IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oFOx101; VII.A5.20

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$$HO + CF_3CH_2CHO \rightarrow CF_3CH_2CO + H_2O \quad (1)$$
$$\rightarrow CF_3CHCHO + H_2O \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.96 \pm 0.04) \times 10^{-12}$	298	Kelly et al. (2005)	PLP-LIF (a)
$(7.8 \pm 2.2) \times 10^{-12} \exp(-314 \pm 90)/T$	263-358	Antinolo et al. (2010)	PLP-LIF (b)
$(2.59 \pm 0.50) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(3.87 \pm 0.16) \times 10^{-12}$	298	Sellevåg et al. (2004)	RR (c)
$(3.07 \pm 0.08) \times 10^{-12}$			
$(2.48 \pm 0.27) \times 10^{-12}$	296	Hurley et al. (2005)	RR (d)
$(2.65 \pm 0.36) \times 10^{-12}$			

Comments

(a) HO radicals were generated by the 248 nm (KrF excimer laser) photolysis of H_2O_2 in 100 Torr (133 mbar) of helium diluent at 298 K.

(b) HO radicals were generated by the 248 nm (KrF excimer laser) photolysis of H_2O_2 in 50-215 Torr (67-286 mbar) of helium diluent at 263-358 K.

(c) Experiments were performed in 1013 mbar of air diluent. HO radicals were generated by the photolysis of O_3 at $\lambda \approx 310$ nm in the presence of H_2O vapor. The loss of CF_3CH_2CHO was monitored relative to C_2H_5OH and $HC(O)OC_2H_5$ in separate experiments using FTIR spectroscopy and rate coefficient ratios of $k(HO+CF_3CH_2CHO)/k(HO+C_2H_5OH) = 1.21 \pm 0.05$ and $k(HO+CF_3CH_2CHO)/k(HO+HC(O)OC_2H_5) = 3.51 \pm 0.09$ were reported. Scaling these ratios using $k(HO+C_2H_5OH) = 3.2 \times 10^{-12}$ (Atkinson et al., 2006) and $k(HO+HC(O)OC_2H_5) = 8.74 \times 10^{-13}$ (Calvert et al., 2011) gives $k(HO+CF_3CH_2CHO) = (3.87 \pm 0.16) \times 10^{-12}$ and $(3.07 \pm 0.08) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(d) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air in the presence of NO. C_2H_2 and C_2H_4 were used as reference compounds in separate experiments. The loss of CF_3CH_2CHO and the reference compounds were monitored using FTIR spectroscopy. Rate coefficient ratios of $k(HO+CF_3CH_2CHO)/k(HO+C_2H_2) = 3.18 \pm 0.35$ and $k(HO+CF_3CH_2CHO)/k(HO+C_2H_4) = 0.336 \pm 0.045$. Scaling these ratios using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ and $k(HO+C_2H_4) = 7.9 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO+CF_3CH_2CHO) = (2.48 \pm 0.27) \times 10^{-12}$ and $(2.65 \pm 0.36) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	2.7 x 10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	8.34 x 10^{-12} exp(-334/T)	260-360
Reliability		
$\Delta \log k$	0.15	298
Δ (E/R)	± 150	260-360

Comments on Preferred Values

With the exception of one of the two relative rate determinations by Sellevåg et al. (2004), the data from the relative and absolute rate studies by Antinolo et al. (2010), Hurley et al. (2005), Kelly et al. (2005), and Sellevåg et al. (2004) are consistent within the combined experimental uncertainties. Taking an average of the data from Antinolo et al. (2010), Hurley et al. (2005), and Kelly et al. (2005) gives the recommended value at 298 K. The recommended Arrhenius expression is based upon a fit to the combined absolute rate data from Antinolo et al. (2010) and Kelly et al. (2005). The reaction is expected to proceed predominantly via abstraction of the aldehydic hydrogen giving $CF_3CH_2C(O)$ radicals.

