IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oFOx93; VII.A5.10

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.

$$\mathbf{HO + \textit{n}\text{-}C_4F_9CH_2CH_2OH \rightarrow \textit{n}\text{-}C_4F_9CHCH_2OH + H_2O} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow \textit{n}\text{-}C_4F_9CH_2CHOH + H_2O} \quad \mathbf{(2)}$$
$$\mathbf{\rightarrow \textit{n}\text{-}C_4F_9CH_2CH_2O + H_2O} \quad \mathbf{(3)}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(0.92 \pm 0.12) \times 10^{-12}$	296	Ellis et al. (2003)	RR (a)
$(1.03 \pm 0.14) \times 10^{-12}$	296		

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air. Experiments were performed with n-$C_4F_9CH_2CH_2OH$, n-$C_6F_{13}CH_2CH_2OH$, and n-$C_8F_{17}CH_2CH_2OH$. There was no discernable difference in the reactivity of the three alcohols and the composite data set was analyzed together. Rate coefficient ratios of $k(HO+C_xF_{2x+1}CH_2CH_2OH)/k(HO+C_2H_2) = 1.18 \pm 0.15$ and $k(HO+C_xF_{2x+1}CH_2CH_2OH)/k(HO+C_2H_4) = 0.131 \pm 0.018$ were reported. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ and $k(HO+C_2H_2) = 7.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO+n\text{-}C_4F_9CH_2CH_2OH) = (0.92 \pm 0.12) \times 10^{-12}$ and $(1.03 \pm 0.14) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.0×10^{-12}	298
Reliability		
$\Delta \log k$	0.15	298

Comments on Preferred Values

The recommendation is based upon the average of the two determinations by Ellis et al. (2003). As discussed by Calvert et al. (2011), HO radicals are approximately an order of magnitude less reactive towards $C_xF_{2x+1}CH_2OH$ than towards $C_xF_{2x+1}CH_2CH_2OH$ and it seems likely that the majority (>90%) of reaction of HO with n-$C_4F_9CH_2CH_2OH$ proceeds via attack on the terminal $-CH_2-$ group. As with other α-hydroxy alkyl radicals, the atmospheric fate of n-$C_4F_9CH_2CHOH$ radicals will be reaction with O_2 to give the corresponding aldehyde.

$$n\text{-}C_4F_9CH_2CH_2OH + HO \rightarrow n\text{-}C_4F_9CH_2CHOH + H_2O$$
$$n\text{-}C_4F_9CH_2CHOH + O_2 \rightarrow n\text{-}C_4F_9CH_2CHO + HO_2$$

Product studies of the chlorine atom initiated oxidation of n-$C_4F_9CH_2CH_2OH$ in 700 Torr of air at

296 K by Hurley et al. (2004) and Andersen et al. (2005) have shown that n-$C_4F_9CH_2CH_2OH$ is oxidized to give n-$C_4F_9CH_2CHO$ in a yield which is indistinguishable from 100%.

References

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