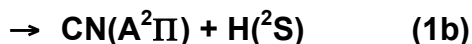


**Authors: Ian Smith (University of Cambridge)**  
**Jean-Christophe Loison (Université de Bordeaux 1)**



#### Thermodynamic Data

$$\Delta H_{298}^{\circ}(1a) = -414 \text{ kJ mol}^{-1}$$

Thermochemical data are taken from ref. (\*)

#### Rate Coefficient Data *k*

<i>k</i> / cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	<i>T</i> / K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$(2.1 \pm 0.5) \times 10^{-11}$	298	Messing <i>et al.</i> 1981	(1)
$(1.66 \pm 0.12) \times 10^{-10} (T/298)^{(0.09 \pm 0.2)}$	216 - 584	Brownsword <i>et al.</i> , 1996	(2)
$(1.4 \pm 0.4) \times 10^{-10} (T/298)^{(0.41 \pm 0.05)}$	56-296	Daranlot <i>et al.</i> , 2013	(3)
<i>Reviews and Evaluations</i>			
$(1.66 \pm 0.12) \times 10^{-10} (T/298)^{(0.09 \pm 0.2)}$	222 - 584	UMIST database	
$(1.66 \pm 0.12) \times 10^{-10} (T/298)^{(0.09 \pm 0.2)}$	all temperatures	OSU website	

### Comments

The reactants correlate with triplet and quintet states, the products with only triplet states. The potential energy surfaces for this reaction are discussed in detail by Rayez *et al.* (4). A <sup>3</sup>A' PES connects the reactants with ground state products (reaction (1a)) and a <sup>3</sup>A'' PES connects the reactants with CN(B<sup>2</sup>Π) + H (reaction (1b)). Therefore, there is an electronic degeneracy factor of *ca.* 3/8. The reaction probably proceeds *via* energised intermediates (excited triplet states of HCN).

Calculations have been performed (5) using long-range transition state theory (6). The long-range interaction between reactants is assumed to arise from dispersion forces and dipole-induced dipole forces. Spin-orbit effects are ignored and the rotation of CH is treated quasi-classically. The calculated rate constants between 10 and 320 K fit:  $k(T) = 1.87 \times 10^{-10} (T/298)^{0.18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The results in the temperature range covered in the measurements in ref. (3) agree quite well with the experimental values.

The experiments of Brownsword *et al.* (2) should be reliable. The large values of the observed rate coefficients, and their agreement with the values calculated by long-range transition state theory, suggest that the reaction rate is determined by capture under the influence of long-range forces. We recommend the calculated rate constant scaled to the experimental results at 298K.

### Preferred Values

*Between 56 and 300 K :*

$$k(T) = 1.4 \times 10^{-10} \times (T/298)^{0.41} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

#### Reliability

$$F = 1.3, g = 4.0$$

#### Comments on Preferred Values

The UMIST and OSU data bases adopt the rate coefficients measured by Brownsword *et al.* (2) – and their *T*-dependence. The reason for the 'low' values reported by Messing *et al.* (1) is not clear. We recommend the new rate constant obtained in CRESU experiment. For temperatures below 56 K,

the rate constant is more uncertain so we introduced a large “g”.

### References

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