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단 신

Ultrasonic Monitoring of Reaction of Fullerene[C_{60}] with 3 - Chloroperoxy Benzoic acid

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풀러렌[C_{60}]과 3 - Chloroperoxy Benzoic acid 반응의 초음파적 조사

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ABSTRACT : The reaction of fullerene [C_{60}] and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene was monitored by high resolution ultrasonic spectroscopy and the product of reaction by fullerene [C_{60}] and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene was characterized using MALDI-TOF-MS spectra.

요 약 : 1,2-dichlorobenzene 용액에서 풀러렌[C_{60}]과 3-chloroperoxy benzoic acid 의 반응을 고분해능 초음파 분광기를 사용하여 조사하였다. 또한 1,2-dichlorobenzene 용액에서 풀러렌[C_{60}]과 3-chloroperoxy benzoic acid의 반응 생성물을 MALDI-TOF-MS를 가지고 확인하였다.

Keywords : ultrasonic monitoring, fullerene[C_{60}], 3- chloroperoxy benzoic acid, MALDI-TOF-MS

Ⅰ. Introduction

High resolution ultrasonic spectroscopy is a spectroscopic technique for material analysis utilizing high frequency acoustical (ultrasonic) waves with a frequency greater than 100 kHz.[1-2] Ultrasonic spectrometry (often named spectroscopy) in liquids become an important tool for basic and applied research in many scientific fields such as physics, physical chemistry, material sciences, biology, and medicine.[3-6] The measurements by ultrasonic spectroscopy have been used successfully to monitor many types of phase transitions in solution.[7-12,17]

The two major parameters measured in ultrasonic spectrometry are the velocity and the attenuation of the waves. Ultrasonic velocity is determined by the density and the elasticity of the medium it travels through. It is sensitive to intermolecular interactions and composition of the sample. Ultrasonic attenuation is determined by the energy losses in the ultrasonic wave propagating through the sample and is proportional to the high frequency viscosity. It allows the analysis of kinetics of chemical reactions. This paper shows the application of ultrasound techniques for the purpose of investigating the kinetics of products which reacted with

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fullerene[C_{60}] and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene.

Ⅱ. Experimental

1. Measurement principles[18]

It is well known that attenuation is a good property for characterizing dispersed phase composition and particle size, while speed of sound is useful for characterizing chemical compositions at a molecular level.[13] The attenuation value at any particular frequency has two component parts, intrinsic, α_1 and excess, α_2, attenuation relating 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 value is proportional to the concentration of insolubles.[13] Speed of sound, C, is inversely proportional to the density, ρ, and compressibility, ε, of the sample;

$$C = 1/\sqrt{\varepsilon\rho}$$

This value can be correlated to the amount of dissolved solids in the sample.[14] The ability to use a single technique to investigate the insoluble, dissolved and total solids is one of the strengths of diagnostic ultrasound. It's worth noting that both these parameters vary with temperature, which must be accounted for any calculation.

2. Experimental instrument, procedure, and sample preparation

The ultrasonic parameters (velocity, attenuation) were measured by a high resolution ultrasonic spectrometer(HR-US 101) made by Ultrasonic Scientific Ltd (Dublin, Ireland). This instrument allows high resolution measurement of both the velocity and the attenuation of acoustic waves propagating through fluids at high ultrasonic frequencies (4-14 MHz).[15,16] It provides fast and non-destructive analysis of a wide spectrum of properties of materials in fluids. Measurement was done at single frequency (at 5.1 MHz) at 25℃.

Temperature of sample and reference cells was controlled with an accuracy of ±0.01 K. Prior to each experiment, the test solution was transferred into the sample cell using positive pressure pipette. 1,2-dichlorobenzene was also filled to the reference cell using a plastic pipette. Care was taken to prevent generating air bubbles inside the cell during the transfer process. Both cells were tightly capped and allowed to reach thermal equilibrium at set temperature for at least 10 min prior to a measurement. After each experiment, the sample cell was thoroughly cleaned several times with 1,2-dichlorobenzene and air-dried. Stock solutions of fullerene [C_{60}] in 1,2-dichlorobenzene (1 mg/g) were prepared by mixing of fullerene [C_{60}] powder and 1,2-dichlorobenzene. 3-chloroperoxy benzoic acid powder was mixed with 1,2-dichlorobenzene giving a total concentration of 40 mg/g. Prepared solution was cloudy, but it was stable without visible particles or sediment.

Small amount of 3-chloroperoxy benzoic acid stock solution was added to preweighted amount of fullerene [C_{60}] stock solutions to obtain final concentration: 5 mg/g of 3-chloroperoxy benzoic acid/1,2-dichlorobenzene and 0.88 mg/g of fullerene [C_{60}]/1,2-dichlorobenzene in sample. Prepared sample (after mixing for 1 min) was added to sample chamber of HR-US and reference was filled with 1,2-dichlorobenzene. Ultrasonic velocity and attenuation in loaded samples(mixtures) were monitored continuously up to 24 hr at 25℃ in a frequency at 5.1 MHz.

