Computational Screening of Metallofullerenes for Nanoscience: X@C_{74} Series (X = Ca, Sr, Ba)

Zdeněk Slanina,[*,**] Filip Uhlík[***] and Shigeru Nagase[*]

[*]Department of Theoretical Molecular Science, Institute for Molecular Science
Myodaiji, Okazaki 444-8585, Aichi, Japan
[**]Institute of Chemistry, Academia Sinica, Nankang, Taipei 11529, Taiwan-ROC
[***]School of Science, Charles University, 128 43 Prague 2, Czech Republic

ABSTRACT

The paper reports computations for Ca@C_{74}, Sr@C_{74} and Ba@C_{74} based on encapsulation into the IPR (isolated pentagon rule) C_{74} cage. Their production abundancies are estimated using the encapsulation Gibbs-energy terms and saturated metal pressures. The saturated pressures can substantially modulate the yields. The Gibbs-energy based evaluations of the production abundancies can be applied generally and thus, the method has a promising prediction potential for fullerene nanoscience.

Keywords: Endohedral fullerenes; carbon-based nanotechnology; molecular electronics; optimized syntheses; Gibbs-energy evaluations.

1 INTRODUCTION

Although empty C_{74} fullerene [1] is not yet available in solid form, several related endohedral species have been known like Ca@C_{74} [2,3], Sr@C_{74} [4], Ba@C_{74} [5], La@C_{74} [6-8], Eu@C_{74} [9], Yb@C_{74} [10], Sc_2@C_{74} [11] or Er_3@C_{74} [12]. In the Yb@C_{74} case, even two isomers were isolated [10] - as there is just one [13] C_{74} cage that obeys the isolated pentagon rule (IPR), namely of D_{3h} symmetry, a non-IPR structure is to be involved [14] (as it is the case with Ca@C_{72} [15] or La@C_{72} [16]). The C_{74} IPR cage was experimentally confirmed for Ca@C_{74} [3], Ba@C_{74} [5] and La@C_{74} [8].

The C_{74} metallofullerene family has also been of computational interest. First such computations were performed for Ca@C_{74} [2,17-19] and it was shown that the non-IPR encapsulations are not significant for Ca@C_{74} (in contrast to Ca@C_{72} [20,21]). The present paper deals with computational evaluations of the relative stabilities in the series Ca@C_{74}, Sr@C_{74} and Ba@C_{74}. In order to respect high temperatures in fullerene/metallofullerene syntheses, the Gibbs energies have been used in stability evaluations [22,23] rather than the mere potential energy terms. Moreover, also saturated metal pressures (extracted from observed data [24]) are newly taken into consideration with the stability evaluations.

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 while another concept of quantum computing aims at an exploitation of spin states of N@C_{60} or fullerene-based molecular transistors. At present, however, a still deeper knowledge of various molecular aspects of the endohedral compounds is needed before their tailoring to nanotechnology applications is possible.

2 COMPUTATIONS

The computations deal with encapsulation into the unique D_{3h} C_{74} IPR cage. The resulting metalofullerenes exhibit [25] C_{2v} symmetry (Fig. 1). The geometry optimizations were 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 the combined basis set of the 3-21G basis for C atoms and a dz basis set [28] with the effective core potential (ECP) for the metal atoms (denoted here by 3-21G∼dz). The B3LYP/3-21G∼dz geometry optimizations were carried out with the analytically constructed energy gradient as implemented in the Gaussian 03 program package [29]. 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 the empty cage.

In the optimized B3LYP/3-21G∼dz geometries, the harmonic vibrational analysis was carried out with the analytical force-constant matrix. In the same B3LYP/3-21G∼dz 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 level. The Gibbs energies were evaluated using the rotational-vibrational partition functions constructed [30] from the calculated structural and vibrational data using the rigid rotator and harmonic oscillator (RRHO) approximation. Although the temperature region where fullerene or metallofullerene electric-arc synthesis takes place is not yet known, the new observations [31] supply some arguments to expect it around or above 1500 K. Thus, the computations here are presented for two illustrative temperatures of 1500 and 2000 K.

