IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet iClOx12

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Cl + CO + M → ClCO + M

$\Delta H° = -32.6$ kJ·mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(9.1 \pm 3.0) \times 10^{-34}$ [Ar]	300	Clark, Clyne, and Stedman, 1966	DF (a)
$1.05 \times 10^{-34} \exp[(810 \pm 70)/T]$ [N_2]	185-260	Nicovich, Kreutter and Wine, 1990	PLP-RF (b)
1.6×10^{-33} [N_2]	298		
Relative Rate Coefficients			
$(1.4 \pm 0.3) \times 10^{-33}$ [N_2]	298	Hewitt et al., 1996	(c)

Comments

(a) Cl atoms were generated from the photolysis of Cl_2-He mixtures and were measured by titration with nitrosyl chloride using the red chlorine afterglow spectrum. The total pressure was 2.7-5.3 mbar. From additional experiments carried out at 195 K, an activation energy of about -8.4 kJ mol^{-1} was obtained.

(b) Pulsed laser photolysis of Cl_2-CO-M (M = N_2, CO, Ar and CO_2) mixtures at 355 nm. The pressure was 19-267 mbar. By second- and third-law analyses of the temperature dependence of the equilibrium constant, a value of $\Delta H°(298\ K) = -(32.2 \pm 2.5)$ kJ mol^{-1} was derived. The relative collision efficiencies were $\beta_c(CO_2) : \beta_c(CO/N_2) : \beta_c(Ar) = 3.2 : 1.0 : 0.8$.

(c) Steady state photolysis of Cl_2 in the presence of CO and a reference gas (CH_4 or $CHCl_3$). Long-path FTIR spectroscopy of CO and CO_2. Measurements of k_0 in 1 bar of air at 298 K relative to $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k_0 = 1.3 \times 10^{-33} (T/300)^{-3.8}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 180-300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The recommended rate coefficients are based on the measurements of Nicovich et al. (1990) which agree well with the relative rate measurements from Hewitt et al. (1996). No signs for deviations from third-order behavior were detected.

References

Clark, T. C., Clyne, M. A. A. and Stedman, D. H.: Trans. Faraday Soc., 62, 3354, 1966.

Hewitt, A. D., Brahan, K. M., Boone, G. D. and Hewitt, S. A.: Int. J. Chem. Kinet. 28, 765, 1996.

Nicovich, J. M., Kreutter, K. D. and Wine, P. H.: J. Chem. Phys., 92, 3539, 1990.