References

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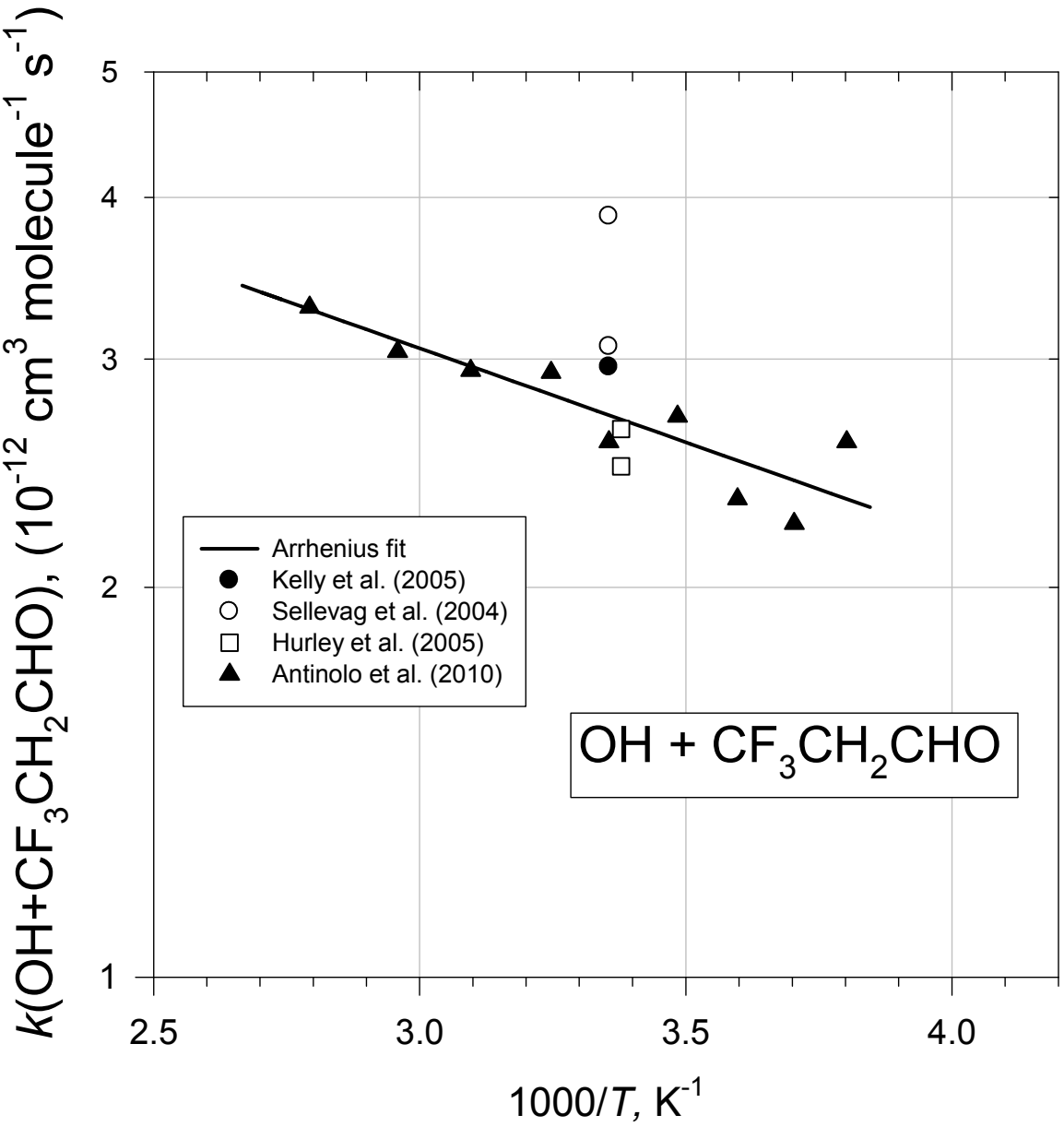
Sellevåg, S. R., Kelly, T., Sidebottom, H., and Nielsen, C. J.: Phys. Chem. Chem. Phys., 6, 1243, 2004.


k(OH+CF3CH2CHO), (10-12 cm3 molecule-1 s-1)
5
4
3
2
1
2.5
3.0
3.5
4.0
1000/T, K-1
Arrhenius fit
Kelly et al. (2005)
Sellevag et al. (2004)
Hurley et al. (2005)
Antinolo et al. (2010)
OH + CF3CH2CHO