Birch Reduction of C$_{60}$—a New Appraisal

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Contrary to a previous report that Birch reduction of C$_{60}$ affords C$_{60}$H$_{36}$ as the principal product, laser desorption–laser photoionisation time-of-flight (L^{2}TOF), laser desorption Fourier transform ion cyclotron resonance (FTICR), and liquid secondary ion mass spectrometry (LSIMS) show collectively that a mixture of polyhydrofullerenes, containing C$_{60}$H$_{18}$ through to C$_{60}$H$_{36}$ with a skewed distribution centred on C$_{60}$H$_{32}$ is formed, the discrepancy in results arising from the thermal lability of this mixture of polyhydrofullerenes when subjected to the elevated temperatures (>250 °C) required for mass spectroscopic studies using direct-insertion heated probes.

Subsequent to the discovery by Krätschmer *et al.*[1] of a method for the macroscopic synthesis of C$_{60}$ **1**, there has been an explosion of activity in fullerene research.[2] Our interest in the theory that a mixed population of the hydrides of the fullerenes are responsible for certain unexplained lines in the IR spectra observed from nebulae in the Galaxy,[3] led us to carry out the Birch reduction of C$_{60}$. Haufler *et al.*[4] had already reported the isolation of an off-white compound of formula C$_{60}$H$_{36}$ as the principal product, albeit from the reduction of fullerite (a *ca.* 85:15 mixture of C$_{60}$ and C$_{70}$). They pointed out that this formula is consistent with a caged hydrocarbon in which twelve isolated double bonds remain, possibly in pentagonal rings. Such a structure is shown as **2** where the remaining sp^2 hybridised carbon atoms are shown as solid circles. We believe their conclusion to be misconceived. The results reported here establish that the Birch reduction of C$_{60}$ gives rise to a mixture of polyhydrofullerenes containing C$_{60}$H$_{18}$ through to C$_{60}$H$_{36}$ with a skewed distribution centred on C$_{60}$H$_{32}$.

Pure C$_{60}$ (*cf* ref. 4) for use in our study was obtained by differential Soxhlet extraction of carbon-arc soot,[5] followed by a novel preparative HPLC protocol using FullereneSep.[6] For the Birch reduction,[7] we used lithium metal added to a suspension of C$_{60}$ in liquid NH$_3$–tetrahydrofuran (THF) at −78 °C under argon, followed by addition of *tert*-butyl alcohol after 30 min. The product was isolated by normal work-up[8] as a pale-yellow solid whose IR spectrum showed *only* C–H vibrations in the region above 2800 cm^{-1}.

Characterisation of the Birch product was initially carried out using laser desorption laser–photoionisation time-of-flight mass spectrometry (L^{2}TOFMS). A pulsed TEA CO$_2$ laser (Alltec 854 MS) was used for desorption of the sample,

deposited in the form of a toluene slurry, from a stainless steel probe; the resultant sample vapour was then entrained in a supersonic molecular beam of helium. Photoionisation of the desorbed neutrals was accomplished using the 193 nm output from a Lumonics TE-861T-4 excimer laser, operating on the ArF line. Fig. 1 shows the time-of-flight mass spectrum that was obtained. It is notable that the spectrum consists of just a single approximately symmetric feature, centred on mass 750 u. This feature, which has a FWHM of 7 u, is due to an unresolved distribution of hydrogenated products, ranging from 740 to 760 u, which cannot be resolved with the limited instrumental resolution of 300 (FWHM) available under the experimental conditions used. There is no evidence for the formation of a unique product (C$_{60}$H$_{36}$) as reported by Haufler *et al.*[4] Also there is no evidence of fragment peaks such as C$_{60}^+$ under the soft ionisation conditions used. We believe, therefore, that this mass spectrum represents the nascent distribution of polyhydrofullerene products resulting from the Birch reduction.

