

## Preparation of Fullerene Oxides by Fullerenes[C<sub>60</sub>,C<sub>70</sub>] with Several Oxidants under Ultrasonic Condition

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### 초음파 조건에서 산화제를 이용한 풀러렌 산화물의 제조

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**ABSTRACT** : Synthesis of fullerene oxides by fullerenes [C<sub>60</sub>, C<sub>70</sub>] and several oxidants such as benzoylperoxide, trichloroisocyanuric acid, methyltrioxorhenium(VII), iodobenzene, phosphorous pentoxide take place under ultrasonic condition at room temperature. The MALDI-TOF MS, UV-visible spectra and HPLC analysis confirmed that the products of fullerenes oxidation are [C<sub>60</sub>(O)<sub>n</sub>], (n=1~3 or n=1) and [C<sub>70</sub>(O)<sub>n</sub>], (n=1~2 or n=1). As compared with the reactivity of epoxidation of fullerenes [C<sub>60</sub>, C<sub>70</sub>], the reaction rate of C<sub>70</sub> was lower than that of C<sub>60</sub> under same reaction condition.

**요약** : 풀러렌[C<sub>60</sub>, C<sub>70</sub>]을 benzoylperoxide, trichloroisocyanuric acid, methyltrioxorhenium(VII), iodobenzene 그리고 phosphorous pentoxide 등의 산화제를 사용하여 상온, 초음파 조건에서 풀러렌 산화물을 제조하였다. MALDI-TOF MS, UV-VIS 그리고 HPLC를 사용하여 분석한 결과 생성된 풀러렌 산화물은 [C<sub>60</sub>(O)<sub>n</sub>](n=1~3, 또는 n=1) 과 [C<sub>70</sub>(O)<sub>n</sub>](n=1~2 또는 n=1)임을 알 수 있었다. 한편, 동일한 실험 조건에서 C<sub>60</sub> 반응속도는 C<sub>70</sub>보다 높았다.

**Keywords** : Fullerene oxides, Several oxidants, Ultrasonic condition, MALDI-TOF MS.

## I. Introduction

The reactivity of the fullerenes,<sup>1</sup> C<sub>60</sub> in particular, with both ultrasonic and some oxidizing agents is likely to be an important consideration in any technological application of these substances. The [C<sub>60</sub>(O)<sub>n</sub>] (n=1~3) has been obtained by a number of oxidation processes in solution. These include the photo-oxygenation of C<sub>60</sub>,<sup>2,3</sup> the electrochemical oxidation of C<sub>60</sub>,<sup>4</sup> the addition of dimethyldioxirane

to C<sub>60</sub>,<sup>5</sup> the ozonolysis of C<sub>60</sub>,<sup>6</sup> and the ultrasound-induced oxidation of C<sub>60</sub>.<sup>14</sup> Although C<sub>70</sub> displays many characteristics similar to C<sub>60</sub>, its chemistry has remained much less explored than that of C<sub>60</sub>. C<sub>70</sub>O was discovered by Diederich *et al.*<sup>7</sup>, in fullerene containing soot from the condensation of carbon vapor. C<sub>70</sub>O is also known to form via oxygen-starved benzene combustion,<sup>8</sup> by ozonolysis in toluene solution<sup>9</sup> and by photo-oxygenation.<sup>6</sup> Peracid oxidation of C<sub>70</sub> yielded considerably more of the 5, 6 than of the 1, 2 isomer.<sup>10</sup> Van Cleempoel *et al.*<sup>11</sup>, have reported that C<sub>70</sub>O and higher C<sub>70</sub>

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oxides in toluene solution oxidize further upon standing by the addition of one O atom to each oxide.  $C_{70}$  can be also oxidized with various oxidants by ultrasonication.<sup>12,13</sup> Ultrasonic waves in liquids are known to cause chemical reactions either in homogeneous or in heterogeneous systems.<sup>14,15</sup> The chemical reactions are promoted by cavitation of liquids caused by ultrasonic waves traveling in the liquid. Here, cavitation implies the formation of micro-bubbles in a liquid subjected to sonication, which implode and generate high pressures and temperatures in their surroundings.<sup>14,15</sup> The ultrasonic process was applied to the synthesis of fullerene [ $C_{60}$ ].<sup>16</sup> We report that the reaction of fullerenes [ $C_{60}$ ,  $C_{70}$ ] with several kind of oxidants

such as benzoylperoxide, trichloroisocyanuric acid, methyltrioxorhenium(VII), iodosobenzene, phosphorous pentoxide, give rise to the oxidation of fullerenes [ $C_{60}$ ,  $C_{70}$ ] at room temperature under ultrasonic condition, with the formation of [ $C_{60}(O)_n$ ], ( $n=1\sim3$  or  $n=1$ ) and [ $C_{70}(O)_n$ ], ( $n=1\sim2$  or  $n=1$ ).

