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Hydrogen storage on fullerenes: hydrogenation of $C_{59}N^{\cdot}$ using $C_{60}H_{36}$ as the source of hydrogen

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$C_{60}H_{36}$ has been used as the source of hydrogen for the *in situ* hydrogenation of $(C_{59}N)_2$, leading to $C_{59}NH_5$ as the main reaction product identified by negative-ion mass spectrometry and providing evidence of the usage of C_{60} as a storage device for hydrogen.

The evaluation of the use of carbon nanotubes as storage devices for molecular hydrogen has been a focal point of recent investigations into potential applications of new, carbon-based materials. However, while the development of many potential applications towards their applicability has reached clearly advanced stages, the use as hydrogen storage devices seems "clouded by controversy".[1]

The material properties of hydrogenated fullerenes such as $C_{60}H_{36}$[2] are also under scrutiny and some of the features revealed so far may indicate a certain potential in the context of hydrogen storage. A variety of inexpensive and efficient methods is at hand to produce $C_{60}H_{36}$, the most prominent representative of this class of compounds.[3–5] In contrast to the attractive forces operative in connection with the storage of hydrogen on nanotubes, which are essentially weak intermolecular interactions, hydrofullerenes feature comparatively strong σ C–H bonds. This in turn raises the issue of the means whereby the stored hydrogen may be released. While accurate data on the energetics involved are sparse,[6,7] there exist clear evidence that hydrogen release is commonly observed following the activation of hydrofullerenes. In fact, the ease by which partial hydrogen loss occurs already upon comparatively gentle activation has hampered previously the assignment of the accurate number of hydrogen atoms attained on C_{60}.[8–12] Although small hydrocarbons could be detected following the thermal treatment of deutero[60]fullerenes,[13] indicating that cage rupture may play a role, there is recent evidence that the C_{60}^{+} signal observed in most mass spectra of these compounds is essentially due to a complete thermal removal of all hydrogen atoms from the neutral molecule.[14] The fact that the carbon core can be completely released from the stored hydrogen and thus be regenerated is a rare feature, as hydrocarbons normally degrade *via* C–C bond rupture.

The present report describes an experiment in which the hydrogen that was initially stored on C_{60} is released, resulting in the hydrogenation of a particular target molecule. As reactant for this reduction serves the aza-fullerenyl radical, $C_{59}N^{\cdot}$, which is readily formed by thermal decomposition of the synthetically accessible $(C_{59}N)_2$ dimer.[15,16] It is known that the reduction of $(C_{59}N)_2$ leads to two major products, namely $C_{59}NH_x$ with $x = 1$[17] and 5.[18,19] Both molecules have also been generated recently through *in situ* hydrogenation of $C_{59}N$.[20]

The latter experiments were carried out in a specially designed entrance channel to a mass spectrometer and residual organic impurities of unknown composition acted as the source of hydrogen. $C_{59}NH$ was found to be an intermediate towards the formation of $C_{59}NH_5$.[20] Computational chemistry confirmed the assumed structure of $C_{59}NH_5$.[18,19,21]

The present experiments feature the use of $C_{60}H_{36}$ as the source of hydrogen, utilizing the [60]fullerene as a storage device for hydrogen. The hydrogenation has been carried out using widely available, commercial instrumentation, applying negative-ion Desorption Chemical Ionisation (DCI) mass spectrometry. DCI is routinely available in many laboratories for the analysis of thermolabile solids and has been successfully applied to the analysis of derivatised fullerenes. For DCI, $(C_{59}N)_2$ and $C_{60}H_{36}$ were dissolved in toluene in a 1 : 1 ratio. A droplet of this solution was then placed onto a heatable Pt wire probe tip, dried and placed into the ion source of a triple sector mass spectrometer (Autospec, Micromass, Altrincham UK) of EBE configuration. E stands for electric sector and B denotes the magnet. The Pt wire was resistively heated to allow the desorption of material. The electron beam energy was 20 eV and ammonia was used as a buffer gas to promote the attachment of secondary electrons to the desorbed compounds.

The mass resolution in this experiment would not allow distinction between isobaric ions (*i.e.* ions of the same nominal mass). In order to avoid confusion between $C_{59}NH_x$ and $C_{60}H_y$ ions of the same nominal mass, a strategy has been adopted that takes advantage of the distinctly different appearance of negatively *versus* positively charged ions derived from $C_{60}H_{36}$ under the applied conditions. In the positive-ion mode, $C_{60}H_{36}$ produces signals from the molecular ion down to C_{60}^{+} on every nominal *m*/*z* value, which would complicate the identification of minor amounts of $C_{59}NH_x$ ions formed. The negative-ion mass spectrum of $C_{60}H_{36}$, however, is characterized by a sharp decline in the ion abundances between C_{60}^{-} and $C_{60}H_x^{-}$ ions where x is approximately 10. This behaviour is primarily the result of the descending electron affinities of the corresponding neutral counterparts of these anionic species. At higher masses, $C_{60}H_{18}^{-}$ may be detected, which has been recently identified as currently the highest hydrogen-containing [60]fullerene that still possesses a positive electron affinity.[22]

