# Formation of Fullerols *via* Hydroboration of Fullerene–$C_{60}$

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Reaction of fullerene–$C_{60}$ with an excess of $BH_3$–THF complex followed by hydrolysis with either glacial acetic acid, sodium hydroxide/hydrogen peroxide or sodium hydroxide gives water soluble fullerols; oxidation of initially formed C–H bonds is believed to accompany the reaction.

Fullerenes are closed cage alkenes capable of undergoing a wide variety of additions.[1] The attachment of hydroxy groups to fullerene–$C_{60}$ by various methods was described recently,[2,3] and involved: (*a*) reaction with mixed nitric acid–sulfuric acid followed by basic work-up (believed to involve nucleophilic substitution by OH of the initial nitronium adduct); (*b*) reaction with nitronium borofluoride and a carboxylic acid, followed by basic hydrolysis of the nitro-organocarboxylated fullerene intermediate; (*c*) hydrolysis of epoxides formed by reaction of fullerene–$C_{60}$ with MCPBA; (*d*) reaction with solid KOH under vacuum. The IR spectra of the products obtained under conditions (*a*) and (*b*) are reproduced in Figs. 1(*a*) and 1(*b*); notable features include the absence of C–H stretching bands (consistent with the expected product), and the strong broad absorptions at 3424, 1595, 1392, 1084, *ca.* 470 $cm^{-1}$ [conditions (*a*)], and 3432, 1590, 1380, 1045, and 600 $cm^{-1}$ [conditions (*b*)]. LSIMS mass spectrometry indicated that up to *ca.* thirty hydroxy groups may be attached to the cage, although the average incorporation was about twenty.

As part of an investigation of additions to fullerenes we studied hydroboration of fullerene–$C_{60}$, using an excess of $BH_3$–THF. Given the normal behaviour of organoboranes, we anticipated that the intermediate would react with $H_2O_2$–NaOH to produce fullerene–$C_{60}$ possessing adjacent H and OH groups, and that treatment with HOAc would generate extensively hydrogenated fullerene–$C_{60}$. We were encouraged in this latter expectation by the report that reaction of 2 equiv. of $BH_3$–THF with fullerene–$C_{60}$ followed by decomposition by HOAc gave $C_{60}H_2$,[4] a result which we readily reproduced. However, the outcome of our experiments was unexpected; both reactions give a product which is effectively identical to that obtained from the hydroxylations (*a*)–(*c*) described above. The implication is that C–H bonds on the fullerene cage are readily oxidised to C–OH bonds. We believe that allylic oxidation (known to be catalysed by single oxygen,[5] of which fullerene–$C_{60}$ is a potent producer[6] may occur subsequent to initial formation of the C–H bond. This conclusion has implications with regard to the generation of some derivatives of fullerenes.

When an excess of 1 mol $dm^{-3}$ $BH_3$–THF complex (0.6 ml, 0.6 mmol) was added to a solution of fullerene–$C_{60}$ (35 mg, 0.049 mmol) dissolve in dry toluene (50 ml), a rapid colour change from magenta to brown occurred. The reaction mixture, stirred for 2–3 h, became increasingly brown owing to precipitation of a solid, [assumed to be the intermediate $C_{60}(HBH_2)_n$], leaving the supernatent toluene colourless. Intermediates with either two, or three fullerene–$C_{60}$ molecules attached to a single boron can reasonably be ruled out on the grounds of steric hindrance.

The IR of some of the intermediate, removed by filtration and recorded after only brief contact with air, shows a strong absorption at 3212 $cm^{-1}$, superimposed upon a broader band at higher wave number, an intense broad band at 1451 $cm^{-1}$, and less intense bands at 1197 (sharp) and 831 $cm^{-1}$ (broad). Only a very weak C–H stretching band at 2956 $cm^{-1}$ is evident, and on prolonged standing in air, this disappeared, the other bands remaining effectively unaltered. Since phenylboric acid (benzeneboronic acid) shows broad intense bands at 3275 and 1360 $cm^{-1}$ (the latter due to B–O stretch[7]) our results suggest that the intermediate is of the form $C_{60}(OH)B(OH)_2$, arising from oxygen insertions.

