

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.62 NO_x32

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This data sheet last evaluated: November 2017; last change in preferred values: June 2012.



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

Low-pressure rate coefficients Rate coefficient data

| k_0/s^{-1} | Temp./K | Reference | Technique/ Comments |
|--|---------|-----------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $1.15 \times 10^{-5} \exp(-9910/T) [\text{N}_2]$ | 285-384 | Viggiano et al., 1981 | (a) |
| $4.15 \times 10^{-20} [\text{N}_2]$ | 298 | | |
| $1.04 \times 10^{-3} (T/300)^{-3.5} \exp(-11000/T) [\text{N}_2]$ | 253-384 | Cantrell et al., 1993 | (b) |
| $9.9 \times 10^{-20} [\text{N}_2]$ | 298 | | |

Comments

- Thermal decomposition of N₂O₅ in a flow system with detection of N₂O₅ 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 $F_c = 0.57$.
- Thermal decomposition of N₂O₅ in the presence of NO and N₂ in a static reactor with FTIR analysis of N₂O₅ using a multiple path optics. Falloff curves analyzed with $F_c = 2.5 \exp(-1950/T) + 0.9 \exp(-T/430)$, i.e. $F_c(298 \text{ K}) = 0.45$. Data from Connell and Johnston (1979) and Viggiano et al. (1981) were taken into account in the analysis.

Preferred Values

$$k_0 = 1.2 \times 10^{-19} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 1.3 \times 10^{-3} (T/300)^{-3.5} \exp(-11000/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 200\text{-}400 \text{ K.}$$

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 $3.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K is consistent with the equilibrium constant from Osthoff et al. (2007) of $3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$.

High-pressure rate coefficients Rate coefficient data

| k_{∞}/s^{-1} | Temp./K | Reference | Technique/ Comments |
|---|---------|-----------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $1.21 \times 10^{17} \exp(-12790/T)$ | 285-384 | Viggiano et al., 1981 | (a) |
| $6.22 \times 10^{14} (T/300)^{-0.2} \exp(-11000/T)$ | 253-384 | Cantrell et al., 1993 | (b) |
| $1.36 \times 10^{15} \exp[-(11300 \pm 200)/T]$ | 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

$$k_{\infty} = 6.9 \times 10^{-2} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

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

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} | $1.2 \times 10^{-19} [\text{N}_2]$ | 298 |
| k_0/s^{-1} | $1.3 \times 10^{-3} (T/300)^{-3.5} \exp(-11000/T) [\text{N}_2]$ | 200-400 |
| k_{∞}/s^{-1} | 6.9×10^{-2} | 298 |
| k_{∞}/s^{-1} | $9.7 \times 10^{14} (T/300)^{0.1} \exp(-11000/T)$ | 200-400 |
| $k(1 \text{ bar } \text{N}_2)/s^{-1}$ | 4.4×10^{-2} | 298 |
| F_c | 0.35 | 200-400 |
| <i>Reliability</i> | | |
| $\Delta \log k_0$ | ± 0.3 | 298 |
| Δn_0 | ± 0.5 | 200-400 |
| $\Delta \log k_{\infty}$ | ± 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 :

$$=((1.3e-3*(T/300)^{-3.5}*\exp(-11000/T))*M*(9.7e14*(T/300)^{0.1}*\exp(-11080/T)))/((1.3e-3*(T/300)^{-3.5}*\exp(-11000/T))*M+(9.7e14*(T/300)^{0.1}*\exp(-11080/T))*10^{(\log_{10}(0.35)/(1+(\log_{10}((1.3e-3*(T/300)^{-3.5}*\exp(-11000/T))*M/(9.7e14*(T/300)^{0.1}*\exp(-11080/T))))/(0.75-1.27*\log_{10}(0.35)))^2)}$$

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

References

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