



On the accuracy of DFT methods for calculating the activation characteristics of the Pd-catalyzed allylation of norbornadiene



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Introduction

More recently, an increasing number of studies have been devoted to studying the reaction of norbornadiene (NBD) allylation in the presence of metal complex catalysts [1], which leads to various carbocyclic compounds, fig. 1. Post-experimental theoretical modeling [2] using the DFT-PBE/L11 method allowed us to detail the mechanism of this reaction. At the same time, the question of the reliability of the calculation method used remains debatable, since the obtained values of activation barriers turned out to be noticeably overestimated ($\Delta G_{298}^\ddagger > 30$ kcal/mol). The aim of this work was to study the influence of the basis set and the type of exchange-correlation functional on the activation and structural characteristics of intermediates and transition states corresponding to the critical points of the energy profiles of the Pd-catalyzed allylation of norbornadiene.

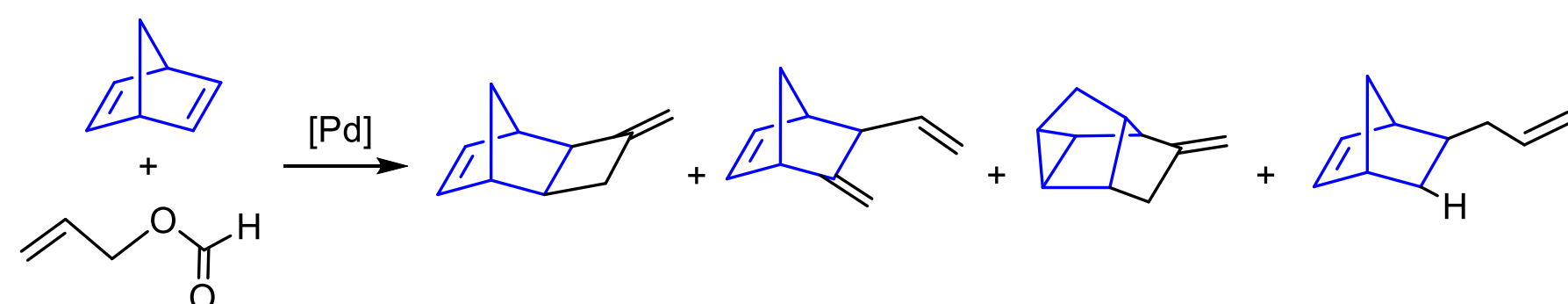


Fig. 1. The main products of Pd-catalyzed allylation of NBD.

