

Efficient and Convenient Preparation of Water-Soluble Fullerenol[†]

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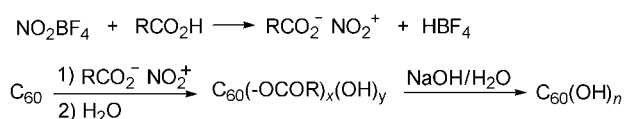
An efficient and convenient preparation of fullerenols was described. With polyethylene glycol (PEG) 400 as catalyst, fullerenols were conveniently synthesized via the direct reaction of fullerene with aqueous NaOH. By control of reaction conditions, either water-soluble C₆₀ fullerenol or water-insoluble C₆₀ fullerenol could be obtained selectively.

Keywords fullerene, water-soluble fullerenol, polyethylene glycol, sodium hydroxide

Introduction

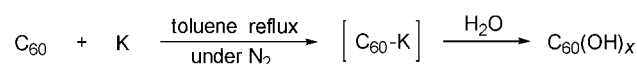
Fullerenols, polyhydroxylated fullerene derivatives, being soluble in water and bearing polar hydroxy groups, have potential applications to aqueous solution chemistry, electrochemistry and biochemistry, as well as synthesis of new fullerene derivatives. Moreover, fullerenols may be useful building blocks for the synthesis of various polymer networks. Synthetic methods leading to the preparation of water-soluble fullerenols have been extensively investigated.¹⁻¹² For example, Chiang *et al.*¹ reported the reaction of fullerene with nitronium tetrafluoroborate in the presence of arenecarboxylic acid in a nonaqueous medium. Hydrolysis of the ester moieties of polyorganocarboxylated fullerene derivatives provided an alternative efficient route for the preparation of water-soluble fullerenols (Scheme 1)

Scheme 1



Li *et al.*⁴ also demonstrated their improved synthetic method of fullerenols via the direct reaction of fullerene with an aqueous NaOH in the presence of tetrabutylammonium hydroxide (TBAH). Recently, Sun *et al.*⁵ found that the fullerenols could also be synthesized by the reaction of C₆₀ with metal potassium in a refluxing toluene solution (Scheme 2). However, they found that the obtained fullerenol was unstable to light, heat and even the basic solution.

Scheme 2



Due to the similar structure of PEG and crown ether, PEG is usually regarded as an efficient substitute for crown ether.¹³ Encouraged by the results of Li *et al.*,⁴ we chose the appropriate PEG as the phase transfer catalyst (PTC) to substitute TBAH. In this paper, a novel direct route to fullerenols by the reaction of C₆₀ with aqueous NaOH in the presence of PEG 400 under aerobic conditions at room temperature was developed. Compared with previous techniques, PEG has manageable and good phase transfer catalytic merits. By control of reaction conditions, either water-soluble C₆₀ fullerenol or water-insoluble C₆₀ fullerenol could be obtained selectively. To the best of our knowledge, this is the first convenient example to prepare the fullerenols using PEG under mild conditions. Herein we wish to report these results.

Results and discussion

In the presence of PEG 400, the reaction of C₆₀ in benzene solution with aqueous NaOH was first studied (Scheme 3). It was found that the reaction proceeded smoothly under aerobic conditions at room temperature. By general work-up water-insoluble product **1** and water-soluble product **2** were isolated successfully.

The IR spectra of products **1** and **2** showed a similar broad hydroxyl absorption centered at 3432 cm⁻¹, a C—O stretching absorption at 1063 cm⁻¹ and a C=C ab-

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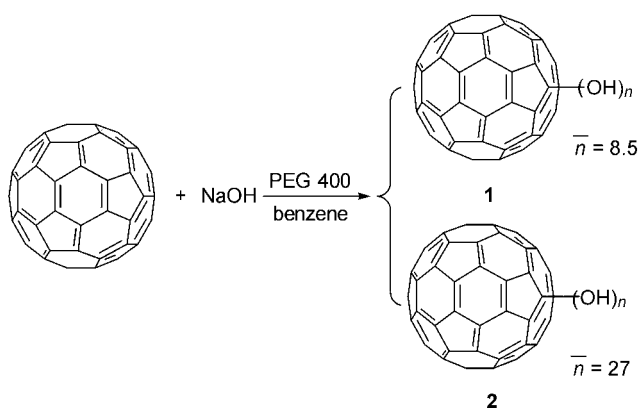
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sorption at 1600 cm^{-1} . It is quite similar to the IR spectrum of the fullereneol reported by Chiang¹ and Li.⁴ As expected, the simple polyhydroxylated fullerene structures of **1** and **2** showed a single strong peak centered at 3.35, corresponding to hydroxyl protons in the ¹H NMR spectra. These protons were further substantiated by deuterium exchange. A clear disappearance of the hydroxyl proton (C—OH) peaks was observed. In their mass spectra, the obvious peaks at m/z 720 indicated that the cage structure was not destroyed during the reaction process. The elemental analyses of **1** (found C 82.51, H 2.01) and **2** (found C 60.42, H 2.38) showed an average composition of $\text{C}_{60}(\text{OH})_n$ ($n=8.5$ and 27 for **1** and **2**, respectively).

