IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oRClOx46

This data sheet updated: 27th January 2006.

$CCl_3O_2NO_2 + M \rightarrow CCl_3O_2 + NO_2 + M$

$\Delta H° = 105.6$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
6.3 x 10^{-3} exp(-10235/T) [N_2]	260-300	Köppenkastrop and Zabel, 1991	(a)

Comments

(a) Thermal decomposition of $CCl_3O_2NO_2$ studied in a temperature-controlled 410 liter reaction chamber. The reactant was monitored by *in situ* long-path IR absorption. Pressures of N_2 of 11, 82, and 800 mbar were employed. The data were extrapolated with $F_c = 0.22$ and $k_\infty = 4.8 \times 10^{16}$ exp(-11820/T) s^{-1}.

Preferred Values

$k_0 = 4.3 \times 10^{-3}$ exp(-10235/T) [N_2] s^{-1} over the temperature range 260-300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

There is a single study of the falloff curve only. However, it is consistent with data for the reverse reaction from Caralp et al. (1988). Some readjustment will be necessary to make F_c identical for the forward and reverse reaction, for which $F_c = 0.32$ was chosen. If $F_c = 0.32$ replaces $F_c = 0.22$, k_0 for the dissociation decreases by about a factor of 0.7 such as preferred here.

High-pressure rate coefficients
Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.42 x 10^{16} exp(-11500/T)	274-305	Simonaitis, Glavas,and Heicklen, 1979	(a)
0.24	298		
6.6 x 10^{16} exp(-12240/T)	260-300	Köppenkastrop and Zabel, 1991	(b)
0.29	298		

Comments

(a) Steady-state photolysis of Cl_2-$CHCl_3$-O_2-N_2–NO-NO_2 mixtures at 1 bar. Product formation monitored by IR spectroscopy. Some assumption about the mechanism had to be made. The reaction was assumed to be at the high pressure limit.
(b) See comment (a) for k_0.

Preferred Values

$k_\infty = 4.8 \times 10^{16}$ (-11820/T) s^{-1} over the temperature range 260-300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The two available measurements are in close agreement such that k_∞ appears well established. For the falloff curve see Comments on Preferred Values for k_0.

References

Köppenkastrop, D. and Zabel F.: Int. J. Chem. Kinet., 23, 1, 1991.
Simonaitis, R., Glavas, S. and Heicklen, J.: Geophys. Res. Lett., 6, 385, 1979.