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Dynamics of carbon clusters: chemical equilibration of rings and bi-cyclic rings

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Abstract

Quantum-chemical calculations, at the self-consistent-charge density-functional-based non-orthogonal tight binding (SCC-DFTB) level, are used to provide the input for unimolecular reaction rate theory calculations to predict the temperatures at which rapid, i.e., microsecond timescale, equilibration between mono-cyclic and bi-cyclic carbon clusters can occur. The computational results are discussed in the form of a set of trends for their variation with the size of the cluster, the length of the carbon–carbon bond broken or formed, the vibrational frequencies, the energy differences and the rate constants. The temperatures used experimentally to prepare fullerenes and nanotubes are compatible with the rapid equilibration of rings and bi-cyclic rings, a factor that explains the lack of defects in these higher forms of carbon clusters and the general trend towards the formation of the most stable fullerene for a given nuclearity. © 2002 Published by Elsevier Science B.V.

1. Introduction

In the gas phase, carbon molecules assemble and exist in a variety of structures which comprise linear chains, mono-, bi- and tri-cyclic rings, graphitic sheets and fullerenes [1]. A large region of isomeric overlap appears for mono- and bi-cyclic rings for which ion mobility studies, obtained by gas-phase ion chromatography, have shown that their co-existence extends between 20 and 40 carbon atoms [2]. The investigations proved that the ranges of presence are rather similar for cations and anions and suggest a relatively small influence of the molecular charge on the final shape of a cluster.

The co-existence of clusters of differing topology and the tendency of fullerenes to ultimately form the most stable isomer for a given nuclearity [3] pose the fundamental question of estimating qualitatively and quantitatively the equilibration processes that occur in the self-assembly of carbon clusters. Indeed, in the timescale of fullerene formation, the self-assembly of the covalent bonds proceeds so efficiently that as final products (a) only fullerenes with isolated pentagons are formed
and (b) of the isolated pentagon isomers the most stable species is the most abundant. Importantly, while the introduction of a pentagon-pentagon abutting bond involves an energy penalty of 70–150 kJ mol\(^{-1}\) [4], the energy separation of pentagon-isolated isomers can be as low as a few kJ mol\(^{-1}\). Annealing must therefore be extremely efficient in the experimental conditions.

Partial or complete severance of at least one bond is the minimal feature common to all the rearrangements that take place during the formation of these systems. The simplest bond breaking one can envisage is the snapping of a ring to form a linear chain or the formation of a large macrocycle from a bi-cyclic system. The former has already been investigated [5], while understanding the latter is the goal of this work. The question we try to answer here is whether the rate constants of inter-conversion between rings and bi-cyclic rings (and vice versa) make it feasible and in the time-scale of the production at the standard temperatures at which carbon clusters are prepared. To achieve this goal a combination of quantum chemistry and model calculations is exploited. First tight binding calculations are performed to locate the minimum energy structures of the two isomers from C\(_{16}\) to C\(_{30}\). Then the transition states connecting the two systems are located. Finally, the energy barriers and vibrational frequencies are used to obtain the kinetic rate constants for the transformation of a ring into a bi-cyclic ring and a bi-cyclic ring into a ring.

2. Computational background

Quantum chemical calculations were performed with self-consistent charge non-orthogonal density-functional-based tight-binding (SCC-DFTB), which has been described elsewhere [7]. In contrast to other TB models, the Hamiltonian and overlap matrix elements are not empirical quantities but are calculated from first-principle density functionals. The method penalizes charge fluctuations within the molecule in a Hubbard-like self-consistent way. SCC-DFTB has been successfully applied to determine structures, energetics and properties of hydrocarbon molecules, small carbon clusters, fullerenes, bulk systems, surfaces and proteins [6–9]. This level of calculations is deemed adequate to obtain structures and energies of the both isomeric species together with the interconnecting transitions states. Vibrational frequencies were also calculated with the same method (see below).

