From major to minor and back—a decisive assessment of $C_{60}H_{36}$ with respect to the Birch reduction of C_{60}

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Hydrogenated fullerenes derived from the Birch reduction and from hydrogen transfer reduction of [60]fullerene have been examined by matrix-assisted laser desorption ionization; applying 9-nitroanthracene as the matrix, it has been possible to desorb and ionise the samples with such a low degree of fragmentation as to enable the establishment of the amount of hydrogen bound to the fullerene; in contrast to the currently assumed polyhydrofullerene distribution featuring $C_{60}H_{36}$ only as a minor component, evidence has been obtained which re-establishes $C_{60}H_{36}$ as the major product of the Birch reduction.

The hydrogenation of fullerenes has been achieved by a large variety of synthetic methods including the Birch reduction,[1] transfer hydrogenation,[2] reactions with elemental hydrogen,[3] reduction in metal/acid systems[4] and others.[5] Thirty-six often represents a 'magic number' for the quantity of hydrogen attached to [60]fullerene. According to semiempirical and *ab initio* SCF calculations, the thermodynamically most stable structure of $C_{60}H_{36}$ possesses T symmetry.[6] This structure was initially suggested by Taylor[7] and is characterised by four isolated benzenoid rings located at the corners of a tetrahedron. A recent X-ray investigation provides evidence for the existence of the benzenoid rings in $C_{60}H_{36}$.[8] Two isomers in a ratio of 2:1 have been found applying ^{3}He NMR[9] and their structures have been proposed to exhibit C_3 and T symmetry. The coexistence of the C_3 isomer, which is thermodynamically less stable than the T isomer, probably indicates that kinetic factors play an important role in the hydrogenation of C_{60}. It seems reasonable to assume that variations in the way the reduction is achieved can lead to the formation of alternative structures of $C_{60}H_{36}$. It has even been proposed that in the case of the Birch reduction,[1] $C_{60}H_{36}$, which is commonly referred to as the first ever synthesised fullerene derivative, is only a minor product of the obtained distribution of hydrogenated [60]fullerenes of the type $C_{60}H_x$, with x ranging from 18 to 36.[10] These conclusions were derived from mass spectrometry-based experiments in which the reaction product resulting from the Birch reduction of C_{60} has been laser-desorbed into the gas phase to be in a second step, subsequently laser-ionised. A distribution of $C_{60}H_x^+$ ions was obtained which was centred at $x = 30$ and 32 with only a minor contribution attributed to $C_{60}H_{36}$. The fact that signals due to C_{60}^+ fragment ions were entirely absent was taken as evidence for the softness of the method revealing the true distribution of the hydrogenated [60]fullerenes. A similar distribution was obtained using liquid secondary ion mass spectrometry (LSIMS) and an almost perfect fit to a theoretical distribution based on Monte Carlo calculation supported the experimental findings. The comparison with other approaches for ionization, especially when electron impact (electron ionization, EI) was used, for which the sample had to be heated to achieve evaporation, revealed a clear shift in the observed $C_{60}H_x^+$ distribution towards $C_{60}H_{36}$. However, since C_{60}^+ was also prominently observed under these conditions, it was concluded that the excitation of the sample resulted in the dissociation of the initial $C_{60}H_x$ species with x being centred at around 30 and that the observed ions with a larger hydrogen content represent more stable species which resist dissociation. Interestingly, for the transfer hydrogenation of [60]fullerene by 9,10-dihydroanthracene (DHA), $C_{60}H_{36}$ has been established beyond any doubt as the major product utilising field desorption mass spectrometry.[2] Roger, Birkett and Campbell (RBC) have recently re-examined the hydrogenated product from transfer reduction of C_{60} with DHA by matrix-assisted laser desorption/ionization (MALDI) mass spectrometry.[11] A matrix combination of 5-methoxysalicylic acid and $NaBF_4$ was found to provide the softest conditions, and a spectrum was recorded which consisted almost entirely of only one signal arising from $C_{60}H_{35}^+$, which can be taken as direct evidence for the exclusive production of $C_{60}H_{36}$. The Birch reduction[1] and the hydrogen transfer reduction[2] differ in the actual reaction mechanism. The Birch reduction proceeds *via* anionic intermediates and the transfer reduction most probably involves neutral radicals, so that the findings by RBC[11] are not necessarily in conflict with those obtained by Banks *et al.*[10] In order to reveal whether or not the two reductions lead to different product distributions, we investigated the products derived from both reactions by MALDI time-of-flight mass spectrometry. In line with recently reported experiments by others,[12] our own initial efforts to apply the above mentioned matrix combination were unsuccessful, as the desorption/ionization process was always accompanied by efficient fragmentation. The reason for this has to be seen as due to slightly differing experimental conditions from those reported originally,[11] rather than in a failure of the method as such. RBC pointed out that the wavelength of the laser light, the laser fluence and the pulse duration were of crucial importance.[11] Employing a nitrogen laser of 337 nm wavelength with a variable laser fluence, the most pronounced difference in the present experiments is the pulse duration of 3 ns, which is two orders of magnitude longer and is probably the cause of the enhanced fragmentation. Unexpectedly, a much simpler approach was found to be more suitable for the present study. Using 9-nitroanthracene (9-NA) as the matrix (using a matrix:analyte ratio of 50:1) led to conditions which allow conclusive insight. Although there exists no comprehensive screening of matrices for the analysis of fullerene derivatives by MALDI, 9-NA has been used successfully in several earlier investigations involving related compounds.[13–17] The signals obtained at the threshold for ion formation from hydrogenated [60]fullerene, derived by transfer reduction[2] from DHA for which the synthetic details have been published elsewhere,[18] are depicted in Fig. 1(a). The base peak corresponds to $C_{60}H_{35}^+$ in line with the findings reported by RBC[11] and very little fragmentation is observed. The same experiment performed with the sample derived from the Birch reduction[1] gave rise to the spectrum shown in Fig. 1(b), which is almost identical to the

