

## NO<sub>2</sub> Adducts of C<sub>60</sub>: Synthesis of Polynitro–Polyhydroxy Fullerenes

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C<sub>60</sub> is nitrated by multiple addition of NO<sub>2</sub>; the product isomerizes partly to the nitrito form with subsequent hydrolysis by atmospheric moisture to yield nitrofullerols consisting of 6–8 nitro and 7–12 hydroxy groups per C<sub>60</sub>.

Buckminsterfullerene, C<sub>60</sub>, has stimulated intense interest.<sup>1–8</sup> Herein, we report the polynitration of C<sub>60</sub>.

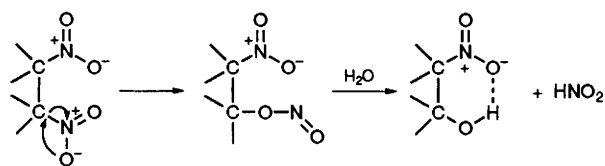
NO<sub>2</sub> gas† was passed through a toluene solution of C<sub>60</sub>,‡ resulting in a colour change to deep orange within 5 min at ambient conditions. Addition of an excess of light petroleum (40–60 °C) or *n*-hexane precipitated a yellow–brown solid **1** in high yield, with an average 6–8 nitro and 7–12 hydroxy groups per C<sub>60</sub> molecule (elemental analyses of **1**). IR (Fig. 1) of the solid showed typical NO<sub>2</sub> vibrations at 1560, 1336 and 809 cm<sup>-1</sup>. Additionally, a broad vibration (*ca.* 3400–3250 cm<sup>-1</sup>) is assignable to ν(OH) and a band centred at 1050 cm<sup>-1</sup> may be due to coupled ν(C<sub>n</sub>–O).

**1** is unstable in air and slowly loses its nitrogen content (completely after six weeks). It is soluble in organic polar solvents and sparingly soluble in water giving a pale-yellow solution which responded positively with Griess's reagent<sup>10</sup> confirming the presence of NO<sub>2</sub><sup>-</sup>. IR spectroscopy (Fig. 1) showed a weak vibration at 1624 cm<sup>-1</sup> which may be due to the presence of the ν(NO) of the nitrito group. This was confirmed by the absence of this band from the IR spectrum of a vacuum dried, washed sample of **1**. The band did, however, reappear on ageing. In the course of the nitration some mixed nitro–nitrito adducts may be formed, which rapidly hydrolyse in the atmosphere. However, the nitro group is isomerised to a nitrito group, which was confirmed by Griess's reaction by continuous washing at several intervals for days with water. This conversion is apparently a kinetically controlled process.§ These observations suggest the conversion as shown in Scheme 1. The appearance of ν(OH) around 3250 cm<sup>-1</sup> thus may be due to hydrogen bonding. The XPS spectrum of **1** (Fig.

2) shows the presence of a nitro group (N 1s B.E. at 406 eV with respect to C 1s B.E. 285.5 eV).

The radical nature of the NO<sub>2</sub> addition in the synthesis of **1** is observed by EPR. A very broad EPR spectrum at room temp. which did not saturate even at 200 mW microwave power (Fig. 3) suggests the formation of an intermediate of a [C<sub>60</sub>(NO<sub>2</sub>)<sub>5</sub>]<sup>•</sup> type radical.<sup>7,¶</sup>

The FAB mass spectrum of **1** did not show any molecular ion peak. Instead, an intense peak for C<sub>60</sub> was observed along with its fragments with the loss of C<sub>2</sub> units ranging from C<sub>58</sub> to C<sub>50</sub> (Fig. 4). *m/z* 737, 754, 768, and 805 corresponding to C<sub>60</sub>OH, C<sub>60</sub>(OH)<sub>2</sub>, C<sub>60</sub>O<sub>3</sub> and C<sub>60</sub>(OH)<sub>5</sub> could be identified. Under the ionisation conditions of FAB mass spectroscopy pure C<sub>60</sub> did not show any fragmentation with the loss of C<sub>2</sub> units. This could be due to oxidative degradation.



Scheme 1

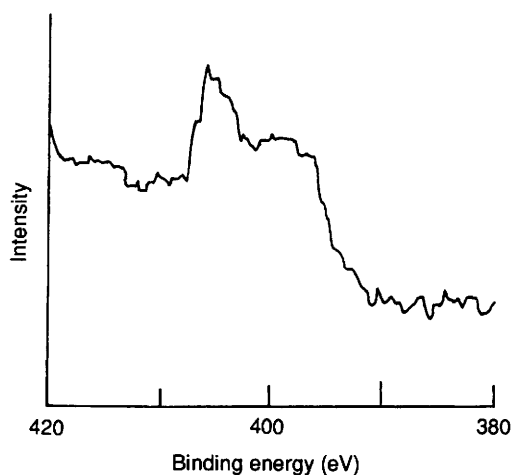


Fig. 2 XPS spectrum of **1** in the range 380–420 eV using PE/ESCA-SAM-550 spectrometer

