Formation of Methylene Derivatives of [60]-, [70]-, [78]- and [84]-Fullerenes by Reaction of Fullerene-containing Soot Extract with Tetrahydrofuran

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If a mixture of carbon clusters extracted from soot produced by the arc-discharge procedure is either heated or sonicated with tetrahydrofuran (THF), a range of methylene derivatives $C_m[CH_2]_n$, where *m* is 60, 70, 78 or 84 and *n* is variously 1–6 are produced. These results constitute the first formation of [78]fullerene derivatives; [76]fullerene does not appear to react under these conditions. Species with $n = 3$ are dominant, believed to be due to addition of trimethylene chains, through loss of formaldehyde from THF. This conclusion is supported by the prominence of $[CH_2]_4$ adducts in the product if [60]fullerene is heated under reflux with dihydropyran. Reaction of pure [60]fullerene with THF results in the addition of up to 10 methylene groups to the cage.

The formation of methylene adducts of [60]- and [70]-fullerene was first reported by Cooks and co-workers, who found evidence for $C_{60}CH_2$ and $C_{60}CH_2$ in the mass spectra of the extract (benzene) of soot produced by the arc-discharge procedure; mass spectra were obtained using both EI and electron attachment (ammonia as chemical ionizing agent) techniques.[1] After UV irradiation of an ethereal solution of the soot extract, the mass spectrum of the products then showed the presence of species $C_{60}[CH_2]_x$, $x = 1$–6, and $C_{70}[CH_2]_y$, $y = 1, 2$, suggesting that a process involving radicals was involved. A series of $C_{60}[CH_2]_x$ species, $x = 1$–5 have been identified from the reaction of [60]fullerene with either epoxypropane or 1-chloro(bromo)-2,3-epoxypropane.[2] Various CR_2 groups have been added to [60]fullerene through the use of diazirene precursors and it is probable that some, if not all, involve carbene intermediates.[3–7] Up to six groups have been added in some cases and an octahedral disposition of these is probable.[8]

We now find that a range of fullerenes react slowly with THF to give various methylene derivatives. Our observation arose from an (unsuccessful) attempt to devise a chemical separation of [60]fullerene from soot extract *via* bromination, isolation of the derivative and debromination. The recovered fullerene was then either heated or sonicated with THF to remove any soluble material, washed with THF and dried under vacuum. The mass spectrum of the soluble material revealed the presence of many methylene-containing species (Fig. 1; this spectrum is normalized to the peak at 762 u). Comparable results were obtained if the soot extract was heated directly with THF, although the concentrations of the methylene-containing derivatives appeared to be lower. No clear explanation for this difference is evident at present and we have not investigated this aspect further; fullerene particle size could be a contributing factor.