## II. Experimental

Fullerenes [ $C_{60}$ ,  $C_{70}$ ] used in this work were Golden grade from Southern Chemical Group Inc, benzene (Daejung Chemicals & Metals Co. Ltd, 99%), toluene (Duksan Pure Chemical Co. Ltd, 99.5%), methylene Chloride (Duksan Pure Chemical Co. Ltd, 99.0%), benzoylperoxide (Fluka, 97.0%),

**Table 1. The MALDI-TOF MS and HPLC Analysis of  $C_{60}(O)_n$  ( $n=1\sim3$  or  $n=1$ ) and  $C_{70}(O)_n$  ( $n=1\sim2$  or  $n=1$ ) Produced in the Reaction with Various Oxidants Under Ultrasonic Condition for 5h.**

Oxidants	Fullerenes	Formation of $C_{60}(O)_n$ ( $n=1\sim3$ or $n=1$ ) and $C_{70}(O)_n$ ( $n=1\sim2$ or $n=1$ )	Mass unit (m/z)	Retention times, min
Trichloroisocyanuric acid	$C_{60}$	$C_{60} O_3$	769	6.68
	$C_{60}$	$C_{60} O_2$	753	9.04
	$C_{60}$	$C_{60} O_1$	737	12.72
	$C_{60}$	$C_{60}$	721	17.14
	$C_{70}$	$C_{70} O_2$	873	14.21
	$C_{70}$	$C_{70} O_1$	857	20.10
	$C_{70}$	$C_{70}$	841	28.15
Benzoylperoxide	$C_{60}$	$C_{60} O_2$	753	9.03
	$C_{60}$	$C_{60} O_1$	737	12.79
	$C_{60}$	$C_{60}$	721	17.10
	$C_{70}$	$C_{70} O_1$	857	20.07
	$C_{70}$	$C_{70}$	841	28.11
Iodosobenzene	$C_{60}$	$C_{60} O_2$	753	9.01
	$C_{60}$	$C_{60} O_1$	737	12.58
	$C_{60}$	$C_{60}$	721	17.32
	$C_{70}$	$C_{70} O_1$	857	20.45
	$C_{70}$	$C_{70}$	841	28.20
Methyltrioxorhenium(VII)	$C_{60}$	$C_{60} O_1$	737	12.75
	$C_{60}$	$C_{60}$	721	17.16
	$C_{70}$	$C_{70} O_1$	857	20.27
	$C_{70}$	$C_{70}$	841	28.36
Phosphorous pentoxide	$C_{60}$	$C_{60} O_1$	737	12.71
	$C_{60}$	$C_{60}$	721	17.18
	$C_{70}$	$C_{70} O_1$	857	20.15
	$C_{70}$	$C_{70}$	841	28.23

Note: MALDI-TOF MS (Voyager-DE STR) analysis conditions: the matrix was a cyano-4-hydroxy cinnamic acid. HPLC analysis conditions: model number: Hewlett Packard 1100; Column: ZorbaxSB  $C_{18}$ ; Detector: 340 nm; Flow rate: 1.0 ml/min; Mobile phase: acetonitrile-toluene 50:50 (v/v); Injection volume: 10.00  $\mu$ l; Pump pressure: 1.000 psi

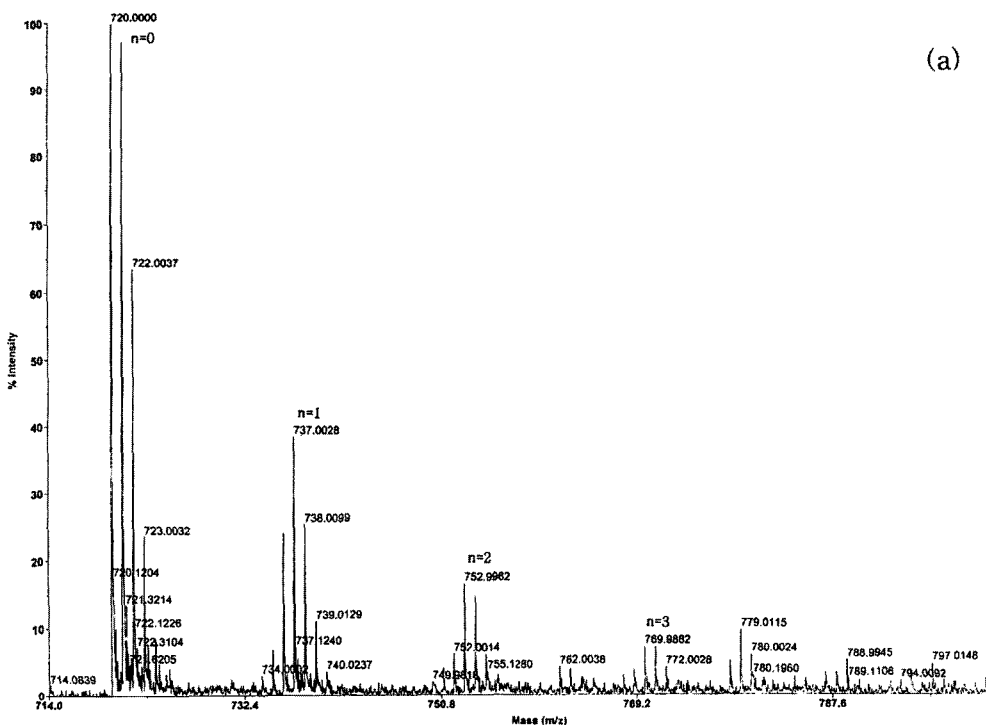
trichloroisocyanuric acid (Aldrich, 97.0%), methyltrioxorhenium(VII) (TCI, 97.0%), iodosobenzene (TCI, 90.0%), phosphorous pentoxide (Daejung Chemicals, 97.0%) were used. The ultrasonication of all the samples was conducted in pulse mode with an Ultrasonic Generator UG 1200 made by Hanil Ultrasonic Co, LTD. Ultrasonic equipment employed in this research having frequency 20 kHz, power 750 W, the configuration of the equipment is a horn type system, and the size of the horn tip is 13 mm in diameter. All the samples were analyzed by MALDI-TOF MS (Voyager-DE STR) and the matrix was a cyano-4-hydroxy cinnamic acid. HPLC analysis conditions: Model number: Hewlett Packard 1100; Column: Zorbax SB C<sub>18</sub>; Detector: 340 nm; Flow rate: 1.0 ml/min; Mobile phase: acetonitrile/ toluene 50:50 (v/v); Injection volume 10.00  $\mu$ l; Pump pressure: 1.000 psi. The electronic absorption spectra were obtained by Varian Cary 100 UV-visible spectrophotometer.

