IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx82

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This data sheet last evaluated: May 2012; last change in preferred values: May 2012.

$$\mathbf{ClO + CH_3O_2 \rightarrow ClOO + CH_3O} \quad (1)$$
$$\mathbf{\rightarrow OClO + CH_3O} \quad (2)$$
$$\mathbf{\rightarrow HCHO + HCl + O_2} \quad (3)$$
$$\mathbf{\rightarrow CH_3Cl + O_3} \quad (4)$$
$$\mathbf{\rightarrow CH_3OCl + O_2} \quad (5)$$

$\Delta H°$ (1) = 4.1 kJ·mol^{-1}
$\Delta H°$ (2) = 1.2 kJ·mol^{-1}
$\Delta H°$ (3) = -311.5 kJ·mol^{-1}
$\Delta H°$ (4) = -49.9 kJ·mol^{-1}
$\Delta H°$ (5) = -174.6 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.1 \pm 1.7) \times 10^{-12}$	300	Simon et al., 1989	MM-UVA (a)
$3.25 \times 10^{-12} \exp[-(114 \pm 38)/T]$	225-355	Helleis et al., 1993	DF-MS (b)
2.22×10^{-12}	295		
$(1.9 \pm 0.4) \times 10^{-12}$	293	Kenner et al., 1993	DF-MS (c)
$2.0 \times 10^{-12} \exp[(80 \pm 50)/T]$	233-300	Kukui et al., 1994	DF-MS (d)
$(2.5 \pm 0.3) \times 10^{-12}$	300		
$1.96 \times 10^{-11} \exp[-(626 \pm 35)/T]$	223-298	Leather et al., 2012	TF-CIMS (e)
2.4×10^{-12}	300		
Branching Ratios			
$k_1/k > 0.70$	300	Simon et al., 1989	IR, UV (f)
$k_2/k < 0.05$			
$k_3/k < 0.02$			
$k_1/k = 1.51 \exp[-(218 \pm 93)/T]$	225-295	Helleis et al., 1993	DF-MS (g)
$k_3/k = < 0.02$			
$k_5/k = 0.08 \exp[(377 \pm 178)/T]$			
$k_1/k = 0.50 \pm 0.2$	300	Kukui et al., 1994	DF-MS (h)
$k_1/k = 0.63 \pm 0.2$	273		
$k_1/k = 0.38 \pm 0.2$	253		
$k_1/k = 0.26 \pm 0.1$	233		
$k_5/k = 0.011 \exp[(836 \pm 140)/T]$	233-300		
$k_5/k = (T/300)^{-1.65} - 0.223\exp(411/T)$	215-295	Helleis et al., 1994	DF-MS (i)
$k_1/k = 0.21 - 0.51$	298	Biggs et al., 1995	DF-LIF (j)
$k_1/k = 0.3 \pm 0.1$	298	Daële and Poulet, 1996	DF-LIF (k)

Comments

(a) Broad band photolysis of slowly flowing Cl_2-Cl_2O-CH_4-O_2 mixtures at 312 ± 7 mbar. CH_3O_2 and ClO were detected by absorption at 240 nm and 292.2 nm, respectively. The rate constant was derived by fitting time dependent optical density measurements at 240 nm and 292.2 nm to a chemical model.

(b) Flow tube at 2.3 – 4 mbar He. CH_3O_2 formed in F + CH_4 in presence of O_2, ClO formed from Cl + Cl_2O, or Cl + OClO or Cl + O_3. Both reactants were monitored at their parent ions by mass spectrometry, and the pseudo first order decay of CH_3O_2 in excess concentration of ClO used to derive *k* directly.

(c) Flow tube at 2.5 mbar He. CH_3O_2 formed in F + CH_4 in presence of O_2, ClO formed from Cl + O_3. Both reactants were monitored at their parent ions by mass spectrometry, and the pseudo first order decay of CH_3O_2 in excess concentration of ClO used to derive *k* directly.

