Evidence of Hemiketals Incorporated in the Structure of Fullerols Derived from Aqueous Acid Chemistry

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Abstract: We have characterized and elucidated the chemical structure of fullerols, prepared from the aqueous acid reaction of C_{60} in the presence of sulfuric acid and nitric acid, consisting of hemiketal moieties in addition to tertiary hydroxy groups. In the aqueous reaction, a high yield of fullerols was obtained utilizing potassium nitrate as an effective precursor for generating nitric acid in situ. Evidence for the hemiketal structure is given by an observation of chemical shifts of vinyl ether carbons and ketal carbons centered at δ 170.3 and 100.0, respectively, in the ^{13}C NMR spectrum of fullerols. This structure was also substantiated by several spectroscopic methods including XPS, TGA–MS, and TGA–FTIR. Interestingly, the reversible interconversion reaction of hemiketal moieties in fullerol to the corresponding ketone upon variation of pH in aqueous solution provided conclusive results to verify the presence of hemiketal functions. This is the first observation of hemiketal functions incorporated onto the fullerene cage structure.

Introduction

Nucleophilic,[1] electrophilic,[2–5] and organoradical[6] addition reactions were found to be among the most efficient methods for the polyfunctionalization of C_{60} fullerene molecules. To demonstrate the electrophilic approach, we developed an aqueous acid reaction for introducing multiple hydroxyl groups directly onto fullerenes.[7] The reaction was best carried out at 85–95 °C in a solution mixture of sulfuric acid, potassium nitrate, and water without any hydrocarbon-containing reagents. The resulting polyhydroxylated fullerene derivatives (fullerols **1**) exhibit a high solubility in an acidic aqueous medium but precipitate from a basic medium when the pH of the solution is higher than roughly 9.0. This unusual solubility property of fullerols allowed isolation and purification of the nearly salt-free solid products. The chemical composition of fullerols was characterized as consisting of 14–15 hydroxyl functional groups on average.[7] Here we provide evidence to substantiate the incorporation of hemiketal functional moieties in the chemical structure of fullerol molecules in addition to hydroxyl groups.

Experimental Section

^{13}C NMR solution spectra were measured with either a Brucker 360 spectrometer or a JEOL FX-100 Fourier transform spectrometer. Solid-state ^{13}C NMR spectra were collected on a SDS360 spectrometer, operating at a frequency of 91.3695 MHz, utilizing a Doty Scientific CP/MAS (cross polarization/magic angle spinning) probe. For the CP/MAS experiment, chemical shifts were referenced to external TMS. The X-ray photoelectron spectroscopic measurement (XPS) was carried out on a Perkin-Elmer 5600 XPS spectrometer using Al K_α radiation at 1486.6 eV. All peak positions in the XPS measurement were calibrated using the binding energy of Si_{2p} as reference at 102.2 eV. Infrared spectra were recorded on a Perkin-Elmer 680 series spectrometer as KBr pellets. Mass spectroscopic studies of fullerols were performed using the fast cesium ion bombardment (or liquid secondary ion mass spectrometry (LSIMS)) technique. A VG ZAB-T four-sector instrument at the Center of Advanced Food Technology of Rutgers University was used for positive ion LSIMS experiments. TGA (thermogravimetric analysis)–mass spectroscopy data of fullerol were collected on a Mettler-TA2000C thermogravimetric analyzer interfaced with a Balzers QMG511 quadrupole mass spectrometer at a heating rate of 6 °C per min. Trifluoromethanesulfonic acid and potassium nitrate were purchased from Aldrich Chemicals and used as received. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of Polyhydroxylated Fullerene Derivatives 1. Method A. A reaction flask (50 mL) was charged with a fullerene mixture of C_{60} (84%) and C_{70} (16%) (500 mg) and fuming sulfuric acid (15 mL), and the solution was stirred at room temperature for 10 min to give a green solution with suspensions. The use of fuming sulfuric acid provided good wetting of fullerenes with the acid solution. The suspension was treated with distilled water (5.0 mL) dropwise at 5 °C with vigorous stirring. A slow addition rate of water was necessary to avoid a sharp increase of temperature. To this acid suspension was then added potassium nitrate (3.5 g) portionwise at 5 °C. The mixture was slowly heated to 90 °C and stirred at that temperature for 6–8 h. It was cooled to room temperature and poured slowly into ice (100 g). The resulting aqueous acid solution was filtered through Celite under vacuum to remove insoluble particles. The clear, brown-orange filtrate was basified by an aqueous sodium hydroxide solution (2 N) until the pH of the product solution reached 9.0 or higher. During base neutralization, the color of the solution slowly turned dark with fine, brown suspensions. It was allowed to stand at room temperature for 5 h to complete the precipitation. The precipitate was separated from solution by a centrifuge technique. It was then washed, centrifuged three times with a dilute NaOH solution (1 N) and twice with methanol, and dried in vacuum at 50 °C to afford brown solids of polyhydroxylated fullerene derivatives **1** (860 mg).