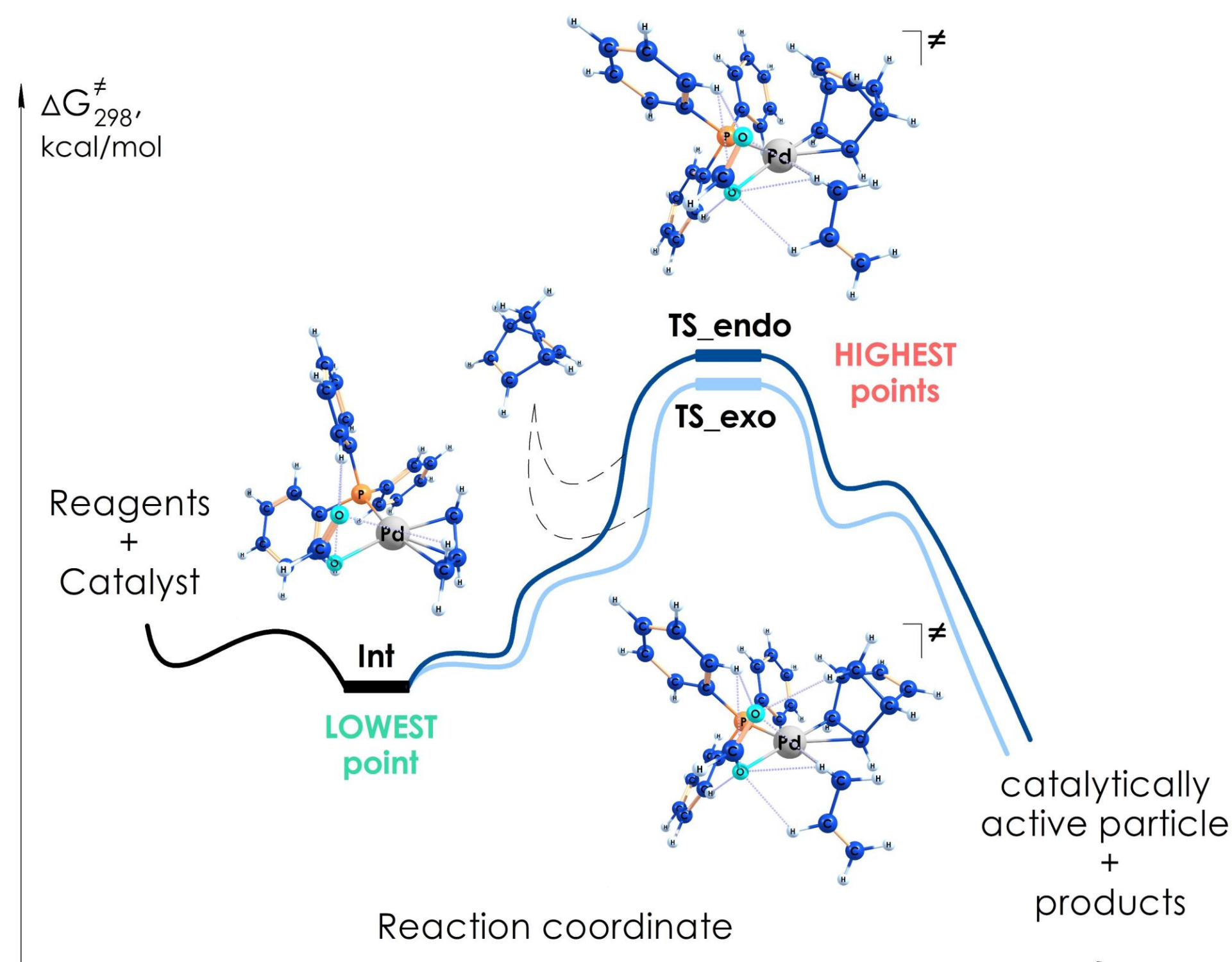


Fig. 2. Critical points of the energy profile of the reaction.

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Calculation method

- Scalar-relativistic approximation of the density functional theory.
- Calculations were performed in Priroda software[3], and ORCA software[4].
- The Priroda's basis sets (L1, L11, L22) and the ORCA's basis sets (ZORA-def2-SVP, ZORA-def2-TZVP, ZORA-def2-QZVPP) were used.
- In this work, functionals of different types were used, as well as taking into account dispersion corrections.

Results

To assess the influence of the size of the basis set and the complexity of the DFT-functional on the activation and structural characteristics of the studied reaction, 3 critical points of the energy profile were selected, fig. 2: profile global minimum (**Int**) and rate-determining states of the whole process (**TS_exo** and **TS_endo**), which correspond to the stage of formation of the C-C bond. Expansion of the basis set by more than 4 times (649→2820) does not lead to a significant change in the Gibbs energy of activation of the entire process, fig. 3. The closest to the energy values obtained in the L11 basis set were the results obtained in the ZORA-def2-TZVP basis set.

Calculations in GGA-functionals (*PBE*, *OLYP*, *BP86*) as well as in hybrid functionals (*B3LYP*, *PBE0*, *B97*) give high values of activation barriers ($\Delta G_{298}^\ddagger = 29.5 - 47.8$ kcal/mol). The use of the meta-GGA functional (*TPSS*) leads to a similar result ($\Delta G_{298}^\ddagger = 32.6 - 36.5$ kcal/mol), fig. 4.

The inclusion of dispersion corrections according to Grimme [5] significantly lowers the activation barriers of the reaction (*PBE-D3*: $\Delta G_{298}^\ddagger = 20.4 - 23.4$ kcal/mol; *B97-D3*: $\Delta G_{298}^\ddagger = 20.7 - 23.4$ kcal/mol) due to the presence of interactions such as intramolecular hydrogen bonds. Consideration of such non-covalent interactions is not implemented in the classical DFT-functionals, and their contribution can be significant. However, the results obtained using *PBE-D3* and *B97-D3* seem to be understated. The moderate ΔG_{298}^\ddagger values were obtained using a more accurate LRC functional: ω B97X with the improved dispersion corrections from DFT-D3: ω B97X-D3 with Becke-Johnson damping. As a result, the energies of **TS_exo** and **TS_endo** become equal to 24.4 and 26.0 kcal/mol, respectively. Moreover, using ω B97X-D3, the energy difference between **TS_exo** and **TS_endo** is reduced from about 3.6 (when using any other DFT-functional) to 1.7 kcal/mol. This fact agrees better with the experimental data.

As regards the change in the key internuclear distances: the transition from the GGA functionals to the LRC leads, on average, to a slight reduction by 0.01 – 0.04 Å. The intramolecular hydrogen bonds (O...H) decrease more noticeably by 0.02 – 0.08 Å.

