

Kinetics of the O + HCN Reaction

Patrícia R. P. Barreto¹, Washington B. Silva², Eberth A. Correa³, Alessandra Albernaz⁴

¹Laboratório Associado de Plasma, INPE, CP515, São José dos Campos, SP, CEP 12247-970
²Instituto Federal de Brasília, Campus Ceilândia, Ceilândia, DF, CEP 72220-260
³Universidade de Brasília, Campus do Gama – Engenharias, Brasília, DF, CEP 72444-240
⁴Instituto de Física, Universidade Brasília, CP04455, Brasília, DF, CEP 70919-970

Abstract: The reactions of the decomposition products, such as HCN and O, CH and NO, NH and CO, OH and CN, also play important roles in the combustion of N-containing hydrocarbon fuels [1-5]. Kinetics of these species are therefore of considerable interest in developing improved models for the combustion of fuels containing organically bound nitrogen. The elucidation of chemical mechanisms in flames is difficult, because there are several pathways involving reactants that are equilibrated among themselves. Even if a mechanism predicts the correct dependence on temperature and composition, it may not be unique. The goal of this work is to investigate global features of potential energy surface (PES) for the exit and isomerization channels on both singlet and triplet O + HCN reactions, represented by:

1	2
\rightarrow ¹ NH + CO $\Delta H = 8.41 \text{ kcal/mol} (\text{R})$	2)
\rightarrow ³ NH + CO $\Delta H = -32.20$ kcal/mol (R	3)
\rightarrow H + NCO Δ H = -9.79 kcal/mol (R	4)
$\rightarrow 0 + HNC$ $\Delta H = 14.07 \text{ kcal/mol} (R)$	5)
$\rightarrow N + HCO$ $\Delta H = 37.25 \text{ kcal/mol} (R)$	5)
$\rightarrow CH + NO$ $\Delta H = 71.55 \text{ kcal/mol} (R)$	7)

The singlet and triplet PES (see Figure 1) were calculated using the complete basis set model chemistry, CBS-QB3. The vibrational frequencies and geometries for all species involved in the reaction were calculated using B3LYP/6-311G(2d,d,p) level, internal level of CBS-QB3 method. Seven different channels were analyzed and the results from the potential energy surface calculations were used to determine rate constant with Master Equation Solver for Multi-Energy Well Reactions (MESMER) [6] and APUAMA [7] programs. Ab initio transition state theory (TST) based master equation simulations are used to predict the temperature and pressure dependence of the O+HCN reaction rate and product branching. In the singlet state, isocyanic acid, HNCO, has been found to be the most stable isomer (-119.17 kcal/mol) followed by cyanic acid, HOCN (-94.26 kcal/mol), fulminic acid, HCNO (-51.41 kcal/mol), isofulminic acid, HONC (-35.77 kcal/mol), NC(H)O (-33.51 kcal/mol) , N(H)CO (-11.97 kcal/mol) and O(H)CN (-6.00 kcal/mol). In the triplet state, the ³HNCO is 9.50 kcal/mol higher than O+HCN (reactants), the branched ³NC(H)O isomer is -33.46 kcal/mol energetically lower than, followed by ³HNCO (-31.71 kcal/mol). The cyclic c-³NC(H)O is by 49.63



Figure 1. Schematic potential energy diagram for the O + HCN reaction calculated using CBS-QB3 level. Solid lines denote singlet states, while dashed lines denote triplet states.

Key-words: HCN; O+HCN; Transition State Theory; Master Equation; Reaction Rate

Support: This work has been supported by CNPq

References:

- [1] J. A. Miller and C. T. Bowman, Prog. Energy Combust. Sci., 15, 287 (1989).
- [2] B. S. Haynes, D. Iverach, and N. Y. Kirov, "Fifteenth Symposium (International) on Combination" The Combustion Institute, 1103 (1975).
- [3] B. S. Haynes, Combust. Flume, 28, 113 (1977).
- [4] C. Morley, Combust. Flume, 27, 189 (1976).
- [5] A. Szekely, Ph.D. thesis, Department of Mechanical Engineering, Stanford University (1984).
- [6] D. R. Glowacki, C.-H. Liang, C. Morley, M. J. Pilling and S. H. Robertson; J. Phys. Chem. A, 116, 9545 (2012).
- [7] H. O. Euclides, P. R. P. Barreto, J. Mol. Model., 23, 176 (2017).