IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oFOx94; VII.A5.11

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$$\mathbf{HO + \textit{n}\text{-}C_6F_{13}CH_2CH_2OH} \rightarrow \mathbf{\textit{n}\text{-}C_6F_{13}CHCH_2OH + H_2O} \quad (1)$$
$$\rightarrow \mathbf{\textit{n}\text{-}C_6F_{13}CH_2CHOH + H_2O} \quad (2)$$
$$\rightarrow \mathbf{\textit{n}\text{-}C_6F_{13}CH_2CH_2O + H_2O} \quad (3)$$

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			
$(9.2 \pm 1.2) \times 10^{-13}$	296	Ellis et al. (2003)	RR (a)
$(7.79 \pm 0.35) \times 10^{-13}$	298	Kelly et al. (2005)	RR (b)
$(7.91 \pm 0.53) \times 10^{-13}$	298		RR (c)

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. A rate coefficient ratio of $k(HO+C_xF_{2x+1}CH_2CH_2OH)/k(HO+C_2H_2) = 1.18 \pm 0.15$ was reported. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO+n\text{-}C_6F_{13}CH_2CH_2OH) = (9.2 \pm 1.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(b) HO radicals were generated by the photolysis of either H_2O_2 or O_3 (in the presence of H_2O vapor) in one atmosphere of air. Experiments were performed using two different reference compounds; $HC(O)OC_4H_9$ and n-C_6H_{14}. Rate coefficient ratios of $k(HO+C_6F_{13}CH_2CH_2OH)/k(HO+HC(O)OC_4H_9) = 0.22 \pm 0.01$ and $k(HO+C_6F_{13}CH_2CH_2OH)/k(HO+n\text{-}C_6H_{14}) = 0.15 \pm 0.01$ were reported. Using $k(HO+HC(O)OC_4H_9) = 3.54 \times 10^{-12}$ (Le Calvé et al., 1997) and $k(HO+n\text{-}C_6H_{14}) = 3.27 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Calvert et al., 2008) gives $k(HO+n\text{-}C_6F_{13}CH_2CH_2OH) = (7.79 \pm 0.35) \times 10^{-13}$ and $(7.91 \pm 0.53) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	8.3×10^{-13}	298
Reliability		
$\Delta \log k$	0.15	298

Comments on Preferred Values

The rate coefficients reported in the relative rate studies by Ellis et al. (2003) and Kelly et al. (2005) are in agreement and an average gives our recommended value. 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-$C_6F_{13}CH_2CH_2OH$ proceeds via attack on the terminal $–CH_2–$ group. As with other α-hydroxy alkyl radicals, the atmospheric fate of n-$C_6F_{13}CH_2CHOH$ radicals will be reaction with O_2 to give the corresponding aldehyde.

$$n\text{-}C_6F_{13}CH_2CH_2OH + OH \rightarrow n\text{-}C_6F_{13}CH_2CHOH + H_2O$$
$$n\text{-}C_6F_{13}CH_2CHOH + O_2 \rightarrow n\text{-}C_6F_{13}CH_2CHO + HO_2$$

References

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