Author:

Jean-Christophe Loison (Univ. of Bordeaux - CNRS, Fr)

$$N(^4S) + NH_2(X^2B_1) \rightarrow N_2(X^1\Sigma^+) + H(^2S) + H(^2S) \quad \Delta H_r^{298} = -227 \text{ kJ mol}^{-1}$$ *(Baulch* et al.*, 2005)*

Rate Coefficient Data *k*

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
Rate Coefficient Measurements (k)			
$(1.21 \pm 0.14) \times 10^{-10}$	296	Whyte and Phillips, 1983	(1)
$(1.15 \pm 0.21) \times 10^{-10}$	298	Dransfeld and Wagner, 1987	(2)
Mechanistic study	296	Whyte and Phillips, 1984	(3)
Reviews and Evaluation			
this reaction is not included		UMIST database	
this reaction is not included		OSU website	

Comments

There have been two experimental investigations of the rate coefficient for this reaction[1-2] at room temperature, both giving similar results. The reaction is found to be rapid at room temperature ($k = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}), so it has no barrier and should have a high rate at low temperature. This reaction has two exothermic product channels $N_2 + H_2$ or $N_2 + H + H$. The $N_2 + H_2$ channel is spin forbidden. Whyte and Phillips[3] performed a H atom branching ratio measurement for this reaction showing that the exit channel is the $N_2 + H + H$ one. The absence of a barrier in the entrance channel means that the reaction is driven by long range interactions, mainly through dispersion. The high value of the rate coefficient at room temperature shows that there is no submerged barrier and the long range interaction term will lead to no substantial temperature dependence. We assume a constant value of the rate coefficient the 10-500 K range, the endothermic $NH(X^3\Sigma^-) + NH(X^3\Sigma^-)$ channel playing eventually a role only at even higher temperature.

Preferred Values

Rate coefficient (10 – 500 K)

k (T) = 1.2×10^{-10} cm^3 molecule^{-1} s^{-1}

Reliability

F_0 = 1.3, g = 6

Comments on Preferred Values

References

DL Baulch, CT Bowman, CJ Cobos, RA Cox, T Just, JA Kerr, MJ Pilling, D Stocker, J Troe, W Tsang, RW Walker, J Warnatz: J. Phys. Chem. Ref. Data 34 (2005) 757-1397.

(1) AR Whyte, LF Phillips: Chem. Phys. Lett. 102 (1983) 451.

(2) P Dransfeld, HG Wagner: Z. Phys. Chem. (Munich) 153 (1987) 89.

(3) AR Whyte, LF Phillips: J. Phys. Chem. 88 (1984) 5670-73.