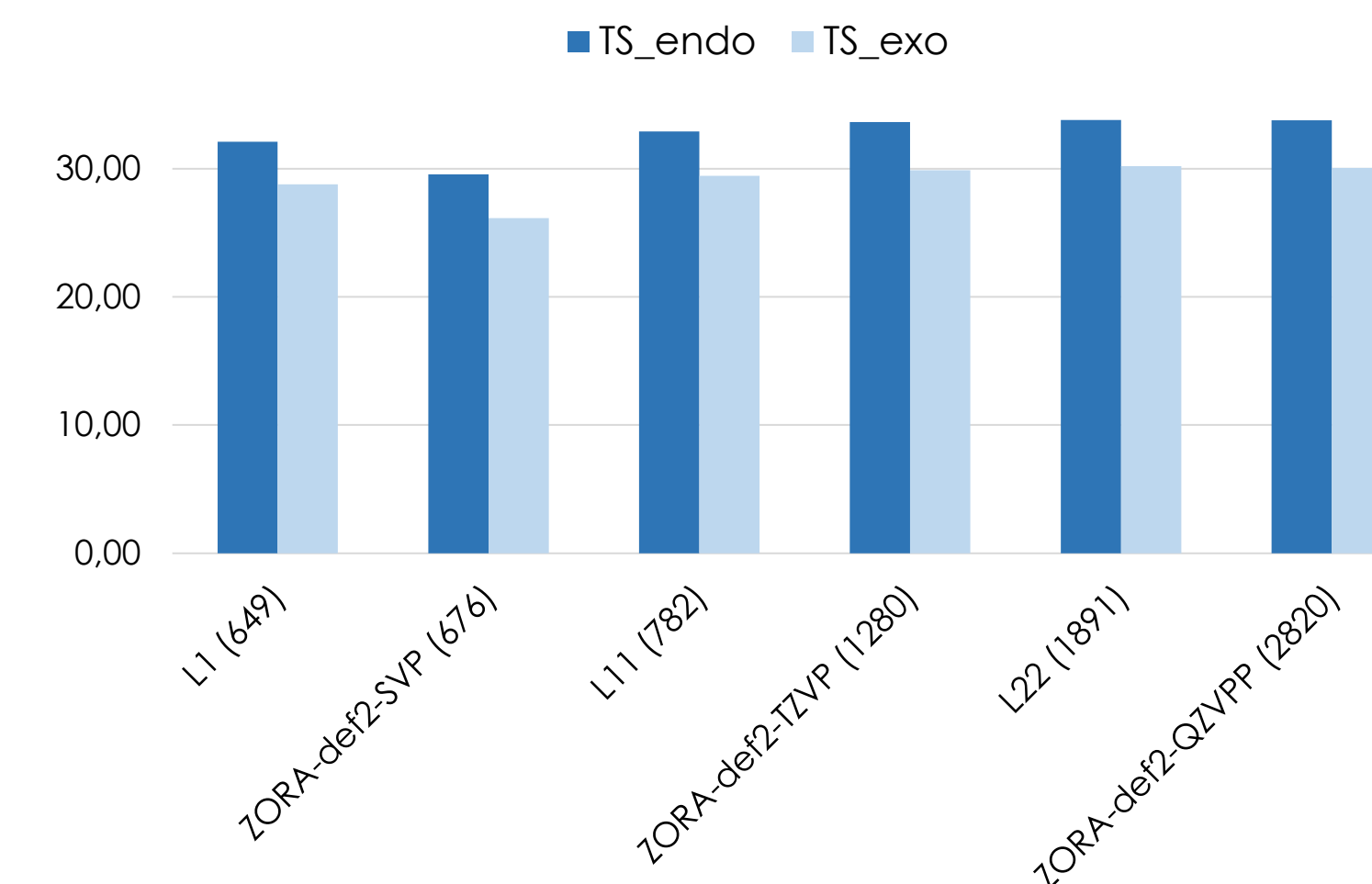


Fig. 3. Influence of the size of the basis set on the activation characteristic (ΔG_{298}^\ddagger) of the reaction. The number of basis functions is given in parentheses.