(d) Flow tube at 5-6 mbar He. CH_3O_2 formed in F + CH_4 in presence of O_2, ClO formed from Cl + O_3. Both reactants were monitored at their parent ions by mass spectrometry, and the pseudo first order decay of CH_3O_2 in excess concentration of ClO used to derive *k* directly.

(e) Turbulent flow reactor operated at 100 or 200 Torr N_2. CH_3O_2 (1-50 × 10^{11} molecule cm^{-3}) was generated via the reaction of CH_3 with O_2, ClO (1-10 × 10^{10} molecule cm^{-3}) was made via reaction of Cl + O_3. Both CH_3O_2 and ClO were detected (as FO_2^- and ClO^-, respectively) using SF_6^- chemi-ions. Measurements made with CH_3O_2 as excess reagent over ClO with ClO decaying only 10-30 %.

(f) FTIR and UV analysis of flowing gas-mixture (as described in comment (a)). No evidence for OClO formation enabled the upper limit of $k_2/k < 0.05$ to be derived. Also, no evidence for O_3 formation from channel (4). Observed products by FTIR were HCHO, CH_3OH, HCl and HC(O)OH. HC(O)OH profiles were analysed with the assumption that it was formed in reactions of HCHO with HO_2 which allows some differentiation between channels (1) and (3), both of which generate HCHO if O_2 is present, but only one of which generates HO_2. The yield of HCOOH was compatible with $k_1/k > 0.7$ and $k_3/k < 0.3$.

(g) (see also comment b). Mass spectrometric detection of products. No evidence was found for formation of OClO, O_3 or CH_3Cl, suggesting that channels 2 and 4 are unimportant. Use of CD_3O_2 enabled sensitive measurement of DCl formation, and an upper limit of 2 % for channel 3. HCHO, HOCl and CH_3OCl were positively identified as products. Branching ratios were derived by assuming that CH_3OCl is formed directly in channel (5), whereas HCHO and HOCl arise from channel (1) followed by rapid reaction of CH_3O with ClO, and by calibrating the CH_3O_2 and HCHO signals. The branching ratio to channel (5) was derived by assuming that only channels (1) and (5) are significant (i.e. sum to unity), though the predicted negative temperature dependence of the CH_3OCl yield was observed.

(h) (see also comment d). CH_3O_2 formed in F + CH_4 in presence of O_2, ClO formed from Cl + O_3. No evidence fround for formation of OClO or CH_3Cl. Observed products were CH_3OCl, HOCl and HCHO. Branching ratios for CH_3OCl and HCHO derived by quantitative mass spectrometric detection of both CH_3O_2 loss and CH_3OCl or HCHO formation. The parameterisation of the branching ratio k_5/k was derived by fitting to the authors tabulated data. HOCl signals were also converted to temperature dependent values of k_1/k by normalising to $(k_1 + k_5)/k = 1$ at 300 K.

(i) Flow tube at 2.3 mbar He. CH_3O_2 formed in F + CH_4 in presence of O_2, ClO formed from Cl + Cl_2O. Branching ratios derived by quantitative mass spectrometric detection of both CH_3O_2 loss and CH_3OCl formation.

(j) Flow tube at 2.7 mbar He. CH_3O_2 (not detected) formed in F + CH_4 in presence of O_2, ClO (detected by MS) formed from Cl + O_3. CH_3O detected by LIF at 292.8 nm. Derivation of the branching ratio for channel (1) involved modelling CH_3O profiles that were influenced by the presence of CH_3O impurity in the CH_3O_2 source, and reactions of both CH_3O_2 and CH_3O with Cl atoms, and loss of CH_3O by reaction with ClO and at the wall.