The combined aqueous solution obtained from the above separation procedure was diluted with water to a total volume of 800 mL and allowed to stand at room temperature overnight to cause the further precipitation of fine, brown solids. The solids were separated from solution and repeatedly washed with 1 N NaOH (aqueous) and methanol. After the solids were dried in vacuum at 50 °C, a second crop of fullerols **1** (190 mg) was obtained as a brown solid.

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If triflic acid (trifluoromethanesulfonic acid) was used in the above reaction instead of sulfuric acid, the reaction resulted in fullerols **1** (225 mg) with a recovery of the unreacted mixture of C_{60} and C_{70} fullerenes (350 mg).

The physical data of compound **1** are as follows: IR ν_{max} (KBr) 3424 (br, OH), 1595 (br), 1392 (br), 1084 (br), 593 (br) cm^{-1}; ^{13}C NMR (D_2O, peak center) δ 170.3, 140.3, 100.0, 79.0; solid-state ^{13}C NMR (3.8-kHz spinning speed, peak center) δ 179.3, 138.3, 103.2, 81.5; solid-state ^{13}C NMR (3.0-kHz spinning speed, peak center) δ 175.0, 141.1, 103.2, 78.3; MS (desorption chemical ionization (DCI) technique, negative ion)[8] *m/z* 720 (rel intensity 100), 734, 750, 763, 768, 840, 860; MS (LSIMS, positive ion, mass of the highest ion peak in the fragmentation group) *m/z* 654, 668, 684, 698, 714, 726, 742, 758, 774, 790 (rel intensity 100), 804, 814, 818, 834, 846, 860, 876, 894, 910, 926, 942, 952, 966, 982. Elemental analysis of hydrated fullerols: C, 43.5; H, 3.1; O, 46.9; N, 0.52; Na, 2.3; S, 1.64. XPS (atomic %): C, 58.0–62.0; O, 27.4–35.0; Na, 0.8–2.3; S, 0.5–1.0. Owing to the high compatibility of fullerols with water and Na_2SO_4, the product often contained one to several sodium sulfate molecules per fullerene derivative in addition to water from the work-up procedure. Therefore, the elemental analysis gives slight variation of the product composition upon change of the amount of these two residues.

Method B. A reaction flask (50 mL) was charged with a fullerene mixture of C_{60} (84%) and C_{70} (16%) (500 mg) and distilled water (4.0 mL), and the solution was treated with concentrated sulfuric acid (10 mL) dropwise at 5 °C with vigorous stirring. A slow addition rate of acid was necessary to avoid a sharp increase of temperature. To this acid suspension was then added concentrated nitric acid (10 mL) dropwise at 5 °C. The mixture was slowly heated to 115 °C and stirred at that temperature for 4–6 h. It was cooled to room temperature and poured slowly into ice (100 g). The resulting aqueous acid solution was filtered through Celite under vacuum to remove insoluble particles. The clear, brown-orange filtrate was basified by an aqueous sodium hydroxide solution (2 N) until the pH of the product solution reached 9.0 or higher. During base neutralization, the color of the solution slowly turned dark with fine, brown suspensions. It was allowed to stand at room temperature for 5 h to complete the precipitation. The precipitate was separated from solution by a centrifuge technique. It was then washed, centrifuged three times with a dilute NaOH solution (1 N) and twice with methanol, and dried in vacuum at 50 °C to afford brown solids of polyhydroxylated fullerene derivatives **1** (620 mg).

