IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx33

This data sheet updated: 23th July 2003.

$$\mathbf{ClO + NO_3 \rightarrow ClOO + NO_2} \qquad (1)$$
$$\mathbf{\rightarrow OClO + NO_2} \qquad (2)$$

$\Delta H°(1) = -44.7$ kJ·mol^{-1}
$\Delta H°(2) = -47.5$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(4.0 \pm 1.6) \times 10^{-13}$	296	Cox *et al.*, 1984[1]	MM-A
$1.6 \times 10^{-12} \exp[-(420 \pm 200)/T]$	278-338	Cox *et al.*, 1987[2]	MM-A (a)
4.0×10^{-13}	300		
$(5.0 \pm 1.4) \times 10^{-13}$	210-353	Biggs *et al.*, 1991[3]	DF-A/MS (b)
$(4.61 \pm 0.6) \times 10^{-13}$	300	Kukui *et al.*, 1994[4]	DF-MS (c)
$k_2 = (1.46 \pm 0.4) \times 10^{-13}$	300		
Branching Ratios			
$k_1/k = 0.73$	300	Cox *et al.*, 1987[2]	MM-A (a)
$k_2/k = 0.14 \pm 0.13$	216	Biggs *et al.*, 1991[3]	DF-A/MS (b)
$k_2/k = 0.20 \pm 0.10$	297		
$k_2/k = 0.035 \pm 0.05$	353		

Comments

(a) Derived from computer analysis of the NO_3 radical and ClO radical profiles.
(b) Pseudo-first-order decay of NO_3 in excess ClO was determined by optical absorption at 662 nm, using a cross-section of 1.7×10^{-17} cm^2 molecule^{-1}. Product branching ratios were measured with a quadrupole mass spectrometer.
(c) Rate coefficients k were obtained from the first-order NO_3 radical decays in the presence of excess ClO radicals and O_3. Rate coefficients k_2 were obtained from the decays of ClO radicals in the presence of excess NO_3 radicals, with ClOO radicals formed in channel (1) reforming ClO radicals by the reactions $ClOO \rightarrow Cl + O_2$ and $Cl + NO_3 \rightarrow ClO + NO_2$. This study[4] supersedes the earlier study of Becker *et al.*[5] from the same laboratory.

Preferred Values

$k = 4.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 210 K to 360 K.
$k_2 = 1.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta \log k_2 = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred 298 K value is based on the results of Kukui *et al.*,[4] which are in agreement with the data of Cox *et al.*[1,2] and Biggs *et al.*[3] The results of Cox *et al.*[2] are consistent with those of Biggs *et al.*,[3] who reported that the rate coefficient is independent of temperature over the range 210 K to 353 K. The two direct measurements of the branching ratio k_2/k, of 0.20 ± 0.10 at 297 K[3] and 0.32 ± 0.1 at 300 K,[4] are in agreement that channel (1) dominates, and the preferred value of k_2 is based on the results of these two studies.[3,4] From a study of the OClO-NO_3 system, Friedl *et al.*[6] conclude that at 220 K and 298 K the major reaction channel is channel (1), in agreement with the conclusions of Cox *et al.*,[2] Biggs *et al.*[3] and Kukui *et al.*[4]

References

[1] R. A. Cox, R. A. Barton, E. Ljungstrom, and D. W. Stocker, Chem. Phys. Lett. **108**, 228 (1984).
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[3] P. Biggs, M. H. Harwood, A. D. Parr, and R. P. Wayne, J. Phys. Chem. **95**, 7746 (1991).
[4] A. Kukui, T. P. W. Jungkamp, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **98**, 1619 (1994).
[5] E. Becker, U. Wille, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **95**, 1173 (1991).
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