Peaks evident on Fig. 1 are at m/z = 734, 748, 762, 776, 804

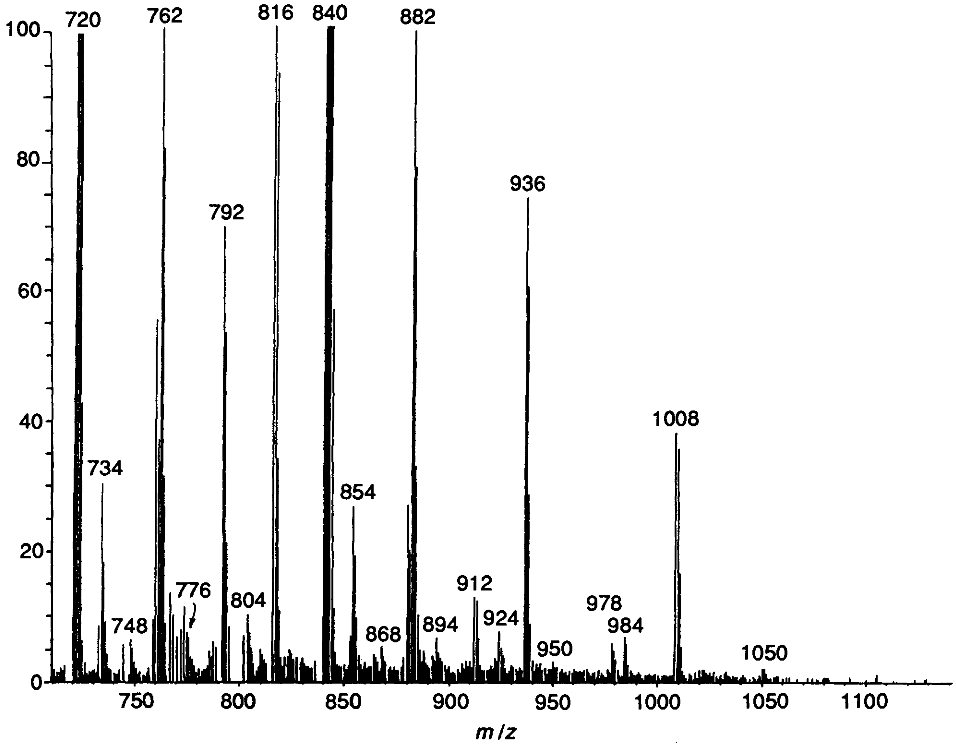

Fig. 1 Mass spectrum of bromine-treated soot extract, after heating with THF

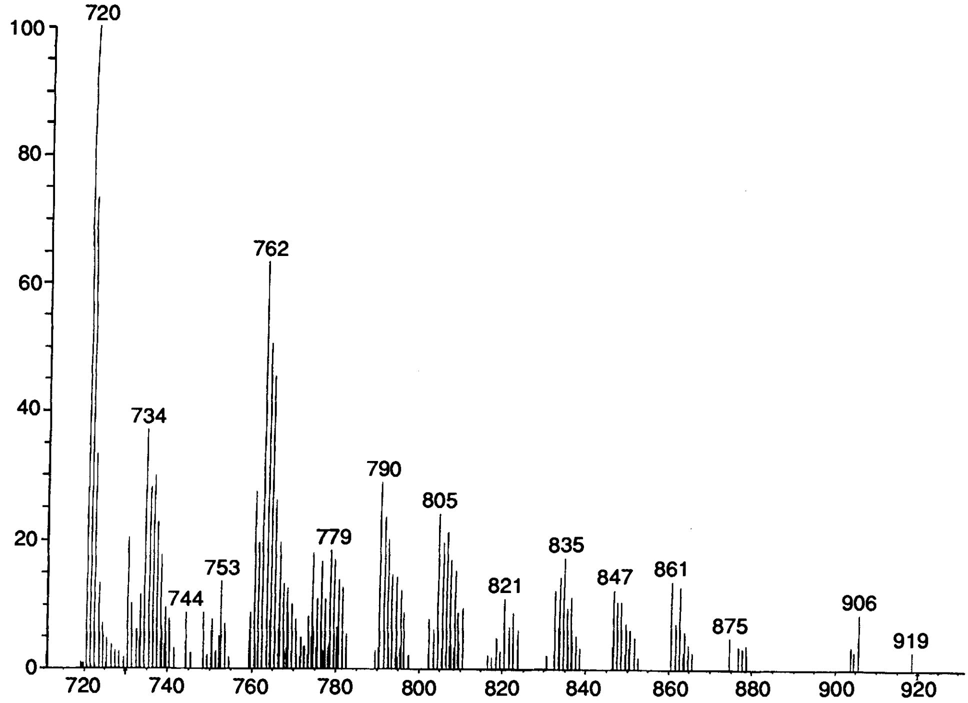

Fig. 2 Mass spectrum of the product of heating [60]fullerene with THF under reflux for 5 days

($C_{60}[CH_2]_n$, $n = 1$–4, 6), 854, 868, 882, 924 ($C_{70}[CH_2]_n$, $n = 1$–3, 6), 950, 978 ($C_{78}[CH_2]_n$, $n = 1, 3$) and 1050 ($C_{84}[CH_2]_3$). The main features of this result are as follows.

(*i*) Methylene derivatives are formed from [60]-, [70]-, [78]- and [84]-fullerenes. This is the first report of the formation of a derivative of [78]fullerenes and only the second[9] for [84]fullerene.

