IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx5

$$O + Cl_2O \rightarrow ClO + ClO$$
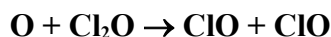
$\Delta H° = -123$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
2.7×10^{-11} exp[-(560 ± 80)/T]	236-295	Miziolek and Molina, 1978	DF-CL (a)
$(4.1 ± 0.5) \times 10^{-12}$	295		
3.3×10^{-11} exp[-(700 ± 150)/T]	237-297	Wecker et al., 1982	DF-EPR (b)
$(3.1 ± 0.5) \times 10^{-12}$	297		
2.7×10^{-11} exp[-(510 ± 30)/T]	230-380	Stevens and Anderson, 1992	DF-RF (c)
$(4.7 ± 0.2) \times 10^{-12}$	298		
1.51×10^{-11} exp[-(477 ± 26)/T]	230-357	Papanastasiou and Burkholder, 2011	LP-RF (d)
$(2.93 ± 0.3) \times 10^{-12}$	298		

Comments

(a) O(^{3}P) were generated by reaction of N atoms (microwave discharge of N$_2$) with NO and detected by afterglow following conversion to NO$_2$. Experiments were carried out at one Torr (1.33 mbar).

(b) Rate coefficients derived either by analysis of O(^{3}P) signals at different injector positions in a constant excess of Cl$_2$O or by varying the [Cl$_2$O] at constant injector position.

(c) O(^{3}P) (2.5-6×10^{11} molecule cm^{-3}) was generated by a microwave discharge of O$_2$ in He. Experiments carried out at 1.9 to 2.1 Torr (2.5-2.8 mbar) He. The concentration of the excess reagent, Cl$_2$O was measured online using absorption spectroscopy.

(d) O(^{3}P) (1-11×10^{11} molecule cm^{-3}) was generated by the 248 nm photolysis of O$_3$ in N$_2$ or the 193 nm photolysis of Cl$_2$O. The concentration of the excess reagent, Cl$_2$O was measured online using absorption spectroscopy. Rate coefficients were independent of pressure over the range 12-32 Torr (16-43 mbar) N$_2$.

Preferred Values

| Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.9×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	1.65×10^{-11} exp(-515/T)	205-580
Reliability		
$\Delta \log k$	± 0.15	298
$\Delta E/R$	± 100	

Comments on Preferred Values

Even when disregarding the earliest rate coefficients reported by Freeman and Phillips (1968) and Basco and Dogra (1971) which have subsequently been shown to be much too high owing to secondary chemistry, there is considerable scatter in the remaining room temperature rate coefficients, although three of the studies (Miziolek and Molina, 1978; Stevens and Anderson, 1992; Papanastasiou and Burkholder, 2011) derive similar *E/R* parameters.

Papanastasiou and Burkholder (2011) minimized the effects of secondary loss of O(^{3}P) via the fast reaction with ClO by using the smallest possible radical concentrations. Guided by simulations of secondary processes, they took data with [Cl$_2$O]/[radical] ratios of >500 (using the 248 nm radical source) and [Cl$_2$O]/[radical] ratios of >90 (using the 193 nm radical source). In a numerical simulation of the dataset of Miziolek and Molina (1978) using updated rate coefficients, Papanastasiou, and Burkholder (2011) showed that an overestimate of *k* by ~ 20 % was likely. We note that reducing the rate coefficient of Miziolek and Molina by 20 % would bring them into agreement (within combined error bounds) with Papanastasiou and Burkholder at 298 K. The numerical simulations of Papanastasiou, and Burkholder (2011) also indicated that the rate coefficient of Stevens and Anderson, (1992) may have been enhanced by secondary chemistry, though the difference of 60 % at room temperature compared to their own data could not be explained.

Papanasasiou and Burkholder have showed that in studies of this reaction, systematic errors will generally lead to a larger rate coefficient than the true one. Their online measurement of the Cl$_2$O concentration and working at large [Cl$_2$O] / [radical] ratios should make the pulsed photolysis study more reliable and we prefer their room temperature rate coefficient. The preferred Arrhenius expression takes an average *E/R* from Miziolek and Molina (1978), Stevens and Anderson (1992) and Papanastasiou and Burkholder (2011), with the pre-exponential factor adjusted to return the preferred value of *k* at 298 K.

References

Basco, N. and Dogra, S. K.: Proc. Roy. Soc. London A, 323, 29, 1971.
Freeman, C. G. and Phillips, L. F.: J. Phys. Chem. 72, 3025, 1968.
Miziolek, A. W. and Molina, M. J.: J. Phys. Chem. 82, 1769, 1978.
Papanastasiou, D. K., and Burkholder, J. B., Int. J. Chem. Kinet., 43, 312-321, 2011.
Stevens, P. S. and Anderson, J. G.: J. Phys. Chem. 96, 1708, 1992.
Wecker, D., Johanssen, R. and Schindler, R. N.: Ber. Bunsenges. Phys. Chem. 86, 532, 1982.
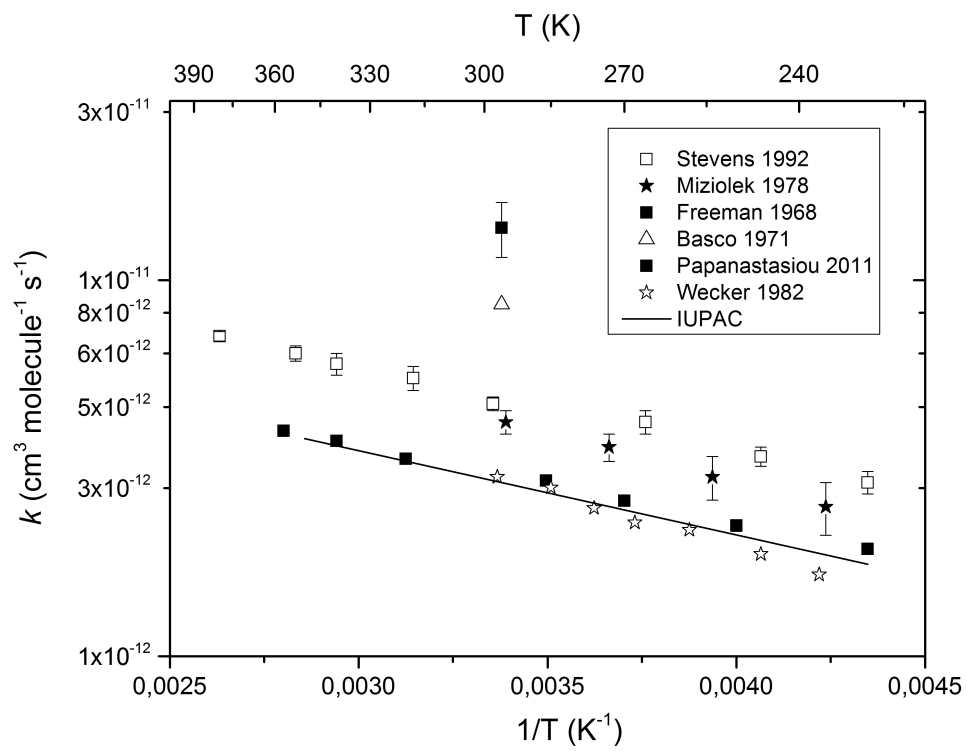
Temperature dependent rate coefficients for the reaction $O(^3P) + Cl_2O$.