IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.59 NOx29

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$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$

$\Delta H^\circ = -57.3$ 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			
(1.4 ± 0.2) x 10^{-33} [N_2]	298	Borrell et al., 1988	PLP (a)
(1.0 ± 0.1) x 10^{-33} [N_2]	224	Brunning et al., 1988	FP (b)
(2.1 ± 0.2) x 10^{-12} $T^{(-9.0 \pm 0.9)}$ [He]	255-273	Markwalder et al., 1992	(c)

Comments

(a) Relaxation of NO_2-N_2O_4-N_2 equilibrium mixtures after low intensity pulsed laser photolysis of N_2O_4 at 248 nm. The relaxation to equilibrium was obtained by measuring the change in N_2O_4 absorption at 220 nm. Falloff curves over the range 1-207 bar were extrapolated with $F_c = 0.40$.

(b) Perturbation of equilibrium mixture of N_2O_4 and NO_2 by photolysis of a fraction of the N_2O_4. The relaxation rate was monitored by IR absorption of N_2O_4 at 1565.5 cm^{-1}.

(c) Temperature jumps induced by IR absorption of SiF_4 in equilibrium mixtures of NO_2-N_2O_4-He-SiF_4. The relaxation to equilibrium was followed by measuring NO_2 and N_2O_4 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

$k_0 = 1.4 \times 10^{-33} (T/300)^{-3.8}$ [N_2] cm^3 molecule^{-1} s^{-1} 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_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(8.3 ± 1.0) x 10^{-13}	298	Borrell et al., 1988	PLP (a)
(3.7 ± 0.3) x 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_∞ = 1.0 x 10^{-12} cm^3 molecule^{-1} 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/cm^3 molecule^{-1} s^{-1}	1.4 x 10^{-33} [N_2]	298
k_0/cm^3 molecule^{-1} s^{-1}	1.4 x 10^{-33} (T/300)$^{-3.8}$ [N_2]	250-300
k_∞/cm^3 molecule^{-1} s^{-1}	1.0 x 10^{-12}	298
k_∞/cm^3 molecule^{-1} s^{-1}	1.0 x 10^{-12}	250-300
k(1 bar N_2)/cm^3 molecule^{-1} s^{-1}	2.3 x 10^{-14}	298
F_c	0.6	250-300
Reliability		
Δlog k_0	± 0.3	298
Δn_0	± 1	250-300
Δlog k_∞	± 0.3	298
Δn$_\infty$	± 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 = 7.243×10^{21}P(bar)/T(K)

References

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Gozel, P., Calpini, B., and van den Bergh, H.: Isr. J. Chem. 24, 210, 1984.
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