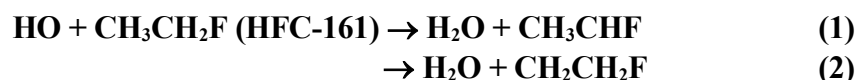


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx14

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This datasheet last evaluated: June 2015; last change in preferred values: March 2005.



$$\Delta H^\circ(1) = -74.4 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -59.6 \text{ kJ mol}^{-1}$$

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>			
$(2.32 \pm 0.37) \times 10^{-13}$	297 ± 2	Nip et al., 1979	FP-RA
$2.69 \times 10^{-12} \exp[-(750 \pm 100)/T]$	243-373	Schmoltnner et al., 1993	PLP/FP-LIF
$(2.17 \pm 0.29) \times 10^{-13}$	298		
$6.78 \times 10^{-12} \exp[-(1033 \pm 74)/T]$	298-480	Kozlov et al., 2003	FP-RF
$2.42 \times 10^{-12} \exp[-(716 \pm 36)/T]$	210-298		
$(2.20 \pm 0.033) \times 10^{-13}$	298		
<i>Relative Rate Coefficients</i>			
$1.73 \times 10^{-17} T^2 \exp[-(657 \pm 36)/T]$	285-364	Hsu and DeMore, 1995	RR (a)
1.69×10^{-13}	298		

Comments

- (a) HO radicals were generated by the photolysis of H₂O at 185 nm or of H₂O-O₃ mixtures in the UV in H₂O (or H₂O-O₃)-CH₃CH₂F-C₂H₆-O₂-N₂ mixtures. The concentrations of CH₃CH₂F and C₂H₆ were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{CH}_2\text{F})/k(\text{HO} + \text{C}_2\text{H}_6) = (1.16 \pm 0.13) \exp[-(158 \pm 36)/T]$ is placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{C}_2\text{H}_6) = 1.49 \times 10^{-17} T^2 \exp(-499/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

$$k = 2.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.7 \times 10^{-12} \exp(-765/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 210\text{-}300 \text{ K.}$$

$$k_1/k = 0.85 \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

$$\Delta k_1/k = \pm 0.15 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The rate coefficients of Nip et al. (1979), Schmoltner et al. (1993) and Kozlov et al. (2003) are in good agreement over the temperature range 243-373 K. The relative rate coefficients of Hsu and DeMore (1995) display a higher temperature dependence compared to that observed by Schmoltner et al. (1993) and Kozlov et al. (2003). At room temperature, the rate coefficients of Hsu and DeMore (1995) are ~35% lower than those of Nip et al. (1979), Schmoltner et al. (1993) and Kozlov et al. (2003). The source of the disagreement is not known although impurities in the reactant were ruled out (Kozlov et al. 2003). Above 298 K (329-364 K), the agreement between the data of Hsu and DeMore (1995), Schmoltner et al. (1993) and Kozlov et al. (2003) is better. The study by Kozlov et al. (2003) shows curvature in the Arrhenius plot. Singleton et al. (1980) determined that 85% of the abstraction by OH is from the CH₂F group at 298 K. Therefore, at least some of the observed curvature is probably due to the increasing importance of H atom abstraction from the unsubstituted methyl group (CH₃) with increasing temperature. The absolute rate coefficients of Nip et al. (1979), Schmoltner et al. (1993) and Kozlov et al. (2003) were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 6.12 \times 10^{-18} T^2 \exp(-275/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 210-480 K. The preferred Arrhenius expression $k = A \exp(-B/T)$ is centered at 245 K and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The relative rate data of Hsu and DeMore (1995) are approximately 20-30% lower than the preferred value at 298 K.

References

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