Inorganica Chimica Acta, *198–200* (1992) 133–138

On the structures, stabilities and fragmentation patterns of carbon clusters including Buckminsterfullerene

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Abstract

The heats of formation and optimum structures of various neutral C_n clusters ($n \leqslant \sim 60$) and linear C_n^+ cations ($n \leqslant 40$) were determined by quantum chemical calculations. Buckminsterfullerene is thermodynamically more stable than the next stable form of C_{60} by about 600 kcal/mol. C_{60} and C_{70} fullerenes belong to a series of fullerenes C_{10m+40} ($m \geqslant 2$) that are derived from C_{10m} cylinders and C_{20} capping units. In the fragmentation of C_n and C_n^+ clusters, the preference for the C_2 or C_3 loss is predicted to depend upon whether the clusters have structures with mainly two- or three-coordinate carbon atoms.

Introduction

Since Buckminsterfullerene, C_{60}, was identified from a laser-produced carbon plasma [1], carbon clusters have received much attention [2]. However, studies of the physical properties and the chemical reactivities of C_{60} became possible only recently with the advent of the method of isolating C_{60} in macroscopic quantities [3]. The recent, explosive research efforts on C_{60} were touched off by the finding that alkali-metal doped Buckminsterfullerene, A_xC_{60} ($x \cong 3$, A = K, Rb), are superconductors with relatively high critical temperatures ($T_c = 18$ [4] and 28 K [5] for A = K and Rb, respectively).

Numerous quantum chemical calculations dealing with C_{60} [6–8] and small C_n clusters [9, 10] have been reported, but several important questions have not been fully answered. How stable is Buckminsterfullerene with respect to other possible forms of C_{60}? What is the conceptual structure-building principle for a series of fullerenes consisting of Buckminsterfullerene and C_{70} fullerene? Why does the fragmentation pattern of C_n^+ cations depend upon the cluster size? The $C_n^+ \rightarrow C_3 + C_{n-3}^+$ fragmentation dominates for $n < 30$, but only the $C_n^+ \rightarrow C_2 + C_{n-2}^+$ fragmentation is observed for $n \geqslant 32$ [11–13]. In the present study, we probe these problems by systematically calculating the heats of formation ($\Delta H_f°$) and the optimum structures of various neutral C_n clusters ($n \leqslant \sim 60$) and linear C_n^+ cations ($n \leqslant 40$) on the basis of the quantum chemical AM1 method [14]† incorporated in the MOPAC program [15]. In our study, all geometries of the carbon clusters were fully optimized, and the unrestricted Hartree–Fock (UHF) method was employed for open-shell state calculations. All the C_n and C_n^+ clusters reported in the following are minimum-energy structures.

Linear and cyclic C_n clusters

Table 1 lists the $\Delta H_f°$ values calculated for various linear C_n and C_n^+ as well as cyclic C_n clusters. Singlet and triplet states were considered for the neutral linear and cyclic clusters, while doublet and quartet states were considered for the linear cation clusters.

Figure 1(a) shows the $\Delta H_f°$ values calculated for the singlet and triplet states of linear C_n, and those calculated for the doublet and quartet states of linear C_n^+ cations for n values upto 20. The $\Delta H_f°$ values of singlet-state linear C_n ($2 \leqslant n \leqslant 6$) increase in the order

$$C_3 < C_2 \ll C_5 < C_4 \ll C_6 \qquad (1)$$

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†The AM1 method was parametrized to provide a quantitative description for the ground state properties of various types of molecules containing primarily carbon, hydrogen, oxygen, and nitrogen. For instance, the average error of the $\Delta H_f°$ values of the 58 hydrocarbons tested by Dewar *et al.* [14] is about 5 kcal/mol.

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TABLE 1. $\Delta H_f°$ values (kcal/mol) calculated for linear C_n, linear C_n^+ and cyclic C_n

