Multi-hydroxy Additions onto C_{60} Fullerene Molecules

Long Y. Chiang,* John W. Swirczewski, Chang S. Hsu, S. K. Chowdhury, Steve Cameron and Kathy Creegan
Corporate Research Laboratory, Exxon Research and Engineering Company, Annandale, NJ 08801, USA

An efficient aqueous acid chemistry for the preparation of fullerols, consisting of 14–15 hydroxy moieties in an average structure, from C_{60} molecules is described.

Recent macroscopic isolation of the unusual structural skeleton of fullerene carbon clusters[1] has initiated intensive research activities aimed at addition across the high order bonds of fullerene molecules to give derivatives with tertiary carbons. These reactions include hydrogenation,[2] fluorination,[3] photochemical oxygenation,[4] methylation,[5] osmylation,[6] radical addition,[7] chlorination[8] and diphenyl carbene addition.[9] The creation of polar functionality on fullerene molecules from a bulk reaction, involving covalent carbon–hydroxy bonds, remains unknown. Here we report the first synthesis of fullerols **1** as polyhydroxylated fullerene derivatives.

We found that the aqueous acid chemistry is an efficient method to introduce multiple hydroxy groups onto fullerene molecules.[10] The chemistry produces hydrated fullerols in a high yield (more than double the quantity of starting materials was obtained). Either pure C_{60} or a mixture of C_{60} (84%) and C_{70} (16%) in an aqueous acid medium containing sulfuric acid (40% by volume of conc. H_2SO_4) and nitric acid (40% by volume of conc. HNO_3) at different temperatures was used in the reaction. Without nitric acid only a low yield of fullerol related products was obtained. The reaction was found to proceed most efficiently at temperatures between 85 and 115 °C using potassium nitrate as a precursor for nitric acid. The completion of reaction was easily determined when the reaction mixture became a clear yellowish-brown solution, indicating a high solubility of polyhydroxylated fullerene products **1** in the acidic aqueous medium. After the reaction was completed, the acid solution was diluted with water and filtered through celite to remove any unreacted fullerene particles. Neutralization with NaOH in order to precipitate products followed; full precipitation was achieved at $pH > 9.0$. The resulting fine amorphous brown solid product was found to be moderately soluble in water and very soluble in acidic water at $pH < 5.0$. In general, the partial removal of water from hydrated products in vacuum at 50 °C affords a brittle brown solid with a slightly lower solubility in water. However, its solubility in acidic water remains unchanged.

Only a trace amount of starting C_{60} was recovered from this hydroxylation reaction; which was attributed to the partially hydroxy-substituted fullerene intermediate having a higher solubility in acidic water than unreacted fullerenes themselves. Thus, the reaction tended to continue onto the intermediate until completion. Elemental analysis of samples from several different batches showed a high oxygen : carbon ratio of 0.4 : 0.5 with only a trace quantity of nitrogen (<0.6% by mass). Because of the high compatibility of polyhydroxylated fullerene derivatives **1** with sodium sulfate in aqueous solution, the product often contained one to several sodium sulfate molecules per fullerene derivative in addition to water from the workup procedure. Further purification by redissolving them in dilute hydrochloric acid (0.1 mol dm^{-3}), followed by reprecipitation after neutralization with NaOH, reduced the sodium sulfate content to a minimum level of less than 0.1 molecule per fullerene derivative. Complete removal of sodium sulfate can be achieved by repeating the above described procedure of washing the product with dilute NaOH solution.

The IR spectrum of fullerols clearly indicates the disappearance of all C_{60} fullerene characteristic peaks; it shows a very strong hydroxy absorption band at 3424 cm^{-1} and three broad absorption bands centred at 1595, 1392 and 1084 cm^{-1}. The broad absorption band is presumably owing to the heterogeneous nature of the product. Several conventional soft ionization techniques have been used for the mass spectrometry study of fullerol molecules but no molecular ions of the products were captured. For example, when desorption electron capture ionization technique was used, only C_{60} and