Because the resolution of this time-of-flight mass spectrometer was insufficient to resolve the product distribution, the sample was then analysed by laser desorption Fourier transform ion cyclotron resonance (FTICR) mass spectrometry on a 3 Tesla Nicolet FTMS 2000 spectrometer, incorporating a Tachisto Model 216 CO$_2$ laser. Samples were prepared by depositing a toluene slurry of the sample onto a steel target. After evaporation of the solvent the target was exposed to pulses from the CO$_2$ laser. Ions were trapped at a potential of 0.2 V and, after a 10 s delay, were excited (1 kHz ms^{-1}, 200 kHz to 0, zero attenuation) and detected in
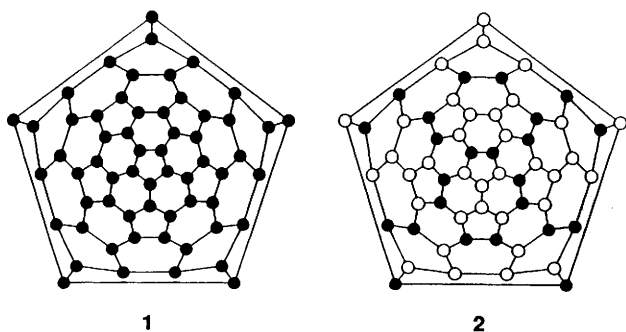
Schematic Schlegl diagram representation of C$_{60}$ **1**, and one possible isomer of C$_{60}$H$_{36}$ **2**. Open circles: C–H; filled circles: sp^2 C. Filled circles are used for C to emphasise the positions of the remaining double bonds.
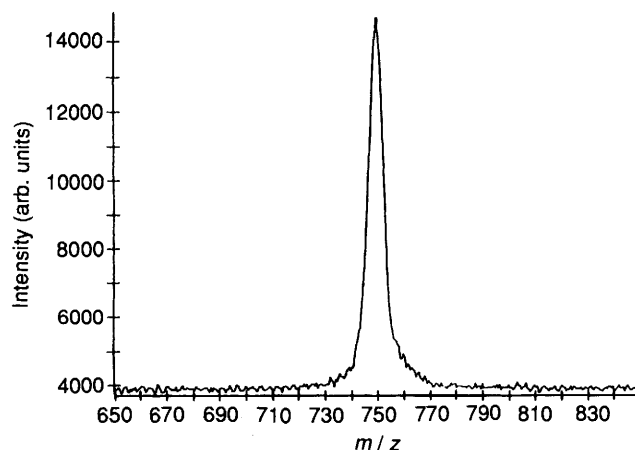

Fig. 1 Laser desorption laser photoionisation time-of-flight mass spectrum of Birch-reduced C$_{60}$

the source side of the dual cell. A detection bandwidth of 100 kHz was employed and signals from 16 laser shots were averaged. Rotation of the target ensured that a fresh region of the target was exposed to each laser pulse. The final spectrum was obtained by Fourier transformation of 32k data points after 3-term Blackman Harris apodisation. The effective mass resolution was 4000 (FWHM). Fig. 2 shows the spectrum obtained. The principal feature in this spectrum is the prominent well-resolved series of peaks centred around the base peak at 753 u, corresponding to the distribution of polyhydrofullerenes. There is clear evidence of fragmentation as witnessed by the relatively strong peak due to C_{60}^+, and its ^{13}C isotope fingerprint, the weaker peaks between 720 and 730 u corresponding to fragmentation to lower molecular weight polyhydrofullerenes. However, the overall intensity profile of the distribution of polyhydrofullerenes is very similar to the unresolved feature in the L²TOF mass spectrum (vide supra). Another striking feature of the product distribu-

tion shown in Fig. 2 is the pronounced even–odd intensity alternation, with the odd number mass peaks substantially more intense than the adjacent even number mass peaks. This result, at first sight, is at odds with the expected even distribution of products from the Birch reduction, which is generally thought to proceed by 1,4-hydrogen addition.[7] We believe that this is due to facile proton attachment during the desorption process. The true experimental distribution of polyhydrofullerene products is also somewhat obscured by the very intense underlying ^{13}C isotope distribution.

