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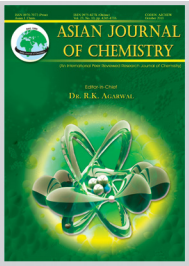

Synthesis and Characterization of Fullerenol using Sodium Stannite as an Electrophilic Reagent

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An electrophilic addition reaction of sodium stannite (Na_2SnO_2) with C_{60} in THF/aqueous NaOH solution can lead to the efficient synthesis of fullerenol. It is found that molecular component and yield of the fullerenol largely depend on the ratio of Na_2SnO_2 to C_{60}, but less on the concentration of NaOH, as evidenced from FTIR, XPS and elemental analysis results. Samples are characterized as weak electrolyte using conductivity testing. TEM study indicates the dependence of aggregation morphology on structure of fullerenol.

Key Words: Fullerenol, Carbon materials, Weak electrolyte.

INTRODUCTION

Fullerenols, polyhydroxylated fullerene derivatives have potential applications in the fields of polymer materials science[1], medical therapeutics[2], biochemistry[3], *etc*. In addition, alkali metalated fullerenols also show promise for electrochemistry[4]. Several methods of preparing metalated fullerenols through the use of tetrabutylammonium hydroxide (TBAH)[5], halogenated fullerenes precursor[6], sulfuric acid and nitric acid[7], have been reported. Husebo *et al*.[5] reported the reaction of an aqueous NaOH solution in contact with a toluene or benzene solution of C_{60} using TBAH as a phase transfer agent to prepare $Na^+_n[C_{60}O_x(OH)_y]^{n-}$. The reaction was performed in liquid phase with toxic organic solvents such as benzene or toluene as reaction media. Troshin *et al*.[6] developed a halofullerene method, which required reaction times of up to 2 weeks. However, the acidic method, reported by Vileno *et al*.[7] required repeated washing and purification treatments. These have become the methods of choice for polyhydroxylation of fullerenes when only a small quantity of material is available. The availability of higher efficiency of metalated fullerenol production would increase significantly the potential use in electrochemistry. Therefore, a novel and efficient procedure must be developed for further applications.

In this report, we describe the facile one-pot synthesis of alkali metal fullerenols with Na_2SnO_2 used as an electrophilic reagent to activate the olefinic bonds of C_{60} molecules. The compound can be readily obtained in high yield within 5 h. The first ionization and aggregation characterization as a function of fullerenol structure have been carried out using conductivity testing and TEM measurement.

EXPERIMENTAL

Synthesis: A small amount of solid C_{60} (150 mg) and THF (50 mL) were placed in a vial and sonicated under very mild conditions (90 W, 40 kHz) for 1.5-2 h at room temperature under argon condition. Then, an aqueous NaOH solution (240 mg, 20 mL), with some dissolved sodium stannite (20.8 mg, 1 equiv per C_{60}), was added. The reaction mixture was then sonicated under the same conditions for at least 3 h. The red-brown product, collected by centrifugation from the aqueous solution, was washed several times with a water-methanol mixture to remove salt, alkali and unreacted C_{60} (if any) completely.

FT-IR spectra were recorded on a Fourier transformation intermediate infrared system (EQUINOX55, BRUKER), using KBr pellets. The fullerenols were also characterized using X-ray photoelectron spectrometer (K-Alpha, VG), CHNS/O element analyzer (EA3000, EURO). The conductivities of the samples were recorded on a conductivity meter (Auto-3000 DL, Fischer) in aqueous solution. TEM was done using H-7650 microscope (Hitachi), with sample solution prepared with high purity water.

Using the relative XPS composition analysis results and above C1s curve-futted data, it is possible to estimate the average number of hydroxyl and hemiketal, along with a Na^+/fullerenol ratio for each sample. In combination with elemental analysis results, molecular formulas for the three fullerenol samples have been calculated as fullerenol-1 [$C_{60}(OH)_6(ONa)_8$], fullerenol-2 ($C_{60}(OH)_5(ONa)_9$) and fullerenol-3 [$C_{60}(OH)_5(ONa)_{11}$] (Table-2). In this manner, molecular formulae for fullerenols prepared in this work can be estimated.