Scheme 3



It is noteworthy that in contrast to previous several reports¹⁻³ in the present study fullereneols were obtained under basic conditions. Moreover, the products contain more hydroxyl groups and are consequently more soluble in water than those reported previously.¹⁻⁴ In addition, the fullereneols are stable to heat and light, which hence could be stored for several weeks without change.

Addition of PEG significantly accelerated the conversion of fullerene to fullereneols, which can be attributed to the phase-transfer catalysis of PEG. The reaction rate depended strongly on the kinds of PEG and the molar ratio of the PEG. Firstly, PEG 200 and PEG 400 were studied in detail. The results were summarized in Table 1. As can be seen from the table, under different concentrations of NaOH (from 5 to $20\text{ mol}\cdot\text{L}^{-1}$), all the reaction time was obviously shorter in PEG 400 than in PEG 200, *i.e.*, PEG 400 was more effective catalyst in the present study. Then effect of different molar ratio of the PEG 400 was discussed in fixed basic concentration ($25\text{ mol}\cdot\text{L}^{-1}$). Table 2 showed that the reaction rate in the initial step, in which the violet C_{60} benzene solution became colorless, increased dramatically with increase in the molar ratio of PEG 400. The reaction proceeded very slowly without PEG 400 even prolonging the time to one day, and no obvious color changed. When the amount of PEG 400 reached a certain value, the time for the solution to become colorless was nearly invariable.

In the presence of PEG 400, the effects of different concentrations of NaOH on the reaction rate and the

amount of water-soluble fullereneols **2** were investigated. It was found that the ratios of **1** to **2** were influenced seriously by the base concentration. With the increase of the base concentration, the reaction time became shorter and the ratio of water-soluble product **2** was increased (Table 3). When the concentration reached a certain value, the variation was not obvious.

Table 1 Effects of different PEG on the reaction rate under basic conditions^a

Entry	$c_{\text{NaOH}}/(\text{mol}\cdot\text{L}^{-1})$	Time/min	
		PEG200	PEG400
1	5	110	65
2	10	55	40
3	15	48	40
4	20	35	30

^a PEG (20 mol%) was used.

Table 2 Effects of the molar ratio of PEG 400 on the reaction rate in air^a

Molar ratio of PEG400/%	0	5	10	15	20	25	30
Time ^b /min	>1440	120	80	45	30	30	30

^a $c_{\text{NaOH}}=25\text{ mol}\cdot\text{L}^{-1}$. ^b Time for C_{60} benzene solution to become colorless.

Table 3 Effects of different concentrations of NaOH on the reaction rate and the percents of **2** in the presence of PEG 400 (20 mol%) in air or N_2 atmosphere

Entry	$c_{\text{NaOH}}/(\text{mol}\cdot\text{L}^{-1})$	In air		In N_2	
		2 /%	Time/min	2 ^a /%	Time/min
1	10	44.9	40	—	55
2	15	67.3	40	—	50
3	20	77.2	35	—	40
4	25	80.4	30	—	30
5	30	81.1	30	—	30

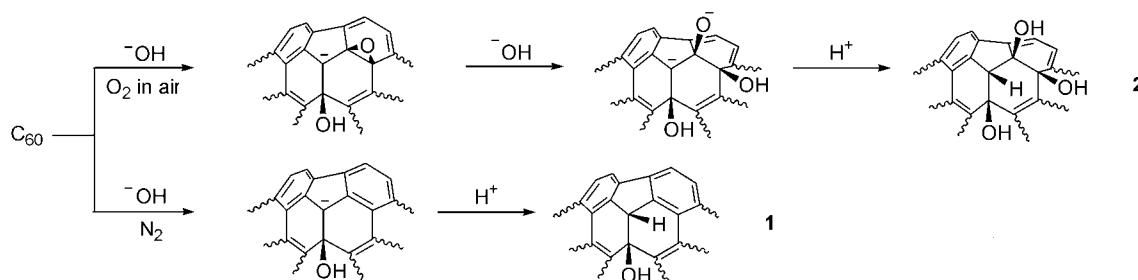
^a Only **1** was obtained.

