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Monitoring Oxidation Behavior of [C_{70}]Fullerene by Ultrasonic Spectroscopy

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[C_{70}]풀러렌 산화 반응의 거동에 관한 초음파 분광학적 고찰

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ABSTRACT : High resolution ultrasonic spectroscopy was used to observe the oxidation of [C_{70}]fullerene with 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene. UV-vis spectroscopy and X-ray diffraction confirmed the resulting products of [C_{70}] fullerene oxidation.

요 약 : 1,2-dichlorobenzene용액에서 [C_{70}]풀러렌 과 3-chloroperoxy benzoic acid 산화반응의 거동을 고분해능 초음파 분광기를 사용하여 고찰하였다. UV-vis spectroscopy, X-ray diffraction 을 가지고 [C_{70}]풀러렌 산화 반응의 생성물을 확인하였다.

Keywords : ultrasonic spectroscopy, oxidation of [C_{70}]fullerene, uv-vis spectroscopy, x-ray diffraction

Ⅰ. Introduction

High resolution ultrasonic spectroscopy using high frequency acoustical waves with a frequency greater than 100 kHz is a new spectroscopic technique for nanomaterials analysis.[1-4]

High resolution ultrasonic spectroscopy is a novel analytical technique with strong potential for analyzing a wide range of samples and molecular processes. This technique is based on precise measurements of the parameters of ultrasonic waves propagating through the samples.

Ultrasonic spectroscopy in the liquid state becomes an important tool in various scientific fields, such as materials science, biology, medicine, physics, physical chemistry, and nanochemistry.[5-8] Ultrasonic spectroscopy has been used successfully to observe many types of phase transitions in the liquid state.[9-15] The two main parameters measured by ultrasonic spectrometry are the attenuation and the velocity of the waves. Ultrasonic attenuation is determined by the energy losses in the ultrasonic wave propagating through the sample. Ultrasonic velocity is determined by the elasticity and density of the medium. This ultrasonic velocity is sensitive to the composition and intermolecular interactions of the sample. High resolution ultrasonic spectroscopy was used to analyze the oxidation of [C_{70}]fullerene for a mixture of [C_{70}]fullerene and 3-chloroperoxxy benzoic acid in 1,2-dichlorobenzene.

This paper describes the changes in the ultrasonic velocity and ultrasonic attenuation at the oxidation of [C_{70}]fullerene with 3-chloroperoxy benzoic acid by high resolution ultrasonic spectroscopy.

Ⅱ. Experimental

1. Chemicals

[C_{70}]fullerene and 3-chloroperoxy benzoic acid were purchased from Sigma-Aldrich Co. 1,2–Dichlorobenzene was obtained from Samchun Chemicals.

2. Measurement principles [16]

Ultrasonic spectroscopy is based on measurements of the sound speed (c) and ultrasonic attenuation. When a sound wave travels through a system, it loses some energy depending on the structure of the system itself. In a liquid system, the ultrasound velocity is related to the adiabatic compressibility (βs) and medium density (ρ) according to the Laplace equation;

$$C = 1/\sqrt{\beta s \times \rho}$$

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As a consequence, this parameter is related directly to the high frequency elasticity of the medium and is extremely sensitive to the intermolecular interactions and composition of the sample. The speed of sound, C, is inversely proportional to the density, ρ, and compressibility, βs, of the sample. This value can be correlated with the amount of dissolved solids in the sample.[17]

The other parameter, attenuation, is a good property for characterizing dispersed phase composition and particle size. It reflects the energy loss due to scattering and absoption.[4] The attenuation value at any particular frequency has two component parts, intrinsic, α_1 and excess, α_2, attenuation related to the dispersed and continuous phase, respectively.

$$\alpha_{total} = \alpha_1 + \alpha_2(1- \varphi)$$

where φ is the volume fraction of the dispersed phase. Assuming that the intrinsic attenuation remains constant, the total attenuation is proportional to the concentration of insoluble components.[18]