3 RESULTS AND DISCUSSION

There is a general stability problem related to fullerenes and metallofullerenes - either the absolute stability of the species or the relative stabilities of clusters with different stoichiometries. One can consider an overall stoichiometry of a metallofullerene formation:

$$X(g) + C_n(g) = X@C_n(g). \quad (1)$$

[**] *The corresponding author e-mail: zdenek@ims.ac.jp*

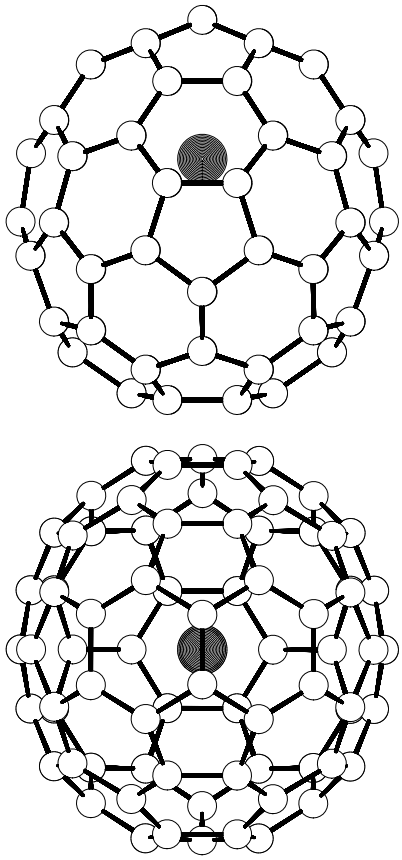

Fig. 1. B3LYP/3-21G∼dz optimized $Sr@C_{74}$ structure with the IPR cage.

The encapsulation process is thermodynamically characterized by the standard changes of, for example, enthalpy $\Delta H^o_{X@C_n}$ or the Gibbs energy $\Delta G^o_{X@C_n}$. Table 1 presents the computed encapsulation $\Delta H^o_{X@C_n}$ and $\Delta G^o_{X@C_n,T}$ terms for $Ca@C_{74}$, $Sr@C_{74}$, and $Ba@C_{74}$ computed for two illustrative temperatures. The potential-energy changes are computed at the B3LYP/6-31G*∼dz level and the entropy part at the B3LYP/3-21G∼dz level.

The equilibrium composition of the reaction mixture is controlled by the encapsulation equilibrium constants $K_{X@C_n,p}$:

$$K_{X@C_n,p} = \frac{p_{X@C_n}}{p_X p_{C_n}}, \tag{2}$$

expressed in the terms of partial pressures of the components. The encapsulation equilibrium constant is interrelated with the the standard encapsulation Gibbs energy change:

$$\Delta G^o_{X@C_n} = -RTlnK_{X@C_n,p}. \tag{3}$$

Temperature dependency of the encapsulation equilibrium constant $K_{X@C_n,p}$ is then described by the van't Hoff equation:

$$\frac{dlnK_{X@C_n,p}}{dT} = \frac{\Delta H^o_{X@C_n}}{RT^2} \tag{4}$$

where the $\Delta H^o_{X@C_n}$ term is typically negative so that the encapsulation equilibrium constants decrease with increasing temperature.

Let us further suppose that the metal pressure p_X is actually close to the respective saturated pressure $p_{X,sat}$. With this presumption, we shall deal with a special case of clustering under saturation conditions [32]. While the saturated pressures $p_{X,sat}$ for various metals are known from observations [24], 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. As already mentioned, the computed equilibrium constants $K_{X@C_n,p}$ have to show a temperature decrease with respect to the van't Hoff equation (4). However, if we consider the combined $p_{X,sat}K_{X@C_n,p}$ term:

$$p_{X@C_n} \sim p_{X,sat}K_{X@C_n,p} = \lambda_{X,n}, \tag{5}$$

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 can frequently (though not necessarily) be increasing with temperature so that a temperature enhancement of metallofullerene formation in the electric-arc technique is still possible. An optimal production temperature could be evaluated in a more complex model that also includes temperature development of the empty-fullerene partial pressure.

