

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.61 NO_x31

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$$\Delta H^\circ = -95.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$9.6 \times 10^{-33} \exp(1550/T) [\text{N}_2]$	262-295	Connell and Johnston, 1979	(a)
$1.7 \times 10^{-30} [\text{N}_2]$	298		
$1.35 \times 10^{-32} \exp(1270/T) [\text{N}_2]$	285-384	Viggiano et al., 1981	(b)
$9.6 \times 10^{-31} [\text{N}_2]$	298		
$(4.5 \pm 1.1) \times 10^{-30} (T/300)^{-(3.4 \pm 1.3)} [\text{N}_2]$	236-358	Kircher et al., 1984	FP-A (c)
$2.12 \times 10^{-30} [\text{N}_2]$	298	Smith et al., 1985	DF-A (d)
$2.8 \times 10^{-30} (T/300)^{-3.5} [\text{N}_2]$	236-358	Orlando et al., 1991	DF-LIF (e)
$(3.1 \pm 0.8) \times 10^{-30} [\text{N}_2]$	288	Nakano et al., 2011	LP-CRDS (f)

Comments

- From study of N₂O₅ decomposition. Static reaction vessel with multi-reflection White-cell optical arrangement for the time-resolved detection of N₂O₅ by IR absorption at 8.028 μ. Converted to recombination rate coefficients with the equilibrium constant $K_c = 8.4 \times 10^{26} \exp(-11180/T) \text{ molecule cm}^{-3}$ from Graham and Johnston (1978).
- From study of N₂O₅ decomposition. Flow system reactors of various size. N₂O₅ was detected by ion-molecule reactions in a flowing afterglow system. Measurements were carried out at $[\text{N}_2] = 2.5 \times 10^{17} \text{ to } 2.7 \times 10^{19} \text{ molecule cm}^{-3}$. Converted to recombination rate coefficients with the equilibrium constant $K_c = 8.4 \times 10^{26} \exp(-11180/T) \text{ molecule cm}^{-3}$ from Graham and Johnston (1978).
- Visible absorption of NO₃ monitored under pseudo-first order conditions. Falloff curve measured over the pressure range 20-700 Torr and extrapolated using falloff curve representation with $F_c = 0.34$ at 298 K.
- Visible absorption of NO₃ monitored. Pressure range 1-8 Torr in He, and 0.5-6 Torr in N₂. Falloff curves extrapolated with $F_c = 0.47$ for N₂ at 298 K.
- Detection of NO₃. Experiments were conducted over the pressure range 0.5-8 Torr and evaluated using $F_c = \{2.5 \exp(-1950/T) + 0.9 \exp(-T/430)\}$, i.e. $F_c(298 \text{ K}) = 0.45$.

- (f) Detection of NO₃. Pressure range 20-700 Torr of N₂. Experiments at 283 and 298 K evaluated with $F_c = 0.6$ leading to $k_0 = 3.1(\pm 0.8) \times 10^{-30} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{N}_2]$ and $k_\infty = 1.6(\pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Preferred Values

$k_0 = 3.6 \times 10^{-30} (T/300)^{-4.1} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200-300 K.

Comments on Preferred Values

The preferred values are based on the data of Orlando et al. (1991) and the falloff extrapolation from Hahn et al. (2000) using the theoretically derived $F_c = 0.35$ independent of the temperature between 200 and 400 K. The temperature dependence is from the theoretical modelling of Hahn et al. (2000). Different choices of F_c lead to different values of the extrapolated k_0 and k_∞ , although the various representations all agree well with the experimental data. New measurements of the equilibrium constant by Osthoff et al. (2007) give $K_c = 1.96 \times 10^{26} \exp(-10871/K) \text{ molecule cm}^{-3}$. Using this value instead of that from Graham and Johnston (1978), increases the values for k_0 from Connell and Johnston (1979) and Viggiano et al. (1981) by a factor of 1.5. The results from Nakano et al. (2011) agree very well with the falloff-curve preferred in the present evaluation while they are about 30 % higher than those from Kircher et al. (1984) at 1 bar.

