FULLERENIC SYSTEMS FOR NANOSCIENCE: COMPUTATIONAL SCREENING ILLUSTRATED ON $X@C_{74}$ METALLOFULLERENES

Zdeněk Slanina,a Filíp Uhlík,b Shyi-Long Lee,c Ludwik Adamowiczd and Shigeru Nagasea

aDepartment of Theoretical Molecular Science, Institute for Molecular Science, Okazaki 444-8585, Japan
bSchool of Science, Charles University, 128 43 Prague 2, Czech Republic
cDepartment of Chemistry and Biochemistry, National Chung-Cheng University, Chia-Yi 62117, Taiwan
dDepartment of Chemistry, University of Arizona, Tucson, AZ 85721-0041, USA

ABSTRACT

The objects of fullerene science - fullerenes, metallofullerenes & other fullerene endohedrals, and nanotubes - are discussed in a wider context of nanoscience and nanotechnology applications for molecular memories and quantum computing. The emerging concepts and nanotube-based endohedrals, especially Ca@C74, Ba@C74, and Yb@C74. A set of six C74 cages is considered, namely one cage with isolated pentagons, three isomers with a pentagon-pentagon junction, two structures with one pentagon-pentagon pair and one heptagon. Special interest is paid to the enthalpy-entropy evaluations for estimations of the relative as well as absolute populations.

1. INTRODUCTION

Although empty C74 fullerene [1] is not yet available in solid form, several related endohedral species have been known like Ca@C74 [2,3], Sr@C74 [4], Ba@C74 [5], La@C74 [6-8], Eu@C74 [9], Yb@C74 [10], Sc2@C74 [11] or Er3@C74 [12]. In the Yb@C74 case, two isomers were in fact isolated [10]. This isomerism finding is particularly interesting as there is just one [13] C74 cage that obeys the isolated pentagon rule (IPR), namely of $D_{5h}$ symmetry. The cage was experimentally confirmed in Ca@C74 [2], Ba@C74 [4] and La@C74 [8]. Obviously, with Yb@C74 a non-IPR cage should be involved as it is the case of Ca@C72 [14] (empty C72 could also not be isolated yet, possibly owing to solubility problems [2,15-17]).

The metallofullerene family is naturally of computational interest. First such computations were performed for Ca@C74 with considerations of selected non-IPR cages [2,16,18,19]. However, the non-IPR encasulations are not significant with Ca@C74, in contrast to Ca@C72 [20,21]. The present paper surveys the computations also for the Ba@C74 and Yb@C74 species. In order to respect high temperatures in fullerene/metallofullerene preparations, the Gibbs energies are to be used [22,23] in relative stability considerations rather than the mere potential energy terms.

2. COMPUTATIONS

The computations treat a set of six metallofullerene isomers, using the carbon cages investigated with Ca@C74, namely the three structures selected from di-anion energetics [2,18], and three additional cages with non-negligible populations as empty C74 cages [24,25]. In the computations [18,19,24] the cages have been labeled by some code numbers that are also used here, combined with the symmetry of the complexes: 1/C2v, 4/C1, 52/C2, 103/C1, 368/C1, and 463/C1. The 1/C2v, endohedral is the species derived from the unique C74 IPR structure. The previously considered [16] two non-IPR C74 cages are now labeled by 4/C1 and 103/C1. A pair of connected pentagons is also present in the 52/C2 structure. The remaining two species, 368/C1 and 463/C1, contain a pentagon/pentagon pair and one heptagon.

The present geometry optimizations were primarily carried out using density-functional theory (DFT), namely employing Becke’s three parameter functional [26] with the non-local Lee-Yang-Parr correlation functional [27] (B3LYP) in a combined basis set. In the case of Ba@C74, the combined basis set consists of the 3-21G basis for C atoms and a dz basis set [28] with the effective core potential (ECP) on Ba (denoted here by 3-21G~dz) while with Yb@C74 (where the dz-type basis set [28] is not available for Yb) the 3-21G basis on C atoms is combined with the CEP-4G basis set [29,30] employing the compact effective (pseudo)potential (CEP) for Yb (denoted here by 3-21G~CEP-4G). The B3LYP/3-21G~dz or B3LYP/3-21G~CEP-4G geometry optimizations were carried out with the analytically constructed energy gradient. The reported computations were performed with the Gaussian 03 program package [31]. In the optimized B3LYP/3-21G~dz or B3LYP/3-21G~CEP-4G geometries, the harmonic vibrational analysis was carried out with the analytical force-constant matrix. In the same optimized geometries,
higher-level single-point energy calculations were also performed, using the standard 6-31G* basis set for C atoms, i.e., the B3LYP/6-31G*~dz single-point treatment for Ba@C{sub 74} and the B3LYP/6-31G*~CEP-4G level with Yb@C{sub 74}. Moreover, in the latter case the SDD (Stuttgart/Dresden) basis set [32,33] was also employed (with the SDD ECP for Yb) for the single-point calculations, and for the carbon atoms the SDD, 6-31G*, or 6-311G* basis set was stepwise used. In point calculations, and for the carbon atoms the SDD, employed (with the SDD ECP for Yb) for the single-SDD (Stuttgart/Dresden) basis set [32,33] was also employed.

