J. Phys. Chem. A **2002,** *106,* 11371−11374

Many Reactive Fullerenes Tend To Form Stable Metallofullerenes

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Received: June 11, 2002; In Final Form: September 3, 2002

It was found that very many isolable or extractable metallofullerenes employ kinetically unstable isomers of C_{78}, C_{80}, and C_{82} as carbon cages. These fullerene isomers are supposed to be stabilized by accepting one or more electrons from the encapsulated metal atoms. It seems that nature prefers to generate metallofullerenes with chemically reactive fullerene isomers. Some kinetically stable isomers of C_{84} likewise form isolable metallofullerenes. All stability considerations were made using a bond resonance energy (BRE) model.

Introduction

The isolability of metallofullerenes cannot be predicted from that of the empty fullerene molecules. For example, the trimetallic nitride template process with Sc_2O_3-doped graphite rods generates $Sc_3N@C_{80}$, $Sc_3N@C_{68}$, and $Sc_3N@C_{78}$, the carbon cages which are different from the isolable isomers of the corresponding hollow fullerenes.[1−3] It should be noted that these carbon cages are produced only when they are negatively charged by the encapsulated species. If an Sc_3N moiety is not encapsulated in these cages, they must possibly be very reactive in arc-discharge conditions. It is very interesting to see that empty fullerene isomers isolated so far are often different from the carbon cages found in isolable metallofullerenes.[4]

Theoretical calculations indicate that the thermodynamic stability of a fullerene molecule depends strongly upon the negative charge that resides on it.[5] Even though low-energy fullerene isomers are chosen successfully, one cannot always say that they are kinetically stable. Here, kinetic stability means stability against any chemical reaction or decomposition.[6,7] We have been studying the kinetic stability of fullerenes and metallofullerenes using a bond resonance energy (BRE) model.[8−13] Isolable fullerenes and metallofullerenes were then found to be devoid of reactive CC bonds with large negative BREs. In this paper, we show explicitly that kinetically unstable fullerenes tend to form kinetically stable metallofullerenes. Fortunately, molecular structures of many metallofullerenes are now available.[4]

Theory

The BRE, defined in Hückel theory, represents the contribution of a given π bond to the topological resonance energy (TRE) of the molecule.[7−9] Full definition of BRE is given in ref 8. The minimum BRE (min BRE) signifies the smallest BRE in the molecule. If the min BRE of a given molecule or its molecular ion has a large negative value, it will be kinetically very unstable with chemically reactive sites. We have presumed that if the min BRE is smaller than $-0.100\ |\beta|$, the molecule or the molecular ion will be kinetically very unstable or chemically reactive in arc-discharge conditions.[8−13] Most fullerene isomers that violate the isolated pentagon rule (IPR) have a min BRE $< -0.100\ |\beta|$.[8−10,13] However, the converse is not generally true. The kinetic stability of metallofullerenes can be reasonably predicted from the min BRE for the fullerene cage.[12,13]

Results and Discussion

There are 51 isolated-pentagon isomers in all for fullerenes with 60−84 carbon atoms.[14] Fifteen of them (29%) are likely to be chemically reactive with a min BRE $< -0.100\ |\beta|$.[11,12] The min BREs for these fullerene isomers and their molecular anions are listed in Table 1. Min BREs $< -0.100\ |\beta|$ are therein printed in bold. Isomers of fullerenes and metallofullerenes are denoted by Arabic and Roman numerals, respectively. The numbering system employed for fullerene isomers are the one proposed by Fowler and Manolopoulos.[14] For the min BREs for other fullerene isomers, see ref 12.

Among 51 isolated-pentagon fullerene isomers with up to 84 carbon atoms, C_{76}(**2**), C_{80}(**6**), C_{80}(**7**), and C_{82}(**7**) have no HOMO−LUMO energy gaps. All these isomers have min BREs $< -0.100\ |\beta|$. Therefore, they must be extremely reactive in the neutral electronic state. We examine below the min BREs for charged carbon cages in individual isolable metallofullerenes.

