

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.60 NOx30

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This data sheet last evaluated: June 2012; last change in preferred values: June 2012.



$$\Delta H^\circ = 57.3 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients Rate coefficient data

k_0/s^{-1}	Temp./ K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.29 \times 10^{-5} (T/300)^{-3.8} \exp(-6460/T) [\text{N}_2]$	300-500	Borrell et al., 1988	PLP (a)
$1.6 \times 10^{19} T^{-(10.0 \pm 1.0)} \exp[-(6790 \pm 700)/T] [\text{He}]$	255-273	Markwalder et al., 1992	(b)
$8.6(\pm 2) \times 10^{-18} [\text{N}_2]$	231	Christensen et al., 2004	PLP-UVA (c)

Comments

- Relaxation of $\text{NO}_2\text{-N}_2\text{O}_4\text{-N}_2$ equilibrium mixtures after pulsed laser photolysis of N_2O_4 at 248 nm. The relaxation to equilibrium was followed by observing N_2O_4 in absorption at 220 nm. Falloff curves over the range 1-207 bar were extrapolated with $F_c = 0.40$. The equilibrium constant from Chao et al. (1974) was employed.
- Temperature jumps induced by IR absorption of SiF_4 in equilibrium mixtures of $\text{NO}_2\text{-N}_2\text{O}_4\text{-He-SiF}_4$. The relaxation to equilibrium was followed by absorption spectroscopy of NO_2 and N_2O_4 at 420 and 250 nm, respectively. Falloff curves over the range 0.3-200 bar were extrapolated with $F_c = 0.52$. Equilibrium constants from Vosper (1970) were employed.
- Measurement in a study of the reaction $\text{HO}_2 + \text{NO}_2 + \text{N}_2 \rightarrow \text{HO}_2\text{NO}_2 + \text{N}_2$ at 100 Torr.

Preferred Values

$$k_0 = 6.1 \times 10^{-15} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 1.3 \times 10^{-5} (T/300)^{-3.8} \exp(-6400/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 300\text{-}500 \text{ K.}$$

Comments on Preferred Values

The preferred values are from the measurements of Borrell et al. (1988) in combination with the equilibrium constants from Chao et al. (1974). These data are based on the most complete part of the falloff curve at 300 K using $F_c = 0.40$. The single measurement from Christensen et al. (2004) at 231 K near to the low pressure range of the reaction is a factor of 3.7 lower than extrapolated with the preferred values from Borrell et al. (1988) from the range 300-500 K, but it

agrees within the uncertainty with the values from Markwalder et al. (1992). A change of the preferred values for temperatures below 300 K thus is expected.

High-pressure rate coefficients Rate coefficient data

k_{∞}/s^{-1}	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$7.7 \times 10^{15} (T/300)^{-1.1} \exp(-6460/T)$	300-600	Borrell et al., 1988	PLP (a)
$2.8 \times 10^{13} T^{(1.3 \pm 0.2)} \exp[-(6790 \pm 700)/T]$	255-273	Markwalder et al., 1992	(b)

Comments

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

Preferred Values

$k_{\infty} = 4.4 \times 10^6 s^{-1}$ at 298 K.

$k_{\infty} = 1.15 \times 10^{16} \exp(-6460/T) s^{-1}$ over the temperature range 250-300 K.

Comments on Preferred Values

The preferred rate coefficient at room temperature is from the average of the values of Borrell et al. (1988) and Markwalder et al. (1992) for the reverse combination and the equilibrium constant from Chao et al. (1974). However, there is some uncertainty in the equilibrium constant (about a factor of 2 near 300 K) such as discussed by Estupiñán et al. (2001) and Tuchler et al. (2005) which is accounted for by the given reliability. The recommended temperature coefficient corresponds to a temperature-independent value of k_{∞} for the reverse recombination. Measurements from Fiedler and Hess (1990) and Van Roozendael and Herman (1990) in the intermediate falloff range at 298 K are consistent with the preferred values of k_0 , k_{∞} , and $F_c = 0.4$ at 300 K.

Preferred Values

Parameter	Value	T/K
k_0/s^{-1}	$6.1 \times 10^{-15} [N_2]$	298
k_0/s^{-1}	$1.3 \times 10^{-5} (T/300)^{-3.8} \exp(-6460/T) [N_2]$	300-500
k_{∞}/s^{-1}	4.4×10^6	298
k_{∞}/s^{-1}	$1.15 \times 10^{16} \exp(-6460/T) [N_2]$	300-500
$k(1 \text{ bar } N_2)/s^{-1}$	1.0×10^5	298
F_c	0.4	300-500
<i>Reliability</i>		
$\Delta \log k_0$	± 0.4	298
$\Delta E_0/R$	$\pm 500 \text{ K}$	300-500
$\Delta \log k_{\infty}$	± 0.4	298
$\Delta E_{\infty}/R$	$\pm 500 \text{ K}$	300-500

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 :

$$= \frac{(1.3e-5*(T/300)^{-3.8*\exp(-6400/T)}*M*(1.15e16*\exp(-6460/T)))}{((1.3e-5*(T/300)^{-3.8*\exp(-6400/T)}*M+(1.15e16*\exp(-6460/T))*10^{(\log_{10}(0.4)/(1+\log_{10}((1.3e-5*(T/300)^{-3.8*\exp(-6400/T)}*M/(1.15e16*\exp(-6460/T))))/(0.75-1.27*\log_{10}(0.4)))^2})}$$

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

References

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