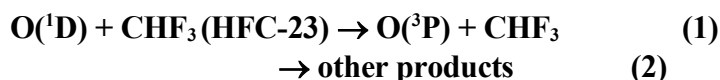


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx4

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., 9, 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>			
$(8.4 \pm 0.8) \times 10^{-12}$	298	Force and Wiesenfeld, 1981	PLP-RA
$(9.76 \pm 0.60) \times 10^{-12}$	298	Schmoltner et al., 1993	PLP-RF
$(8.7 \pm 0.3) \times 10^{-12} \exp[(30 \pm 10)/T]$	217-373	Baasandorj et al., 2013	PLP-CR (a)
$(9.6 \pm 0.7) \times 10^{-12}$	296		
<i>Relative Rate Coefficients</i>			
$k_2 = (2.35 \pm 0.35) \times 10^{-12}$	296	Baasandorf et al., 2012	RR (b)
<i>Branching Ratios</i>			
$k_1/k = 0.77 \pm 0.15$	298	Force and Wiesenfeld, 1981	PLP-RA (c)
$k_1/k = 1.02 \pm 0.03$	298	Schmoltner et al., 1993	PLP-RF (d)
$k_2/k = 0.26$	296	Schmoltner et al., 1993	PLP-RF (e)

Comments

- (a) Pulsed laser photolysis competitive kinetics method used. $\text{O}(^1\text{D})$ atoms were produced by 248 nm pulsed laser (KrF excimer) photolysis of O_3 in the presence of CHF_3 and $n\text{-C}_4\text{H}_{10}$. $\text{O}(^1\text{D})$ atoms react with $n\text{-C}_4\text{H}_{10}$ 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 $\text{O}(^1\text{D})$ in the system from which the rate coefficient for loss of $\text{O}(^1\text{D})$ atoms by reaction with CHF_3 can be determined.
- (b) $\text{O}(^1\text{D})$ atoms were produced by 248 nm pulsed laser (KrF excimer) photolysis of O_3 in the presence of CHF_3 and NF_3 . The loss of CHF_3 and NF_3 was monitored by FTIR and a reactive rate coefficient ratio of $k(\text{O}(^1\text{D}) + \text{CHF}_3)/k(\text{O}(^1\text{D}) + \text{NF}_3) = 0.106 \pm 0.001$ was measured. Using a reactive rate coefficient of $k(\text{O}(^1\text{D}) + \text{NF}_3) = (2.21 \pm 0.33) \times 10^{-11}$ (Baasandorf et al., 2012) gives the reactive rate coefficient $k(\text{O}(^1\text{D}) + \text{CHF}_3) = k_2 = (2.35 \pm 0.35) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (c) $\text{O}(^3\text{P})$ atoms were monitored by resonance absorption at 130.4 nm and compared to $\text{O}(^3\text{P})$ atoms in the presence of ozone in He diluent where the $\text{O}(^3\text{P})$ atom yield from the $\text{O}(^1\text{D}) + \text{O}_3$ reaction is 1.0.
- (d) Branching ratio was determined from the ratio of the $\text{O}(^3\text{P})$ yield from $\text{O}(^1\text{D}) + \text{CHF}_3$ relative to that for $\text{O}(^1\text{D}) + \text{N}_2$.

- (e) Branching ratio determined from the ratio of $k_2 = (2.35 \pm 0.35) \times 10^{-11}$ to the preferred value of $k = 9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

$$k = 9.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 8.77 \times 10^{-12} \exp(30/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

$$k_1/k = 0.75 \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.04 \text{ at } 298 \text{ K.}$$

$$\Delta(k_1/k) = \pm 0.05 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The absolute determinations of the total rate coefficient k at, and near, 298 K by Force and Wiesenfeld (1981), Schmoltner et al. (1993), and Baasandorj et al. (2013) are in good agreement. The preferred value of k is the average of the values reported by Schmoltner et al. (1993), and Baasandorj et al. (2013). Baasandorj et al. (2013) studied the kinetics as a function of temperature and reported a small negative temperature dependence described by $E/R = -30 \pm 10$. Our preferred Arrhenius expression was derived by taking the temperature dependence reported by Baasandorj et al. (2013) with an A factor chosen to reproduce the preferred $k(298\text{K})$ value. Branching ratios for k_2/k have been reported by Force and Wiesenfeld (1981), Schmoltner et al. (1993), and Baasandorj et al. (2012). The finding by Schmoltner et al. (1993) that channel (2) plays essentially no role in the reaction is inconsistent with values of $k_2/k = 0.23 \pm 0.15$ and $k_2/k = 0.26$ derived from the work by Force and Wiesenfeld (1981) and Baasandorj et al. (2012). The branching ratio determined by Schmoltner et al. (1993) is also inconsistent with the observation of stimulated emissions from vibrationally excited HF by Burks and Lin (1981) and Aker et al. (1987) and with the observation of COF₂ product by FTIR spectroscopy (although its yield was not quantified). The preferred value of the branching ratio k_1/k is the average of the values derived from the work of Force and Wiesenfeld (1981) and Baasandorj et al. (2012).

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