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Synthesis of Hydrogenated Fullerenes by Zinc/Acid Reduction[1]

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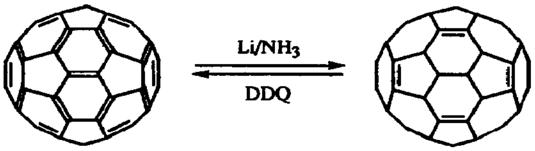
Abstract: Reduction of C_{60} with zinc and acid results in the formation of $C_{60}H_2$, $C_{60}H_4$, and more highly hydrogenated fullerenes.

The chemical modification of fullerenes is currently a highly active area of research.[2,3] One of the simplest types of chemical modification of fullerenes is hydrogenation of individual double bonds. The synthesis of $C_{60}H_{36}$ by the Birch reduction[4] was among the first chemical reactions of a fullerene reported in the literature. Treatment of C_{60} (1) with lithium in ammonia and using t-butanol as a proton source leads to the formation of a series of polyhydrofullerenes ranging from $C_{60}H_{18}$ to $C_{60}H_{36}$.[5] The formation of $C_{60}H_{36}$ rather than more highly reduced species has been rationalized as being the result of the deconjugation of double bonds, and one such structure (2) has been proposed. Fully hydrogenated "fullerane" ($C_{60}H_{60}$) is predicted to be a high-energy species due to the interactions of so many eclipsed hydrogen atoms,[6] and these interactions may contribute to the Birch reduction stopping at the $C_{60}H_{36}$ stage.



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The reductive electrochemistry of fullerenes, C_{60} in particular, has been extensively investigated.[7-16] Lithium is an aggressive reducing agent with a Li^+/Li potential of -3.0 V versus Fc^+/Fc, very close to the $C_{60}^{5-/6-}$ reduction potential. The protonated products, $C_{60}H_2$ being the simplest, would be easily reduced under these conditions,[17] leading to the eventual formation of $C_{60}H_{36}$. We are interested in the products that might result from dissolving metal reduction of C_{60} using less highly reducing metals. There are a number of metals with suitable reduction potentials, and we chose to investigate tin (ε^o (Sn^{2+}/Sn) = -0.75 V vs Fc^+/Fc), iron (ε^o (Fe^{2+}/Fe) = -1.05 V vs Fc^+/Fc), and zinc (ε^o (Zn^{2+}/Zn) = -1.37 V vs Fc^+/Fc). These three reagents conveniently allow reaction at a potential where C_{60} is not electrochemically reduced, as well as near the $C_{60}^{0/-1}$ and at the $C_{60}^{-1/-2}$ potentials (-0.98 V and -1.37 V vs Fc^+/Fc, respectively).[9] Herein we report the synthesis of the reduced fullerenes $C_{60}H_2$, $C_{60}H_4$, $C_{60}H_6$ and others by dissolving metal reduction using zinc and acid.

Results and Discussion

Heating a heterogeneous mixture of C_{60}, toluene, tin dust, and aqueous HCl for periods of up to six hours under a nitrogen or argon atmosphere leads to very little reaction as indicated by gel permeation chromatography (GPC). The same was found using iron dust instead of tin, suggesting that if any C_{60} radical anion is produced under these conditions it is fairly unreactive toward acid. However, treatment of C_{60} with an excess of zinc dust and acid in refluxing toluene under argon or nitrogen results in a change in color from the magenta color of C_{60} to a dark brown. GPC analysis of the reaction mixture shows three new, evenly spaced bands that elute after C_{60}. Different acids (6 M HCl, 12 M HCl, glacial HOAc, and concentrated H_2SO_4) as well as catalytic hydrogenation (35 psi H_2, 10% Pd/C, 24 hours) lead to the formation of the same three new bands. The relative concentrations of the new species differ somewhat, reflecting different extents of reaction over the six hour reaction period. Control experiments with each acid alone and with zinc alone do not, under these conditions, show the formation of any new compounds. Treatment of the Zn/H^+ reaction mixture with DDQ results in smooth conversion of the mixture back to C_{60}, consistent with the assignment of these new bands as reduced fullerenes.[4]

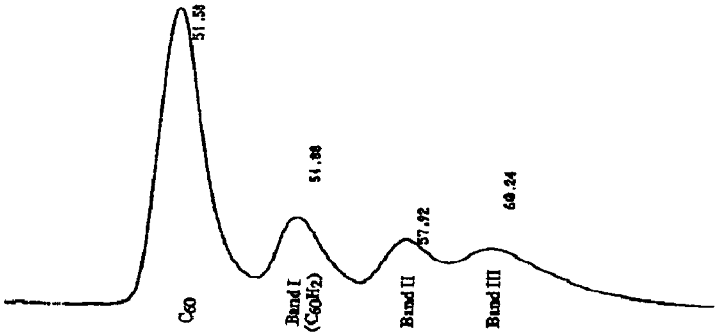
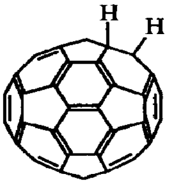


Fig. 1. Gel Permeation Chromatogram of Zn/HOAc Reduction Mixture. See text for specific conditions.

We have separated the new bands by preparative GPC[16,18] using a bank of four 19 mm diameter columns operating at ambient temperature with toluene as the mobile phase. Each band was isolated and rechromatographed twice. The known lability of $C_{60}H_2$, particularly the sensitivity toward oxidation when solutions are evaporated to dryness, dictated that samples were handled in solution and not evaporated unless necessary.

