Stability Computations in a Series of Extraction-Derivatized Metallofullerenes: $La@C_x$ / $La@C_x$-$C_6H_3Cl_2$

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Recently, an extraction of metallofullerenes from soot using 1,2,4-trichlorobenzene has been developed and applied to to $La@C_{72}$ [1], $La@C_{74}$ [2] $La@C_{80}$ [3] and $La@C_{82}$ [4]. In all four cases the cages were derivatized by the solvent, forming $La@C_x$-$C_6H_3Cl_2$, and the following X-ray analysis moreover disclosed that in some cases rather unexpected cages are involved - non-IPR $C_{72}(C_2)$, $C_{80}(C_{2v};3)$, and $C_{82}(C_{3v};7)$ cage. In order to interpret the interesting discoveries, a two step computational treatment is used. The first step deals with the high-temperature gas-phase formation of the pristine (underivatized) endohedrals like $La@C_{80}(C_{2v};3)$ and $La@C_{80}(C_{2v};5)$. The second step models the reaction with the solvent that produces the $La@C_{80}$-$C_6H_3Cl_2$ derivatives. In order to have a more reliable description of the thermodynamic terms, the Gibbs free energies were evaluated instead of mere potential-energy values and a representative temperature of 1500 and 298 K was considered with the first and second reaction, respectively. Although the underivatized $La@C_{80}(C_{2v};5)$ species is lower in energy, the derivatization changes the energy order so that after the derivatization the $La@C_{80}(C_{2v};3)$ isomer should prevail in the solution. When the computed Gibbs free energy terms are converted into the equilibrium constants and concentrations, the model evaluation suggests that the $\frac{La@C_{80}(C_{2v};3)-C_6H_3Cl_2}{La@C_{80}(C_{2v};5)-C_6H_3Cl_2}$ concentration ratio in solution should be equal to about 67 (at the B3LYP/6-31G*∼SDD computational level). A similar enhancement of $La@C_{80}(C_{2v};3)$-$C_6H_3Cl_2$ is also found with respect to the $La@C_{80}(D_{5h};6)$-$C_6H_3Cl_2$ production. The computational treatment is applied throughout the $La@C_x$ / $La@C_x$-$C_6H_3Cl_2$ series.

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