IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oFOx100; VII.A5.19

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HO + *n*-C_4F_9CHO → *n*-C_4F_9CO + H_2O

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.5) \times 10^{-12} \exp[-(356 \pm 70)/T]$	253 – 373	Solignac et al. (2007)	PLP-LIF (a)
$(6.4 \pm 0.3) \times 10^{-13}$	299		
Relative Rate Coefficients			
$(5.68 \pm 0.74) \times 10^{-13}$	296	Sulbaek Andersen et al. (2004)	RR (b)
$(6.42 \pm 0.75) \times 10^{-13}$			

Comments

(a) HO radicals were generated by the photolysis of H_2O_2 at 248 nm in the presence of C_4F_9CHO in 100 Torr (133 mbar) of helium diluent.

(b) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air in the presence of NO. In separate experiments C_2H_2 and C_2H_4 were used as reference compounds. The loss of C_4F_9CHO and the reference compounds were monitored using FTIR spectroscopy. Experiments were performed using CF_3CHO, C_3F_7CHO, and C_4F_9CHO. There was no discernable difference in reactivity of the three fluorinated aldehydes. An analysis of the combined data set gave rate coefficient ratios of $k(HO+ C_xF_{2x+1}CHO)/k(HO+C_2H_2) = 0.73 \pm 0.10$ and $k(HO+C_xF_{2x+1}CHO)/k(HO+C_2H_4) = 0.0813 \pm 0.0095$. 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 $k(HO+C_xF_{2x+1}CHO) = (5.68 \pm 0.74) \times 10^{-13}$ and $(6.42 \pm 0.75) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	6.1×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$2.07 \times 10^{-12} \exp(-363/T)$	250-380
Reliability		
$\Delta \log k$	0.12	298
$\Delta E/R$	± 150	250-380

Comments on Preferred Values

There is excellent agreement between the absolute rate data reported by Solignac et al. (2007) and the relative rate data reported by Sulbaek Andersen et al. (2004) at temperatures near

298 K. A fit to the data from Solignac et al. (2007) gives the recommendation of k(HO+C_4F_9CHO) = 2.07 x 10^{-12} exp(-363/T) which gives 6.1 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K. As shown by Sulbaek Andersen et al. (2004), the reaction proceeds via abstraction of the aldehydic hydrogen to give $C_4F_9C(O)$ radicals.

References

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Solignac, G., Mellouki, A., Le Bras, G., Yujing, M., and Sidebottom, H.: Phys. Chem. Chem. Phys., 9, 4200, 2007.

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