3. Experimental instrument, procedure and sample preparation

The ultrasonic attenuation (α) and ultrasonic velocity (u) were measured using a high resolution ultrasonic spectrometry (HR-US 101), which made by Ultrasonic Scientific Ltd (Dublin, Ireland). This instrument allows high resolution measurements of both the velocity and attenuation of acoustic waves propagating through the fluids within the 4-14 MHz frequency range. The temperature of the sample and reference cells was controlled with an accuracy of ± 0.01K. The reference cell was filled with 1,2-dichlorobenzene using a plastic pipette.

Stock solutions of [C_{70}]fullerene in 1,2-dichlorobenzene (1 mg/g) were prepared by mixing [C_{70}]fullerene powder and 1,2-dichlorobenezne. 3-chloroperoxy benzoic acid powder was mixed with 1,2-dichlorobenzene to give a total concentration of 40 mg/g. The prepared solution was cloudy, but stable without sedimentation or visible particles.

A small amount of 3-chloroperoxy benzoic acid stock solution was added to a preweighed amount of a [C_{70}]fullerene stock solution to obtain a final concentration of 5 mg/g of 3-chloroperoxy benzoic acid/1,2-dichlorobenzene and 0.88 mg/g of [C_{70}]fullerene/1,2-dichlorobenezne.

The prepared sample (after mixing for 1 min) was added to the sample chamber of HR-US and the reference was filled with 1,2-dichlorobenzene. The ultrasonic velocity and attenuation in the loaded samples (mixtures) were monitored continuously for up to 24 hr at 25 ° at the frequency of 5.1 MHz.

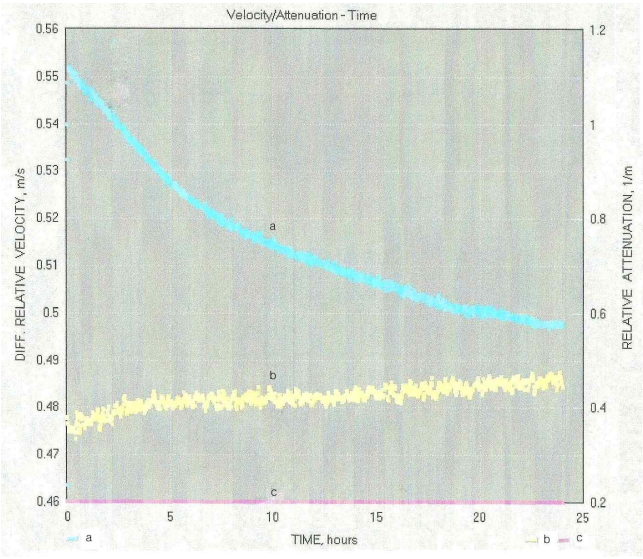

Figure 1. High resolution ultrasonic spectrum of the reaction between [C_{70}]fullerene and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene at 25 ℃; a-velocity l/m, b-attenuation l/m, c-reference(from 0 to 24 hr).

Ⅲ. Results and Discussion

Ultrasonic high resolution spectroscopy is a useful tool for characterizing nanomaterials produced by a reaction of [C_{70}]fullerene and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene.

In Figure 1, two stages were detected in the reaction of [C_{70}]fullerene and 3-chloroperoxy benzoic acid. The reaction in the first stage showed a rapid change within 5 hr after mixing, and the second stage showed a slow rate of change in the ultrasonic values from 5 to 24 hr.

The change in the ultrasonic velocity and attenuation represents the interaction of [C_{70}]fullerene and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene. The ultrasonic velocity decreased during the reaction due to the density increase of the product.