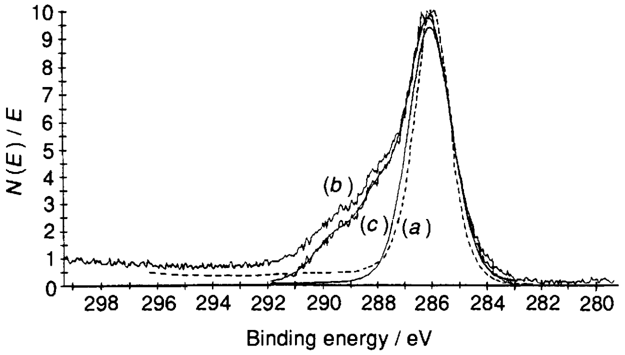

Fig. 1 XPS spectrum of the C_{1s} binding energy of fullerols **1** (*a*), C_{60} fullerene (*b*) and the curve-fitting analysis for non-oxygenated carbons (*c*) in fullerols showing higher oxidation states of carbons in (*b*)

C_{70} anions were detected in the spectrum. Since C_{60} and C_{70} fullerenes themselves are are not water soluble,† the presence of C_{60} and C_{70} anions observed in the negative ion desorption chemical ionization is apparently a result of thermal decomposition of fullerols occurring during the desorption process. The spectrum is also indicative of the products being C_{60} derivatives.

X-Ray photoelectron spectroscopic (XPS) measurement of fullerol **1** gave mainly C_{1s} (58%) and O_{1s} (35%) peaks. There were no detectable peaks for N_{1s} or S_{2p} binding energy in the XPS spectrum, indicating no incorporation of nitro (from nitric acid) or sulfonyl-analogue (from sulfuric acid) functional groups in the fullerol structure. Since there were no carbon containing chemical reagents or solvents used in the reaction, the carbon peak in the spectrum should correspond solely to fullerene derivatives. Fig. 1 shows the overlay of the C_{1s} binding energy of fullerols [curve (*b*)] and the C_{60} fullerene [curve (*a*)], which peaks at 285.9 eV with a full width at half maximum (FWHM width) of 1.49 eV. The slight shift of peak position to the higher energy from the normal C_{1s} binding energy at about 285 eV for hydrocarbons reveals that these samples were homogeneously charged. Interestingly, we observed a clear deviation of the C_{1s} peak of fullerol from that of C_{60}. The large shift indicates a high percentage of carbons in fullerol arising from a higher oxidation state than that of fullerene carbons. Simple curve-fitting analysis of the fullerol carbon peak indicates the presence of more than two differerent oxidation states of carbons, assuming that the first peak [curve (*c*)] matches with the lower binding energy region of the experimental curve. With fullerol solids of a heterogeneous composition, a slightly larger FWHM width of about 1.85 eV for the peak was expected. Based upon this procedure of analysis, we have assigned the absorption with a binding energy at 286.1 eV (68%) to non-oxygenated carbons and the remaining absorptions (32%) to carbons with a higher oxidation state. These higher oxidation state carbons spread over a range of about 4 eV in the spectrum, which is too broad to account for monooxygenated carbons such as etheral or hydroxylated carbons alone. It indicates the existence of a certain quantity of dioxygenated carbons such as carbonyl (C=O), ketal (RO–C–OR) or hemi-ketal (RO–C–OH) carbons in the fullerol structure. Owing to the lack of carbonyl absorption bands in the IR spectrum of fullerols and the low probability of ketal formation on C_{60}, we suggest that carbon atoms with the highest oxidation state in fullerols **1** are attributed to the hemi-ketal functionality.

