

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.59 NO_x29

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



$$\Delta H^\circ = -57.3 \text{ kJ}\cdot\text{mol}^{-1}$$

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>			
$(1.4 \pm 0.2) \times 10^{-33} [\text{N}_2]$	298	Borrell et al., 1988	PLP (a)
$(1.0 \pm 0.1) \times 10^{-33} [\text{N}_2]$	224	Brunning et al., 1988	FP (b)
$(2.1 \pm 0.2) \times 10^{-12} T^{(-9.0 \pm 0.9)} [\text{He}]$	255-273	Markwalder et al., 1992	(c)

Comments

- Relaxation of NO₂-N₂O₄-N₂ equilibrium mixtures after low intensity pulsed laser photolysis of N₂O₄ at 248 nm. The relaxation to equilibrium was obtained by measuring the change in N₂O₄ absorption at 220 nm. Falloff curves over the range 1-207 bar were extrapolated with $F_c = 0.40$.
- Perturbation of equilibrium mixture of N₂O₄ and NO₂ by photolysis of a fraction of the N₂O₄. The relaxation rate was monitored by IR absorption of N₂O₄ at 1565.5 cm⁻¹.
- Temperature jumps induced by IR absorption of SiF₄ in equilibrium mixtures of NO₂-N₂O₄-He-SiF₄. The relaxation to equilibrium was followed by measuring NO₂ and N₂O₄ concentrations by absorption spectroscopy at 420 and 250 nm, respectively. Falloff curves over the range 0.3-200 bar were extrapolated with $F_c = 0.52$ (see also earlier data from Gozel et al., 1984).

Preferred Values

$$k_0 = 1.4 \times 10^{-33} (T/300)^{-3.8} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 300-500 K.}$$

Comments on Preferred Values

The preferred values are from the most extensive study of Borrell et al. (1988), where a nearly complete falloff curve was measured. Earlier less extensive measurements are in reasonable agreement with this curve which uses $F_c = 0.40$. The temperature dependence given is from the theoretical modeling of Borrell et al. (1988), rather than from the limited experimental information of Markwalder et al. (1992).

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>			
$(8.3 \pm 1.0) \times 10^{-13}$	298	Borrell et al., 1988	PLP (a)
$(3.7 \pm 0.3) \times 10^{-18} T^{(2.3 \pm 0.2)}$	255-273	Markwalder et al., 1992	(b)

Comments

- (a) See comment (a) for k_0 .
 (b) See comment (b) for k_0 .

Preferred Values

$k_{\infty} = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250-300 K.

Comments on Preferred Values

The preferred rate coefficient is the mean of the values of Borrell et al. (1988) and Markwalder et al. (1992). The temperature dependence of k_0 and k_{∞} derived from the measurements of Markwalder et al. (1992) appears to be inadequate because it results from the fitting of incomplete parts of the falloff curves. $F_c = 0.4$ is chosen such as derived in Borrell et al. (1988).

Preferred Values

Parameter	Value	T/K
$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.4 \times 10^{-33} [\text{N}_2]$	298
$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.4 \times 10^{-33} (T/300)^{-3.8} [\text{N}_2]$	250-300
$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.0×10^{-12}	298
$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.0×10^{-12}	250-300
$k(1 \text{ bar N}_2)/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.3×10^{-14}	298
F_c	0.6	250-300
<i>Reliability</i>		
$\Delta \log k_0$	± 0.3	298
Δn_0	± 1	250-300
$\Delta \log k_{\infty}$	± 0.3	298
Δn_{∞}	± 0.5	250-300

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 :

$$= ((1.4e-33*(T/300)^{-3.8}*M*(1.0e-12))/((1.4e-33*(T/300)^{-3.8}*M+(1.0e-12))*10^{(\log10(0.4)/(1+(\log10((1.4e-33*(T/300)^{-3.8}*M/(1.0e-12))/(0.75-1.27*\log10(0.4))))^2}))$$

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

References

Borrell, P., Cobos, C. J., and Luther, K.: *J. Phys. Chem.* 92, 4377, 1988.
Bunning, J., Frost, M. J., and Smith, I. W. M.: *Int. J. Chem. Kinet.* 20, 957, 1988.
Gozel, P., Calpini, B., and van den Bergh, H.: *Isr. J. Chem.* 24, 210, 1984.
Markwalder, B., Gozel, P., and van den Bergh, H.: *J. Chem. Phys.* 97, 5472, 1992.