IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oRClOx57

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$$CH_2ClCH_2O_2 + CH_2ClCH_2O_2 \rightarrow CH_2ClCH_2OH + CH_2ClCHO + O_2 \quad (1)$$
$$\rightarrow CH_2ClCH_2O + CH_2ClCH_2O + O_2 \quad (2)$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$k_{obs} = 1.1 \times 10^{-13} \exp[(1020 \pm 170)/T]$	228-380	Dagaut et al., 1988	FP-UVA (a,b)
$k_{obs} = (3.57 \pm 0.57) \times 10^{-12}$	298		
$k_{obs} = (6.0 \pm 0.8) \times 10^{-12}$	295	Maricq et al., 1993	FP-UVA (a,c)
$k_{obs} = 4.0 \times 10^{-14} \exp[(1376 \pm 60)/T]$	253-345	Chakir et al., 2003	MM-UVA(a,d)
$k_{obs} = (4.5 \pm 0.4) \times 10^{-14}$			
Branching Ratios			
$k_1/k = 0.31$	295	Wallington et al., 1990	UV-P-FTIR (e)
$k_2/k = 0.69$			
$k_1/k = 0.43$	296	Yarwood et al., 1992	UV-P-FTIR(e)
$k_2/k = 0.57$			

Comments

(a) k_{obs} is based on the measured overall second-order decay of $CH_2ClCH_2O_2$, defined by $-d[CH_2ClCH_2O_2]/dt = 2k_{obs}[CH_2ClCH_2O_2]^2$. As described in detail by Lesclaux (1997), HO_2 radicals formed from the subsequent chemistry of CH_2ClCH_2O (formed from channel (2)) are expected to lead to secondary removal of $CH_2ClCH_2O_2$. The true value of k is expected to fall in the range $k_{obs}/(1+\alpha) < k < k_{obs}$, where $\alpha = k_2/k$.

(b) Flash photolysis of Cl_2 in the presence of C_2H_4-O_2-N_2 mixtures over the pressure range 33-533 mbar. $CH_2ClCH_2O_2$ concentrations measured by UV absorption spectroscopy using $\sigma_{250\ nm} = (3.64 \pm 0.39) \times 10^{-18}$ cm^2 molecule^{-1}.

(c) Pulsed photolysis of Cl_2 in the presence of C_2H_4-O_2-N_2 mixtures at 1013 mbar pressure. Kinetics determined from time-resolved UV absorption spectra of $CH_2ClCH_2O_2$ and HO_2. The values of $\sigma(CH_2ClCH_2O_2)$ obtained are ca. 13% greater than those reported by Dagaut et al. (1988).

(d) Modulated photolysis of Cl_2 in the presence of C_2H_4-O_2-N_2 mixtures over the pressure range 67-267 mbar. k_{obs} determined from analysis of modulated absorption waveforms in the wavelength range 215-270nm. The UV absorption spectrum of $CH_2ClCH_2O_2$ characterized simultaneously, agrees well with that of Dagaut et al. (1988) at $\lambda \geq 240$ nm, with $\sigma_{250\ nm} = (3.56 \pm 0.20) \times 10^{-18}$ cm^2 molecule^{-1}. At shorter wavelengths, cross sections are up to 20% greater.

(e) Steady-state photolysis of Cl_2-C_2H_4-O_2-N_2 mixtures at total pressures of 933 mbar with FTIR spectroscopic monitoring of the removal of C_2H_4 and the formation of CH_2ClCHO, CH_2ClCH_2OOH, and CH_2ClCH_2OH. The listed branching ratios were derived from the yields of CH_2ClCH_2OH and CH_2ClCHO relative to the decay of C_2H_4.

Preferred Values

$k = 3.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.2 \times 10^{-14} \exp(1300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-380 K.
$k_1/k = 0.37$ at 298 K.
$k_2/k = 0.63$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.
$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The studies of Wallington et al. (1990) and Yarwood et al. (1992) provide reasonably consistent determinations of k_2/k, and the preferred value at 298 K is the average of these determinations. Chakir et al. (2003) also used steady state concentrations of HO_2 and $CH_2ClCH_2O_2$, inferred from their modulated photolysis study, to draw conclusions about the temperature dependence of the branching ratio for HO_2 formation, k_2/k. Using the 298 K values of Wallington et al. (1990) and Yarwood et al. (1992) as a reference, they estimated that k_2/k varies from ca. 0.3 at 253K to ca. 0.7-0.9 at 345 K. k_2/k is expected to tend to unity as T increases.

The preferred values of k were calculated from the reported values of k_{obs} and k_2/k, using a methodology similar to that employed by Lesclaux (1997) for peroxy radicals with self reaction rate coefficients $\geq$ ca. 2×10^{-12} cm^3 molecule^{-1} s^{-1} at room temperature. k is estimated to be $k_{obs}/(1+0.5(k_2/k))$, with this approximation assuming that the secondary reaction of HO_2 with $CH_2ClCH_2O_2$ competes equally with its removal via $HO_2 + HO_2$. The preferred values are based on the temperature dependence kinetics results of Dagaut et al. (1988) and Chakir et al. (2003), and the preferred value of k_2/k at 298 K, with the assumption that k_2/k increases to $\approx$ 1 at the high end of the studied temperature range, 380 K. The 298 K value of k_{obs} reported by Maricq et al. (1993) is ca. 50% greater than the average of the values of Dagaut et al. (1988) and Chakir et al. (2003), but is encompassed by the uncertainty range in the preferred value. The discrepancy is not fully resolved, but is partially explained by the greater absorption cross-sections for $CH_2ClCH_2O_2$ reported by Maricq et al. (1993).

References

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