The combined aqueous solution obtained from the above separation procedure was diluted with water to a total volume of 800 mL and allowed to stand at room temperature overnight to cause the further precipitation of fine, brown solids. The solids were separated from solution and repeatedly washed with 1 N NaOH (aqueous) and methanol. After the solids were dried in vacuum at 50 °C, a second crop of fullerols **1** (80 mg) was obtained as a brown solid.

Results and Discussion

The existence of fullerolic carbons with a higher oxidation state than that of a monooxygenated carbon was first indicated in the X-ray photoelectron spectroscopic (XPS) study. The analysis of a peak corresponding to C_{1s} binding energy in the spectrum showed a large absorption deviation from that of C_{60} fullerene, indicating a high percentage of carbons in fullerols arising from a higher oxidation state than that of fullerene carbons. These higher oxidation-state carbons spread over a range of more than 4 eV in the spectrum, which is too broad to be caused only by monooxygenated carbons such as etheral or hydroxylated carbons. It revealed the presence of dioxygenated carbons in the structure. The curve-fitting analysis of the fullerol carbon peak allowed one to reasonably fit three different oxidation states of carbon by assuming that the peak separation between each oxidation state is in a similar range of 1.8 eV. With fullerol solids in a heterogeneous composition, a slightly larger FWHM width of about 1.85 eV for each fitted peak was expected. Based upon this procedure of analysis, we assigned the fitted peaks with a binding energy at 286.1 eV (68%) to nonoxygenated carbons, 287.9 eV (23%) for monooxygenated carbons such as etheral or hydroxylated carbons, and 289.7 eV (9%) to dioxygenated carbons such as carbonyl (C=O), ketal (RO—C—OR) or hemiketal (RO—C—OH) carbons. Since the infrared spectrum of fullerols consists of no obvious carbonyl absorption bands, we suggested that carbon atoms with the highest oxidation state in fullerol **1** attribute to hemiketal carbons. Even though this arbitrary curve fitting provides no absolute quantity of carbons at different oxidation states, it does provide a valuable estimation of the average number of hydroxyl additions, 14–16, consistent with that obtained from the chemical method,[7] with proximately 6–7 hemiketal moieties per fullerene molecule. The chemical method determines the number of hydroxyl groups per fullerene molecule from the proton integration ratio of hydroxyl protons:predefined ester C–H protons in the ^1H NMR spectrum of partially esterified fullerol derivatives.

Solid-state ^{13}C NMR study of fullerols, using the CP/MAS (cross polarization/magic angle spinning) technique, was performed at different spinning speeds of 3.8 KHz and 3.0 KHz, as shown in Figures 1a and 1b, respectively. Both spectra show three distinct carbon peaks with chemical shifts centered at roughly δ 80, 140, and 170–180 and one weak carbon peak centered at δ 103.2. These spectra were reproduced in D_2O solution, showing two major bands with a chemical shift centered at δ 79.0 and 140.3, corresponding to hydroxylated carbons (C_a) and unreacted olefinic carbons, respectively. The third downfield band at δ 170.3 was assigned to vinyl ether carbons (C_c) owing to the lack of carbonyl absorptions in the infrared spectrum of fullerols (Figure 4a) that excludes the possible ester or related functions in the structure of **1**. The fourth weak band centered at δ 100.0 corresponds clearly to dioxygenated carbons such as ketal (RO–C–OR) or hemiketal (RO–C–OH) carbons. From the low probability of ketal formation on C_{60}, we suggest that the dioxygenated carbons in fullerols **1** are attributed to the hemiketal functionality. These spectra provide consistent evidence to support the structural assignment of fullerols containing hemiketals with vinyl ether linkages.