TABLE-1
XPS AND EA ANALYSIS RESULTS OF FULLERENOLS

S. No	Results						
	XPS Composition analysis results (At %)				Elemental analysis (EA, mass %)		
	C	O	Na	C:O:Na (atom ratio)	C	H	C/H ratio
Sample No. 1	73.47	17.58	8.95	60:14:8	63.12	0.54	60:6
Sample No. 2	72.48	17.17	10.35	60:14:9	61.88	0.45	60:5
Sample No. 3	69.38	18.03	12.59	60:16:11	58.89	0.42	60:5

TABLE-3
XPS AND EA ANALYSIS RESULTS OF FULLERENOLS

S. No	Results						
	XPS Composition analysis results (At %)				Elemental analysis (EA, mass %)		
	C	O	Na	C:O:Na (atom ratio)	C	H	C/H ratio
Sample No. 4	78.72	18.62	2.65	60:14:2	71.48	1.21	60:12
Sample No. 5	73.47	17.58	8.95	60:14:8	63.12	0.54	60:60
Sample No. 6	66.06	19.39	14.55	60:18:13	54.21	0.37	60:50

RESULTS AND DISCUSSION

In a typical reaction, the addition of an aqueous NaOH solution (240 mg, 20 mL), with some dissolved Na_2SnO_2 (20.8 mg, 1 equiv per C_{60}) to a THF (50 mL) solution of C_{60} (150 mg) results in the formation of fullerenol, as confirmed by FT-IR spectrum and XPS experiment. The FT-IR spectrum shows the characteristic features of fullerenols: a broad hydroxyl group-related absorption band centered at 3411 cm^{-1}, C=C band (1570 cm^{-1}), C-O bending band (1406 cm^{-1}) and C-O stretching bands (1056, 1019 cm^{-1}). We attribute the high frequency C-O stretching band to the C-OH band, the low frequency band to the C-ONa band (as Na is much higher than H). The fitting analysis of the sample 1 allowed the assignment of three different oxidation states of carbon. The fitted peak with a banding energy at 284.7 ev (76.6 % of total area) is assigned to nonoxygenated carbon, the peak at 286.5 eV (13.3 % of total area) to monoxygenated carbon (C-OH) and the peak at 288.1 eV (10.1 % of total area) to deoxygenated carbon. Besides of the C1s (At % 73.47) peaks in the sample 1, O1s (At % 17.58) and Na 1s (At % 8.95) peak at 1070.8 eV were also observed. It is remarkable that the molar ratio of C, Na and O is close to 60:8:14. The elemental analysis of the powder yielded the following weight fractions: % C 63.12, % H 0.54 %. Using XPS results, in combination with elemental analysis data, it is possible to calculate the molecule formula for sample 1 as $C_{60}(OH)_8(ONa)_8$. In this manner, molecular formulas for other fullerenol samples, which were prepared with different mole ratio of Na_2SnO_2 to C_{60} and NaOH concentrations, have been estimated (Tables 1-4).

TABLE-2
DEPENDENCE OF FULLERENOL MOLECULAR FORMULA, YIELD, SOLUBILITY ON THE MOLE RATIO OF Na_2SnO_2:C_{60}

S. No.	Na_2SnO_2:C_{60}[a] (mol)	m.f.	Yield (%)
0	0	-	0
1	1:1	$C_{60}(OH)_6(ONa)_8$	74.9
2	2:1	$C_{60}(OH)_5(ONa)_9$	92.5
3	3:1	$C_{60}(OH)_5(ONa)_{11}$	98.8

C_{NaOH} (g/L) = 3.42

As can be seen from Table-5, molecular components and yields of these fullerenols are influenced by the different mole ratio of Na_2SnO_2 to C_{60}. It is noteworthy that fullerenol can not be synthesized without the use of Na_2SnO_2. When mole ratio of Na_2SnO_2 to C_{60} is less than 2:1, the yields of these fullerenols increase evidently and number of functional groups in the fullerenols is constant as mole ratio of Na_2SnO_2:C_{60} increases. The yield rises to 98.8 % and number of functional groups increases clearly when Na_2SnO_2:C_{60} is up to 3:1. The results show that mole ratio of Na_2SnO_2:C_{60} affects yields of these fullerenols then number of functional groups in the fullerenols. In addition, the effect of the concentration of NaOH was also investigated. Na_2SnO_2 and C_{60} were dissolved in THF/aqueous NaOH solutions (5:2 by volume) with mole ratio of 1:1. Therefore, we propose that higher concentrations of NaOH can increase the yield and number of functional groups of the fullerenol by enhancing reaction efficiency of Na_2SnO_2 with C_{60}. It has been found that the ratio of initial reagents and alkalinity are critical influencing factors for the molecular formulae of our samples.

