Computing Isomeric Higher and Smaller Fullerenes: Materials Controlled by a Profound Enthalpy/Entropy Interplay

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ABSTRACT

Early results from the eighties for small carbon clusters like C_4 or C_6 have suggested that the combined quantum-chemical and statistical-mechanical computations could show some interesting temperature effects also for isomeric fullerenes. This feature was first demonstrated on some C_{50} isomers. The fullerene research has indeed supplied several sets of isomeric higher fullerenes. At present over twenty stable fullerenes C_n have been identified with n varying from 60 to 96. Several such mixtures of fullerene isomers have been computed (C_{76} till C_{94}) and an agreement with observations found. Hence, the computations have demonstrated that the presumption of partial, inter-isomeric thermodynamic equilibrium is actually well working. One of the biggest systems computed within the partial thermodynamic-equilibrium treatment so far is C_{92} with 86 IPR isomers. The reported computations are based on semiempirical (SAM1), *ab initio* SCF (HF/4-31G), and DFT (B3LYP/6-31G*) approaches and RRHO partition functions. The entropy considerations also indicate an interesting way for non-IPR structures stabilization, illustrated on the C_{72} system. The approach is also applied to smaller fullerenes like C_{36}. As fullerenes are formed at high temperatures, entropy effects should be important owing to the temperature enhancement. It turns out for C_{36} that in the most sophisticated computational approximation used, B3LYP/6-31G*, just two structures are controlling the region of higher temperatures: the conventional fullerenes D_{6h} and D_{2d}. Although the D_{2d} ground state has to prevail at low temperatures, the stability order is reversed by entropy effects already at a temperature of 1500 K. The case of non-isomeric species is also discussed. Fullerenes and nanotubes have been considered as new agents and materials for molecular electronics including molecular memories. Optimized preparation and understanding of the material properties is not possible without this new type of enthalpy/entropy evaluations.

INTRODUCTION

Higher fullerenes have vigorously been studied - at present over thirty higher fullerenes C_n with n from 76 till 94 have been identified [1-4] especially by means of ^{13}C NMR in solution. Elucidation of their structures has widely been based on the isolated-pentagon-rule (IPR) concept [5]. The lowest IPR stoichiometry which allows for a structural isomerism is $n = 76$, though the case is Jahn-Teller controlled [6]. Otherwise, a coexistence of two or more isomers is a rather typical feature of higher fullerenes and several mixtures of fullerene isomers have been computed: C_{78} (e.g. [7]), C_{80} (e.g. [8]), C_{82} (e.g. [9]), C_{84} (e.g. [10]), C_{86} (e.g. [11]), C_{88} (e.g. [12]), C_{90} (e.g. [13]) and some preliminary results are available for even higher members [14]. The thermodynamic computations have clearly shown that temperature effects are truly essential for understanding higher fullerenes. The inter-isomeric separation energies are important as a starting point, nevertheless, they alone cannot predict the isomeric relative stabilities.

Several pertinent aspects of the combined quantum-chemical and statistical-mechanical treatment are illustrated on the complete sets of the IPR C_{88} and C_{90} isomers. The treatment is also applied to C_{36} fullerenes and *quasi*-fullerenes. Finally, IPR and non-IPR structures are treated simultaneously for C_{72}.

COMPUTATIONS

The treatment starts from geometry optimizations, typically with some semiempirical method like [15] SAM1, or still more common AM1 and PM3 methods [16,17]. The computations were carried out primarily with the AMPAC program package [18] and also with the MOPAC program [19]. The geometry optimizations are performed with no symmetry constraints in Cartesian coordinates and with analytically constructed potential-energy gradient. In the optimized geometries, the harmonic vibrational analysis is carried out by a numerical differentiation of the analytical potential-energy gradient.