The change in velocity, which is related directly to the change in chemical composition of the solution, was found to be inversely proportion to the concentration from the reactants, [C_{70}]fullerene and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene, to the products as a function of the time. A change in attenuation was found to be directly proportional to the change in concentration of the reactants to the products in the reaction with [C_{70}]fullerene and 3-chloroperoxy benzoic acid in 1,2-dichlorbenzene. A decrease in phase velocity was observed in the [C_{70}]fullerene and 3-chloroperoxy benzoic acid system (e.g.-5.2 cm/s at 5.1 MHz), whereas an increase in attenuation was observed in [C_{70}]fullerene and 3-chloroperoxy benzoic acid (e.g., 0.196 l/m at 5.1 MHz).

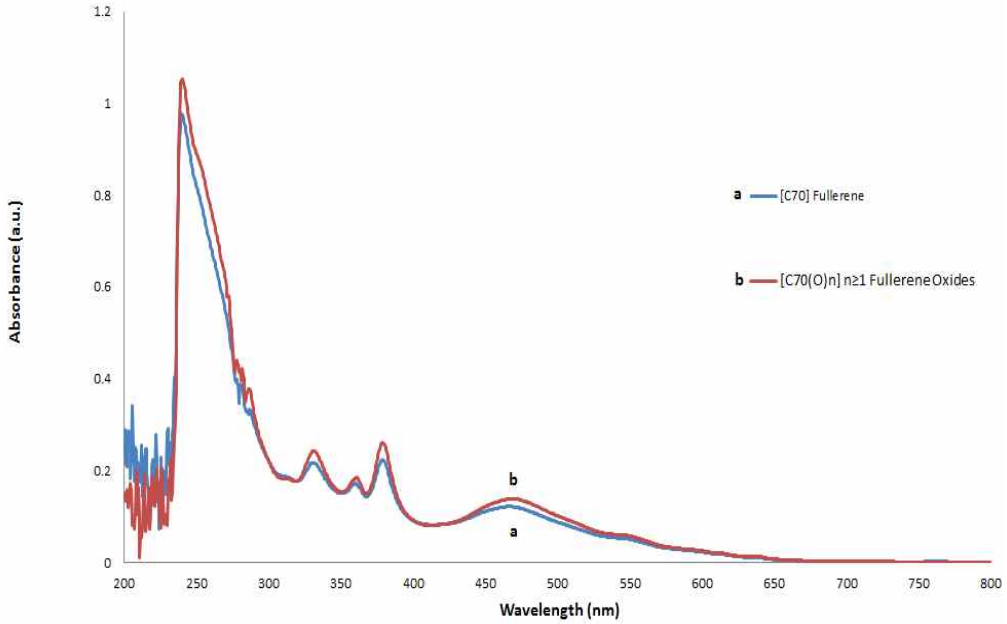

Figure 2. UV-vis spectra of [$C_{70}(O)_n$, n≥1]fullerene oxides and [C_{70}]fullerene.