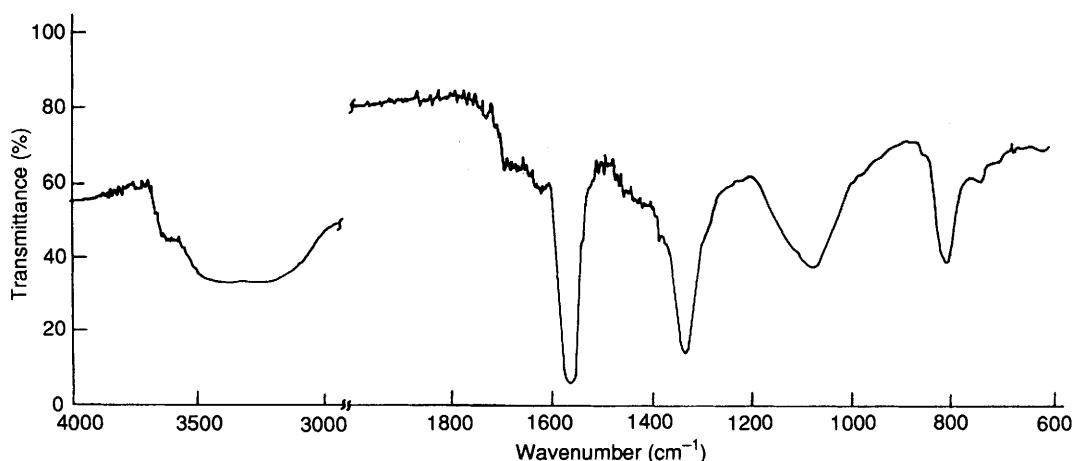
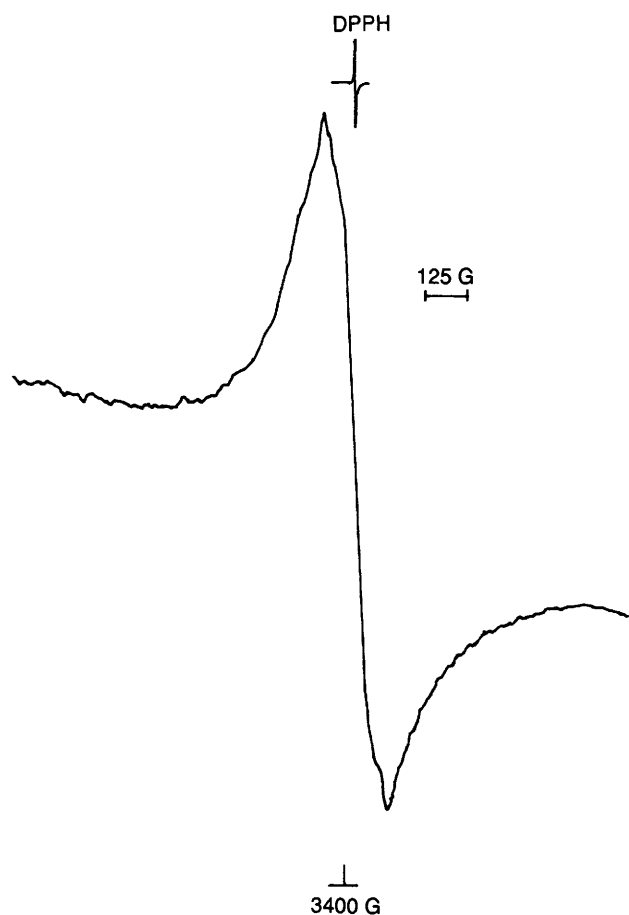


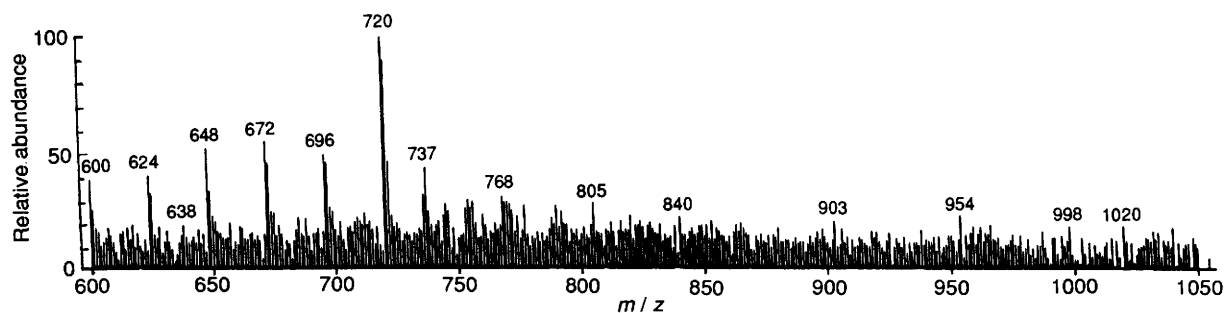
Fig. 1 IR spectrum of nitrofullerols in KBr using PE-1320 IR spectrometer

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**Fig. 3** Room temp. EPR spectrum (Varian E-109 spectrometer) at 200 mW microwave of a solution of  $C_{60}$  in toluene with  $NO_2$  at the initial reaction stage when the purple colour just changed. The solution was evacuated prior to EPR measurement to remove any unreacted  $NO_2$ .



**Fig. 4** Part of the FAB mass spectrum of nitrofullerols using a JEOL SX 102/DA-6000 mass spectrometer with argon in a *m*-nitrobenzyl alcohol matrix

### Footnotes

† Generated by reacting  $NaNO_2$  and  $FeSO_4$  in aqueous  $H_2SO_4$  and mixing the gas with air.

‡  $C_{60}$  was isolated from a home-made reactor by resistive heating and purified by column chromatography.<sup>9</sup>

§ The intensity of the dye colour (Griess's test) increases with time (h) in water but on quick washing (min) of the product the centrifugate turns pale. This gives an idea of the time required for hydrolysis.

¶ A blank experiment did not give any EPR signal for  $NO_2$  under identical conditions.

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