The semiempirical isomeric separation energies should be checked through some *ab initio* calculations. We have used the G94 program package [20] for the purpose. First, the Hartree-Fock (HF) SCF computation was performed with the standard 4-31G basis in the fixed optimized SAM1 geometries, HF/4-31G//SAM1. At the HF/4-31G computational level the stability of the SCF solution was checked (i.e., if it is really a local minimum in wavefunction space). After this step, density-functional computations at the B3LYP/6-31G* level followed, using the HF/4-31G SCF solution as the starting guess, again in the fixed optimized SAM1 geometries, i.e., the B3LYP/6-31G*//SAM1 approach.

Rotational-vibrational partition functions were constructed from the SAM1 calculated structural and vibrational data (though, only of the rigid rotator and harmonic oscillator quality, and with no frequency scaling). Relative concentrations (mole fractions) w_i of m isomers can be expressed through the partition functions q_i and the ground-state energy $\Delta H_{0,i}^o$ by a master formula [21]:

$$w_i = \frac{q_i exp[-\Delta H_{0,i}^o/(RT)]}{\sum_{j=1}^m q_j exp[-\Delta H_{0,j}^o/(RT)]}, \qquad (1)$$

where R is the gas constant and T the absolute temperature. The semiempirical heats of formation at room temperature $\Delta H_{f,298}^o$ have to be converted to the heats of formation at the absolute zero temperature $\Delta H_{f,0}^o$.

The geometrical symmetries of the optimized cages are determined by a flexible procedure [8]. Chirality contributions are considered accordingly with Eq. (1), too.

ISOMERIC FULLERENES

The thirty five IPR isomers of C_{88} are labeled by a conventional numbering system suggested in [5]. The original topological symmetries can sometimes be lowered - it happens at any quantum-chemical level of geometry optimizations. The SAM1 computed symmetry actually in five cases falls below the topological expectation [5]. However, out of the five cases, only for isomer **34** we face a Jahn-Teller distortion (namely from T to D_2). The isomer labeled by **17** (C_s symmetry) is the ground state of the C_{88} IPR set. The species richest in energy is located about 300 kJ/mol above the system ground state.

The system is to be analyzed using the temperature evolution of the relative concentrations, w_i - Eq. (1), for the full, thirty-five-membered mixture under the conditions of the inter-isomeric thermodynamic equilibrium (evaluated with the HF/4-31G//SAM1 energetics). At very low temperatures the ground-state structure has to be prevailing. The species second lowest in energy, **7** with a C_2 symmetry, exhibits a fast relative-stability increase with a maximum share of about 30% at a temperature of 1270 K. The third lowest species, **33** with a C_2 symmetry, also exhibits a temperature profile with a maximum, though rather modest. There is however a structure with a steady increase which eventually becomes dominant at very high temperatures - **20** with a C_1 symmetry (actually reduced down from a C_2 topological expectation [5]).

^{13}C NMR spectrum of C_{88} in solution had originally been interpreted by Achiba *et al.* [1-4] as consistent with an isomer of C_2 symmetry as a major structure. However, a more recent interpretation [4] allows for more structures and the finding is actually in a better agreement with the computations. Although our thermodynamic computations give a different picture for moderate and high temperatures, we can speak in both regions on a symmetry triad: C_s, C_2, C_2. This interesting conclusion is linked to the fact that the isomer labeled **20** exhibits a C_2 topological symmetry which is reduced to C_1 in the quantum-chemical optimization. Such symmetry reductions are connected with rather small coordinate distortions [8].

Recently, Zettl *et al.* [22] isolated a new solid fullerene, C_{36}, and from its solid-state ^{13}C NMR concluded a D_{6h} cage structure. The system has also been computed at several levels of theory [23]. The original topological search [24] was limited to conventional fullerenes and to *quasi*-fullerenes with one or two squares (no heptagon), one heptagon (no square), or one square and one heptagon - there are 598 such cages. It turns out, however, that no more than twelve structures lowest in energy can play some significant role. Among the twelve selected low-energy cages, seven are the conventional fullerenes. There are however a few cases of significant differences between the SAM1 and B3LYP/6-31G* methods in the set.

