THEORETICAL STUDIES OF THE REACTIONS OF H_2 + CN: COMPETITION BETWEEN H-ABSTRACTION IN H + HCN/HNC CHANNELS.

Alessandra F. Albernaz[1]*, Patrícia R. P. Barreto*[2]
[1]*Instituto de Física, Universidade Brasília, CP04455, Brasília, DF, CEP 70919-970*
[2]*Laboratório Associado de Plasma, Instituto Nacional de Pesquisas Espaciais, CP515, São José dos Campos, SP, CEP 12247-970*

1. Introduction

Reactions involving [H,C,N] systems are of wide interest in several chemical processes that occur in flames, comets, lasers and planetary atmospheres. Hydrogen cyanide (HCN) and its isomer, hydrogen isocyanide (HNC), have been detected in such diverse molecular astrophysical environments as diffuse interstellar clouds, prestellar disks, outflowing circumstellar envelopes, Titan's atmosphere and planetary nebulae. There are studies that show the importance of the nitriles/isonitriles compounds in prebiotic chemistry as possible precursors of molecules of biological interest. There is a variety of theoretical studies on the mechanisms of reactions that lead to the formation of the HCN/HNC radicals. In most of these studies, the HNC formation mechanism occur via $HCNH^+ + e$, $H_2CN^+ + e^-$,H_2C + N, H_2N + C, CH + NH and H + HCN[1].

Thus a complete understanding of the HNC/HCN abundance ratio requires, in addition to some explanation for the low temperature enhanced abundance of the metastable HNC, a further explanation for the disappearance of this species with increasing temperature. Like, at present moment, there is no record of the location of any transition structure for hydrogen abstraction converting H_2 + CN to H + HNC; in this work, we propose investigate the production of HCN/HNC via neutral H_2 + CN reaction, with a linear configurations, leading to the formation of the H + HCN

$$H_2 + CN \rightarrow H + HCN \qquad \Delta H_f = -21.58\, kcal/mol$$

and H + HNC

$$H_2 + CN \rightarrow H + HNC \qquad \Delta H_f = -6.68\, kcal/mol$$

channels.

2. Theory Methods

The G3 Method were employed in our work to determine the potential energy surface (PES), geometries, vibrational frequencies and energies of the reactants, transition states and products of the H_2+CN reactive process. Vibrational frequencies were used to characterize the stationary points as minimum or transition states, the number of imaginary frequencies (0 or 1) indicate whether a minimum or a transition state has been located. To confirm that the transition state really connects reactants and products, the intrinsic reaction coordinate (IRC) calculations were performed. All calculations were performed with Gaussian 09 program. The rate constants for the present simple reactions have been calculated by conventional transition state theory (TST) and canonical variational transition state theory (CVT) with the APUAMA program [2]. The quantum effect corrections for the CVT rate constants have been made by zero-curvature tunneling (ZCT) and small-curvature tunneling (SCT) calculations. The results of these calculations will be compared later with experimental data and theoretical results.

3. Results and Discussions

For the H_2 + CN reaction system, the two product channels, as alluded to in the introduction, have been considered: H-atom abstraction processes by the carbon of the CN molecule $H_2 + CN \rightarrow H + HCN$ and H-atom abstraction processes by the nitrogen of the CN molecule $H_2 + CN \rightarrow H + HNC$. The optimized geometries of the reactants, transition states, products and relative energies, ΔE, (in parentheses) are calculated using G3 method can be seen in Fig. 1.

The schematic potential energy surfaces for the reaction between H_2 and CN are plotted in Fig. 1 with the following products: H + HCN and H + HNC. Note that energy of reactants is set to be zero as reference. To H + HCN channel, we found a barrier among the transition state TS_1 of the 3.40 kcal mol^{-1} that is close to the value found by Horst et al. of the 3.2 kcal mol^{-1} [3]. To H + HNC channel, the barrier height of the transition state TS_2 is 13.37 kcal mol^{-1}. At present moment, there is no record of the location of any transition structure for hydrogen abstraction converting H_2 + CN to H + HNC. The product energy goes from –22.83 kcal mol^{-1}, for H + HCN channel to –8.18 kcal mol^{-1} for H + HNC channel. The rate constants, calculated as conventional, Wigner correction tunneling and CVT to $H_2 + CN \rightarrow H + HCN$ and $H_2 + CN \rightarrow H + HNC$ reactions, are presented in Fig. 2 and 3, respectively. The branching ratios as a function of

* alessandra@fis.unb.br

temperature for channel 1 and 2 are displayed in Fig. 4. These results show that H+HCN product is the most important in range of temperature of 300–1700 K, with a probability of 100% of the total reaction, at 300 K. While, the H+HNC product is more favorable to high temperatures (T > 1700 K), with a probability of 100% of the total reaction, at 3000 K.