In previous literatural reports, it was noticed that the addition of hydroxyl group to fullerene was very slow in the absence of oxygen. However, in the present study a similar reaction in N_2 gave a water-insoluble mass solely. In addition, under the same base concentration, longer reaction time was usually needed when the reaction was carried out in N_2 than in air. To our surprise, under different basic concentrations, the reaction could also proceed smoothly under N_2 atmosphere, which is contrary to the literatures reported,¹⁻⁵ proving that the PEG 400 was more effective catalyst than other catalysts such as TBAH.

Possible mechanisms for the selective formation of products **1** and **2** in air or in N_2 atmosphere were proposed as Scheme 4.

Finally, the adding fashion of the substrates also influenced the percents of **2**. For example, adding the

Scheme 4



aqueous NaOH to the benzene solution of C₆₀ (Method A) resulted in different results with the sequence reversed (Method B) (Table 4). From the table, it was found that the higher percents of **2** were obtained by method B. So the high percents of water-soluble fullereneol **2** could be obtained in relatively low basic concentration.

Table 4 Effects of the adding fashion on the percents of **2** (20 mol% PEG400)

Entry	$c_{\text{NaOH}}/(\text{mol}\cdot\text{L}^{-1})$	2/%	
		Method A ^a	Method B ^b
1	5	10.9	31.3
2	10	45.0	65.6
3	15	67.3	75.9
4	20	77.2	85.6
5	25	80.4	87.2

^aMethod A: The NaOH solution was added to the benzene solution of C₆₀. ^bMethod B: The benzene solution of C₆₀ was added to NaOH solution.

Conclusions

In summary, an efficient and convenient synthetic method of preparing fullereneols was developed. With polyethylene glycol (PEG) 400 as catalyst, fullereneols were conveniently synthesized via the direct reaction of fullerene with aqueous NaOH. By control of reaction conditions, either water-soluble C₆₀ fullereneol or water-insoluble C₆₀ fullereneol were obtained selectively. Further studies on the chemical transformations of fullereneols and their applications to the synthesis of various polymer networks are on the way in our laboratory.

Experimental

¹H NMR spectra were recorded in (CD₃)₂SO on a Bruker AM-300 instruments with Me₄Si as the internal standard. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Lower resolution mass spectra were obtained on an Ionspect instrument using matrix-assisted laser desorption-ionization technique (MALDI). Elemental analyses were performed by this Institute. All solvents were purified before use. C₆₀ (99.9%) was purchased from Wuhan University.

Typical procedure for the reaction of C₆₀ with aqueous NaOH solution in air or N₂

To the benzene solution of C₆₀ (50 mg in 70 mL) vigorously stirred were added slowly 2 mL of NaOH (25 mol·L⁻¹) and PEG 400 (20 mol%) at room temperature in air (or N₂). After being stirred for 30 min, the originally deep violet benzene solution turned colorless and a black sludge precipitated. After removal of benzene by evaporation under reduced pressure, water (15 mL) was added and stirred for 5 min to dissolve the sludge completely. After filtration the water-insoluble product **1** (11.3 mg, 19.6%) was obtained. ¹H NMR [(C-D₃)₂SO, 300 MHz] δ : 3.35(br); IR (KBr) ν : 3433, 1605, 1063, 574, 524 cm⁻¹; MS (MALDI) m/z (%): 720 (C₆₀⁺, 75). Anal. calcd for C₆₀(OH)_{8.5}H_{8.5}: C 82.47, H 1.95; found C 82.51, H 2.01.

The brown filtrate was concentrated and MeOH was added to produce a brown precipitate. The precipitation process was repeated three times to ensure complete removal of PEG and NaOH. Drying the precipitate under reduced pressure gave a brown solid product **2** (64.6 mg, 80.4%). ¹H NMR [(CD₃)₂SO, 300 MHz] δ : 3.35(br); IR (KBr) ν : 3433, 1601, 1064, 573, 524 cm⁻¹; MS (MALDI) m/z (%): 720 (C₆₀⁺, 100). Anal. calcd for C₆₀(OH)₂₇H_{8.5}: C 60.63, H 2.98; found C 60.42, H 2.38.

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