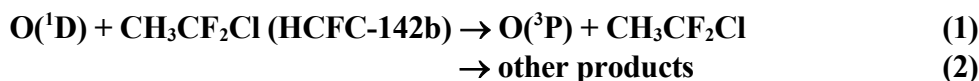


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet IV.A2.77 oClOx3

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.



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

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>			
$(2.15 \pm 0.20) \times 10^{-10}$	298	Warren et al., 1991	PLP-RF
$(1.80 \pm 0.12) \times 10^{-10} \exp[(-0 \pm 45)/T]$	217-373	Baasandorj et al., 2013	PLP-CR (a)
$(1.86 \pm 0.09) \times 10^{-10}$	296		
<i>Branching Ratios</i>			
$k_1/k = 0.26 \pm 0.05$	298	Warren et al., 1991	PLP-RF (b)
<i>Relative Rate Coefficients</i>			
$k_2 = (1.39 \pm 0.35) \times 10^{-10}$	297	Green and Wayne, 1976	RR (c)
$k_2 = (1.06 \pm 0.03) \times 10^{-10}$	296	Baasandorj et al., 2013	RR (d)
$k_2 = (1.15 \pm 0.02) \times 10^{-10}$			

Comments

- (a) Pulsed laser photolysis competitive kinetics method used. O(¹D) atoms were produced by 248 nm pulsed laser (KrF eximer) photolysis of O₃ in the presence of CH₃CF₂Cl 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 CH₃CF₂Cl was determined.
- (b) Branching ratio was determined from the ratio of the O(³P) yield from O(¹D) + CH₃CF₂Cl relative to that for O(¹D) + N₂.
- (c) O(¹D) produced by photolysis of NO₂ at 229 nm. Δ(CH₃CF₂Cl)/Δ(N₂O) monitored by IR absorption spectroscopy. Measured rate coefficient ratio of $k_2/k(\text{O}(^1\text{D}) + \text{N}_2\text{O}) = 1.2 \pm 0.3$ is placed on an absolute basis using $k(\text{O}(^1\text{D}) + \text{N}_2\text{O}) = 1.16 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2004). The cited rate coefficient refers to chemical reaction only and does not include physical quenching.
- (d) O(¹D) atoms were produced by 248 nm pulsed laser (KrF eximer) photolysis of O₃ in the presence of CH₃CF₂Cl and the reference compounds CHF₂Cl or CF₃CF₂Cl. The loss of CH₃CF₂Cl and the reference compounds were monitored by FTIR and reactive rate coefficient ratios of $k(\text{O}(^1\text{D}) + \text{CH}_3\text{CF}_2\text{Cl})/k(\text{O}(^1\text{D}) + \text{CHF}_2\text{Cl}) = 1.38 \pm 0.03$ and $k(\text{O}(^1\text{D}) + \text{CH}_3\text{CF}_2\text{Cl})/k(\text{O}(^1\text{D}) + \text{CF}_3\text{CF}_2\text{Cl}) = 2.23 \pm 0.03$ was measured. Using reactive rate coefficients $k(\text{O}(^1\text{D}) + \text{CHF}_2\text{Cl}) = (7.70 \pm 0.13) \times 10^{-11}$ and $k(\text{O}(^1\text{D}) + \text{CF}_3\text{CF}_2\text{Cl}) = (5.16 \pm 0.18) \times 10^{-11}$ (Baasandorj et al., 2013) gives reactive rate coefficients $k(\text{O}(^1\text{D}) + \text{CH}_3\text{CF}_2\text{Cl}) = k_2$ of $(1.06 \pm 0.03) \times 10^{-10}$ and $(1.15 \pm 0.02) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.0×10^{-10}	215-375
k_1/k	0.36	298
<i>Reliability</i>		
$\Delta \log k$	± 0.06	298
$\Delta(k_1/k)$	± 0.1	298

Comments on Preferred Values

The preferred value of k is based upon the results from Warren et al. (1991) and Baasandorj et al. (2013) which are in good agreement. Combining the values of k_2 measured by Green and Wayne (1976) and Baasandorj et al. (2013) with the preferred value of k gives branching ratios of $k_2/k = 0.70 \pm 0.18$, 0.53 ± 0.08 , and 0.58 ± 0.09 . The results from Warren et al. (1991) provide a value of $k_2/k = 0.74 \pm 0.05$. Clearly there are some discrepancies between the reported results. Taking an average gives $k_2/k = 0.64$ which gives $k_1/k = 0.36$.

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., 4, 1461, 2004; IUPAC Subcommittee for Gas Kinetic Data Evaluation, <http://www.iupac-kinetic.ch.cam.ac.uk>
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- Warren, R., Gierczak, T. and Ravishankara, A. R.: Chem. Phys. Lett., 183, 403, 1991.