DFT response theory [34] at the B3LYP/3-21G [39] level was used for the three lowest isomers, the geometry optimizations were also carried out at the B3LYP/6-31G*~SDD level. The electronic excitation energies were evaluated by means of time-dependent (TD) DFT response theory [34] at the B3LYP/3-21G~dz or B3LYP/3-21G~CEP-4G level.

Relative concentrations (mole fractions) $x_i$ of $m$ isomers can be evaluated [35] through their partition functions $q_i$ and the enthalpies at the absolute zero temperature or ground-state energies $\Delta H_{0,i}^*$ (i.e., the relative potential energies corrected for the vibrational zero-point energies) by a compact formula:

$$x_i = \frac{q_i \exp(-\Delta H_{0,i}^* / (RT))}{\sum_{j=1}^{m} q_j \exp(-\Delta H_{0,j}^* / (RT))},$$

(1)

where $R$ is the gas constant and $T$ the absolute temperature. Eq. (1) is an exact formula that can be directly derived [35] from the standard Gibbs energies of the isomers, supposing the conditions of the inter-isomeric thermodynamic equilibrium. Rotational-vibrational partition functions were constructed from the calculated structural and vibrational data using the rigid rotator and harmonic oscillator (RRHO) approximation. No frequency scaling is applied as it is not significant [36] for the $x_i$ values at high temperatures. The geometrical symmetries of the optimized cages were determined not only by the Gaussian built-in procedure [31], but primarily by a procedure [37] which considers precision of the computed coordinates. The electronic partition function was constructed by direct summation of the TD B3LYP/3-21G~dz or B3LYP/3-21G~CEP-4G electronic excitation energies. Finally, the chirality contribution was included accordingly [38] (for an enantiomeric pair its partition function $q_i$ is doubled).

In addition to the conventional RRHO treatment with eq. (1), also a modified approach to description of the encapsulate motions can be considered [39], following findings [14,16,40] that the encapsulated atoms can exercise large amplitude motions, especially so at elevated temperatures (unless the motions are restricted by cage derivatizations [41]). One can expect that if the encapsulate is relatively free then, at sufficiently high temperatures, its behavior in different cages will bring about the same contribution to the partition functions. However, such uniform contributions would then cancel out in eq. (1). This simplification is called [39] free, fluctuating, or floating encapsulate model (FEM) and requires two steps. In addition to removal of the three lowest vibrational frequencies (belonging to the metal motions in the cage), the symmetries of the cages should be treated as the highest (topologically) possible, which reflects averaging effects of the large amplitude motions. There are several systems [39,42] where the FEM approach improves agreement with experiment.

As for the temperature intervals to be considered, it is true that the temperature region where fullerene or metallofullerene electric-arc synthesis takes place is not yet known, however, the new observations [43] supply some arguments to expect it around 1500 K. Very low excited electronic states can be present in some fullerenes like C{sub 80} [44] or even the C{sub 74} IPR cage [45] which makes the electronic partition function particularly significant at such high temperatures. Interestingly enough, there is a suggestion [25] that the electronic partition function, based on the singlet electronic states only, could actually produce more realistic results for fullerene relative concentrations in the fullerene soot. Incidentally, the electronic excitation energies can in some cases (like empty fullerenes) be evaluated by means of a simpler ZINDO method [46,47].

\[ \text{Fig. 1. B3LYP/3-21G~CEP-4G optimized structures of three Yb@C}_{74} \text{ isomers and B3LYP/3-21G~dz structure of the lowest Ba@C}_{74} \text{ species.} \]