If we however want to evaluate production abundances in a series of metallofullerenes like $Ca@C_{74}$, $Sr@C_{74}$ and $Ba@C_{74}$, just the product $p_{X,sat}K_{X@C_{74},p}$ terms can straightforwardly be used. The results in Table 2 show several interesting features. While for $Ca@C_{74}$ the $p_{X,sat}K_{X@C_{74},p}$ quotient increases with temperature, it is about constant for $Sr@C_{74}$ for the considered temperatures, and it decreases with temperature for $Ba@C_{74}$. The behavior results from competition between the decreasing encapsulation equilibrium constants and increasing saturated metal pressures. As the encapsulation enthalpy $\Delta H^o_{X@C_n}$ has the most negative value for $Ba@C_{74}$ (Table 1), its encapsulation equilibrium constant has to exhibit the fastest temperature decrease that already cannot be overcompensated by the temperature increase of the saturated metal pressure so that the $p_{X,sat}K_{X@C_{74},p}$ quotient decreases with temperature in this case. In order to allow for cancellation of various factors introduced by the computational approximations involved, it is better to deal with the relative quotient $\frac{p_{X,sat}K_{X@C_{74},p}}{p_{Ba,sat}K_{Ba@C_{74},p}}$. Table 2 shows that the production yield of $Sr@C_{74}$ should be by two or three orders of magnitude smaller than that for $Ba@C_{74}$. For $Ca@C_{74}$ the production yield for the considered temperatures is computed to be between three and five orders of magnitude lower than for $Ba@C_{74}$. In principle, an endohedral with lower value of the encapsulation equilibrium constant can still be produced in larger yields if a convenient over-compensation by higher saturated metal pressure can take place. In this way, we can employ a parameter, saturated metal pressure, that has never been taken into consideration before, and with this we can distinguish three different types of temperature developments of the production yields.

Table 1. The encapsulation[a] enthalpy $\Delta H^o_{X@C_n,T}$ and Gibbs energy $\Delta G^o_{X@C_n,T}$ for Ca@C_{74}, Sr@C_{74}, and Ba@C_{74} computed[b] for illustrative temperatures T = 1500 and 2000 K

Endohedral	$\Delta H^o_{X@C_{74},T}$ (kcal/mol)	$\Delta G^o_{X@C_{74},T}$ (kcal/mol)
	T=1500K	
Ca@C_{74}	-22.37	13.98
Sr@C_{74}	-35.51	1.96
Ba@C_{74}	-58.10	-21.45
	T=2000K	
Ca@C_{74}	-21.84	26.01
Sr@C_{74}	-34.97	14.36
Ba@C_{74}	-57.59	-9.31

[a] The standard state - ideal gas phase at 101325 Pa pressure.
[a] The potential-energy change evaluated at the B3LYP/6-31G*~dz level and the entropy part at the B3LYP/3-21G~dz level.

Although the energy terms are likely still not precise enough, their errors could be comparable in the series and thus, they should cancel out in the relative term $\frac{p_{X,sat}K_{X@C_{74},p}}{p_{Ba,sat}K_{Ba@C_{74},p}}$. This should be the case of, for example, the basis set superposition error important for evaluation of the encapsulation potential-energy changes. A similar cancellation should also operate for the higher corrections to the RRHO partition functions, including motions of the encapsulate. Incidentally, the computed stability proportions do correlate with qualitative abundances known from observations. For Ba@C_{74} even microsrystals could be prepared [5] so that a diffraction study was possible, while for Sr@C_{74} at least various spectra could be recorded [4] in solution, and Ca@C_{74} was studied [3] only by NMR spectroscopy.

The encapsulation equilibrium constants themselves result from both the standard enthalpy and entropy changes connected with the encapsulation process. It can be argued [33] that the encapsulation enthalpy changes in a series (like Ca@C_{74}, Sr@C_{74}, Ba@C_{74}) should be related to the ionization potentials of the free metals (in the given series, just sum of the first and second ionization potential). The stabilization of metallofullerenes is mostly electrostatic [34]. This feature can be documented [35] using the topological concept of 'atoms in molecules' (AIM) [36,37] which shows that the metal-cage interactions form ionic, and not covalent, bonds. Then, for a series like Ca@C_{74}, Sr@C_{74}, Ba@C_{74} three formal steps can be considered: (i) double-ionization of the free metal, (ii) double charging of the empty cage, and (iii) placing the metal dication into the dianionic cage (the formal description [38] of Ca in metallofullerenes is known to be about Ca^{2+}). The (ii) energy is identical for all members of the series, and the (iii) terms should be similar as they are controlled by electrostatics. Hence, the free-metal ionization potentials represent a critical factor, their order

Table 2. The products $\lambda_{X,n}$ of the encapsulation equilibrium constant[a] $K_{X@C_n,p}$ with the metal saturated-vapor pressure[b] $p_{X,sat}$ for Ca@C_{74}, Sr@C_{74}, and Ba@C_{74} computed for illustrative temperatures T = 1500 and 2000 K