As a consequence of the declining abundances of $C_{60}H_x^{-}$ ions in the mass range of interest, the co-formation of even minor amounts of $C_{59}NH_x^{-}$ ions should be detectable with much higher accuracy than in the positive-ion mode. A prerequisite for this procedure, however, is that the potentially formed $C_{59}NH_x$ molecules would form long-lived negative ions, possessing lifetimes long enough to allow their detection on the timescale of the experiment. This has in fact been recently established for $C_{59}NH$ and $C_{59}NH_5$, representing the two major hydrogenation products of $C_{59}N$.[20]

Fig. 1 displays the total ion current obtained upon heating the loaded probe tip from an initial operating temperature of 150 °C to 300 °C (peak labelled A) and then up to 400 °C (peak labelled B). The mass spectra obtained in both these temperature intervals were accumulated and also displayed in Fig. 1. The mass spectrum representative for the temperature range up to 300 °C is clearly indicative for the formation of $C_{60}H_n^{-}$ ions, showing $C_{60}H_{18}^{-}$ as the base peak. Obviously, up to a temperature of 300 °C, the evaporation of $C_{60}H_{36}$ is more pronounced than of $(C_{59}N)_2$. It is well established that hydrogen loss from $C_{60}H_{36}$ occurs very efficiently already at much lower temperatures,[8] generating in the present case a hydrogen atmosphere for the reduction of $C_{59}N$, which, however, requires even higher temperatures to be efficiently evaporated from the sample holder. The efficient co-evaporation of $C_{59}N$ is achieved upon further increase of the temperature to 400 °C and the mass spectrum dramatically changes, featuring now *m*/*z* 727 as the most intense peak. It is clear from what has been outlined above that the ion abundance at *m*/*z* 727 must correspond predominantly to $C_{59}NH_5^{-}$, indicating the efficient hydrogenation of $C_{59}N$. In several control experiments without admixture of

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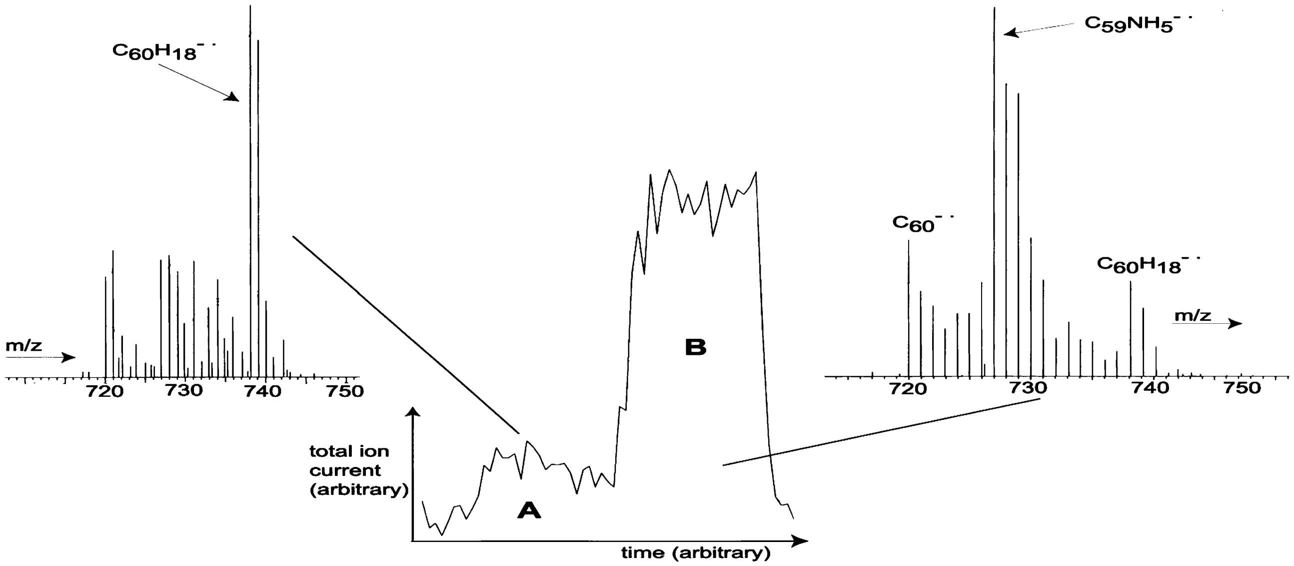

Fig. 1 Total ion current and negative-ion mass spectra for the co-evaporation of $(C_{59}N)_2$ and $C_{60}H_{36}$ at temperatures up to 300 °C (A) and 400 °C (B).

$C_{60}H_{36}$, no $C_{59}NH_5^-$ could be detected. Only $C_{59}N^-$ was observed and occasionally a minute amount of $C_{59}NH^-$ from hydrogenation by background impurities. This clearly establishes $C_{60}H_{36}$ as the source of hydrogen. Neither $C_{59}N$ nor $C_{59}NH$ are clearly identifiable in the present experiment, indicating that a sufficiently high amount of hydrogen has been liberated from $C_{60}H_{36}$, in order to drive the reaction to the higher hydrogenated $C_{59}NH_5$. The fact that hydrogenation is only observed at higher temperatures (300–400 °C) is entirely caused by the low vapour pressure of $(C_{59}N)_2$. Efficient hydrogen release from $C_{60}H_{36}$, which has the remarkable hydrogen storage capacity of 4.8 wt%, already occurs at 150 °C, the lowest temperature possible in the present set-up.

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