In order conclusively to identify the nascent product distribution the sample was also characterised by liquid secondary ion mass spectrometry (LSIMS) using a Fisons VG Analytical ZAB2-T tandem mass spectrometer of BEBE geometry in which the first two sectors were utilised. Samples were prepared for analysis in a 3-nitrobenzyl alcohol (3-NOBA) matrix. A positive ion LSIMS experiment was carried out at an acceleration voltage of 8000 V with the caesium gun
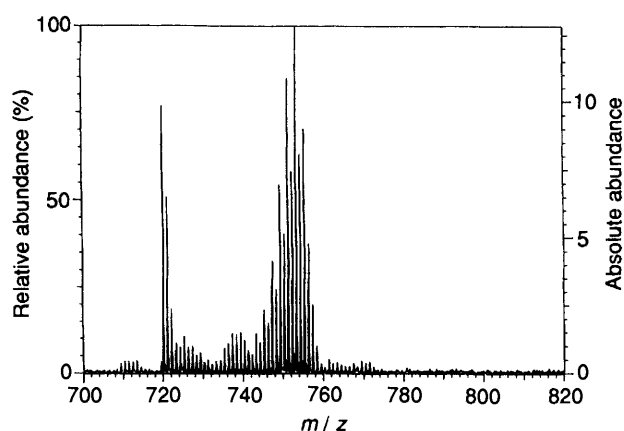

Fig. 2 Laser desorption Fourier transform ion cyclotron resonance mass spectrum of Birch-reduced C_{60}

Table 1 Experimental and calculated (Monte Carlo simulation) product distribution from Birch reduction of C_{60}

Polyhydrofullerene composition	Experimental distribution[a] (% of base peak)	Monte Carlo distribution[b] (% of base peak)
$C_{60}H_{24}$	39 (24)	0.2
$C_{60}H_{26}$	53 (35)	3
$C_{60}H_{28}$	72 (57)	19
$C_{60}H_{30}$	96 (89)	53
$C_{60}H_{32}$	100 (100)	100
$C_{60}H_{34}$	71 (62)	98
$C_{60}H_{36}$	11 (10)	55
$C_{60}H_{38}$	— (—)	14
$C_{60}H_{40}$	— (—)	0.3

[a] Derived from LSIMS data of Fig. 3 and (in parentheses) FTICRMS data of Fig. 2. [b] Based on reduction of 20000 molecules of C_{60}.
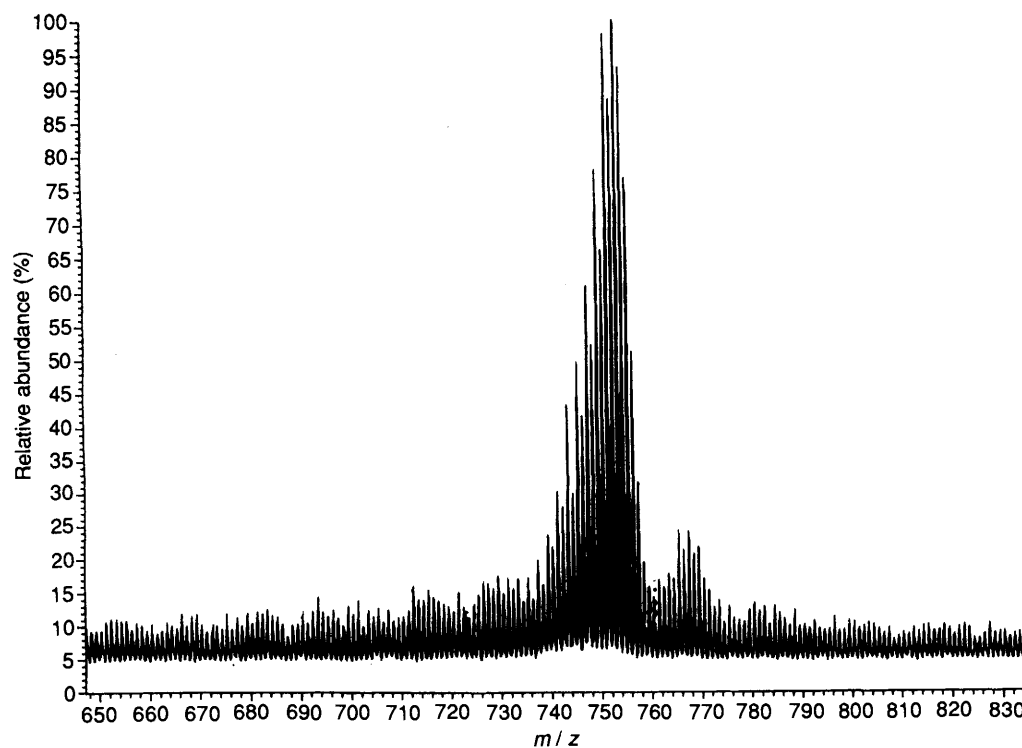

