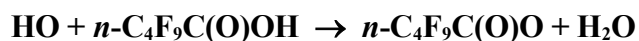


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet of FOx107; VII.A5.29

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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 2014; 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>Relative Rate Coefficients</i>			
$(1.54 \pm 0.17) \times 10^{-13}$	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<sub>3</sub>ONO in C<sub>4</sub>F<sub>9</sub>C(O)OH/CH<sub>3</sub>ONO/NO/(C<sub>2</sub>H<sub>2</sub> or C<sub>2</sub>H<sub>4</sub>) mixtures in 700 Torr (933 mbar) of air. The loss of the reference compounds C<sub>2</sub>H<sub>2</sub> or C<sub>2</sub>H<sub>4</sub> was monitored by FTIR spectroscopy. The loss of C<sub>4</sub>F<sub>9</sub>C(O)OH was small and difficult to observe directly. The loss of C<sub>4</sub>F<sub>9</sub>C(O)OH was calculated from the formation of COF<sub>2</sub> observed by FTIR spectroscopy. Experiments performed using C<sub>2</sub>F<sub>5</sub>C(O)OH, C<sub>3</sub>F<sub>7</sub>C(O)OH, and C<sub>4</sub>F<sub>9</sub>C(O)OH gave indistinguishable values of the rate coefficient ratio  $k(\text{HO}+\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH})/k(\text{HO}+\text{reference})$ . Analysis of the composite data set gave  $k(\text{HO}+\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH})/k(\text{HO}+\text{C}_2\text{H}_2) = 0.197 \pm 0.022$  and  $k(\text{HO}+\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH})/k(\text{HO}+\text{C}_2\text{H}_4) = 0.0198 \pm 0.0014$ . 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 the values of  $k(\text{HO}+\text{C}_x\text{F}_{2x+1}\text{CHO})$  listed in the table above.

### Preferred Values

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

### Comments on Preferred Values

The recommendation is based on the study by Hurley et al. (2004). The C<sub>4</sub>F<sub>9</sub>C(O)O radical decomposes rapidly to give CO<sub>2</sub> and a C<sub>4</sub>F<sub>9</sub> radical. As discussed by Ellis et al. (2005), the C<sub>4</sub>F<sub>9</sub> radical will be converted mainly into COF<sub>2</sub> with CF<sub>3</sub>C(O)OH, C<sub>2</sub>F<sub>5</sub>C(O)OH, and C<sub>3</sub>F<sub>7</sub>C(O)OH formed as minor products. As might be expected from their similar molecular structure, C<sub>4</sub>F<sub>9</sub>C(O)OH has a reactivity towards HO radicals which is indistinguishable from those of C<sub>2</sub>F<sub>5</sub>C(O)OH and C<sub>3</sub>F<sub>7</sub>C(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.