IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx25

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

HO + CF$_3$CH$_2$CF$_3$ (HFC-236fa) $\rightarrow$ H$_2$O + CF$_3$CHCF$_3$
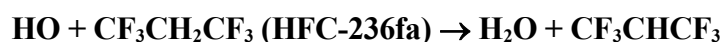
Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.0 x 10^{-14} exp[-(906 ± 151)/T]	257-311	Garland et al., 1993	PLP-LIF
9.6 x 10^{-16}	298		
(5.1 ± 0.7) x 10^{-16}	294	Nelson et al., 1995	DF-LIF
(4.15 ± 0.33) x 10^{-16}	298	Garland and Nelson, 1996	PLP-LIF
(1.6 ± 0.4) x 10^{-12} exp [-(2540± 150)/T]	273-413	Gierczak et al., 1996	FP-LIF
(3.20 ± 0.60) x 10^{-16}	298		
Relative Rate Coefficients			
1.16 x 10^{-18} T^2 exp[-(1700 ± 109)/T]	298-367	Hsu and DeMore, 1995	RR (a)
3.43 x 10^{-16}	298		
(3.5 ± 1.5) x 10^{-16}	298	Barry et al., 1997	RR (b)

Comments

(a) Relative rate method. HO radicals were generated from the photolysis of H$_2$O at 185 nm or of O$_3$-H$_2$O mixtures in the UV in H$_2$O (or O$_3$-H$_2$O)-CF$_3$CH$_2$CF$_3$-CHF$_2$CF$_3$-O$_2$-N$_2$ mixtures. The concentrations of CF$_3$CH$_2$CF$_3$ and CHF$_2$CF$_3$ were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of k(HO + CF$_3$CH$_2$CF$_3$)/k(HO + CHF$_2$CF$_3$) = (1.26 ± 0.41) exp[-(580 ± 109)/T] is placed on an absolute basis by using a rate coefficient of k(HO + CHF$_2$CF$_3$) = 9.24 x 10^{-19} T^2 exp(-1120/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) Relative rate method. HO radicals were generated by UV photolysis of O$_3$ at 254 nm in the presence of H$_2$O vapour. Mixtures of O$_3$/CF$_3$CH$_2$CF$_3$/CF$_3$CH$_2$CF$_2$CH$_3$/H$_2$O were photolysed in air at 298 K, k(HO + CF$_3$CH$_2$CF$_3$)/k(HO + CF$_3$CH$_2$CF$_2$CH$_3$) was found to be 0.06 ± 0.02. Using the experimentally derived value of k(HO + CF$_3$CH$_2$CF$_2$CH$_3$) = 2.0 x 10^{-12} exp(-(1750 ± 400)/T) cm^3 molecule^{-1} s^{-1} gives k(HO + CF$_3$CH$_2$CF$_3$) = (3.5 ± 1.5) x 10^{-16} cm^3 molecule^{-1} s^{-1}.

Preferred Values

k = 3.3 x 10^{-16} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 1.3 x 10^{-12} exp(-2465/T) cm^3 molecule^{-1} s^{-1} over the temperature range 270-340 K.

Reliability
   Δlog k = ± 0.3 at 298 K.

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

Comments on Preferred Values

The preferred values are derived from the relative rate coefficients of Hsu and DeMore (1995) and the absolute rate coefficients of Gierczak et al. (1996). The agreement between the data of Hsu and DeMore (1995), when placed on an absolute basis as described above, and the data of Gierczak et al. (1996) is very good over the temperature range 298-367 K. The absolute rate coefficients of Garland et al. (1993) over the temperature range 257-311 K are consistently higher than those of Hsu and DeMore (1995) and Gierczak et al. (1996) and were not used in the evaluation. The absolute rate coefficient of Nelson et al. (1995) is also relatively large and has a large uncertainty; this value was also not used in the evaluation.

The data of Hsu and DeMore (1995) and Gierczak et al. (1996) were fitted to the three parameter equation, $k = CT^2 \exp(-D/T)$, resulting in $k = 1.91 \times 10^{-18}\ T^2 \exp(-1865/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 273-413 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 (270-340 K); rather, the full three parameter expression should be used.

The relative rate study of Barry et al. (1997) at 298 K is in very good agreement with the recommended value. However, the very small rate constant ratio would lead to large uncertainties, therefore the rate coefficient derived by Barry et al. (1997) was not used in the evaluation. The preferred value at 298 K is 30% lower than the absolute rate coefficient of Garland and Nelson (1996), but taking into account the uncertainty in the Garland and Nelson (1996) value, the agreement is reasonable.

References

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