Fig. 3 Positive ion liquid ion secondary ion mass spectrum of Birch-reduced C_{60} in 3-NOBA matrix
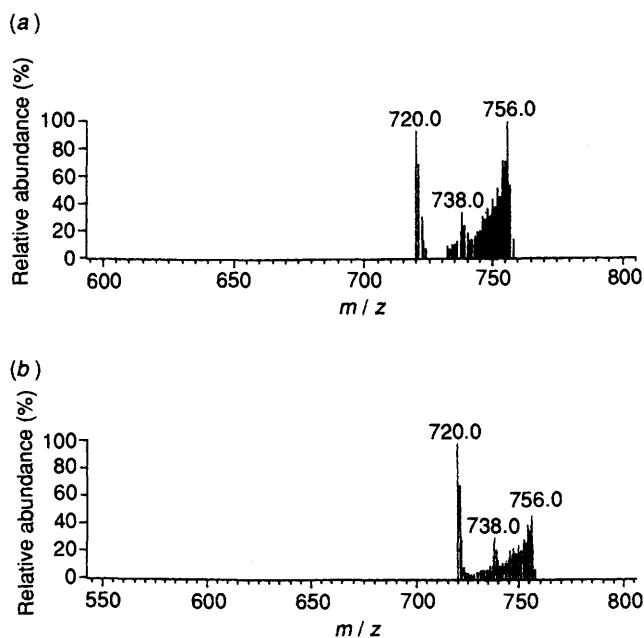
(a)

(b)

Fig. 4 Electron impact mass spectra (Kratos MS50TC) of Birch-reduced C_{60}: (a) source temperature 295 °C; probe temperature 390 °C; (b) source temperature 310 °C; probe temperature 400 °C
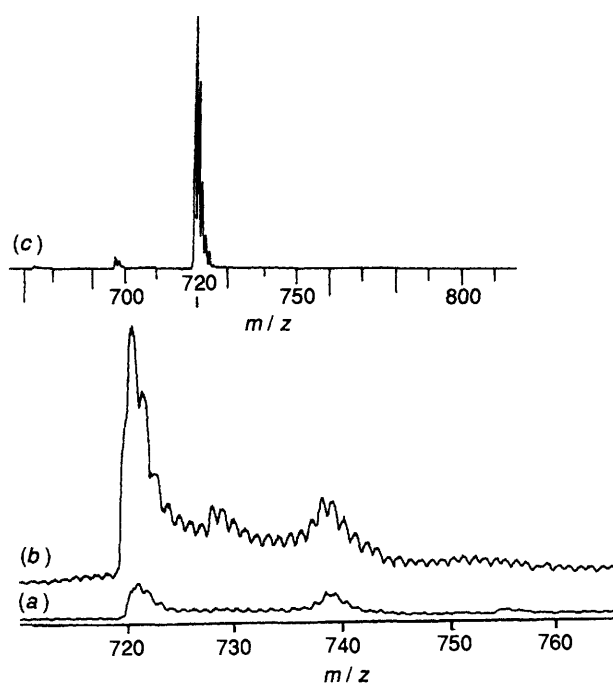
(c)