We utilized TGA–mass spectroscopy data of fullerol to detect the thermal evolution of H_2O, CO, and CO_2. In this case, thermal cleavage of monooxygenated carbons is the main source of CO whereas the thermal cleavage of dioxygenated carbons leads to the release of CO_2. As shown in Figure 2, the physically absorbed H_2O (6% by weight) can be eliminated before 200 °C. The subsequent evolution of water owing to the dehydration of polyol moieties of **1** was clearly observed between 280 and 430 °C, indicating the polyhydroxy nature of fullerol. This chemical dehydration process corresponds to a weight loss of 8%. Thermal elimination of CO and CO_2 occurred in two stages starting from 450 °C with CO_2 as the major gas detected. A much higher intensity of CO_2 evolved in the first stage, with a peak maximum at 555 °C, than in the second stage at 700 °C. The intensity of CO is relatively weak with two weak maxima at 575 and 695 °C. The combined weight loss due to the elimination of CO_2 and CO is 19%. Even though the chemical mechanism of thermal bond cleavage at high temperatures may be greatly complicated, at lower temperatures, we resolved the evolution of CO_2 arising from the thermal cleavage of dioxygenated carbons such as hemiketal carbons in fullerol. Interestingly, in the TGA–FTIR study of fullerols, we detected the CO_2 absorption band in the infrared spectrum at a temperature as low as 175 °C, as shown in Figure 3. Since thermal elimination of CO_2 from the structural skeleton of fullerol involves several σ-bond cleavages, it normally requires a temperature higher than 400 °C to accomplish the process. A conceivable explanation for the elimination of CO_2 at low temperatures coincides with a bond-cleavage initiation via the chemical dehydration process of polyols in conjunction with

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(8) The fullerol sample was dissolved in water and filtered through Celite prior to the mass spectrum measurement to exclude any water-insoluble hydrocarbons. Since C_{60} and C_{70} are not water-soluble, the presence of C_{60} and C_{70} anions observed in the negative ion spectrum is apparently a result of the thermal decomposition of fullerols occurring during the desorption process.