n	Linear C_n		Linear C_n^+		Cyclic C_n	
	Singlet	Triplet	Doublet	Quartet	Singlet	Triplet
1	170.89					
2	216.24	221.88	488.45	467.13		
3	212.45	257.60	461.79	521.90		
4	279.88	266.11	491.97	497.00	364.99	369.82
5	270.13	315.43	501.49	545.77		388.48
6	326.53	316.71	524.56	530.87	407.21	373.93
7	330.86	360.73	544.43	577.09	408.26	381.23
8	379.35	371.56	567.18	595.84	417.89	385.96
9	391.35	410.67	589.56	615.04	431.45	387.86
10	434.54	427.91	614.39	637.06	403.90	406.18
11	451.63	462.92	636.42	657.33	446.04	410.81
12	490.97	485.03	659.83	680.98	438.61	439.99
13	511.83	508.27	683.63	701.89	481.56	440.92
14	548.12	542.60	707.24	726.64	465.19	474.93
15	571.98	556.95	731.26	747.90	517.05	474.94
16	605.74	580.47	755.11	773.35	504.90	514.32
17	632.10	605.73	779.26	794.86	558.80	512.85
18	663.64	629.65	803.27	820.78	543.91	555.05
19	692.22	654.55	827.51	842.45	600.50	552.94
20	721.75	716.52	851.67	868.71	587.08	597.54
21	752.34				645.31	594.84
22	779.99				630.71	641.23
23	809.57				690.07	637.89
24	838.33				676.16	685.73
25	872.55				736.59	
26	896.15				723.12	
27	925.60				783.29	
28	955.17				769.22	
29	984.15				829.89	
30	1013.65				817.31	
31	1042.95				878.48	
32	1072.68				865.01	
33	1084.28				927.08	
34	1130.70				913.09	
35	1159.11				975.59	
36	1189.46				961.84	
37	1218.38				1024.80	
38	1247.89				1010.67	
39	1277.14				1073.65	
40	1306.46				1059.67	

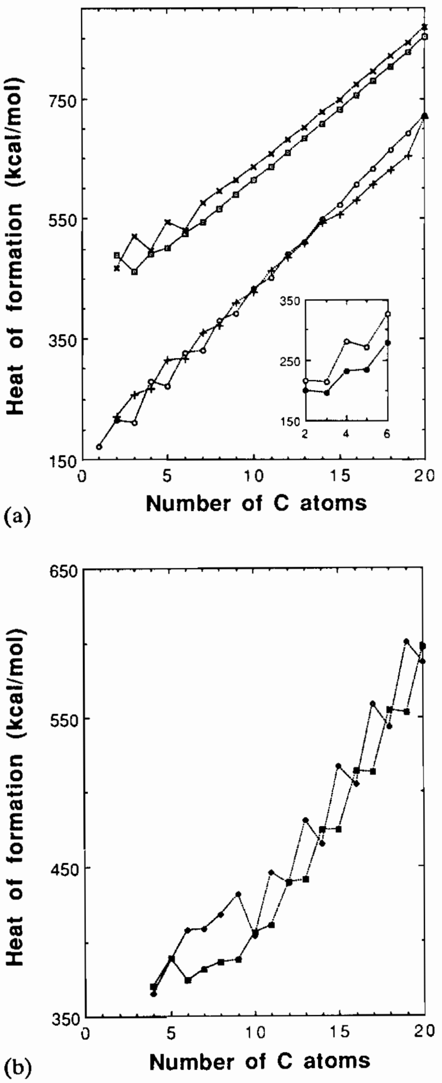

Fig. 1. (a) Heats of formation calculated for the linear C_n and linear C_n^+ chains. The labels are defined as follows: –○–, singlet-state linear C_n; · · · + · · ·, triplet-state linear C_n; –□–, doublet-state linear C_n^+; –×–, quartet-state linear C_n^+; –●–, experimental linear C_n. (b) Heats of formation calculated for the monocyclic C_n rings. The labels are defined as follows: –◇–, singlet-state C_n ring; –■–, triplet-state C_n ring.

The inset of Fig. 1(a) compares the calculated and experimental [16, 17]* $\Delta H_f°$ values of singlet-state linear C_n ($2 \leqslant n \leqslant 6$). The step-like increase in $\Delta H_f°$ as a function of n is well reproduced by the AM1 calculations. Beyond $n > 6$, the $\Delta H_f°$ values of singlet-state linear C_n increase almost linearly as n increases (see also Fig. 2) with the slope

$$\Delta\Delta H_f°/\Delta n \cong 22 \text{ kcal/mol} \qquad (2)$$

For an even-membered linear $C_n (n \leqslant 12)$, the triplet state is calculated to be more stable than the singlet state, as expected [18]. For an odd-membered linear C_n with $13 \leqslant n < 20$, the AM1 calculations predict the triplet state to be more stable than the singlet state, due mainly to the spin contamination of the UHF calculations. For the linear C_n^+ cations, with the exception of C_2^+, the doublet state is more stable than the quartet state.

