IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NOx7

This data sheet last evaluated: 12 July 2007; revision of preferred value.

$O(^1D) + N_2O$	**$\rightarrow N_2 + O_2$**	**(1)**
	$\rightarrow 2NO$	**(2)**
	$\rightarrow O(^3P) + N_2O$	**(3)**

$\Delta H^\circ(1) = -521.0$ kJ·mol^{-1}
$\Delta H^\circ(2) = -340.4$ kJ·mol^{-1}
$\Delta H^\circ(3) = -189.7$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.1 \pm 0.2) \times 10^{-10}$	204-359	Davidson et al., 1977	PLP (a)
$(1.20 \pm 0.1) \times 10^{-10}$	295	Amimoto et al., 1979	PLP-RA (b)
$(1.17 \pm 0.12) \times 10^{-10}$	298	Wine and Ravishankara, 1981	PLP-RF (b)
$(1.17 \pm 0.2) \times 10^{-10}\exp(40 \pm 50/T)$	210-370	Dunlea and Ravishankara, 2004	PLP-RF (b)
$(1.27 \pm 0.08) \times 10^{-10}$	298		
$(1.07 \pm 0.10) \times 10^{-10}$	294	Blitz et al, 2004	PLP-VUV/LIF (c)
$(1.13 \pm 0.08) \times 10^{-10}$	195		
$(1.35 \pm 0.08) \times 10^{-10}$	295	Takahashi et al., 2005	PLP-VUV/LIF (c)
$(1.43 \pm 0.08) \times 10^{-10}$	295	Carl	PLP-CL (d)
Branching Ratios			
$k_2/k = 0.62 \pm 0.02$	298	Marxet al., 1979	P-GC/CL
$k_2/k = 0.62 \pm 0.09$	177-296	Lam et al., 1981	P-CL
$k_2/k = 0.61 \pm 0.08$	296	Cantrell et al., 1994	(e)
$k_3/k = 0.04 \pm 0.02$	298	Nishida et al., 2004	PLP-VUV/LIF
$k_3/k = 0.056 \pm 0.009$	295	Carl	PLP-CL (d)

Comments

(a) $O(^1D)$ atoms were monitored by time-resolved detection of $O(^1D) \rightarrow O(^3P)$ emission.
(b) $O(^1D)$ atoms were produced by 248 nm photolysis of O_3. k determined by analysis of time resolved production of $O(^3P)$ atoms, monitored by VUV resonance fluorescence .
(c) $O(^1D)$ atoms were produced by 193 nm photolysis of N_2O, and monitored by on-resonant VUV LIF at $\lambda = 115.2$ nm.
(d) $O(^1D)$ atoms were produced by photolysis of N_2O at 193 nm and monitored by time-resolved emission at 431 nm from $CH(A^2\Delta)$, produced in the reaction of $O(^1D)$ with C_2H, formed concurrently by photolysis of C_2H_2. k determined directly from first order decay of $O(^1D)$ in excess N_2O. Residual emission from reaction of $O(^3P)$ with C_2H allows any quencing to be determined with high sensitivity.

(e) Static photolysis of N_2O-O_3 mixtures at λ>240 nm with product analysis by FTIR spectroscopy. The amount of NO formed in reaction (2) was determined from the yield of HNO_3 formed by total oxidation and hydration of NO_x products, corrected for losses to the wall. The value of k_2/k obtained from the experimental data was 0.57 ± 0.08; the value given in the table was obtained by averaging the experimental value with selected literature data.

Preferred Values

$k_1 = 4.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200-350 K.
$k_2 = 7.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200-350 K.
$k_3 = 6.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200-350 K.

Reliability

$\Delta\log k_1 = \Delta\log k_2 = \pm 0.05$ at 298 K.
$\Delta(E_1/R) = (E_2/R) = \pm 50$ K.

Comments on Preferred Values

The recent measurements of the overall rate coefficient are in good agreement with the earlier data at room temperature and are generally of higher precision. The recommendations are based on a mean value of k (= $k_1 + k_2 + k_3$) = 1.25×10^{-11} cm^3 molecule^{-1} s^{-1}, from the results Davidson et al. (1977), Amimoto et al. (1979) and Wine and Ravishankara (1981), Dunlea and Ravishankara (2004), Blitz et al. (2004), Takahashi et al. (2005) and Carl (2005), and the respective branching ratios. The branching ratio recommended for NO production at room temperature of k_2/k = 0.61 ± 0.08 is that given by Cantrell et al. (1994) , which is in accord with the earlier results of Marx et al. (1979) and Lam et al. (1981). The recent measurements of the branching ratio for quenching at room temperature agree well and we recommend a mean k_3/k = 0.05 ± 0.01. The temperature dependence studies reported by Davidson et al. (1977, 1979), Dunlea and Ravishankara (1981), and Blitz et al. (2004) all show no significant temperature of k.

References

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