang et al., 2013 | (g) k/k(NO2)=6.4±1.7 x 1011 |
| 8.9 ±0.9 | 293 | Berndt et al., 2014 | (h) k/k(SO2)=2.6±0.32 x 1011 |
|  |  |  |  |

**Comments**

(a) CH2OO (formaldehyde oxide) was produced by the reaction of CH2I + O2. CH2I was generated by 248-nm laser photolysis of di-iodomethane, CH2I2, at 293 K and 4 torr, 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] decay at m/z = 46. The first order decay CH2OO in the presence of excess known concentrations of H2O was used to determine the rate constants, at a total pressure of 4.5 Torr. The upper limit determined on the basis of absence of any effect of [H2O] = 3 x 1016 molecule cm-3

(b) Photolysis of CH2I2-O2-N2 mixtures. in the absence of added reactant under pseudo-first-order conditions. Kinetics of CH2OO were followed by time-resolved monitoring of HCHO product by laser-induced fluorescence (LIF) spectroscopy (pressure range: 50 – 450 Torr). Rate coefficients for CH2OO + H2O was investigated at 200 Torr, using up to [H2O] = 1.7 x 1017 molecule cm-3. The cited value of *k* is an upper limit based on the assumption that HCHO detected is derived solely from decomposition of CH2OO.

(c) 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 absence of added reactant (SO2 or HFA) the decomposition life-time of CH2OO was ~8 ms, corresponding to the cited lower limit for *k*d.

(d) CH2OO prepared by PLP (266 nm) of CH2I2 in O2/Ar mixtures at 5.1 Torr total pressure. CH2OO kinetics observed by time-resolved UV absorption spectrum at in the B̃ (1A′) ← X̃(1A′) electronic transition between 350 – 420 nm. Decays were first order in the absence of added reagent and *decreased* with total pressure between 3.5 and 9.3 mbar at 294K, suggesting it is dominated by diffusion limited wall loss. Decomposition rate coefficient therefore is an upper limit.

(e) Cavity ring-down spectroscopy was used to perform kinetic measurements at 293 K under low pressure (10 to 30 Torr) conditions, for reactions of CH2OO generated by (248-nm) laser photolysis of CH2I2 in the presence of O2.and SO2 . The *k* value for the unimolecular decomposition of CH2OO was determined from analysis of pseudo first order decay constants at low [SO2], accounting for contribution from self-reaction of CH2OO and the proposed SO2 catalysed CH2OO isomerization, which gives rise to non-linear dependence of the decay constant with [SO2]. An upper limit for the unimolecular CH2OO loss rate coefficient of (11.6 ± 8.0) s-1 was deduced from the analysis.

(f) CH2OO generated by laser flash photolysis of CH2I2/O2/He at *λ* = 266 nm. Monitoring of CH2OO by broadband multipass UV absorption spectroscopy. Absorbance spectra contain contributions from CH2OO, the CH2I2 precursor and IO. Decay of CH2OO well-described by first-order kinetics indicates removal dominated by decomposition. Fit first-order loss to find *k*dec At elevated temperature (450-650 K), rate of decomposition increases with increasing temperature and pressure (2.6 – 395 mbar). CH2OO kinetics also determined by measurement of HO (v = 0 and v = 1) produced in decomposition; kdedc from LIF expts. lower than from UV expts., shown to be due to multilevel OH production. Analysis of data using Troe formalism gave high and low pressure limiting rate coefficients and fall off parameters.

(g) Photolysis of CH2I2 – O2 – N2- NO2 mixtures at 348 nm in continuous flow conditions at 760 Torr pressure. CH2OO produced in this system was allowed to react with NO2. Simultaneous measurement of products NO3 and [N2O5+NO2] was made in a dual channel BB-CEAS at 663 nm. Analysis of these data as function of [NO2] allowed evaluation of the rate constant ratio: (kd(CH2OO)/k(CH2OO + NO2) = (6.4 ± 1.7) x 1012 molec.cm-3, where kd is the total loss rate constant for competing first order processes. Using *k*(NO2) = 3 x 10-12 (IUPAC, 2015) gives the tabulated value of *k*d above, which is an upper limit of *k* for thermal decomposition.

