IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oFOx99; VII.A5.18

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.

This datasheet last evaluated: June 2015; last change in preferred values: June 2009.

HO + *n*-C_3F_7CHO → *n*-C_3F_7CO + H_2O

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.6) \times 10^{-12}$ exp[-(369 ± 90)/T]	252 - 373	Solignac et al. (2007)	PLP-LIF (a)
5.55×10^{-13}	297		(b)
Relative Rate Coefficients			
$(5.68 \pm 0.74) \times 10^{-13}$	296	Sulbaek Andersen et al. (2004)	RR (c)
(6.42 ± 0.75) x 10^{-13}			

Comments

(a) HO radicals were generated by the photolysis of H_2O_2 at 248 nm in the presence of C_3F_7CHO in 100 Torr (133 mbar) of helium diluent.

(b) Average of values given at 297 K

(c) 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_3F_7CHO 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 ± 0.10 and k(HO+ $C_xF_{2x+1}CHO$)/k(HO+C_2H_4) = 0.0813 ± 0.0095. Scaling these ratios using k(HO+C_2H_2) = 7.8 x 10^{-13} and k(HO+C_2H_4) = 7.9 x 10^{-12} (Atkinson et al., 2006) gives k(HO+ $C_xF_{2x+1}CHO$) = (5.68 ± 0.74) x 10^{-13} and (6.42 ± 0.75) x 10^{-13} cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	5.9 x 10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	2.02 x 10^{-12} exp(-368/T)	250-380
Reliability		
Δ log k	0.12	298

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

298K. A fit to the data from Solignac et al. (2007) gives the recommendation of $k(HO+C_3F_7CHO)$ = 2.02 x 10^{-12} exp(-368/T) which gives 5.9 × 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 $C_3F_7C(O)$ 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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