Potential energy surfaces for the Reaction of the Methylidyne Radical (CH $X^2\Pi$) with the Propionitrile C_2H_5CN ($X^1\sum^+$) Molecule

Lubov I. Krikunova[1,2], A.A. Nikolayev[1,2], D.P. Porfirev[1,2], A.M. Mebel[3]

[1] Lebedev Physical Institute, Samara 443011, Russia; [2] Samara National Research University, Samara 443086, Russia; [3] Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, USA

The reaction of the methylidyne (CH; $X^2\Pi$) radical with ethyl cyanide (C_2H_5CN; $X^1\sum+$) molecule was studied at a collision energy of 4.0 kJ/mol with ab initio calculations of the potential energy surface (PES). At low temperatures in deep space, a large amount of nitriles are present in the atmosphere of Saturn's moon Titan [1, 2], as well as in interstellar molecular clouds. Reactions of nitriles with the methine radical CH are of interest, as potencial initial step in the study of biological molecules. In particular, in the course of the reaction with cyanide molecules, a nitrogenous base, structural blocks in DNA chains, can be formed. In addition, the formation of linear and cyclic radicals is possible with the release of the corresponding products: atoms, molecular particles, ethylene, etc.

Geometries and potential energies of reactants, products, intermediates and transition states for the reaction were found by means of ab initio quantum chemical method ωB97xd/cc-pVTZ [3, 4] and the higher-level corrections were evaluated at the CCSD(T)-F12 level of theory[5, 6, 7] with the cc-pVQZ-f12 (E_1) basis set [8, 9].

Those results were utilized in Rice–Ramsperger–Kassel–Marcus calculations of the product branching ratios at the zero pressure limit – common approach in modelling of the cold molecular clouds chemistry. Mechanism identified emphasizes importance of the CH+C_2H_5CN reaction as an important supplier of the initial bricks for building heterocyclic hydrocarbons in extreme environments [10, 11].

References

1. R.I. Kaiser, A.M. Mebel, V.V. Kislov, S.J. Klippenstein, L.B. Harding, M.C. Liang, and Y.L. Yung. Acrossed molecular beams study on the formation of the exotic cyanoethynyl radical in titan's atmosphere x. Gu1, / astrophysical journal V. 701, – i 2, – 2009, – p. 1797-1803
2. X.Gu, Y.S. Kim, R.I. Kaiser, A.M. Mebel, M.C. Liang, Y.L. Yung Chemical dynamics of triacetylene formation and implications to the synthesis of polyynes in Titan's atmosphere // Proceedings of the National Academy of Sciences of the United States of AmericaV. 106, – I. 38, – 2009, – P. 16078-16083
3. D. Xu and D. Li, «CH as a molecular gas tracer and c-shock tracer across a molecular cloud boundary in Taurus» Astrophys. J., 2016, 833, 90.
4. Frisch, M.J. «Gaussian 09 (Revision A.1): Gaussian, Inc., Wallingford (CT)». – 2009. https://gaussian.com
5. Werner, H.-J. MOLPRO, Version 2010.1, A «Package of Ab Initio Programs MOLPRO.NET: University of Cardiff, UK». – 2010. – URL: https://www.molpro.net/info/release/doc/manual/index.html
6. Adler, T.B. «A simple and efficient CCSD(T)-F12 approximation» The Journal of Chemical Physics. – 2007. – Vol. 127(22). – P. 1-4.
7. Knizia, G. «Simplified CCSD(T)-F12 methods: Theory and benchmarks» The Journal of Chemical Physics. – 2009. – Vol. 130(5). – P. 1-21.
8. Chai, J.-D. «Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections» Physical Chemistry Chemical Physics. – 2008. – Vol. 10. – P. 6615-6620.
9. J.-D. Chai and M. Head-Gordon, «Systematic optimization of long-range corrected hybrid density functionals» Physics Chemical Journal. – 2008. 128 – 084106.
10. Marcus, R.A. «Unimolecular reactions, rates and quantum state distribution of products Philosophical Transactions of the Royal Society» A. – 1990. – Vol. 332. – P. 283-296.
11. P. J. Robinson, K. A. Holbrook, «Unimolecular Reactions», Wiley: New York, 1972.