

# Hydrogenation of [76]-, [78]- and [84]-fullerenes: cage degradation

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The title fullerenes have been reduced under conditions (Zn, conc. HCl, toluene solution, 1 h, N<sub>2</sub>, dark, room temp.) that give C<sub>60</sub>H<sub>36</sub> from [60]fullerene and C<sub>70</sub>H<sub>36-40</sub> from [70]fullerene. Reduction of [76]fullerene gives C<sub>76</sub>H<sub>46-50</sub>, [78]fullerene gives a broader spectrum of reduction products (consistent with the diverse isomeric composition of the parent fullerene), the most abundant species being C<sub>78</sub>H<sub>36</sub> and C<sub>78</sub>H<sub>48</sub> (main component), and [84]fullerene yields mainly C<sub>84</sub>H<sub>48-52</sub>. In each case, reduction of the higher fullerenes is accompanied by cage breakdown to C<sub>60</sub>H<sub>36</sub> and C<sub>70</sub>H<sub>36-40</sub>, the relative proportions of which vary with the starting fullerene. Thus reduction of [76]fullerene gave only a trace of C<sub>70</sub>H<sub>36-40</sub>, whereas [78]fullerene gave considerably more. Reduction of [84]fullerene over an extended period (5 h) resulted in complete degradation to C<sub>60</sub>H<sub>36</sub>. HPLC separation of the hydrogenated fullerenes on a Cosmosil column (toluene eluent), showed them to elute more rapidly the larger the cage, as found previously for C<sub>60</sub>H<sub>36</sub> and C<sub>70</sub>H<sub>36-40</sub>. By contrast, on the same column and under the same conditions, the parent fullerenes elute more slowly the higher the molecular weight.

Although some hundreds of papers describe the chemistry of [60]- and [70]-fullerenes, only three studies concern the chemistry of higher fullerenes. Hawkins and Meyer reported the resolution of [76-D<sub>2</sub>]fullerene into its enantiomers through the formation of osmium derivatives,<sup>1</sup> Balch and co-workers described the isolation of an iridium complex of [84-D<sub>2</sub>]fullerene,<sup>2</sup> whilst we have observed the formation of methyl-

ene adducts of [78]- and [84]-fullerenes.<sup>3</sup> A major problem in this area of research is the very low availability of the higher fullerenes. Accordingly, hydrogenation followed by mass spectrometric analysis of the reaction products appeared to be an ideal method for obtaining some preliminary information concerning the chemistry of the higher fullerenes. In particular, the hydrogenation method which we used

