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

$\Delta H°$ (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[1]	MM-UVA (a)
$3.25 \times 10^{-12} \exp[-(114 \pm 38)/T]$	225-355	Helleis, Crowley, and Moortgat, 1993[2]	DF-MS (b)
2.22×10^{-12}	295		
$(1.9 \pm 0.4) \times 10^{-12}$	293	Kenner, Ryan, and Plumb, 1993[3]	DF-MS (c)
$2.0 \times 10^{-12} \exp[(80 \pm 50)/T]$	233-300	Kukui, Jungkamp, and Schindler, 1994[4]	DF-MS (d)
$(2.5 \pm 0.3) \times 10^{-12}$	300		
Branching Ratios			
$k_1/k > 0.70$	300	Simon *et al.*,1989[1]	IR, UV (e)
$k_2/k < 0.05$			
$k_3/k < 0.02$			
$k_1/k = 1.51 \exp[-(218 \pm 93)/T]$	225-295	Helleis, Crowley, and Moortgat, 1993[2]	DF-MS (f)
$k_3/k = < 0.02$			
$k_5/k = 0.08 \exp[(377 \pm 178)/T]$			
$k_1/k = 0.50 \pm 0.2$	300	Kukui, Jungkamp, and Schindler, 1994[4]	DF-MS (g)
$k_1/k = 0.63 \pm 0.2$	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, Crowley, and Moortgat, 1994[5]	DF-MS (h)
$k_1/k = 0.21 - 0.51$	298	Biggs *et al.*, 1995[6]	DF-LIF (i)
$k_1/k = 0.3 \pm 0.1$	298	Daële and Poulet, 1996[7]	DF-LIF (j)

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) 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 $k_3/k < 0.3$.

(f) (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.

(g) (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.

(h) 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.

(i) 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.

(j) 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

$k = 2.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.4 \times 10^{-12} \exp(-20/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220 K to 360 K.

$k_1/k = 0.73$ at 298 K
$k_1/k = 1.51 \exp -(218/T)$ from 220 to 300 K
$k_5/k = 0.15$ at 298 K
$k_5/k = 0.018 \exp(630/T)$ from 220 to 300 K

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

$\Delta(k_1/k) = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 150$ K.

$\Delta(k_5/k) = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

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.*,[2] Kenner *et al.*,[3] and Kukui *et al.*,[4] who all measured the CH_3O_2 radical directly by MS, under pseudo first-order conditions. The recommended value also encompasses the result of Simon *et al.*[1] which was obtained indirectly, and is consistent with the upper limit of $k(200\text{ K}) < 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} set by De More.[8] The temperature dependence of k was derived by averaging the values of E/R presented by Helleis *et al.*[2] and Kukui *et al.*[4] and adjusting the pre-exponential factor to obtain the recommended value of k(298 K).

Although there is consensus that formation of CH_3Cl, O_3, OClO and HCl are insignificant,[1,2,4,8] 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.*[5] and Kukui *et al.*[4] The data of Helleis *et al.*[5] 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.*[4] to obtain the preferred expression for the temperature dependence of branching to channel (5).

There are two direct measurements[6,7] 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.[9,10] Helleis *et al.*[2] and Kukui *et al.*[4] 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.*[4] 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.*[2] This data is in excellent agreement with the values of k_1/k which Kukui *et al.*[4] 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.

References

1. F. G. Simon, J. P. Burrows, W. Schneider, G. K. Moortgat and P. J. Crutzen, J. Phys. Chem. **93**, 7807 (1989).
2. F. Helleis, J. N. Crowley and G. K. Moortgat, J. Phys. Chem. **97**, 11464 (1993).
3. R. D. Kenner, K. R. Ryan and I. C. Plumb, Geophys. Res. Lett. **20**, 1571 (1993).
4. A. S. Kukui, T. P. W. Jungkamp and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **98**, 1298 (1994).
5. F. Helleis, J. Crowley and G. Moortgat, Geophys. Res. Lett. **21**, 1795 (1994).
6. P. Biggs, C. E. Canosa-Mas, J.-M. Fracheboud, D. E. Shallcross and R. P. Wayne, Geophys. Res. Lett. **22**, 1221 (1995).
7. V. Daële and G. Poulet, J. Chim. Phys. **93**, 1081 (1996).
8. W. B. DeMore, J. Geophys. Res. **96**, 4995 (1991).
9. V. Daële, G. Laverdet and G. Poulet, Int. J. Chem. Kinet. **28**, 589 (1996).
10. P. Biggs, C. E. Canosa-Mas, J.-M. Fracheboud, G. Marston, D. E. Shallcross and R. P. Wayne, J. Chem. Soc. Faraday Trans. **91**, 3045 (1995).