IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oFOx90; VII.A5.7

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$$HO + CF_3CHFCF_2CH_2OH \rightarrow CF_3CFCF_2CH_2OH + H_2O \quad (1)$$
$$\rightarrow CF_3CHFCF_2CHOH + H_2O \quad (2)$$
$$\rightarrow CF_3CHFCF_2CH_2O + H_2O \quad (3)$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.46\pm0.26) \times10^{-12} \exp[-(880\pm40)/T]$	250-430	Chen et al. (2003)	LP-LIF (a)
1.3×10^{-13}	298		FP-LIF (a)
Relative Rate Coefficients			
$6.03 \times 10^{-13} \exp(-510/T)$	230-308	Chen et al. (2003)	RR (b)
$(1.04 \pm 0.04) \times 10^{-13}$	298		
$9.41 \times 10^{-13} \exp(-591/T)$	230-308	Chen et al. (2003)	RR (b)
$(1.27 \pm 0.03) \times 10^{-13}$	298		

Comments

(a) Two different absolute rate methods were employed by Chen et al. (2003): LP-LIF and FP-LIF. HO radicals in the LP-LIF experiments were generated by the photolysis (ArF laser) of N_2O to produce $O(^1D)$ atoms in the presence of H_2O in 20-80 Torr (27-107 mbar) of helium diluent. HO radicals in the FP-LIF experiments were generated by the photolysis (Xe flash lamp) of H_2O in 20-80 Torr (27-107 mbar) of argon diluent. There was good agreement between the results from experiments using the three different techniques. The Arrhenius expression is from a fit to the combined data set from both sets of absolute rate experiments. The value at 298 K cited above is the average obtained using the different techniques.

(b) HO radicals were generated by the photolysis of O_3 at $\lambda \geq 260$ nm using the output from Xe arc lamps in the presence of H_2O vapor in 100 Torr (133 mbar) of helium diluent. CH_2Cl_2 and $CHCl_3$ were used as reference compounds. Arrhenius fits to the rate coefficient ratios reported by Chen et al. (2003) give $k(HO+CF_3CHFCF_2CH_2OH)/k(HO+CH_2Cl_2) = 0.335 \exp(350/T)$ and $k(HO+CF_3CHFCF_2CH_2OH)/k(HO+CHCl_3) = 0.523 \exp(259/T)$. Placing these ratios on an absolute basis using $k(HO+CH_2Cl_2) = 1.8 \times 10^{-12} \exp(-860/T)$ and $k(HO+CHCl_3) = 1.8 \times 10^{-12} \exp(-850/T)$ (Atkinson et al., 2008) gives $k(HO+CF_3CHFCF_2CH_2OH) = 6.03 \times 10^{-13} \exp(-510/T)$ and $9.41 \times 10^{-13} \exp(-591/T)$ cm^3 molecule^{-1} s^{-1}, respectively. Over the temperature range were comparison is possible, the results from the relative rate studies are consistent with those from the absolute study.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.3×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$2.26 \times 10^{-12} \exp(-848/T)$	250-430
Reliability		
$\Delta \log k$	0.12	298

$\Delta E/R$	± 300	250-430

Comments on Preferred Values

The results from the absolute rate (two different techniques) and the relative rate (two different references) of Chen et al. (2003) are in good agreement. A fit to the absolute rate data set gives $k(HO+CF_3CHFCF_2CH_2OH) = 2.26 \times 10^{-12} \exp(-848/T)$ cm^3 molecule^{-1} s^{-1}. The HO radical initiated oxidation of $CF_3CHFCF_2CH_2OH$ is expected to proceed mainly via abstraction from the $-CH_2-$ group leading to essentially quantitative conversion into CF_3CHFCF_2CHO as discussed by Calvert et al. (2011).

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Wallington, T. J.: Atmos. Chem. Phys., 8, 4141, 2008; IUPAC Subcommittee for Gas Kinetic Data Evaluation, http://iupac.pole-ether.fr.

Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M., and Wallington T. J.: The Mechanisms of Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, NY, 2011.

Chen, L., Tokuhashi, K., Kutsuna, S., Sekiya, A., Yonei, Y., and Yamamoto, A.: Chem. Phys. Lett., 382, 277, 2003.