Metallofullerene with C_{78}. This fullerene has five isolated-pentagon fullerene isomers.[14] We previously pointed out that fullerenes with 6*n* carbon atoms, such as C_{78} ($n = 13$), have many kinetically stable isomers with large highest occupied molecular orbital−lowest unoccupied molecular orbital (HOMO−LUMO) energy separations.[15,16] Here, *n* is a positive integer larger than 12. Isomers **1**−**3** have been isolated from the fullerene soot.[17,18] Recently the fourth isomer was isolated and identified as C_{78}(**4**).[19] Only one of the five isomers, C_{78}(**5**), has a min BRE $< -0.100\ |\beta|$ and is presumed to be chemically very reactive.

$Sc_3N@C_{78}$ employs C_{78}(**5**) as the carbon cage.[1] This metallofullerene can be described formally as $(Sc_3N)^{6+}C_{78}{}^{6-}$. The C_{78}(**5**) hexaanion has a min BRE of as much as 0.162 $|\beta|$, which indicates that all CC bonds contribute much to the TRE. It is impressive that the reactive carbon cage acquires large kinetic stability by accepting six electrons from the encapsulated species. This must be why C_{78}(**5**) can accommodate a highly charged cation. $Sc_3N@C_{78}$ is the only metallofullerene with a C_{78} cage that has been isolated in a significant quantity.[1]

Metallofullerenes with C_{80}. This fullerene has seven isolated-pentagon isomers.[14] Isomers **1** and **2** have so far been isolated from the fullerene soot.[20,21] Since C_{80} consists of $6n + 2$ carbon atoms ($n = 13$), it has many kinetically unstable isomers.[16]

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10.1021/jp021390+ CCC: $22.00

TABLE 1: Min BREs for 15 Kinetically Unstable Fullerene Isomers and Their Molecular Anions

	min BRE/$|\beta|$						
isomer	neutral	anion	dianion	trianion	teraanion	pentaanion	hexaanion
C_{76}(**2**,T_d)	**−0.109**	**−0.109**	**−0.109**	0.007	0.123	0.094	0.053
C_{78}(**5**,D_{3h})	**−0.147**	−0.050	0.027	0.004	−0.050	0.057	0.162
C_{80}(**3**,C_{2v})	**−0.153**	−0.006	0.073	0.074	0.053	0.023	−0.029
C_{80}(**5**,C_{2v})	**−0.119**	−0.049	−0.043	0.065	0.086	0.057	0.018
C_{80}(**6**,D_{5h})	**−0.125**	−0.063	−0.063	−0.066	−0.070	0.066	0.165
C_{80}(**7**,I_h)	**−0.148**	**−0.148**	**−0.148**	**−0.148**	**−0.148**	0.025	0.193
C_{82}(**5**,C_2)	**−0.117**	−0.001	0.035	0.018	−0.027	0.046	0.094
C_{82}(**6**,C_s)	**−0.162**	−0.059	−0.065	0.048	0.079	0.049	−0.001
C_{82}(**7**,C_{3v})	**−0.241**	−0.044	0.077	0.065	0.030	−0.003	−0.065
C_{82}(**8**,C_{3v})	**−0.188**	**−0.116**	**−0.107**	0.028	0.081	0.007	−0.085
C_{82}(**9**,C_{2v})	**−0.227**	−0.087	0.015	0.020	0.015	0.087	0.098
C_{84}(**3**,C_s)	**−0.161**	−0.023	0.032	0.056	0.027	0.069	0.038
C_{84}(**9**,C_2)	**−0.156**	−0.008	0.058	0.075	0.052	0.026	−0.002
C_{84}(**13**,C_2)	**−0.147**	−0.005	0.054	0.032	−0.008	0.051	0.091
C_{84}(**17**,C_{2v})	**−0.108**	0.026	0.079	0.023	−0.051	−0.063	−0.074

Isomers **3**, **5**, **6**, and **7** are presumed to be kinetically unstable with a min BRE $< -0.100\ |\beta|$.

