IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A6.128 ROO_9

This datasheet last evaluated: 4th June 2009. Last change in preferred values: 12th June 2003.

$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$

$\Delta H° = -92.7$ 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			
$(2.33 \pm 0.08) \times 10^{-30}$ [N_2]	298	Sander and Watson, 1980[1]	FP-AS (a)
2.2×10^{-30} $(T/300)^{-2.5}$ [N_2]	253-353	Ravishankara, Eisele, and Wine, 1980[2]	FP-AS (b)
$(1.46 \pm 0.50) \times 10^{-30}$ [SF_6]	295	Wallington, Nielsen, and Sehested, 1999[3]	(c)

Comments

(a) Pressure range 70 mbar to 900 mbar for the bath gases He, N_2, and SF_6. Analysis of the falloff curve was carried out with a theoretical F_c value of 0.39, in good agreement with the fitted value of $F_c = 0.4 \pm 0.10$.

(b) Pressure range 100 mbar to 950 mbar. Analyses of the falloff curves at 253 K, 298 K and 353 K were carried out with $F_c = 0.4$ independent of temperature.

(c) Pulse radiolysis study in 0.5-14 bar of SF_6. Evaluating of the falloff curve with $F_c = 0.40$.

Preferred Values

$k_0 = 2.5 \times 10^{-30}$ $(T/300)^{-5.5}$ [N_2] cm^3 molecule^{-1} s^{-1}, over the temperature range 250 to 350 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the results from refs. 1 and the theoretical analysis from ref. 4. These values are based on a theoretically determined value of $F_c = 0.36$ at 300 K.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
$(8.0 \pm 1.0) \times 10^{-12}$	298	Sander and Watson, 1980[1]	FP-AS (a)
7×10^{-12} $(T/298)^{-3.5}$	253-353	Ravishankara, Eisele, and Wine, 1980[2]	FP-AS (b)
$(1.8 \pm 0.25) \times 10^{-11}$	295	Wallington, Nielsen, and Sehested, 1999[3]	(c)

Comments

(a) See comment (a) for k_0.
(b) See comment (b) for k_0. The large negative temperature coefficient is probably an artifact of the interpretation. If a larger negative temperature exponent for k_0 and a smaller F_c value at higher temperature are used, the large negative temperature exponent of k_∞ will decrease.
(c) See comment (c) for k_0.

Preferred Values

$k = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k_\infty = 1.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250 to 350 K.

Reliability
$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values
The preferred values are based on the high pressure study from ref. 3. An experimental value of $F_c = 0.36$ at 298 K appears well established. Less complete information on the falloff range is obtained from the experiments by Cox and Tyndall,[5] who measured $k = 1.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 700 mbar of N_2 and 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 66 mbar of Ar at 275 K, and Bridier, Lesclaux, and Veyret[6] who measured $k = 4.4\ (\pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K in 1 bar of air. The apparent observation of a pressure independent rate coefficient k over the range 66 mbar to 760 mbar of Ar, reported by Adachi and Basco,[7] is not confirmed by refs. 1 and 2. ΔH is taken from the equilibrium measurements of ref. 6.
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:

=((2.5e-30*(T/300)^-5.5)*M*(1.8e-11))/((2.5e-30*(T/300)^-5.5)*M+(1.8e-11))*10^(log10(0.36)/(1+(log10((2.5e-30*(T/300)^-5.5)*M/(1.8e-11))/(0.75-1.27*log10(0.36)))^2))

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

References

[1] S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).
[2] A. R. Ravishankara, F. L. Eisele, and P. H. Wine, J. Chem. Phys. **73**, 3743 (1980).
[3] T. J. Wallington, O. J. Nielsen, and K. Sehested, Chem. Phys. Lett. **313**, 456 (1999).
[4] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[5] R. A. Cox and G. S. Tyndall, J. Chem. Soc. Faraday Trans. 2, **76**, 153 (1980).
[6] I. Bridier, R. Lesclaux, and B. Veyret, Chem. Phys. Lett. **119**, 259 (1992).
[7] H. Adachi and N. Basco, Int. J. Chem. Kinet. **12**, 1 (1980).