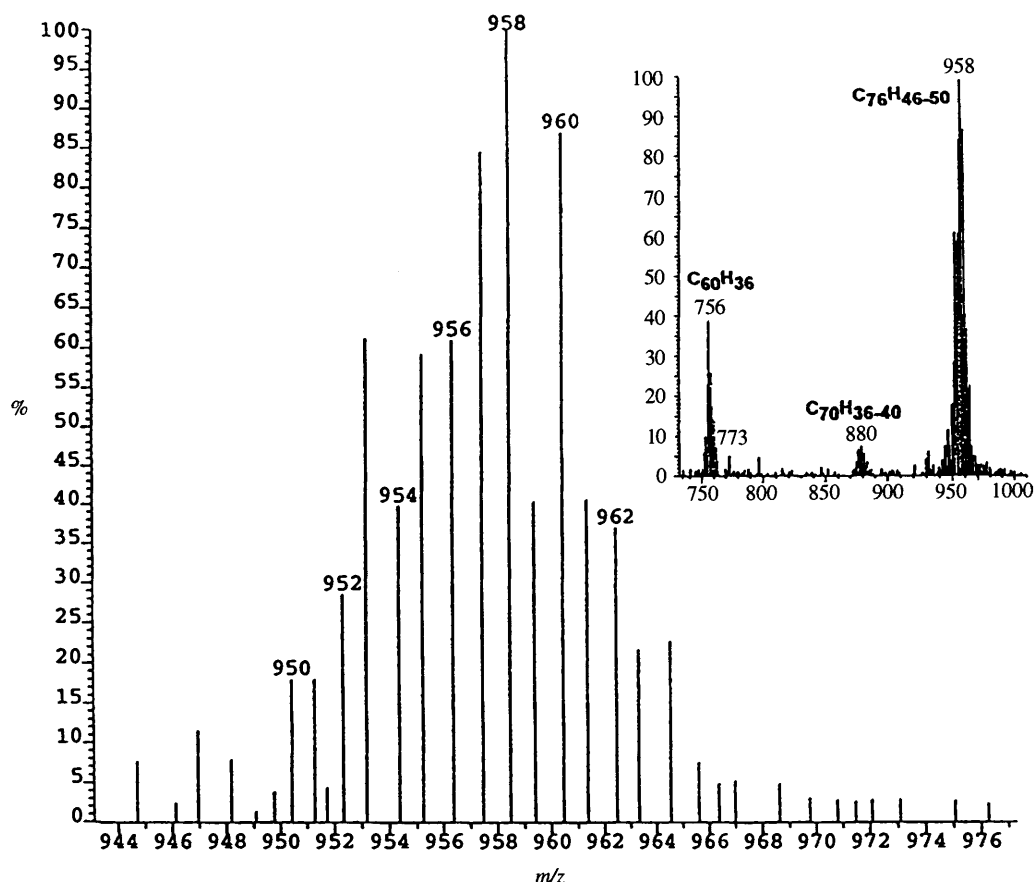


Fig. 1 Expanded EI mass spectrum of the product of reduction of [76]fullerene; inset shows the full spectrum, with the hydrogenated [60]- and [70]-fullerene products evident

previously (Zn, conc. HCl, toluene solution, 1 h, N<sub>2</sub>, dark, room temp.) is very simple and can be carried out on < 1 mg scale. Moreover, if the reaction products are analysed rapidly by mass spectrometry (EI conditions), reliable data may be obtained without interference from oxidative degradation of the products.<sup>4</sup>

### Experimental

Higher fullerenes, available to us from a previous study,<sup>5</sup> had been stored in the dark and open to air for three years. The

