IUPAC Task Group on Atmospheric Kinetic Data Evaluation – Data Sheet IV.A1.62 oFOx63

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$CF_3O_2 + NO_2 + M \rightarrow CF_3O_2NO_2 + M$

$\Delta H° = -105$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.7 \pm 0.8) \times 10^{-29} (T/298)^{-4.7}$ [O_2]	233-373	Caralp et al., 1988	PLP-MS (a)
$6.3 \times 10^{-33} \exp(2710/T)$ [N_2]	264-297	Mayer-Figge, Zabel and Becker, 1996	(b)
$5.6 \times 10^{-29} (T/298)^{-9.1}$ [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 $k_\infty = 8.9 \times 10^{-12} (T/298)^{-0.72}$ cm^3 molecule^{-1}s^{-1} from RRKM model.

(b) From measurements of the reverse dissociation of $CF_3O_2NO_2$. Equilibrium constants $K_c = 3.80 \times 10^{27} \exp(-12140/T)$ 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 $k_\infty = 7.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k_0 = 5.6 \times 10^{-29} (T/298)^{-9}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 260-300 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ 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_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$8.9 \times 10^{-12} (T/298)^{-0.72}$	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

$k_\infty = 7.7 \times 10^{-12} (T/298)^{-0.67}$ cm^3 molecule^{-1} 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 = 7.243×10^{21}P(bar)/T(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.