A conventional chemical method was used to substantiate the hydroxy functional groups in fullerols by carrying out the esterification reaction with alkanoyl chlorides and verifying the carbonyl absorption band in the IR spectrum of resulting products. In this case, the reaction was performed at 85 °C in either dimethylformamide solution using 5-bromovaleryl chloride as a reagent or tetrahydrofuran solution with 4-bromobutyric acid in the presence of carbodiimide to afford partially esterified fullerols **2** or **3**, respectively. Both compounds **2** and **3** show a significant solubility change from water to organic solvents. A clear ester carbonyl absorption at 1720–1740 cm^{-1} was observed in the infrared spectrum of solids **2** and **3**.‡ Both elemental analysis and X-ray photoelectron spectroscopic measurement of the compound **2** gave a carbon : bromine ratio of 29 indicating, on average, two and a half 5-bromovaleryl ester substitutions per C_{60} molecule. The hydroxy content of ester **2** was characterized by ^1H NMR spectroscopy. The spectrum {Fig. 2(*a*) in [$^2H_6$]acetone} showed three groups of carbon proton peaks centred at δ 1.9, 2.9 and 3.7 corresponding to protons on C-3 and C-4 carbons, C-2 carbon (α carbon) and C-5 carbon of the 5-bromovaleryl ester group, respectively. The hydroxy proton peak centred at δ 3.3 was verified and removed by the deuterium exchange with D_2O as shown in Fig. 2(*b*). Even though the three different types of protons between δ 2.5 and 4.0 displayed a certain degree of overlap, we were able to estimate a ≈1.2 : 1 intensity ratio of hydroxy protons : combined protons at C-2 and C-5 carbons from the proton integration. This corresponds to a ratio of the number of hydroxy groups : 5-bromovaleryl ester groups of 4.8. By combining this data with that obtained from the elemental analysis, we calculated an average chemical structure of **2** in good agreement with an addition of 12 hydroxy groups and 2.5 5-bromovaleryl ester groups per C_{60} molecule, which correlates to an average of 14–15 hydroxy moieties in a fullerol moelcule **1**.

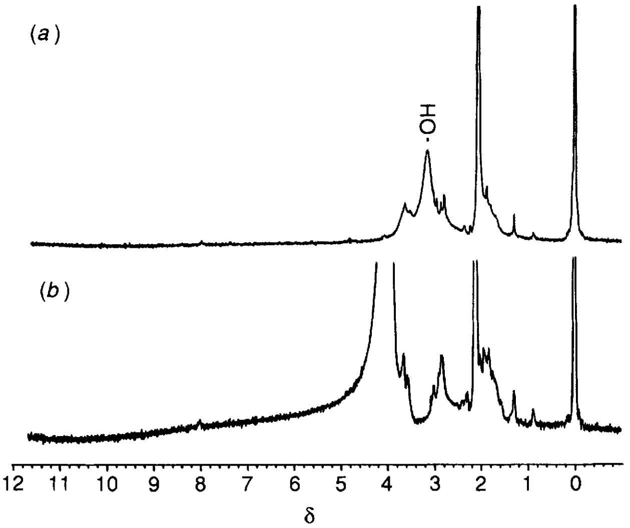

Fig. 2 ^1H NMR spectrum of partially esterified fullerols **2**, in (*a*) [$^2H_6$]acetone and (*b*) [$^2H_6$]acetone–D_2O

Partially esterified fullerols **2** were also investigated by the matrix-assisted laser desorption mass spectrometry[11,12] using 4-hydroxy-α-cyanocinnamic acid as a matrix. The distinct peaks at *m*/*z* 720 and 840 respectively represent the C_{60} and C_{70} fragment ions arising from the laser ablation of **2**. A broad unresolved distribution of ions ranging from *m*/*z* 940 to 1900 with its centre at *m*/*z* 1425 was observed as shown in Fig. 3. The spectrum is consistent with the average molecular mass of **2** [*m*/*z* 1464 corresponds to $C_{60}(\text{-OCOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-Br})_3(\text{OH})_{12}$] described above. The higher end of the ion distribution (*m*/*z* 1840–1875) represents the upper limit of the molecular mass distribution of **2**. This corresponds to a C_{60}

---

† The fullerol sample was dissolved in H_2O and filtered through celite prior to the mass spectrum measurement.

‡ *IR data* for **2** ν/cm^{-1} (KBr) 3434, 2938, 1733 (C=O), 1629, 1411, and 1162br. For **3** ν/cm^{-1} (KBr) 3422, 2927, 2855, 1727 (C=O), 1613, 1503w, 1450 and 1080br.