Endohedral	$K_{X@C_{74},p}$ (atm^{-1})	$p_{X,sat}$ (atm)	$\lambda_{X,74}$	$\frac{\lambda_{X,74}}{\lambda_{Ba,74}}$
		T=1500K		
Ca@C_{74}	0.00919	0.162	0.00149	4.3×10^{-5}
Sr@C_{74}	0.518	0.355	0.184	5.3×10^{-3}
Ba@C_{74}	1332.6	0.0261	34.82	1.00
		T=2000K		
Ca@C_{74}	0.00144	3.773	0.00542	9.9×10^{-4}
Sr@C_{74}	0.02694	6.124	0.1650	0.030
Ba@C_{74}	10.399	0.528	5.489	1.00

[a] See Table 1.
[b] Extracted from available observed data [24].

being [39] Ca > Sr > Ba (with a substantial separation between them). Even if the metal saturated pressures are included, the metallofullerene yields should follow the order Ca@C_{74} < Sr@C_{74} < Ba@C_{74} which is supported by the already mentioned fact that only for Ba@C_{74} microcrystals were prepared.

The saturation regime is a useful simplification - it is well defined, however, it is not necessarily always achieved. Under some experimental arrangements, under-saturated or perhaps super-saturated metal vapors are also possible. This reservation is applicable not only to the electric-arc treatment but even more likely to newly introduced ion-bombardment production technique [40,41]. Still, eqs. (2) and (5) remain valid, however, the metal pressure has to be described by the values actually relevant [42]. For some volatile metals their critical temperature could be overcome and the saturation region thus abandoned (though practically speaking, this could rarely come into consideration, some examples could be metals with low melting points like mercury and cesium - moreover, for some metals their critical temperatures are so high that they are not even well known). Still, the saturation regime can give a kind of upper-limit estimates of the production yields.

ACKNOWLEDGMENTS

The reported research has been supported by a Grant-in-aid for NAREGI Nanoscience Project, for Scientific Research on Priority Area (A), and for the Next Generation Super Computing Project, Nanoscience Program, MEXT, Japan, and by the Czech National Research Program 'Information Society' (Czech Acad. Sci. 1ET401110505).

REFERENCES

[1] M. D. Diener and J. M. Alford. Nature, 393, 668, 1998.

