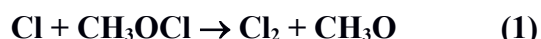


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet IV.A2.89 oClOx15

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 retransmitted or disseminated either electronically or in hardcopy without explicit written permission. The citation for this data sheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Wallington, T. J.: Atmos. Chem. Phys., 8, 4141, 2008; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

This data sheet last evaluated: June 2015; last change in preferred values: November 2003.



$$\Delta H^\circ(1) = -39.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -14.2 \text{ kJ}\cdot\text{mol}^{-1}$$

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>			
$(6.0 \pm 0.2) \times 10^{-11}$	300	Kukui et al., 1997	DF-MS/LIF (a)
<i>Relative Rate Coefficients</i>			
$(6.3 \pm 0.1) \times 10^{-11}$	295	Carl et al., 1996	RR (b)
<i>Branching ratios</i>			
$k_1/k = 0.8 \pm 0.2$	295	Carl et al., 1996	FTIR /UV (c)
$k_2/k = 0.2 \pm 0.1$	295		
$k_1/k = 0.85 \pm 0.06$	300	Kukui et al., 1997	DF-MS/LIF (a)

Comments

- Flow tube operated at 2.5 – 3.5 mbar of He. Cl and Cl₂ monitored as their parent ions, CH₃O was monitored by LIF, but not quantified. The relative sensitivity of the MS to Cl and Cl₂ was determined by titration of Cl to Cl₂ via reaction with NOCl. Rate coefficients were obtained from the Cl decay in excess CH₃OCl, and the branching ratio, k_1/k , was derived by numerical modeling of Cl loss and Cl₂ production processes both in the desired reaction and secondary processes.
- Relative rates of removal of CH₃OCl and C₂H₆ (reference reactant) monitored by FTIR in air and N₂ bath gas at total pressure of 133 to 988 mbar. The value $k/k(\text{Cl} + \text{C}_2\text{H}_6) = 1.07 \pm 0.02$ was combined with $k(\text{Cl} + \text{C}_2\text{H}_6) = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) to yield the value for k listed in the table.
- Branching ratios determined by quantitative analysis of CH₃OCl loss combined with HCl formation (FTIR experiments) and also by CH₃OCl loss combined with Cl₂ formation (UV experiments). The chemistry was initiated by photolysis of Cl₂ or CH₃OCl itself. The HCl formation was modeled to assess the effects of secondary reactions such as Cl + HCHO.

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	6.1×10^{-11}	298
k_1/k	0.85	298
k_2/k	0.15	298
<i>Reliability</i>		
$\Delta \log k$	± 0.1	298
$\Delta(k_1/k)$	± 0.1	298
$\Delta(k_2/k)$	± 0.1	298

Comments on Preferred Values

The preferred values of $k(298 \text{ K})$ is an average of the absolute and relative rate experiments, which are in excellent agreement. A consistent result for the branching ratios also emerges from these studies, and the value obtained by Kukui et al. (1997) for k_1/k is adopted. The product analysis of Carl et al. (1996) provides confirmation of this result, and that channel (2) provides the rest of the product formation. Theoretical work confirms the existence of these two reaction channels, and suggests comparable efficiencies at room temperature and dominance of hydrogen abstraction at higher temperatures (He et al., 2005).

References

- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>
- Carl, S. A., Roehl, C. M., Müller, R., Moortgat, G. K. and Crowley, J. N.: J. Phys. Chem. 100, 17191, 1996.
- He, H.-Q., Liu, J.-Y., Li, Z.-S. and Sun, C.-C.: J. Comput. Chem. 26, 642, 2005.
- Kukui, A., Roggenbuck, J. and Schindler, R. N.: Ber. Bunsenges. Phys. Chem. 101, 281, 1997.