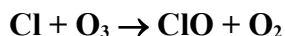


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx14

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 updated: 25th September 2003.



$$\Delta H^\circ = -162.4 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$3.08 \times 10^{-11} \exp[-(290 \pm 25)/T]$	220-350	Watson et al., 1976	FP-RF
$(1.20 \pm 0.10) \times 10^{-11}$	298		
$2.17 \times 10^{-11} \exp[-(171 \pm 30)/T]$	205-366	Zahniser et al., 1976	DF-RF (a)
$(1.23 \pm 0.25) \times 10^{-11}$	298		
$2.72 \times 10^{-11} \exp[-(298 \pm 39)/T]$	213-298	Kurylo and Braun, 1976	FP-RF (a)
$(1.02 \pm 0.15) \times 10^{-11}$	298		
$5.18 \times 10^{-11} \exp[-(418 \pm 28)/T]$	221-629	Clyne and Nip, 1976	DF-RF
$(1.33 \pm 0.26) \times 10^{-11}$	298		
$(1.3 \pm 0.3) \times 10^{-11}$	295	Leu and DeMore, 1976	DF-MS (b)
$(1.3 \pm 0.2) \times 10^{-11}$	298	Toohey et al., 1988	DF-RF
$2.49 \times 10^{-11} \exp[-(233 \pm 46)/T]$	269-385	Nicovich et al., 1990	PLP-RF (c)
$1.19 \times 10^{-11} \exp[-(33 \pm 37)/T]$	189-269		
$(1.14 \pm 0.17) \times 10^{-11}$	298		
$1.59 \times 10^{-11} \exp[-(87 \pm 57)/T]$	206-296	Seeley et al., 1996	DF-RF (d)
$(1.21 \pm 0.13) \times 10^{-11}$	295		
$3.1 \times 10^{-11} \exp[-(280 \pm 100)/T]$	184-298	Beach et al., 2002	DF-RF
$(1.41 \pm 0.08) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
1.17×10^{-11}	197	DeMore, 1991	(e)
1.24×10^{-11}	217		

Comments

- The A factors tabulated are ~8% lower than those originally reported due to a revision of the value used for the O_3 absorption cross-sections.
- Discharge flow system with MS detection of O_3 .
- A change in slope of the Arrhenius plot was observed at ~270 K. The data were fitted to two separate Arrhenius expressions over the temperature ranges 189 K to 269 K and 269 K to 385 K.
- Turbulent flow conditions were used with total pressures in the range 66 mbar to 330 mbar.
- Competitive chlorination of O_3 - CH_4 mixtures. Cl atoms were produced by the photolysis of Cl_2 at 300 nm to 400 nm. The measured rate coefficient ratios $k(\text{Cl} + \text{O}_3)/k(\text{Cl} + \text{CH}_4)$ are placed on an absolute basis using a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Vanderzanden and Birks, 1982).

Preferred Values

$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.8 \times 10^{-11} \exp(-250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 180 K to 300 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta(E/R) = {}^{+100}_{-150} \text{ K}$.

Comments on Preferred Values

The majority of the rate coefficients for this reaction have been obtained at temperatures at and below 298 K, and our evaluation is restricted to that temperature regime. The preferred value of k at 298 K is the mean of the absolute room temperature rate coefficients of Watson et al. (1976), Zahniser et al. (1976), Kurylo and Braun (1976), Clyne and Nip (1976), Leu and DeMore (1976), Toohey et al. (1988), Nicovich et al. (1990) and Seeley et al. (1996), all of which are in excellent agreement. In the recent study of Beach et al. (2002) a slightly, but significantly higher value was obtained at 298 K but the Arrhenius expression for k derived by Beach et al. (2002) from the results over the whole temperature range covered, gives a value of $k(298 \text{ K})$ in excellent agreement with the recommended value. The Arrhenius temperature dependence of k is obtained from a least-squares fit to all of the data at and below 298 K from the studies of Watson et al. (1976), Zahniser et al. (1976), Kurylo and Braun (1976), Clyne and Nip (1976), Leu and DeMore (1976), Toohey et al. (1988) and Beach et al. (2002). This temperature dependence is combined with a pre-exponential factor adjusted to fit the value of k at 298 K.