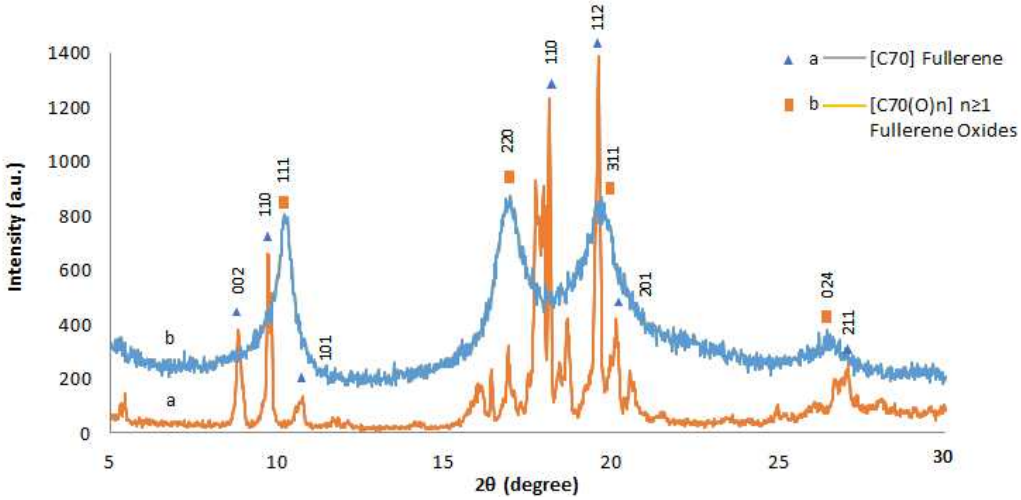

Figure 3. XRD patterns of [$C_{70}(O)_n$, n≥1]fullerene oxides and [C_{70}]fullerene.

Ultrasonic attenuation increases during the reaction as a result of the decrease in the density of the reactant. This can be explained by the aggregation of [C_{70}]fullerene and 3-chloroperoxy benzoic acid. The increase in attenuation can be attributed to the flocculation of dispersed solution by a reaction of [C_{70}]fullerene and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene.

The UV-vis spectrum of [$C_{70}(O)_n$, n≥1]fullerene oxides revealed absorption bands at 240, 331, 360, 379, and 467 nm, as shown in Figure 2. This spectrum showed a slight hypsochromic shift relative to [C_{70}]fullerene[19] (UV-vis(THF): λ_{max} [nm] = 241, 332, 361, 380, 468), which is a characteristic absorption pattern for [$C_{70}(O)_n$, n≥1]fullerene oxides.

Figure 3 presents an XRD pattern of fullerene oxides [$C_{70}(O)_n$, n≥1]. Distinctive peaks for [$C_{70}(O)_n$, n≥1]fullerene oxides were observed at 10.20°, 16.97°, 20.03°, and 26.63° 2θ, which were assigned to the plane indices (111), (220), (311), and (024), respectively. The distinctive peaks for [C_{70}]fullerene in Figure 3 were observed at 8.82°, 9.70°, 10.75°, 18.13°, 19.61°, 20.14°, and 27.09° 2θ, which were assigned to the (002), (110), (101), (110), (112), (201), (211) plane indices, respectively.[20-25]

According to XRD, the crystallinity of [$C_{70}(O)_n$, n≥1]full-

erene oxides decreased compared to [C_{70}]fullerene. This suggests that the oxygen was bonded to [C_{70}]fullerene.

Ⅳ. Conclusions

High resolution ultrasonic spectroscopy was an efficient tool for examining the oxidation of [C_{70}]fullerene. The ultrasound parameters of velocity and attenuation showed the process of a reaction with [C_{70}]fullerene and 3-chloroperoxy benzoic acid. The ultrasonic velocity and attenuation data were effective for examining the behavior of [C_{70}]fullerene oxidation.

Two stage reactions were detected in the reaction of [C_{70}] fullerene and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene. A steep slope in the ultrasonic parameters indicated a rapid change in the reaction at the first stage within the 5 hr after mixing. At the second stage, however, the gentle slope indicated a slow change in the ultrasonic values for the reaction from 5 to 24 hr.

The change in velocity, which is related directly to a change in the chemical composition of the solution, was found to be inversely proportional to the change in the concentration from the reactants to products in the reaction of [C_{70}]fullerene and 3-chloroperoxy benzoic acid in 1,2-dichorobenzene as a function of time. The change in attenuation was found to be directly proportional to the change in the concentration of reactants and products during the reaction with [C_{70}]fullerene and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene.

UV-vis spectroscopy showed that the wavelength of [$C_{70}(O)_n$, $n\geq1$]fullerene oxides had shifted to a shorter wavelength in the range, 200 nm to 800 nm. XRD indicated that [$C_{70}(O)_n$, $n\geq1$]fullerene oxides had lower crystallinity than [C_{70}]fullerene due to the presence of oxygen bonded to the carbon atoms of [C_{70}]fullerene.

Acknowledgments

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