Interaction of Nitrogen with Fullerenes: Nitrogen Derivatives of C_{60} and C_{70}

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On the basis of N(1s) core-level spectroscopic studies, it is found that nitrogen interacts with multimolecular films of C_{60}. More interestingly, mass spectrometric studies show that contact-arc vaporization of graphite in a partial atmosphere of N_2 or NH_3 yields nitrogenous products tentatively assigned to species such as $C_{70}N_2$, $C_{59}N_6$, $C_{59}N_4$, and $C_{59}N_2$ involving addition of or substitution by nitrogen along with the species due to C_2 and C_4 losses.

Research on C_{60} has progressed at an enormous pace in the last few months. One of the important aspects of research in this area relates to the reactivity of C_{60}. It is known that C_{60} readily produces singlet oxygen in high quantum yields[1] and reacts with oxygen.[2] C_{60} interacts strongly with nickel deposited on it.[3] We were interested in studying the interaction of C_{60} with nitrogen and employed X-ray photoelectron spectroscopy (XPS) to investigate the nature of the surface nitrogen species formed on a multimolecular films of C_{60} on exposure to gaseous N_2. This study revealed that N_2 molecules bind strongly to C_{60}. Prompted by this observation and encouraged by the finding of Guo et al.[4] that carbon can be replaced by boron in C_{60}, we sought to explore whether we can produce nitrogenous derivatives of C_{60} and C_{70} by carrying out the contact-arc vaporization of graphite in a partial atmosphere of gaseous N_2 or NH_3. We have indeed found that nitrogen containing derivatives of C_{60} and C_{70} involving the addition of nitrogen as well as substitution of carbon by nitrogen are formed in such a process. We report the preliminary results of our study in this letter. An understanding of the exact nature of these nitrogenous derivatives of fullerenes would, however, require further experimentation.

We shall first examine the results of our XPS study of the interaction of gaseous N_2 with multimolecular films of C_{60} deposited on a gold foil. The N(1s) spectrum of N_2 adsorbed on a multilayer film of C_{60} at 80 K (Figure 1) has a single sharp feature around 400.6 eV, unlike N_2 adsorbed (in the γ-state) on most transition-metal surfaces wherein two relatively broad features around 401 and 405 eV are generally found due to the screened and the unscreened final states, respectively.[5] The absence of a feature due to the unscreened state suggests that the N_2 species is strongly bound to the surface. A single N(1s) feature in the 399–400-eV range is found on transition-metal surfaces when N_2 is strongly chemisorbed in the α-state[5] with a N–N bond order between 1 and 2. We believe that the N(1s) peak around 400.6 eV found at 80 K on the C_{60} films is due to a strongly chemisorbed molecular species, the sharpness of the feature indicating the presence of a well-defined single species.[6] This N_2 species, I, does not desorb even at 300 K, unlike the weakly chemisorbed γ-species on transition-metal surfaces. The N(1s) spectrum at 300 K shows a new sharp feature at a lower binding energy (400.2 eV) representing another chemisorbed state, II, of N_2 on C_{60}. On warming I to 450 K, we only see the 400.2-eV feature, indicating that species I completely transforms to II. The occurrence of a strongly chemisorbed state of N_2 clearly indicates the high reactivity of the C_{60} surface with respect to N_2.

We carried out contact-arc vaporization of graphite in the presence of N_2 by leaking N_2 gas at a rate of 1 cm^3 s^{-1}; helium was simultaneously leaked at the same rate. The soot obtained was soxhlet-extracted with toluene. The solvent was evaporated from the toluene solution, and the resulting light brown product contained nitrogen as shown by elemental analysis. The mass spectrum of the sample given in Figure 2 (JEOL direct inlet, 70-eV EI source) shows new peaks at m/z 792, 764, and 736 (along with the corresponding, dication peaks). Since the 792 peak is unlikely to arise from the substitution of 36 carbons of C_{60} by nitrogen, we suggest that this is due to the addition of five nitrogen atoms (N_a) and substitution of one carbon atom by nitrogen (N_s) giving a composition $C_{59}N_6$. Other possible alternatives are compounds with $(5 - n)N_a + (1 + 7n)N_s$ with $n = 1$, 2, or 3; even with $n = 1$, the formula works out to be $C_{52}N_{12}$ with more nitrogen than the structure can probably tolerate. We therefore feel that the assignment of the 792 peak to $C_{59}N_6$ may be reasonable; this is also justified by the internally consistent set of assignments of the other observed features that becomes possible on this basis. The 764 peak can be considered to be due to $C_{59}N_4$ (with $3N_a + 1N_s$) arising from a loss of N_2 from $C_{59}N_6$, while the 736 feature is due to $C_{59}N_2$ (with $1 N_a + N_s$) arising from a further N_2 loss. The other peaks in the mass spectra (Figure 2) at m/z 778, 768, and 744 can be explained as due to loss of N, C_2, and C_4, respectively, from $C_{59}N_6$. We also see peaks at m/z 722–728 which can be due to nitrogen substitution in C_{60} giving molecules in the range $C_{59}N$ to $C_{56}N_4$. The m/z 868 peak (dication peak at 434) in the mass spectrum is clearly due to $C_{70}N_2$ with two N_a; the feature around 856 can also be due to $C_{69}N_2$ with 1 N_a and 1 N_s.