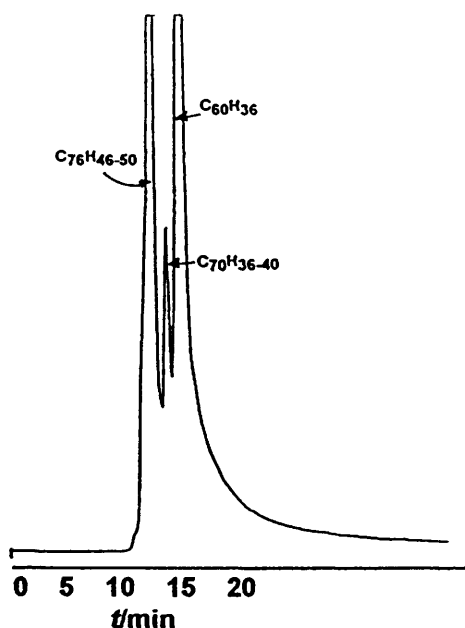


Fig. 2 HPLC trace of the products of reduction of [76]fullerene

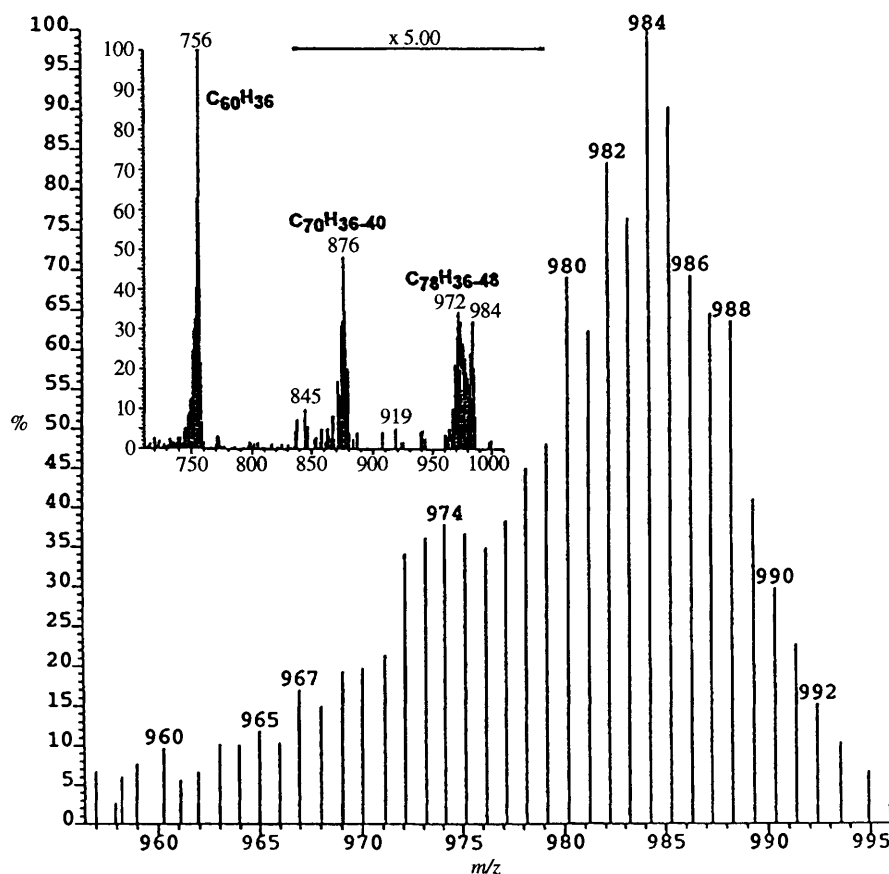


Fig. 3 Expanded EI mass spectrum of the product of reduction of [78]fullerene; inset shows the full spectrum of a duplicate run with the hydrogenated [60]- and [70]-fullerene products evident

samples were repurified, using improved HPLC (high pressure liquid chromatography) conditions (Cosmosil 4.5 mm × 25 cm column, toluene eluent), and each sample was *entirely* free of either [60]- or [70]-fullerene. Notably, a significant proportion of the original [84]fullerene would no longer dissolve in carbon disulfide, a carbonaceous residue remaining, indicating that the long-term stability of [84]fullerene is limited.

Each fullerene (*ca.* 1 mg) was dissolved in toluene and reduced as described previously.<sup>4</sup> The solutions lost colour rapidly and became completely colourless after 1 h. The products were analysed by EI mass spectrometry (70 eV) immediately after work-up. As each product showed substantial decomposition to generate hydrides of [60]- and [70]-fullerene, and to confirm that this was not taking place during mass spectrometric analysis, the samples were also analysed by HPLC using the conditions (4.5 mm × 25 cm Cosmosil column, toluene eluent, 0.25 ml min<sup>-1</sup> flow rate, 23 bar, UV detector at 285 nm), previously employed<sup>4</sup> for the analysis of the products of hydrogenation of [60]- and [70]-fullerene. The retention times of the hydrides derived from [60]-, [70]-, [76]-, [78]- and [84]-fullerenes were 15.1, 13.9, 12.4, 12.1 and 11.9 min, respectively.

### Discussion

#### Reduction of [76-D<sub>2</sub>]fullerene

The mass spectrum of the product obtained after 1 h reaction time is shown in Fig. 1. There is a spectrum of reduction products, the most intense even-mass ions corresponding to C<sub>76</sub>H<sub>44</sub>, C<sub>76</sub>H<sub>46</sub> (main) and C<sub>76</sub>H<sub>48</sub> at 956, 958 and 960 amu, respectively. The nature of the species giving the most intense ion is somewhat dependent upon the temperature of the DCI probe, and at lower probe temperatures C<sub>76</sub>H<sub>46</sub> dominates. In a duplicate run, the main species were either C<sub>76</sub>H<sub>46</sub>, C<sub>76</sub>H<sub>48</sub> or C<sub>76</sub>H<sub>50</sub>, depending upon the probe temperature.

Both runs show common features in that (i) C<sub>60</sub>H<sub>36</sub> is a

major degradation product and (ii)  $C_{70}H_{ca.40}$  is a very minor one. HPLC analysis (Fig. 2) confirmed that these products are present in the reduced mixture and are not an artefact of EI mass spectrometry. Previously we have found that, under EI conditions, the larger fullerene cages fragment to [60]- and [70]-fullerenes. The present work shows that this degradation can occur during reduction and this fact must be taken into account in future work. The degradation is confirmed in the reduction of the other fullerenes described below.