3. RESULTS AND DISCUSSION

Let us first survey, for a more complete picture, the empty C{sub 74} cages (B3LYP/6-31G*~B3LYP/3-21G energetics, ZINDO electronic partition functions). The
relative populations computed according to eq. (1) show that the sole IPR cage \(D_{3h}\) is prevailing. Shinohara et al. [48] recently recorded electronic spectrum of \(C_{74}\) anion and concluded that the cage could have \(D_{3h}\) symmetry. Moreover, it was observed by Achiba et al. [3] that the only available IPR \(C_{74}\) cage is actually employed also in the \(Ca@C_{74}\) endohedral species. At a temperature of 1500 K, the \(1/C_{2v}\), \(4/C_1\), and \(103/C_1\) \(Ca@C_{74}\) isomeric populations are computed [19] in the FEM scheme as 88.4, 8.0, 3.5 %, respectively.

\[ \text{Yb@C}_{74} \] relative stability proportions differ from those previously computed [19] for \(Ca@C_{74}\). For example, at a temperature of 1500 K the \(1/C_{2v}\), \(4/C_1\), and \(103/C_1\) species when evaluated with the conventional RRHO treatment should form 99.5, 0.3, 0.2 % of the equilibrium isomeric mixture, respectively. With the more realistic FEM scheme, the relative concentration are changed to 97.8, 1.2 and 1.0 %. The proportions are in agreement with the observation of Reich et al. [5] in which just one \(Ba@C_{74}\) species was isolated, namely possessing the IPR carbon cage.

\[ \text{Yb@C}_{74} \] is actually a more interesting system as Xu et al. [10] isolated two isomers and even found their production ratio as 100:3. In the computations support the experimental finding [10] of two \(Yb@C_{74}\) isomers and point out that the major species should have the IPR cage while the minor one should contain one pentagon-pentagon junction in the carbon cage. A similar situation should be met with \(Ca@C_{74}\) but rather not with \(Ba@C_{74}\).

There is a more general stability problem [49-52] related to fullerenes and metallofullerenes, viz. the absolute stability of the species or the relative stabilities of clusters with different stoichiometries. We shall illustrate the issue just on the most stable (i.e., \(1/C_{2v}\)) structures of \(Ba@C_{74}\) and \(Yb@C_{74}\), thus ignoring the remaining five isomers in each set. Let us consider formation of a metallofulleren:

\[ X(g) + C_n(g) = X@C_n(g). \]  

(2)

Under equilibrium conditions, we shall deal with the encapsulation equilibrium constant \(K_{X@C_n,p}\):

\[ K_{X@C_n,p} = \frac{p_{X@C_n}}{p_X p_{C_n}}, \]  

(3)

expressed in the terms of partial pressures of the components. Temperature dependency of the encapsulation equilibrium constant \(K_{X@C_n,p}\) is described by the van’t Hoff equation:

\[ \frac{d\ln K_{X@C_n,p}}{dT} = \frac{\Delta H_{X@C_n}^\circ}{RT^2} \]  

(4)

where \(\Delta H_{X@C_n}^\circ\) stands for the (negative) standard change of enthalpy upon encapsulation. Let us further suppose that the metal pressure is close to the respective saturated pressure \(p_{X,sat}\). With this presumption, we shall deal with a special case of clustering under saturation conditions [53,54]. While the saturated pressures \(p_{X,sat}\) for various metals are known from observations [55,56], the partial pressure of \(C_n\) is less clear as it is obviously influenced by a larger set of processes (though, \(p_{C_n}\) should exhibit a temperature maximum and then vanish). Therefore, we avoid the latter pressure in our considerations at this stage. The
computed equilibrium constants $K_X@C_{n,p}$ show a temperature decrease as it must be the case with respect to the van’t Hoff equation (4) for the negative encapsulation enthalpy. However, if we consider the combined $p_{X,sat}K_X@C_{n,p}$ term:

$$p_{X,sat}K_X@C_{n,p} \sim p_{X,sat}K_{X@C_{n,p}}$$

that directly controls the partial pressures of various $X@C_{n}$ encapsulates in an endohedral series (based on one common $C_{n}$ fullerene), we get a different picture. The considered $p_{X,sat}K_X@C_{n,p}$ term typically increases with temperature which is the basic scenario of the metallofullerene formation in the electric-arc technique. An optimal production temperature could be evaluated in a more complex model that also includes temperature development of the empty fullerene partial pressure.