High-pressure rate coefficients Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$2.1 \times 10^{-10} \exp(-1360/T)$	262-295	Connell and Johnston, 1979	(a)
2.2×10^{-12}	298		
$1.5 \times 10^{-10} \exp(-1610/T)$	285-384	Viggiano et al., 1981	(b)
6.8×10^{-13}	298		
$(2.2 \pm 0.5) \times 10^{-12}$	293	Croce de Cobos et al., 1984	(c)
$(1.65 \pm 0.15) \times 10^{-12} (T/300)^{-0.4 \pm 0.5}$	236-358	Kircher et al., 1984	FP-A (d)
1.85×10^{-12}	298	Smith et al., 1985	DF-A (e)
$1.7 \times 10^{-12} (T/300)^{-0.2}$	236-358	Orlando et al., 1991	DF-LIF (f)
$(1.9 \pm 0.3) \times 10^{-12} (T/300)^{0.2}$	300-400	Hahn et al., 2000	PLP (g)
$(1.6 \pm 0.3) \times 10^{-12}$	298	Nakano et al., 2011	LP-CRDS (h)

Comments

- (a) See comment (a) and comments on preferred values for k_0 .
- (b) See comment (b) comments on preferred values for k_0 . Data obtained from extrapolation of data in a relatively narrow pressure range near to the center of the falloff curve.
- (c) Laser flash photolysis of N₂O in the presence of NO₂. NO₃ radicals were monitored by visible absorption under pseudo-first order conditions. The falloff curve was measured over the pressure range 1-200 bar in N₂, and extrapolated with $F_c = 0.34$.
- (d) See comment (c) for k_0 .
- (e) See comment (d) for k_0 .
- (f) See comment (e) for k_0 .

- (g) See comment (c); measurements over the pressure range 30-900 bar evaluated with k_0 from Orlando et al. (1991) and $F_c = 0.35$.
- (h) see comment (f) for k_0 .

Preferred Values

$$k_\infty = 1.9 \times 10^{-12} (T/300)^{0.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200-400 K.}$$

Comments on Preferred Values

The preferred values are based on the high pressure measurements from Hahn et al. (2000) which within experimental uncertainty agree well with the extrapolated values from Kircher et al. (1984), Smith et al. (1985), Hahn et al. (2000) and Croce de Cobos et al. (1984). The theoretically calculated value of $F_c = 0.35$ does not influence the derivation of k_∞ but influences the extrapolation towards k_0 . The values from Viggiano et al. (1981) also agree with the preferred values if equilibrium constants from Osthoff et al. (2007) instead of those from Graham and Johnston (1978) are employed. The results from Nakano et al. (2011) agree well with the preferred values.

Preferred Values

Parameter	Value	T/K
$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.6 \times 10^{-30} [\text{N}_2]$	298
$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.6 \times 10^{-30} (T/300)^{-4.1} [\text{N}_2]$	200-400
$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.9×10^{-12}	298
$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.9 \times 10^{-12} (T/300)^{0.2}$	200-400
$k(1 \text{ bar N}_2)/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.2×10^{-12}	298
F_c	0.35	200-400
<i>Reliability</i>		
$\Delta \log k_0$	± 0.1	298
Δn_0	± 0.5	200-400
$\Delta \log k_\infty$	± 0.2	298
Δn_∞	± 0.6	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 :

$$=((3.6\text{e-}30*(T/300)^{-4.1}*M*(1.9\text{e-}12*(T/300)^{0.2}))/((3.6\text{e-}30*(T/300)^{-4.1}*M+(1.9\text{e-}12*(T/300)^{0.2}))*10^{(\log10(0.35)/(1+(\log10((3.6\text{e-}30*(T/300)^{-4.1}*M/(1.9\text{e-}12*(T/300)^{0.2}))/((0.75-1.27*\log10(0.35))))^2))}$$

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

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