TABLE-4
DEPENDENCE OF FULLERENOL MOLECULAR FORMULA, YIELD ON THE NaOH CONCENTRATION

S. No.	NaOH (g/L)	Molecular formula	Yield (%)
Sample No. 4	1.71	$C_{60}(OH)_{12}(ONa)_2$	70.0
Sample No. 5	3.42	$C_{60}(OH)_6(ONa)_8$	74.9
Sample No. 6	5.13	$C_{60}(OH)_5(ONa)_{13}$	77.6

$NaSnO_2$: C_{60} : 1:1

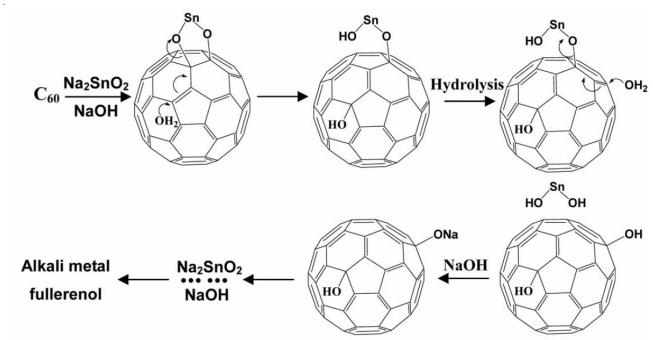
TABLE-5
DEPENDENCE OF FULLERENOL MOLECULAR FORMULA, YIELDS ON THE MOLE RATIO OF Na_2SnO_2:C_{60} AND NaOH CONCENTRATION

Sample			Molecular formula	Yields of 1 (%)
No. 0		0	-	0
No. 1	Mole ratio of	1:1	$C_{60}(OH)_6(ONa)_8$	74.9
No. 2	Na_2SnO_2:C_{60}[a]	2:1	$C_{60}(OH)_5(ONa)_9$	92.5
No. 3		3:1	$C_{60}(OH)_5(ONa)_{11}$	98.8
No. 4		1.71	$C_{60}(OH)_{12}(ONa)_2$	69.0
No. 5	C_{NaOH} (g/L)[b]	3.42	$C_{60}(OH)_6(ONa)_8$	74.9
No. 6		5.13	$C_{60}(OH)_5(ONa)_{13}$	77.6

[a]C_{NaOH} = 3.42 g/L; [b]Na_2SnO_2:C_{60} = 1:1

As shown in **Scheme-I**, synthesis mechanism of fullerenol is proposed to be an electrophilic addition reaction of Na_2SnO_2

with fullerene C_{60} in the NaOH condition. The initial nucleophilic attack of SnO_2^{2-} ions on fullerene in alkaline conditions may give reactive intermediates of $C_{60}(SnO_2^{2-})_x$ adducts. The subsequent hydrolysis of these adducts in NaOH solution, followed by a proton transfer reaction, generates the corresponding polyhydroxyl derivatives of fullerene. Alkali metal fullerenols are then prepared by the reaction between hydroxyl and NaOH at strong alkalinity.



Scheme-I: Mechanism for the formation of fullerenol based upon electrophilic property of Na_2SnO_2 under strong basic conditions

When the concentration is below 0.01 mol dm^3, Kohlrausch figured out that the molar conductivity (Λ_m) of strong electrolyte can be related to the square root of concentration ($\sqrt{C}$) by the equation:

$$\Lambda_m = \Lambda_m^{\infty}(1-\beta\sqrt{C}) \quad (1)$$

The limiting molar conductivity (Λ_m^{∞}) and constant (β) were determined from the Λ_m *vs.* $\sqrt{C}$ plots, where the two parameters exhibit a linear relationship. Moreover, Kohlrausch indicated that Λ_m and $\sqrt{C}$ of weak electrolyte have nonlinearity relation, despite with low concentration below 0.005 mol dm^3. The resulting fullerenols in this work, also called alkali metal fullerenols, have been characterized as a structurally and electronically complex C_{60} anion[5,7]. To further characterize these Na^+-fullerenols, we investigated the molar conductivity of samples in water as a function of concentration. As shown in Fig. 1, there exists a nonlinear relationship between the molar conductivity and the square root of concentration of all four samples, which demonstrates alkali metal fullerenol would ionize in aqueous solution as weak electrolyte based on the Kohlrausch's dilution law.