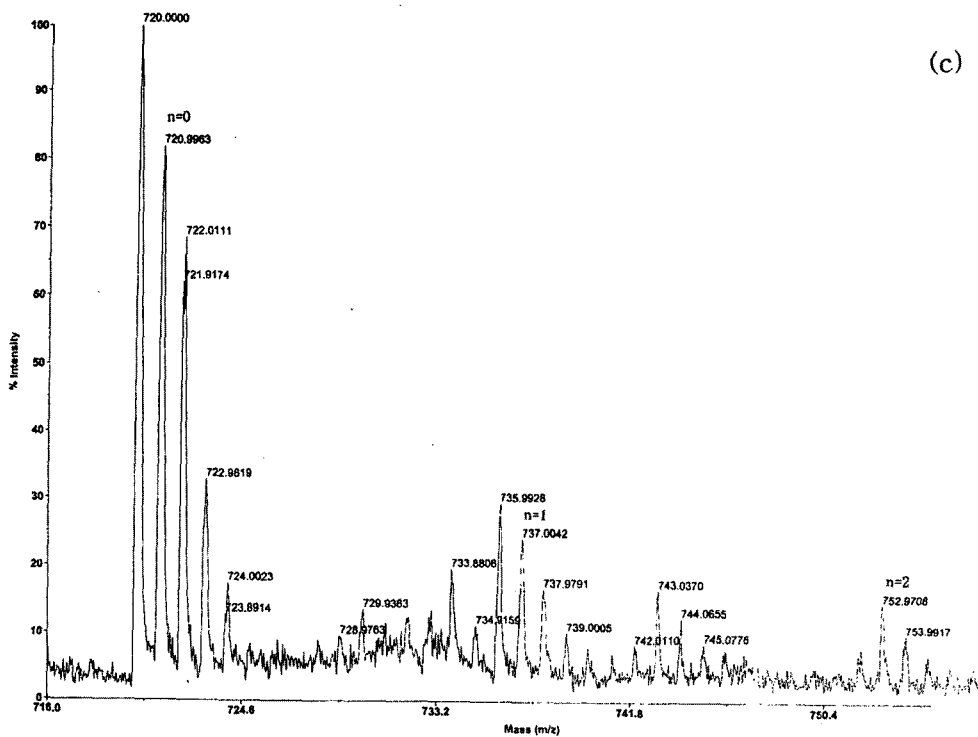
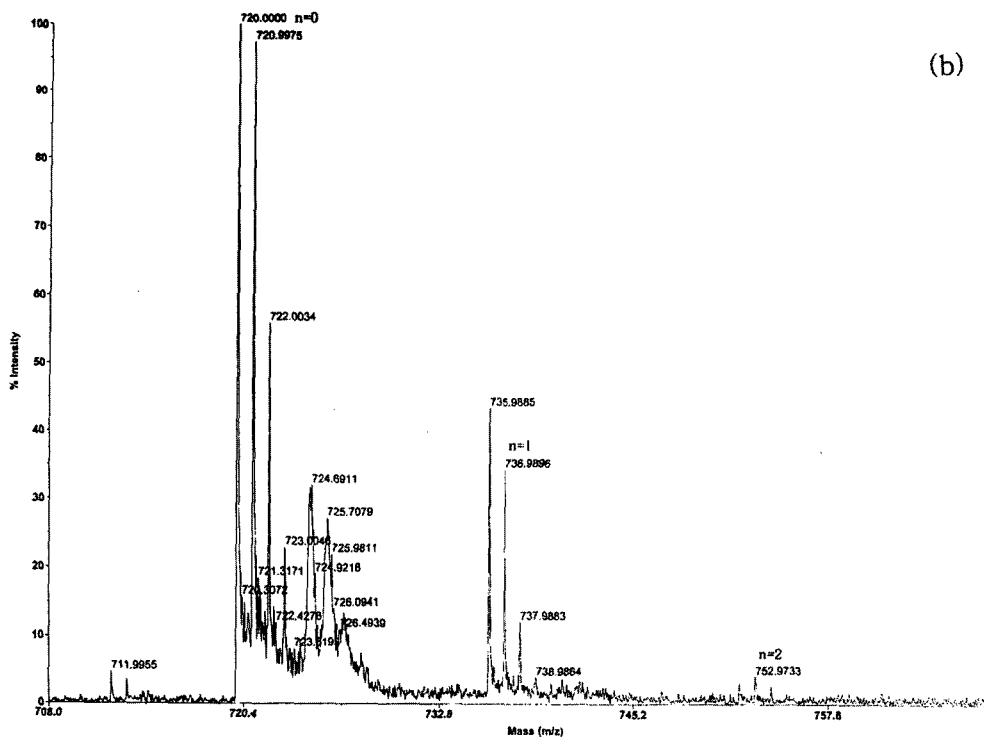
### 1. The reaction of fullerene[C<sub>60</sub>] by ultrasonication with various oxidants.