Table 1. The computed products of the encapsulation equilibrium constant $\Xi_X = K_X@C_{n,p}$ with the metal saturated-vapor pressure $\Psi_X = p_{X,sat}$ for $Ba@C_{74}$ and $Yb@C_{74}$ at a temperature $T = 1500$ K.

<table>
<thead>
<tr>
<th>Species</th>
<th>$K_X@C_{74,p}$ (atm$^{-1}$)</th>
<th>$p_{X,sat}$ (atm)</th>
<th>$\Psi_X\Xi_X$</th>
<th>$\Psi_{Ba,sat}\Xi_{Ba}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba@C_{74}</td>
<td>1332.6</td>
<td>0.0261</td>
<td>34.82</td>
<td>1.00</td>
</tr>
<tr>
<td>Yb@C_{74}</td>
<td>81.77</td>
<td>1.42</td>
<td>116.13</td>
<td>3.34</td>
</tr>
</tbody>
</table>

$^a$ Ba@C_{74}: the potential-energy change evaluated at the B3LYP/6-31G$^*$—dz level and the entropy part at the B3LYP/3-21G—dz level; Yb@C_{74}: the potential-energy change evaluated at the B3LYP/6-31G$^*$—SDD level and the entropy part at the B3LYP/3-21G—CEP-4G level. $^b$ The standard state - ideal gas phase at 101325 Pa pressure.

If we however want to evaluate production abundances for two metallofullerenes like Ba@C_{74} and Yb@C_{74}, just the product $p_{X,sat}K_X@C_{n,p}$ term can straightforwardly be used. Let us consider a temperature of 1500 K as the observations [43] suggest that fullerene synthesis should happen in the temperature region. The results in Table 1 show for 1500 K that the $p_{Ba,sat}K_{Ba@C_{74,p}}$ quotient is about three times smaller than the $p_{Yb,sat}K_{Yb@C_{74,p}}$ product term. The ratio is enabled by a higher saturated pressure of Yb compared to Ba though the equilibrium constants show the reversed order. The B3LYP/6-31G$^*$—dz potential-energy change upon Ba encapsulation into the IPR $C_{74}$ cage is $\Delta E = -59.5$ kcal/mol while the B3LYP/6-31G$^*$—SDD term for Yb encapsulation is computed at -55.9 kcal/mol. Although the energy terms are likely still not precise enough, their errors could be comparable and thus they should cancel out in the relative term $p_{Ba,sat}K_{Ba@C_{74,p}}/p_{Yb,sat}K_{Yb@C_{74,p}}$. Let us mention that the combined basis sets require in the Gaussian program specification through a GEN keyword and for the sake of consistency the GEN approach is to be used even with empty cages (for example, the GEN-consistent approach gives for the B3LYP/6-31G$^*$—dz La@C_{60} encapsulation energy [57] the value -54.7 kcal/mol). Let us also note that the FEM treatment is not used in a full extent with the product quotient $p_{X,sat}K_X@C_{74,p}$ evaluation as the three lowest vibrational frequencies are not removed in contrast to the isomeric treatment by eq. (1), and also the electronic partition functions were ignored in the quotient evaluations. Finally, this new stability criterion also suggests (as Yb@C_{74} should come in higher yields than Ba@C_{74}) that the conditions for the isolation of a minor isomer are more convenient in the Yb@C_{74} case (in addition to the computed higher fraction of the non-IPR species in the case of Yb encapsulation compared to Ba [58]).

Various endohedral cage compounds have been suggested as possible candidate species for molecular memories and other future nanotechnological applications. One approach is built on endohedral species with two possible location sites of the encapsulated atom [59], while another concept of quantum computing aims at a usage of the spin states of N@C_{60} [60], and still another would employ fullerene-based molecular transistors [61]. In the connection, low potential barriers for a three-dimensional rotational motion of encapsulates in the cages [14,16,40,62-64] or at least large amplitude oscillations [65,66] can be a significant factor. The low barriers are responsible for simplifications of the NMR patterns at room temperature. This simplification is made possible by a fast, isotropic endohedral motions inside the cages that yield a time-averaged, equalizing environment [59,60] on the NMR timescale. The internal motion can however be restricted by a cage derivatization [41,67] thus in principle allowing for a versatile control of the endohedral positions needed, for example, in molecular memory applications. In overall, a still deeper experimental and computational knowledge of various molecular aspects of the endohedral compounds is at present needed before tailoring of their nanoscience to future nanotechnology applications becomes possible.

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