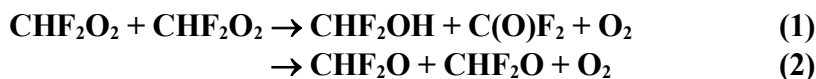


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx66

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This data sheet updated: 24<sup>th</sup> January 2006.



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = (5.0 \pm 0.7) \times 10^{-12}$	298	Nielsen et al., 1992	PR-UVA (a,b)
<i>Branching Ratios</i>			
$k_2/k \approx 1.0$	298	Nielsen et al., 1992	UVP-FTIR (c)

## Comments

- (a)  $k_{\text{obs}}$  is based on the measured overall second-order decay of  $\text{CHF}_2\text{O}_2$ , defined by  $-\text{d}[\text{CHF}_2\text{O}_2]/\text{dt} = 2k_{\text{obs}}[\text{CHF}_2\text{O}_2]^2$ . As described in detail by Lesclaux (1997),  $\text{HO}_2$  radicals formed from the subsequent chemistry of  $\text{CHF}_2\text{O}$  (formed from channel (2)) are expected to lead to secondary removal of  $\text{CHF}_2\text{O}_2$ . The true value of  $k$  is expected to fall in the range  $k_{\text{obs}}/(1+\alpha) < k < k_{\text{obs}}$ , where  $\alpha = k_2/k$ .
- (b) Pulse radiolysis study of  $\text{CH}_2\text{F}_2\text{-O}_2\text{-SF}_6$  mixtures at a total pressure of 1000 mbar.  $\text{CHF}_2\text{O}_2$  radicals were monitored by UV absorption with  $\sigma_{240 \text{ nm}} = (2.66 \pm 0.46) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .
- (c)  $\text{CHF}_2\text{O}_2$  radicals were generated from the steady-state photolysis of  $\text{Cl}_2\text{-CH}_2\text{F}_2$  mixtures in the presence of air at a total pressure of 933 mbar. The decay of  $\text{CH}_2\text{F}_2$  and the formation of  $\text{C(O)F}_2$  were monitored by FTIR spectroscopy. The yield of  $\text{C(O)F}_2$  was  $104 \pm 2\%$  of the removal of  $\text{CH}_2\text{F}_2$ .

## Preferred Values

$k = (2.5\text{-}5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_2/k \approx 1.0$  at 298 K.

### Comments on Preferred Values

We have recommended a range of values for the rate coefficient at 298 K, based on the determination by Nielsen et al. (1992). The upper limit is the measured value of  $k_{\text{obs}}$  with no correction for possible secondary  $\text{CHF}_2\text{O}_2$  removal by  $\text{HO}_2$  radicals, and the lower limit is a factor of two less than the upper limit, corresponding to a maximum correction for the  $\text{HO}_2$  radical reaction.

The product study in the same paper (Nielsen et al., 1992) showed that the only carbon-containing product was  $\text{COF}_2$ , indicating that channel (2) is the predominant, if not the only, pathway, formed followed by the reaction  $\text{CHF}_2\text{O} + \text{O}_2 \rightarrow \text{C(O)F}_2 + \text{HO}_2$ . The absence of the product  $\text{CHF}_2\text{O}_2\text{H}$  expected from the reaction  $\text{CHF}_2\text{O}_2 + \text{HO}_2 \rightarrow \text{CHF}_2\text{O}_2\text{H} + \text{O}_2$ , raises several possibilities, including a slow reaction between  $\text{CHF}_2\text{O}_2$  and  $\text{HO}_2$  radicals or an alternative reaction pathway, such as  $\text{CHF}_2\text{O}_2 + \text{HO}_2 \rightarrow \text{C(O)F}_2 + \text{H}_2\text{O} + \text{O}_2$ . More information is needed on the kinetics and mechanism of the  $\text{CHF}_2\text{O}_2 + \text{HO}_2$  reaction to define  $k$  and  $k_2/k$  more

accurately.

### References

Lesclaux, R.: Combination of peroxy radicals in the gas phase. In 'Peroxy Radicals', edited by Z.B. Alfassi. John Wiley and Sons, 1997.

Nielsen, O. J., Ellermann, T., Bartkiewicz, E., Wallington, T.J. and Hurley, M.D.: Chem. Phys. Lett. 192, 82, 1992.