IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx76

This data sheet last evaluated: June 2015; last change in preferred values: December 2004.

$$HO_2 + CCl_3O_2 \rightarrow CCl_3O_2H + O_2 \quad (1)$$
$$\rightarrow C(O)Cl_2 + HOCl + O_2 \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.8 \times 10^{-13} \exp[(706 \pm 31)/T]$	298-374	Catoire et al., 1996	FP-UVA (a)
$(4.9 \pm 0.6) \times 10^{-12}$	300		
Branching Ratios			
$k_2/k = 1.0$	295	Catoire et al., 1996	UVP-FTIR (b)

Comments

(a) Flash photolysis of CCl_4 in the presence of CH_3OH-O_2-N_2 mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from CCl_3O_2 and HO_2) were recorded in the wavelength range 220 nm to 250 nm. k derived from simulations of the decay traces using a six reaction mechanism.

(b) Steady-state photolysis of Cl_2 or F_2 in the presence of $CHCl_3$-H_2-O_2-N_2 mixtures at a total pressure of 933 mbar with FTIR spectroscopic monitoring of the removal of $CHCl_3$ and formation of $C(O)Cl_2$ as a function of the initial concentration ratio $[H_2]/[CH_2Cl_2]$. $C(O)Cl_2$ was the only carbon-containing product observed, with a yield of 100% (within experimental error) under all conditions.

Preferred Values

$k = 5.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.7 \times 10^{-13} \exp(710/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280-440 K.
$k_2/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 300$ K.
$\Delta(k_2/k) = {}^{+0.0}_{-0.1}$ at 298 K.

Comments on Preferred Values

The results of the product study of Catoire et al. (1996) are consistent with the reaction proceeding exclusively via channel (2). The preferred rate coefficient values are based on the results of the same study, which is the only study of this reaction. 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.