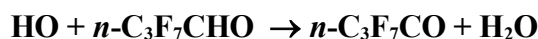


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oFOx99; VII.A5.18

Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

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/<br>Comments |
|-------------------------------------------------------|--------------|--------------------------------|------------------------|
| <i>Absolute Rate Coefficients</i>                     |              |                                |                        |
| $(2.0 \pm 0.6) \times 10^{-12} \exp[-(369 \pm 90)/T]$ | 252 - 373    | Solignac et al. (2007)         | PLP-LIF (a)            |
| $5.55 \times 10^{-13}$                                | 297          |                                | (b)                    |
| <i>Relative Rate Coefficients</i>                     |              |                                |                        |
| $(5.68 \pm 0.74) \times 10^{-13}$                     | 296          | Sulbaek Andersen et al. (2004) | RR (c)                 |
| $(6.42 \pm 0.75) \times 10^{-13}$                     |              |                                |                        |

## Comments

- (a) HO radicals were generated by the photolysis of  $\text{H}_2\text{O}_2$  at 248 nm in the presence of  $\text{C}_3\text{F}_7\text{CHO}$  in 100 Torr (133 mbar) of helium diluent.
- (b) Average of values given at 297 K
- (c) 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  $\text{C}_3\text{F}_7\text{CHO}$  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                               | $T/\text{K}$ |
|------------------------------------------------------|-------------------------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $5.9 \times 10^{-13}$               | 298          |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $2.02 \times 10^{-12} \exp(-368/T)$ | 250-380      |
| <i>Reliability</i>                                   |                                     |              |
| $\Delta \log k$                                      | 0.12                                | 298          |

## 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

298K. A fit to the data from Solignac et al. (2007) gives the recommendation of  $k(\text{HO}+\text{C}_3\text{F}_7\text{CHO}) = 2.02 \times 10^{-12} \exp(-368/T)$  which gives  $5.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. As shown by Sulbaek Andersen et al. (2004), the reaction proceeds via abstraction of the aldehydic hydrogen to give  $\text{C}_3\text{F}_7\text{C}(\text{O})$  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.

