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$$\mathbf{O(^3P) + NH_2(^2\mathit{B}_1) \rightarrow HNO(^1\mathit{A}') + H(^2S)} \quad \mathbf{(1)} \quad \Delta Hr^{298} = -\ 113.7\ \text{kJ mol}^{-1} \quad (*)$$

$$\mathbf{\rightarrow NO(^2\Pi) + H_2(^1\Sigma_g^+)} \quad \mathbf{(2)} \quad \Delta Hr^{298} = -\ 348.4\ \text{kJ mol}^{-1} \quad (*)$$

$$\mathbf{\rightarrow OH(^2\Pi) + NH(^3\Sigma^-)} \quad \mathbf{(3)} \quad \Delta Hr^{298} = -\ 45\ \text{kJ mol}^{-1} \quad (*)$$

Rate Coefficient Data $k = k_1 + k_2 + k_3$

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
Rate Coefficient Measurements			
$k = 7.6 \times 10^{-11}$	296	(a) Dransfield *et al.*	all studies use variants of the flow-discharge method and should be quite reliable – in respect of the overall rate coefficient
$k = 6.5 \times 10^{-11}$	295	(b) Adamson *et al.*	
$k = (1.2 \pm 0.3) \times 10^{-11}$	242 - 473	(c) Inomata and Washida	
Reviews and Evaluations			
$4.56 \times 10^{-11}\ \exp(10/T)$	200 – 3000	UMIST database	
8×10^{-11}	no T-dependence	OSU website	

Comments

This radical-radical reaction is strongly exothermic and spin-allowed to all channels – though the reactants correlate with quartet, as well as doublet, surfaces.

The values of the overall rate coefficient at 'room temperature' obtained in (a) and (b) are in good agreement; that in (c) is slightly higher but probably within combined errors. Consequently, k can be assumed to be quite well-determined. Reaction probably proceeds through an ONH_2^* complex whose formation does not require passage over a barrier.

Refs (a) and (b) also agree that (1) is the major channel with k_3 being about 10% of k. There is no experimental indication that channel (2) proceeds at a measurable rate.

Preferred Values

Total rate coefficient (10 – 300 K)

$k(300\ \text{K}) = 7.0 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}

$k(10\ \text{K}) = 1.0 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1}

$\mathbf{k(T) = 7 \times 10^{-11}\ (T/300)^{-0.1}\ cm^3\ molecule^{-1}\ s^{-1}}$

Branching Ratios

$\mathbf{k_1 / (k_1 + k_2 + k_3) = 0.9}$

$\mathbf{k_2 / (k_1 + k_2 + k_3) = 0.0}$

$\mathbf{k_3 / (k_1 + k_2 + k_3) = 0.1}$

Reliability

$\Delta \log k\ (300\ \text{K}) = \pm 0.3$

$\Delta \log k\ (10\ \text{K}) = \pm 0.5$

$\mathbf{F_0 = 2\ ;\ g = 4}$

Comments on Preferred Values

I recommend values for the overall rate coefficient similar to those in the UMIST and Ohio compilations. For k(298 K), I take an average of the room temperature measurements in (a) and (b). I assume a mild negative T-dependence.

If all three channels proceed via formation of an energised ONH_2 complex, then the branching ratios are unlikely to have a strong temperature-dependence.

References

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(c) S. Inomata and N. Washida, J. Phys. Chem. *A* **103**, 5023 (1999).