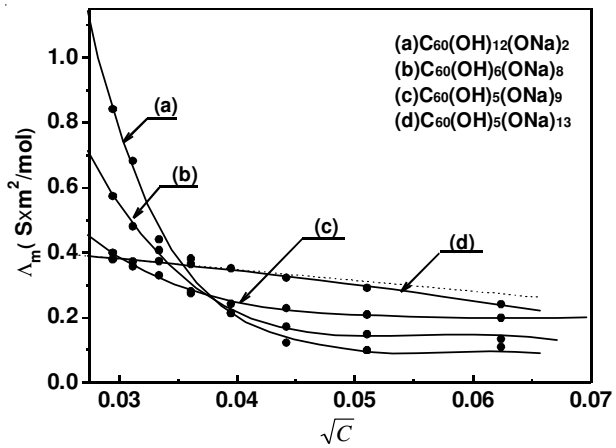


Fig. 1. Molar conductivity of fullerenols in water as a function of concentration at 291K

Furthermore, under conditions of concentration lower than 0.0016 mol dm^3 ($\sqrt{C} = 0.04$), the four samples exhibit quite a different Λ_m increasing rate with the decreases of concentrations. Higher Λ_m increasing rate of these samples corresponds to lower ionizability, because the weak electrolyte with lower ionizability can be the most affected by the decreasing concentration. So, in order of increasing ionizability, the four weak electrolytes are $C_{60}(OH)_{12}(ONa)_2$, $C_{60}(OH)_6(ONa)_8$, $C_{60}(OH)_5(ONa)_9$ and $C_{60}(OH)_5(ONa)_{13}$. Therefore, it is concluded that more -ONa bands will improve the ionizability of fullerenols.

Fullerenols showed various aggregation morphologies in different literatures[4,5,7]. To investigate the possible morphology influences, we performed TEM measurements to image the fullerenol samples with different molecular formula in this work. Fig. 2 shows a comparison of the TEM images of the fullerenols in water (9×10^{-5} mol/L). As shown in Fig. 2a, fullerenol molecules gather to large amorphous aggregation. However, spherical assemblies are observed in Fig. 2b and 2c. In Fig. 2d, the spherical clusters exist with smaller sizes and obvious boundaries. On both theory and empirical studies, a weaker hydrogen bond network of -OH and a stronger repulsive forces of negatively charged groups (-ONa) can be contribute to an improved spherical morphology, smaller cluster diameter and more obvious boundaries. Therefore, the aggregation morphology of fullerenol is highly dependent on the relative strength of the two bonds.

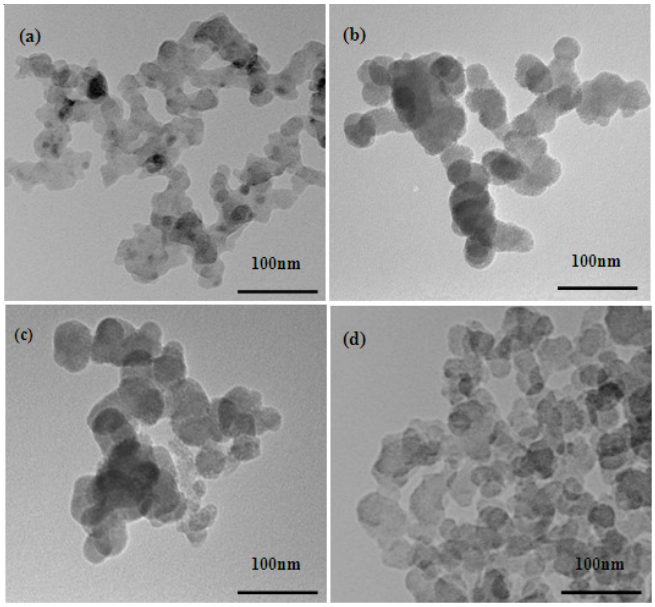


Fig. 2. TEM image of fullerenol prepared using different conditions: (a) $C_{60}(OH)_{12}(ONa)^2$; (b) $C_{60}(OH)_6(ONa)_8$; (c)$C_{60}(OH)_5(ONa)_9$; (d) $C_{60}(OH)_5(ONa)_{13}$

Conclusion

In conclusion, alkali metal fullerenol has been synthesized by the electrophilic addition of Na_2SnO_2 in THF under strong basic conditions. Molecular formula and yields of synthesis fullerenols can be determined by the mole ratio of Na_2SnO_2:C_{60} and NaOH concentration. The resulting fullerenols would ionize in water as weak electrolytes and more -ONa bands of these molecules will improve the ionizability. TEM results

indicate that relative strength of -OH and -ONa bands have an impact on the aggregation morphology of fullerenol.

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