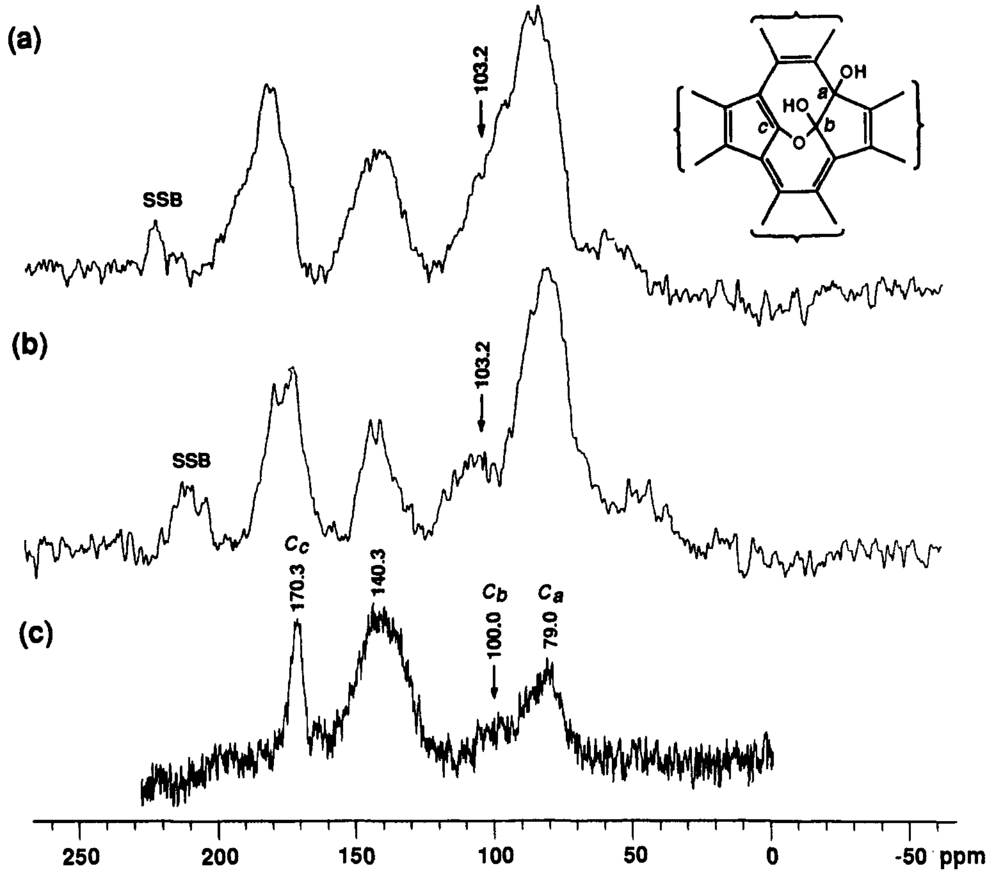


Figure 1. ^{13}C NMR spectrum of fullerols: (a) solid-state CP/MAS at 3.8-kHz spinning speed; (b) solid-state CP/MAS at 3.0-kHz spinning speed; and (c) in D_2O solution.

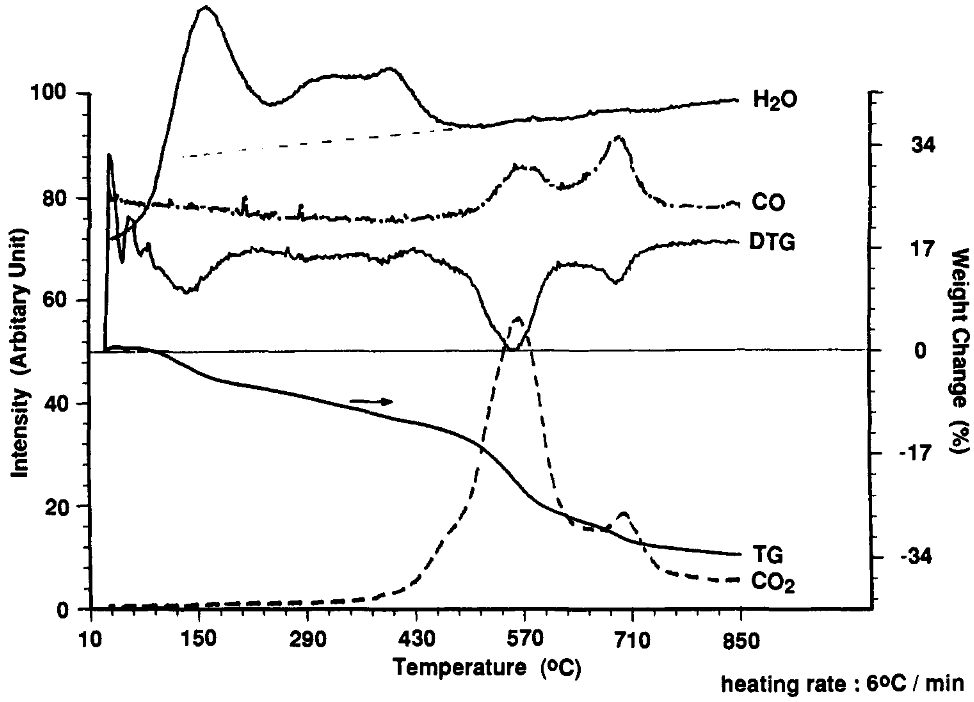


Figure 2. TGA–mass spectroscopic data of fullerols, prepared from pure C_{60}, showing the percent weight change (TG), differential weight change (DTG), and intensity of H_2O, CO, and CO_2 gases evolved upon thermal treatment at a rate of 6 °C/min.

the thermally labile hemiketal structure. The intensity of the CO_2 absorption band in the infrared spectrum was observed to rise to a maximum at 605 °C upon the increase of temperature. The on-set temperature for detection of the CO absorption band is 650 °C with a peak maximum at 735 °C. Weight loss of the fullerol sample used in this measurement was 14% and 27.5%, corresponding to the chemical dehydration and thermal elimination of CO_2 and CO, respectively.