$La_2@C_{80}$(**7**) is generated abundantly.[22,23] This endohedral complex is formally represented as $(La^{3+})_2C_{80}$.[6−23,24] According to theoretical calculations,[23,24] C_{80}(**7**) is the highest-energy isomer of C_{80}, but forms the lowest-energy isomer of $La_2@C_{80}$. Thus, complexation markedly changes the relative energies of C_{80} isomers.[5] $Ce_2@C_{80}$ is likewise predicted to consist of the C_{80}(**7**) hexaanion and two Ce^{3+} ions.[26] Although Ce can take an oxidation number of 4, it is unlikely that two Ce^{4+} ions are encapsulated in the C_{80}(**7**) octaanion. This octaanion has an open-shell electronic configuration with a min BRE of -0.117 $|\beta|$.

The HOMOs in C_{80}(**7**) are quadruply degenerate with only two electrons. Therefore, this isomer needs six more electrons to close the electronic shells. C_{80}(**7**) becomes the lowest-energy isomer when it is in the -4 or -6 charge state.[5] The C_{80}(**7**) hexaanion has a min BRE of 0.193 $|\beta|$. However, the tetraanion is not suited for metallofullerenes since it has a large negative min BRE of -0.148 $|\beta|$ with an open-shell electronic configuration. The min BRE for C_{80}(**7**) hexaanion is the largest one among the IPR fullerene isomers with up to 84 carbon atoms. Next come hexaanions of C_{80}(**6**) and C_{78}(**5**), both with a min BRE $> 0.160\ |\beta|$. As has been seen,[2] the C_{78}(**5**) hexaanion is isolable in the form of $Sc_3N@C_{78}$.

Isolated $Sc_3N@C_{80}$ also employs C_{80}(**7**) as a carbon cage.[1,27] The Sc_3N unit donates six electrons to the C_{80}(**7**) cage. The generation and isolation of $Er_2ScN@C_{80}$(**7**) and $Y_3N@C_{80}$(**7**) can be rationalized in the same manner.[28,29] Kobayashi et al. predicted that unknown $La_3N@C_{80}$ is formally described as $(La_3N)^{8+}C_{80}$.[8−27] This endohedral complex must be kinetically unstable since it contains the C_{80}(**7**) octaanion with a min BRE of -0.117 $|\beta|$.

Metallofullerenes with C_{82}. This fullerene has nine IPR fullerene isomers.[14] Only isomer **3** has been isolated from the fullerene soot.[18] Since C_{82} consists of $6n - 2$ carbon atoms ($n = 14$), it has many reactive isomers.[16] Isomers **5**−**9** are predicted to be kinetically unstable with a min BRE $< -0.100\ |\beta|$.

It is noteworthy that four isomers of $Ca@C_{82}$ have been isolated, which are denoted by **I**, **II**, **III**, and **IV**.[30−32] All the electronic configurations can be described as $Ca^{2+}C_{82}{}^{2-}$. Carbon cages in **I**, **II**, **III**, and **IV** have C_s, C_{3v}, C_2, and C_{2v} symmetry, respectively.[31,32] A carbon cage in **IV** is nothing other than C_{82}(**9**) since it is the only isomer with C_{2v} symmetry. A cage in **I** is C_{82}(**2**) or C_{82}(**4**) or C_{82}(**6**). A cage in **II** is either C_{82}(**7**) or C_{82}(**8**). A cage in **III** is C_{82}(**1**) or C_{82}(**3**) or C_{82}(**5**). There is no doubt that the carbon cages adopted in **II** and **IV** have a min BRE $< -0.100\ |\beta|$ in the neutral electronic state. Theoretical calculations indicate that isomers **5**, **6**, **7**, and **9** of C_{82} form the low-energy molecular dianions and hence are likely to form low-energy isomers of $Ca@C_{82}$.[34,35] Therefore, it is probable that carbon cages in **I**, **II**, and **III** are C_{82}(**6**), C_{82}(**7**), and C_{82}(**5**), respectively. Note that all these C_{82} isomers have a min BRE $< -0.100\ |\beta|$ in the neutral electronic state. The ultraviolet photoelectron spectrum and molecular orbital calculations support the view that the carbon cage in **III** is C_{82}(**5**).[36]

