

Synthesis of Water-Soluble Fullerols

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Water-soluble fullerol, $C_{60}(OH)_n$ with $n=24-26$, was synthesized by a reaction of fullerene with NaOH in aqueous solution. C_{60} fullerene oxides was generated in-situ during the reaction in the presence of oxygen and hydroxide anion. The reaction rate was enhanced significantly by oxidation of fullerene and catalyzation of quaternary ammonium hydroxides.

1. INTRODUCTION

The chemical modification on fullerene can yield a new class of materials for potential uses. Fullerol, a polyhydroxylated fullerene derivative, has been synthesized recently by Chiang et al. by the reaction of fullerene with an aqueous acid or by the hydrolysis of ester moieties of a polyorganocarboxylated fullerene derivative.^{1,2} The isolated fullerene derivative, due to being highly soluble in water and having polarized hydroxyl groups, is expected to find potential applications in aqueous solution chemistry, electrochemistry and biochemistry, as well as in synthesis of new fullerene compounds. Here we describe a novel route to synthesize C_{60} fullerol. We found that the formation of C_{60} fullerol is more efficient under basic conditions by the reaction of fullerene with an aqueous NaOH solution in the presence of tetrabutylammonium hydroxide (TBAH) at an ambient temperature.

2. EXPERIMENTAL

80 mg of chromatographically purified C_{60} was dissolved in 60 mL benzene. The

C_{60} solution was vigorously stirred with an aqueous NaOH solution (2 g in 2 mL water) containing 3 drops of TBAH (40% in water) at room temperature. Within a few minutes, the benzene solution, originally deep violet, turned to be colorless and gave rise to a brown sludge precipitated from the solution. After removal of benzene by decantation and evaporation under reduced pressure for a few hours, the sludge and remaining water solution was stirred with additional 10 mL of water for 10 h. After another 20 mL water was added at the completion of reaction, a clear reddish brown aqueous solution was filtered to remove a trace amount of water-insoluble residue. The filtrate was concentrated to about 5 mL, and then 50 mL of MeOH was added to produce a brown precipitate. The precipitation was repeated for 3 times in order to completely remove TBAH and NaOH. Drying the precipitate under reduced pressure gave 115 mg of brown solid product 1. The same reaction carried out in argon was found to be difficult to obtain water-soluble fullerol.

3. RESULTS AND DISCUSSION

The IR spectrum of product **1** showed a broad hydroxyl absorption band centered at 3430 cm^{-1} , a C-O stretch absorption band centered at 1070 cm^{-1} and a C=C absorption band centered at about 1600 cm^{-1} . It is quite similar to the IR spectrum of the fullerol reported by Chiang et al.¹ ^1H NMR spectrum of fullerene derivative **1** in DMSO-d_6 showed only one broad peak of hydroxyl protons at δ 3.35 ppm. The elemental analysis of **1** (Found: C, 61.47; H, 2.25; N, <0.01) was in good agreement with the theoretical composition of $\text{C}_{60}(\text{OH})_{26.5}$ (Calcd.: C, 61.51; H, 2.25). Due to the possibility of the presence of a small amount of water in the fullerol obtained, the number of hydroxyl groups could be slightly less than 26.5.

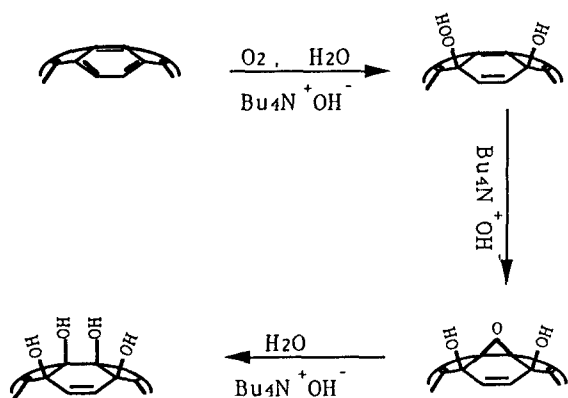
It has been known that $\text{C}_{60}\text{Br}_{24}$ (T_h) has a high symmetry structure without any two adjacent Br atoms to avoid the steric hindrance.³ But no isomer of $\text{C}_{60}(\text{OH})_{24}$ had been isolated yet in the present study. A 1,2-diol structure in the fullerol had been suggested by Chiang et al.^{1,2} In this case, adjacent 1,2-attachment of hydroxyl groups in fullerol may exist. It is noteworthy that C_{60} fullerol is obtained under basic conditions in the present study in contrast to the case reported.^{1,2} Moreover, the C_{60} fullerol obtained in the present reaction has more hydroxyl groups and is consequently more soluble in water than those reported previously.^{1,2}

