

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx10

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$$\Delta H^\circ = -78.2 \text{ kJ mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp/K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.60 \pm 0.35) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
$(2.18 \pm 0.18) \times 10^{-14}$	297	Nip et al., 1979	FP-RA
$8.11 \times 10^{-12} \exp[-(1887 \pm 61)/T]$	292-480	Jeong et al., 1984	DF-RF (a)
$(1.40 \pm 0.09) \times 10^{-14}$	292		
$(1.71 \pm 0.24) \times 10^{-14}$	298	Bera and Hanrahan, 1988	PR-A
$1.75 \times 10^{-12} \exp[-(1300 \pm 100)/T]$	243-373	Schmoltnner et al., 1993	PLP/FP-LIF
$(2.09 \pm 0.08) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$(1.71 \pm 0.08) \times 10^{-14}$	296 ± 2	Wallington and Hurley, 1993	RR (b)
$(1.41 \pm 0.07) \times 10^{-14}$	296 ± 2	Wallington and Hurley, 1993	RR (c)
$(1.32 \pm 0.12) \times 10^{-14}$	295	Møgelberg et al., 1994	RR (d)
$2.77 \times 10^{-18} T^2 \exp[-(754 \pm 34)/T]$	298-363	Hsu and DeMore, 1995	RR (e)
1.96×10^{-14}	298		
$4.21 \times 10^{-18} T^2 \exp[-(856 \pm 82)/T]$	308-393	DeMore, 1996	RR (f)

Comments

- The rate expression cited in Jeong et al. (1984) supersedes that reported in Jeong and Kaufman (1982). Jeong et al. (1984) also corrects an erroneously reported rate measurement at 480 K.
- HO radicals were generated by photolysis of CH_3ONO at 933 mbar total pressure of air. The decay of CH_3F was inferred from the measured formation of HC(O)F , using a formation yield of HC(O)F of 0.90 as measured in separate $\text{Cl}_2\text{-CH}_3\text{F-NO-air}$ irradiations. The concentrations of HC(O)F and acetylene were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{F})/k(\text{HO} + \text{C}_2\text{H}_2) = 0.0201 \pm 0.0009$ was placed on an absolute basis by using $k(\text{HO} + \text{C}_2\text{H}_2) = 8.49 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K and 1013 mbar air (Sørensen et al. 2003).
- HO radicals generated by the photolysis of O_3 at 254 nm in the presence of H_2 . The concentrations of CH_4 and CH_3F were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{F})/k(\text{HO} + \text{CH}_4) = 2.30 \pm 0.11$ was placed on an absolute basis by using $k(\text{HO} + \text{CH}_4) = 6.14 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- HO radicals generated by the photolysis of O_3 at 254 nm in the presence of H_2 . The decay of

CH₄ and CH₃F concentrations was monitored by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{F})/k(\text{HO} + \text{CH}_4) = 2.2 \pm 0.2$ was placed on an absolute basis by using $k(\text{HO} + \text{CH}_4) = 6.01 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (IUPAC, current recommendation).

- (e) HO radicals were generated by the photolysis of H₂O at 185 nm or of O₃-H₂O mixtures in the UV in H₂O (or O₃-H₂O)-CH₃F-CH₃CHF₂-O₂-N₂ mixtures. The concentrations of CH₃F and CH₃CHF₂ were measured by IR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{F})/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (0.99 \pm 0.10) \exp[-(174 \pm 34)/T]$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 2.80 \times 10^{-18} T^2 \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- (f) HO radicals generated by the photolysis of O₃ at 254 nm in the presence of H₂O vapour. The decay of CH₃Cl and CH₃F concentrations was monitored by FTIR spectroscopy. The rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{F})/k(\text{HO} + \text{CH}_3\text{Cl}) = (0.97 \pm 0.23) \exp[-(156 \pm 82)/T]$ was measured over the temperature range 308-393 K. The rate coefficient ratio was placed on an absolute basis by using $k(\text{HO} + \text{CH}_3\text{Cl}) = 4.34 \times 10^{-18} T^2 \exp(-700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

$k = 2.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.9 \times 10^{-12} \exp(-1350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240-300 K.

Reliability

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

$\Delta(E/R) = \pm 400 \text{ K}$.

Comments on Preferred Values

The absolute rate coefficients of Schmoltner et al. (1993) are higher than those reported previously by Jeong and Kaufman (1982) and Jeong et al. (1984), although the discrepancy decreases with increasing temperature. The absolute rate coefficients of Schmoltner et al. (1993), although exhibiting scatter at temperatures $\sim 273 \text{ K}$, are in good agreement with the relative rate coefficients of Hsu and DeMore (1995) and DeMore (1996) at 298 K and above. The absolute rate coefficient of Nip et al. (1979) is in good agreement with the data of Schmoltner et al. (1993), Hsu and DeMore (1995) and DeMore (1996). Because secondary reactions of HO radicals with CH₂F radicals and other radical species were expected to have occurred in the study of Bera and Hanrahan (1988), their rate coefficient was consequently not used in the evaluation. The absolute rate coefficients of Howard and Evenson (1976), Jeong and Kaufman (1982), Wallington and Hurley (1993), and Møgelberg et al. (1994) appear to be systematically lower than other studies, and therefore they were not used in the evaluation.

The data of Nip et al. (1979), Schmoltner et al. (1993), Hsu and DeMore (1995) and DeMore (1996) were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 3.66 \times 10^{-18} T^2 \exp(-818/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 243-393 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

Marinkovic et al. (2008) investigated the carbon-13 and deuterium kinetic isotope effects and determined $k(\text{HO} + \text{CH}_3\text{F})/k(\text{OH} + \text{CD}_3\text{F}) = 4.067 \pm 0.018$ and $k(\text{HO} + \text{CH}_3\text{F})/k(\text{OH} + {}^{13}\text{CH}_3\text{F}) = 1.067 \pm 0.006$.

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- Howard and Evenson (1976)
- ▲ Nip et al. (1979)
- Jeong and Kaufman (1982)
- Schmoltnner et al. (1993)
- Hsu and DeMore (1995) relative to CH_3CHF_2
- ◆ Wallington and Hurley (1993) relative to C_2H_2
- ◀ Wallington and Hurley (1993) relative to CH_4
- ▲ Mogelberg et al. (1994) relative to CH_4
- ◆ DeMore (1996) relative to CH_3Cl