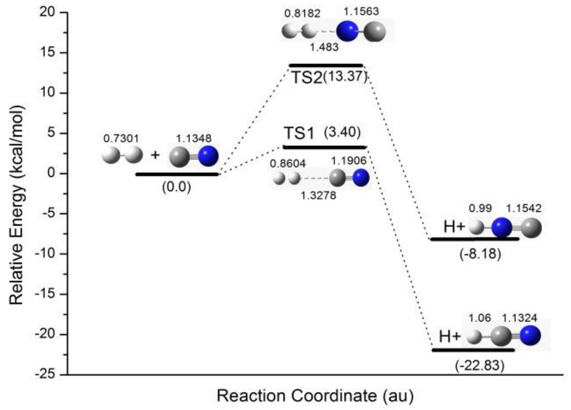

Fig. 1: *The profile of the doublet Potential Energy Surface of the H_2+CN→ H+HCN/HNC reactions with optimized geometries calculated at G3 Method, with ZPE correction.*

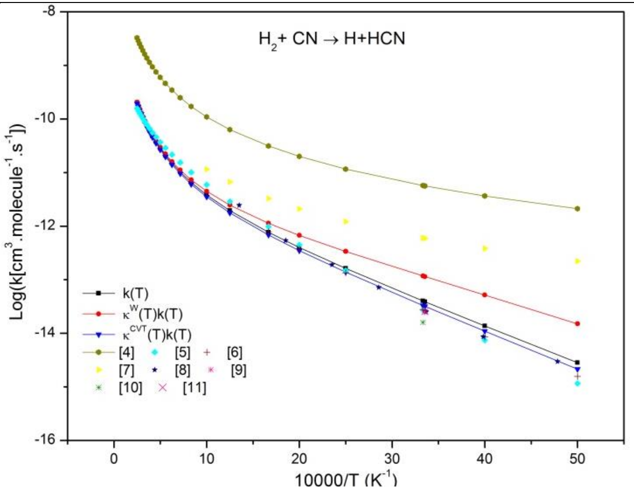

Fig. 2: *Comparison of the present thermal rate constants for the H_2+CN→ H+HCN reaction as a function of temperature (solid lines with symbols) are reported together with the corresponding values of references (symbols only).*

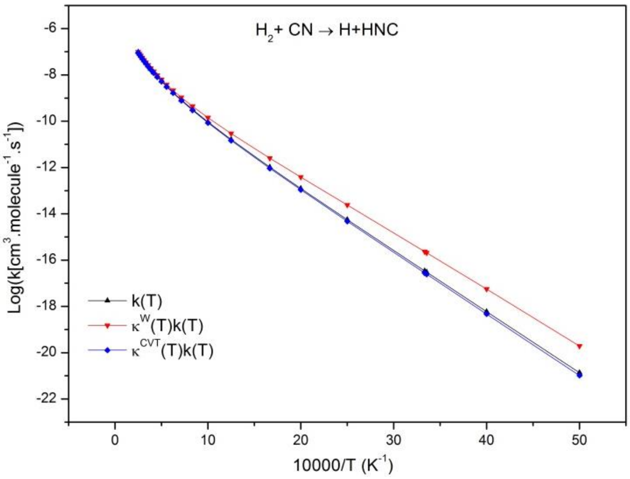

Fig. 3: T*hermal rate constants for the H_2+CN→ H+HNC reaction as a function of temperature.*

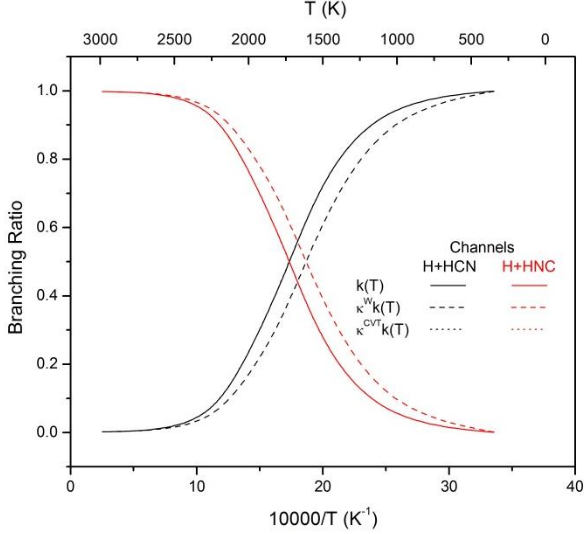

Fig. 4: *The branching ratios of the H_2+CN→ H+HCN and H_2+CN→ H+HNC reactions, at temperature range of 300-3000 K*

4. References

[1] Correa, E., da Silva, W.B., Barreto, P.R.P., Albernaz, A. F., J. Mol. Model. (2017) 23: 169.
[2] H. O. Euclides, P. R. P. Barreto, J. Mol. Model. (2017) 23: 176.
[3] M. A. ter Horst, G. C. Schatz, and L. B. Harding. J. Chem. Phys., (1996) 105:558.
[4] A. F. Wagner and R. A. Bair. Int. Chem. Kinet., (1986) 18:473.
[5] W. Tsang. J. Phys. Chem. Ref. Data, (1992) 21:753.
[6] I. R. Sims and I. W. M. Smith. Chem. Phys. Lett., (1988) 149:565.
[7] B. Atakan, A. Jacobs, M. Wahl, R. Weller, and J. Wolfrum. Chem. Phys. Lett., (1989)154:449.
[8] Q. Sun and J. M. Bowman. J. Chem. Phys., (1990) 92:5201.
[9] J. de Juan, I. W. M. Smith, and B. Veyrets. J. Phys. Chem., (1987) 91: 69.
[10] X. Li, N. Sayah, and W. M. Jacson. J. Chem. Phys., (1984) 81: 833.
[11] R. J. Balla and L. Pasternack. J. Phys. Chem., (1987) 91:73.

* alessandra@fis.unb.br