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Short communication

C_{60} Inflation: Production of C_{62}, C_{64}, ...

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Abstract

The fullerenes, C_{60} and C_{70}, incorporate multiple C_2 groups into the cage when the solid is bombarded by a kiloelectron volt polyatomic ion beam. In the case of C_{60}, C_{62} to at least C_{74} are produced but there is no enhanced formation of C_{70}. The C_2 groups are derived from fullerene fragmentation and addition apparently occurs with subsequent cage expansion. This new process of fullerene inflation was recently predicted by ab initio molecular dynamics methods (Yi and Bernholc, Phys. Rev. B, 48 (1993) 5724).

Keywords: C_{60}; C_{70}; Cage expansion; Fullerenes

Among the most interesting aspects of the chemistry of fullerenes is their ability to form new C–C bonds, for example by cycloaddition [1]. Cycloaddition of benzyne [2] and addition of the elements of benzene [3] have been of particular interest in this laboratory while additions of many other groups and atoms, including oxygen, fluorine, hydrogen, methylene, methyl, and halogen have also been reported [4]. Ion/molecule reactions in the mass spectrometer have also been used to generate fullerene derivatives and many examples of this are known [5] including the remarkable formation of endohedral complexes [6]. The process of C–C bond formation in all-carbon systems is important in the mechanism of fullerene formation [7]. Fullerene formation in pure carbon plasmas has been investigated by Bowers and co-workers [8] and Jarrold and co-workers [9]. Both studies show that large planar ring systems coalesce to fullerenes upon collisional heating. In order to cool the superheated nascent fullerene, small carbon particles are evaporated. These particles are exclusively C_2 units for clusters with an even number of carbon atoms [8].

There is expected to be a strong thermodynamic driving force for fullerenes to undergo cage expansions and/or coalescence since the cohesive energy per carbon atom increases and it would ultimately reach the value of graphite [10]. Whetten and co-workers [11], Marshall and co-workers [12], and Hettich and co-workers [13] have shown that laser desorption can give rise to such coalescence. Amster, Duncan and co-workers [14] have shown that ultraviolet irradiation can also cause coalescence of fullerenes and it

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has recently been reported by Hertel and co-workers [15] that coalescence occurs upon bombardment of a fullerene target by a fullerene ion/beam. Although Yeretzian et al. [11] have shown that fullerenes undergo laser induced coalescence and that the resulting higher fullerenes undergo processes which are ascribed to C_2 additions, C_{60} inflation has not been reported. Nevertheless, a recent theoretical study [16] predicts that C_2 additions should occur without an activation barrier to give the inflated product.

The above considerations regarding cycloaddition, coalescence and the growth of all-carbon compounds, led to the present study of reactive collisions of C_2 with C_{60}. Neutral C_2 is not readily accessible, but fullerene molecular ions fragment by C_2 loss [17]. Hence it might be possible to generate C_2 in situ at a fullerene surface by ion beam bombardment. Since SIMS is known [18] to yield $C_{60}^{\cdot+}$ molecular ions, it is possible that C_2 additions to $C_{60}^{\cdot+}$ could be observed in the course of ion/surface collisions under the appropriate conditions. Intermolecular reactions are known to occur during ion bombardment in the energized phase known as the selvedge [19] or spinoidal phase [20]. The best known of the interfacial reactions is reduction [21] but a wide variety of other reactions occur [22] among which cycloaddition [23] is most relevant to this study.

The bombardment of solid C_{60} and C_{70} employed keV beams of several projectile ions, including $Cr(CO)_6^{\cdot+}$, $Mo(CO)_6^{\cdot+}$, $W(CO)_6^{\cdot+}$, p-$C_6H_4Br_2^{\cdot+}$, $CBr_4^{\cdot+}$ and $Xe^{\cdot+}$. The experiments were carried out in a BEEQ [24] instrument designed for ion/surface collisions. Primary beams of 1800 eV at a current of approx. 1 nA/2 mm^2 were used in the experiment. These conditions allow approximately 20 seconds before a monolayer is affected by the beam and therefore they do not correspond to static SIMS conditions. C_{60} was obtained commercially (Texas Fullerenes,

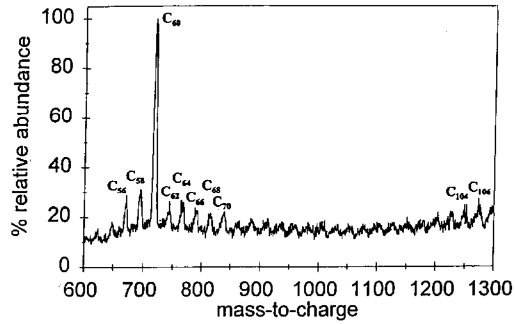

Fig. 1. 1800 eV $Cr(CO)_6^{\cdot+}$ secondary ion mass spectrum for a pure C_{60} film on a stainless steel sample holder. The probe area was approx. 2 mm^2 and the beam current was 1 nA. The peaks above 600 dalton/charge are separated at 24 dalton.

purity > 99.5%). Electron impact mass spectra did not show any impurities. C_{70} was from the same supplier, estimated purity 95%. A few microlitres of a toluene or CS_2 solution of the sample was used to make a film of the material with a typical estimated average thickness of 3 μm on a stainless steel holder of 16 mm diameter. The dried samples were introduced into the scattering chamber held at 10^{-8} Torr. Primary ions were produced by 80 eV electron impact and selected by mass analysis. The secondary ions were mass analyzed using a quadrupole mass filter, scanned at a rate of 0.5 dalton s^{-1}.