(k) Flow tube at 1.3 mbar He. CH_3O_2 formed in F + CH_4 in presence of O_2, ClO (detected by MS) formed from Cl + O_3. CH_3O was detected quantitatively by LIF at 298.3 nm, and CH_3OCl was observed but not quantified. As in comment (i), derivation of the branching ratio required numerical simulation of several processes.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.2 x 10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	3.2 x 10^{-12} exp(-110/T)	220-360
k_1/k	0.73	298
k_1/k	1.51 exp -(218/T)	220-300
k_5/k	0.15	298
k_5/k	0.018 exp(630/T)	220-300
Reliability		
$\Delta \log k$	± 0.15	298
Δ E/R	± 300	220-360
$\Delta(k_1/k)$	± 0.2	298
$\Delta(E/R)$	± 150	220-300
$\Delta(k_5/k)$	± 0.1	298
$\Delta(E/R)$	± 300	220-300

Comments on Preferred Values

The preferred value of k at 298 K is the unweighted average k from the direct studies of Helleis et al. (1993), Kenner et al. (1993) and Kukui et al. (1994) who all measured the CH_3O_2 radical directly by MS, under pseudo first-order conditions with excess ClO. The recommended value also encompasses the result of Simon et al. (1989), which was obtained indirectly, and is consistent with the upper limit of k(200 K) < 4.0 x10^{-12} cm^3 molecule^{-1} s^{-1} set by DeMore (1991). It is also consistent with the most recent measurement of Leather et al. (2012), which was obtained using CH_3O_2 as excess reagent whereby pseudo-first order conditions could not be confirmed as ClO decayed over only 10-30 percent of its initial concentration and plots of pseudo-first-order decay rates of ClO versus [CH_3O_2] showed large scatter. Additionally, it is not clear to what extent formation of HO_2 (via reaction of CH_3O from channel (1) with O_2) would have perturbed the ClO decay in the experiments of Leather et al (2012) especially at higher temperatures where channel (1) dominates (see below). k appears to be independent of pressure between ~1 Torr (1.33 mbar) He and 1 bar air.

The temperature dependence of k is less well defined, with both Helleis et al (1993) and Kukui et al (1993) returning only weak dependencies but with opposite sign, whereas Leather et al. (2012) obtaining a much larger value of E/R = 626. Of these three studies, that of Helleis et al (1993) appears to be the most comprehensive, covering the largest range of temperature and also using several different chemical sources of ClO. We therefore adopt the value of E/R given by Helleis et al. (1993) with increased errors to reflect different results obtained in the other studies.

Although there is consensus that formation of CH_3Cl, O_3, OClO and HCl are insignificant, (Simon et al., 1989; Helleis et al., 1993; Kenner et al., 1993; DeMore, 1991) ruling out channels (2-4), there is disagreement in the branching ratio to channels (1) and (5). The most reliable branching ratio is that to CH_3OCl formation (5), as CH_3OCl is easiest to calibrate, and is a non-reactive product. The preferred branching ratio at 298 K for channel (5) is the

averaged result of Helleis et al. (1993) and Kukui et al. (1994). The data of Helleis et al. (1993) are reproduced by the expression: $k_5/k = 0.034 \exp(430/T)$, which was combined with $k_5/k = 0.011 \exp(836/T)$ from Kukui et al. (1994) to obtain the preferred expression for the temperature dependence of branching to channel (5).

There are two direct measurements (Biggs et al., 1995; Daële et al., 1996) of CH_3O formation in reaction (1), which required extensive modelling of its further reactions, and which had to take its presence as impurity in the CH_3O_2 source into account (see comments i and j). There are also indirect measurements, which assume rapid conversion of CH_3O to HCHO and HOCl via reaction with the excess ClO, which is borne out in separate studies of the kinetics of this reaction (Daële et al. 1996, Biggs et al. 1995). Helleis et al. (1993) and Kukui et al. (1994) observed formation of both HCHO and HOCl, with kinetics consistent with formation in channel (1) as rate limiting step. Although only HCHO could be accurately calibrated, HOCl signals were consistent with expected ionization efficiencies compared to ClO. The data of Kukui et al. (1994) suffered from a large background under the HCHO peak, which introduced severe uncertainty into their measurement of k_1/k, and the preferred branching ratio for channel (1) at 298 K, and its temperature dependence is therefore taken from Helleis et al. (1993). This data is in excellent agreement with the values of k_1/k which Kukui et al. (1994) derived from HOCl signals and assuming that only channels (1) and (5) contribute at 300 K.