(*ii*) No derivatives of [76]fullerene were detected. Although this might be thought to have some bearing on the reported different electrochemical behaviour of [76]fullerene behaviour from other fullerenes[10] (being able to both accept and donate electrons, *i.e.* to have both oxidizing and reducing properties), the phenomenon has been reported recently to be unreproducible.[11]

(*iii*) The dominant species present for each fullerene contains three methylene groups attached to the cage and the next most intense species has one methylene group so attached. Accurate mass measurements for the derivatives of [60]fullerene are: $n = 1$, 734.0162 (measured), 734.0157 u (calc.), error 0.7 ppm; $n = 3$, 762.0468 (measured), 762.0470 u (calc.), error 0.2 ppm. The excellent agreement between observed and calculated masses confirms the correct interpretation of the peaks. {It also confirms that the interpretation of peaks at 734 and 854 u in the mass spectra of processed [60]- and [70]-fullerenes in terms of nitrogen adducts (with inexplicable bonding)[12] is incorrect.}

(*iv*) Whilst one and two methylene groups must be either attached across high order bonds, or inserted into 5,6-ring junctions to give methanofullerene or homofullerene structures, respectively, this is not the case for the addition of three methylene groups. Whilst the addition of three such groups, predicted on theoretical grounds,[13] could account for the high intensities, it is evident that for the reaction of [60]- and [70]-fullerene further species corresponding to the addition of 40 u, are present. Moreover these species (evident in a number of spectra, see also Fig. 2) become more intense the longer the residence time in the mass spectrometer, showing that they are elimination products, not feasible from three separately added methylenes. We believe that one addition product has a $-[CH_2]_3-$ group attached across one of the high order bonds {giving *e.g.*, 1,2-propano[60]fullerene, Fig. 3(*a*)} and that hydrogen elimination then gives the corresponding $-CH_2CH{=}CH-$ derivative. We discount the alternative insertion into the 1,9-bond, which methylene can undergo,[4] because of the severe strain thereby introduced.

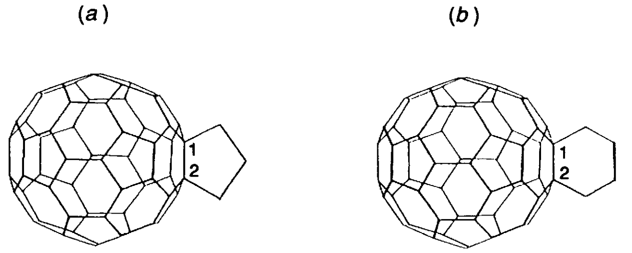

Fig. 3 Proposed structure for (*a*) 1,2-propano[60]fullerene; (*b*) 1,2-butano[60]fullerene

(*v*) It is not possible to formulate a mechanism for the trimethylene abstraction from THF without an extensive study of the behaviour of a range of its substituted derivatives. However, since such an abstraction will produce formaldehyde as a leaving group, we heated [60]fullerene (which contained a small amount of [70]fullerene) with dihydropyran, from which loss of formaldehyde would correspondingly give tetramethylene and hence formation of butano[60]fullerene [Fig. 3(*b*)]. This conjecture proved to be correct; Fig. 4 shows an intense peak at $m/z = 776$ u. Moreover, stepwise loss of at least two hydrogen molecules can now be seen.

(*vi*) Fig. 2 shows the expanded mass spectrum of the dark red THF-soluble material produced in *ca.* 60% yield by heating pure [60]fullerene with THF under reflux for five days. The trimethylene derivative is again the most prominent species present and the dehydro-trimethylene derivative is particularly evident. The presence of some $C_{60}O$ is also apparent. Most notable is the addition of up to 10 methylene groups. Because of the combination of methylene, dehydro-trimethylene and oxygenated species, the peaks at higher mass are more clustered