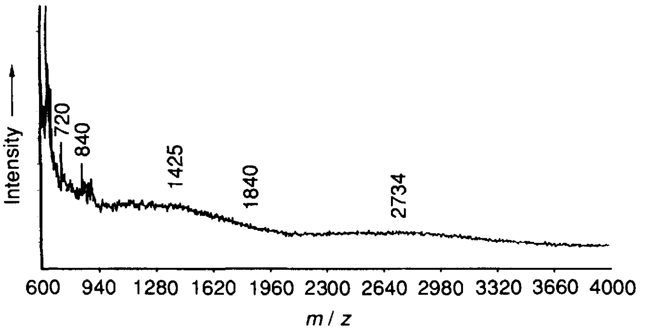

Fig. 3 Mass spectrum of **2** using the laser desorption technique in 4-hydroxy-α-cyanocinnamic acid matrix

molecule with 18–20 hydroxy groups and five 5-bromovaleryl ester groups, which correlates to a total of 23–25 hydroxy additions per C_{60} molecule prior to esterification. The second broad distribution of ions centred at *m/z* 2734 is the dimer of **2** resulted from the mass spectrometric experiment. In conclusion, we have described an efficient aqueous acid chemistry for the preparation of fullerols. The structure of fullerols has been characterized to consist of, on average, 14–15 hydroxy groups.§

We thank B. T. Chait of Rockefeller University for stimulating discussions and valuable assistance in obtaining laser desorption mass spectra. We also thank P. Tindall and D. Cox of Exxon Research for the preparation of fullerenes and R. Polizzotti of Exxon Research for the discussion of XPS data.

Received, 19th May 1992; Com. 2/02612K

References

1 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354; R. Taylor, J. P. Hare, A. K. Abdul-Sada and H. W. Koroto, *J. Chem. Soc., Chem. Commun.*, 1990, 1423.

2 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. Curl and R. E. Smalley, *J. Phys. Chem.*, 1990, **94**, 8634.

3 H. Selig, C. Lifshitz, T. Peres, J. E. Fischer, A. R. McGhie, W. J. Romanow, J. P. McCauley Jr. and A. B. Smith, *J. Am. Chem. Soc.*, 1991, **113**, 5475; J. H. Holloway, E. G. Hope, R. Taylor, G. J. Langley, A. G. Avent, J. T. Dennis, J. P. Hare, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1991, 966.

4 J. M. Wood, B. Kahr, S. H. Hoke, L. Dejarme, R. G. Cooks and D. Ben-Amotz, *J. Am. Chem. Soc.*, 1991, **113**, 5907; F. Diederich, R. Ettl, Y. Rubin, R. L. Whetten, R. Beck, M. Alvarez, S. Anz, D. Sensharma, F. Wudl, K. Khemani and A. Koch, *Science*, 1991, **252**, 548.

5 J. W. Bausch, G. K. S. Prakash and G. A. Olah, *J. Am. Chem. Soc.*, 1991, **113**, 3205.

6 J. M. Hawkins, *Acc. Chem. Res.*, 1992, **25**, 150.

7 P. J. Krusic, E. Wasserman, P. N. Keizer, J. R. Morton and K. F. Preston, *Science*, 1991, **254**, 1183.

8 G. A. Olah, I. Bucsi, C. Lambert, R. Aniszfeld, N. J. Trivedi, D. K. Sensharma and G. K. S. Prakash, *J. Am. Chem. Soc.*, 1991, **113**, 9385; F. N. Tebbe, J. Y. Becker, D. B. Chase, L. E. Firment, E. R. Holler, B. S. Malone, P. J. Krusic and E. Wasserman, *J. Am. Chem. Soc.*, 1991, **113**, 9900.

9 T. Suzuki, Q. Li, K. C. Khemani, F. Wudl and O. Almarsson, *Science*, 1991, **254**, 1186.

10 L. Y. Chiang, paper presented at the Symposium of Organic Solid State Materials in the Materials Research Society Fall Meeting, Boston, Massachusetts, December 4, 1991.

11 R. C. Beavis and B. T. Chait, *Rapid Commun., Mass Spect.*, 1989, **3**, 233.

12 R. C. Beavis and B. T. Chait, *Anal. Chem.*, 1990, **62**, 1836.

---

§ In addition to hydroxy groups, there is evidence of hemi-ketal moieties incorporated in the fullerols structure. A detailed structural study is currently underway.