Shinohara et al. pointed out that electronic absorption spectra of $M@C_{82}$-type metallofullerenes are very similar to each other if the cage structures and the negative charges they carry are the same.[4] For example, electronic spectra of $Sr@C_{82}$ and $Ba@C_{82}$ are similar to that of $Ca@C_{82}$(**III**).[37] Two isomers of $Sc@C_{82}$ have been isolated. One of them, isomer **I**, consists of Sc^{2+} and a C_{82}(**9**) dianion.[33,38] Its electronic absorption spectrum is similar to that of $Ca@C_{82}$(**IV**).[4] Three isomers of $Tm@C_{82}$ were isolated separately.[39] Measured electronic and ^{13}C NMR spectra suggest that the carbon cages in isomers **I**, **II**, and **III** of $Tm@C_{82}$ are iso-π-electronic with those in isomers **I**, **III**, and **IV** of $Ca@C_{82}$, respectively.[40] The carbon cage in $Tm@C_{82}$(**III**) was found to be C_{82}(**9**).[40]

Two isomers of $La@C_{82}$ were described formally as $La^{3+}C_{82}{}^{3-}$ and structurally characterized[41,42] One isomer contains the C_{82}(**9**) trianion[41] and another the C_{82}(**6**) trianion.[42] One of the $Pr@C_{82}$ isomers was also found to contain the C_{82}(**9**) trianion.[43] $Sc_3@C_{82}$ contains a carbon cage that turned out to be a C_{82}(**7**) trianion.[44] As shown in Table 1, the min BREs for C_{82}(**6**), C_{82}(**7**), and C_{82}(**9**) markedly increases by forming molecular trianions. Recently the carbon cage in one of three $Er_2@C_{82}$ isomers was identified as C_{82}(**6**) from crystallographic data.[45] Er usually takes an oxidation number of $+3$.[46] If this is the case for this metallofullerene isomer, the carbon cage in it exists as $C_{82}{}^{6-}$ with a min BRE of -0.001 $|\beta|$.

Metallofullerenes with C_{84}. This fullerene has 24 IPR isomers.[14] Since C_{84} is one of the fullerenes with $6n$ carbon atoms ($n = 4$), it has many kinetically stable isomers.[16] Ten isomers have so far been isolated.[18,47−51] and eight of them, **4**, **5**, **11**, **16**, **19**, **22**, **23**, and **24**, structurally identified.[18,47−50] Only four isomers, **3**, **9**, **13**, and **17**, are predicted to be kinetically unstable with a min BRE $< -0.100\ |\beta|$. It is worth noting that these unstable isomers have not been isolated from the fullerene soot although many isomers have been isolated. This further supports the validity of the present approach based on the BRE values.

Three $Sc_2@C_{84}$ isomers were isolated and identified as $Sc_2@C_{84}$(**10**), $Sc_2@C_{84}$(**17**), and $Sc_2@C_{84}$(**23**).[52−54] Bare C_{84}-

(**17**) is predicted to be kinetically very unstable but is stabilized by acquiring one or more excess electrons. The formal charge on each Sc later proved to be close to +3, which indicate that the carbon cage is a C_{84} molecular hexaanion.[55] C_{84}(**10**) and C_{84}(**23**) are among the kinetically stable isomers of C_{84}. According to theoretical calculations,[5] C_{84}(**10**) and C_{84}(**23**) form the low-energy tetraanions whereas the C_{84}(**17**) tetraanion is fairly higher in energy. This is consistent with the observation that the relative yield and kinetic stability of $Sc_2@C_{84}$(**17**) are much lower than those of the other two isomers.[54] C_{84}(**10**) and C_{84}(**23**) are kinetically stable, even in the neutral electronic state.[11,12]