There is one high symmetry species, a conventional D_{6h} fullerene [5] in the selected twelve-membered isomeric set. In fact, the D_{6h} point group is a topological symmetry, however, our more flexible symmetry diagnostic tool [8] gives only a C_{6v} symmetry. A closer inspection suggests that we are actually dealing with a Jahn-Teller distortion owing to the degenerate frontier orbitals. Although the symmetry distortion is rather small, it can be further relaxed at the B3LYP/6-31G* level.

In the best computational approximation applied, B3LYP/6-31G*, just two structures are controlling the region of higher temperatures, the conventional fullerenes D_{6h} and D_{2d}. Although the D_{2d} ground state has to prevail at low temperatures, the stability order is reversed soon. In overall, the B3LYP/6-31G* treatment gives the best agreement with the experiment [22].

Let us now move to C_{72}, a not yet isolated fullerene. For this system, there is just one IPR cage [5] exhibiting a high symmetry, D_{6d}. In fact, it was already reported [25] for Ca@C_{72} that the IPR rule indeed did not work for the species. Even if we consider [26] the pristine C_{72}, with no metals inside, we can get some significant non-IPR structures, in particular a C_2 isomer with one pentagon-pentagon junction. In the context of this work we are however really interested not in potential energies but in the Gibbs functions. The SAM1 computations of the temperature evolution of the isomeric relative stabilities for the C_{72} IPR/non-IPR set are already available. The IPR D_{6d} structure, in spite of being the system ground state, decreases its relative population pretty fast. At higher temperatures the equilibrium isomeric mixture is in fact governed by the non-IPR C_2 isomer with one pentagon-pentagon junction.

This result is a further indication that non-IPR structures cannot always be ignored. With this result in mind, computations should check the temperature effects on relative stabilities of selected non-IPR isomers in the whole series C_{76} - C_{94}.

Let us close this section with the C_{90} system as still another isomeric set to which the combined quantum-chemical and statistical-mechanical treatment can be applied. The computed energetics is pretty much similar at the SAM1 and HF/4-31G levels of theory. The temperature evolution of the five most significant C_{90} species is available [13] for the SAM1 computed energetics. A structure of C_2 symmetry, labeled **45** according to [5], is the system ground state. Achiba *et al.* [1] reported altogether five C_{90} species in ^{13}C NMR spectra. They treated [1] three HPLC fractions - one C_{2v}, three C_2, and one C_1; their C_{2v} species exhibits 25 lines, 5 of them weaker (a further development in the interpretation is however possible [4]). The SAM1 computations indeed indicate that there are just five structures which exhibit a significant population in a high-temperature region: C_2 **45**, C_{2v} **46**, C_s **35**, C_2 **18**, and C_1 **9**. Again, at very low temperatures the ground-state structure must be the dominant species, though it exhibits a fast stability decrease. Its equimolarity with the **18** structure is reached at a temperature of 2012 K. Two other structures, **35** and **46**, show moderate maxima close to 1500 K. The last structure, **9**, becomes quite important at very high temperatures.

One may expect that the temperatures relevant for fullerene synthesis are somewhere beyond 800 K. Our computations predict that at elevated temperatures we primarily deal with five C_{90} structures: C_2, C_2, C_s, C_{2v}, and C_1. Hence, we have only three direct coincidences with the experiment [1] as the computed C_{2v} structure has a different NMR pattern (24 lines, 3 of them weaker). The other structure considered only in

the computation is a C_s species with 46 lines (2 of them weaker). If we now combine together the NMR patterns of the two structures predicted by theory, C_{2v} and C_s, we get 70 lines (5 of them weaker). In the considered experiment [1] one fraction also gave exactly 70 lines, five of them weaker, and it was interpreted as mixture of a C_2 symmetry and C_{2v} structure with 25 lines (5 of them weaker). Hence, the experimental finding could be interpreted in two different ways, but only one of them is consistent with the quantum-chemical computations.