Figure 1(b) shows the $\Delta H_f°$ values calculated for the singlet and triplet states of monocyclic C_n rings. For $n \geqslant 4$, with exception of C_5, the C_n rings are stable in both singlet and triplet states. The C_5 ring is stable

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*Ref. 17 gives only the lower limit value for the $\Delta H_f°$ of C_6, that is, $\Delta H_f° \geqslant 279.6$ kcal/mol. The electronic state of C_6 corresponding to this value is unknown.

only in the triplet state. For $n>6$, an even-membered C_n ring has a circular shape of alternating C–C and C≡C bonds (that is, $\cdots$C–C≡C–C≡C–C≡C$\cdots$), while an odd-membered C_n ring has a 'tear-drop' shape made up of a carbene center and a string of alternating C–C and C≡C bonds (that is, $\cdots$C–C≡C–C–C≡C–C$\cdots$) (see C_{10} and C_{11} in Scheme 1). An alternative form to this carbene structure is a 1,3-diradical (that is, $\cdots$C≡C–C=C=C–C≡C$\cdots$), which is slightly less stable than the carbene form. For $n \geqslant 10$, singlet-state C_n rings become more stable than singlet-state C_n chains. For even-membered C_n rings ($n \geqslant 10$), the singlet state is more stable than the triplet state. For odd-membered C_n rings ($n \geqslant 7$), the triplet state is more stable than the singlet state, as expected from their carbene-like character.

It is important to note from Fig. 1 that, for linear C_n chains, linear C_n^+ cations or C_n rings, the global features of the $\Delta H_f°$ versus n plots calculated for different electronic states are similar. Consequently, in the following, we consider only the $\Delta H_f°$ values of various C_n clusters calculated for their singlet states.

C_n derived from [*N*] radialene frameworks

Besides the chain and cyclic ring structures, C_n clusters may adopt various fused-ring structures, and when such clusters form cage structures, all carbon atoms are three-coordinate. Otherwise, two-coordinate carbon atoms are present at the edges of such clusters. As for C_n clusters with fused-ring structures, we consider only those derived from the [*N*] radialene ($N=3$–7) and hexatriene π frameworks (see Scheme 1). Starting with the 'nucleus' of an [*N*] radialene framework constructed from *N* units of C_2, C_n clusters may be built as follows. (i) We add C_2 units successively to the nucleus to form hexatriene units until the *N*-membered ring of the nucleus is completely encircled with hexatriene units. (ii) To the hexatriene units of the resulting cluster, we add C_2 units successively to form [*N*] radialene units. (iii) We repeat the above two processes until a cage structure is reached, when possible. All the C_n clusters thus generated may now be referred to as the $C_{n[N]}$ clusters. Table 2 summarizes the $\Delta H_f°$ values calculated for various $C_{n[N]}$ clusters, and Scheme 1 shows the structures of some of the $C_{n[N]}$ clusters ($N=3$–7) determined by the present AM1 calculations.

