$$CH_2OO\ (+\ M) \rightarrow H_2 + CO_2 \qquad (1)$$
$$CO_2 + 2H \qquad (2)$$
$$H + HOCO \qquad (3)$$
$$CO + H_2O \qquad (4)$$
$$OH + HCO \qquad (5)$$

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

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(NO$_2$)=6.4±1.7 x 10
8.9 ±0.9	293	Berndt et al., 2014	(h) k/k(SO$_2$)=2.6±0.32 x 10

Comments

(a) CH$_2$OO (formaldehyde oxide) was produced by the reaction of CH$_2$I + O$_2$. CH$_2$I was generated by 248-nm laser photolysis of di-iodomethane, CH$_2$I$_2$, at 293 K and 4 torr, 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$_2$OO and its reaction products over the region 9.5 – 11.5 eV, Time-resolved direct detection of [CH$_2$OO] decay at m/z = 46. The first order decay CH$_2$OO in the presence of excess known concentrations of H$_2$O 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 [H$_2$O] = 3 x 10^{16} molecule cm^{-3}

(b) Photolysis of CH$_2$I$_2$-O$_2$-N$_2$ mixtures. in the absence of added reactant under pseudo-first-order conditions. Kinetics of CH$_2$OO were followed by time-resolved monitoring of HCHO product by laser-induced fluorescence (LIF) spectroscopy (pressure range: 50 – 450 Torr). Rate coefficients for CH$_2$OO + H$_2$O was investigated at 200 Torr, using up to [H$_2$O] = 1.7 x 10^{17} 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 CH$_2$OO.

(c) CH$_2$OO molecule generated by 351-nm laser flash photolysis of CH$_2$I/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$_2$OO. Using the OH signals as a proxy for the [CH$_2$OO] concentration, in the absence of added reactant (SO$_2$ or HFA) the decomposition life-time of CH$_2$OO was ~8 ms, corresponding to the cited lower limit for k_d.

(d) CH$_2$OO prepared by PLP (266 nm) of CH$_2$I$_2$ in O$_2$/Ar mixtures at 5.1 Torr total pressure. CH$_2$OO kinetics observed by time-resolved UV absorption spectrum at in the $\tilde{B}$ (1A′) ← $\tilde{X}$(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 CH$_2$OO generated by (248-nm) laser photolysis of CH$_2$I$_2$ in the presence of O$_2$.and SO$_2$. The k value for the unimolecular decomposition of CH$_2$OO was determined from analysis of pseudo first order decay constants at low [SO$_2$], accounting for contribution from self-reaction of CH$_2$OO and the proposed SO$_2$ catalysed CH$_2$OO isomerization, which gives rise to non-linear dependence of the decay constant with [SO$_2$]. An upper limit for the unimolecular CH$_2$OO loss rate coefficient of (11.6 ± 8.0) s^{-1} was deduced from the analysis.

(f) CH$_2$OO generated by laser flash photolysis of CH$_2$I$_2$/O$_2$/He at λ = 266 nm. Monitoring of CH$_2$OO by broadband multipass UV absorption spectroscopy. Absorbance spectra contain contributions from CH$_2$OO, the CH$_2$I$_2$ precursor and IO. Decay of CH$_2$OO 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). CH$_2$OO 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 $CH_2I_2 - O_2 - N_2$- NO_2 mixtures at 348 nm in continuous flow conditions at 760 Torr pressure. CH_2OO produced in this system was allowed to react with NO_2. Simultaneous measurement of products NO_3 and $[N_2O_5+NO_2]$ was made in a dual channel BB-CEAS at 663 nm. Analysis of these data as function of $[NO_2]$ allowed evaluation of the rate constant ratio: $(k_d(CH_2OO)/k(CH_2OO + NO_2)) = (6.4 \pm 1.7) \times 10^{12}$ molec.cm^{-3}, where k_d is the total loss rate constant for competing first order processes. Using $k(NO_2) = 3 \times 10^{-12}$ (IUPAC, 2015) gives the tabulated value of k_d above, which is an upper limit of k for thermal decomposition.

(h) CH_2OO produced from $O_3 + C_2H_4$ reaction in atmospheric pressure FT at 293 ± 0.5 K. H_2SO_4 formation from the reaction $CH_2OO + SO_2$ as a function of RH (= 2% to 50%) for close to atmospheric conditions, was measured using NO_3^-–CI–APi–TOF MS, sampling the centre flow at the tube outlet. The uncertainty in the $[H_2SO_4]$ estimated to be $\pm45\%$. Second-order kinetics with regard to water vapour concentration indicates a preferred reaction of CH_2OO with the water dimer. Measurements at the lowest relative humidity (RH ~2%) yield an upper limit of the rate coefficient ratio $k_{uni}/k(SO_2) = 2.4 \times 10^{11}$ molecule cm^{-3}, where k_{uni} is the total first order loss coefficient for CH_2OO in the absence of water. Combining this ratio with $k(SO_2) = 3.7 \times 10^{-11}$ (IUPAC, 2015) gives the tabulated value of k_{uni} above.

