IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oRClOx42

This data sheet updated: 27th January 2006.

$CF_2ClO_2NO_2 + M \rightarrow CF_2ClO_2 + NO_2 + M$

$\Delta H° = 107$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.8 x 10^{-3} exp(-10500/T) [N_2]	273-288	Köppenkastrop and Zabel, 1991	(a)
1.1 x 10^{-3} exp(-10762/T) [N_2]	276-289	Xiong and Carr, 1994	(b)

Comments

(a) Thermal decomposition of $CF_2ClO_2NO_2$ in a temperature-controlled (± 0.1°C) 420 liter reaction chamber. The reactant was monitored *in situ* by long-path IR absorption. N_2 pressures of 11, 82, and 800 mbar were employed. Falloff extrapolations with $F_c = 0.30$ and $k_\infty = 1.6 \times 10^{16}$ exp(-11990/T) s^{-1}.

(b) Continuous-flow temperature-controlled (± 1°C) photoreactor coupled to MS. N_2 pressures of 4-53 mbar were employed. Falloff extrapolations made with $F_c = 0.45$ and $k_\infty = 6.7 \times 10^{16}$ exp(-11871/T) s^{-1}.

Preferred Values

$k_0 = 1.8 \times 10^{-3}$ exp(-10500/T) [N_2] s^{-1} over the temperature range 270-290 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The measurements of Köppenkastrop and Zabel (1991) and of Xiong and Carr (1994) differ markedly in their pressure dependences which is reflected by large differences of the extrapolated k_∞. As the pressure dependence observed by Xiong and Carr (1994) is much larger than given by theoretical falloff curves from Destriau and Troe (1990) and Caralp et al. (1988), the measurements by Xiong and Carr (1994) have to be in error for some unknown reason and are not considered here. Instead, the results from Köppenkastrop and Zabel (1991), which were obtained over a ten times larger pressure range, here are preferred with $F_c = 0.30$ and k_∞ such as given below.

High-pressure rate coefficients
Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.6 \times 10^{16} \exp(-11990/T)$	273-288	Köppenkastrop and Zabel, 1991	(a)
$6.7 \times 10^{16} \exp(-11871/T)$	276-289	Xiong and Carr, 1994	(b)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0. The given value for k_∞ actually stems from a combination of recombination data, equilibrium constants and theoretical modelling. It is consistent with the observed pressure dependence.

Preferred Values

$k_\infty = 1.6 \times 10^{16} (-11990/T)\ s^{-1}$ over the temperature range 270-290 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

See Comments on Preferred Values of k_0.

References

Caralp, F., Lesclaux, R., Rayez, M.-T., Rayez, J.-C. and Forst, W.: J. Chem. Soc. Faraday Trans. 2, 84, 569, 1988.

Destriau, M. and Troe, J.: Int. J. Chem. Kinet., 22, 915, 1990.

Köppenkastrop, D. and Zabel F.: Int. J. Chem. Kinet., 23, 1, 1991.

Xiong, J. Q. and Carr, R. W.: J. Phys. Chem., 98, 9811, 1994.