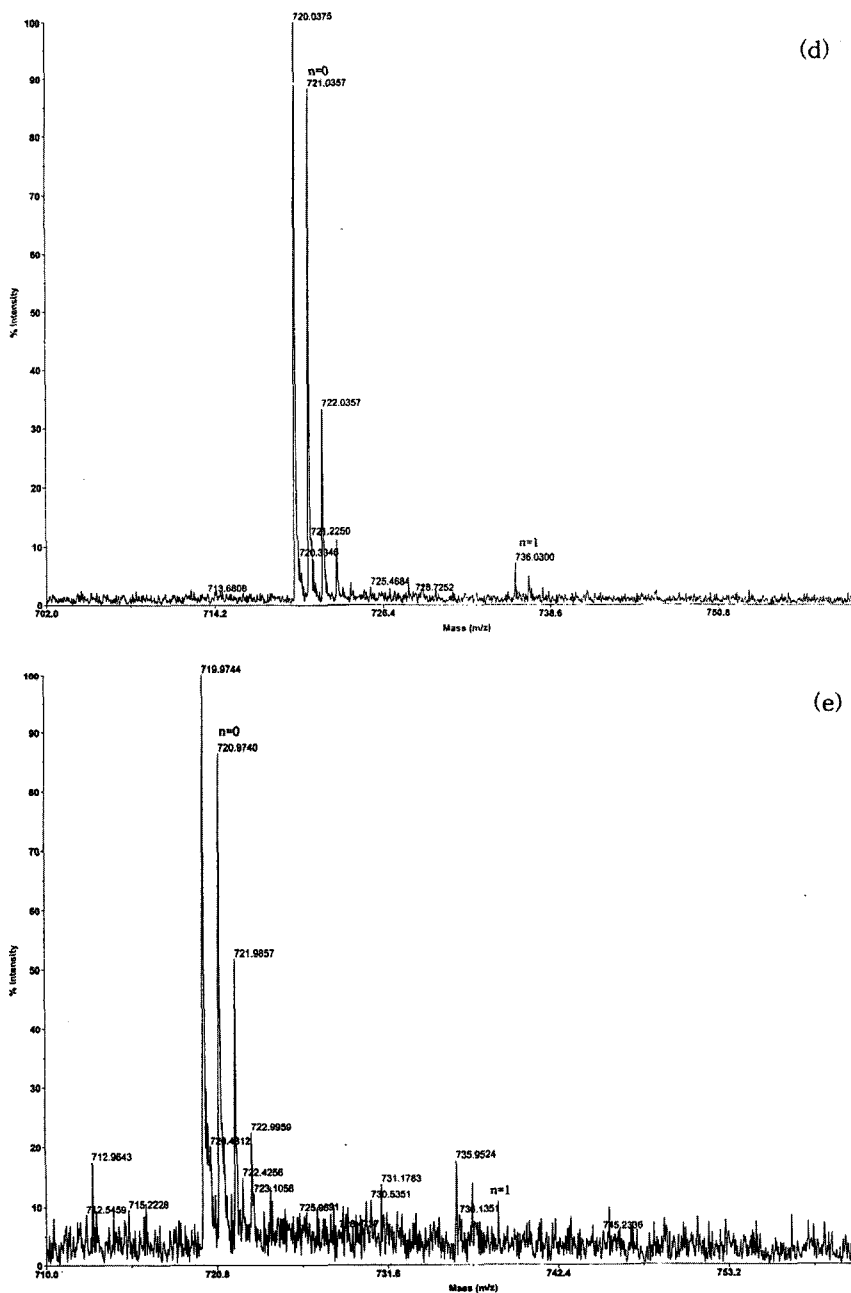
Solutions of C<sub>60</sub> (20 mg, 0.028 mmol) dissolved in 60ml of benzene with benzoylperoxide (136.0 mg, 0.56 mmol), in 50 ml of methylene chloride with trichloroisocyanuric acid (130.0 mg, 0.56 mmol), in 50 ml of toluene with methyltrioxorhenium (VII)(140.0 mg, 0.56 mmol), in 50ml of toluene with iodosobenzene(123.0 mg, 0.56 mmol), in 50ml methylene chloride with phosphorous pentoxide (80.0 mg, 0.56 mmol) reacted under ultrasonic condition in air at room temperature for 5h. Each resulting solution was evaporated, the remaining solid material was obtained as a mixture of fullerene oxidation products, and was dried in the vacuum oven.