Ⅲ. Results and Discussion

High resolution ultrasonic spectroscopy has proven to be valueable tool in the characterization of nanomaterial by reaction of fullerene[C_{60}] and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene.

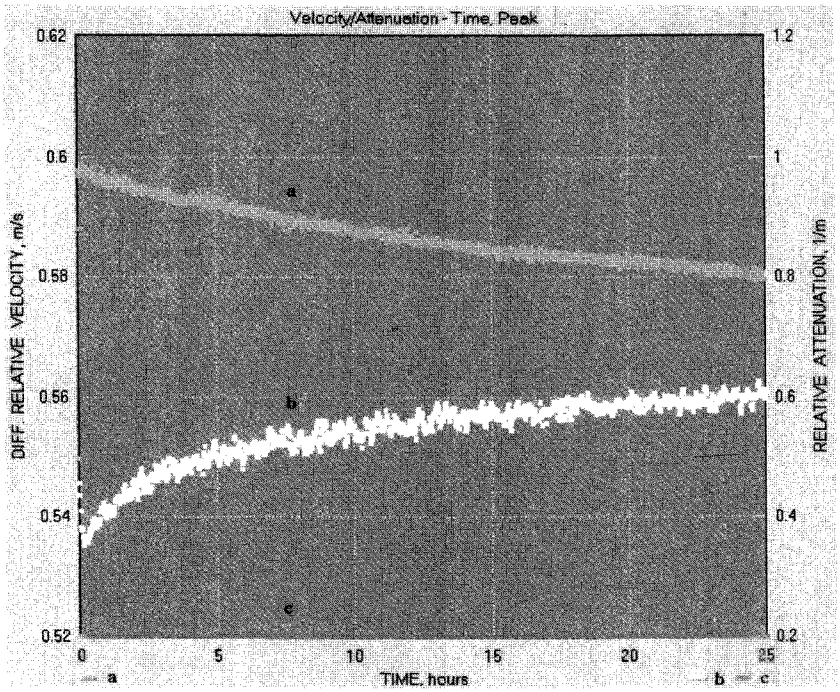
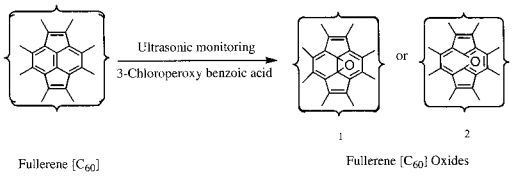


Figure 1. High resolution ultrasonic spectra of the reaction between fullerene[C_{60}] and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene at 25℃; a-Velocity m/s, b-attenuation1/m, c-reference(from 0hr to 24hr).

As shown in Figure 1, reactions of two stage are detected in fullerene[C_{60}] and 3-chloroperoxy benzoic acid. The reaction of first stage shows fast change from 0 hr to 3 hr, second stage shows slow change from 3 hr to 24 hr. It is demonstrated that the measurements of both velocity and attenuation has sufficient accuracy and precision. The change of ultrasonic velocity and attenuation represent the interaction of fullerene[C_{60}] and 3- chloroperoxy benzoic acid in 1,2-dichlorobenzene. Ultrasonic velocity decreases during the reaction as a result of increase of density of product. The change in velocity which is directly related to the change in chemical composition of the solution is found to be inversely proportion to the concentration from reactants to products in the reaction by the time with fullerene [C_{60}] and 3- chloroperoxy benzoic acid in 1,2-dichlorobenzene. The change in attenuation is found to be directly proportion to the changed concentration from reactants to products in the reaction with fullerene [C_{60}] and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene. The magnitude of decrease in phase velocity is observed in C_{60} and 3-chloroperoxy benzoic acid system (e.g. -1.8 cm/s at 5.1 MHz), while the magnitude of increase in attenuation also is observed in C_{60} and 3-chloroperoxy benzoic acid (e.g. 0.24 1/m at 5.1 MHz). Ultrasonic attention increases during the reaction as a result of a decrease of density of reactant. This can be explained by aggregation of fullerene [C_{60}] and 3-chloroperoxy benzoic acid and the increase in the attenuation can be attributed to the flocculation dispersed solution by the reaction of



