IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.56 NOx26

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

$\Delta H° = 40.6$ kJ·mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients $5.0 \times 10^{14}\ T^{-(8.7 \pm 0.9)}$ exp(-4880/*T*)[Ar]	225-260	Markwalder et al., 1993	(a)

Comments

(a) CO_2 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. Dissociation rate coefficients were derived from the measured recombination rate coefficients and the equilibrium constant from Chao et al. (1974) of $K_c = 1.8 \times 10^{29}\ T^{-1}$ exp(-4880/*T*) molecule cm^{-3}. Falloff curves with M=Ar were obtained over the pressure range 0.5-200 bar and extrapolated to k_0 and k_∞ with $F_c = 0.6$. $k_0(N_2)/k_0$ (Ar) = 1.36 was taken from Smith and Yarwood (1987) (see reaction NO + NO_2 + M → N_2O_3 + M).

Preferred Values

$k_0 = 1.6 \times 10^{-14}$ [N_2] s^{-1} at 298 K.
$k_0 = 1.9 \times 10^{-7}\ (T/300)^{-8.7}$ exp(-4880/*T*) [N_2] s^{-1} over the temperature range 225-300 K.

Comments on Preferred Values

The preferred values are based on the data of Markwalder et al. (1993), which are consistent with a theoretical analysis of the results (leading to collision efficiencies β_c(Ar) = 0.3). The preferred values correspond to an analysis of the falloff curve with $F_c = 0.6$ and the value of k_∞ given below.

High-pressure rate coefficients
Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$4.8 \times 10^{14}\ T^{(0.4 \pm 0.1)}\ \exp(-4880/T)$	225-260	Markwalder et al., 1993	(a)

Comments

(a) See comment (a) for k_0.

Preferred Values

$k_\infty = 3.6 \times 10^{8}$ s^{-1} at 298 K.
$k_\infty = 4.7 \times 10^{15}\ (T/300)^{0.4} \exp(-4880/T)$ s^{-1} over the temperature range 225-300 K.

Comments on Preferred Values

The preferred values are based on the values of Markwalder et al. (1993) converted to dissociation data with the equilibrium constant from Chao et al. (1974).

Preferred Values

Parameter	Value	T/K
k_0/s^{-1}	1.6×10^{-14} [N_2]	298
k_0/s^{-1}	$1.9 \times 10^{-7}\ (T/300)^{-8.7} \exp(-4880/T)$ [N_2]	225-300
k_∞/s^{-1}	3.6×10^{8}	298
k_∞/s^{-1}	$4.7 \times 10^{15}\ (T/300)^{0.4} \exp(-4880/T)$	225-300
k(1 bar N_2)/s^{-1}	3.6×10^{5}	298
F_c	0.6	225-300
Reliability		
$\Delta \log k_0$	± 0.4	225-300
$\Delta E_0/R$	± 500 K	298
$\Delta \log k_\infty$	± 0.3	225-300
$\Delta E_\infty/R$	± 400 K	298

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:

=((1.9e-7*(*T*/300)^-8.7*exp(-4880/*T*))*M*(4.7e15*(*T*/300)^0.4*exp(-4880/*T*)))/((1.9e-7*(*T*/300)^-8.7*exp(-4880/*T*))*M+(4.7e15*(*T*/300)^0.4*exp(-4880/*T*)))*10^(log10(0.6)/(1+(log10((1.9e-7*(*T*/300)^-8.7*exp(-4880/*T*))*M/(4.7e15*(*T*/300)^0.4*exp(-4880/*T*)))/(0.75-1.27*log10(0.6)))^2))

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

References

Chao, J., Wilhoit, R. C., and Zwolinski, B. J.: Thermochim. Acta 10, 359, 1974.
Markwalder, B., Gozel, P., and van den Bergh, H.: J. Phys. Chem. 97, 5260, 1993.
Smith, I. W. M., and Yarwood, G.: Faraday Disc. Chem. Soc. 84, 205, 1987.