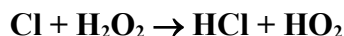


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClO_x9

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be re-transmitted or disseminated either electronically or in hard copy without explicit written permission.

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



$$\Delta H^\circ = -62.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(5.8^{+5.8}_{-2.9}) \times 10^{-13}$	298	Watson et al., 1976	FP-RF (a)
$(6.2 \pm 1.5) \times 10^{-13}$	295	Leu and DeMore, 1976	DF-MS
$1.24 \times 10^{-12} \exp[-(384 \pm 168)/T]$	265-400	Michael et al., 1977	FP-RF (b)
$(3.64 \pm 0.52) \times 10^{-13}$	299		
$(4.0 \pm 0.4) \times 10^{-13}$	298	Poulet et al., 1978	DF-MS
$1.05 \times 10^{-11} \exp[-(982 \pm 102)/T]$	298-424	Keyser, 1980	DF-RF
$(4.1 \pm 0.2) \times 10^{-13}$	298		

Comments

- (a) A recalculated rate coefficient of $(5.2^{+5.2}_{-2.6}) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is cited in Michael et al. (1977).
- (b) Obtained using H_2O_2 concentrations measured after the reaction cell. Using an average of the H_2O_2 concentrations measured in the reactant flow prior to and after the reaction cell, a rate coefficient of $k = (3.14 \pm 0.56) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 265-400 K, was obtained.

Preferred Values

$k = 4.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.1 \times 10^{-11} \exp(-980/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260-430 K.

Reliability

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

$\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The room temperature rate coefficients measured by Watson et al. (1976), Leu and DeMore (1976), Michael et al. (1977), Poulet et al. (1978) and Keyser (1980) cover the range $(3.6\text{--}6.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The studies of Michael et al. (1977), Poulet et al. (1978) and Keyser (1980) are considered to be the most reliable. The recommended Arrhenius expression is that reported by Keyser (1980). The rate coefficient measured by Michael et al. (1977) at 265 K is in good agreement with the recommendation; however, the A -factor reported is considerably

lower than that expected from theoretical considerations and may be attributed to decomposition of H_2O_2 above 300 K (which was indeed observed, especially at 400 K). More data are required before the Arrhenius parameters can be considered to be well established. Heneghan and Benson (1983), using mass spectrometry, confirmed that this reaction proceeds only by H-atom abstraction.

References

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