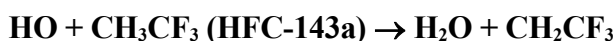


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx16

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



$$\Delta H^\circ = -47.4 \text{ kJ mol}^{-1}$$

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./ K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.92 \pm 1.20) \times 10^{-11} \exp[-(3200 \pm 500)/T]$	333-425	Clyne and Holt, 1979	DF-RF (a)
$<1.0 \times 10^{-15}$	293		
$(1.71 \pm 0.43) \times 10^{-15}$	298	Martin and Paraskevopoulos, 1983	FP-RA
$2.12 \times 10^{-12} \exp[-(2200 \pm 200)/T]$	261-374	Talukdar et al., 1991	DF-LMR/FP-LIF (b)
$(1.35 \pm 0.25) \times 10^{-15}$	298		
$9.51 \times 10^{-13} \exp[-(1979 \pm 65)/T]$	298-370	Orkin et al., 1996	FP-RF
$(1.24 \pm 0.09) \times 10^{-15}$	298		
<i>Relative Rate Coefficients</i>			
$7.96 \times 10^{-21} T^{2.82} \exp[-(1210 \pm 90)/T]$	298-403	Hsu and DeMore, 1995	RR (c,d)
$1.30 \times 10^{-15}$	298		
$2.00 \times 10^{-18} T^2 \exp[-(1490 \pm 21)/T]$	298-383	Hsu and DeMore, 1995	RR (c,e)
$1.20 \times 10^{-15}$	298		

## Comments

- Although experiments were conducted over the temperature range 293-425 K, only an upper limit to the rate coefficient was obtained at 293 K.
- Kinetic data were obtained over the temperature range 223-374 K. Because the Arrhenius plot exhibited curvature below 261 K, the Arrhenius expression cited in the table was derived from the rate coefficients between 261-374 K.
- HO radicals generated by the photolysis of H<sub>2</sub>O at 185 nm or of O<sub>3</sub>-H<sub>2</sub>O mixtures in the UV in H<sub>2</sub>O (or O<sub>3</sub>-H<sub>2</sub>O)-CH<sub>3</sub>CF<sub>3</sub>-CH<sub>4</sub>(or CHF<sub>2</sub>CF<sub>3</sub>)-O<sub>2</sub>-N<sub>2</sub> mixtures. The concentrations of CH<sub>3</sub>CF<sub>3</sub> and CH<sub>4</sub> (or CHF<sub>2</sub>CF<sub>3</sub>) were measured by FTIR spectroscopy.
- The measured rate coefficient ratio  $k(\text{HO} + \text{CH}_3\text{CF}_3)/k(\text{HO} + \text{CH}_4) = (0.43 \pm 0.12) \exp[-(223 \pm 90)/T]$  was placed on an absolute basis by use of the rate coefficient  $k(\text{HO} + \text{CH}_4) = 1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).
- The measured rate coefficient ratio  $k(\text{HO} + \text{CH}_3\text{CF}_3)/k(\text{HO} + \text{CHF}_2\text{CF}_3) = (2.16 \pm 0.14) \exp[-(370 \pm 21)/T]$  was placed on an absolute basis by use of the rate coefficient  $k(\text{HO} + \text{CHF}_2\text{CF}_3) = 9.24 \times 10^{-19} T^2 \exp(-1120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

## Preferred Values

$$k = 1.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$k = 9.2 \times 10^{-13} \exp(-1970/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220-300 K.

#### *Reliability*

$\Delta \log k = \pm 0.15$  at 298 K.

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

#### *Comments on Preferred Values*

The room temperature absolute rate coefficients of Martin and Paraskevopoulos (1983) and Talukdar et al. (1991) agree to within 20%, and taking into account the respective uncertainties in both studies, the agreement is reasonable. The rate coefficients of Hsu and DeMore, (1995) relative to the rate coefficients for the reactions of the HO radical with CH<sub>4</sub> and CHF<sub>2</sub>CF<sub>3</sub>, are in excellent agreement with each other. The rate coefficients of Orkin et al. (1996) are also in quite good agreement with the rate coefficients of Talukdar et al. (1991) and both sets of relative rate coefficients determined by Hsu and DeMore (1995). The rate coefficients of Clyne and Holt (1979) are not used in the evaluation because their rate coefficients at 333 K and 378 K are significantly higher than those of the other studies and have large associated uncertainties.

The rate coefficients of Martin and Paraskevopoulos (1983), Talukdar et al. (1991) (using their entire data set over the temperature range 223-374 K), Orkin et al. (1996), and Hsu and DeMore (1995) have been fitted to the three parameter equation  $k = CT^2 \exp(-D/T)$ , resulting in  $k = 1.91 \times 10^{-18} T^2 \exp(-1456/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 223-403 K. The preferred Arrhenius expression  $k = A \exp(-B/T)$ , is centered at 255 K and is derived from the three parameter equation with  $A = C e^2 T^2$  and  $B = D + 2T$ . The preferred values are 13 % lower and 9 % higher than the values of Talukdar et al. (1991) at 223 K and 261 K, respectively.

#### **References**

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