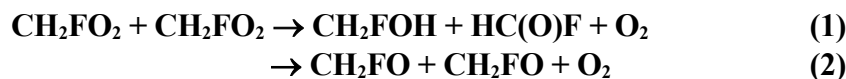


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FO<sub>x</sub>65

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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>			
$k_{\text{obs}} = 3.3 \times 10^{-13} \exp[(700 \pm 100)/T]$	228-380	Dagaut et al., 1988	FP-UVA (a,b)
$k_{\text{obs}} = (3.07 \pm 0.65) \times 10^{-12}$	298		
$k_{\text{obs}} = (4.01 \pm 0.52) \times 10^{-12}$	298	Wallington et al., 1992	PR-UVA (a,c)
<i>Branching Ratios</i>			
$k_2/k > 0.77$	298	Wallington et al., 1992	UVP-FTIR (d)

## Comments

- (a)  $k_{\text{obs}}$  is based on the measured overall second-order decay of  $\text{CH}_2\text{FO}_2$ , defined by  $-\text{d}[\text{CH}_2\text{FO}_2]/\text{dt} = 2k_{\text{obs}}[\text{CH}_2\text{FO}_2]^2$ . As described in detail by Lesclaux (1997),  $\text{HO}_2$  radicals formed from the subsequent chemistry of  $\text{CH}_2\text{FO}$  (formed from channel (2)) are expected to lead to secondary removal of  $\text{CH}_2\text{FO}_2$ . 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) Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{F-O}_2\text{-N}_2$  mixtures at total pressures of 33-533 mbar.  $\text{CH}_2\text{FO}_2$  radicals were monitored by UV absorption with  $\sigma_{240 \text{ nm}} = (3.72 \pm 0.45) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .
- (c) Pulse radiolysis study of  $\text{CH}_3\text{F-O}_2\text{-SF}_6$  mixtures at a total pressure of 1000 mbar.  $\text{CH}_2\text{FO}_2$  radicals were monitored by UV absorption with  $\sigma_{240 \text{ nm}} = (4.11 \pm 0.67) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .
- (d)  $\text{CH}_2\text{FO}_2$  radicals were generated from the steady-state photolysis of  $\text{Cl}_2\text{-CH}_3\text{F}$  mixtures at 933 mbar pressure of air. The decay of  $\text{CH}_3\text{F}$  and the formation of products was monitored by FTIR spectroscopy. No  $\text{CH}_2\text{FOH}$  was observed within the detection limits of the apparatus. Significant amounts of  $\text{HC(O)F}$  were observed ( $86 \pm 5\%$ ) and, in experiments with high conversions,  $\text{CH}_2\text{FOOH}$  was observed ( $11 \pm 4\%$ ).

## Preferred Values

$k = 2.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 2.5 \times 10^{-13} \exp(700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220-380 K.

$k_2/k = 1.0$  at 298 K.

## Reliability

$\Delta \log k = \pm 0.3$  at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$ .

$\Delta(k_2/k) = {}^{+0.0}_{-0.2}$  at 298 K.

### Comments on Preferred Values

The product study of Wallington et al. (1992) showed no formation of CH<sub>2</sub>FOH, suggesting that channel (1) is negligible at 298 K. The high yields of HC(O)F are also consistent with the dominance of channel (2), followed by reaction of CH<sub>2</sub>FO with O<sub>2</sub> to form HC(O)F and HO<sub>2</sub>. A more recent product study of the CH<sub>2</sub>FO<sub>2</sub> + HO<sub>2</sub> reaction (Wallington et al., 1994) has shown that the only ca. 30% of that reaction produces CH<sub>2</sub>FO<sub>2</sub>H and O<sub>2</sub>, with the remainder forming HC(O)F, H<sub>2</sub>O and O<sub>2</sub>. The low yields of CH<sub>2</sub>FO<sub>2</sub>H observed by Wallington et al. (1992) are thus partially explained by this, but also suggest that HO<sub>2</sub> is probably removed by its self reaction in competition with reaction with CH<sub>2</sub>FO<sub>2</sub>.

The preferred value of  $k$  at 298 K is derived from the  $k_{\text{obs}}$  values reported by Dagaut et al. (1988) and Wallington et al. (1992), adjusted to be consistent with the re-evaluation of  $\sigma_{240 \text{ nm}}(\text{CH}_2\text{FO}_2) = 4.03 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  by Nielsen and Wallington (1997). Similar to a procedure adopted by Lesclaux (1997) for peroxy radicals for which the self reaction rate coefficients are  $\geq \text{ca. } 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k$  is estimated to be  $k_{\text{obs}}/(1+0.5(k_2/k))$ , with this approximation assuming that the secondary reaction of HO<sub>2</sub> with CH<sub>2</sub>FO<sub>2</sub> competes equally with its removal via HO<sub>2</sub> + HO<sub>2</sub>. The reliability range reflects that  $k$  has been derived by this approximate procedure. The preferred value of  $E/R$  is based on the  $k_{\text{obs}}$  expression of Dagaut et al. (1988). This assumes that the above competition remains valid over the entire temperature range, consistent with the CH<sub>2</sub>FO<sub>2</sub> and HO<sub>2</sub> self reactions, and reaction of CH<sub>2</sub>FO<sub>2</sub> with HO<sub>2</sub> possessing similar temperature dependences.

### References

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