An established chemical method to substantiate the hemiketal function is the conversion of a hemiketal to its ketone analogue by acid treatment. This transformation can be detected readily by the observation of carbonyl absorption in the infrared spectrum

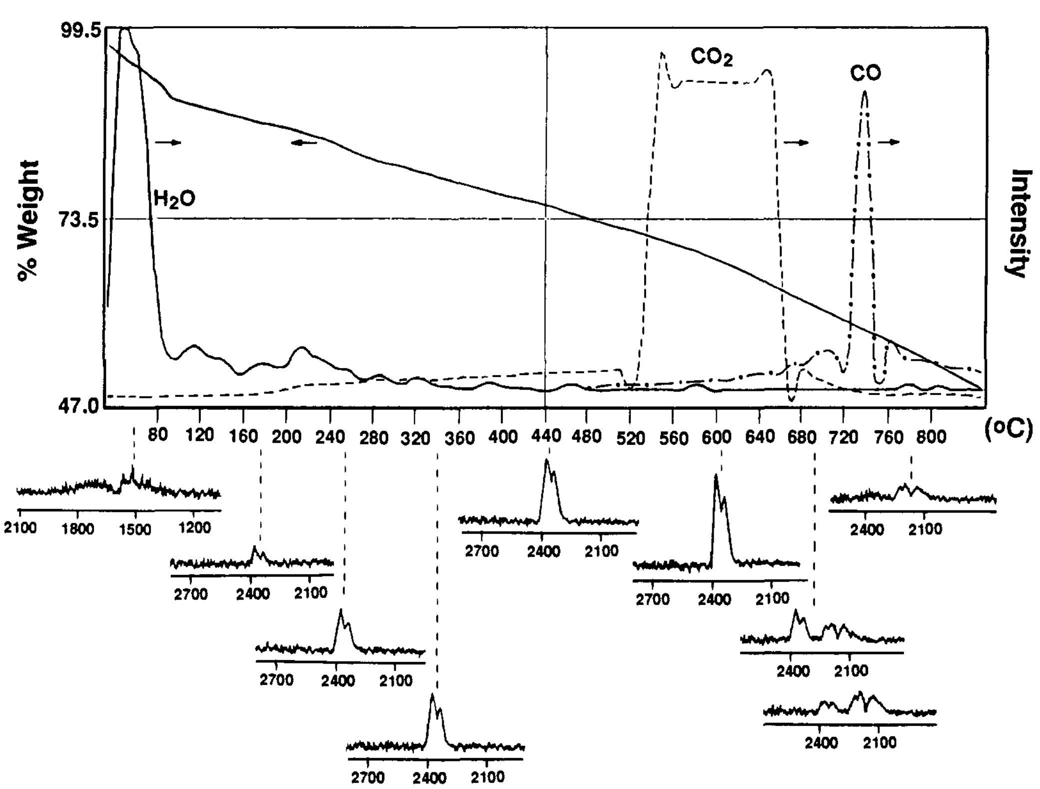
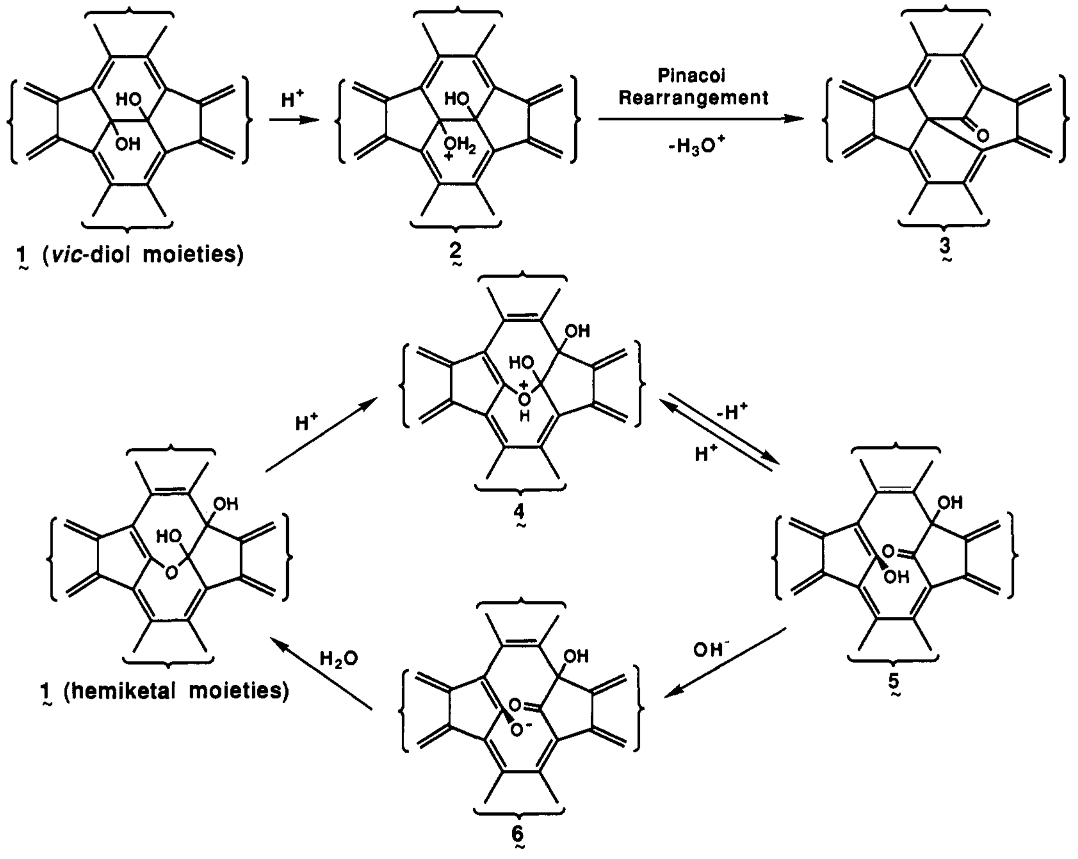