The results obtained from the contact-arc vaporization of graphite in the presence of NH_3 (leak rate of 1 cm^3 s^{-1}, same as for He), are more satisfying. The soot, on soxhlet extraction with toluene, gave a pale yellow solid containing nitrogen as found by chemical analysis. The yellow solid gave three fractions in column chromatography (with neutral alumina) which could be eluted out with CH_2Cl_2, leaving one band at the top of the column. Mass spectra of the three fractions show the total absence of the m/z 720 peak due to C_{60} (Figure 3) but instead show peaks which can be assigned to nitrogeneous products[7] similar to those obtained in the vaporization of graphite in the presence of N_2. Accordingly, the mass spectrum of fraction 1 shows peaks at m/z 764 and 736 (along with the corresponding dication peaks at m/z 382 and 368) due to $C_{59}N_4$ and $C_{59}N_2$. The peaks at m/z 740 and 716 are considered to be due to C_2 and C_4 loss respectively from $C_{59}N_4$; the other peaks in the mass spectra can also be interpreted in terms of similar combinations of N_a and N_s. Fraction 2 shows peaks at m/z 792 and 764 due to $C_{59}N_6$ and $C_{59}N_4$ (Figure 3); peaks

(1) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Auz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11.

(2) Kroll, G. H.; Benning, P. J.; Chen, Y.; Ohno, T. R.; Weaver, J. H.; Chibante, L. P. F.; Smalley, R. E. *Chem. Phys. Lett.* **1991**, *181*, 112.

(3) On depositing Ni on multimolecular films of C_{60}, we have observed that both the C(1s) and C(2p) features undergo large progressive shifts to lower binding energies.

(4) Guo, T.; Jin, C.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 4948.

(5) Rao, C. N. R.; Ranga Rao, G. *Surf. Sci. Rep.* **1991**, *13*, 221.

(6) It should be noted that N_2 does not interact with the graphite surface at 80 or 300 K.

(7) The compounds present in these fractions show absorption only in the ultraviolet region. The infrared spectra are completely different from those of C_{60} and C_{70}. While there could be some hydrogenation, we have not found evidence for C–H or N–H bonds. Contact-arc vaporization of graphite in a partial atmosphere of CH_3NH_2 also gives similar nitrogenous products, completely transforming C_{60}; $C_{59}N_4$, $C_{59}N_2$, and the associated peaks have been found by us in the mass spectrum.

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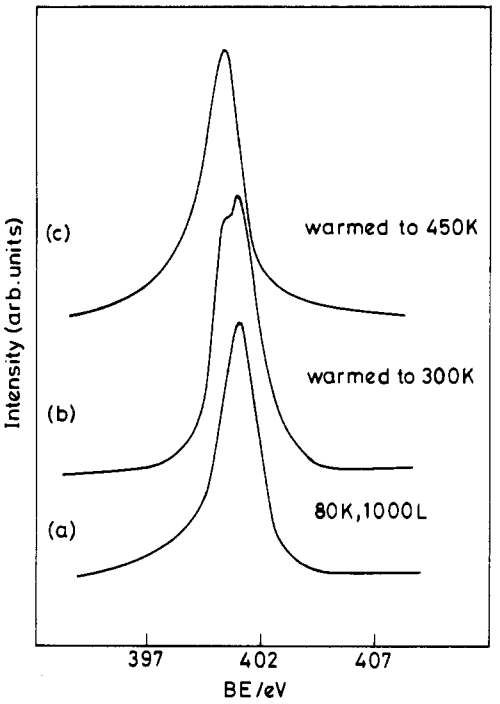

Figure 1. N(1s) spectra of nitrogen adsorbed on a multilayer film of C_{60}.

