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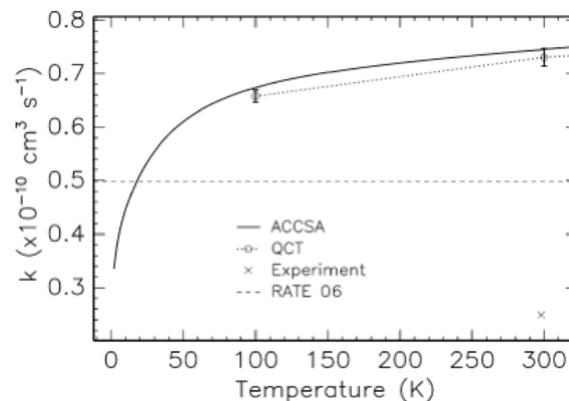
Rate Coefficient Data k

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T / K	Reference	
<i>Rate Coefficient Measurements</i>			
2.49×10^{-11}	298	Hack <i>et al.</i> , 1994	(1)
<i>Theory</i>			
$1.95 \times 10^{-11} \times (T/300)^{-0.51} \times \exp(-6.3/T)$	300-3000	Caridade et al, 2005	(2)
$7.3 \times 10^{-11} \times (T/300)^{0.094}$	100-3000	Caridade et al, 2007	(3)
$7.6 \times 10^{-11} \times (T/300)^{0.116} \times \exp(-0.792/T)$	2-300	Frankcombe and Nyman (2007)	(4)
<i>Reviews and Evaluation</i>			
this reaction is not included		UMIST database	
this reaction is not included		OSU website	

Comments

The $\text{N}(^4\text{S}) + \text{NH}(\text{X}^3\Sigma^-)$ correlate with sextuplet, quadruplet and doublet states and $\text{N}_2(\text{X}^1\Sigma^+) + \text{H}(^2\text{S})$ only with doublet states. Then, there is a $2/(2+4+6)=1/6$ degeneracy factor. There has been only one direct experimental investigation of the rate coefficient for this reaction at room temperature.(1) The reaction is found to be relatively rapid at room temperature ($k = 2.49 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Ab-initio calculations have been performed on this system showing no barrier for $^2\text{N-NH}$ formation. (3) Along the minimum energy path the reaction proceeds to a strongly bound collision complex (N_2H) without a potential barrier. A very small barrier exists on the exit channel from N_2H to the $\text{N}_2 + \text{H}$ products, well below the energy of the entrance channel. The overall reaction is exothermic by 613 kJ/mol (6.33 eV), implying a very strong tendency for any N_2H formed to go on to produce the $\text{N}_2 + \text{H}$ products. Various kinetic calculations have been performed on this system such as quasi-classical trajectory (QCT)(2,3), capture theory(3) and adiabatic capture, centrifugal sudden approximation (ACCSA).(4) It should be noted that dynamics calculations of Caridade et al in 2005(2) were affected by an error in the collision energy sampling, favoring high-energy values.

The results summarized on the figure below (from Frankcombe and Nyman (4)):



There is clear disagreement between the calculated rates constant and the single existing experimental measurement. The agreement between the QCT and ACCSA calculations indicate that the calculated rate coefficients represent the true rate coefficients on the potential energy surface, itself derived from high quality ab initio data. The difference with the experimental measurements may be due to the fact that the experimental rate coefficient have been determined by modeling NH reactant concentrations profiles as a function of the reaction time, with and without N atoms and then is very sensitive to the atomic concentrations. However, as noted by Caridade et al(3), the partition of the total rate of NH removal may not be equal for both doublet electronic states. Thus, the observed discrepancies between the calculated and measured rate coefficients may be attributed both to experimental difficulties and to the non-inclusion of non-adiabatic effects in the theory as complicated electronic crossings.

We recommend the use of the T dependency obtained by making an average of the very similar

theoretical T dependency, with k(300K) value being the average of theoretical and experimental values.

Preferred Values

Rate coefficient (10 – 500 K)

$$k(T) = 5 \times 10^{-11} (T/300)^{0.1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Reliability

$$F_0 = 2 ; g = 6$$

Comments on Preferred Values

(*) 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) W Hack, HG Wagner, A Zaspypkin: Ber. Bunsenges. Phys. Chem. 98 (1994) 156-64.

(2) PJSB Caridade, SPJ Rodrigues, F Sousa, AJC Varandas: The Journal of Physical Chemistry A 109 (2005) 2356-63.

(3) PJSB Caridade, LA Poveda, SPJ Rodrigues, AJC Varandas: The Journal of Physical Chemistry A 111 (2007) 1172-78.

(4) TJ Frankcombe, G Nyman: The Journal of Physical Chemistry A 111 (2007) 13163-67.

References