Fig. 5 Electron impact quadrupole (Ribermag R10-10C) mass spectra of Birch-reduced C_{60}: (a) at 460 °C; (b) at 460 °C after 1 min; (c) at 560 °C

operating at 35 kV. The instrument was scanned from 2000 to 50 u at 10 seconds per decade. Fig. 3 shows the mass spectrum obtained at a resolution of 5000. An even–odd intensity distribution, similar to that observed in the FTICR mass spectrum (*vide supra*) is also apparent here; proton attachment is a commonly observed phenomenon in LSIMS. It is interesting to note the complete absence of any daughter ion peak in the spectrum obtained using this sample introduction technique due to C_{60}^+. The distribution of hydrogenated products can be clearly identified from this very high resolution spectrum. Deconvolution of the underlying ^{13}C isotope fingerprint† yields the product distribution shown in column 2 of Table 1, which is in good agreement with model calculations (using Monte Carlo sampling) of the product distribution to be expected for 1,4-addition in the Birch reduction (*vide infra*).

Clearly these results are at odds with those of Haufler *et al.*,[4] who reported only two products, $C_{60}H_{36}$ as the major product, and $C_{60}H_{18}$ as a minor product. We believe that these conflicting observations can be attributed to the different mass spectrometric methods used for analysis. We have also recorded electron impact mass spectra (EIMS) of the Birch product on a Kratos MS50TC double-focusing instrument. The sample was introduced using a heated direct-insertion probe into the EI source which was initially heated to 145 °C. The probe and source were then ramped manually up to the maximum temperature attainable (source temperature maximum 310 °C, probe temperature maximum 400 °C). Fig. 4(a) shows one such spectrum obtained at a source temperature of 295 °C and a probe temperature of 390 °C. The base peak in this spectrum is now at 756 u and there is also a prominent secondary maximum in the distribution at 738 u, together with a strong peak at 720 u due to C_{60}^+. Fig. 4(b) shows another

spectrum recorded a short time later at a source temperature of 310 °C and a probe temperature of 400 °C. The distribution of polyhydrofullerene ions has now clearly shifted to lower mass and the base peak in the spectrum is now the fragment ion C_{60}^+.

On the basis of these results we argue that the radically different mass spectra obtained under the rather severe sample introduction conditions required for EI mass spectroscopic studies can be attributed to thermal decomposition of the polyhydrofullerenes.‡ In further support of this argument we have also examined the behaviour of the said fullerenes as a function of temperature using quadrupole mass spectroscopy. The spectra shown in Fig. 5 were recorded using a Ribermag R 10-10C instrument. As can be seen from the mass spectrum, near unit mass-resolution is available in the C_{60} region. After the mass spectrum had been recorded at 400 °C, when nothing was seen, the temperature was raised to 460 °C within a minute, and the mass spectrum shown in Fig. 5(a) obtained. After about a minute at this temperature the sample was observed to be decomposing, see Fig. 5(b). At higher temperatures (550 °C) the only peaks that could be detected in the mass spectrum were due to fragment ion C_{60}^+, see Fig. 5(c).

Finally, further to these experimental studies we have used Monte Carlo methods to numerically simulate the product distribution to be expected under different modes of 1,4-hydrogen addition in the Birch reduction. The results, given in column 2 of Table 1, appear to indicate that the mechanism of hydrogenation is not restricted to the 'benzene moieties' alone, which would lead to a maximum in the distribution centred on $C_{60}H_{36}$. Instead a simple mechanism involving reduction of *all* 1,3-diene groupings appears to account

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† Deconvolved data were obtained from the experimentally observed peak intensities, following background subtraction, by a least-squares fitting procedure incorporating the ^{13}C natural isotope abundances up to the $^{13}C_4{}^{12}C_{56}$ isotopomer.

‡ Fluorination of C_{60} has been reported by several groups[9–11] with somewhat conflicting results, the origin of which may also partly lie in the method of sample introduction employed for their mass spectrometric characterisation.

satisfactorily for the observed polyhydrofullerene distribution.

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