Solutions of hydrogen peroxide (14 ml, 27%) followed by sodium hydroxide (10 ml, 10%) were added to the intermediate, and the mixture when stirred for 3 h, changed from brown to orange. It was allowed to settle overnight, and the toluene layer was removed to leave a yellow–orange aqueous layer, together with a brown precipitate, which was separated by filtration. The precipitate gave the IR shown in Fig. 2, (bands at 3430, 1631, 1385, *ca.* 1090 and 450–550 $cm^{-1}$), commensurate with a fullerol. The relative band intensities at 1631, 1385 and 1090 $cm^{-1}$ are somewhat batch-dependent, but the similarity to the spectra shown in Figs. 1(*a*),(*b*) is most striking. Other notable features are the absence of C–H stretching bands, and the variability of the position of the lowest wavenumber band, (as in the work described in ref. 1).

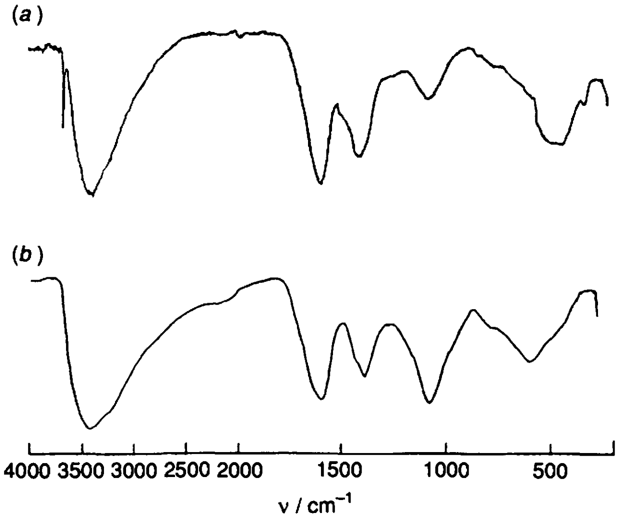

**Fig. 1** (*a*) IR Spectrum of the product of reaction of $C_{60}$ with nitric acid–sulfuric acid followed by base.[2] (*b*) IR spectrum of the product of reaction of $C_{60}$ with $NO_2^+BF_4^-$ followed by basic hydrolysis.[2]

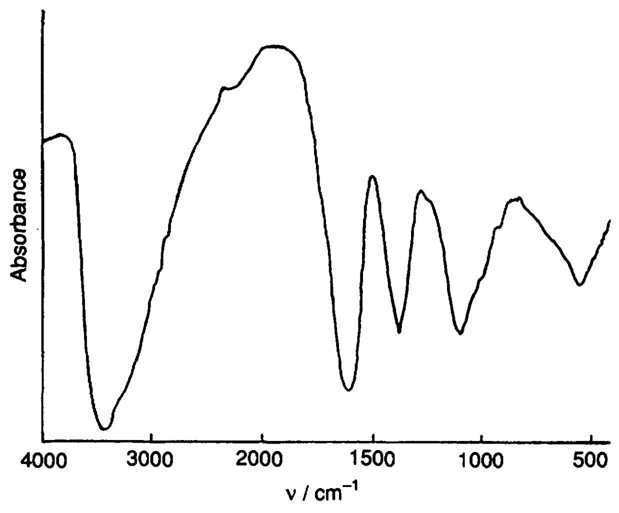

**Fig. 2** IR Spectrum of the product of reaction of $C_{60}$ with diborane (excess) followed by $H_2O_2$–NaOH

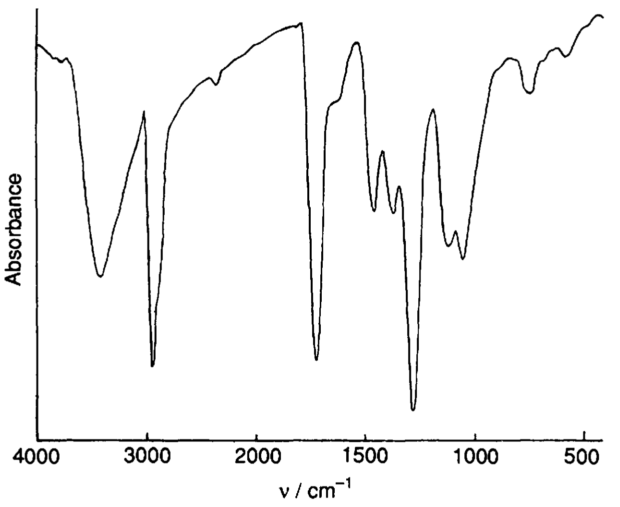

**Fig. 3** IR Spectrum of the product of reaction of $C_{60}$ with diborane (excess) followed by HOAc, under an atmosphere of nitrogen

