THERMODYNAMIC FEASIBILITY OF REDUCING ORGANOPLATINUM(IV) SPECIES BY IODIDE IONS AS A KEY STEP FOR CROSS-ELECTROPHILE COUPLING

Mitchenko S.A., *Krasnyakova T.V., Nikitenko D.V., Gogilchin A.S.*
L.M. Litvinenko Institute of Physical Organic and Coal Chemistry
283048, Donetsk, R. Luxemburg st., 70

Exploiting the vast synthetic potential of reductive cross-electrophile coupling, i.e., the direct coupling of two C-electrophiles, remains challenging due to issues with controlling chemoselectivity caused by the identical chemical nature of both substrates [1]. A model Pt(II)–NaI–acetone catalytic system for reductive cross-electrophilic coupling was recently designed [2], providing a useful tool for exploring the causes of selectivity. In this system, the key intermediates of C-C coupling, bis-organic $Pt^{IV}(R_1)(R_2)$ complexes, are generated in a sequence of steps: oxidative addition (OA) of R_1-I to PtI_2 forming $Pt^{IV}(R_1)$ species – reduction of the latter by I^- to give $Pt^{II}(R_1)$ and I_3^- – OA of R_2-I generating $Pt^{IV}(R_1)(R_2)$. The reduction step here is facilitated by the solvent-specific binding of the released iodine with acetone and NaI into a poorly soluble polymeric complex tris(μ_2-acetone-κ^2O:O)-sodium polyiodide [3]. Reductive elimination of two organic ligands yields the C-C coupling product, R_1-R_2, and regenerates the catalyst. Thus, the reduction of organic Pt^{IV} derivatives by iodine ions to the corresponding Pt^{II} organometallic compounds, being one of the key steps in the overall catalytic process, could have an impact on the chemoselectivity.

To elucidate the possible contribution of the reduction step to the selectivity of C-C coupling, we estimated the Gibbs free energy and enthalpy of this transformation for a series of organic derivatives of Pt^{IV} using density functional theory (DFT) calculations. The results of DFT-modeling the energy profiles of the reactions, as well as correlations between the free Gibbs energies of the reactions and the calculated values of Pt^{IV} electrophilicity indices, will be presented and discussed.

1. Ehehalt L. E., Beleh O. M., Priest I. C. [et al.]. Cross-Electrophile Coupling: Principles, Methods, and Applications in Synthesis // Chemical Reviews. 2024. Vol. 124, №. 23. P. 13397-13569. https://doi.org/10.1021/acs.chemrev.4c00524

2. Krasnyakova T. V., Nikitenko D. V., Gogil'chin A. S. [et al.]. Reductive Cross-Electrophile C(sp^2)-C(sp^3) Coupling Catalyzed by PtI_2: In Situ Structural Determination of the Intermediates by X-ray Absorption Spectroscopy and Multinuclear NMR // Organometallics. 2024. Vol. 43, № 1. P. 55–67. https://doi.org/10.1021/acs.organomet.3c00400

3. Howie R. A.; Wardell J. L. Polymeric tris(μ_2-acetone-k^{2}O:O)-sodium polyiodide at 120 K. Acta Cryst. Section C, Crystal Structure Communications 2003. C59, m184–m186. https://doi.org/10.1107/S0108270103006395

This work was supported by the Ministry of Science and Higher Education of the Russian Federation through State Assignment "Design of C-C and C-X coupling reactions catalyzed by simple transition metal complexes using acetylene and organic halides", Grant No. FRES-2026-0010.