### 2. The reaction of fullerene[C<sub>70</sub>] by ultrasonication with various oxidants.

Solutions of C<sub>70</sub> (20 mg, 0.024 mmol) dissolved

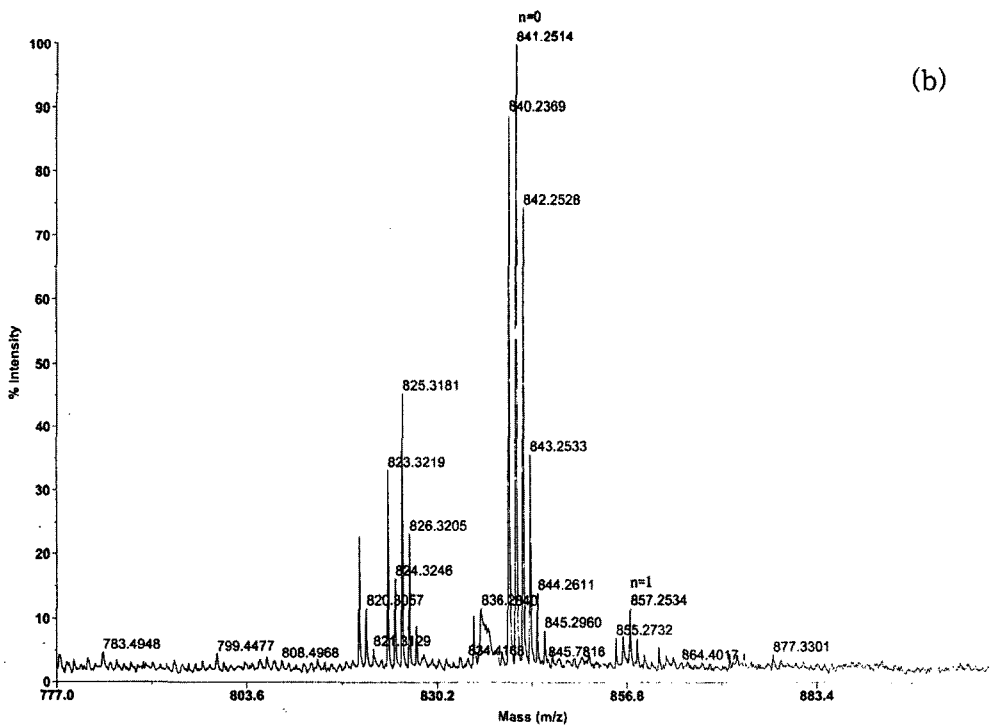
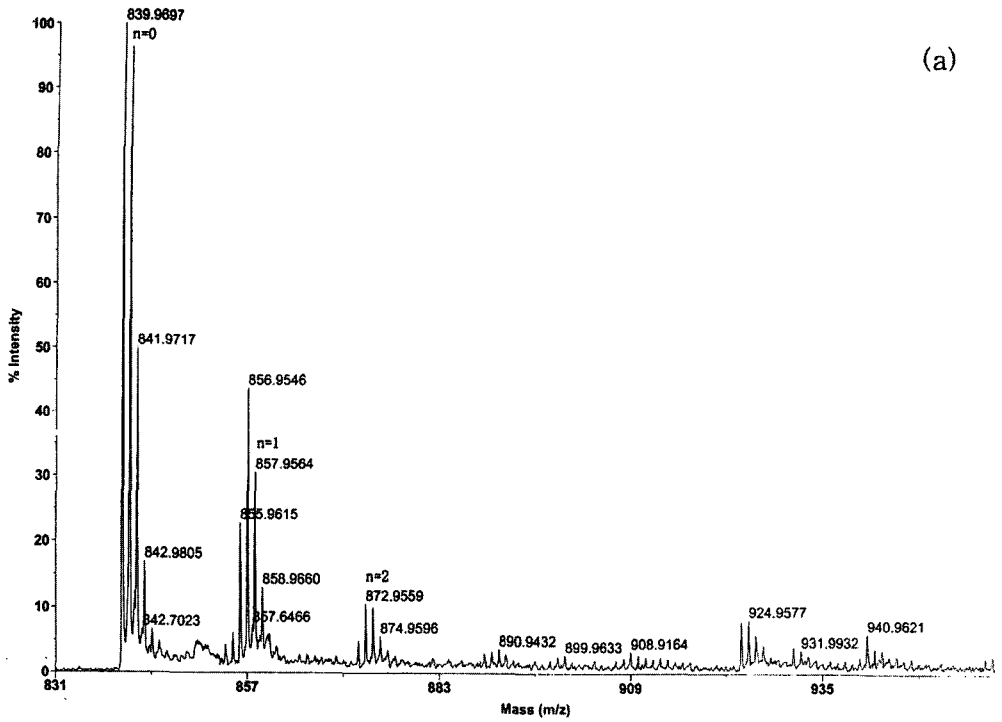


