IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx20

This data sheet last evaluated: 28th June 2007; no revision of preferred values.

$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$

$\Delta H° = -70.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$6.3 \times 10^{-12} \exp(150/T)$	219-298	Margitan, 1983	FP-RF (a)
$(1.04 \pm 0.16) \times 10^{-11}$	298		
$7.3 \times 10^{-12} \exp(165/T)$	220-296	Kurylo et al., 1983	FP-RF (b)
$(1.20 \pm 0.24) \times 10^{-11}$	296		
$6.0 \times 10^{-12} \exp[(140 \pm 30)/T]$	195-298	Yokelson et al., 1995	PLP-RF/
$(9.6 \pm 1.0) \times 10^{-12}$	298		TDLS (c)
$(9.1 \pm 1.2) \times 10^{-12}$	298	Tyndall et al., 1997	PLP-RF

Comments

(a) The O(^{3}P) atom abstraction channel to give ClO + ClONO was shown to be unimportant based on results of experiments with added NO, in which Cl was not regenerated by the fast reaction ClO + NO → Cl + NO_2.

(b) Supersedes earlier results of Kurylo and Manning (1977) from the same laboratory.

(c) Decays of Cl atoms were measured by RF over the temperature range 195-354 K ($k = 6.5 \times 10^{-12} \exp[(120 \pm 20)/T]$ cm^3 molecule^{-1} s^{-1}) and formation of NO_3 radicals were measured by tuneable diode laser spectroscopy (TDLS) over the temperature range 200-298 K ($k = 6.0 \times 10^{-12} \exp[(140 \pm 30)/T]$ cm^3 molecule^{-1} s^{-1}). The values cited in the table are the combined results of experiments using both detection systems for the temperature range 195-298 K.

Preferred Values

$k = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.2 \times 10^{-12} \exp(145/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 190-360 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 50$ K.

Comments on Preferred Values

The recommended Arrhenius equation is derived from the data of Margitan (1983) and Yokelson et al. (1995), which are in excellent agreement. The data of Kurylo et al. (1983) and Tyndall et al. (1997) agree with the preferred values within the recommended uncertainty limits. Margitan (1983) showed that the reaction proceeds by Cl-atom abstraction rather than by O-atom abstraction and this was confirmed by Yokelson et al. (1995), who determined that more than 95% of the reaction forms Cl_2 and NO_3 at 298 K.

References

Kurylo, M. J. and Manning, R. G.: Chem. Phys. Lett. 48, 279, 1977.

Kurylo, M. J., Knable, G. L. and Murphy, J. L.: Chem. Phys. Lett. 95, 9, 1983.

Margitan, J. J.: J. Phys. Chem. 87, 674, 1983.

Tyndall, G. S., Kegley-Owen, C. S., Orlando, J. J. and Calvert, J. G.: J. Chem. Soc. Faraday Trans. 93, 2675, 1997.

Yokelson, R. J., Burkholder, J. B., Goldfarb, L., Fox, R. W., Gilles, M. K. and Ravishankara, A. R.: J. Phys. Chem. 99, 13976, 1995.