IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx74

$$HO_2 + CHCl_2O_2 \rightarrow CHCl_2O_2H + O_2 \qquad (1)$$
$$\rightarrow C(O)Cl_2 + H_2O + O_2 \qquad (2)$$
$$\rightarrow HC(O)Cl + HOCl + O_2 \qquad (3)$$
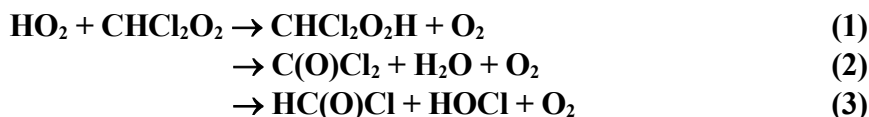
Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
5.6 x 10^{-13} exp[(700 ± 64)/T]	286-440	Catoire et al., 1996	FP-UVA (a)
(5.46 ± 0.77) x 10^{-12}	300		
Branching Ratios			
k_2/k = 0.71	295	Catoire et al., 1996	UVP-FTIR (b)
k_3/k = 0.29			

Comments

(a) Flash photolysis of CHCl$_3$ in the presence of CH$_3$OH-O$_2$-N$_2$ mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from CHCl$_2$O$_2$ and HO$_2$) were recorded in the wavelength range 220 nm to 250 nm. k derived in conjunction with optimization of the rate coefficient for the self-reaction of CHCl$_2$O$_2$, using a five reaction mechanism.

(b) Steady-state photolysis of Cl$_2$ or F$_2$ in the presence of CH$_2$Cl$_2$-H$_2$-O$_2$-N$_2$ mixtures at a total pressure of 933 mbar with FTIR spectroscopic monitoring of the removal of CH$_2$Cl$_2$ and formation of HCOCl and COCl$_2$ as a function of the initial concentration ratio [H$_2$]/[CH$_2$Cl$_2$].

Preferred Values

k = 5.9 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 5.6 x 10^{-13} exp(700/T) cm^3 molecule^{-1} s^{-1} over the temperature range 280-440 K.
k_2/k = 0.7 at 298 K.
k_3/k = 0.3 at 298 K.

Reliability
   Δlog k = ± 0.3 at 298 K.
   $\Delta(E/R)$ = ± 300 K.
   $\Delta(k_1/k)$ = ± 0.2 at 298 K.
   $\Delta(k_2/k)$ = ± 0.1 at 298 K.

Comments on Preferred Values
   The preferred branching ratios are based on the results of the product study of Catoire et al. (1996), which provide evidence for the participation of reaction channels (2) and (3), through

observation of $C(O)Cl_2$ and $HC(O)Cl$ formation, respectively. No evidence for formation of the hydroperoxide, $CHCl_2OOH$, by channel (1) was obtained. The existence of an alternative channel forming O_2, OH and $CHCl_2O$ (and therefore $HC(O)Cl$ from $CHCl_2O$ decomposition) could not be ruled out on the basis of the product studies alone; but no evidence for a radical-forming channel was apparent from the kinetics measurements in the same study.

The preferred rate coefficient values are based on the sole kinetics study of Catoire et al. (1996). These results indicate that the rate coefficients of the reactions of CH_3O_2, CH_2ClO_2, $CHCl_2O_2$ and CCl_3O_2 radicals with the HO_2 radical at 298 K are similar, as are their temperature dependences. This is in marked contrast to the self-reactions, for which chlorine substitution greatly enhances the rate coefficient. Confirmation of the above sole determination is required.

References

Catoire, V., Lesclaux, R., Schneider, W. F. and Wallington, T. J.: J. Phys. Chem. 100, 14356, 1996.