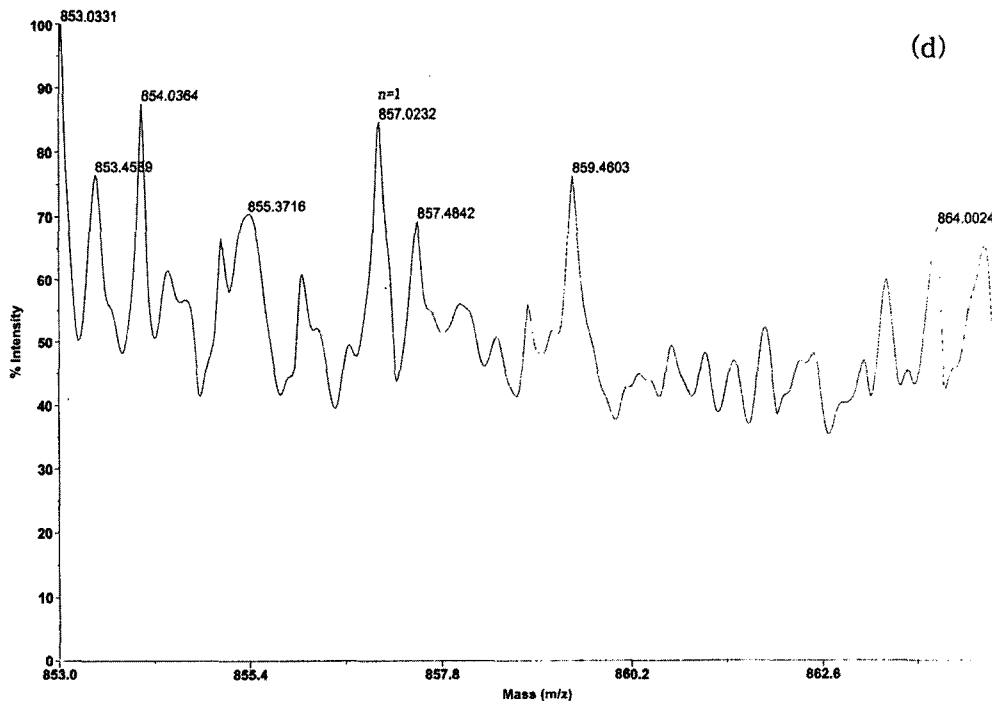
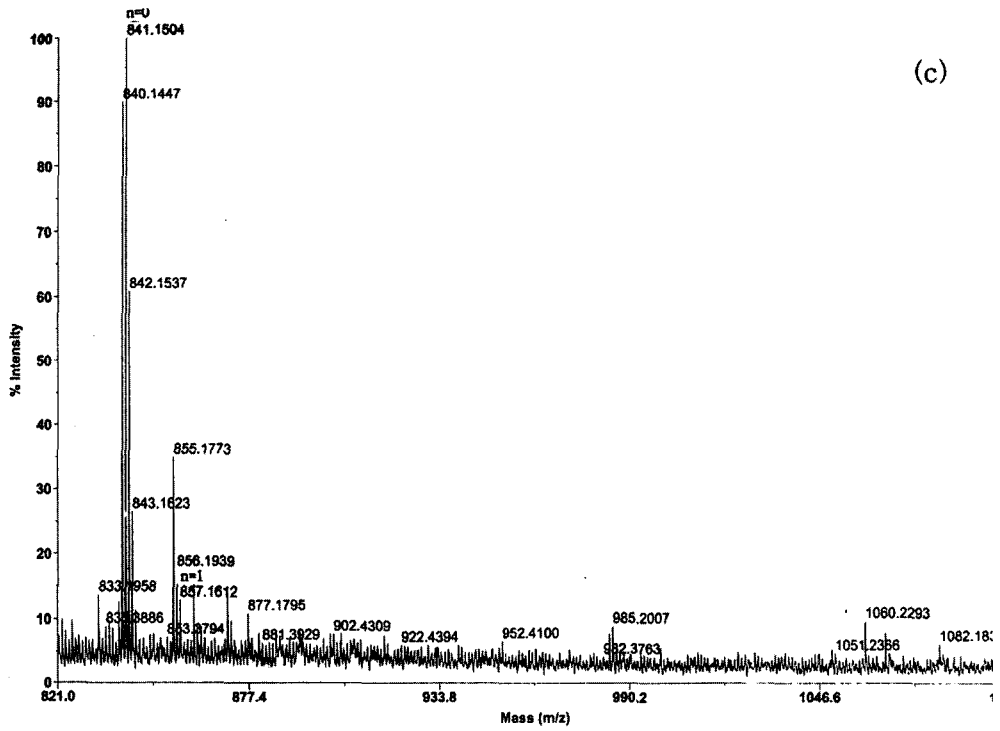