$Sc_2C_2@C_{84}$ contains the C_{84}(**23**) dianion as a charged carbon cage.[56] The formal electronic structure of this endohedral complex is described as $(Sc_2C_2)^{2+}C_{84}{}^{2-}$.[56] All molecular anions of C_{84} isomers have min BREs larger than $-0.100\ |\beta|$.[11,12]

Exceptional Metallofullerene. Recently, Cao et al. isolated two isomers of $Ti_2@C_{80}$ and characterized them as $Ti_2@C_{80}$(**6**) and $Ti_2@C_{80}$(**7**).[57] As stated above, C_{80}(**6**) and C_{80}(**7**) have large negative min BREs in the neutral electronic state. Electron energy loss spectra of these complexes revealed that the valency of each titanium atom in the carbon cages must be lower than +2.[57] There is no problem with $Ti_2@C_{80}$(**6**) because all molecular anions derived from C_{80}(**6**) have min BREs $> -0.100\ |\beta|$. However, the mono- to tetra-anions of C_{80}(**7**) are predicted to be kinetically very unstable. Therefore, it seems that the isolability of $Ti_2@C_{80}$(**7**) cannot be predicted by the present BRE model. This is the only exception to our prediction based on the BRE model. There may be some covalent interaction between Ti_2 and the C_{80}(**7**) cage.[58]

Main Origin of Kinetic Stability. We have seen that most fullerenes, including chemically reactive ones, are kinetically stabilized by acquring one or more electrons. Such kinetic stabilization of fullerenes must be closely related to the low-lying LUMOs that arise from the presence of twelve pentagons. In fact, LUMOs in most fullerenes are either slightly bonding or nonbonding in nature,[6] which reflects the electron-deficient character of the molecules.[59] Therefore, they can be kinetically stabilized by filling such vacant molecular orbitals with electrons. In particular, kinetically unstable fullerene isomers have very low-lying LUMOs together with no or very small HOMO−LUMO energy separations.[6,15,16] This must constitute the main reason molecular anions of kinetically unstable fullerene isomers are often kinetically very stable. The HOMOs in fullerenes are fairly low in general.

Concluding Remarks

C_{80} and C_{82} are magic fullerenes with which many metallofullerenes are produced.[4] Such an aspect of fullerene chemistry is apparently associated with the fact that these two fullerenes not only consist of $6n \pm 2$ carbon atoms but also provide the optimum size of the cavity for the accommodation of one or more metal atoms. C_{80} and C_{82} have four and five kinetically unstable isomers with min BREs $< -0.100\ |\beta|$, respectively. Furthermore, they have no or very small HOMO−LUMO energy separations. Many metallofullerenes indeed employ kinetically unstable isomers of C_{78}, C_{80}, and C_{82} as carbon cages. We can safely say that nature prefers to generate metallofullerenes with chemically reactive fullerene isomers.

Many IPR-violating fullerenes are also stabilized kinetically by forming molecular anions.[13] Carbon cages in two nonclassical metallofullerenes, $Sc_2@C_{66}$[60] and $Sc_3N@C_{68}$,[3] are such examples. There is no doubt that these abutting-pentagon fullerenes are kinetically stable only in some negatively charged states. However, it seems unlikely that there are many such nonclassical metallofullerenes. Most of abutting-pentagon fullerenes must be higher in energy than the isolated-pentagon isomers even if they are negatively charged.

Acknowledgment. We thank Prof. Hisanori Shinohara (Nagoya University), Prof. Ken Kodama (Tokyo Metropolitan University), and Prof. Kaoru Kobayashi (Institute for Molecular Science) for many valuable suggestions. This work was supported by a Grant-in-Aid for Scientific Research (No. 11640502) from the Ministry of Education, Science, Sports and Culture, Japan. Computations were carried out at the Information Processing Center at Shizuoka University and the Computer Center at the Institute for Molecular Science.

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