

Indenyl radical self-reaction study

Vlad Krasnoukhov^{1,2}, Marsel Zagidullin¹, Alexander Mebel³

¹ Lebedev Physical Institute, Samara Branch, 221 Novo-Sadovaya str., Samara, Russia, 443011

² Samara National Research University, 34, Moskovskoye shosse, Samara, Russia, 443086

³ Florida International University, 11200 SW 8th Street Miami, Florida 33199

vladya11@gmail.com

When theoretically considering the mechanism of the reaction of two indenyl radicals, the first step is to find and refine the energies, structures of the reactants, intermediate and transition states, and products using non-empirical quantum mechanical methods of density functional theory, in this case B3LYP / 6-311G **. The results of theoretical studies of the reaction of five-membered carbon rings C₅H₅ and C₅H₄ by the G3(MP2, CC)//B3LYP methods, leading to the formation of two-ring PAHs, have already been presented in¹⁻³, as well as data from a previous work showing the pathways for the formation of multi-ring PAHs and their energy profitability, which served as the goal and basis for further study of the formation of four membered ring PAHs and their kinetics. Vibrational frequencies and zero-point energies E(ZPE) were also calculated by a similar method. The final energy refinement was based on a modified combined scheme: E[G3] = E[CCSD(T)/6-311G**] + E[MP2/G3Large] - E[MP2/6-311G**] + E(ZPE), where CCSD(T) is the paired cluster method with the 6-311G** basis, and MP2 is the Möller-Plesset second-order perturbation theory method with the 6-311G** and G3Large basis sets.

The interaction of two radicals firstly forms a C₁₈H₁₄ complex, where further abstraction of hydrogen from the five-membered ring of one bicyclic indenyl system leads to the barrier-free formation of the i1 isomer, the energy of which is 23.6 kcal/mol higher than the energy of the reagents. In the future, a similar abstraction of a hydrogen atom can immediately lead to the formation of a product p1 of the dibenzofulvalene type with an energy of 66.6 kcal/mol. Isomerization can occur in two ways, one of which is the creation of a three-membered compound between the rings to form a spiro structure with an energy i1-1 of 37.4 kcal/mol. Subsequently, this three-membered compound breaks with an energy of 72.3 kcal/mol to form a six-membered ring, obtaining a four-ring spiran structure. Similarly, the last five-membered ring grows into a six-membered one. Further, after the detachment of hydrogen from i4-2, the product p3 is formed with an energy of 29.9 kcal/mol of the tetraphene type.

It is also possible to create a four-membered ring bond in the i1-2 intermediate with an energy of 70.0 kcal/mol. This compound involves the creation of a larger carbon ring (i2-2; 43.3 kcal/mol). The detachment of hydrogen can lead to the formation of a product p2 of the dibenzoazulene type with a relative energy of 67.8 kcal/mol. Also, like in the first route, it is also possible to obtain the i4-22 isomer with a relative energy of 13.1 kcal/mol. Removal of hydrogen will lead to the formation of the p4 product of the chrysene type with a relative energy of 27.4 kcal/mol. However, by getting rid of the intercarbon bond in c i4-22, it is possible to create a twelve-membered ring in the center, in which another bond can be made to create a sequential four-ring structure. As a result, after the removal of hydrogen from intermediate i5-2 (36.3 kcal/mol), the product p5 of the "tetracene" type can be formed with a relative energy of 38.5 kcal/mol. These results allow us to begin work on the study of reaction rate constants and relative yields of products to determine the energy preference.

References

1. Kislov V.V., Mebel A.M. *The Journal of Physical Chemistry A*. 2007. V. 111(38). P. 9532-9543.
2. Mebel A. M., Landera A., Kaiser R.I. *The Journal of Physical Chemistry A*. 2017. V. 121(5). P. 901-926.
3. Krasnoukhov V.S., Zagidullin M.V., Zavershinskiy I.P., Mebel A.M. *The Journal of Physical Chemistry A*. 2020. V. 124(48). P. 9933-9941.