

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.56 NO<sub>x</sub>26

Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. The citation for this datasheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys. 4, 1461, 2004; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>).

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



$$\Delta H^\circ = 40.6 \text{ kJ}\cdot\text{mol}^{-1}$$

### Low-pressure rate coefficients Rate coefficient data

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

### Comments

- (a) CO<sub>2</sub> laser-induced temperature jump measurements with NO<sub>2</sub>-N<sub>2</sub>O<sub>4</sub>-N<sub>2</sub>O<sub>3</sub>-NO-SiF<sub>4</sub>-Ar equilibrium mixtures. The subsequent relaxation toward equilibrium was monitored by UV absorption of N<sub>2</sub>O<sub>3</sub> 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<sup>-3</sup>. Falloff curves with M=Ar were obtained over the pressure range 0.5-200 bar and extrapolated to  $k_0$  and  $k_\infty$  with  $F_c = 0.6$ .  $k_0(\text{N}_2)/k_0(\text{Ar}) = 1.36$  was taken from Smith and Yarwood (1987) (see reaction NO + NO<sub>2</sub> + M → N<sub>2</sub>O<sub>3</sub> + M).

### Preferred Values

$$k_0 = 1.6 \times 10^{-14} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 1.9 \times 10^{-7} (T/300)^{-8.7} \exp(-4880/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 225\text{-}300 \text{ K.}$$

### 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  $\beta_c(\text{Ar}) = 0.3$ ). The preferred values correspond to an analysis of the falloff curve with  $F_c = 0.6$  and the value of  $k_\infty$  given below.

## High-pressure rate coefficients Rate coefficient data

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

### Comments

(a) See comment (a) for  $k_0$ .

### Preferred Values

$k_{\infty} = 3.6 \times 10^8 \text{ s}^{-1}$  at 298 K.

$k_{\infty} = 4.7 \times 10^{15} (T/300)^{0.4} \exp(-4880/T) \text{ s}^{-1}$  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
$k_0/s^{-1}$	$1.6 \times 10^{-14} [\text{N}_2]$	298
$k_0/s^{-1}$	$1.9 \times 10^{-7} (T/300)^{-8.7} \exp(-4880/T) [\text{N}_2]$	225-300
$k_{\infty}/s^{-1}$	$3.6 \times 10^8$	298
$k_{\infty}/s^{-1}$	$4.7 \times 10^{15} (T/300)^{0.4} \exp(-4880/T)$	225-300
$k(1 \text{ bar N}_2)/s^{-1}$	$3.6 \times 10^5$	298
$F_c$	0.6	225-300
<i>Reliability</i>		
$\Delta \log k_0$	$\pm 0.4$	225-300
$\Delta E_0/R$	$\pm 500 \text{ K}$	298
$\Delta \log k_{\infty}$	$\pm 0.3$	225-300
$\Delta E_{\infty}/R$	$\pm 400 \text{ K}$	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  $k$ :

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

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.