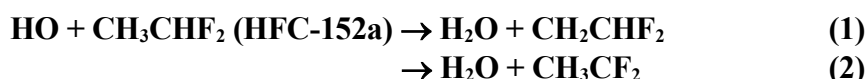


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx15

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This datasheet last evaluated: June 2015; last change in preferred values: March 2006.



$$\Delta H^\circ(1) = -53.8 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -69.8 \text{ kJ mol}^{-1}$$

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>			
$(3.12 \pm 0.70) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
$(3.50 \pm 0.50) \times 10^{-14}$	293	Handwerk and Zellner, 1978	FP-RA
$2.92 \times 10^{-12} \exp[-(1200 \pm 100)/T]$	293-417	Clyne and Holt, 1979	DF-RF
$(4.66 \pm 0.16) \times 10^{-14}$	293		
$(3.7 \pm 0.4) \times 10^{-14}$	297±2	Nip et al., 1979	FP-RA
$1.42 \times 10^{-12} \exp(-1050/T)$	220-423	Brown et al. 1990	DF-RF
4.2×10^{-14}	298		
$9.6 \times 10^{-13} \exp[-(940 \pm 130)/T]$	270-400	Liu et al., 1990	FP-RF
$(4.22 \pm 0.45) \times 10^{-14}$	298		
$1.0 \times 10^{-12} \exp[-(980 \pm 50)/T]$	212-349	Gierczak et al., 1991	DF-LMR/FP-LIF
$(3.76 \pm 0.6) \times 10^{-14}$	293		
$3.9 \times 10^{-12} \exp[-(1370 \pm 260)/T]$	295-388	Nielsen, 1991	PR-RA
$(4.7 \pm 1.1) \times 10^{-14}$	295		
$3.24 \times 10^{-12} \exp[-(1372 \pm 89)/T]$	298-480	Kozlov et al., 2003	FP-RF
$9.36 \times 10^{-13} \exp[-(998 \pm 56)/T]$	210-298		
$(3.38 \pm 0.05) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$(3.86 \pm 0.67) \times 10^{-14}$	298±2	DeMore, 1992	RR (a)
$(3.45 \pm 0.34) \times 10^{-14}$	298±2	DeMore, 1992	RR (b)
$3.44 \times 10^{-18} T^2 \exp[-(690 \pm 57)/T]$	298-358	Hsu and DeMore, 1995	RR (c)
3.02×10^{-14}	298		
$1.18 \times 10^{-20} T^{2.82} \exp[-(388 \pm 67)/T]$	298-358	Hsu and DeMore, 1995	RR (b)
3.05×10^{-14}	298		
$2.53 \times 10^{-18} T^2 \exp[-(557 \pm 19)/T]$	286-403	Wilson et al., 2003	RR (d,e)
3.47×10^{-14}	298		
$1.22 \times 10^{-18} T^2 \exp[-(329 \pm 42)/T]$	290-391	Wilson et al., 2003	RR (d,f)
3.59×10^{-14}	298		
$(3.12 \pm 0.58) \times 10^{-14}$	295±2	Taketani et al., 2005	RR (g, h)
$(3.03 \pm 0.53) \times 10^{-14}$	295±2	Taketani et al., 2005	RR (g, i)

Comments

- (a) HO radicals were generated by the photolysis of H₂O at 185 nm in H₂O-CH₃CHF₂-C₂H₆-N₂-O₂ mixtures. The concentrations of CH₃CHF₂ and C₂H₆ were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{CHF}_2)/k(\text{HO} + \text{C}_2\text{H}_6) = 0.161 \pm 0.028$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{C}_2\text{H}_6) = 2.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- (b) HO radicals were generated by the photolysis of H₂O at 185 nm or of O₃-H₂O mixtures in H₂O (or O₃-H₂O)-CH₃CHF₂-CH₄-N₂-O₂ mixtures. The concentrations of CH₃CHF₂ and CH₄ were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CH}_3\text{CHF}_2)/k(\text{HO} + \text{CH}_4) = 5.2 \pm 0.54$ (DeMore, 1992) and $k(\text{HO} + \text{CH}_3\text{CHF}_2)/k(\text{HO} + \text{CH}_4) = (0.64 \pm 0.13) \exp[(599 \pm 67)/T]$ (Hsu and DeMore, 1995) are placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_4) = 1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- (c) HO radicals were generated by the photolysis of H₂O at 185 nm or of O₃-H₂O mixtures in the UV in H₂O (or H₂O-O₃)-CH₃CHF₂-CH₃CCl₃-O₂-N₂ mixtures. The concentrations of CH₃CHF₂ and CH₃CCl₃ were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{CHF}_2)/k(\text{HO} + \text{CH}_3\text{CCl}_3) = (1.53 \pm 0.28) \exp[(220 \pm 57)/T]$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- (d) Relative rate method. HO radicals were generated by photolyzing H₂O vapour at 185 nm. Reactant and reference compound concentrations were monitored by GC/MS.
- (e) Relative to C₂H₆. An Arrhenius plot of the data gives the temperature dependence of the measured ratios as $(0.17 \pm 0.01) \exp[-(58 \pm 19)/T]$, which 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).
- (f) Relative to cyclopropane. An Arrhenius plot of the data gives the temperature dependence of the measured ratios as $(0.29 \pm 0.10) \exp[(125 \pm 42)/T]$, which is placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{cyclo-C}_3\text{H}_6) = 4.21 \times 10^{-18} T^2 \exp(-454/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003).
- (g) Relative rate method. HO radicals were generated by the UV photolysis of CH₃ONO in the presence of the reactant in 700 Torr total pressure of air diluent. Reference compound concentrations were monitored by FTIR. CH₃CHF₂ loss was measured indirectly from the observed formation of COF₂.
- (h) Relative to C₂H₄. The measured rate coefficient ratio of $k(\text{CH}_3\text{CHF}_2 + \text{HO})/k(\text{C}_2\text{H}_4 + \text{HO}) = (3.59 \pm 0.27) \times 10^{-3}$ is placed on an absolute basis by using a rate coefficient of $k(\text{C}_2\text{H}_4 + \text{HO}) = 8.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (Calvert et al., 2000).
- (i) Relative to C₂H₂. The measured rate coefficient ratio of $k(\text{CH}_3\text{CHF}_2 + \text{HO})/k(\text{C}_2\text{H}_2 + \text{HO}) = (3.58 \pm 0.12) \times 10^{-2}$ is placed on an absolute basis by using a rate coefficient of $k(\text{C}_2\text{H}_2 + \text{HO}) = 8.45 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (Sørensen et al., 2003).

