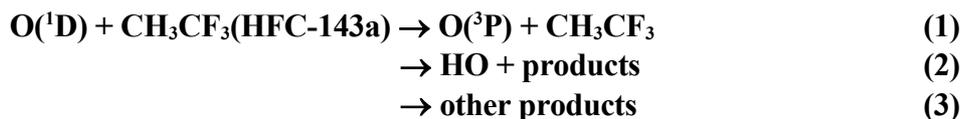


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx7

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This datasheet last evaluated: June 2015; last change in preferred values: July 2007.



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

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>			
$(4.0 \pm 0.5) \times 10^{-11}$	298	Kono and Matsumi, 2001	PLP-LIF (a)
$(5 \pm 1) \times 10^{-11}$	298?		PLP-LIF (b)
$(6.5 \pm 0.6) \times 10^{-11} \exp[(20 \pm 25)/T]$	217-373	Baasandorj et al., 2013	PLP-CR (c)
$(7.08 \pm 0.44) \times 10^{-11}$	296		
<i>Relative Rate Coefficients</i>			
$k_2 + k_3 = (5.8 \pm 2.0) \times 10^{-11}$	298	Green and Wayne, 1976	RR (d)
$k_2 + k_3 = (4.23 \pm 0.08) \times 10^{-11}$	298	Baasandorj et al., 2013	RR (e)
$k_2 + k_3 = (3.80 \pm 0.15) \times 10^{-11}$	298	Baasandorj et al., 2013	RR (e)
$k_2 + k_3 = (3.70 \pm 0.15) \times 10^{-11}$	298	Baasandorj et al., 2013	RR (e)
<i>Branching Ratios</i>			
$k_1/k = 0.18 \pm 0.04$	298	Kono and Matsumi, 2001	PLP-LIF (f)
$k_2/k = 0.38 \pm 0.06$			(g)
$k_3/k = 0.44 \pm 0.07$			(h)

Comments

- 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.
- Rate constant for the overall reaction ($k_1 + k_2 + k_3$) determined by using LIF (at 130.22 nm) to monitor the rate of formation of O(³P) atoms from the O(¹D) + CH₃CF₃ reaction.
- 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 CH₃CF₃ 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 CH₃CF₃ can be determined.
- O(¹D) produced by photolysis of NO₂ at 229 nm. Δ(CH₃CF₃)/Δ(N₂O) monitored by IR absorption spectroscopy. Measured rate coefficient ratio of $k_2/k(\text{O}(^1\text{D}) + \text{N}_2\text{O}) = 0.5 \pm 0.1$ 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.

- (e) O(¹D) atoms were produced by 248 nm pulsed laser (KrF eximer) photolysis of O₃ in the presence of CH₃CF₃ and a reference compound (NF₃, CF₃CF₂Cl or CHClF₂). The loss of CH₃CF₃ and the reference compound were monitored by FTIR and reactive rate coefficient ratios of $k(\text{O}^1\text{D}) + \text{CH}_3\text{CF}_3 / k(\text{O}^1\text{D}) + \text{NF}_3 = 1.93 \pm 0.04$, $k(\text{O}^1\text{D}) + \text{CH}_3\text{CF}_3 / k(\text{O}^1\text{D}) + \text{CF}_3\text{CF}_2\text{Cl} = 0.74 \pm 0.03$, and $k(\text{O}^1\text{D}) + \text{CH}_3\text{CF}_3 / k(\text{O}^1\text{D}) + \text{CHClF}_2 = 0.49 \pm 0.01$ were measured. Using reactive rate coefficients of $k(\text{O}^1\text{D}) + \text{NF}_3 = (2.2 \pm 0.3) \times 10^{-11}$, $k(\text{O}^1\text{D}) + \text{CF}_3\text{CF}_2\text{Cl} = (5.16 \pm 0.18) \times 10^{-11}$, and $k(\text{O}^1\text{D}) + \text{CHClF}_2 = (7.70 \pm 0.13) \times 10^{-11}$ (Baasandorj et al., 2012; Baasandorj et al., 2013) gives reactive rate coefficients $k_2 + k_3 = (4.23 \pm 0.08) \times 10^{-11}$, $(3.80 \pm 0.15) \times 10^{-11}$ and $(3.70 \pm 0.15) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.
- (f) Branching ratio determined by monitoring the yield of O(³P) atoms (using LIF at 115.22 nm) from O(¹D) + CH₃CHF₂ 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) + CH₃CHF₂ relative to that for O(¹D) + H₂O.
- (h) Inferred from $k_3/k = 1 - (k_1/k + k_2/k)$

Preferred Values

$k = 7.1 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

$k = 6.5 \times 10^{-11} \exp(20/T)$ cm³ molecule⁻¹ s⁻¹.

$k_1/k = 0.45$ at 298 K.

$k_2/k + k_3/k = 0.55$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$

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

$\Delta(k_2/k + k_3/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

There is a significant discrepancy between the values of k reported by Kono and Matsumi (2001) and Baasandorj et al. (2013). In addition to the absolute rate measurement of k , Baasandorj et al. (2013) measured $k_2 + k_3$ using a relative rate method. Baasandorj et al. (2013) reported consistent results from experiments using three different reference compounds with substantially different absolute rates. The branching ratio of $(k_2 + k_3) = 0.55 \pm 0.04$ reported by Baasandorj et al. (2013) is consistent with the expectation that a substantial fraction of the reaction proceeds via reactive channels. Baasandorj et al. (2013) report a large body of self-consistent data and is adopted as the preferred values. The results from the study by Green and Wayne (1976) are consistent with the preferred values.

References

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