The reported considerable thermal effects on various isomeric fullerene sets result from a complex interplay between rotational, vibrational, potential-energy terms, and chirality factors. The whole scheme however deals with the inter-isomeric thermodynamic equilibrium. It is still difficult to check the presumption under the real experimental conditions. Anyhow, the thermodynamic-equilibrium treatment already produced a reasonable theory-experiment agreement in eight isomeric systems (C_{76}, C_{78}, C_{80}, C_{82}, C_{84}, C_{86}, C_{88}, and C_{90}). This relatively strong evidence clearly supports our belief in a good applicability of the combined quantum-chemical and statistical-mechanical treatment. The general technique should represent a key tool in further search of particularly stable higher fullerenes as agents for applications in materials science and nanotechnology.

NON-ISOMERIC FULLERENES

We have been computing equilibrium compositions of isomeric fullerene mixtures and the computations have agreed well with the available experiments. This finding can suggest that the inter-isomeric thermodynamic equilibrium does exist in experiment. There may also be other interpretation, viz. that although the inter-isomeric equilibrium is not yet reached, the relative non-equilibrium and equilibrium isomeric concentrations do not differ significantly. The computational treatment of isomeric mixtures has several interesting features: The results depend on temperature but not on pressure, only the relative and not the absolute values of the heats of formation are needed, the form of the master equation allows for an ample cancellation of terms in the partition functions (in particular, the cluster mass is canceled out exactly).

There is a subsequent, more general task - relative stabilities of fullerenes of different dimensions, i.e., of non-isomeric fullerenes [27-30]. In its most general form, the problem can be treated as a complex kinetic scheme described by a huge number of kinetic differential equations. The scheme can be solved if the values of the rate constants for all reaction channels are known. The equilibrium composition comes as the limiting case of infinite time. If we treat the problem from thermodynamic point of view, we should realize that the conventional standard pressure of 1 atm is considerably different from actual fullerene-synthesis conditions. Apparently, we should expect considerably lower cluster pressures in the carbon-arc synthesis. The actual entropy and Gibbs free energy change considerably with pressure as can be demonstrated on the C_{60} and C_{70} cases based on quantum chemical methods. For example, the equilibrium constant $K_{60/70}$ for an interconversion between the two clusters, expressed in partial pressures p, offers a deeper insight into the problem:

$$K_{60/70} = \frac{p_{70}^{6/7}}{p_{60}} = \frac{(1 - x_{60})^{6/7}}{x_{60}} P^{-1/7}, \qquad (2)$$

(where P stands for the total pressure of the two clusters and x_{60} is the mole fraction of buckminsterfullerene). At 1 atm, C_{70} is more populated than C_{60}, but at the conditions of a saturated carbon vapor (simulated simply as a mixture of seven cluster at present) the stability order is reversed in favor of C_{60} so that agreement with experiment is obtained. The pressure effects are studied based on the MNDO, AM1, PM3, SAM1 methods or using the available experimental data. The results point out a need for a reliable evaluation of the absolute values of the heats of formation and other input information before the pressure-dependent scheme can be applied to other higher fullerenes.

One should consider all the clusters C_n, i.e., all the values for n, and for each n value all the isomers. At present we have been considering just seven clusters: n = 1, 2, 3, 4, 5, 60, and 70. Clearly enough, expansion to any larger set of cluster is just a technical, not a conceptual problem. Let us suppose that the thermodynamic equilibrium between the carbon gas phase and graphite is established, i.e, the partial chemical equilibria:

$$nC(s) = C_n(g) \qquad (3)$$

satisfy the related equilibrium constants:

$$K_{p,n} = p_n \qquad (4)$$

where p_n denotes the partial pressure of C_n (it is actually expressed in atm; 1 atm = 101325 Pa). If all the partial equilibria (2) are satisfied, we reach the state of the saturated carbon vapor with a unique total saturated pressure p^* (for a given temperature T). In our model truncated se of carbon aggregates it means:

$$p^* = p_1 + p_2 + p_3 + p_4 + p_5 + p_{60} + p_{70}. \qquad (5)$$

There is also an alternative, and more general formulation of the problem. The alternative formulation is related to the mono-atomic carbon cluster $C_n(g)$:

$$nC(g) = C_n(g) \qquad (6)$$

and is described by a set of equilibrium constants $K'_{p,n}$:

$$K'_{p,n} = \frac{p_n}{p_1^n}. \qquad (7)$$

The equilibrium constants $K'_{p,n}$ are related to the starting equilibrium constants $K_{p,n}$ by:

$$K'_{p,n} = \frac{K_{p,n}}{K_{p,1}^n}. \qquad (8)$$

Now, we can consider any total pressure p, not just the saturated p^* but also any under-saturated or super-saturated pressure. However, it remains true that:

$$p = p_1 + p_2 + p_3 + p_4 + p_5 + p_{60} + p_{70}. \qquad (9)$$

In order to simplify the scheme, we can introduce a variable x_1 with a meaning of the mole fraction of the monoatomic cluster $C_n(g)$. This substitution converts Eq. (9) into the following algebraic equation of the 70th order:

$$1 = x_1 + \sum_{i=2}^{70} K'_{p,i} x_1^i p^{i-1} \; , \quad (i = 2-5, 60, 70). \quad (10)$$

We can solve Eq. (10) for a selected temperature T and pressure p numerically with any required precision. Once the term x_1 is known, other mole fractions are simply given:

$$x_n = K'_{p,n} x_1^n p^{n-1}. \quad (11)$$

The equilibrium constants $K'_{p,n}$ can be derived from quantum-chemical and statistical mechanical calculations, the constant $K_{p,1}$ comes from experiment.

The scheme is pressure dependent - the pressure does not reflect the He pressure but the carbon-vapor pressure itself (never measured, after all it is always covered by the He pressure). At very low pressures around the saturated carbon-vapor pressure the scheme gives the correct order of the populations of C_{60} and C_{70}. If we increase the pressure to very high, unrealistic values like 1 atm, we can reverse the order. The scheme is quite sensitive to the heats of formation. Thus, before the scheme itself is applied in a large scale, we have to be able to produce accurate values of the total heats of formation (i.e., not only the relative energetics like for the isomeric problem). Heats of formation cannot be, at present, well produced by most of our theoretical tools. At the semiempirical levels they are considerably overestimated. In *ab initio* treatments some adjustment to the observed values is necessary as the top levels, like G2, cannot be performed at present. Hence, further research activities are needed before we can fully explore the thermodynamic treatment of the stabilities of fullerenes with different dimensions.

