IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.33 NOx3

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$O + NO_2 + M \rightarrow NO_3 + M$

$\Delta H° = -208.6$ 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			
3×10^{-31} $(T/300)^{-1.75}$ [N_2]	220-296	Burkholder and Ravishankara, 2000	PLP (a)
$(1.3\pm0.3) \times 10^{-31}$ $(T/300)^{-1.5}$ [N_2]	300-400	Hahn et al., 2000	PLP (b)
Relative Rate Coefficients			
$(9.2 \pm 1) \times 10^{-32}$ [N_2]	297	Harker and Johnston, 1973	RR (c)
$(8.0 \pm 1) \times 10^{-32}$ [N_2]	295	Hippler et al., 1975	RR (d)

Comments

(a) Oxygen atoms generated by laser photolysis of NO_2 at 352 nm, NO_3 monitored by long-path diode laser absorption at 662 nm. Measurements were made in N_2 over the pressure range 20-800 Torr; falloff curves were represented with $F_c = 0.6$ and $k_\infty = 3.75 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} independent of the temperature.

(b) Oxygen atoms generated by laser photolysis of N_2O at 193 nm, NO_3 monitored by light absorption at 578 nm. Falloff curves measured at 300 and 400 K in N_2 over the presure range 1-900 bar. Falloff curves represented with $F_c = 0.71 \exp(-T/1700)$, which corresponds to $F_c = 0.6$ at 300 K, and $k_\infty = (2.3 \pm 0.2) \times 10^{-11}$ $(T/300)^{0.24}$ cm^3 molecule^{-1} s^{-1}.

(c) $O(^3P)$ atoms were generated by the photolysis of NO_2 in the presence of 1 bar of N_2. NO_2 and N_2O_5 concentrations were monitored by IR absorption. The measured value of $k/k(O + NO_2)$ was evaluated with $k(O + NO_2) = 9.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The rate coefficient has been reevaluated by increasing the measured rate coefficient by 10% to account for a 10% falloff below k_0, as measured by in ref. 5.

(d) $O(^3P)$ atoms were generated by the photolysis of NO_2 at various N_2 pressures. NO_2 was monitored by UV absorption. The measured value of $k/k(O + NO_2)$ was evaluated with $k(O + NO_2) = 9.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, taking N_2O_5 reactions and falloff effects into account.

Preferred Values

$k_0 = 1.3 \times 10^{-31}$ $(T/300)^{-1.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200-400 K.

Reliability

$\Delta \log k_0 = \pm 0.30$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are from the falloff extrapolations of the absolute rate measurements of Hahn et al. (2000) and the relative rate measurements of Harker and Johnston (1973), Hippler et al. (1975), Gaedtke and Troe (1975), Schuck et al. (1966) and Troe (1969). The discrepancy between the absolute rate measurements below 800 Torr from ref. 1 and above from Hahn et al. (2000) may be due to difficulties in separating the reactions O + $NO_2 \rightarrow O_2$ + NO and O + NO_2 + M $\rightarrow NO_3$ + M with subsequent $NO_2 + NO_3$ + M $\rightarrow N_2O_5$ + M. Because the data from Hahn et al. (2000) are in better consistency with the relative rate measurements from Hahn et al. (2000), Harker and Johnston (1973), and Hippler et al. (1975), they are preferred here. It should be emphasized that falloff effects are important at atmospheric pressures; these effects are represented with $F_c = 0.6$ and $k_\infty = 2.3 \times 10^{-11}$ $(T/300)^{0.24}$ cm^3 $molecule^{-1}$ s^{-1} from the measurements and theoretical analysis of Hahn et al. (2000).

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
$(2.3\pm0.2) \times 10^{-11}$ $(T/300)^{0.24}$	300-400	Hahn et al., 2000	PLP (a)
Relative Rate Coefficients			
$(2.2 \pm 0.4) \times 10^{-11}$	300	Gaedtke and Troe, 1975	(b)

Comments

(a) See comment (b) for k_0.
(b) Analysis of the pressure dependence of the quantum yield of NO_2 photolysis between 1 and 1000 bar of N_2. Measurements of $k_\infty/k(O + NO_2 \rightarrow O_2 + NO)$ evaluated with $k(O + NO_2) = 9\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

Preferred Values

$k_\infty = 2.3 \times 10^{-11}$ $(T/300)^{0.24}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200-400 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over the temperature range 200-400 K.

Comments on Preferred Values

The absolute and relative rate measurements of the falloff curve over a very wide pressure range from Hahn et al. (2000) and Gaedtke and Troe (1975), on which the preferred values are based, allow for a reliable extrapolation to the high pressure limit of the reaction. Falloff curves are constructed with $F_c = 0.6$ and $k_0 = 1.3 \times 10^{-31}(T/300)^{-1.5}$ $[N_2]$ cm^3 $molecule^{-1}$ s^{-1}.

Preferred Values

Parameter	Value	T/K
k_0/cm^3 molecule^{-1} s^{-1}	1.3 x 10^{-31} $(T/300)^{-1.5}$ [N_2]	200-400
k_∞/cm^3 molecule^{-1} s^{-1}	2.3 x 10^{-11} $(T/300)^{0.24}$	200-400
k(1 bar N_2)/cm^3 molecule^{-1} s^{-1}	2.1 x 10^{-12}	298
F_c	0.6	200-400
Reliability		
$\Delta\log k_0$	± 0.3	298
Δn_0	± 1	200-400
$\Delta\log k_\infty$	± 0.1	298
Δn_∞	± 0.1	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*:

=((1.3e-31*(*T*/300)^-1.5)*M*(2.3e-11*(*T*/300)^0.24))/((1.3e-31*(*T*/300)^-1.5)*M+(2.3e-11*(*T*/300)^0.24))*10^(log10(0.6)/(1+(log10((1.3e-31*(*T*/300)^-1.5)*M/(2.3E-11*(*T*/300)^0.24))/(0.75-1.27*log10(0.6)))^2))

The molecular density, M = 7.243×10^{21}P(bar)/T(K)

References

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