IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A6.134

This datasheet last evaluated: 12th June 2003.

$C_2H_5C(O)O_2NO_2 + M \rightarrow C_2H_5C(O)O_2 + NO_2 + M$

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
1.7 x 10^{-3} exp(-11280/T) [N_2]	291-320	Kirchner *et al.*, 1999[1]	(a)

Comments

(a) Experiments in a 420 l reaction chamber with photolytic generation of radicals forming peroxynitrates. Decomposition of propionyl peroxynitrate followed in the dark by FTIR spectrometry. Experiments between 11.5 and 1013 mbar of N_2. Falloff extrapolations with F_c = 0.36.

Preferred Values

k_0 = 1.7 x 10^{-3} exp(-11280/T) [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 290-320 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 2000$ K.

Comments on Preferred Values

The only available low pressure data from ref. 1 appear consistent with the more extensive data base for the high-pressure range. The falloff curve is constructed with F_c = 0.36.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
2 x 10^{15} exp (-12800/*T*)	300-315	Mineshos and Glavas, 1991[2]	(a)
4.4 x 10^{-4}	298*		
8.3 x 10^{16} exp(-13940/*T*)	291-320	Kirchner *et al.*, 1999[1]	(b)
4.0 x 10^{-4}	298		

Comments

(a) Thermal decomposition of propionyl peroxynitrate (PPN) in a 4.5 liter glass flask in the presence of 1 bar of N_2. PPN and the products ethyl nitrate, NO_2, and methyl nitrate were analyzed by GC at 323 K. In the presence of NO, ethyl nitrate was the major product observed.

(b) See comment (a) for k_0. Limited data from earlier work are also considered.

Preferred Values

k = 3.6 x 10^{-4} s^{-1} at 298 K and 1 bar of air.
k_∞ = 4.0 x 10^{-4} s^{-1} at 298 K.
k_∞ = 8.3 x 10^{16} exp(-13940/*T*) s^{-1} over the temperature range 290 K to 320 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values

The values from refs. 1 and 2 which are in very good agreement.

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:

=((1.7e-3*exp(-11280/*T*))*M*(8.3e16*exp(-13940/*T*)))/((1.7e-3*exp(-11280/*T*))*M+(8.3e16*exp(-13940/*T*)))*10^(log10(0.36)/(1+(log10((1.7e-3*exp(-11280/*T*))*M/(8.3e16*exp(-13940/*T*)))/(0.75-1.27*log10(0.36)))^2))

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

References

1 F. Kirchner, A. Mayer-Figge, F. Zabel, and K. H. Becker, Int. J. Chem. Kinet. **31**, 127 (1999).
2 G. Mineshos and S. Glavas, React. Kinet. Catal. Lett. **45**, 305 (1991).