

PATHWAYS AND KINETICS OF POLYCYCLIC CARBON CLUSTERS CONVERSION TO FULLERENES

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1. Introduction

Despite the huge amount of investigations, the mechanism of fullerenes formation still remains an unresolved mystery.

The experimental results evidently show [1,2] that clusters larger than 20 atoms grow mostly by the coalescence of smaller ring isomers. It was discovered in [3-5], and also observed in [6] that thus forming polycyclic clusters are efficiently collapsing to fullerenes. This fact still cannot explain the great abundance of C_{60} and the absence of smaller fullerenes in condensing carbon, although this may be possibly explained by the 'fullerene road' growth mechanism [7], but it requires further investigations. However, it is evident that fullerenes are produced by the coalescence of rings with subsequent conversion to the energetically favorable closed shell structure. So the study of polycycles' conversion to fullerenes is of great interest.

We present an attempt to consider the mechanism of conversion and to estimate numerically the efficiency and rate of such transitions. We propose a statistical model describing the isomerization process. The polycyclic isomer transforms to fullerene by a sequence of bond formations. At each step of conversion, we calculate the isomer energy, the isomerization barrier height and the partition functions (PF) for each pair of isomers and also for the transition state. This allows to evaluate the kinetics of isomerization. The main problem is the lack of information about the isomers energy and PF.

2. Energetics of isomerization

Since the quantum chemical methods are extremely CPU-time consuming, we decided to use classical interatomic potential. We chose the model of Brenner [8], but had to modify it slightly [9] in order to fit the vibrational spectra of clusters, which was necessary for PF calculations. The simulation of cluster evolution by Monte-Carlo method has shown that for temperatures less than 0.3 eV bond formations and breakings occur rarely and the kinetics of isomerization can be

described through single acts of bond formation being considered as separate isomerization steps.

The relative efficiency of bicyclic and tricyclic isomers conversion to fullerene has not been reported now, but it can be noticed, that fullerene and tricyclic isomer appears simultaneously at 30 atoms and the fullerene formation efficiency increases with size similarly to the tricyclic isomer abundance in parent ions. We considered the conversion of tricyclic structures which are the most abundant isomer in size interval $N = 40 \div 60$ [1]. Using MINDO/3 we find two most stable tricyclic isomers - three rings bound by hexagon and those bound by additional central atom.

Since new bond formations decrease the cluster entropy, but increase the binding energy, there appears a minimum of isomer's PF at a certain step of conversion. We have shown, that this step is a bottle neck to the whole conversion process, and the kinetics is determined by the PF meaning there. As the rate of entropy decreasing appeared to be nearly constant, the effectivity of a conversion path depends upon how soon the loss of entropy will be compensated by the energy gain. So we looked for the isomerization pathways giving increase in energy as soon as possible. We find that the main principle in choosing the pathway is to avoid dangling bonds and radical orbitals. Formation of adjacent pentagons is more preferable.

The conversion proceeds mostly by bonding atoms near the rings bases and resembles the closure of bud. The resulting shell structure would not be a perfect fullerene, but its further rearrangement is evidently thermodynamically favorable, with low change of entropy (because the number of bonds remains constant) and significant gain in energy, and can proceed by the Stone-Wales isomerizations [10]. As the conversion is highly exothermic, the isomerization barriers would be easily overcome.

3. Results and discussion

To evaluate the rate of conversion we determined also the barrier heights and rates for the initial critical steps of isomerization. We assumed that at the early

stage of conversion, when the energy changes slowly, the temperature is nearly constant. The process may be described by solving a set of kinetic equations for the isomers abundances. We found that the quasi-steady state approximation works quiet well, and the kinetics is really limited by the bottle neck. The details are to be published in [9].

We calculated the fraction of clusters transformed to fullerene and the characteristic conversion time t_f in temperature interval $0.12 \div 0.25$ eV for a variety of pathways. We have found only one non-radical path for the tricycle with a central atom, and the best evaluated t_f for it was $3 \cdot 10^{-4}$ s. Other pathways, requiring appearance of radical orbitals, have t_f of a few orders of magnitude larger. The appearance of radical delays the gain in energy and so strongly decreases the PF at the bottle neck.

The pathways of direct construction of buckyball structure require a lot of atoms with radical orbitals and cannot be efficient. For example, the path considered in [5] creates up to six such atoms and in our potential the energy gain appears only after 11-12 isomerization steps (instead of 4-5 for the best pathways), when a huge loss in entropy arises, so the bottle neck on this path is extremely narrow.

We can conclude that the assembly of fullerene must proceed by the paths with the best energies of intermediate isomers rather than by instant construction of perfect structure. Besides, so high relative efficiency of the non-radical path also points that, in reality, there are probably only a few certain dominant paths responsible for efficient conversion. The radical orbital appearance must be avoided at their first steps.

The size of rings in the tricycle isn't important for the kinetics since at the limiting stage of conversion the rearrangement of structure is local and the size of ring fragments doesn't influence on the energetics (while the fragments remain larger than $10 \div 12$ atoms and their angular strain is low). So our model doesn't predict any advantages for C_{60} or C_{70} fullerene formation. However, this is in agreement with experiment [5], where nothing special was observed for these sizes. We compared the conversion rates of C_{40} and C_{60} tricycles through the non-radical path and found that they didn't differ significantly. The barrier heights on this path for C_{60} are mostly $1 \div 1.5$ eV, with the maximal value observed of 2.7 eV. For C_{40} the corresponding barrier is 2.9 eV, the others are almost the same. For comparison, the estimated activation ener-

gy for cluster cation conversion in [5] was 2.4 eV for C_{60} and 2.8 eV for C_{40} . So the size dependence of conversion rate may be considered as weak.

We can assume from this, that the conversion process is really limited by few initial isomerization steps, when the ring fragments size does not affect much. The observed in [3-5] increase of fullerene formation efficiency with cluster size may be explained by increase of the abundance of some certain initial isomers, possibly tricyclic, which can efficiently transform to fullerene. The bicyclic isomers, predominant for size less than 40 atoms [1], may rather anneal to monocyclic rings because need to break less number of bonds for this.

As the kinetics is very sensitive to the intermediate isomers energies, the more reliable estimation of conversion rate needs more accurate information about energies and PF, which is out of reach now. Comparison with experiment is impossible yet, the only guess is that the t_f for cations must be significantly less than the measured gas tube drift time (for example, 10^{-4} s in [3]).

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