Molecular partition functions were obtained in the harmonic oscillator approximation in analogy with a previous treatment [6–9]. In the Transition State Theory approximation [10,11] temperature dependent, canonical, rate constants, \(K(T)\), were calculated as

\[
K(T) = \frac{k_B T}{h} \frac{Q_{ts}}{Q_{r,br}} \exp \left( - \frac{\Delta E_{att}}{k_B T} \right),
\]

where \(T\) is the temperature, \(Q\) is the partition functions of either the transition state, ts, or the reactant system, ‘r’ stands for ring and ‘br’ for bi-cyclic ring, and \(\Delta E_{att}\) is the activation energy. The vibrational partition function were calculated in the harmonic approximation, while the rotational partition function were calculated in the rigid rotor approximation.

3. Results and discussion

In a recent review paper [1] VanOrder and Saykally asked the following: ‘An interesting

<table>
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<th>N atoms</th>
<th>(\Delta E_{r,br})</th>
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<th>(\Delta E_{br,ts})</th>
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question regarding clusters in the C_{11} to C_{30} size range is, at what size does the closed cage fullerene-like structure begin to emerge as a stable isomer? Similar questions address the shape and the nature of the inter-conversion between the various forms of carbon clusters. While it is known that fullerenes are the most stable and dominant species from about 40 atoms and upwards, the C_{11}-C_{30} region can at best be described as not entirely well understood in its dynamical features and yet that is the region where the initial game of carbon cluster formation is played. Importantly, however, a very large amount of work has been carried out on the stability of the possible isomers [12], an illustrative case is C_{20} for which three different isomers were synthesised [13] and the PES has been theoretically well studied [14].

Presence of a given isomeric form of carbon clusters in the fullerene or carbon nanotube formation process is not only a matter of stability and the experimental temperatures of the self-assembly is likely to play an important role. Production is achieved at ~1800 °C in flames [15]. Somewhat higher temperatures are used in experiments in which carbon cylinders in a He atmosphere at 150 kPa are treated with high frequency (500 kHz) inductive heat where carbon starts to sublime at 2500 °C [16]. The standard electric arcs for fulle-

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Fig. 1. Structures and shape of the lowest frequency vibrations of the ring, bi-cyclic ring and transition state for C_n, n = 15–30. Also the corresponding wavenumbers and the carbon–carbon distance of the bond broken/formed are given.
rene production reach temperatures well above 4000 °C [17]. In the case of smaller clusters, it is known that production of C₂ to C₇ requires temperatures of 2660–2850 K [18–20]. Similar high-temperature conditions are also likely to occur in the production of carbon clusters in acetylene electric discharge [21]. Annealing studies [22–27] have shown that equilibration to the most stable structure can be achieved by injecting electrons in the production chamber at 150 eV which result in an effective carbon cluster temperature somewhat above the carbon melting temperature of 3740 K. It can be concluded that the temperatures of self-assembly of carbon clusters are well above 1000 K and reach up to 4000 K depending on the experimental set-up.

To investigate some dynamical aspects connected to small carbon clusters, Cₙ, n = 15–30, we decided to use the quantum chemical results as input for the calculations of isomerisation rates within unimolecular reaction rate theory. Specifically, the intent was to investigate breaking/formation of a carbon–carbon that leads to the formation of single- or bi-rings. Unimolecular reaction rate theory requires the vibrational frequencies of reactants, i.e., minima, and transition states, i.e., saddle points. Frequencies of odd-numbered carbon rings and chains were reported a number of times [28]. A comprehensive comparison of calculated and experimental frequencies for organic molecules is reported in [7]. The agreement with the experiment is rather good and
no systematic deviation is observed. Moreover, the comparison between experiment and theory, with some controversies, were reported for Raman spectra for C\textsubscript{16}, C\textsubscript{18} and C\textsubscript{20} [29]. Density-Functional calculations of carbon clusters C\textsubscript{2n}, \(n=2\text{--}16\), were presented recently [30,31]. The present SCC-DFTB approach gives frequency values comparable to LDA calculations. Interestingly, other frequency dependent properties of non-fullerene clusters have been studied. For instance, the second Order Jahn–Teller effect found in carbon 4N + 2 ring clusters [32] and the vibrational fine structure in photoelectron spectra [33].