Scheme

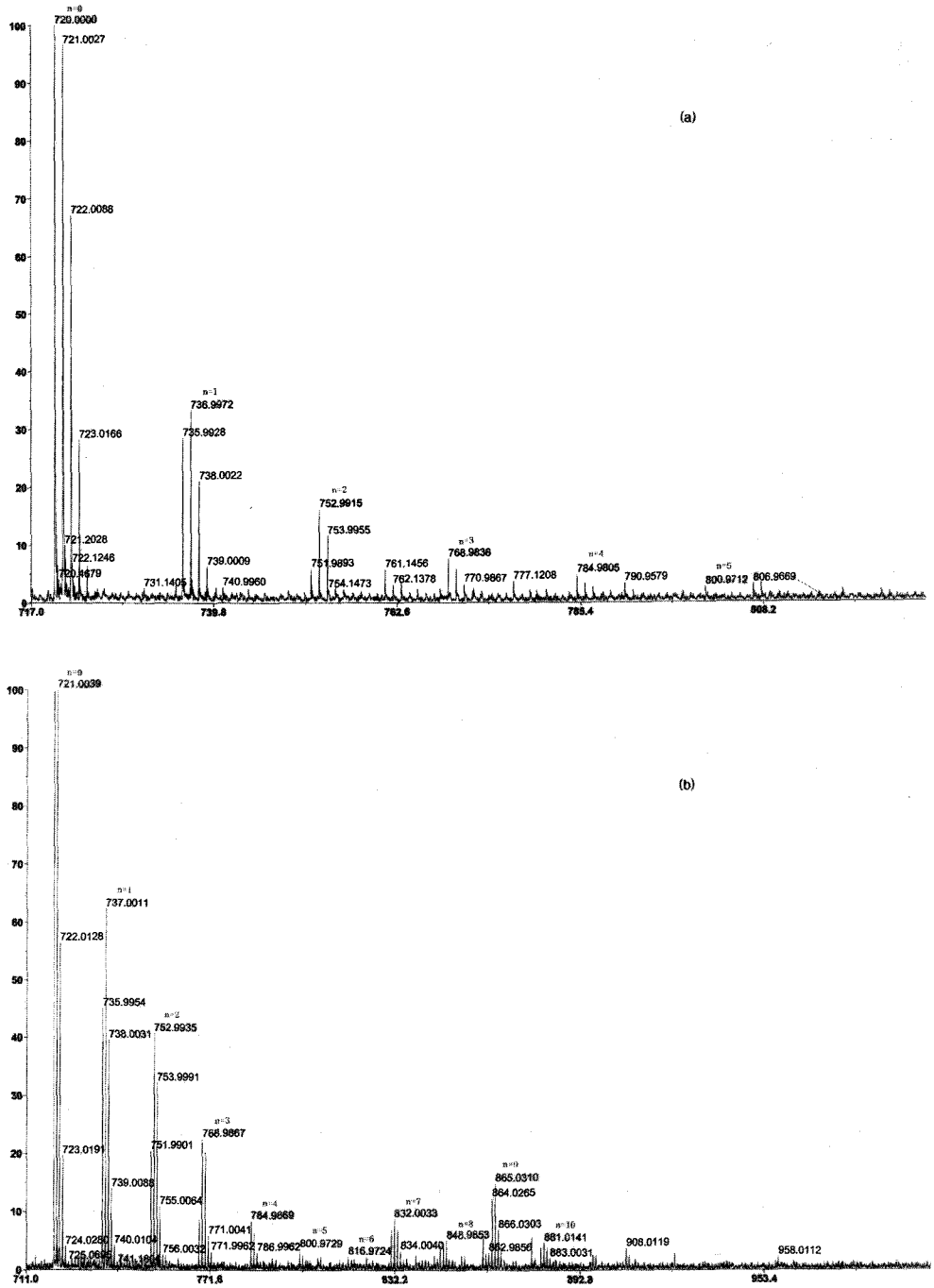


Figure 2. MALDI-TOF-MS spectra of the reaction between fullerene[C_{60}] and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene at 25 ℃; (a) product of reaction from 0 hr to 3 hr, $C_{60}(O)_n$ n=1~5. (b) product of reaction from 3 hr to 24 hr, $C_{60}(O)_n$ n=1~10.

fullerene[C_{60}] and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene. The reaction steps is proposed as following scheme.

The products of reaction by the fullerene[C_{60}] and 3-chloroperoxy benzoic acid at room temperature are formed $C_{60}(O)n$ n=1~5 from 0 hr to 3 hr, $C_{60}(O)n$ n=1~10 from 3 hr to 24 hr, which were observed by MALDI-TOF-MS spectra in Figure 2.

Ⅳ. Conclusion

High resolution ultrasonic spectroscopy has been proven to be valueable tool in the characterization of nanomaterial by reaction of fullerene[C_{60}] and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene. The two stage reactions are detected in the reaction of fullerene [C_{60}] and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene. A steep slope means a fast change of reaction in ultrasonic parameters as seen at the first stage within the first 3 hr after mixing, but at the second stage, a gentle slope means a slow change of reaction in ultrasonic values after 3 hr to 24 hr in Figure 1.

The change in velocity which is directly related to the change in chemical composition of the solution is found to be inversely proportion to the changed concentration from reactants to products in the reaction by the time with fullerene [C_{60}] and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene. The change in attenuation is found to be directly proportion to the changed concentration from reactants to products in the reaction with fullerene [C_{60}] and 3-chloroperoxy benzoic acid in 1,2-dichlorobenzene. The products of reaction are formed $C_{60}(O)_n$ n=1~5 from 0 hr to 3 hr, $C_{60}(O)_n$ n=1~10 from 3 hr to 24 hr, which were observed by MALDI-TOF-MS spectra.

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