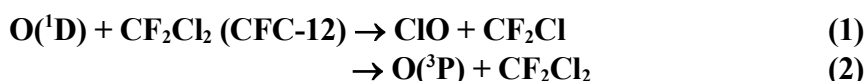


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet IV.A2.83 oClOx9

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Datasheets 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 datasheet last evaluated: June 2015; last change in preferred values: June 2013.



$$\Delta H^\circ(1) = -123 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -190 \text{ kJ mol}^{-1}$$

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>			
$(1.45 \pm 0.5) \times 10^{-10}$	173-343	Davidson et al., 1978	PLP (a)
$(1.4 \pm 0.2) \times 10^{-10}$	298	Force and Wiesenfeld, 1981	PLP-RA
$(1.47 \pm 0.12) \times 10^{-10} \exp[(-25 \pm 8)/T]$	217-372	Baasandorj et al., 2013	PLP-CR (b)
$(1.57 \pm 0.13) \times 10^{-10}$	296		
<i>Branching Ratios</i>			
$k_2/k = 0.14 \pm 0.07$	298	Force and Wiesenfeld, 1981	PLP-RA (c)
$k_1/k = 0.87 \pm 0.18$	298	Takahashi et al., 1996	PLP-LIF (d)
$k_2/k = 0.19 \pm 0.05$	298	Takahashi et al., 1996	PLP-LIF (e)
$k_1/k = 0.76 \pm 0.06$	296	Feierabend et al., 2010	PLP-CRDS (f)

Comments

- Pulsed laser photolysis of O₃ at 266 nm. O(¹D) atoms were monitored by time-resolved emission at 630 nm.
- Pulsed laser photolysis competitive kinetics method used. O(¹D) atoms were produced by 248 nm pulsed laser (KrF excimer) photolysis of O₃ in the presence of CF₂Cl₂ and *n*-C₄H₁₀. O(¹D) atoms react with *n*-C₄H₁₀ to give HO radicals which were monitored by LIF. The initial rate of rise of the HO radical concentration provides a measure of the pseudo-first order loss of O(¹D) in the system from which the rate coefficient for loss of O(¹D) atoms by reaction with CF₂Cl₂ was determined.
- O(¹D) atoms were monitored by resonance absorption at 130.4 nm and compared to O(³P) atoms in the presence of ozone in He diluent where the O(³P) atom yield from the O(¹D) + O₃ reaction is 1.0.
- Branching ratio for ClO formation was determined by measurement of the LIF signal intensity of ClO normalized to that from O(¹D) + HCl.
- Branching ratio for quenching of O(¹D) to O(³P) was determined by comparison of the VUV-LIF signal intensity for CF₂Cl₂ with that of N₂.
- O(¹D) produced by laser photolysis of O₃ at 248 nm. ClO radicals were monitored using cavity ring-down differential absorption spectroscopy near the peak and valley of the 10-0 transition band

head at 279.67 and 279.56 nm of the $A^2\pi \leftarrow X^2\pi$ system. Experiments were performed in 400 – 800 mbar of helium diluent.

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.5×10^{-10}	170-375
k_1/k	0.76	298
k_2/k	0.24	298
<i>Reliability</i>		
$\Delta \log k$	± 0.04	170-350
$\Delta(k_1/k)$	± 0.1	298
$\Delta(k_2/k)$	± 0.1	298

Comments on Preferred Values

The measurements of k near 298 K by Davidson et al. (1978), Force and Wiesenfeld (1981), and Baasandorj et al. (2013) are in excellent agreement and the preferred value is an average of results from these studies. The studies by Davidson et al. (1978) and Baasandorj et al. (2013) show that there is no discernible effect of temperature on k over the range 170 – 375 K. The branching ratio k_1/k is taken from Feierabend et al. (2010) which is consistent with, but more precise than, the result reported by Takahashi et al. (1996). The preferred value of the branching ratio k_2/k is equal to $1 - k_1/k$ and is consistent with the values reported by Force and Wiesenfeld (1981) and Takahashi et al. (1996).

References

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