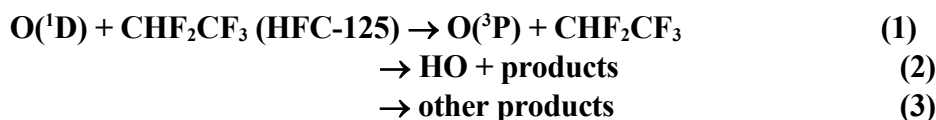


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx9

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

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_2 + k_3 = (4.6 \pm 1.2) \times 10^{-11}$	297	Green and Wayne, 1976	RR (a)
$k = (1.23 \pm 0.06) \times 10^{-10}$	298	Warren et al., 1991	PLP-RF (b)
$k = 1 \left(\begin{smallmatrix} +1.0 \\ -0.5 \end{smallmatrix} \right) \times 10^{-11}$	298	Kono and Matsumi, 2001	PLP-LIF (c)
$(9.5 \pm 1.1) \times 10^{-12} \exp[(25 \pm 30)/T]$	217-373	Baasandorj et al., 2013	PLP-CR (d)
$(1.01 \pm 0.04) \times 10^{-11}$	296		
<i>Relative Rate Coefficients</i>			
$k_2 + k_3 = (7.95 \pm 0.70) \times 10^{-12}$	296	Baasandorj et al., 2013	RR (e)
$k_2 + k_3 = (6.72 \pm 0.66) \times 10^{-12}$			
<i>Branching Ratios</i>			
$k_1/k = 0.85 \left(\begin{smallmatrix} +0.15 \\ -0.22 \end{smallmatrix} \right)$	298	Warren et al., 1991	PLP-RF (b,f)
$k_1/k = 0.24 \pm 0.04$	298	Kono and Matsumi, 2001	PLP-LIF (c,f)
$k_2/k = 0.6 \pm 0.1$			(g)
$k_3/k = 0.2 \pm 0.1$			(h)

Comments

- (a) O(¹D) produced by photolysis of NO₂ at 229 nm. Δ(CHF₂CF₃)/Δ(N₂O) monitored by IR absorption spectroscopy. Measured rate coefficient ratio of $(k_2+k_3)/k(\text{O}(^1\text{D}) + \text{N}_2\text{O}) = 0.4 \pm 0.1$ is placed on an absolute basis by use of $k(\text{O}(^1\text{D}) + \text{N}_2\text{O}) = 1.16 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2004). The cited rate coefficient refers to chemical reaction only and does not include physical quenching.
- (b) O(¹D) produced by photolysis of O₃ at 248 nm. Resonance fluorescence used to follow O(³P) atoms, Rate constant for the overall reaction $(k_1 + k_2 + k_3)$ determined from rate of formation of O(³P).
- (c) O(¹D) produced by photolysis of N₂O at 193 nm. Rate constant for the overall reaction $(k_1 + k_2 + k_3)$ determined by using LIF (at 115.22 nm) to monitor the rate of loss of O(¹D) atoms in presence of CHF₂CF₃.
- (d) 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 CHF₂CF₃ 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 CHF₂CF₃ was determined.

- (e) O(¹D) atoms were produced by 248 nm pulsed laser (KrF excimer) photolysis of O₃ in the presence of CHF₂CF₃ and a reference compound (NF₃ or CHF₃). The loss of CHF₂CF₃ and the reference compound were monitored by FTIR and reactive rate coefficient ratios of $k(\text{O}^1\text{D}) + \text{CHF}_2\text{CF}_3 / k(\text{O}^1\text{D}) + \text{NF}_3 = 0.356 \pm 0.030$ and $k(\text{O}^1\text{D}) + \text{CHF}_2\text{CF}_3 / k(\text{O}^1\text{D}) + \text{CHF}_3 = 2.86 \pm 0.14$ was measured. Using reactive rate coefficients of $k(\text{O}^1\text{D}) + \text{NF}_3 = (2.21 \pm 0.33) \times 10^{-11}$ (Baasandorj et al., 2012) and $k(\text{O}^1\text{D}) + \text{CHF}_3 = (2.35 \pm 0.04) \times 10^{-12}$ gives reactive rate coefficients $k(\text{O}^1\text{D}) + \text{CHF}_2\text{CF}_3 = k_2 + k_3 = (7.95 \pm 0.70) \times 10^{-12}$ and $(6.72 \pm 0.66) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (f) Branching ratio was determined from the ratio of the O(³P) yield from O(¹D) + CHF₂CF₃ relative to that for O(¹D) + N₂.
- (g) Branching ratio determined by monitoring the yield of OH radicals (using LIF at 282 nm) from O(¹D) + CHF₂CF₃ relative to that for O(¹D) + H₂O.
- (h) Inferred from $k_3/k = 1 - (k_1/k + k_2/k)$