Preferred Values

$$k = 3.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.25 \times 10^{-12} \exp(-1070/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 210\text{-}300 \text{ K.}$$

Reliability

$$\Delta \log k = {}^{0.10}_{-0.20} \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = {}^{+200}_{-400} \text{ K.}$$

Comments on Preferred Values

The absolute rate coefficients of Handwerk and Zellner (1978), Nip et al. (1979), Gierczak et al. (1991), and Kozlov et al. (2003) are in good agreement, and the relative rate coefficients of

DeMore (1992), Wilson et al. (2003) and Taketani et al. (2005) agree well with these absolute rate coefficients. The absolute rate coefficients of Clyne and Holt (1979) and Nielsen (1991) are systematically higher than the other absolute or relative rate coefficients, hence these data were not used in the evaluation. The data of Brown et al. (1990) is scattered and subject to large uncertainties, and that of Liu et al. (1990) exhibits a lower temperature dependence than the other absolute or relative rate coefficients – these studies were also not used in the evaluation. It is possible that the studies of Clyne and Holt (1979), Brown et al. (1990), Liu et al. (1990) and Nielsen (1991) were affected by reactant impurities. Of the data of Wilson et al. (2003), the rate data relative to C₂H₆ agrees very well with the absolute rate coefficients of Gierczak et al. (1991) and Kozlov et al. (2003). The Wilson et al. (2003) data relative to cyclopropane exhibits a lower temperature dependence compared with the data of Gierczak et al. (1991), Kozlov et al. (2003) and Wilson et al. (2003) relative to C₂H₆. This is attributed to uncertainties in the recommended rate constant for the cyclopropane reaction. Hence, only the Wilson et al. (2003) data relative to C₂H₆ were used in the evaluation. The relative rate coefficients of DeMore (1992) relative to C₂H₆ and CH₄ are in good agreement with each other, and in good agreement with the absolute rate coefficients of Howard and Evenson (1976), Handwerk and Zellner (1978), Nip et al. (1979), Gierczak et al. (1991), Kozlov et al. (2003), and the rate coefficients of Wilson et al. (2003) relative to C₂H₆. The relative rate coefficients of Hsu and DeMore (1995) are systematically lower and exhibit a slightly higher temperature dependence than the data of Gierczak et al. (1991), Kozlov et al. (2003), and Wilson et al. (2003) relative to C₂H₆.

The rate coefficient data of Howard and Evenson (1976), Handwerk and Zellner (1978), Nip et al. (1979), Gierczak et al. (1991) (using all data in the temperature range 212-422.5 K), DeMore (1992), Kozlov et al. (2003) and Wilson et al. (2003) (relative to C₂H₆) were fitted to a three parameter equation $k = CT^2 \exp(-D/T)$ giving $k = 2.80 \times 10^{-18} T^2 \exp(-580/T)$ 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 16-18% lower than the preferred value at 298 K.

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- △ Howard and Evenson (1976)
- ◇ Handwerk and Zellner (1978)
- ▼ Nip et al. (1979)
- ▲ Gierczak et al. (1991)
- ◊ DeMore (1992), relative to C₂H₆
- ◆ DeMore (1992), relative to CH₄
- Hsu and DeMore (1995), relative to CH₄
- ▲ Hsu and DeMore (1995), relative to CH₃CCl₃
- Kozlov et al. (2003)
- Wilson et al. (2003), relative to C₂H₆
- Taketani et al. (2005) relative to C₂H₄
- Taketani et al. (2005) relative to C₂H₂
- IUPAC three parameter fit
- Recommendation

