IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx26

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$HO + CF_3CHFCF_3$ (HFC-227ea) $\rightarrow H_2O + CF_3CFCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$3.7 \times 10^{-13} \exp[-(1615 \pm 190)/T]$	294-369	Nelson et al., 1993	DF-LIF
$(1.64 \pm 0.28) \times 10^{-15}$	295		
$3.8 \times 10^{-13} \exp[-(1596 \pm 77)/T]$	298-463	Zellner et al., 1994	PLP-LIF
$(1.8 \pm 0.2) \times 10^{-15}$	298		
$3.63 \times 10^{-13} \exp[-(1613 \pm 135)/T]$	270-365	Zhang et al., 1994	FP-RF
$(1.62 \pm 0.03) \times 10^{-15}$	298		
$6.19 \times 10^{-13} \exp[-(1830 \pm 100)/T]$	250-430	Tokuhashi et al. 2004	FP/PLP-LIF (a)
$(1.34 \pm 0.08) \times 10^{-15}$	298		
Relative Rate Coefficients			
$3.15 \times 10^{-21} T^{2.82} \exp[-(870 \pm 105)/T]$	296-398	Hsu and DeMore, 1995	RR (b,c)
1.55×10^{-15}	296		
$7.67 \times 10^{-19} T^{2} \exp[-(1082 \pm 89)/T]$	298-367	Hsu and DeMore, 1995	RR (b,d)
1.80×10^{-15}	298		

Comments

(a) HO radical concentration monitored by laser induced fluorescence.

(b) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or O_3 at 254 nm in H_2O (or H_2O-O_3) - CF_3CHFCF_3 - CH_4 (or CHF_2CF_3) - O_2 - N_2 mixtures. The concentrations of CF_3CHFCF_3 and CH_4 (or CHF_2CF_3) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratios of $k(HO + CF_3CHFCF_3)/k(HO + CH_4) = (0.17 \pm 0.05) \exp[(117 \pm 105)/T]$ and $k(HO + CF_3CHFCF_3)/k(HO + CHF_2CF_3) = (0.83 \pm 0.22) \exp[(38 \pm 89)/T]$ are placed on an absolute basis by use of rate coefficients of $k(HO + CH_4) = 1.85 \times 10^{-20} T^{2.82} \exp(-987/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation) and $k(HO + CHF_2CF_3) = 9.24 \times 10^{-19} T^{2} \exp(-1120/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) Relative to $k(HO + CH_4)$.

(d) Relative to $k(HO + CHF_2CF_3)$.

Preferred Values

$k = 1.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.3 \times 10^{-13} \exp(-1770/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-380 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are derived from absolute rate coefficients of Zhang et al. (1994) and Tokuhashi et al. (2004). The relative rate coefficients of Hsu and DeMore (1995), and the absolute rate coefficients of Nelson et al. (1993) and Zellner et al. (1994) are 10-30% higher than those of Tokuhashi et al. (2004) over the temperature range 298-380 K, with the agreement being better at the higher temperatures. Tokuhashi et al. (2004) used highly purified reactants in their study, suggesting that the previous studies may have been affected by reactant impurities.

The data of Zellner et al. (1994), Zhang et al. (1994) and Tokuhashi et al. (2004) were fitted to the three parameter equation, $k = CT^2 \exp(-D/T)$, resulting in $k = 8.0 \times 10^{-19}\ T^2 \exp(-1170/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-430 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three parameter equation with $A = C\ e^2\ T^2$ and $B = D + 2T$. Note that the preferred Arrhenius expression should not be used outside the specified temperature range (250-380 K); rather, the full three parameter expression should be used.