Addition of the aqueous layer to methanol resulted in an orange–brown precipitate, which was washed several times with methanol so as to remove some of the sodium borate byproduct; further separation was achieved by centrifugation. An IR spectrum showed this precipitate to be essentially the same as the dark-brown material. Both materials were soluble only in $Me_2SO$, pyridine, water (slightly), and hydrochloric acid, this latter being also observed by the Exxon group.[2] The $^1H$ NMR spectrum of a solution in MeSO showed an intense band at δ 3.4, but this was largely due to water in $Me_2SO$ which is difficult to remove. The presence of water was confirmed by the addition of TFA, which caused the expected 2.3 ppm downfield shift. Microanalysis of samples of this material gave O/C values of 0.31–0.47; these are subject to considerable error because of the difficulty in removing all sodium borate from the (water-soluble) samples. Nevertheless they indicate that a substantial number of the cage sites are occupied, as also found in the fullerols produced by nitration.[2]

Fullerene–$C_{60}$ in toluene was reacted with 2 equiv. of $BH_3$–THF for 3 h, followed by stirring for 2 h with glacial acetic acid. The separated toluene layer was washed (water, sodium bicarbonate) and dried. The IR of the toluene-soluble material differed from that given in Fig. 2 only in showing C–H stretching bands and much stronger O–H stretching bands; the relative intensities of these bands varied from run to run, suggesting that a mixture of products is formed. The $^1H$ NMR spectrum showed a singlet at δ 5.88, ($C_6D_6$) confirming (*cf.* ref. 4) that $C_{60}H_2$ was formed. (We also observed singlets at δ 6.08 and 6.03 but discussion of these is deferred.) Repeating this reaction using 30 equiv. of $BH_3$–THF with stirring over 19 h and hydrolysis (HOAc, 3 h) gave a product showing the very strong O–H bands in the IR, but only very weak C–H stretching bands. The IR of the residual solid that had been washed with dichloromethane and toluene was virtually identical to Fig. 1(*b*). The material dissolved in solvents as described above for fullerols, and also in base.

In order to confirm the presence of the hydroxy groups, we adopted the esterification method used by the Exxon group.[2] They employed alkanoyl chlorides and observed a peak in the IR at 1720–1740 cm$^{-1}$, coupled with a change to solubility in organic solvents and insolubility in water. We esterified with benzoyl chloride in dichloromethane, catalysed by triethylamine. The product gave in the IR a peak at *ca.* 1730 (C=O) and 1600 cm$^{-1}$ (typical of benzoates) and also a peak at 1788 cm$^{-1}$. Whilst this latter absorption suggested lactone formation (a mechanism for which process would be hard to conceive), heating the sample under vacuum caused the peak to slowly disappear. We believe therefore that it arises from acid chloride trapped in the fullerene lattice; similar trapping of solvents is a well-established feature of fullerene behaviour.[8] The heated material gave a multiplet at δ 7.3–7.5 (ArH) in the $^1H$ NMR and a singlet at δ 162.3 in the $^{13}C$ NMR (CO), confirming benzoate formation.

Further experiments confirmed that reaction with oxygen (at least in part) takes place during hydroboration. Two runs were performed in parallel using an excess of diborane–THF; one under nitrogen at all stages, the other in air. The sequence of colour changes that accompanied the reactions were significantly different, moreover only a small amount of precipitate formed on adding diborane to the toluene solution of the fullerene under nitrogen. The reaction products were quenched with acetic acid, washed with water, sodium carbonate, and water, and the resultant brown aq. toluene solutions/suspensions concentrated to dryness. The IR spectrum for the product of the reaction carried out in air is again similar to that shown in Fig. 2; minor differences probably reflect the degree of reproducibility of the process at present. The spectrum of the product of reaction carried out under nitrogen (Fig. 3) is quite different, and shows now the expected strong C–H stretching bands. However, OH groups (of unclear origin) are also present, but they are less intense relative to the rest of the spectrum as compared with reactions carried out in air. There are also strong bands at 1720 and 1280 cm$^{-1}$, which could not removed by baking, and so are unlikely to be due to occluded acetic acid, and suggest the presence of an ester. The band at 1720 cm$^{-1}$ can also be discerned in the other spectra in which C–H stretching bands are evident.

Research on fullerols presents a considerable challenge because these derivatives have low solubility in common organic solvents, are difficult to separate from inorganic materials, and degrade readily during mass spectrometry.

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