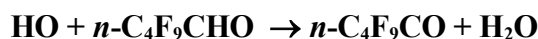


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet of FOx100; VII.A5.19

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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.



### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(2.0 \pm 0.5) \times 10^{-12} \exp[-(356 \pm 70)/T]$	253 – 373	Solignac et al. (2007)	PLP-LIF (a)
$(6.4 \pm 0.3) \times 10^{-13}$	299		
<i>Relative Rate Coefficients</i>			
$(5.68 \pm 0.74) \times 10^{-13}$	296	Sulbaek Andersen et al. (2004)	RR (b)
$(6.42 \pm 0.75) \times 10^{-13}$			

### Comments

- (a) HO radicals were generated by the photolysis of  $\text{H}_2\text{O}_2$  at 248 nm in the presence of  $\text{C}_4\text{F}_9\text{CHO}$  in 100 Torr (133 mbar) of helium diluent.
- (b) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO}$  in 700 Torr (933 mbar) of air in the presence of NO. In separate experiments  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  were used as reference compounds. The loss of  $\text{C}_4\text{F}_9\text{CHO}$  and the reference compounds were monitored using FTIR spectroscopy. Experiments were performed using  $\text{CF}_3\text{CHO}$ ,  $\text{C}_3\text{F}_7\text{CHO}$ , and  $\text{C}_4\text{F}_9\text{CHO}$ . There was no discernable difference in reactivity of the three fluorinated aldehydes. An analysis of the combined data set gave rate coefficient ratios of  $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CHO})/k(\text{HO} + \text{C}_2\text{H}_2) = 0.73 \pm 0.10$  and  $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CHO})/k(\text{HO} + \text{C}_2\text{H}_4) = 0.0813 \pm 0.0095$ . Scaling these ratios using  $k(\text{HO} + \text{C}_2\text{H}_2) = 7.8 \times 10^{-13}$  and  $k(\text{HO} + \text{C}_2\text{H}_4) = 7.9 \times 10^{-12}$  (Atkinson et al., 2006) gives  $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CHO}) = (5.68 \pm 0.74) \times 10^{-13}$  and  $(6.42 \pm 0.75) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

### Preferred Values

Parameter	Value	$T/\text{K}$
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$6.1 \times 10^{-13}$	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.07 \times 10^{-12} \exp(-363/T)$	250-380
<i>Reliability</i>		
$\Delta \log k$	0.12	298
$\Delta E/R$	$\pm 150$	250-380

### 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

298 K. A fit to the data from Solignac et al. (2007) gives the recommendation of  $k(\text{HO}+\text{C}_4\text{F}_9\text{CHO}) = 2.07 \times 10^{-12} \exp(-363/T)$  which gives  $6.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. As shown by Sulbaek Andersen et al. (2004), the reaction proceeds via abstraction of the aldehydic hydrogen to give  $\text{C}_4\text{F}_9\text{C}(\text{O})$  radicals.

### 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>.
- Solignac, G., Mellouki, A., Le Bras, G., Yujing, M., and Sidebottom, H.: Phys. Chem. Chem. Phys., 9, 4200, 2007.
- Sulbaek Andersen, M. P., Nielsen, O. J., Hurley, M. D., Ball, J. C., Wallington, T. J., Stevens, J. E., Martin, J. W., Ellis, D. A., and Mabury, S. A.: J. Phys. Chem. A, 108, 5189, 2004.