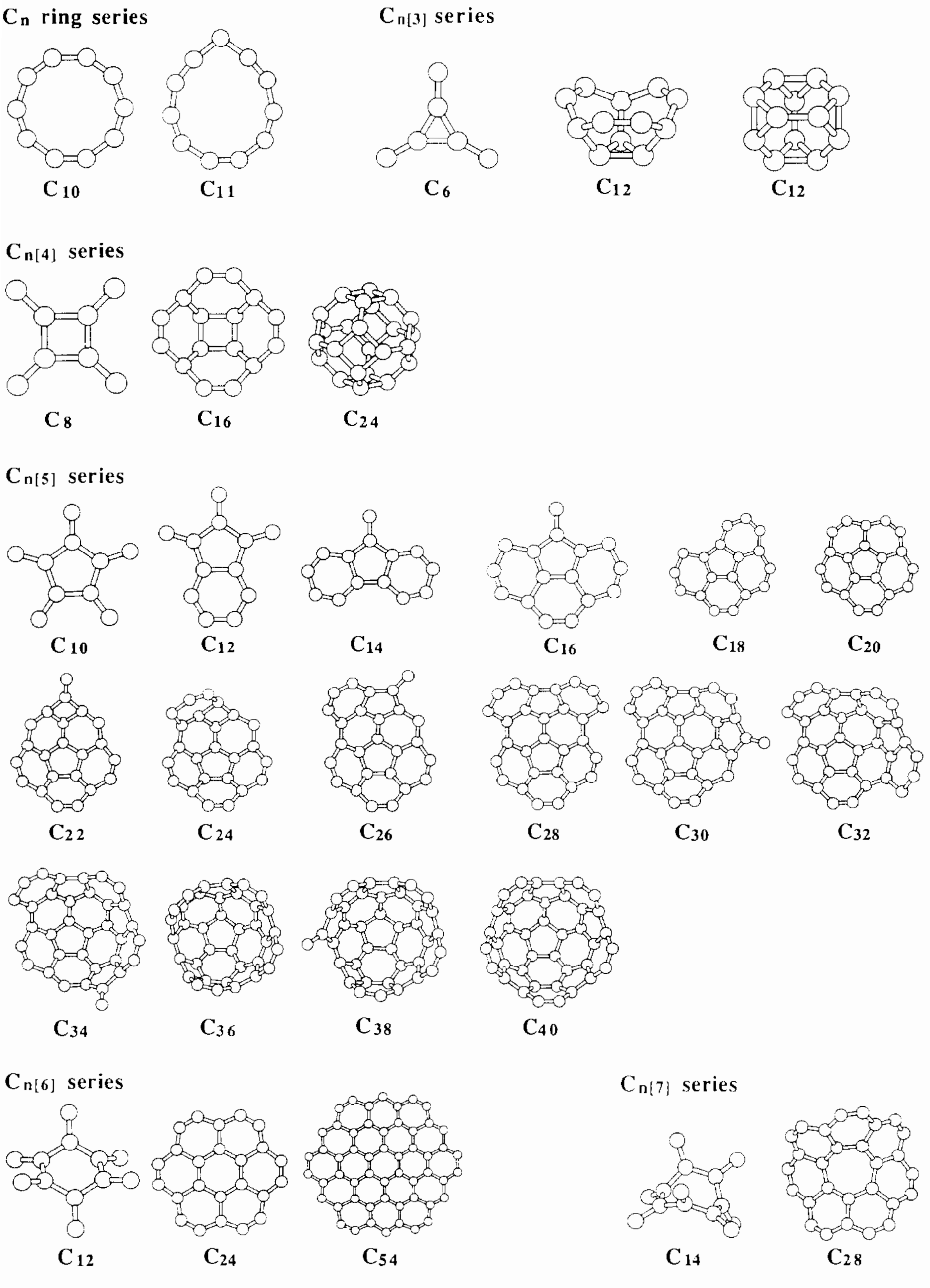
For $N=3$–5, the $C_{n[N]}$ clusters lead to cage structures. The end members of $C_{n[3]}$, $C_{n[4]}$ and $C_{n[5]}$ are $C_{12[3]}$, $C_{24[4]}$ and $C_{60[5]}$, respectively. With the $C_{n[N]}$ notation, Buckminsterfullerene C_{60} is written as $C_{60[5]}$. For $C_{12[3]}$, the cage structure is less stable than the open 'basket' form. The $C_{n[6]}$ clusters are planar, being graphite fragments, while the $C_{n[7]}$ clusters form a saddle-like warped structure. When capped with a $C_{20[5]}$ unit, the $C_{40[5]}$ cluster leads to Buckminsterfullerene $C_{60[5]}$. Formally, $C_{40[5]}$ is fragmented into a $C_{20[5]}$ and C_{20} 'cylinder', so that $C_{60[5]}$ may be viewed as a structure obtained from the C_{20} cylinder by capping with two $C_{20[5]}$ units. This is illustrated in Scheme 2, where the carbon atoms belonging to the C_{20} cylinder of $C_{60[5]}$ are indicated by shading. The proposed structure of C_{70} fullerene [19, 20] is formally derived from a C_{30} cylinder by capping with two $C_{20[5]}$ units, as shown in Scheme 2. In general, one can generate a series of fullerenes C_{10m+40} ($m \geqslant 2$) from C_{10m} cylinders by capping with two $C_{20[5]}$ units, that is, $C_{10m+40} = C_{20[5]} + C_{10m} + C_{20[5]}$. The C_{80} fullerene thus generated is shown in Scheme 2.