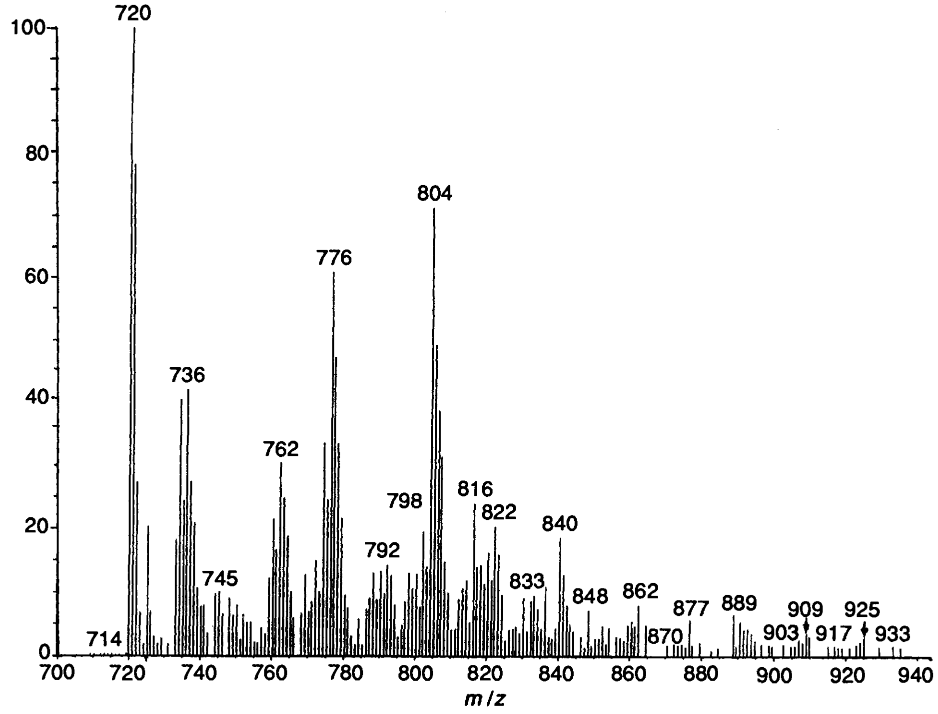

Fig. 4 Mass spectrum of the product of heating [60]fullerene with dihydropyran under reflux for 24 h

and detailed interpretation of them would be too speculative at present. The peaks for $C_{60}[CH_2]_n$, $n = 1–10$, should appear at 734, 748, 762, 776, 790, 804, 818, 832, 846 and 860 u. Investigation of these species can only be realistically undertaken by, *e.g.*, using ion cyclotron resonance techniques.

The methylene groups are readily lost from the fullerenes under EI conditions so that the peak for the parent ion appears as the most intense one. This was confirmed by comparison, for a given sample, of spectra run under EI and Laser-Desorption Time-of-Flight conditions. Under the latter the relative intensities of the derivatives was considerably higher.

(*vii*) The ^1H NMR spectrum (500 MHz, $CDCl_3$) of the material giving rise to Fig. 1 showed a multitude of signals between δ 1.5 and 7.0. Strong broad resonances were centred at δ 1.92, 3.70 and 6.45, and there were some sharp signals around δ 6.80. Weak signals at δ 9.82, 8.09 and 8.04 may correspond to some aldehydic material, which is qualitatively consistent with the reasoning above [see (*v*) above].

(*viii*) The IR spectrum (KBr) showed bands at 2931 and 1462 cm^{-1}, consistent with the presence of methylene derivatives; bands (unassigned) at 1510, 1262, 1195, 1070 and 747 cm^{-1} were also present. Notably however, bands for [60]fullerene were absent, further confirming [see (*vi*) above] that the methylene adducts are not stable under EI conditions. The failure to detect adducts from > [84]fullerene may therefore reflect a lower stability of the derivatives, especially since the higher fullerenes are believed to be less electron-withdrawing and therefore less prone to form stable derivatives.

Experimental

A mixture of fullerite (32 mg), carbon disulfide (3 cm^3) and bromine (1.5 cm^3) was allowed to stand for 24 h, during which time small dark crystals formed. The crystals were collected by decantation, washed with CS_2 (4 × 1 cm^3) and dried under vacuum at room temperature. The solid was heated to 170 °C for 4 h, cooled to room temperature, ground to a fine red solid and heated at 170 °C for a further 2 h. The resultant solid (17 mg) was suspended in THF (20 cm^3) and heated under reflux for 3 h. The orange–brown solution, collected by filtration from the cooled mixture, was concentrated to give a dark residue (8 mg) which was washed with pentane and dried under vacuum. The mass spectrum was run under EI conditions.

Fullerite (20 mg) was also heated directly with THF under reflux for 3 h, the same work-up procedure being used as before, to give *ca.* 5 mg of THF-soluble material. Likewise [60]fullerene also reacted with either THF or dihydropyran; in the latter case, all of the fullerene reacted to produce a soluble material.

EI mass spectra (VG Autospec.) were run at 70 eV, 6 kV accelerating voltage, 100 μA current, source 350 °C, probe ramped up to 400 °C. MALDI-TOF spectra (GSG Vestec Interion Lasertec, Benchtop 2) used an N_2 laser producing 3 ns pulses at 337 nm, 20 Hz repetition rate, operated at 20 kV.

Acknowledgements

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