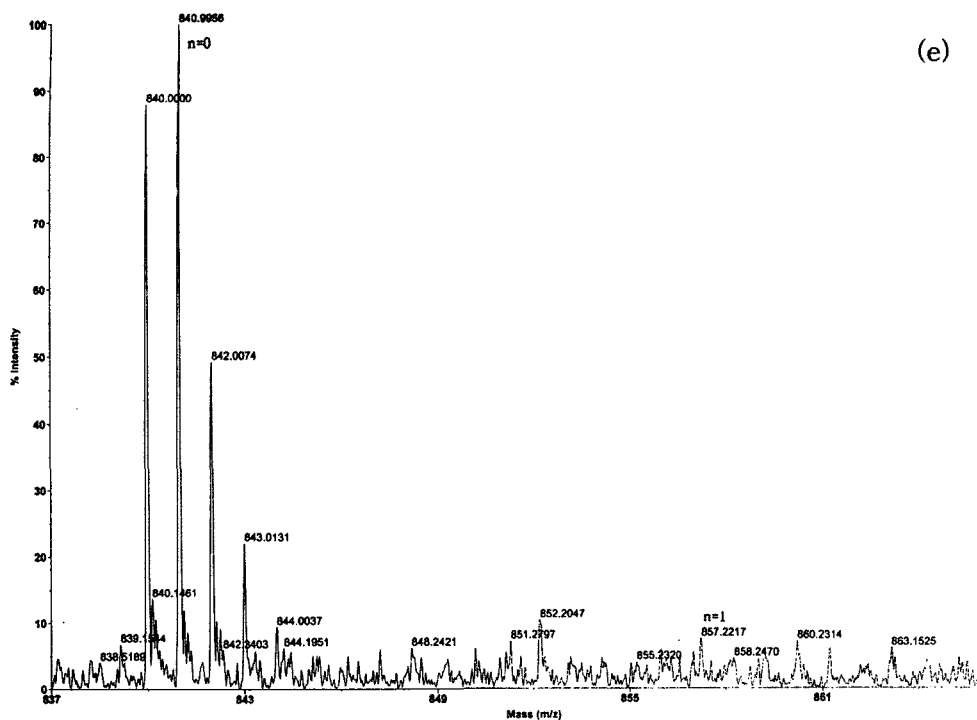


**Figure 1.** MALDI-TOF MS spectra of C<sub>60</sub>(O)<sub>n</sub>, (n=1~3 or n=1)

- (a) the mixture reacted with trichloroisocyanuric acid, n=0, 1, 2, 3 by ultrasonication shows the presence of C<sub>60</sub>, C<sub>60</sub>O<sub>1</sub>, C<sub>60</sub>O<sub>2</sub>, C<sub>60</sub>O<sub>3</sub>
- (b) the mixture C<sub>60</sub> reacted with benzoylperoxide, n=0, 1, 2 by ultrasonication shows the presence of C<sub>60</sub>, C<sub>60</sub>O<sub>1</sub>, C<sub>60</sub>O<sub>2</sub>
- (c) the mixture reacted with iodobenzene, n=0, 1, 2 by ultrasonication shows the presence of C<sub>60</sub>, C<sub>60</sub>O<sub>1</sub>, C<sub>60</sub>O<sub>2</sub>
- (d) the mixture reacted with methyltrioxorhenium (VII), n=0, 1 by ultrasonication shows the presence of C<sub>60</sub>, C<sub>60</sub>O<sub>1</sub>
- (e) the mixture reacted with phosphorous pentoxide, n=0, 1 by ultrasonication shows the presence of C<sub>60</sub>, C<sub>60</sub>O<sub>1</sub>







(e)

**Figure 2.** MALDI-TOF MS spectra of  $C_{70}(O)_n$ , ( $n=1\sim 2$  or  $n=1$ )

- (a) the mixture reacted with trichloroisocyanuric acid,  $n=0, 1, 2$  by ultrasonication shows the presence of  $C_{70}, C_{70}O_1, C_{70}O_2$   
 (b) the mixture reacted with benzoylperoxide,  $n=0, 1$  by ultrasonication shows the presence of  $C_{70}, C_{70}O_1$   
 (c) the mixture reacted with iodosobenzene,  $n=0, 1$  by ultrasonication shows the presence of  $C_{70}, C_{70}O_1$   
 (d) the mixture reacted with methyltrioxorhenium (VII),  $n=0, 1$  by ultrasonication shows the presence of  $C_{70}, C_{70}O_1$   
 (e) the mixture reacted with phosphorous pentoxide,  $n=0, 1$  by ultrasonication shows the presence of  $C_{70}, C_{70}O_1$

in 60 ml of benzene with benzoylperoxide (116.0 mg, 0.48 mmol), in 50 ml of methylene chloride with trichloroisocyanuric acid (112.0 mg, 0.48 mmol), in 50 ml of toluene with methyltrioxorhenium (VII) (120.0 mg, 0.48 mmol), in 50 ml of toluene with iodosobenzene (106.0 mg, 0.48 mmol), in 50 ml methylene chloride with phosphorous pentoxide (68.0 mg, 0.48 mmol) reacted under ultrasonic condition in air at room temperature for 5h. Each resulting solution was evaporated, the remaining solid material was obtained as a mixture of fullerene oxidation products, and was dried in the vacuum oven.

### III. Results and Discussion

The MALDI-TOF MS spectra and HPLC profile revealed that the oxidation of fullerenes [ $C_{60}, C_{70}$ ] by ultrasonication in the presence of various oxidants such as benzoylperoxide (Fluka, 97.0%), trichloroisocyanuric acid (Aldrich, 97.0%), methyltrioxorhenium(VII) (TCI, 97.0%), iodosobenzene (TCI, 90.0%), phosphorous pentoxide (Daejung Chemicals, 97.0%) were [ $C_{60}(O)_n$ ], ( $n=1\sim 3$  or  $n=1$ ) and [ $C_{70}(O)_n$ ], ( $n=1\sim 2$  or  $n=1$ ). The reactivity of fullerenes [ $C_{60}, C_{70}$ ] under ultrasonic conditions increased in the order of trichloroisocyanuric acid > benzoyl peroxide  $\cong$  iodosobenzene > methyltrioxorhenium(VII)  $\cong$  phosphorous pentoxide. The differences between various oxidation reactions with and