TABLE 2. $\Delta H_f°$ values (kcal/mol) calculated for the singlet state of the $C_{n[N]}$ clusters ($N=3$, 4, 5, 6)

n	$C_{n[3]}$	$C_{n[4]}$	$C_{n[5]}$	$C_{n[6]}$	$C_{n[7]}$
6	404.34				
8		518.35			
10			606.16		
12	663.41		643.64	719.11	
14			682.20		842.48
16		712.29	737.78		
18			757.71	824.61	
20			724.88		
22			897.36		
24		911.25	944.51	808.90	
26			978.24		
28			994.79		1012.48
30			1057.32	1097.59	
32			1074.38		
34			1132.28		
36			1106.91		
38			1137.73		
40			1089.60	1213.79	
50			1176.02		
54				1465.74	
58			1083.01		
60			973.34		
64				1656.87	

Relative stability of Buckminsterfullerene C_{60}

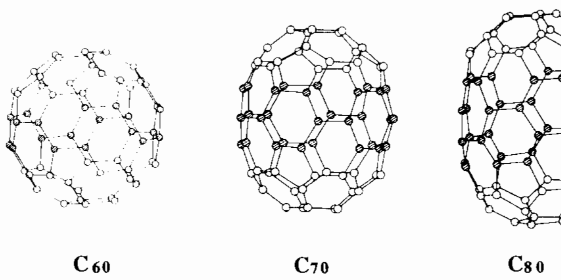
Figure 2 shows the $\Delta H_f°$ values calculated for the C_n chains, C_n rings and $C_{n[N]}$ clusters. As shown in the inset, the $C_{n[N]}$ clusters for $N=3$, 4 and 7 are less stable than the linear C_n chains. The graphite fragments $C_{n[6]}$ are less stable than the C_n rings for n values up to ~60. For $n \geqslant 28$, the $C_{n[5]}$ clusters become more stable than the $C_{n[6]}$ clusters. The striking feature of Fig. 2 is that, for the $C_{n[5]}$ clusters, the $\Delta H_f°$ versus n plot begins to flatten out a $n \cong 34$, and exhibits a negative slope beyond $n \geqslant 50$. It is noteworthy that the $C_{n[5]}$ series shows a remarkable stability for $n=20$. By truncating a single carbon atom from the even-membered $C_{n[N]}$ clusters, odd-membered $C_{n[N]}$ clusters can be generated. Though not shown, the $\Delta H_f°$



Scheme 1.

values of such odd-membered $C_{n[5]}$ clusters closely follow the $\Delta H_f°$ versus n plot obtained for the even-membered $C_{n[5]}$ clusters shown in Fig. 2. For $n > 42$, the $C_{n[5]}$ clusters are more stable than the C_n rings. Figure 2 shows that Buckminsterfullerene is thermodynamically the most stable form of C_{60} (see below).

In view of the fact that the $\Delta H_f°$ (per carbon atom) of graphite is defined to be zero, it is important to recognize why small graphite fragments $C_{n[6]}$ ($n < 60$) are not even as stable as C_n rings. For simplicity, consider a series of graphite fragments C_6, C_{24}, C_{54} etc. which are obtained from a hexagon by adding 'rings' of encircling fused-hexagons (see Scheme 1 for $C_{24[6]}$ and $C_{54[6]}$). In such clusters, the number of carbon atoms and that of σ dangling bonds are given by $6m^2$ and $6m$, respectively, where m is an integer. Thus, the average number of σ dangling bonds per carbon atom is $1/m$, which is not negligible unless the graphite fragment is extremely large. For example, in $C_{54[6]}$ for which $m = 3$, one in every three carbon atoms carries a σ dangling bond on average. That is, the unstable nature of the $C_{n[6]}$ clusters for small values of n stems



Scheme 2.

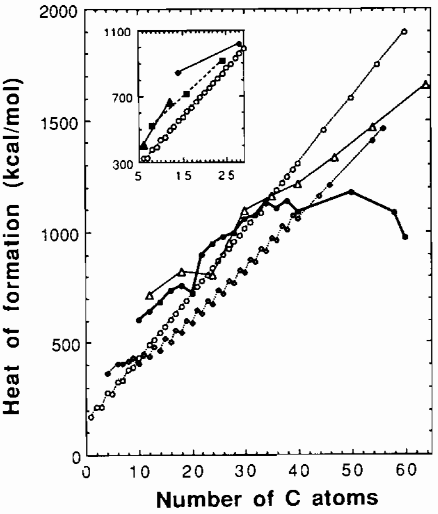


Fig. 2. Heats of formation calculated for the singlet-state linear C_n chains, monocyclic C_n rings, and $C_{n[N]}$ clusters ($N = 3$–7). The labels are defined as follows: -○-, linear C_n; -◇-, monocyclic C_n; -▲-, $C_{n[3]}$; ···□···, $C_{n[4]}$; -●-, $C_{n[5]}$; -△-, $C_{n[6]}$; -◆-, $C_{n[7]}$.

