C_{60} Fullerol Formation catalysed by Quaternary Ammonium Hydroxides

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C_{60} fullerol with 24–26 hydroxy groups was synthesized directly by the reaction of fullerene with aqueous NaOH in the presence of tetrabutylammonium hydroxide (TBAH), the most effective catalyst.

Fullerols, polyhydroxylated fullerene derivatives, which are highly soluble in water, have been synthesized recently by Chiang *et al.* by the reaction of fullerene with an aqueous acid or by the hydrolysis of the ester moieties of a polyorganocarboxylated fullerene derivative.[1,2] The isolated fullerene derivatives, being soluble in water and having polar hydroxy groups, have potential applications in aqueous solution chemistry, electrochemistry and biochemistry, as well as in synthesis of new fullerenes. Moreover, fullerols may be useful building blocks for the synthesis of various polymer networks. Here we describe a novel direct route to C_{60} fullerol by the reaction of C_{60} fullerene with aqueous NaOH in the

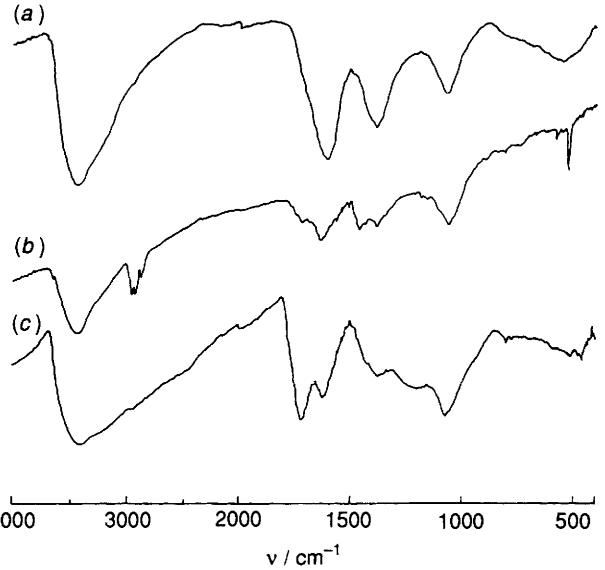

Fig. 1 IR spectra of (*a*) fullerol **1**, (*b*) product **2**, and (*c*) product **3**

presence of tetrabutylammonium hydroxide (TBAH), which was the most effective catalyst under aerobic conditions at ambient temperature.

A benzene solution of C_{60} (80 mg in 60 ml) was vigorously stirred with aqueous NaOH (2 g in 2 ml water) containing 3 drops of TBAH (40% in water) at room temperature under air. Within a few minutes, the benzene solution, originally deep violet, turned colourless and a brown sludge precipitated. After removal of benzene by decantation and evaporation under reduced pressure for a few hours, the sludge and remaining aqueous solution was stirred with an additional 10 ml of water for 10 h. Further water (20 ml) was added at the completion of reaction, and the clear reddish brown aqueous solution obtained was filtered to remove a trace of water-insoluble residue. The filtrate was concentrated to about 5 ml, and MeOH (50 ml) was added to produce a brown precipitate. The precipitation was repeated three times to ensure complete removal of TBAH and NaOH. Drying the precipitate under reduced pressure gave 115 mg of a brown solid product **1**.

The IR spectrum [Fig. 1(*a*)] of product **1** showed a broad hydroxy absorption centred at 3430 cm^{-1}, a C–O stretching absorption centred at 1070 cm^{-1} and a C=C absorption centred at about 1600 cm^{-1}. It is quite similar to the IR spectrum of the fullerol reported by Chiang *et al.*[1] The ^{1}H NMR spectrum of the fullerene derivative **1** in $(CD_3)_2SO$ showed a broad OH peak at δ 3.35 and a weak peak due to the water in the solvent at δ 3.1. The ^{13}C NMR spectrum of the fullerol showed only quite broad peaks. The elemental analysis of **1** (found: C, 61.5; H, 2.25; N, <0.01%) showed an average composition of $C_{60}(OH)_n$ (n = 26.5, Calc.: C, 61.5; H, 2.25%). Since a small amount of water may be present in the fullerol obtained, the number of hydroxy groups could be slightly less than 26.5.

The C_{60} fullerol products obtained may have a variable number of hydroxy groups and be formed in an 'uncontrolled' manner much like other fullerene derivatives such as $C_{60}H_{36}$, $C_{60}F_{36}$ and $C_{60}Cl_{20-22}$. It is known that $C_{60}Br_{24}$ (T_h) has a high-symmetry structure with no adjacent Br atoms to avoid steric hindrance.[3] No isomers, were isolated yet in the present study.

It is noteworthy that C_{60} fullerol is obtained under basic conditions in the present study in contrast to previous reports.[1,2] Moreover, the product contains more hydroxy groups and is consequently more soluble in water than those reported previously.[1,2]

Table 1 Reaction rate of fullerene with NaOH in the presence of quaternary ammonium hydroxides[a]

$R_4N^+{}^-OH$	$Bu_4N^+{}^-OH$	$Et_4N^+{}^-OH$	$Me_4N^+{}^-OH$	Without
Conversion time[b]	3 min	110 min	6 h	>96 h

[a] A benzene solution of C_{60} (10 mg in 10 ml) was stirred with aqueous NaOH (2 ml; 12 mol l^{-1}) and $R_4N^+{}^-OH$ (0.1 ml; 20% w/w in water) in air at room temperature. [b] Time for C_{60} benzene solution to become colourless.

We found that this hydroxy 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 hydroxy 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.

Addition of tetrabutylammonium hydroxide significantly accelerated the conversion of fullerene to fullerol. The reaction rate depended strongly on the alkyl group of the quaternary ammonium hydroxide used. Table 1 shows that the reaction rate in the initial step, in which the C_{60} benzene solution became colourless, increased dramatically with increase in the number of carbon atoms in the alkyl groups of the quaternary ammonium hydroxide. The water-insoluble product **2** from the initial step could be isolated by stopping the reaction after removing benzene, NaOH and TBAH. Product **2** showed an IR spectrum [Fig. 1(*b*)] with the same absorption bands as the water-soluble fullerol except for the C–H absorption bands around 2830–2890 cm^{-1} and the absorption bands around 520–570 cm^{-1} from unreacted C_{60}. The elemental analysis (found: C, 78.8; H, 3.2; N, 1.2%) 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 $C_{60}(OH)_n$ with n = *ca.* 3 which includes some TBAH and unreacted C_{60}. It was insoluble in water because of the small number of hydroxy groups added, and insoluble in benzene. Reaction of C_{60} with only TBAH (40% in water) also produced a fullerol. However, the product was soluble in methanol because it contained a certain amount of TBAH (about 2% N in the samples from elemental analysis). It was difficult to purify the product.

Treatment of **1** with a cation ion-exchanger (Dowex 50X4-400) gave derivative **3** (elemental analysis: C, 55.3; H, 1.9; N < 0.01%). The IR spectrum of the derivative **3** showed a strong C=O absorption centred at 1720 cm^{-1} and a broad weak band at about 1250 cm^{-1} [Fig. 1(*c*)]. This acidic ion-exchanger may lead to conversion of vicinal hydroxy groups to the corresponding ketone structure with ring opening *via* a pinacol-type rearrangement.[2]

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