Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NOx6

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2$$

ΔH° = -189.7 kJ mol^{-1}

Rate coefficient data

k / cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
2.0x10^{-11} exp[(107 ± 8)/T]	104-354	Streit et al.,1976	PLP (a)
(2.8 ± 0.6) x 10^{-11}	300		
(2.4 ± 0.1) x 10^{-11}	295	Amimoto et al., 1979	PLP-RA (b)
(2.52 ± 0.25) x 10^{-11}	297	Wine and Ravishankara, 1981	PLP-RF (c)
2.2x10^{-11} exp[(118 ± 21)/T]	195-673	Blitz et al., 2004	PLP-LIF (d)
(3.06 ± 0.25) x 10^{-11}	295		
1.99x10^{-11} exp[(145 ± 9)/T]	197-427	Strekowski and Wine, 2004	PLP-RF (e)
3.24 x 10^{-11}	294-300		
1.95x10^{-11} exp[(125 ± 20)/T]	197-427	Dunlea and Ravishankara, 2004	PLP-RF (f)
(3.00 ± 0.24) x 10^{-11}	295		
(3.29 ± 0.27) x 10^{-11}	295	Takahashi et al., 2005	PLP-LIF (g)
(3.3 ± 0.6) x 10^{-11}	297-300	Dillon et al., 2008	PLP-LIF (h)

Comments

(a) $O(^1D)$ atoms were monitored by time-resolved detection of $O(^1D) \rightarrow O(^3P)$ emission.

(b) $O(^1D)$ generated by O_3 photolysis at 248 nm and $O(^3P)$ product monitored by RA. Pressures were 13- 26 mbar.

(c) $O(^1D)$ generated by 266 nm photolysis of O_3 and the $O(^3P)$ product monitored by RF. Most experiments conducted at 53 mbar (He bath gas).

(d) $O(^1D)$ generated by the 193 nm photolysis of N_2O and monitored directly by VUV-LIF or indirectly, in a competitive kinetics method, as HO following reaction of $O(^1D)$ with C_4H_{10}. The competitive kinetics method yielded consistently large values of k (factor of 1.13). The value given in the table is from the VUV-LIF experiments only, as the authors suggest that this method is less prone to systematic error.

(e) $O(^1D)$ generated by 248 or 266 nm photolysis of O_3 and the $O(^3P)$ product monitored by RF. Most experiments conducted at ≈ 27 mbar (He bath gas).

(f) $O(^1D)$ generated by 248 nm photolysis of O_3 and the $O(^3P)$ product monitored by RF. Experiments conducted at 6.7 – 67 mbar (He bath gas).

(g) $O(^1D)$ generated by the 193 nm photolysis of N_2O and monitored by VUV-LIF. Experiments at 6.7 mbar (He bath gas).

(h) Competitive kinetics method. $O(^1D)$ was generated in the 248 nm photolysis of O_3 and detected as HO following reaction with n-C_6H_{14} or H_2O.

Preferred Values

$k = 3.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.15 \times 10^{-11} \exp(110/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 190-500 K.

Reliability

$\Delta \log k = \pm 0.05$ at 298 K.
$\Delta(E/R) = \pm 30$ K.

Comments on Preferred Values

Both the room temperature rate coefficient and values of E/R obtained for this reaction are in good agreement, although the datasets obtained prior to 2004 indicate slightly lower numbers for k. Three carefully executed, independent studies of this reaction in 2004 (Blitz et al., 2004; Strekowski and Wine, 2004; Dunlea and Ravishankara, 2004) using VUV-LIF detection of $O(^1D)$ and RF detection of $O(^3P)$ result in values of k that agree to within 5 % of an average value of 3.1×10^{-11} cm^3 molecule^{-1} s^{-1} at room temperature and provide the basis of the preferred value at 298 K. The less comprehensive, room temperature studies of Takahashi et al (2005) and Dillon et al. (2008), which appeared subsequently, are consistent with this value. The preferred values are from Ravishankara et al. (2002) which combines the data from Blitz et al. (2004), Strekowski and Wine (2004) and Dunlea and Ravishankara (2004). Strekowski and Wine (2004) showed that the quenching rate coefficient for synthetic air is consistent with the individual values obtained for N_2 and O_2 with a ratio at 295 K of $k(O(^1D) + O_2) / k(O(^1D) + N_2) = 1.30$.

References

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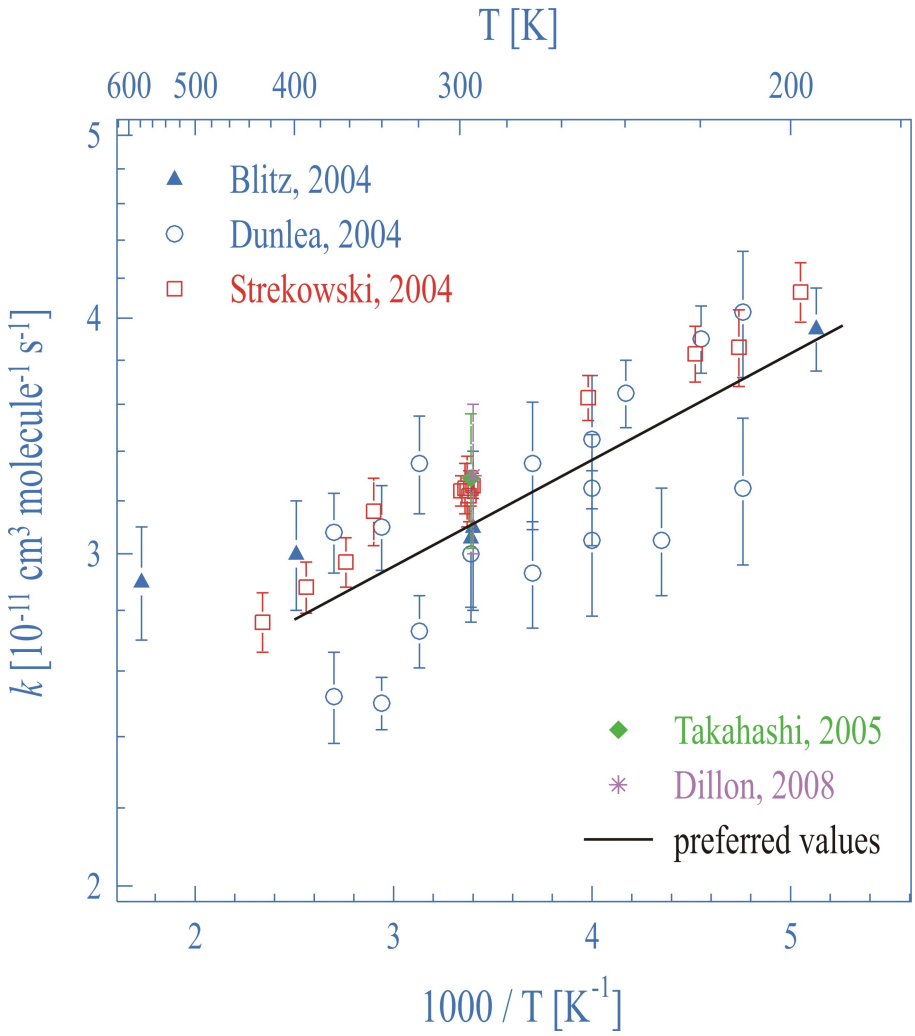

Data on $k(O(^1D) + N_2)$ since 2004.