IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oFOx107; VII.A5.29

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HO + *n*-$C_4F_9C(O)OH$ → *n*-$C_4F_9C(O)O + H_2O$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.54 \pm 0.17) \times 10^{-13}$	296	Hurley et al. (2004)	RR (a)
$(1.56 \pm 0.11) \times 10^{-13}$			

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in $C_4F_9C(O)OH/CH_3ONO/NO/(C_2H_2$ or $C_2H_4)$ mixtures in 700 Torr (933 mbar) of air. The loss of the reference compounds C_2H_2 or C_2H_4 was monitored by FTIR spectroscopy. The loss of $C_4F_9C(O)OH$ was small and difficult to observe directly. The loss of $C_4F_9C(O)OH$ was calculated from the formation of COF_2 observed by FTIR spectroscopy. Experiments performed using $C_2F_5C(O)OH$, $C_3F_7C(O)OH$, and $C_4F_9C(O)OH$ gave indistinguishable values of the rate coefficient ratio $k(HO+C_xF_{2x+1}C(O)OH)/k(HO+reference)$. Analysis of the composite data set gave $k(HO+C_xF_{2x+1}C(O)OH)/k(HO+C_2H_2) = 0.197 \pm 0.022$ and $k(HO+C_xF_{2x+1}C(O)OH)/k(HO+C_2H_4) = 0.0198 \pm 0.0014$. 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 the values of $k(HO+C_xF_{2x+1}CHO)$ listed in the table above.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.5×10^{-13}	298
Reliability		
$\Delta \log k$	0.12	298

Comments on Preferred Values

The recommendation is based on the study by Hurley et al. (2004). The $C_4F_9C(O)O$ radical decomposes rapidly to give CO_2 and a C_4F_9 radical. As discussed by Ellis et al. (2005), the C_4F_9 radical will be converted mainly into COF_2 with $CF_3C(O)OH$, $C_2F_5C(O)OH$, and $C_3F_7C(O)OH$ formed as minor products. As might be expected from their similar molecular structure, $C_4F_9C(O)OH$ has a reactivity towards HO radicals which is indistinguishable from those of $C_2F_5C(O)OH$ and $C_3F_7C(O)OH$.

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Subcommittee for Gas Kinetic Data Evaluation, http://iupac.pole-ether.fr.
Ellis, D. A., Martin, J. W., De Silva, A. O., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P., and Wallington, T. J.: Environ. Sci. Tech., 38, 3316, 2004.
Hurley, M. D., Wallington, T. J., Ellis, D. A., Martin, J. W., and Mabury, S. A.: J. Phys. Chem. A, 108, 615, 2004.