The mass spectrum obtained using $Cr(CO)_6^{\cdot+}$ primary ions (Fig. 1) shows the base peak corresponding to $C_{60}^{\cdot+}$, accompanied by the expected C_2 loss fragments down to $C_{52}^{\cdot+}$, with the expected decreasing abundances with decreasing mass characteristic of the C_{60} mass spectrum [7,18]. Above $C_{60}^{\cdot+}$, there occurs a series of ions separated by 24 dalton; this series actually occurs all the way up to the mass limit of the instrument (C_{118}) with greatest abundance at the high and low mass extremes (Fig. 1). While the signal-to-noise ratio is not high, it is clear that the addition of numerous C_2 units has occurred. Note that there is no enhanced abundance at m/z 840, $C_{70}^{\cdot+}$; the spectrum is therefore quite unlike that of soot extract which shows enhanced peaks at

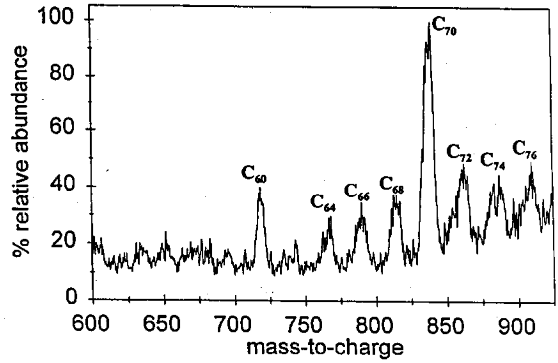

Fig. 2. Part of the SIMS spectrum for a C_{70} sample recorded under identical conditions as in Fig. 1.

particular carbon numbers [25]. A sample rich in C_{70} was investigated similarly and it too showed C_2 additions (Fig. 2). The peaks near the molecular ion are more intense, suggesting that initial C_2 additions occur at a fast rate.

The C_2 addition may occur by cycloaddition followed by incorporation of the added C_2 into the ring by an inflation process, which is predicted to occur without an activation barrier [16]. Additional rearrangement might follow to produce the lowest energy isomer of the fullerene. If only C_2 addition were occurring a rapid drop in ion abundance with mass would be expected; it is possible that addition of units larger than C_2 also occurs. In addition, the relatively high abundance of the ions at very high mass suggests an additional process. This is probably fullerene coalescence to yield products such as C_{120} which undergoes fragmentation by C_2 loss, just as do the lower fullerenes [11]. Note that C_{120} itself is beyond the mass range of the instrument. Although scanning electron and transmission electron microscopy (SEM and TEM) showed no evidence for giant fullerenes in material subjected to ion beam bombardment for long periods, coalescence is not ruled out in the energized selvedge.

A similar product distribution was obtained when other *molecular* projectiles of similar mass were used. However, $Xe^{\cdot+}$ ions did not yield detectable addition products although an abundant C_{60} signal was produced. The ionization energy of the projectile or the difference in the conditions in the energized surface region associated with use of an atomic vs. a polyatomic projectile ion [26] might be responsible for this difference. The time-scale required for fullerene annealing is probably the reason why no additional intensity is seen at m/z 840 corresponding to C_{70}. Sundqvist and co-workers [27] report C_{60} formation in subnanosecond times upon fission fragment bombardment of an organic polymer; they, too, did not observe enhanced C_{70} formation. Anomolous intensity distributions of fullerene ions were observed also by McElvany, Dietrich and co-workers in laser induced cyclocarbonization [28].

An attempt was made to investigate the thickness dependence of the inflation reaction by taking SIMS spectra from a number of samples of varying thicknesses. Similar spectra were obtained from samples varying in color from pale yellow ($\sim 1\,\mu g/cm^2$) to dark brown ($\sim 0.5\,mg/cm^2$). No fluence dependence was seen in the range of 0.1 to 1 nA. However, at lower fluences, the signals due to addition products were significantly weaker.

Since completion of this study, we have learned [29] of fast atom bombardment experiments on aryl derivatives of fullerene, such as $C_{60}Ph_5H$, which show the formation of $C_{60}^{\cdot+}$ as a fragment ion accompanied by what appear to be inflation products at C_{62}, C_{64}, ... etc. We have also learned of experiments [30] in which $C_{60}^{\cdot+}$ collides with a C_{70} surface and picks up C_2 even though collisions at other surfaces do not give inflation [11]. Note the similarities and differences between both these experiments and ours in which the molecular surface is both the source of C_2 and its recipient.

The present results confirm the theoretical prediction of fullerene inflation. They are significant since desorption ionization methods, including SIMS, are often used to characterize fullerene samples; unanticipated interfacial reactions might therefore represent a complication in spectral interpretation. There are also important implications for fullerene formation; C_2 units can definitely be added to $C_{60}^{\cdot+}$, in contrast to the known reluctance of C_{60} to grow in contact with carbon vapor [31]. These processes may be significant in coalescence reactions and the methodology presented here might be extended to investigate a wider range of addition reactions, especially for reagents like C_2 which are not available in conventional form. Details of the mechanism of inflation remain to be elucidated but it appears that the positive ions undergo reaction with the neutral fragments to form the fullerenes. The high local pressure in the spinoidal phase [20] helps account for the observation of multiple dicarbon additions.

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