[2] T. S. M. Wan, H. W. Zhang, T. Nakane, Z. D. Xu, M. Inakuma, H. Shinohara, K. Kobayashi and S. Nagase, J. Am. Chem. Soc., 120, 6806, 1998.
[3] T. Kodama, R. Fujii, Y. Miyake, S. Suzuki, H. Nishikawa, I. Ikemoto, K. Kikuchi and Y. Achiba, Chem. Phys. Lett., 399, 94, 2004.
[4] O. Haufe, M. Hecht, A. Grupp, M. Mehring and M. Jansen, Z. Anorg. Allgem. Chem., 631, 126, 2005.
[5] A. Reich, M. Panthofer, H. Modrow, U. Wedig and M. Jansen, J. Am. Chem. Soc., 126, 14428, 2004.
[6] Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, J. M. Alford and R. E. Smalley, J. Phys. Chem., 95, 7564, 1991.
[7] K. Sueki, K. Akiyama, T. Yamauchi, W. Sato, K. Kikuchi, S. Suzuki, M. Katada, Y. Achiba, H. Nakahara, T. Akasaka and K. Tomura, Full. Sci. Technol., 5, 1435, 1997.
[8] H. Nikawa, T. Kikuchi, T. Wakahara, T. Nakahodo, T. Tsuchiya, G. M. A. Rahman, T. Akasaka, Y. Maeda, K. Yoza, E. Horn, K. Yamamoto, N. Mizorogi and S. Nagase, J. Am. Chem. Soc., 127, 9684, 2005.
[9] H. Matsuoka, N. Ozawa, T. Kodama, H. Nishikawa, I. Ikemoto, K. Kikuchi, K. Furukawa, K. Sato, D. Shiomi, T. Takui and T. Kato, J. Phys. Chem. B, 108, 13972, 2004.
[10] J. X. Xu, X. Lu, X. H. Zhou, X. R. He, Z. J. Shi and Z. N. Gu, Chem. Mater., 16, 2959, 2004.
[11] S. Stevenson, H. C. Dorn, P. Burbank, K. Harich, J. Haynes, C. H. Kiang, J. R. Salem, M. S. Devries, P. H. M. Vanloosdrecht, R. D. Johnson, C. S. Yannoni and D. S. Bethune, Anal. Chem., 66, 2675, 1994.
[12] N. Tagmatarchis, E. Aslanis, K. Prassides and H. Shinohara, Chem. Mater., 13, 2374, 2001.
[13] P. W. Fowler and D. E. Manolopoulos, "An Atlas of Fullerenes," Clarendon Press, Oxford, 1995.
[14] Z. Slanina, F. Uhlík and S. Nagase, J. Phys. Chem. A, 110, 12860, 2006.
[15] T. Ichikawa, T. Kodama, S. Suzuki, R. Fujii, H. Nishikawa, I. Ikemoto, K. Kikuchi and Y. Achiba, Chem. Lett., 33, 1008, 2004.
[16] T. Wakahara, H. Nikawa, T. Kikuchi, T. Nakahodo, G. M. A. Rahman, T. Tsuchiya, Y. Maeda, T. Akasaka, K. Yoza, E. Horn, K. Yamamoto, N. Mizorogi, Z. Slanina and S. Nagase, J. Am. Chem. Soc., 128, 14228, 2006.
[17] S. Nagase, K. Kobayashi and T. Akasaka, J. Mol. Struct. (Theochem), 462, 97, 1999.
[18] K. Kobayashi and S. Nagase, in "Endofullerenes - A New Family of Carbon Clusters," eds. T. Akasaka and S. Nagase, Kluwer Academic Publishers, Dordrecht, p. 99, 2002.
[19] Z. Slanina, K. Kobayashi and S. Nagase, Chem. Phys. 301 (2004) 153.
[20] K. Kobayashi, S. Nagase, M. Yoshida and E. Ōsawa, J. Am. Chem. Soc., 119, 12693, 1997.
[21] Z. Slanina, K. Kobayashi and S. Nagase, Chem. Phys. Lett., 372, 810, 2003.
[22] Z. Slanina, F. Uhlík, X. Zhao and E. Ōsawa, J. Chem. Phys., 113, 4933, 2000.
[23] Z. Slanina, K. Kobayashi and S. Nagase, Chem. Phys. Lett., 388, 74, 2004.
[24] C. B. Alcock, V. P. Itkin and M. K. Horrigan, Can. Metallurg. Quart., 23, 309, 1984.
[25] Z. Slanina and S. Nagase, Chem. Phys. Lett., 422, 133, 2006.
[26] A. D. Becke, J. Chem. Phys., 98, 5648, 1993.
[27] C. Lee, W. Yang and R. G. Parr, Phys. Rev. B, 37, 785, 1988.
[28] P. J. Hay and W. R. Wadt, J. Chem. Phys., 82, 299, 1985.
[29] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, "Gaussian 03, Revision C.01," Gaussian, Inc., Wallingford, CT, 2004.
[30] Z. Slanina, Int. Rev. Phys. Chem., 6, 251, 1987.
[31] R. J. Cross and M. Saunders, J. Am. Chem. Soc., 127, 3044, 2005.
[32] Z. Slanina, J. Cluster Sci., 15, 3, 2004.
[33] Z. Slanina, F. Uhlík, S.-L. Lee, L. Adamowicz and S. Nagase, J. Nanosci. Nanotech., 7, 1339, 2007.
[34] S. Nagase, K. Kobayashi and T. Akasaka, J. Mol. Struct. (Theochem), 398/399, 221, 1997.
[35] K. Kobayashi and S. Nagase, Chem. Phys. Lett., 302, 312, 1999.
[36] R. F. W. Bader, Chem. Rev., 91, 893, 1991.
[37] R. F. W. Bader, J. Phys. Chem. A, 102, 7314, 1998.
[38] Z. Slanina, K. Kobayashi and S. Nagase, J. Chem. Phys., 120, 3397, 2004.
[39] "CRC Handbook of Chemistry and Physics," 85th edition, ed. D. R. Lide, CRC Press, Boca Raton, 2004.
[40] A. Gromov, N. Krawez, A. Lassesson, D. I. Ostrovskii and E. E. B. Campbell, Curr. App. Phys., 2, 51, 2002.
[41] E. E. B. Campbell, "Fullerene Collision Reactions," Kluwer Academic Publishers, Dordrecht, 2003.
[42] Z. Slanina, X. Zhao, N. Kurita, H. Gotoh, F. Uhlík, J. M. Rudziński, K. H. Lee and L. Adamowicz, J. Mol. Graphics Mod., 19, 216, 2001.