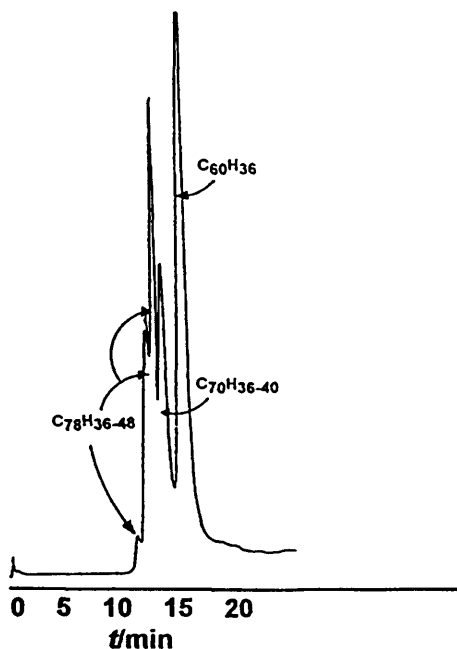


Fig. 4 HPLC trace of the products of reduction of [78]fullerene

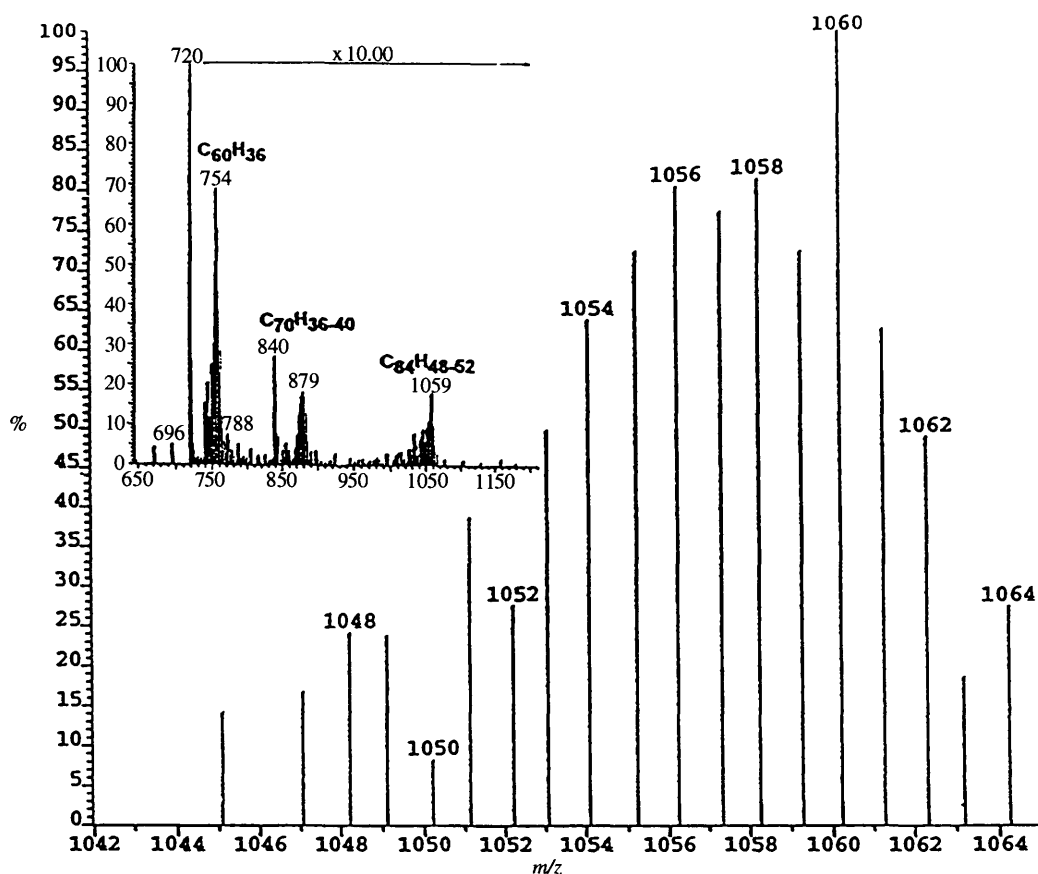


Fig. 5 Expanded EI mass spectrum of the product of reduction of [84]fullerene; inset shows the full spectrum of a duplicate run with the hydrogenated [60]- and [70]-fullerene products evident

#### Reduction of [78- $D_3$ , $C_{2v}(I)$ and $C_{2v}(II)$ ]fullerenes

In contrast to [76]fullerene reduction, a wider spectrum of reaction product species (ranging from *ca.*  $C_{78}H_{34}$  to  $C_{78}H_{54}$ ) was obtained here. The maximum ion intensities occurred for  $C_{78}H_{36}$  (972 amu) and  $C_{78}H_{48}$  (984 amu). The mass spectra for two separate runs are shown in Fig. 3 and the appearance of two maxima in the ion intensities are evident in each case. This result is consistent with the fact that [78]fullerene is a mixture of three components and these are likely to have different regiochemistry as predicted, for example, in bromination.<sup>6</sup> The reduction is accompanied by cage fragmentation, but here reduced [70]fullerene is a much more significant component than in [76]fullerene reduction. It will be interesting to see, when larger amounts of these fullerenes become available, if this pattern is general; if so, it could throw some light on the way in which the higher fullerene cages are assembled.