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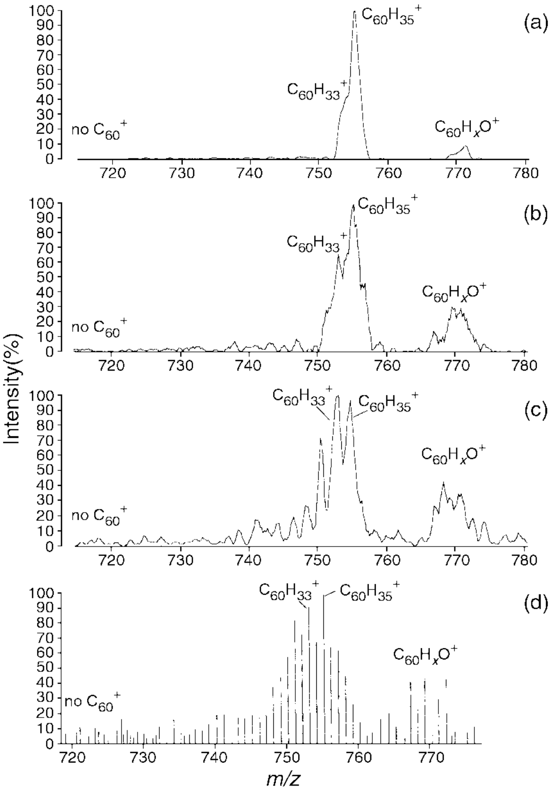

Fig. 1 (a) Threshold positive-ion MALDI mass spectrum of $C_{60}H_{36}$ derived from transfer reduction. (b) Threshold positive-ion MALDI mass spectrum of Birch-reduced C_{60}. (c) Positive-ion MALDI mass spectrum of Birch-reduced C_{60} at slightly higher laser fluence than in (b). (d) Positive-ion liquid secondary ion mass spectrum of Birch-reduced C_{60}.

spectrum in Fig. 1(a). When the laser fluence is only slightly increased, the spectrum depicted in Fig. 1(c) results. Caused by enhanced fragmentation, a clear shift of the ion distribution is observed with $C_{60}H_{33}^+$ now prevailing. Fig. 1(d) shows the liquid secondary ion mass spectrum (LSIMS) of Birch-reduced C_{60} using 3-nitrobenzyl alcohol (3-NBA) as the matrix. With $C_{60}H_{35}^+$ as the major signal and no evident C_{60}^+ peak, LSIMS confirms the MALDI findings. In all spectra, small satellite peaks are observed, arising from oxygenated species. We assume that these are indicative of a partial oxidation of the hydrogenated samples, although we have recently established[19] that oxygen transfer from 9-NA to the analyte can be very pronounced during the desorption/ionization process in MALDI. The observation of these satellite peaks does not affect the interpretation of the present findings, as these species were also observed in the work performed by Banks *et al.*[10] In contrast to the assumption that $C_{60}H_{35}^+$ results under these conditions from protonation of $C_{60}H_{34}$,[10] RCB have provided evidence, that at least in the MALDI experiments, the $C_{60}H_{35}^+$ is directly formed from $C_{60}H_{36}$.[11] A comprehensive MALDI investigation on related, organic ligand-bearing fullerene derivatives confirms that protonation is not important for the ion formation in the present experiments.[19] The observed $C_{60}H_x^+$ ions (with x representing an odd number of hydrogen atoms) are thus indicative for the neutral $C_{60}H_{x+1}$ species. In contrast, the close match reported earlier[10] for the experimental distribution and the distribution derived from a Monte Carlo simulation was based on the assumption that the odd numbered $C_{60}H_x^+$ ions would represent $C_{60}H_{x-1}$ neutrals. On the basis of the present experiments it has to be concluded that the earlier experiments suffered from the partial dissociation of $C_{60}H_{36}$. Obviously, conditions were met by which a certain amount of hydrogen was readily evaporated from $C_{60}H_{36}$ without the complete loss of all attached hydrogen atoms, suggesting soft ionization conditions and leading to a distribution of ions which do not represent the neutrals which were initially present. In this context it is interesting to note that, in line with the assumptions made by Banks *et al.*,[10] fragment ions such as C_{60}^+ are primarily the result of neutral dissociation followed by ionization, rather than caused by fragmentation of energised ions. Recent investigations into the dissociation behaviour of size-selected, hydrogenated fullerene ions reveal that cage rupture efficiently competes with hydrogen losses in these cases.[20] This means the direct formation of C_{60}^+ from $C_{60}H_{36}^+$ is unlikely.

