

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx8

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This data sheet updated: 12th July 2006.



$$\Delta H^\circ(1) = -228.2 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = 2.9 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(4.2 \pm 0.7) \times 10^{-11}$	250-414	Lee and Howard, 1982	DF-LMR (a)
$k_1 = (4.4 \pm 1.5) \times 10^{-11}$	308	Cattell and Cox, 1986	MM (b)
$k_2 = (9.4 \pm 1.9) \times 10^{-12}$	308		
$3.8 \times 10^{-11} \exp[(40 \pm 90)/T]$	230-360	Riffault et al., 2001	DF-MS (c)
$(4.4 \pm 0.5) \times 10^{-11}$	300		
$k_2 = 8.6 \times 10^{-11} \exp[-(660 \pm 100)/T]$	230-360		
$k_2 = (9.9 \pm 2.8) \times 10^{-12}$	295		
$2.8 \times 10^{-11} \exp[(123 \pm 15)/T]$	246-296	Hickson and Keyser, 2005	DF-RF (d)
$(4.3 \pm 0.1) \times 10^{-11}$	296		
$k_1 = 1.6 \times 10^{-11} \exp[(249 \pm 34)/T]$	226-336		
$k_1 = (3.6 \pm 0.1) \times 10^{-11}$	296		
<i>Branching Ratio</i>			
$k_2/k = 1.09 \exp[-(478 \pm 17)/T]$	250-420	Lee and Howard, 1982	DF-LMR (a)
$k_2/k = 0.210 \pm 0.016$	297		
$k_1/k = 0.34 \exp[(222 \pm 17)/T]$	256-296	Hickson and Keyser, 2005	DF-RF/TDLS (d)
$k_1/k = 0.724 \pm 0.020$	296		
$k_2/k = 2.4 \exp[-(733 \pm 41)/T]$	226-336		
$k_2/k = 0.189 \pm 0.003$	296		

Comments

- (a) On the basis of the temperature independent overall rate coefficient and the temperature dependent branching ratio, the authors derived the rate coefficient expressions $k_1 = 1.8 \times 10^{-11} \exp[(170 \pm 80)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_2 = 4.1 \times 10^{-11} \exp[-(450 \pm 60)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (b) Rate coefficients were derived from the observed time-concentration behavior of HO₂ and ClO radicals using computer simulations and a 25-step reaction mechanism. Because of uncertainties in the Cl atom concentrations, the rate coefficients k_1 and k_2 cited above (for 1 bar total pressure) may be low by a factor of 2 and high by a factor of 2, respectively (Cattell and Cox, 1986). The reaction was also studied over the pressure range 67 mbar to 1013 mbar, and no pressure dependence of either k_1 or k_2 over this range was evident.
- (c) k was determined under pseudo-first order conditions with either HO₂ or Cl in excess. Because the reported weak temperature dependence is not significantly different from zero, a temperature independent rate coefficient $k = (4.4 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, was also reported for the temperature range 230-360 K. k_2 was determined from the formation kinetics of both OH and ClO.

- (d) HO₂ radicals were detected by titration to HO, following reaction with NO. k and k_1 were determined under pseudo-first order conditions in experiments with Cl and HO₂ in excess, respectively. Because the reported temperature dependence is weak, a temperature independent rate coefficient $k = (4.5 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, was also reported for the studied temperature range. A value of $k_2 = 7.7 \times 10^{-11} \exp[-(708 \pm 29)/T]$ was inferred from the measurements of k and k_1 , for the temperature range 256-296 K. k_1/k and k_2/k were determined from the respective yields of HCl (measured by TDLS) and HO at reaction completion, relative to initial [HO₂] in experiments with Cl in excess.

Preferred Values

$k = 4.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ independent of temperature over the range 230 - 420 K.

$k_2/k = 0.21$ at 298 K.

$k_2/k = 1.7 \exp(-620/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230 - 420 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta \log (k_2/k) = \pm 0.1$ at 298 K.

$\Delta(E_2/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values for k and k_2/k are based on results of the direct studies of Lee and Howard (1982), Riffault et al. (2001) and Hickson and Keyser (2005), which are in good agreement. Although all three of these studies report very small negative temperature dependences for the overall k , each also recommends a temperature independent value for the studied temperature range. The preferred value of k is the mean of these temperature independent values. The preferred value of k_2/k at 298 K is the mean of the values reported by Lee and Howard (1982) and Hickson and Keyser (2005) and that derived from the k and k_2 values reported by Riffault et al. (2001); the room temperature results of Cattell and Cox (1986) are also in reasonable agreement with this recommendation. The value of E_2/R , which defines the temperature dependence of k_2 and k_2/k , is the rounded mean of the values reported in the k_2/k determinations of Lee and Howard (1982) and Hickson and Keyser (2005), and the k_2 determination of Riffault et al. (2001), with the pre-exponential factor adjusted to give the preferred value of k_2/k at 298 K. The values of k_1 and k_1/k which can be calculated from the preferred values of k and k_2/k , are also in acceptable agreement with those reported by Hickson et al. (2005). Based on the combined results of the available studies, neither channel shows any pressure dependence between 1 mbar and 1 bar, showing that stabilization of the HOOC1* intermediate does not occur, the two bimolecular channels making up the entire reaction pathway. Dobis and Benson (1993) report a total rate coefficient in good agreement with the preferred value but a significantly lower value of the branching ratio k_2/k . Results of earlier indirect studies (Leu and DeMore, 1976; Poulet et al., 1978, Burrows et al., 1979 and Cox, 1980) were not used in the evaluation of the preferred values.

References

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