Nicovich et al. (1990) observed non-Arrhenius behavior in the temperature range studied (189 K to 385 K). The data of Nicovich et al. (1990) are in excellent agreement with the present recommendation above $\sim 250 \text{ K}$; at lower temperatures their data are higher than the recommendation although still within the stated uncertainty down to $\sim 220 \text{ K}$.

Vanderzanden and Birks (1982) have interpreted their observation of oxygen atoms in this system as evidence for some production (0.1% to 0.5%) of $\text{O}_2(^1\Sigma_g)$ in this reaction. The possible production of singlet molecular oxygen in this reaction has also been discussed by DeMore (1981) in connection with the Cl_2 photosensitized decomposition of ozone. However, Choo and Leu (1985) were unable to detect $\text{O}_2(^1\Sigma)$ or $\text{O}_2(^1\Delta)$ in the $\text{Cl} + \text{O}_3$ system and set upper limits to the branching ratios for their production of 5×10^{-4} and 2.5×10^{-2} , respectively. A crossed molecular beam study (Zhang and Lee, 1997) also found no evidence for the production of electronically excited O_2 . Choo and Leu (1985) suggested two possible mechanisms for the observed production of oxygen atoms, involving reactions of vibrationally excited ClO radicals with O_3 or with Cl atoms, respectively. Burkholder et al. (1989) in a study of infrared line intensities of the ClO radical, present evidence in support of the second mechanism. In their experiments with excess Cl atoms, the vibrationally excited ClO radicals produced in the $\text{Cl} + \text{O}_3$ reaction can react with Cl atoms to give Cl_2 and oxygen atoms which can then remove additional ClO radicals (Burkholder et al., 1989). These authors (Burkholder et al., 1989) point out the possibility for systematic error from assuming a 1:1 stoichiometry for $[\text{ClO}] : [\text{O}_3]_0$ when using the $\text{Cl} + \text{O}_3$ reaction as a quantitative source of ClO radicals for kinetic and spectroscopic studies.

References

- Beach, S. D., Smith, I. W. M. and Tuckett, R. P.: *Int. J. Chem. Kinet.* 34, 104, 2002.
- Burkholder, J. B., Hammer, P. D., Howard, C. J. and Goldman, A.: *J. Geophys. Res.* 94, 2225, 1989.
- Choo, K. Y. and Leu, M.-T.: *J. Phys. Chem.* 89, 4832, 1985.
- Clyne, M. A. A. and Nip, W. S.: *J. Chem. Soc. Faraday Trans. 2*, 72, 838, 1976.
- DeMore, W. B.: presented at 182nd National Meeting, American Chemical Society, New York, August, 1981.
- DeMore, W. B. : *J. Geophys. Res.* 96, 4995, 1991.
- IUPAC: Supplement VII, 1999 (see references in Introduction).
- Kurylo, M. J. and Braun, W.: *Chem. Phys. Lett.* 37, 232, 1976.
- Leu, M.-T. and DeMore, W. B.: *Chem. Phys. Lett.* 41, 121, 1976.
- Nicovich, J. M., Kreutter, K. D. and Wine, P. H.: *Int. J. Chem. Kinet.* 22, 399, 1990.
- Seeley, J. V., Jayne, J. T. and Molina, M. J.: *J. Phys. Chem.* 100, 4019, 1996.
- Toohey, D. W., Brune, W. and Anderson, J. G.: *Int. J. Chem. Kinet.* 20, 131, 1988.
- Vanderzanden, J. W. and Birks, J. W.: *Chem. Phys. Lett.* 88, 109, 1982.
- Watson, R. T., Machado, G., Fischer, S. and Davis, D. D.: *J. Chem. Phys.* 65, 2126, 1976.
- Zahniser, M. S., Kaufman, F. and Anderson, J. G.: *Chem. Phys. Lett.* 37, 226, 1976.
- Zhang, J. and Lee, Y. T.: *J. Phys. Chem. A* 101, 6485, 1997.