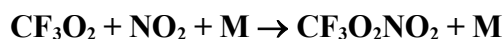


IUPAC Task Group on Atmospheric Kinetic Data Evaluation – Data Sheet IV.A1.62 of FOx63

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$$\Delta H^\circ = -105 \text{ kJ mol}^{-1}$$

Low-pressure rate coefficients Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(2.7 \pm 0.8) \times 10^{-29} (T/298)^{-4.7} [\text{O}_2]$	233-373	Caralp et al., 1988	PLP-MS (a)
$6.3 \times 10^{-33} \exp(2710/T) [\text{N}_2]$	264-297	Mayer-Figge, Zabel and Becker, 1996	(b)
$5.6 \times 10^{-29} (T/298)^{-9.1} [\text{N}_2]$			

Comments

- (a) Pulsed laser photolysis–MS study in 1-10 Torr O_2 . Extrapolation with $F_c = \exp(-T/416)$, i.e., $F_c = 0.49$ at 298 K, and $k_\infty = 8.9 \times 10^{-12} (T/298)^{-0.72} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from RRKM model.
- (b) From measurements of the reverse dissociation of $\text{CF}_3\text{O}_2\text{NO}_2$. Equilibrium constants $K_c = 3.80 \times 10^{27} \exp(-12140/T) \text{ molecule cm}^{-3}$ derived by combining the dissociation data with the recombination data from Caralp et al. (1988) over the falloff curve, assuming equal results for the bath gases N_2 and O_2 . Extrapolation with $F_c = 0.31$ and $k_\infty = 7.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

$$k_0 = 5.6 \times 10^{-29} (T/298)^{-9} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 260-300 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.2 \text{ at 298 K.}$$

$$\Delta n = \pm 3.$$

Comments on Preferred Values

The data by Mayer-Figge et al. (1996) are preferred because they cover a much broader part of the falloff curve and employ a more reasonable value of $F_c = 0.31$, thus allowing for a better extrapolation to the low pressure limit. Nevertheless, the rate data from Caralp et al. (1988) and Mayer-Figge et al. (1996) are identical over the range 1.3-13 mbar because both sets of data have been used for the conversion from dissociation to recombination rate coefficients.

High-pressure rate coefficients Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$8.9 \times 10^{-12} (T/298)^{-0.72}$	233-373	Caralp et al., 1988	PLP-MS(a)
$7.7 \times 10^{-12} (T/298)^{-0.67}$	264-297	Mayer-Figge, Zabel, and Becker, 1996	(b)

Comments

- (a) See comment (a) for k_0 .
 (b) See comment (b) for k_0 .

Preferred Values

$k_{\infty} = 7.7 \times 10^{-12} (T/298)^{-0.67} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260-300 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.2$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

See Comments on Preferred Values for k_0 .

The following text-line combines the preferred values for the high and low pressure limiting rate coefficients to generate a single, cut-and-paste expression for calculation of k :

```
=(5.6e-29*(T/298)^-9)*M*(7.7e-12*(T/298)^-0.67)/((5.6e-29*(T/298)^-9)*M+(7.7e-12*(T/298)^-0.67))*10^(log10(0.31)/(1+(log10((5.6e-29*(T/298)^-9)*M/(7.7e-12*(T/298)^-0.67))/(0.75-1.27*log10(0.31))))^2)
```

The molecular density, $M = 7.243 \times 10^{21} \text{ P}(\text{bar})/\text{T}(\text{K})$

References

- Caralp, F., Lesclaux, R., Rayez, M.-T., Rayez, J.-C. and Forst, W.: J. Chem. Soc. Faraday Trans 2, 84, 569, 1988.
 Mayer-Figge, A., Zabel, F. and Becker, K.H.: J. Phys. Chem., 100, 6587, 1996.