IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx114

This data sheet last evaluated: June 2017; last change in preferred values: June 2017.

$HO + CF_3CF{=}CH_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.41×10^{-12} exp[-(64±27)/T]	252-370	Orkin et al., 1997	FP-RF (a)
$(1.12 \pm 0.02) \times 10^{-12}$	298		
1.26×10^{-12} exp[-(35±10)/T]	207-380	Papadimitriou et al., 2008	PLP-LIF (b)
$(1.12 \pm 0.02) \times 10^{-12}$	296		
1.145×10^{-12} exp[-13/T]	220-298	Orkin et al., 2010	FP-RF (c)
$(1.096 \pm 0.007) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(9.04\pm0.67) \times 10^{-13}$	296	Nielsen et al. (2007)	RR (d)
$(9.82\pm0.55) \times 10^{-13}$	296		

Comments

(a) HO radicals were generated by the photolysis of H_2O by a xenon flash lamp in 100 Torr (133 mbar) of argon diluent. HO radicals were monitored using resonance fluorescence.

(b) HO radicals were produced using the pulsed laser photolysis of either H_2O_2 or HNO_3 at 248 nm. HO radicals were monitored using laser induced fluorescence. Experiments at 296K were conducted in a total pressure of 25-600 Torr (33-800 mbar) using helium, nitrogen, or SF_6 diluent. There was no discernable effect of total pressure or diluent on the kinetics of the reaction.

(c) HO radicals were generated by the photolysis of H_2O by a xenon flash lamp in 30-300 Torr (40-400 mbar) of argon diluent. HO radicals were monitored using resonance fluorescence.

(d) Photolysis of CH_3ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The loss of $CF_3CF{=}CH_2$ was measured relative to those of C_2H_2 and C_2H_4 and used to measure the rate coefficient ratios $k(CF_3CF{=}CH_2)/k(C_2H_2)$ = 1.21±0.09 and $k(CF_3CF{=}CH_2)/k(C_2H_2)$ = 0.125±0.007. Using $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ and $k(HO + C_2H_4) = 7.85 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO + CF_3CF{=}CH_2) = (9.04\pm0.67) \times 10^{-13}$ and $(9.82\pm0.55) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	1.11×10^{-11}	298
k /cm^3 molecule^{-1} s^{-1}	1.15×10^{-12} exp $(-10/T)$	200-300
Reliability		
$\Delta \log k$	± 0.06	298
Δ E/R	± 100	200-300

Comments on Preferred Values

The absolute rate measurements by Orkin et al. (1997), Papadimitriou et al. (2008), and Orkin et al. (2010) are in excellent agreement (within 5% at all temperatures studied) while the relative rate measurements by Nielsen et al. (2008) at 296 K lie approximately 15% below those from the absolute studies. Orkin et al. (1997) and Papadimitriou et al. (2008) showed that for pressures above 25 Torr there is no effect of total pressure and the reaction is at, or near, the high pressure limit. The precision of the absolute rate measurements for this reaction are extraordinary and a small, but discernable, curvature is evident in the Arrhenius plot. A fit of a modified Arrhenius expression to the entire data set from Orkin et al. (1997), Papadimitriou et al. (2008), and Orkin et al. (2010) gives $k = 0.545 \times (T/298)^{0.882}$ exp $(212/T)$ cm^3 molecule^{-1} s^{-1}. A fit of the Arrhenius expression to the data below 300 K with the A-factor adjusted to reproduce the recommended value of k at 298K gives $k = 1.15 \times 10^{-12}$ exp $(10/T)$ cm^3 molecule^{-1} s^{-1}. While the modified Arrhenius expression provides a better representation of the measured data, for simplicity and consistency within the IUPAC recommended database we recommend the simple Arrhenius expression. The HO radical initiated oxidation of $CF_3CF{=}CH_2$ gives $CF_3C(O)F$ and HCHO as products (Hurley et al., 2008). The atmospheric fate of $CF_3C(O)F$ is hydrolysis to give $CF_3C(O)OH$ (trifluoroacetic acid).

References

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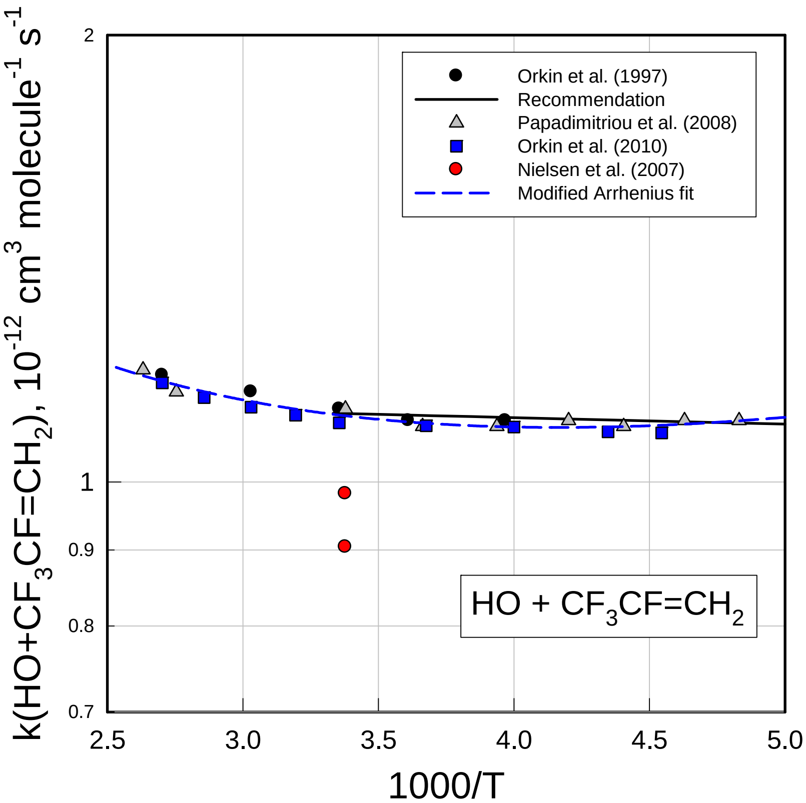
Papadimitriou, V. C.; Talukdar, R. K.; Portmann, R. W.; Ravishankara, A. R.; and Burkholder, J. B.: Phys. Chem. Chem. Phys., 10, 808, 2008.



k(HO+CF3CF=CH2), 10-12 cm3 molecule-1 s-1
1000/T
Orkin et al. (1997)
Recommendation
Papadimitriou et al. (2008)
Orkin et al. (2010)
Nielsen et al. (2007)
Modified Arrhenius fit
HO + CF3CF=CH2
2
1
0.9
0.8
0.7
2.5
3.0
3.5
4.0
4.5
5.0