Authors:

Dahbia Talbi (Univ. of Montpellier – CNRS, Fr)

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

$N(^4S) + CH_2(^3B_1) \rightarrow HCN(X\ ^1\Sigma^+) + H(^2S)$ **(1)** $\Delta Hr_{298} = -510$ kJ/mol (Baulch *et al.* 2005)

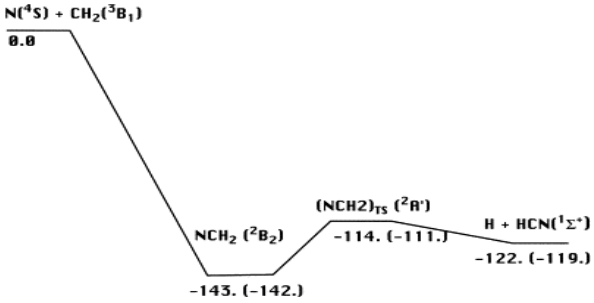
$\rightarrow HNC(X\ ^1\Sigma^+) + H(^2S)$ **(2)** $\Delta Hr_{298} = -455$ kJ/mol (Baulch et al. 2005)

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

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
Rate Coefficient Measurements			
No data was found			
Calculations			
k(T)= 7.89 x 10^{-11}(T/300)$^{1/6}$ cm^{3}s^{-1}	10-300	Herbst et al. (2000)	
Reviews and Evaluations			
k_1 (T) = 3.95 x 10^{-11} (T/300)$^{0.17}$	10-300	UMIST database	
k_2 (T) = 3.95 x 10^{-11} (T/300)$^{0.17}$	10-300	UMIST database	
k_1 (T) = 3.95 x 10^{-11} (T/300)$^{0.167}$		OSU database	
k_2 (T) = 3.95 x 10^{-11} (T/300)$^{0.167}$		OSU database	

Comments

There is no barrier for this reaction as shown by ab-initio calculations (Talbi 1999, Herbst *et al.* 2000, Takahashi & Takayanagi 2007). The ground state ^{4}N nitrogen atom has only one electronic state and $^4N + {}^3CH_2$ correlate adiabatically with sextet, quadruplet and doublet state and products in their ground state correlate only to doublet state so there is an electronic degeneracy equal to 1/6 leading to capture rate constant equal to $8.0\times10^{-11}\times(T/300)^{0.17}$ cm^3 molecule^{-1} s^{-1} (Herbst et al. 2000). It should be noted that the quadruplet surface shows also no barrier in the entrance valley and may participate to the reaction, then the rate constant may be substantially higher, up to $2.4\times10^{-10}\times(T/300)^{0.17}$ cm^3 molecule^{-1} s^{-1} (Herbst et al. 2000). The main products from ab-intio results are the HCN + H. As the isomerization energy of the HCN → HNC is 186 kJ/mol (DePrince III & Mazziotti 2008), there is so much excess energy available in this reaction (510 kJ/mol) that the HCN product is able to undergo efficient isomerization reactions after production leading to near equal production rates of the two isomers. Precise internal energy distribution is necessary to get accurate branching ratio, the HCN being likely more abundant that HNC as all the HCN produced with less than 186 kJ/mol will be not able to isomerize. The final branching ratio will likely in favor of HCN, we propose a ratio HCN/HNC=5/3.



The Energy profiles are for surfaces of doublet multiplicity. Relative energies, given in kcal/mol, have been calculated at the PMP4SDTQ/6-311++G(3df,3pd)//MP2/6-31G(d,p) and CCSD(T)/6-311++G(3df,3pd)//MP2/6-31G(d,p) (numbers in brackets) levels. In all cases, relative energies are corrected for the ZPE and for spin contamination from higher spin state

Preferred Values

Rate coefficient (10 – 300 K)

k_1 (T) = 5.0×10^{-11}(T/300)$^{0.17}$ cm^3 s^{-1}

k_2 (T) = 3.0×10^{-11}(T/300)$^{0.17}$ cm^3 s^{-1}

Reliability
F_0 = 1.5 ; g = 0

Comments on Preferred Values

References

Baulch D.L., Bowman C.T., Cobos C.J., Cox R.A., Just T., Kerr J.A., Pilling M.J., Stocker D., Troe J., Tsang W., Walker R.W., Warnatz J., 2005, J. Phys. Chem. Ref. Data, 34, 757

DePrince III A.E., Mazziotti D.A., 2008, J. Phys. Chem. B, 112, 16158

Herbst E., Terzieva R., Talbi D., 2000, MNRAS, 311, 869

Takahashi K., Takayanagi T., 2007, J. Mol. Struct.: THEOCHEM, 817, 153

Talbi D., 1999, Chem. Phys. Lett., 313, 626

8 october 2013