In summary, using 9-NA as the chosen matrix for the MALDI analysis of hydrogenated fullerenes creates desorption/ionization conditions which are sufficiently free of fragmentation to allow the establishment of the hydrogen content. These findings re-establish $C_{60}H_{36}$ as the major product derived by Birch reduction of C_{60}.

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Notes and references

1 R. E. Haufler, J. Conceicao, L. P. F. Chibante, Y. Chai, N. E. Byrne, S. Flanagan, M. M. Haley, S. C. O'Brien, C. Pan, Z. Xiao, W. E. Billups, M. A. Ciufolini, R. H. Hauge, J. L. Margrave, L. J. Wilson, R. F. Crul and R. E. Smalley, *J. Phys. Chem.*, 1990, **94**, 8634.

2 C. Rückhardt, M. Gerst, J. Ebenhoch, H.-D. Beckhaus, E. E. B. Campbell, R. Tellgmann, H. Schwarz, T. Weiske and S. Pitter, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 584.

3 C. Jin, R. Hettich, R. Compton, D. Joyce, J. Blencoe and T. Burch, *J. Phys. Chem.*, 1994, **98**, 4215.

4 A. D. Darwich, A. K. Abdul-Sada, G. L. Langley, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1995, 2359.

5 N. F. Gol'dshleger and A. P. Moravskii, *Russ. Chem. Rev.*, 1997, **66**, 323.

6 L. D. Book and G. E. Scuseria, *J. Phys. Chem.*, 1994, **98**, 4283.

7 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1667.

8 A. V. Okotrub, L. G. Bulusheva, I. P. Asanov, A. S. Lobach and Yu. M. Shulga, *J. Phys. Chem. A*, 1999, **103**, 716.

9 O. V. Boltalina, M. Bühl, A. Khong, M. A. Saunders, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1475.

10 M. R. Banks, M. J. Dale, I. Gosney, P. K. G. Hodgson, R. C. K. Jennings, A. C. Jones, J. Lecoultre, P. R. R. Langridge-Smith, J. P. Maier, J. H. Scrivens, M. J. C. Smith, C. J. Smyth, A. T. Taylor, P. Thorburn and A. S. Webster, *J. Chem. Soc., Chem. Commun.*, 1993, 1149.

11 I. Rogner, P. Birkett and E. E. B. Campbell, *Int. J. Mass Spectrom. Ion Processes*, 1996, **156**, 103.

12 L. Zhou, A. A. Tuinman, R. N. Compton and A. S. Lahamer, *Electrochem. Soc. Proc.*, 1998, **98**, 493.

13 A. Gromov, S. Lebedkin, S. Ballenwag, A. G. Avent, R. Taylor and W. Krätschmer, *Chem. Commun.*, 1997, 209.

14 S. G. Penn, D. A. Costa, A. L. Balch and C. B. Lebrilla, *Int. J. Mass Spectrom. Ion Processes*, 1997, **169**, 371.

15 R. Taylor, M. P. Barrow and T. Drewello, *Chem. Commun.*, 1998, 2497.

16 M. P. Barrow, N. J. Tower, R. Taylor and T. Drewello, *Chem. Phys. Lett.*,1998, **293**, 302.

17 M. S. Al-Jafari, M. P. Barrow, R. Taylor and T. Drewello, *Int. J. Mass Spectrom.*, 1999, **184**, L1.

18 A. S. Lobach, A. A. Perov, A. I. Rebrov, O. S. Roshchupkina, V. A. Tkacheva and A. N. Stepanov, *Russ. Chem. Bull.*, 1997, **46**, 641.

19 T. Brown, N. L. Clipston, N. Simjee, H. Hungerbühler and T. Drewello, in preparation.

20 M. Möder, M. Nüchter, B. Ondruschka, G. Czira, K. Vekey, M. P. Barrow and T. Drewello, *Int. J. Mass Spectrom.*, 2000, **195**/**196**, 599.