Preferred Values

Parameter	Value	T/K
k / s^{-1}	0.1	298
k_0 /cm^3 molecule^{-1} s^{-1}	1.7×10^{-9} exp(-6650/T)	450 - 650
k_∞ / s^{-1}	1.5×10^9 exp(-7060/T)	450 - 650
Reliability		
$\Delta \log k$	± 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 $CH_2I + O_2$ reaction as a source of stablised CH_2OO is that reported by Chhantyal-Pun, et al. (2015), who presented evidence for an SO_2 catalysed CH_2OO isomerization, which gives rise to non-linear dependence of the decay constant of CH_2OO with $[SO_2]$. The occurrence of this process, together with the non-linearity due to presence of the self-reaction at high $[CH_2OO]$, 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 $CH_2OO + SO_2$ reaction using ozonolysis of ethene as a source of CH_2OO (Berndt et al. 2014).

The recent measurements of Stone at al. (2017), indicate that the rate constant for decomposition of CH_2OO 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 /cm^3 molecule^{-1} s^{-1} = 1.7 x 10^{-9} exp(-6650/T); k_∞ / s^{-1} = 1.5 x 10^9 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' CH$_2$COO 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 CH$_2$OO 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 CH$_2$OO 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 CH$_2$OO 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 CH$_2$OO 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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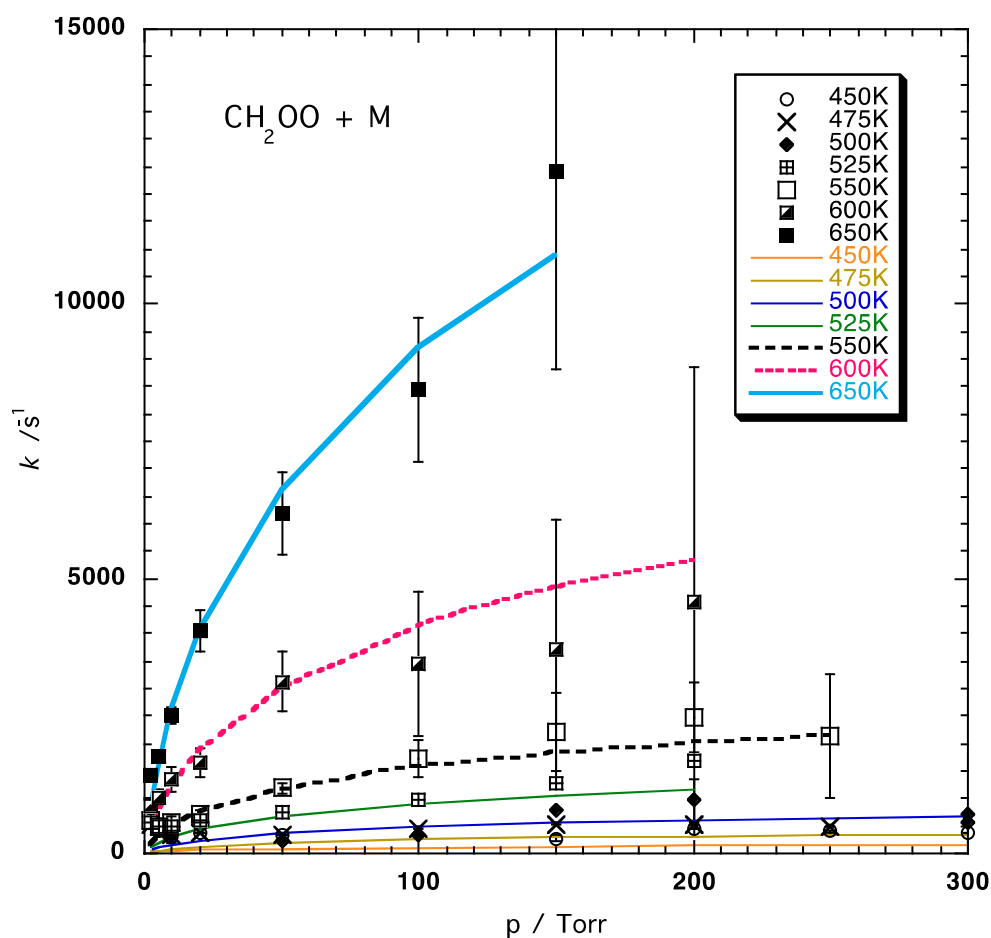
Fig.1: Pressure and temperature dependence of rate coefficients for unimolecular decomposition of CH_2OO. Symbols show experimental data of Stone et al., 2017, with reported error bars; lines show lines calculated using parameters fitted to the data at temperatures above 500 K using the Troe formulation

Fig.2: same data but on expanded pressure axis