Author:

Ian Smith (University of Cambridge, UK)

$$O(^3P) + NH(^3\Sigma^-) \rightarrow NO(^2\Pi) + H(^2S) \quad (1) \quad \Delta Hr^{298} = -297.4 \text{ kJ mol}^{-1} \quad (*)$$

$$\rightarrow OH(^2\Pi) + N(^4S) \quad (2) \quad \Delta Hr^{298} = -95.9 \text{ kJ mol}^{-1} \quad (*)$$

Rate Coefficient Data $k = k_1 + k_2$

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
Rate Coefficient Measurements			
6.6×10^{-11}	295	Adamson *et al*., 1994	(a)
$k_2 < 1.66 \times 10^{-13}$	298	Hack *et al*., 1994	(b)
Reviews and Evaluations			
$1.8 \times 10^{-10} \exp(-300/T)$ $k(298 \text{ K}) = 6.7 \times 10^{-11}$; k_2 (298 K) $< 1.7 \times 10^{-13}$	295 – 3500	Baulch *et al.*, 2005	(*)
$k_1 = k_2 = 1.16 \times 10^{-10}$	250 – 3000	UMIST database	
$k_1 = k_2 = 1.16 \times 10^{-10}$	all temperatures	OSU website	

Comments

Channel (1) is strongly exothermic and could occur via the ground ($^1A'$) state of HNO (and possibly excited states). The reactants correlate with 27 states ($^5A' + 2^5A'', {}^3A' + 2^3A'', {}^1A' + 2^1A''$), the products with 8 states ($^3A' + {}^3A'', {}^1A' + {}^1A''$). Therefore, there is an electronic degeneracy factor of *ca*. 8/27.

There are scarcely any kinetic experiments on this reaction. The principal aim in the experiments described in (a) was to find the rate coefficient for O + NH_2. However, the interpretation of the observations to yield the rate coefficient for O + NH is quite direct and appears sound. Hidden in the text the authors propose a branching ration into channel (2) of 7%. They also refer to an earlier measurement by Wagner's group in fair agreement with their value. Ref. (b) reports a very low branching ratio to channel (2) – in agreement with its lower exothermicity and the notion that reaction may occur *via* HNO.

Preferred Values

Rate coefficients (10 – 300 K)

$k = k_1$ (298 K) = $6.6 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}

$k = k_1$ (10 K) = $6.6 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}

$k_1(T) = 6.6 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}

k_2 (298 K) = k_2 (10 K) = zero

Reliability

$\Delta \log k$ (300 K) = ± 0.5

$\Delta \log k$ (10 K) = ± 0.6

$F_0 = 3$; g = 2.97

Comments on Preferred Values

The value recommended for $k = k_1$ (298 K) is about what one would get by reducing a collisional rate coefficient by the factor of 8/27. I have assumed no temperature-dependence. I also believe that the branching ratio to channel (2) is likely to be small in agreement with the measurement in (b). I don't know where the values in the data bases come from. I recommend values that are lower by a factor of *ca*. 2.

References

(*) D. L. Baulch *et al*., J. Phys. Chem. Ref. Data **34**, 575 (2005).

(a) J. D. Adamson *et al.* J. Phys. Chem. **98**, 5665 (1994).

(b) W. Hack, H. Gg. Wagner and A. Zasypkin, Ber. Bunseb. Gesell. **98**, 156 (1994).