When summed together, channels (1) and (5) are seen to represent 85-90 % of the overall reaction, although these measurements are associated with large errors that do not preclude a significant, so far unconsidered reaction channel, which would potentially also explain the low branching ratios for CH_3O formation obtained. The error limits on k_1/k are expanded to accommodate this. Theoretical work (Drougas et al., 2003) has shown that the reaction proceeds via formation of a CH_3OOOCl association complex on both a singlet surface (decomposing to CH_3O + ClOO, (1)) or a triplet surface (rearranging to form CH_3OCl + O_2 (5)), which is consistent with experimental findings.

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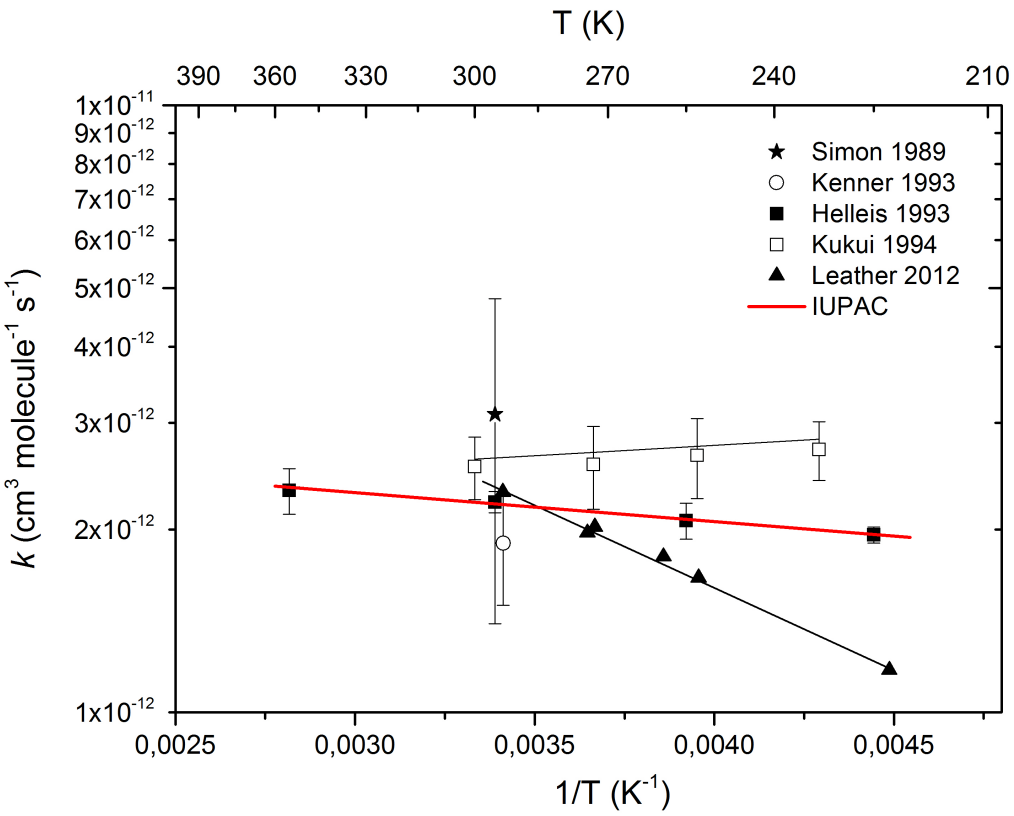

Temperature dependence of $k(CH_3O_2 + ClO)$. The red line is the IUPAC preferred value. The datapoints of Leather et al. were digitized from their Figure.