Preferred Values

$$k = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 9.5 \times 10^{-12} \exp(25/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

$$k_1/k = 0.25 \text{ at } 298 \text{ K.}$$

$$k_2/k = 0.60 \text{ at } 298 \text{ K.}$$

$$k_3/k = 0.15 \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1$$

$$\Delta(k_1/k) = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(k_2/k) = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(k_3/k) = \pm 0.1 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The value of k reported by Warren et al. (1991) is approximately an order of magnitude, larger than those reported by Kono and Matsumi (2001) and Baasandorj et al. (2013). Warren et al. (1991) report that the quenching of O(¹D) to O(³P) is the dominant process (channel (1)). In contrast, Kono and Matsumi (2001) report that production of OH is the dominant process (channel (2)) and Baasandorj et al. (2013) report a reactive (channels (2) + (3)) branching ratio of 0.73 ± 0.09 . Baasandorj et al. (2013) used an absolute rate technique to measure the total reaction rate $k_1 + k_2 + k_3$. Baasandorj et al. (2013) used a relative rate technique to measure $k_2 + k_3$ and obtained consistent results using two reference compounds whose reactivity differed by an order of magnitude. Combining the results from the absolute and relative rate techniques employed by Baasandorj et al. (2013) gives a branching ratio for the quenching channel, k_1/k , of 0.27 ± 0.09 . This result is in good agreement with the direct measurement of the O(³P) yield by Kono and Matsumi (2001) giving $k_1/k = 0.24 \pm 0.04$. The results from the studies by Kono and Matsumi (2001) and Baasandorj et al. (2013) provide a comprehensive and consistent picture of the reaction kinetics and mechanism. The preferred Arrhenius expression and $k(298\text{K})$ are taken from Baasandorj et al. (2013), the preferred branching ratios at 298 K are based on the work of Kono and Matsumi (2001).

Green and Wayne (1976) conducted a relative rate study in which NO₂-CHF₂CF₂-N₂O mixtures were subjected to 229 nm UV irradiation. Photolysis of NO₂ generated O(¹D) atoms and the relative decays of CHF₂CF₃ and N₂O were used to derive the rate constant ratio $(k_2+k_3)/k(\text{O}^1\text{D}) + \text{N}_2\text{O}$. It can be argued that radical products (e.g., HO in channel (2)) could react with CHF₂CF₃ leading to an overestimation of $(k_2+k_3)/k(\text{O}^1\text{D}) + \text{N}_2\text{O}$. It is unclear why the rate coefficient and quenching branching ratio reported by Warren et al. (1991) are substantially greater than observed by Kono and Matsumi (2001) and Baasandorj et al. (2013). Given the consistency of results from these two studies and the comprehensive nature of the

investigation by Baasandorj et al. (2013) we conclude that the data reported by Warren et al. (1991) for this reaction are erroneous.

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://iupac.pole-ether.fr>
- Baasandorj, M., Fleming, E. L., Jackman, C. H., and Burkholder, J. B.: J. Phys. Chem., 117, 2434, 2013.
- Baasandorj, M., Hall, B. D., and Burkholder, J. B.: Atmos. Chem. Phys. 12, 11753, 2012.
- Green, R. G. and Wayne, R. P.: J. Photochem. 6, 371, 1976.
- Kono, M., Matsumi, Y.: J. Phys. Chem. A., 105, 65, 2001.
- Warren, R., Gierczak, T. and Ravishankara, A. R.: Chem. Phys. Lett., 183, 403, 1991.