Figure 3. TGA–FTIR measurement of fullerols showing the temperature-dependent weight loss and infrared absorption bands of H_2O, CO_2, and CO thermally evolved upon heat treatment at a rate of 6 °C/min.

Scheme I



of the resulting ketone. However, the reaction of fullerols containing *vic*-diols (glycols) with acid can be potentially complicated by the pinacol rearrangement, which rearranges tertiary *vic*-diol moieties of **1** to give the corresponding ketone **3**, as shown in Scheme I. Differentiation between the hemiketal and ketone equilibration and the pinacol rearrangement of *vic*-diols under acidic conditions can be made by an examination of full reversibility of the former interconversion, leading conceivably to the formation of several different hydroxy ketone moieties, which can be presented as the partial structure **5** in products.

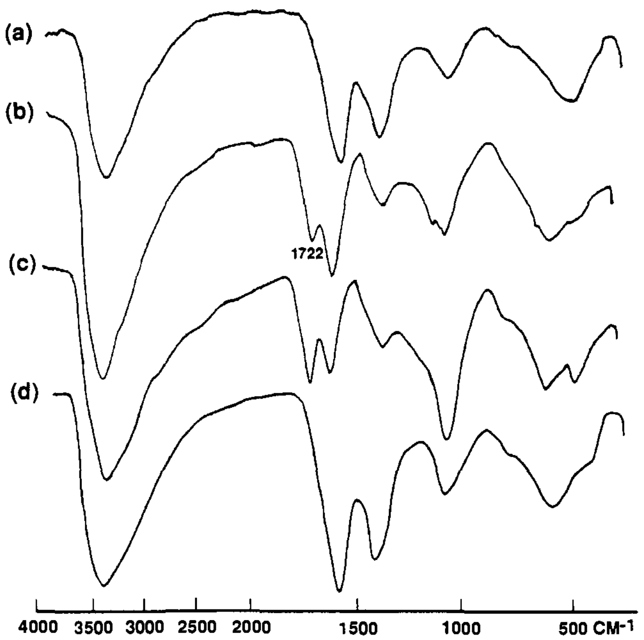


Figure 4. Infrared spectrum of (a) fullerols; (b) water-soluble products **5b** and (c) solid precipitates **5a** from the reaction of fullerols with dilute HCl (0.4 N) at 80 °C; and (d) recovered fullerols from the treatment of **5a** and **5b** with aqueous NaOH.

Whereas the later rearrangement is irreversible, it requires both cleavage and formation of carbon–carbon bonds in the protonated structure of **2** to afford ketone **3**, which contains highly sterically strained tetracyclic 5,5,6,6-membered rings sharing one common carbon. Indeed, fullerols with multiple tertiary hydroxyl groups were found to be sensitive to certain acidic conditions. Acid used in this study was either hydrochloric acid in water solution or HBF_4–Et_2O in methanol solution. Experimentally, fullerol **1** was treated with a dilute aqueous solution of HCl (0.4 N) at 80 °C for 5–16 h. Slow increase of suspended, brown solids in an initially clear, dark brown solution was observed. At the end of the reaction, the solids were collected by a centrifuge technique to afford products **5a** and the remaining solution was dried directly in vacuo at 50 °C to give solid products **5b**.

Both infrared spectra of **5a** (Figure 4c) and **5b** (Figure 4b) show a new, pronounced carbonyl absorption band at 1722 cm^{-1} and the retention of five characteristic absorptions of fullerol at 3424, 1595, 1392, 1084, and 593 cm^{-1} in different intensity from those of the corresponding absorptions of fullerol itself (Figure 4a). The observed carbonyl absorptions confirmed ketone structures in **5**. These spectra also indicate that the chemical structures of **5a** and **5b** are virtually related to each other, presumably, in a different degree of hemiketal to ketone conversion. The driving force for this facile acid conversion is the stabilization of a tertiary alkyl carbocation, derived from the protonation of hemiketal functions in **4**, by an oxygen atom and the elimination of an hydroxy proton by ketone formation. Interestingly, the treatment of **5a** or **5b** with alkaline aqueous solution (2 N NaOH) precipitates brown solids. After the removal of NaOH by repeated aqueous and methanol washings, these brown solids exhibited a nearly identical infrared spectrum (Figure 4d) to that of the starting fullerols. This reversibility of hemiketal and ketone interconversion upon pH variation of aqueous solution clearly excludes the pinacol rearrangement of *vic*-diol moieties in fullerols. To further support the existence of hemiketal structure in fullerols, an ethylation reaction was performed to attack the ketal moiety with triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$) as an alkylation reagent in 1,1,2-trichloroethane at 85 °C. The reaction converted hemiketal groups, through ring opening, to the corresponding ethoxy and ketone structures. As expected, we obtained a carbonyl absorption band at 1726 cm^{-1} in the infrared spectrum of products, indicating ketone formation during the reaction and consistency of the above structural hypothesis.

In conclusion, we characterized and elucidated the chemical structure of fullerols, prepared from an aqueous reaction of C_{60} in the presence of strong acids, consisting of hemiketal moieties in addition to tertiary hydroxyl groups. This is the first observation of hemiketal functions incorporated onto the fullerene ball-structure skeleton. The structure also allows construction of a hypothetical mechanism involving hydroxylated fullerene oxide as one of the reaction intermediates.

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