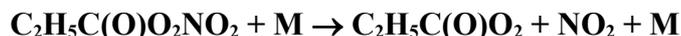


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A6.134

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This datasheet last evaluated: 12th June 2003.



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>			
$1.7 \times 10^{-3} \exp(-11280/T) [\text{N}_2]$	291-320	Kirchner <i>et al.</i> , 1999 ¹	(a)

Comments

- (a) Experiments in a 420 l reaction chamber with photolytic generation of radicals forming peroxy nitrates. Decomposition of propionyl peroxy nitrates 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

$k_0 = 1.7 \times 10^{-3} \exp(-11280/T) [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$2 \times 10^{15} \exp(-12800/T)$	300-315	Mineshos and Glavas, 1991 ²	(a)
4.4×10^{-4}	298*		
$8.3 \times 10^{16} \exp(-13940/T)$	291-320	Kirchner <i>et al.</i> , 1999 ¹	(b)
4.0×10^{-4}	298		

Comments

- (a) Thermal decomposition of propionyl peroxyxynitrate (PPN) in a 4.5 liter glass flask in the presence of 1 bar of N₂. PPN and the products ethyl nitrate, NO₂, 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

$k = 3.6 \times 10^{-4} \text{ s}^{-1}$ at 298 K and 1 bar of air.

$k_{\infty} = 4.0 \times 10^{-4} \text{ s}^{-1}$ at 298 K.

$k_{\infty} = 8.3 \times 10^{16} \exp(-13940/T) \text{ s}^{-1}$ over the temperature range 290 K to 320 K.

Reliability

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

$\Delta(E/R) = \pm 1000 \text{ K}$.

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

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).