(h) CH2OO produced from O3 + C2H4 reaction in atmospheric pressure FT at 293 ± 0.5 K. H2SO4 formation from the reaction CH2OO + SO2 as a function of RH (= 2% to 50%) for close to atmospheric conditions, was measured using NO3-–CI–APi–TOF MS, sampling the centre flow at the tube outlet. The uncertainty in the [H2SO4] estimated to be ±45%. Second-order kinetics with regard to water vapour concentration indicates a preferred reaction of CH2OO with the water dimer. Measurements at the lowest relative humidity (RH ~2%) yield an upper limit of the rate coefficient ratio kuni/k(SO2) = 2.4 x 1011 molecule cm-3, where kuni is the total first order loss coefficient for CH2OO in the absence of water. Combining this ratio with *k*(SO2) = 3.7 x 10-11 (IUPAC, 2015) gives the tabulated value of *k*uni above.

### Preferred Values

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | **T/K** |
|  |  |  |
| *k* */* s-1 | 0.1 | 298 |
| *k*0 */*cm3 molecule-1 s-1 | 1.7 x 10-9 exp(-6650/T) | 450 - 650 |
| *k*∞ */* s-1 | 1.5 x 109 exp(-7060/T) | 450 - 650 |
| *Reliability* |  |  |
| Δ log *k* | ± 0.5 | 298 |
| Δ (E/R) | ± 500 | 283-323 |

*Comments on Preferred Values*

The values of *k*dec from all the experiments carried out at ambient temperature are upper limits because they relate to the total first order loss process, including thermal decomposition. The lowest value from direct studies at room temperature using CH2I + O2 reaction as a source of stablised CH2OO is that reported by Chhantyal-Pun, et al. (2015), who presented evidence for an SO2 catalysed CH2OO isomerization, which gives rise to non-linear dependence of the decay constant of CH2OO with [SO2]. The occurrence of this process, together with the non-linearity due to presence of the self-reaction at high [CH2OO], leads to systematic inaccuracies in the measurement and assignment of the first order loss by slow thermal decomposition. However this low value for *k*dec agrees with that obtained relative to the CH2OO + SO2 reaction using ozonolysis of ethene as a source of CH2OO (Berndt et al. 2014).

The recent measurements of Stone at al. (2017), indicate that the rate constant for decomposition of CH2OO observed directly at higher temperatures exhibits pressure dependence typical of a classic unimolecular decomposition of small molecules, i.e. fall behavior which can be fitted with the Troe formalism. Because the data for *k*I below 500 K may well contain losses from other processes, only the data at 500 K and above was used for fitting to obtain the limiting high pressure and low pressure limiting rate constants for thermal decomposition. For this dataset, and allowing *F*c to vary, the following values of the parameters were obtained by Stone et al: *k*0 */*cm3 molecule-1 s-1 = 1.7 x 10-9 exp(-6650/T); *k*∞ */* s-1 = 1.5 x 109 exp(-7060/T); and *F*c = 0.33. We adopt their values in our recommendation. Fig 1 shows a comparison of the fall-off curves described by the fitted parameters with the experimental data reported by Stone et al. (2017); the magnitude of k becomes increasingly over predicted as the temperature (and the magnitude of *k*uni) decreases, the expected effect of additional losses by other first order processes. Extrapolation to room temperature using these parameters gives: *k*= 0.1 s-1 at 1 bar and 298 K, a value substantially lower than suggested from all room temperature experiments carried out previously. Clearly the stablised formaldehyde oxide Criegee is a relatively stable intermediate under atmospheric conditions. The higher value from the relative rate study of Berndt et al could arise from a contribution from the ‘hot’ CH2COO produced in ozonolysis, which could be dominant. However the removal of stablised formaldehyde oxide Criegee in the atmosphere by bimolecular processes is likely to be the dominant loss.

Olzmann et al. (1997) using electronic structure calculations, estimated the CH2OO unimolecular loss rate coefficient to be 0.33 s-1, which is in keeping with the unimolecular rate coefficient obtained by extrapolation of the high pressure/temperature results of Stone et al.(2017) to 1 bar and 298 K. The pathway for CH2OO losses by catalysed isomerization or ISC could bridge the discrepancies between the prior experimental and the theoretical estimates.

The many studies have identified HO radicals among the products of ozonolysis of alkenes, and decomposition of both stablised and chemically activated CH2OO have been demonstrated experimentally to be the source of HO. No recommendation is made for the branching ratio *k*5/*k*, because of the uncertainty in the fraction of stabilised CH2OO produced in the atmospheric source reactions. The overall yields of HO radicals from ozonolysis of individual alkenes, presented in the corresponding data sheets, could be used to provide estimates of HO production from this source.

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Fig.1: Pressure and temperature dependence of rate coefficients for unimolecular decomposition of CH2OO. Symbols show experimental data of Stone et al., 2017, with reported error bars; lines show lines calculated using parameters fitted to the data at temperatures above 500 K using the Troe formulation

Fig.2: same data but on expanded pressure axis

