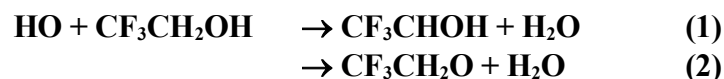


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet of FOx86; VII.A5.3

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The citation for the preferred values in this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

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Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(9.55 \pm 0.71) \times 10^{-14}$	298	Wallington et al. (1988)	FP-RF (a)
$(2.00 \pm 0.37) \times 10^{-12} \exp[-(890 \pm 60)/T]$	250-430	Tokuhashi et al. (1999)	LP-LIF (b)
1.01×10^{-13}	298		FP-LIF (b)
			DF-LIF (b)
$(1.06 \pm 0.30) \times 10^{-13}$	300	Kovacs et al. (2005)	FP-RF (c)
$(1.23 \times 10^{-12} \exp[-(760 \pm 340)/T])$	298-363	Indulkar et al. (2011)	LP-LIF (d)
$(1.03 \pm 0.11) \times 10^{-13}$	298		
<i>Relative Rate Coefficients</i>			
$(1.31 \pm 0.05) \times 10^{-13}$	298	Sellevåg et al. (2004)	RR (e)
$(9.4 \pm 0.8) \times 10^{-14}$	296	Hurley et al (2004)	RR (f)

Comments

- HO radicals were generated by the photolysis ($\lambda \geq 165 \text{ nm}$) of H_2O in 25-50 Torr (33-67 mbar) of argon diluent at 298 K.
- Three different absolute rate methods were employed by Tokuhashi et al. (1999): LP-LIF, FP-LIF, and DF-LIF. HO radicals in the LP-LIF experiments were generated by the photolysis (ArF laser) of N_2O to produce $\text{O}(^1\text{D})$ atoms in the presence of H_2O in 15-70 Torr (20-93 mbar) of helium diluent. HO radicals in the FP-LIF experiments were generated by the photolysis (Xe flash lamp, $\lambda \approx 180 \text{ nm}$) of H_2O in argon diluent. HO radicals in the DF-LIF experiments were generated by the reaction of H atoms with NO_2 in 4-6 Torr (5-8 mbar) of argon diluent. There was good agreement between the results from experiments using the three different techniques. The value at 298 K cited above is the average obtained using the different techniques.
- HO radicals were produced by the photolysis of HNO_3 at 248 nm in $105 \pm 5 \text{ mbar}$ of helium diluent.
- HO radicals were produced by the photolysis of H_2O_2 at 248 nm (KrF excimer laser) in 55 Torr (75 mbar) of helium diluent. HO was excited at 308 nm using a Nd:YAG pumped frequency-doubled dye laser with fluorescence monitored using a broad band filter centered at 310 nm.
- HO radicals were generated by the photolysis of O_3 in the presence of H_2O in 1013 mbar of air diluent at 298 K. A rate coefficient ratio of $k(\text{HO}+\text{CF}_3\text{CH}_2\text{OH})/k(\text{HO}+\text{C}_2\text{H}_6) = 0.547 \pm 0.019$ was measured. Placing this on an absolute basis using $k(\text{HO}+\text{C}_2\text{H}_6) = 2.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{HO}+\text{CF}_3\text{CH}_2\text{OH}) = (1.31 \pm 0.05) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air. A rate coefficient ratio of $k(\text{HO}+\text{CF}_3\text{CH}_2\text{OH})/k(\text{HO}+\text{C}_2\text{H}_2) = 0.12 \pm 0.01$ was reported. Using $k(\text{HO}+\text{C}_2\text{H}_2) = 7.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{HO}+\text{CF}_3\text{CH}_2\text{OH}) = (9.4 \pm 0.8) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.05×10^{-13}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.98 \times 10^{-12} \exp(-875/T)$	250-430
<i>Reliability</i>		
$\Delta \log k$	0.06	298
$\Delta E/R$	± 200	250-430

Comments on Preferred Values

There is good agreement in the room temperature rate coefficients reported in the six studies of this reaction. The recommended value at 298 K is an average of the results from the six studies. The rate coefficients reported by Indulkar et al. (2011) at 318 and 333 K are approximately 20% below those expected from the study by Tokuhashi et al. (1999) but are within the likely combined uncertainties of the two studies. The rate coefficients reported by Indulkar et al. (2011) at 348 and 363 K are in excellent agreement with those expected based on the study by Tokuhashi et al. (1999). The study by Tokuhashi et al. (1999) employed three different absolute rate methods with good agreement between the results from the different techniques. The recommended Arrhenius expression is based on a fit to the combined data set from Tokuhashi et al. (1999) and Indulkar et al. (2011) with the A factor adjusted to reproduce the recommended rate coefficient at 298 K. Hurley et al. (2004) have reported the formation of CF_3CHO in a molar yield of $97 \pm 3\%$ following the chlorine atom initiated oxidation of $\text{CF}_3\text{CH}_2\text{OH}$ in 700 Torr of air. HO and chlorine atom reaction with $\text{CF}_3\text{CH}_2\text{OH}$ are expected to proceed via the same mechanism; hydrogen abstraction from the $-\text{CH}_2-$ group. The HO radical initiated oxidation of $\text{CF}_3\text{CH}_2\text{OH}$ is expected to lead to quantitative conversion of $\text{CF}_3\text{CH}_2\text{OH}$ into CF_3CHO (Calvert et al., 2011).

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