

Detailed computational study of the chlorination-assisted skeletal rearrangement of D₂-19150C₇₆ into C₂-18917C₇₆Cl₂₄

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The Isolated Pentagon Rule (IPR) plays a definitive role in fullerene chemistry. All identified products of the standard arc discharge synthesis without dopants are IPR fullerenes. Non-IPR structures are typically obtained via instant functionalization of the forming cages in the reactor with endohedral metal atoms/clusters or with chlorine addends. Because of lower thermodynamic stability of the non-IPR isomers and presumably high activation energy of the Stone-Wales rearrangements that were generally regarded as key mechanism of skeletal transformations, no one anticipated, until very recently, a possibility of conversion of the conventional IPR fullerenes into non-IPR ones under milder chemical conditions.

In view of that, quite surprising was formation of strongly non-IPR C₂-¹⁸⁹¹⁷C₇₆Cl₂₄ compound in the course of chlorination of the well known IPR-isomer D₂-¹⁹¹⁵⁰C₇₆ in SbCl₅ [1]. The new fullerene chloride was found to have as many as five pairs of adjacent pentagons. To explain this transformation, a modified mechanism of Stone-Wales rearrangements was proposed that involves migration of chlorine atoms to stabilize the transition states and thus to reduce the reaction barriers.

We present a detailed computational analysis of the formation pathway of C₂-¹⁸⁹¹⁷C₇₆Cl₂₄ at the DFT level of theory. We employed the PBE exchange-correlation functional known to be successfully applicable to various fullerene systems. The activation energy calculations were additionally refined with the use of the PBE0 hybrid functional and PCM corrections.

The transformation of the chlorinated D₂-¹⁹¹⁵⁰C₇₆ into C₂-¹⁸⁹¹⁷C₇₆Cl₂₄ was found to require seven Stone-Wales steps plus a step of global chlorine migration over the carbon cage, all steps calculated to be thermodynamically favorable. The Stone-Wales bond rotations in the chlorinated fullerenes are facilitated by formation of stabilized valence-saturated intermediate structures via SbCl₅-mediated transfer of chlorine anions. The activation energy of the first, limiting Stone-Wales step was calculated to be 2.5 eV. Of critical importance for the skeletal rearrangement process is the chlorinating SbCl₅ environment that enables formation of closed-shell ion pair transition states [C₇₆Cl_{2n-1}]⁺[SbCl₆]⁻ and further stabilizes them through polarization interactions.

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- [1] I.N. Ioffe, A.A. Goryunkov, N.B. Tamm, L.N. Sidorov, E. Kemnitz, S.I. Troyanov, *Angew. Chem. Int. Ed.* **48**, 5904 (2009).