IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.55 NOx25

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$NO + NO_2 + M \rightarrow N_2O_3 + M$

ΔH° = -40.6 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			
(6.7 ± 0.6) x 10^{-33} [Ar]	207 ± 2	Smith and Yarwood, 1987	FP (a)
(9.1 ± 0.7) x 10^{-33} [N_2]	208 ± 2		
(2.8 ± 2.8) x 10^{-15} $T^{-(7.7 \pm 0.8)}$ [Ar]	227-260	Markwalder et al., 1993	(b)
4.1 x 10^{-33} [Ar]			

Comments

(a) Partial photodissociation of N_2O_3 in equilibrium NO_2-N_2O_4-NO-N_2O_3-M mixtures with M = He, Ar, Ne, N_2 and CF_4 (see also Smith and Yarwood, 1986). The relaxation to equilibrium was monitored by observing the absorption of N_2O_3 at the ν_1 band at 1829.59 cm^{-1}. The total pressure was 190-500 Torr. Falloff curves were extrapolated using F_c = 0.60 for Ar and N_2.

(b) CO laser-induced temperature jump measurements with NO_2-N_2O_4-N_2O_3-NO-SiF_4-Ar equilibrium mixtures. The subsequent relaxation toward equilibrium was monitored by UV absorption of N_2O_3 at 253 nm.

Preferred Values

k_0 = 3.1 x 10^{-34} (T/300)$^{-7.7}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K.

Comments on Preferred Values

The preferred values are based on the data from Markwalder et al. (1993) after conversion by the ratio $k_0(N_2)/k_0$ (Ar) = 1.36 of Smith and Yarwood (1987). F_c = 0.6 is chosen.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
$(3.4 \pm 1) \times 10^{-12}$	208	Smith and Yarwood, 1987	FP (a)
$(2.7 \pm 0.9) \times 10^{-15}\ T^{(1.4 \pm 0.2)}$	227-260	Markwalder et al., 1993	(b)
4.7×10^{-12}	208		

Comments

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

Preferred Values

$k_\infty = 7.9 \times 10^{-12}\ (T/300)^{1.4}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K.

Comments on Preferred Values

The preferred values are those from Markwalder et al. (1993), where the largest ranges of the falloff curve were investigated. At 208 K, the values of k_∞ from Smith and Yarwood (1987) and Markwalder et al. (1993) are in reasonable agreement.

Preferred Values

Parameter	Value	T/K
k_0/cm^3 molecule^{-1} s^{-1}	3.1×10^{-34} [N_2]	298
k_0/cm^3 molecule^{-1} s^{-1}	$3.1 \times 10^{-34}\ (T/300)^{-7.7}$ [N_2]	200-300
k_∞/cm^3 molecule^{-1} s^{-1}	7.9×10^{-12}	298
k_∞/cm^3 molecule^{-1} s^{-1}	$7.9 \times 10^{-12}(T/300)^{1.4}$	200-300
k(1 bar N_2)/cm^3 molecule^{-1} s^{-1}	7.5×10^{-15}	298
F_c	0.6	200-300
Reliability		
$\Delta \log k_0$	± 0.3	298
Δn_0	± 1	200-300
$\Delta \log k_\infty$	± 0.3	298
Δn_∞	± 0.5	200-300

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:

=((3.1e-34*(*T*/300)^-7.7)*M*(7.9e-12*(*T*/300)^1.4))/((3.1e-34*(*T*/300)^-7.7)*M+(7.9e-12*(*T*/300)^1.4))*10^(log10(0.6)/(1+(log10((3.1e-34*(*T*/300)^-7.7)*M/(7.9e-12*(*T*/300)^1.4))/(0.75-1.27*log10(0.6)))^2))

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

References

Markwalder, B., Gozel, P., and van den Bergh, H.: J. Phys. Chem. 97, 5260, 1993.
Smith, I. W. M. and Yarwood, G.: Chem. Phys. Lett. 130, 24, 1986.
Smith, I. W. M. and Yarwood, G.: Faraday Disc. Chem. Soc. 84, 205, 1987.