References

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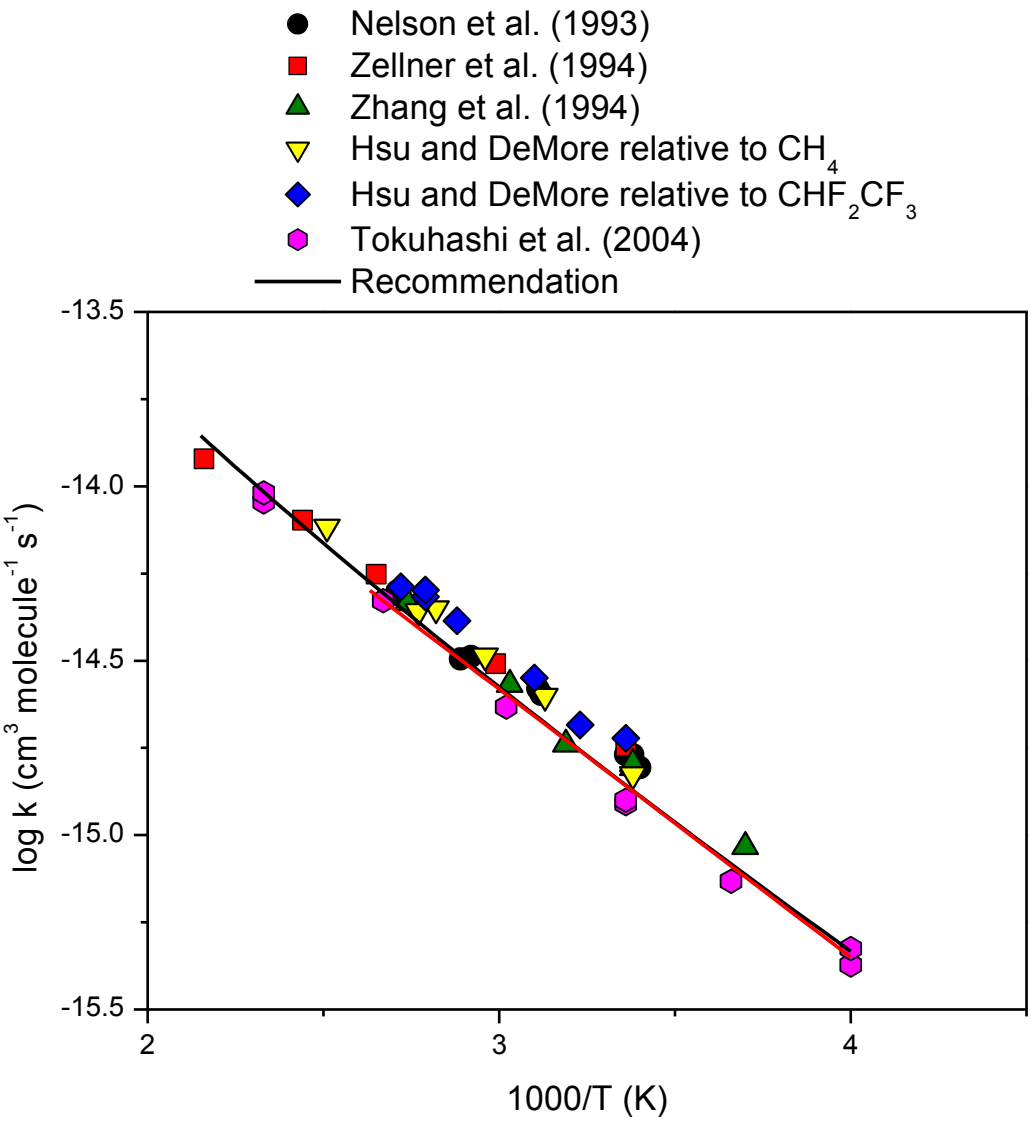
Nelson et al. (1993)
Zellner et al. (1994)
Zhang et al. (1994)
Hsu and DeMore relative to CH4
Hsu and DeMore relative to CHF2CF3
Tokuhashi et al. (2004)
Recommendation
-13.5
-14.0
-14.5
-15.0
-15.5
log k (cm3 molecule-1 s-1)
2
3
4
1000/T (K)