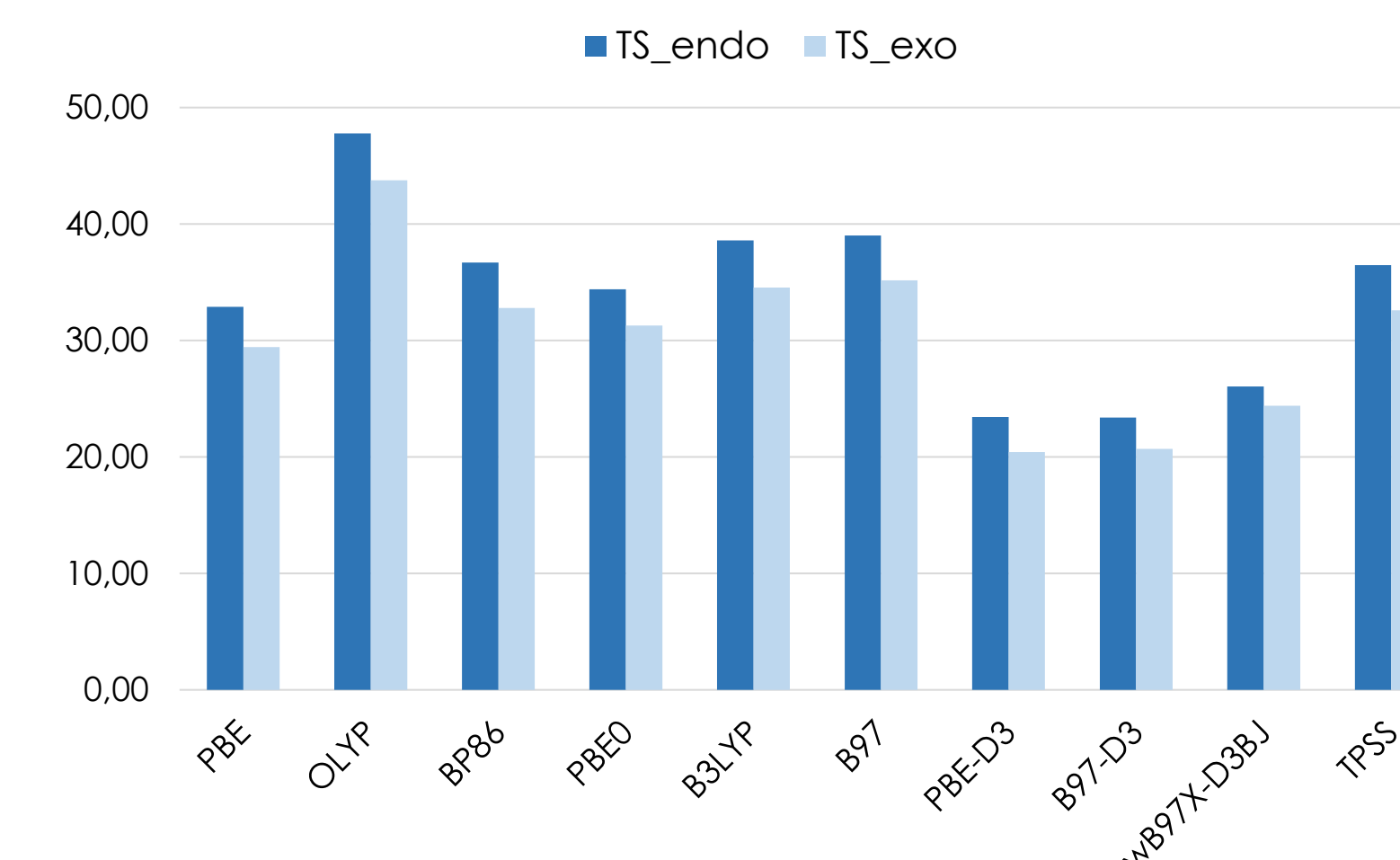


Fig. 4. Influence of the type of exchange-correlation functional on activation characteristic (ΔG_{298}^\ddagger) of the reaction. Calculations using GGA-functionals in combination with L11 basis set were performed, all other calculations were performed with ZORA-def2-TZVP basis set.

Conclusion

1. The expansion of the basis set does not significantly affect the value of ΔG_{298}^\ddagger for the routes of products formation.
2. The replacement of GGA-functionals by hybrid ones leads to an even greater increase in the values of ΔG_{298}^\ddagger (by ~2 kcal/mol). The Grimme dispersion correction (D3) for GGA or hybrid functionals leads to a strong underestimation of ΔG_{298}^\ddagger (by ~10 kcal/mol). Moderate values of ΔG_{298}^\ddagger were obtained using the LRC-functional - ω B97X-D3.

References

- [1] S.A. Durakov, P.V. Melnikov, E.M. Marzinkevich, A.A. Smirnova, R.S. Shamsiev, V.R. Flid Russ. Chem. Bull. 2021, 70(1), pp. 113-121.
- [2] R.S. Shamsiev, K.T. Egiazaryan, V.R. Flid Russ. Chem. Bull. 2022, 71(5), pp. 905-914.
- [3] D.N. Laikov, Yu. A. Ustynyuk Russ. Chem. Bull. 2005, 54(3), pp. 820-826.
- [4] F. Neese, F. Wennmohs, U. Becker, C. Riplinger J. Chem. Phys. 2020, 152, 224108.
- [5] S. Grimme, J. Antony, S. Ehrlich, H. Krieg J. Chem. Phys. 2010, 132, 154104.