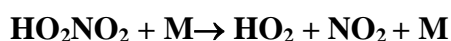


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.47 NO_x17

Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. The citation for this datasheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys. 4, 1461, 2004; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>).

This data sheet last evaluated: November 2017; last change in preferred values: June 2012.



$$\Delta H^\circ = 100.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.5 \times 10^{-20} [\text{N}_2]$	298	Cox and Patrick, 1979	(a)
$5.2 \times 10^{-6} \exp[-(10014 \pm 250)/T] [\text{N}_2]$	261-295	Graham et al., 1978	(b)
$1.3 \times 10^{-20} [\text{N}_2]$	298		
$4.1 \times 10^{-5} \exp[-(10645 \pm 260)/T] [\text{N}_2]$	261-307	Zabel, 1995	(c)
$1.2 \times 10^{-20} [\text{N}_2]$	298		
$2.1 \times 10^{-18} [\text{N}_2]$	348	Gierczak et al., 2005	(d)

Comments

- Derived from measurements of the reverse reaction. Conversion of the data to the dissociation reaction of HO₂NO₂ using the equilibrium constant $K_c = 1.68 \times 10^{28} \exp(-11977/T) \text{ cm}^3 \text{ molecule}^{-1}$ from Uselman et al. (1978) and comparison with earlier dissociation data.
- FTIR study in a 5800 L chamber. Measurements were made at 1-7 Torr of N₂. At higher pressures, deviations from low pressure behavior were observed.
- FTIR study in a 420 L chamber. The pressure range was 10-772 Torr. The falloff curve was evaluated with $F_c = 0.5$.
- Pulsed LIF experiments. NO was added to HO₂NO₂ in equilibrium with HO₂ and NO₂, and OH was detected. Temperatures between 330 and 350 K and pressures of N₂ between 33 and 66 mbar were applied. The resulting rate coefficients agree well with the extrapolated results from Zabel (1995).

Preferred Values

$$k_0 = 1.3 \times 10^{-20} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 4.1 \times 10^{-5} \exp(-10650/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 260\text{-}300 \text{ K.}$$

Comments on Preferred Values

The preferred values are from the study of Zabel (1995), and are in close agreement with those from Graham et al. (1978). The data from Zabel (1995) provide a consistent picture with other RO₂NO₂ dissociation reactions. Falloff curves are constructed with $F_c = 0.5$. A revised equilibrium constant $K_c = 4.76 \times 10^{26} \exp(-10900/T) \text{ cm}^3 \text{ molecule}^{-1}$ from Burkholder et al (2015), together with the preferred value of the present evaluation for the reverse reaction would lead to $k_0 = 6.7 \times 10^{-5} (T/300)^{-3.1} \exp(-10900/T) [\text{N}_2] \text{ s}^{-1}$ and $k_0 = 8.7 \times 10^{-21} [\text{N}_2] \text{ s}^{-1}$ at 298 K.

High-pressure rate coefficients Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
>0.018	278	Graham et al., 1978	(a)
$5.7 \times 10^{15} \exp(-11170/T)$	261-307	Zabel, 1995	(b)
0.30	298		

Comments

- (a) See comment (b) for k_0 . This is a lower limit since a linear Lindemann-Hinshelwood evaluation of the falloff curve (i.e. $F_c = 1$) was made for the pressure range 10-760 Torr of N₂.
 (b) See comment (c) for k_0 .

Preferred Values

$k_\infty = 0.31 \text{ s}^{-1}$ at 298 K.

$k_\infty = 6.0 \times 10^{15} \exp(-11170/T) \text{ s}^{-1}$ over the temperature range 260-300 K.

Comments on Preferred Values

See Comments on Preferred Values for k_0 . The data from Zabel (1995) were reevaluated with $F_c = 0.4$ such as used for the falloff curves of the reverse reaction $\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2 + \text{M}$, because F_c is identical for the forward and backward reaction. Since the measurements from Zabel (1995) were made closer to the low pressure limit, only the extrapolation to k_∞ is noticeably influenced by the change of the used F_c . A revised equilibrium constant $K_c = 4.76 \times 10^{26} \exp(-10900/T) \text{ cm}^3 \text{ molecule}^{-1}$ from Burkholder et al (2015), together with the preferred value of the present evaluation for the reverse reaction would lead to $k_\infty = 1.9 \times 10^{15} \exp(-10900/T) [\text{N}_2] \text{ s}^{-1}$ and $k_\infty = 0.25 \text{ s}^{-1}$ at 298 K.

Preferred Values

Parameter	Value	T/K
k_0/s^{-1}	$1.3 \times 10^{-20} [\text{N}_2]$	298
k_0/s^{-1}	$4.1 \times 10^{-5} \exp(-10650/T) [\text{N}_2]$	260-300
k_∞/s^{-1}	0.31	298
k_∞/s^{-1}	$6.0 \times 10^{15} \exp(-11170/T) [\text{N}_2]$	260-300
$k(1 \text{ bar N}_2)/\text{s}^{-1}$	6.2×10^{-2}	298
F_c	0.4	260-300
<i>Reliability</i>		
$\Delta \log k_0$	± 0.3	298

$\Delta E_0/R$	± 500 K	260-300
$\Delta \log k_\infty$	± 0.5	298
$\Delta E_\infty/R$	± 500 K	260-300

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 :

$$= ((4.1e-5 * \exp(-10650/T)) * M * (6.0e15 * \exp(-11170/T))) / ((4.1e-5 * \exp(-10650/T)) * M + (6.0e15 * \exp(-11170/T))) * 10^{(\log_{10}(0.4) / (1 + (\log_{10}((4.1e-5 * \exp(-10650/T)) * M / (6.0e15 * \exp(-11170/T)))) / (0.75 - 1.27 * \log_{10}(0.4))))^2)}$$

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

References

- Burkholder, J. B., Sander, S. P., Abbatt, J., Barker, J. R., Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, NASA Panel for Data Evaluation, Evaluation Number 18, JPL Publication 15-10, 2015.
- Cox, R. A., and Patrick, K.: Int. J. Chem. Kinet. 11, 635, 1979.
- Gierczak, T., Jiménez, E., Riffault, V., Burkholder, J. B., and Ravishankara, A. R.: J. Phys. Chem. A 109, 586, 2005.
- Graham, R. A., Winer, A. M., and Pitts, J. N.: Chem. Phys. Lett. 51, 215, 1977; J. Chem. Phys. 68, 4505, 1978.
- Uselman, W. M., Levine, S. Z., Chan, W. H., Calvert, J. G., and Shaw, J. H.: Chem. Phys. Lett. 58, 437, 1978.
- Zabel, F.: Z. Phys. Chem. 188, 119, 1995.