without ultrasonication are as follows: the reaction time is shortened due to high pressure and temperature under ultrasonic condition. Epoxidation mediated by ultrasonication with various oxidants is efficient for both electron-rich olefins and fullerenes. MALDI-TOF MS and HPLC analysis data reported in Table 1 show the formation of [C<sub>60</sub>(O)<sub>n</sub>], (n=1~3 or n=1) and [C<sub>70</sub>(O)<sub>n</sub>], (n=1~2 or n=1). MALDI-TOF MS analysis reported in Figures 1 and 2 shows the formation of [C<sub>60</sub>(O)<sub>n</sub>], (n=1~3 or n=1) and [C<sub>70</sub>(O)<sub>n</sub>], (n=1~2 or n=1). The most intense peak was at m/z=721, and m/z=841 in the MALDI-TOF MS spectrum in Figure 1 (a)~(e) and Figure 2 (a)~(e) which is due to the unreacted fullerenes [C<sub>60</sub>, C<sub>70</sub>] and the fragmentation of fullerene oxides [C<sub>60</sub>(O)<sub>n</sub>], (n=1~3 or n=1) and [C<sub>70</sub>(O)<sub>n</sub>], (n=1~2 or n=1). HPLC analysis reported in Table 1 shows the formation of [C<sub>60</sub>(O)<sub>n</sub>], (n=1~3 or n=1) and [C<sub>70</sub>(O)<sub>n</sub>], (n=1~2 or n=1). HPLC analysis data in Table 1 for the oxidation of fullerenes [C<sub>60</sub>, C<sub>70</sub>] under ultrasonic condition with various oxidants show C<sub>60</sub>, C<sub>60</sub>O<sub>1</sub>, C<sub>60</sub>O<sub>2</sub>, C<sub>60</sub>O<sub>3</sub> and C<sub>70</sub>, C<sub>70</sub>O<sub>1</sub>, C<sub>70</sub>O<sub>2</sub> at different retention times respectively. Comparing oxidation of fullerenes[C<sub>60</sub>, C<sub>70</sub>] between C<sub>60</sub> and C<sub>70</sub>, the reactivity of C<sub>70</sub> by ultrasonication with various oxidants such as benzoylperoxide (Fluka, 97.0%), trichloroisocyanuric acid (Aldrich, 97.0%), methyltrioxorhenium(VII) (TCI, 97.0%), iodosobenzene (TCI, 90.0%), phosphorous pentoxide (Daejung Chemicals, 97.0%) looks lower than that of C<sub>60</sub> under the same reaction condition. The reactivity difference probably results from the symmetry in their structures. Electronic absorption bands(λ max) of [C<sub>60</sub>(O)<sub>n</sub>], (n=1~3 or n=1) in benzene were observed at 279, 331, and 407 nm at [C<sub>60</sub>(O)<sub>n</sub>], (n=1~3) and at 279, 335, and 407 nm at [C<sub>60</sub>(O)<sub>n</sub>], (n=1). Electronic absorption bands(λ max) of [C<sub>70</sub>(O)<sub>n</sub>], (n=1~2 or n=1) in benzene were observed at 278, 314, 334, 364, 382 and 474 nm. This electronic absorption spectrum of the oxidation of fullerenes [C<sub>60</sub>, C<sub>70</sub>] by ultrasonication with various oxidants is not similar to that of pure C<sub>60</sub> and C<sub>70</sub> as the number of oxygen atom increases. This

indicates that the multi-epoxide of fullerenes [C<sub>60</sub>, C<sub>70</sub>] perturbs the π molecular orbital in pure C<sub>60</sub> and C<sub>70</sub>, while the mono-epoxide of fullerenes [C<sub>60</sub>, C<sub>70</sub>] does not seriously perturb the π molecular orbital in pure C<sub>60</sub> and C<sub>70</sub>. The reaction of fullerenes [C<sub>60</sub>, C<sub>70</sub>] by ultrasonication with various oxidants may proceed by a nucleophilic attack of various oxidants to a 6-6 bond in the fullerenes[C<sub>60</sub>, C<sub>70</sub>], followed by the heterolytic cleavage of the O-O bond. The consensus mechanism for fullerene oxidation by ultrasonication with various oxidants involves oxygen atom transfer to the fullerenes [C<sub>60</sub>, C<sub>70</sub>]. It is suggested that the fullerene epoxide [C<sub>60</sub>(O)<sub>n</sub>], (n=1~3 or n=1) and [C<sub>70</sub>(O)<sub>n</sub>], (n=1~2 or n=1) may be used as oxygen transfer materials. Also, the fullerene epoxide, [C<sub>60</sub>(O)<sub>n</sub>], (n=1~3 or n=1) and [C<sub>70</sub>(O)<sub>n</sub>], (n=1~2 or n=1) are interesting starting materials for the formation of other fullerene-based entities.

#### IV. Conclusions

By the HPLC profile, UV-visible and MALDI-TOF MS spectra of products which were obtained by sonochemical oxidation reactions, we have identified the [C<sub>60</sub>(O)<sub>n</sub>], (n=1~3 or n=1) and [C<sub>70</sub>(O)<sub>n</sub>], (n=1~2 or n=1) formed in the reaction of C<sub>60</sub> and C<sub>70</sub> by ultrasonication with benzoylperoxide (Fluka, 97.0%), trichloroisocyanuric acid (Aldrich, 97.0%), methyltrioxorhenium(VII) (TCI, 97.0%), iodosobenzene (TCI, 90.0%), phosphorous pentoxide (Daejung Chemicals, 97.0%) at room temperature. We observed that the reaction rate of C<sub>70</sub> was lower than that of C<sub>60</sub>, which may be due to the lower symmetry of the C<sub>70</sub> structure. The epoxidation of olefin by the multi-epoxide of fullerenes, [C<sub>60</sub>(O)<sub>n</sub>], (n=1~3 or n=1) and [C<sub>70</sub>(O)<sub>n</sub>], (n=1~2 or n=1) is presently under investigation.

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