We found that the reaction of hydroxyl group addition to fullerene was very slow in the absence of oxygen. A similar reaction under argon gave mainly a water-insoluble mass which was found to have less than 10 hydroxyl groups per C_{60} molecule from elemental analysis, although its IR spectrum was similar to that of the C_{60} fullerol. This indicates the important role of oxygen in the reaction. Addition of tetrabutylammonium hydroxide significantly accelerated the conversion of fullerene to fullerol. Moreover, the reaction rate strongly

depended on the alkyl groups in the quaternary ammonium hydroxides. The reaction rate in the initial step, in which the C_{60} benzene solution became colorless, increased dramatically with increasing the number of carbons in the alkyl groups of the quaternary ammonium hydroxides. It took only 3 minutes for completion of the initial step reaction in the case of addition of TBAH as a catalyst, but it took about 6 h. by addition of $\text{Et}_4\text{N}^+\text{OH}$ and 96 h. by addition of $\text{Et}_4\text{N}^+\text{OH}$. Without addition of quaternary ammonium hydroxide, only small part of C_{60} was observed from benzene solution into aqueous solution after three days. Water-insoluble product **2** from the initial step reaction could be isolated by stopping the reaction after removing benzene, NaOH and TBAH. Product **2** showed an IR spectrum with the same absorption bands as the water soluble fullerol except for the C-H absorption bands around 2830 to 2890 cm^{-1} and the absorption bands around 520 and 570 cm^{-1} from unreacted C_{60} . The elemental analysis (Found: C, 78.76; H, 3.20; N, 1.18) showed that the C-H absorption bands could be attributed to the butyl group in TBAH. Therefore, product **2** from this step seems to be the fullerol $\text{C}_{60}(\text{OH})_n$ with about $n=3$ which includes some TBAH and unreacted C_{60} . It was insoluble in water due to small number of the hydroxyl groups added, as well as insoluble in benzene.

C_{60} is known to have high electron affinity so that it is more susceptible to nucleophilic addition than to electrophilic addition.⁴⁻⁶ Therefore, based on the observation above, a possible mechanism for the reaction of hydroxyl group addition to fullerene under basic conditions can be proposed, shown in Scheme 1. The initial attack of oxygen on fullerene in the presence of hydroxide anion gave hydroxylated fullerene tertiary hydroxyperoxide or directly gave epoxide,⁷ then the hydroxyperoxide immediately

oxidized to give hydroxylated fullerene oxide, the subsequent nucleophilic ring-opening of the fullerene oxide with hydroxide anions gives rise to the fullerol. The quaternary ammonium hydroxides act as catalysts either in the stage of the oxidation of fullerene or in the stage of nucleophilic ring-opening reaction of fullerene oxide with hydroxide anions.



Scheme 1

An attempt to treat derivative **1** with cation ion-exchanger (Dewox 50X4-400) gave derivative **3** (Elemental analysis: C, 55.30; H, 1.94; N<0.01). The IR spectrum of the derivative **3** showed a strong C=O absorption band centered at 1720 cm⁻¹ and a broad weak absorption band at about 1250 cm⁻¹. A reaction may take place in this acidic ion-exchanger to convert the 1,2-dihydroxyl groups to the corresponding ketone structure with the ring opening through a Pinacol-analog rearrangement.²

4. CONCLUSIONS

This work presents a simple and efficient process for the conversion of C₆₀ fullerene to fullerol C₆₀(OH)_n with n=24-26 under basic conditions. We found that C₆₀

fullerene oxides was generated in-situ during the reaction in the presence of oxygen and hydroxide anion and that reaction rate was enhanced significantly by catalyzation of quaternary ammonium hydroxides. Further studies are in progress in elucidating the reaction mechanism.

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