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$CN + NH_3 \rightarrow HCN + NH_2$ (1) $\Delta Hr^{298} = -65.4$ kJ mol^{-1} (*)

$\rightarrow NCNH_2 + H$ (2) $\Delta Hr^{298} = -49$ kJ mol^{-1} (*)

Rate Coefficient Data ($k = k_1 + k_2$)

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
Rate Coefficient Measurements (k)			
8.8×10^{-12}	687	Boden and Thrush, 1968	
$(2.5 \pm 0.5) \times 10^{-11}$	295	DeJuan, Smith and Veyret	
$(1.52 \pm 0.23) \times 10^{-11} \exp\{(1.50 \pm 0.40)$ kJ/mole/RT$\}$	294 - 761	Sims and Smith	
$(2.9 \pm 0.3) \times 10^{-11}$	296	Meads, Maclagan and Phillips, 1993	
$(2.8 \pm 0.7) \times 10^{-11}$ (T/298 K)$^{(-1.14\pm0.15)}$	25 - 295	Sims *et al.*, 1994	
Branching Ratios			
$k_1 / (k_1 + k_2) = 1.0$; $k_2 / (k_1 + k_2) = 0.0$		Talbi and Smith, 2009	
$k_1 / (k_1 + k_2) = 1.0$; $k_2 / (k_1 + k_2) = 0.0$		Blitz, Seakins and Smith, 2009	
Reviews and Evaluations			
$k_1 = 3.41 \times 10^{-11}$ (T/300 K)$^{-0.90}$ exp(9.9 K / T)	all temperatures	UMIST database	
$k_2 = 1.38 \times 10^{-11}$ (T/300 K)$^{-1.14}$	all temperatures	UMIST database	
$k_1 = 1.38 \times 10^{-11}$ (T/300 K)$^{-1.14}$	all temperatures	OSU website	
$k_2 = 1.3 \times 10^{-11}$ (T/300 K)$^{-1.14}$	all temperatures	OSU website	

Comments

Refs (b), (c) and (e): All these studies used the reliable pulsed photolysis / laser-induced fluorescence method. They yield very similar values for $k_1 + k_2$ at 298 K, which agree with that from Meads *et al*. So the value of $k_1 + k_2$ at 298 K must be judged well-established. By extension the low T measurements reported in (c) can be considered reliable.

Until recently, there was really no evidence as to the major products of this reaction (i.e., the branching ratio between channels (1) and (2)). The UMIST and OSU databases appear to arrive at individual values of k_1 and k_2 by arbitrarily dividing up the overall rate coefficient between the two channels. Meads *et al.* (d) demonstrated the formation of NH_2 but their other efforts to find products did not eliminate channel (2). Nor, unfortunately, did their *ab initio* calculations cast a clear light on this problem.

Recently there have been theoretical (f) and experimental (g) studies of this reaction with the emphasis on determining the branching ratio between reactions (1) and (2). Talbi and Smith (f) found no low energy path to $NCNH_2$ + H and concluded that reaction proceeds exclusively to HCN + NH_2. Likewise, the experiments of Blitz *et al.* (g) found no significant formation to H-atoms and they concluded that reaction must proceed only via channel (1).

Preferred Values

Rate coefficients (10 – 300 K)

k(300 K) = 2.8x10^{-11} cm^3 molecule^{-1} s^{-1}
k(10 K) = 5x10^{-10} cm^3 molecule^{-1} s^{-1}
$k_1(T)$ = 2.8x10^{-11} (T/300)$^{-0.85}$ cm^3 molecule^{-1} s^{-1}

Branching ratios

$k_1 / (k_1 + k_2) = 1.0$
$k_2 / (k_1 + k_2) = 0.0$

Reliability

$\Delta \log k$(298 K) = ± 0.08
$\Delta \log k$(10 K) = ± 0.15

$F_0 = 1.2$; g = 1.6

Comments on Preferred Values

Given the good agreement between the experimental values at 298 K, the estimate of 20% certainty seems generous. The wider uncertainty at 10 K reflects the fact that the measurements in (e) only go down to 25 K and it is not clear if $\{k_1 + k_2\}$ will continue to increase below 25 K. The experiments of Blitz et al. (h) show that k_2 /

(k_1 + k_2) is certainly less than 0.05, and most probably zero.

References

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