FULLERENE FORMATION KINETICS IN CARBON VAPORS. II

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Ab-initio calculations using density functional theory (B3LYP/6- 31G*) and thermodynamical analysis has demonstrated to be a model chemistry with suitable theoretical accuracy for the identification of intermediate structures and reaction pathways in carbon derivatives formation kinetics [1]. Fullerene formation reaction pathways in carbon vapors are proposed in this work using this powerful tool [2].

Four major steps are analyzed in the formation kinetics of fullerenes from a carbon vapor gas.

The first step comprises the selective formation of linear chains with null activation energy. These addition reactions begin with the nucleation of one, two or three carbon atoms originally produced from the ablation or sublimation of graphite in an inert gas (buffer) atmosphere. These reactions can proceed to form linear chains that can have more than 30 carbon atoms. Branched chains can also be formed, but they are not favored by energetic considerations.

The second step is the cyclization of linear chains forming carbon ring structures. Cyclization to tadpole structures can also be competitive in some structures. Some branched chain structures can give origin of tadpole structures by cyclization.

As a third step, carbon ring structures can react between them, preferentially in their triplet state, to form bowl shaped very reactive metastable or stable aromatic polycycles. Polycycles can also be formed after the reaction of a chain and a ring or a tadpole, or directly after the cyclyzation of long linear or branched chain structures.

Finally, as the fourth step, bowl shaped polycycles can react between them in a zip fastener mechanism in which a very exothermic reaction takes place. Energy liberation can be greater than 10 eV, more than enough to produce several Stone-Wales transformations, until the fullerene structure decays to the more stable isomer or isomers thermodynamically possible. Pair of carbon atoms can be loosed in this last reaction process.

The reaction pathway towards fullerene formation is mainly done threw structures in their triplet state and hitherto are governed by very quick free radical reactions. Reaction pathways are totally shown for the particular case of formation of fullerene C60 from two bowls of 30 atoms that can be formed by the isomerization of a 30 atoms carbon ring or the reaction between two 15 atom rings or the reaction of 14 and 16 carbon atom rings. Bowl shaped polycyclic structures were detected in experiments of catalytic dehydrogenation and cyclization of saturated linear hydrocarbons [3].

References

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