The HPLC trace for reduced [78]fullerene (Fig. 4) reveals the presence of two main components (with a trace of a third) due to reduced [78]fullerene, together with  $C_{60}H_{36}$  and  $C_{70}H_{36-40}$ . The HPLC trace also shows that the latter species is present in higher concentration than in the product from [76]fullerene reduction (Fig. 2).

#### Reduction of [84- $D_2$ and $D_{2d}$ ]fullerenes

The main products are  $C_{84}H_{48-52}$ ,  $C_{84}H_{52}$  giving the most intense peak, as indicated in Fig. 5 which shows the spectra from two separate runs. On raising the temperature of the probe to 420 °C, the main component present was  $C_{84}H_{40}$  suggesting that this may be a particularly stable species. It may of course derive from only one of the two main isomers of [84]fullerene that are present initially.<sup>5</sup> As in the case of the reductions of the other higher fullerenes, both  $C_{60}H_{36}$  and  $C_{70}H_{36-40}$  are produced through degradation, and were shown to be present in the reaction mixture by HPLC. The HPLC trace (Fig. 6) indicates that there are two distinct reduced [84]fullerene

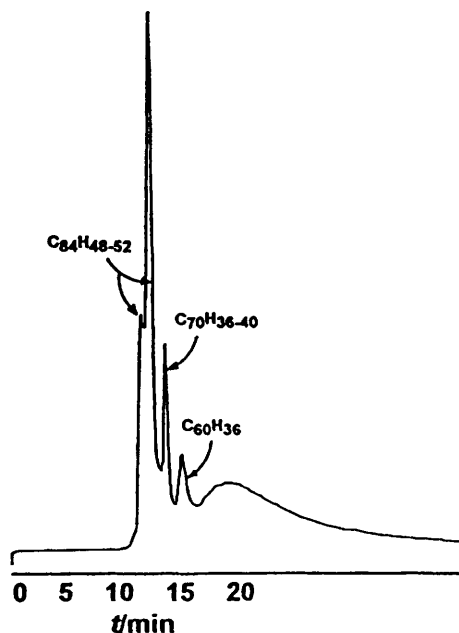


Fig. 6 HPLC trace of the products of reduction of [84]fullerene

species present, but further work on much larger samples would be needed to confirm this.

The occurrence of degradation during reduction was confirmed by allowing the reaction to proceed for 5 h. At this point the mass spectrum showed only the presence of hydrogenated [60]- and [70]-fullerenes, as did the HPLC trace (Fig. 7).

#### HPLC retention times

The retention times of the hydrides decrease the larger the fullerene, and thus the elution order is the reverse of that found for the parent fullerenes. The retention times are also less than for the parents; these are 8.3, 16.8, 19.6, 21.3 and 26.1 min, for [60]-, [70]-, [76]-, [78]- and [84]-fullerenes, respectively, at 1 ml min<sup>-1</sup> flow rate (which lowers the retention time by a factor of ca. 4, compared to the conditions used in the present study). These differences make the separation of the hydrogenated species from the parent fullerenes very easy, increasingly so as the fullerene becomes larger.

#### Acknowledgements

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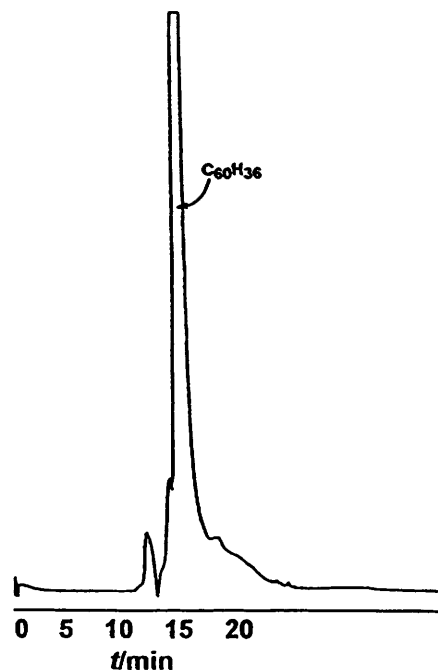


Fig. 7 HPLC trace of the products of extended reduction (5 h, see text) of [84]fullerene

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