ACKNOWLEDGMENTS

REFERENCES

1. Y. Achiba, K. Kikuchi, Y. Aihara, T. Wakabayashi, Y. Miyake, and M. Kainosho, in Science and Technology of Fullerene Materials, Eds. P. Bernier, D. S. Bethune, L. Y. Chiang, T. W. Ebbesen, R. M. Metzger, J. W. Mintmire, Materials Research Society, Pittsburgh, 1995, p. 3.
2. Y. Achiba, K. Kikuchi, Y. Aihara, T. Wakabayashi, Y. Miyake, and M. Kainosho, in The Chemical Physics of Fullerenes 10 (and 5) Years Later, Ed. W. Andreoni, Kluwer Academic Publishers, Dordrecht, 1996, p. 139.
3. R. Mitsumoto, H. Oji, Y. Yamamoto, K. Asato, Y. Ouchi, H. Shinohara, K. Seki, K. Umishita, S. Hino, S. Nagase, K. Kikuchi, and Y. Achiba, *J. Phys. IV*, **7**, C2-525 (1997).
4. Y. Achiba, Y. Miyake, H. Ishiwatari, M. Kainosho, and K. Kikuchi, in MRS Boston 1998 Fall Meeting, MRS, Pittsburgh, 1998, Abstract S2.2.
5. P. W. Fowler, and D. E. Manolopoulos, An Atlas of Fullerenes, Clarendon Press, Oxford, 1995.
6. Z. Slanina, S.-L. Lee, and C.-H. Yu, *Rev. Comput. Chem.*, **8**, 1 (1996).
7. Z. Slanina, J.-P. François, D. Bakowies, and W. Thiel, *J. Mol. Struct. (Theochem)*, **279**, 213 (1993).
8. M.-L. Sun, Z. Slanina, S.-L. Lee, F. Uhlík, and L. Adamowicz, *Chem. Phys. Lett.*, **246**, 66 (1995).
9. Z. Slanina, S.-L. Lee, K. Kobayashi, and S. Nagase, *Theochem*, **339**, 89 (1995).
10. Z. Slanina, J.-P. François, M. Kolb, D. Bakowies, and W. Thiel, *Fullerene Sci. Technol.*, **1**, 221 (1993).
11. Z. Slanina, S.-L. Lee, M. Yoshida, and E. Ōsawa, *Chem. Phys.*, **209**, 13 (1996).
12. Z. Slanina, S.-L. Lee, M. Yoshida, and E. Ōsawa, in Physics and Chemistry of Fullerenes and Their Derivatives, Eds. H. Kuzmany, J. Fink, M. Mehring, S. Roth, World Sci. Publ., Singapore, 1996, p. 389.
13. Z. Slanina, X. Zhao, S.-L. Lee, and E. Ōsawa, *Chem. Phys.*, **219**, 193 (1997).
14. Z. Slanina, X. Zhao, and E. Ōsawa, *Advan. Strain. Inter. Org. Mol.*, **7**, 185 (1999).
15. M. J. S. Dewar, C. Jie, and J. Yu, *Tetrahedron*, **49**, 5003 (1993).
16. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
17. J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209 (1989).
18. AMPAC 6.0, Semichem, Shavnee, KS, 1997.
19. J. J. P. Stewart, MOPAC 5.0, QCPE 455, Indiana University, 1990.
20. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian 94, Gaussian, Inc., Pittsburgh, PA, 1995.
21. Z. Slanina, *Int. Rev. Phys. Chem.*, **6**, 251 (1987).
22. C. Piskoti, J. Yarger, and A. Zettl, *Nature*, **393**, 771 (1998).
23. Z. Slanina, X. Zhao, and E. Ōsawa, *Chem. Phys. Let.*, **290**, 311 (1998).
24. E. Ōsawa, H. Ueno, M. Yoshida, Z. Slanina, X. Zhao, M. Nishiyama, and H. Saito, *J. Chem. Soc., Perkin Trans. 2*, 943 (1998).
25. K. Kobayashi, S. Nagase, M. Yoshida, and E. Ōsawa, *J. Am. Chem. Soc.*, **119**, 12693 (1997).
26. Z. Slanina, X. Zhao, and E. Ōsawa, in Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials, Vol. 6, Eds. K. Kadish and R. S. Ruoff, The Electrochemical Society, Pennington, 1998, p. 19.
27. J. M. Rudziński, Z. Slanina, M. Togasi, E. Ōsawa, and T. Iizuka, *Thermochim. Acta*, **125**, 155 (1988).
28. Z. Slanina, J. M. Rudziński, and E. Ōsawa, *Carbon*, **25**, 747 (1987).
29. Z. Slanina, J. M. Rudziński, and E. Ōsawa, *Collect. Czech. Chem. Commun.*, **52**, 2381 (1987).
30. Z. Slanina, J. M. Rudziński, M. Togasi, and E. Ōsawa, *Thermochim. Acta*, **140**, 87 (1989).