Kinetic rate constants depend also on the energy barriers. As a test case, one can calibrate the results of the DFTB model by calculating the energy for rupture of the CC bonds in ethane and ethyne. The strength of these bonds is similar (and actually exceeds) that of the bonds that are broken in the bicyclic clusters. For C\textsubscript{2}H\textsubscript{4} bond breaking occurs at 192.0 kcal mol\(^{-1}\) versus an experimental value of
146 kcal mol$^{-1}$, while for C$_2$H$_2$ the bond cleavage is calculated at 259.2 kcal mol$^{-1}$ versus an experimental value of 200 kcal mol$^{-1}$ [34]. The overbinding is about 30% and is consistent with the general overbinding of density functional theory. In kinetic terms, a higher transition state results in slower processes. In practice, the present calculations will underestimate the possibility of equilibration.

Table 1 shows the calculated energy differences between the two isomers and their transition state.

Several trends with the increasing number of atoms appear:
1. The activation energy for opening the bi-cyclic ring reaches a plateau of about 2 eV.
2. The activation energy for byclisation of monocyclic ring reaches a plateau of slightly less than 3 eV.
3. The energy difference between the two stable species approaches a value somewhere between 0.5–1 eV.

Fig. 2. Rates of interconversion from the bi-cyclic ring to the mono-cyclic ring (circles) and from the mono-cyclic ring to the bi-cyclic ring for (a) C$_{15}$, (b) C$_{16}$, (c) C$_{17}$, (d) C$_{18}$, (e) C$_{19}$, (f) C$_{20}$, (g) C$_{21}$, (h) C$_{22}$, (i) C$_{23}$, (j) C$_{24}$, (k) C$_{25}$, (l) C$_{26}$, (m) C$_{27}$, (n) C$_{28}$, (o) C$_{29}$, (p) C$_{30}$. 
Fig. 1 shows the optimised structures with the lowest energy vibration and the distance of the forming/breaking carbon–carbon ring. More trends are discernable:

4. From above 20 atoms, the lowest frequency vibration of the rings decreases. The odd-numbered clusters are more rigid and have a higher frequency which, however, tends towards that of the even-numbered clusters which possess a consistently near-zero frequency.

5. The shorter the central bond in the bi-cyclic ring the higher the frequency in the ring of origin.

6. The shorter the incipient bond in the transition state the larger the associated imaginary frequency.

7. Apart from the near zero frequencies of the even-numbered rings, the larger the lowest frequency of the ring the larger the lowest frequency of the bi-cyclic ring.

It is also instructive to compare the energy data of Table 1 with the data reported in Fig. 1. A few more trends emerge:

8. The higher the lowest frequency of the ring the greater its energy gap with the bi-cyclic ring.
9. The shorter the incipient bond of the transition state the greater its energy gap between the ring and the bi-cyclic ring.

10. The shorter the incipient bond in the transition state the greater transition state energy obtained from the ring.

Fig. 2 shows the rates of inter-conversion of the 16 clusters considered in this work. They were calculated from an experimentally not accessible temperature of 50–5000 K in steps of 50 K. Inspection shows some more trends:

11. The rate of conversion from the bi-cyclic ring to the mono-cyclic ring is consistently higher than the opposite rate.

12. At around 1000 K, the rate of bi-cyclic ring to the mono-cyclic ring conversion reaches the microsecond timescale.

13. The rate of bi-cyclic ring to the mono-cyclic ring are higher for the smaller (more strained) clusters.

14. The two rate constants never cross, in agreement with the higher stability of the rings.

4. Conclusion

Rather simple trends emerged from the calculations of the potential energy surface and dynamics of the inter-conversion between cyclic and bi-cyclic forms of carbon clusters between 15 and 30 atoms. Apart from shedding light on the general behaviour of these species, the results indicate that the conversion from bi-cyclic rings to monocyclic rings occurs more efficiently for small clusters. In all cases, however, at the temperatures used experimentally to prepare fullerenes and nanotubes, the annealing can be rapid \( k > 10^6 \text{ s}^{-1} \) and therefore defects are easily removed, in agreement with the experimental observation.

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