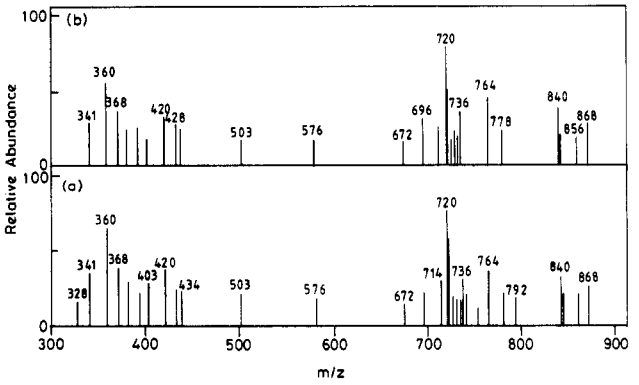

Figure 2. Typical mass spectra of the toluene extract of the soot obtained from the contact-arc vaporization of graphite in a partial nitrogen atmosphere; (a) and (b) are spectra from different runs.

at m/z 778, 768, and 744 are likely to be due to loss of N, C_2, and C_4, respectively, from $C_{59}N_6$, while the other peaks in the m/z 714–742 range can be interpreted as due to combinations of N_a and N_s. Fraction 2 also shows peaks at m/z 868 and 434 due to $C_{70}N_2$; the peak at m/z 842 could be due to $C_{69}N$ with one carbon substituted by nitrogen. Fraction 3 shows a peak at m/z 868 due to $C_{70}N_2$.

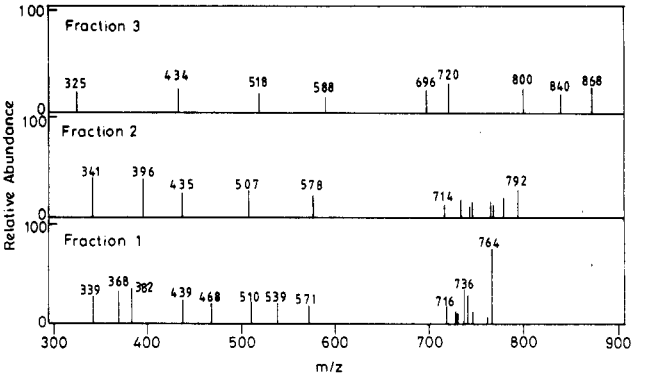

Figure 3. Mass spectra of the chromatographic fractions of the toluene extract of the soot obtained from the contact-arc vaporization of graphite in a partial atmosphere of ammonia.

TABLE I: Nitrogen Derivatives of C_{60} and C_{70} Identified by Mass Spectrometry

mass no.	molecular formula	approx description[a]
868	$C_{70}N_2$	2 N_a
856	$C_{69}N_2$	1 N_a + 1 N_s
842	$C_{69}N$	1 N_s
792	$C_{59}N_6$	5 N_a + 1 N_s (4 N_a + 8 N_s)[b]
764	$C_{59}N_4$	3 N_a + 1 N_s (2 N_a + 8 N_s)[b]
736	$C_{59}N_2$	1 N_a + 1 N_s (8 N_s)[b]
728–722	$C_{56}N_4$ to $C_{59}N$	4 N_s to 1 N_s

[a] N_a and N_s stand for addition of nitrogen and substitution of a carbon by nitrogen, respectively. Alternative combinations of N_a and N_s are possible. [b] Alternative descriptions of m/z 792, 764, and 736 features shown in parentheses would be $C_{52}N_{12}$, $C_{52}N_{10}$, and $C_{52}N_8$, but these seem unlikely.

In summary, the present study demonstrates that C_{60} interacts strongly with nitrogen. The reaction products of the contact-arc vaporization of graphite in a partial atmosphere of N_2 or NH_3 can be identified by mass spectrometry.[7] In Table I, we list the approximate description of the nitrogenous products; the exact characterization of these products however has to await more detailed mass spectrometric and chemical studies. It is possible that $C_{70}N_2$, $C_{59}N_6$, and $C_{59}N_4$ and possibly some of the species with mass numbers in the range 722–728 ($C_{56}N_4$ to $C_{56}N$ with only N_s) are bona fide compounds formed in the vaporization of graphite while the others are fragmentation features. We are not able to comment on the nature of the nitrogen added to C_{60} or C_{70} at this stage, although one possibility is the formation of three- or four-membered rings. A noteworthy feature is that they seem to eliminate N_2 (e.g., $C_{59}N_6 \rightarrow C_{59}N_4 \rightarrow C_{59}N_2$). The likely reason that we have found formation of nitrogenous derivatives in the present study is because we did not backfill the reactor completely with N_2 but only leaked N_2 gas at a slow rate. On backfilling, we found a polymeric product.