from the presence of σ dangling bonds. Our calculations on the $C_{n[N]}$ clusters show that neighboring σ dangling bonds form a σ bond or an in-plane π bond when allowed by geometry. Thus, at the six-membered ring edges of the $C_{n[N]}$ clusters, two adjacent σ dangling bonds tend to form an in-plane π bond. According to the $\Delta H_f°$ values calculated for the even-membered C_n ring (Fig. 2), it is projected that the C_{60} ring is nearly equal in stability with the corresponding graphite fragment, and $C_{60[5]}$ is more stable than C_{60} ring by ~600 kcal/mol. Possible forms of C_{60} other than linear C_{60} chain, C_{60} ring and $C_{60[5]}$ are structures containing four-coordinate carbon atoms, which leads to more dangling bonds than does $C_{60[6]}$. Such C_{60} structures would be less stable than $C_{60[6]}$ or C_{60} ring, so that Buckminsterfullerene should be more stable than the next stable form of C_{60} by about 600 kcal/mol.

Fragmentation patterns of C_n^+

For the $C_n \rightarrow C_m + C_{n-m}$ fragmentation of linear C_n, the enthalpy change (ΔH) is given by $\Delta H = \Delta H_f°(C_m) + \Delta H_f°(C_{n-m}) - \Delta H_f°(C_n)$, which is rewritten for $n \geqslant 6$ *as* $\Delta H \cong \Delta H_f°(C_m) - 29m$ by using eqn. (2). Similarly, the ΔH for the $C_n^+ \rightarrow C_m + C_{n-m}^+$ fragmentation of linear C_n^+ can be written for $n \geqslant 5$ as $\Delta H \cong \Delta H_f°(C_m) - 22m$ by using eqn. (3). Therefore, according to eqn. (1), fragmentation leading to C_3 (or C_5) is enthalpically more favorable than that leading to C_2 (or C_4) for linear $C_n (n \geqslant 6)$ and linear C_n^+ $(n \geqslant 5)$. This argument is also valid for the fragmentation of C_n or C_n^+ rings provided that the fragmentation products of such rings are linear, which is most likely the case.

The above conclusion concerning the fragmentation of the linear and cyclic forms of C_n or C_n^+ does not take the activation energy of fragmentation into consideration, and is not applicable for the fragmentation of the C_n or C_n^+ clusters with fused-ring structures in which most carbon atoms are three-coordinate because loss of a small carbon unit (for example, C_2 or C_3) from such a cluster does not lead to a linear chain fragment. In such a cluster, three-coordinate carbon atoms do not carry σ dangling bonds and are therefore more strongly bound to the cluster than are the two-coordinate carbon atoms present at the edge. Thus, removal of a small carbon atom fragment would require a smaller activation energy if it occurs at the edge than in the interior of the cluster. Furthermore, either at the edge or in the interior, C_2 removal leads to a smaller number of dangling bonds in the remaining fragment than does C_3 removal. Therefore, from C_n or C_n^+ clusters with fused-ring structures, C_2 removal would be kinetically more favorable than C_3 removal. The observation of the exclusive $C_n^+ \rightarrow C_2 + C_{n-2}^+$ fragmentation for even-membered C_n^+ with $n \geqslant 32$ might then imply that these C_n^+ cations have a structure with mostly three-coordinate carbon atoms. Likewise, the observation of the predominant $C_n^+ \rightarrow C_3 + C_{n-3}^+$ fragmentation for C_n^+ clusters with $n < 30$ implies that these C_n^+ cations have a structure with two-coordinate carbon atoms (for example, linear chains and monocyclic rings).

Concluding remarks

In summary, Buckminsterfullerene is thermodynamically more stable than the next stable form of C_{60} by about 600 kcal/mol. Our calculations suggest that C_{60} and C_{70} fullerenes belong to a series of fullerenes $C_{10m+40} (m \geqslant 2)$ derived from C_{10m} cylinders by capping with two $C_{20[5]}$ units. The preference for the C_3 or C_2 loss in the fragmentation of C_n or C_n^+ clusters should depend upon whether these clusters have structures with mainly two- or three-coordinate carbon atoms.

Acknowledgements

Work at North Carolina State University and Argonne National Laboratory is supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Science, under Grant DE-FG05-86ER45259 and Contract W-31-109-ENG-38, respectively. We express our appreciation for computing time on the Cray-2 computer made available by DOE and on the VAX-8700 at Argonne National Laboratory provided by the Chemistry Division. J.J.N. thanks NATO and Ministerio de Educacion y Ciencia (Spain) for Fellowships which made it possible to visit North Carolina State University, and DGICYT PB89-0268.

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