

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx31

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HO + CF₃C(O)OH → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.6 \pm 0.4) \times 10^{-13}$	315	Møgelberg et al., 1994	PR-RA
$(1.5 \pm 0.2) \times 10^{-13}$	348		
<i>Relative Rate Coefficients</i>			
$3.73 \times 10^{-19} T^2 \exp[(375 \pm 400)/T]$	283-323	Carr et al., 1994	RR (a,b)
$(1.14 \pm 0.10) \times 10^{-13}$	298 ± 2		
$(1.21 \pm 0.22) \times 10^{-13}$	298 ± 2	Carr et al., 1994	RR (a,c)
$(1.75 \pm 0.44) \times 10^{-13}$	296	Møgelberg et al., 1994	RR (d)
$(8.70 \pm 1.44) \times 10^{-14}$	296 ± 2	Hurley et al., 2004	RR (e,f)
$(1.00 \pm 0.11) \times 10^{-13}$	296 ± 2	Hurley et al., 2004	RR (e,g)

Comments

- (a) Relative rate method. HO radicals were generated by the 254 nm photolysis of O₃ in the presence of water vapor in O₃-H₂O-CF₃C(O)OH-C₂H₆ (or C₃H₈)-O₂ mixtures. The concentrations of CF₃C(O)OH and C₂H₆ (or C₃H₈) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CF}_3\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{C}_2\text{H}_6) = 0.025 \exp[(874 \pm 400)/T]$ (0.47 ± 0.04 at 298 ± 2 K) and $k(\text{HO} + \text{CF}_3\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{C}_3\text{H}_8) = 0.11 \pm 0.02$ at 298 K are placed on an absolute basis by using rate coefficients of $k(\text{HO} + \text{C}_2\text{H}_6) = 1.5 \times 10^{-17} T^2 \exp(-499/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation) and $k(\text{HO} + \text{C}_3\text{H}_8) = 1.10 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).
- (b) Relative to $k(\text{OH} + \text{ethane})$.
- (c) Relative to $k(\text{OH} + \text{propane})$.
- (d) Relative rate method. HO radicals were generated by the photolysis of O₃ at 254 nm in the presence of H₂ in O₃-H₂-CF₃C(O)OH-C₂H₆-O₂ mixtures at 740 Torr total pressure. The concentrations of CF₃C(O)OH and ethane were measured by FTIR spectroscopy. The measured rate coefficient ratio was $k(\text{HO} + \text{CF}_3\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{C}_2\text{H}_6) = 0.59 \pm 0.04$. If the (CF₃C(O)OH)₂ dimer is unreactive towards the HO radical, then the rate coefficient ratio corrected for dimer formation is 0.84 ± 0.06 . An average value of $k(\text{HO} + \text{CF}_3\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{C}_2\text{H}_6) = 0.72 \pm 0.18$ was preferred and is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{C}_2\text{H}_6) = 2.43 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (e) Relative rate method. HO radicals were generated by the photolysis of CH₃ONO in the presence of NO in air. CH₃ONO-NO-CF₃C(O)OH-reference compound-air mixtures at 700 Torr total pressure were photolysed by UV lamps. Reference compounds were C₂H₂ and C₂H₄. The concentrations of CF₃C(O)OH, C₂H₂ and C₂H₄ were measured by FTIR spectroscopy. The measured rate constant ratios of $k(\text{HO} + \text{CF}_3\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{C}_2\text{H}_2) = 0.103 \pm 0.017$ and $k(\text{HO} + \text{CF}_3\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{C}_2\text{H}_4) = 0.0116 \pm 0.0012$ are placed on an absolute basis by using rate coefficients of $k(\text{HO} + \text{C}_2\text{H}_2) = 8.45 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Sørensen et al., 2003) and $k(\text{HO} + \text{C}_2\text{H}_4) = 8.66 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Calvert et al. 2000), both at 296 K and 700 Torr of air.
- (f) Relative to $k(\text{HO} + \text{acetylene})$.

(g) Relative to $k(\text{HO} + \text{ethene})$.

Preferred Values

$k = 1.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 280-350 K.

Reliability

$\Delta \log k = \pm 0.1$ over the temperature range 280-350 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the relative and absolute rate coefficients of Møgelberg et al. (1994), Carr et al. (1994) and Hurley et al. (2004). The reaction is expected to proceed by overall H-atom abstraction from the -OH group to form $\text{H}_2\text{O} + \text{CF}_3\text{CO}_2$ (see the data sheets on the HO radical reactions with $\text{HC}(\text{O})\text{OH}$ and $\text{CH}_3\text{C}(\text{O})\text{OH}$).

References

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