Mass spectrometric characterization of these compounds indicates a strong tendency for fragmentation back to the parent fullerene.[17] However, negative ion FABS MS analysis of Band I exhibited m/e 722 as the parent ion, along with the expected isotope lines (67% M+1, 24% M+2), corresponding to $C_{60}H_2$. Even under these conditions, extensive fragmentation to C_{60} occurs, and the spectrum shows a prominent line at *m/e* 720, again accompanied by the expected isotope lines. Excess intensity at *m/e* 721, beyond the 67% of the 720 line expected due to the natural abundance of ^{13}C, indicates a small quantity of $C_{60}H$, either a fragment of $C_{60}H_2$ or the adduct of a hydrogen ion[18] from the FABS matrix to the C_{60} formed by fragmentation of $C_{60}H_2$.

Analysis of the $C_{60}H_2$ band by high-resolution C_{18} HPLC (70% CH_2Cl_2, 30% acetonitrile) indicated that this band contains a single component, suggesting that a single isomer is formed. Calculations by Cahill suggest that of the 23 all-*exo* isomers of $C_{60}H_2$,[16] one isomer (1, 9) is 3.8 kcal/mole more stable than any other isomer. This isomer, resulting from the placement of hydrogens across a 6,6 ring fusion, has been prepared by treatment of C_{60} with BH_3•THF followed by protonolysis,[19] and by hydrogenation over rhodium.[20] When we prepare a sample of $C_{60}H_2$ using BH_3•THF, we find that it is chromatographically and spectroscopically (UV/Vis, ^1H NMR) identical to the compound we prepare by zinc/acid reduction, indicating that the same isomer is produced.



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Reversed-phase HPLC indicated that bands II and III each contain a number of components. Analysis of Band II by negative-ion FABS mass spectrometry shows that it is primarily $C_{60}H_4$. Analysis of this band with a "Buckyclutcher" HPLC column showed that three compounds, presumably different isomers, are present. This is consistent with results reported by Cahill, although the relative amounts of the isomers produced by this method are quite different from the relative amounts produced by BH_3•THF. Buckyclutcher analyses made before GPC separation confirm that this ratio is not an artifact of prior GPC treatment.

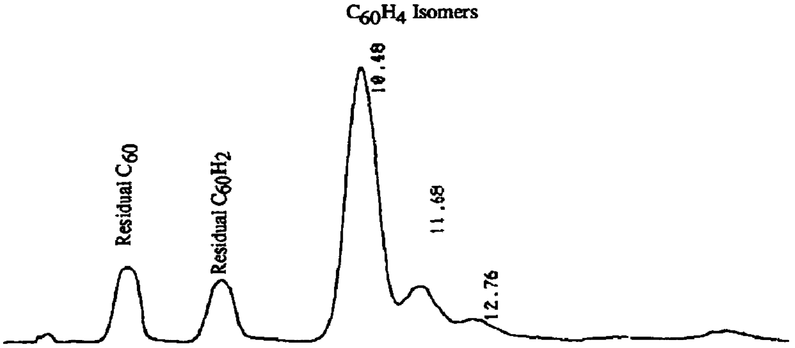

Fig. 2. HPLC (19 mm preparative Buckyclutcher) Chromatogram of Band II ($C_{60}H_4$). Toluene/hexane (70/30, 5 mL/min) mobile phase, UV/Vis detection at 330 nm.

Band III, containing the most highly reduced material produced under these conditions, exhibits mass lines from *m/e* 720 (C_{60}) to 730 (M+2 line from $C_{60}H_8$). Again, the lower mass lines are most likely due to fragmentation from $C_{60}H_6$ or $C_{60}H_8$. Reversed phase HPLC analysis clearly shows that this band is composed of a mixture of a large number of compounds. Given the difficulty in obtaining fragmentation-free mass spectra we can not be certain if $C_{60}H_6$ is the parent and that other lines result from fragmentation.

Clearly, a number of hydrogenated fullerenes $C_{60}H_6$ to $C_{60}H_{22}$ are produced, and these compounds are not separated by GPC.

Reduction of C_{60} with Zinc Dust - General Procedure

To a suspension of 20 mg (0.0278 mmoles) C_{60} in 5 mL toluene was added 360 mg (5.54 mmoles) Zn powder and 0.5 mL 6 M HCl. The suspension was heated at reflux under Ar for a period of 6 hours. The resulting brown suspension was diluted with toluene and filtered to remove the metal salts. The resulting solution was washed with water, then dried (Na_2SO_4) and concentrated to 2 mL before being microfiltered and purified by GPC. Preparative GPC of hydrogenated fullerenes was performed using a bank of four 19 mm x 300 mm GPC columns (#1 - Jordigel E-277 (500Å), #2 and #3 - Waters Ultrastyragel (500Å), #4 - Waters Ultrastyragel (100Å)) using toluene as the mobile phase at a flow rate of 5 mL/min. Injections of up to 5 mL of saturated solutions of the fullerenes in toluene were made. Evaporation to dryness was avoided due to difficulty in redissolving the solid products. Typical mass balances were 70%. In cases where the samples were evaporated to dryness, the yields obtained were $C_{60}H_2$ (7%), $C_{60}H_4$ (3%) and band III ($C_{60}H_{6+}$, 1%).

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