IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.62 NOx32

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$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$

$\Delta H^\circ = 95.6$ kJ·mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.15 x 10^{-5} exp(-9910/T) [N_2]	285-384	Viggiano et al., 1981	(a)
4.15 x 10^{-20} [N_2]	298		
1.04 x 10^{-3}(T/300)$^{-3.5}$ exp(-11000/T) [N_2]	253-384	Cantrell et al., 1993	(b)
9.9 x 10^{-20} [N_2]	298		

Comments

(a) Thermal decomposition of N_2O_5 in a flow system with detection of N_2O_5 by ion-molecule reactions in a flowing-afterglow system. Carrier gas pressures between 15 and 1100 mbar. Representation of the falloff curves with temperature independent $F_c = 0.57$.

(b) Thermal decomposition of N_2O_5 in the presence of NO and N_2 in a static reactor with FTIR analysis of N_2O_5 using a multiple path optics. Falloff curves analyzed with $F_c = 2.5 \exp(-1950/T) + 0.9 \exp(-T/430)$, i.e. F_c (298 K) = 0.45. Data from Connell and Johnston (1979) and Viggiano et al. (1981) were taken into account in the analysis.

Preferred Values

$k_0 = 1.2 \times 10^{-19}$ [N_2] s^{-1} at 298 K.
$k_0 = 1.3 \times 10^{-3}$ (T/300)$^{-3.5}$ exp(-11000/T) [N_2] s^{-1} over the temperature range 200-400 K.

Comments on Preferred Values

The preferred values are based on the study of Cantrell et al. (1993). However, instead of $F_c = 0.45$, like in the reverse reaction, a modelled value of $F_c = 0.35$ independent of the temperature was used for extrapolation to the low pressure limit. The ratio of the preferred dissociation and recombination rate coefficients of 3.1 x 10^{-11} cm^3 molecule^{-1} at 298 K is consistent with the equilibrium constant from Osthoff et al. (2007) of 3.4 x 10^{-11} cm^3 molecule^{-1}.

High-pressure rate coefficients
Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.21 x 10^{17} exp(-12790/T)	285-384	Viggiano et al., 1981	(a)
6.22 x 10^{14}(T/300)$^{-0.2}$ exp(-11000/T)	253-384	Cantrell et al., 1993	(b)
1.36 x 10^{15} exp[-(11300 ± 200)/T]	314-348	Ide et al., 2008	(c)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

(c) Flow system study using NO_3 detection at 662 nm by pulsed laser cavity ring-down spectroscopy. Measurements in 1.01 bar of N_2, corresponding to conditions in the middle part of the falloff curve relatively close to the high pressure limit. The given expression for the rate coefficient is for constant pressure of 1.01 bar and includes data from Viggiano et al. (1981) and Cantrell et al. (1993) down to 263 K.

Preferred Values

k_∞ = 6.9 x 10^{-2} s^{-1} at 298 K.

k_∞ = 9.7 x 10^{14} (T/300)$^{0.1}$ exp(-11080/T) s^{-1} over the temperature range 200-400 K.

Comments on Preferred Values

The preferred values are from the evaluation of the data from Viggiano et al. (1981) and Connell and Johnston (1979) by Malko and Troe (1982) which agrees well with the more recent values from Cantrell et al. (1993) and Ide et al. (2008). Falloff curves are constructed with temperature independent F_c = 0.35.

Preferred Values

Parameter	Value	T/K
k_0/s^{-1}	1.2 x 10^{-19} [N_2]	298
k_0/s^{-1}	1.3 x 10^{-3} (T/300)$^{-3.5}$exp(-11000/T) [N_2]	200-400
k_∞/s^{-1}	6.9 x 10^{-2}	298
k_∞/s^{-1}	9.7 x 10^{14} (T/300)$^{0.1}$exp(-11000/T)	200-400
k(1 bar N_2)/s^{-1}	4.4 x 10^{-2}	298
F_c	0.35	200-400
Reliability		
Δlog k_0	± 0.3	298
Δn_0	± 0.5	200-400
Δlog k_∞	± 0.3	298
Δn_∞	± 0.2	200-400

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*:

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=((1.3e-3*(T/300)^-3.5*exp(-11000/T))*M*(9.7e14*(T/300)^0.1*exp(-11080/T)))/
((1.3e-3*(T/300)^-3.5*exp(-11000/T))*M+(9.7e14*(T/300)^0.1*exp(-11080/T)))*10^(log10(0.35)/(1+
(log10((1.3e-3*(T/300)^-3.5*exp(-11000/T))*M/(9.7e14*(T/300)^0.1*exp(-11080/T)))/(0.75-1.27*log10(0.35)))^2))
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The molecular density, $M = 7.243 \times 10^{21} P(bar)/T(K)$

References

Cantrell, C. A., Shetter, R. E., Calvert, J. G., Tyndall, G. S., and Orlando, J. J.: J. Phys. Chem. 97, 9141, 1993.

Connell, P. and Johnston, H. S.: Geophys. Res. Lett. 6, 553, 1979.

Ide, T., Nakayama, T., Takahashi, K., and Matsumi, Y.: Int. J. Chem. Kinet. 40, 679, 2008.

Malko, M. W. and Troe, J.: Int. J. Chem. Kinet. 14, 399, 1982.

Osthoff, D., Pilling, M. J., Ravishankara, A. R., and Brown, S. S.: Phys. Chem. Chem. Phys. 9, 5785 2007.

Viggiano, A. A., Davidson, J. A., Fehsenfeld, F. C., and Ferguson, E. E.: J. Chem. Phys. 74, 6113, 1981.