

Sonochemical Synthesis of Fullerene Oxides $[C_{70}O_n]$ ($n=1\sim 2$) Using Metal Hexacarbonyl Complexes $M(CO)_6$ ($M=Cr, Mo, W$) Under Air Atmosphere

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공기 중에서 금속 헥사카르보닐 착물 $M(CO)_6$ ($M=Cr, Mo, W$)을 이용한 풀러렌 산화물 $[C_{70}O_n]$ ($n=1\sim 2$)의 초음파화학 합성

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ABSTRACT : Sonochemical synthesis of fullerene oxides $[C_{70}O_n]$ ($n=1\sim 2$) by fullerene $[C_{70}]$ and metal hexacarbonyl complexes $M(CO)_6$ ($M=Cr, Mo, W$) took place under air atmosphere. The reactivity of fullerene $[C_{70}]$ and several metal hexacarbonyl complexes $M(CO)_6$ ($M=Cr, Mo, W$) under same ultrasonic condition increased in the order of $Mo(CO)_6 > W(CO)_6 > Cr(CO)_6$. The MALDI-TOF-MS, UV-visible spectra, and HPLC analysis confirmed that the products of sonochemical reaction were $[C_{70}O_n]$ ($n=1\sim 2$).

요약 : 공기 중 초음파 조건에서 풀러렌 $[C_{70}]$ 과 금속 헥사카르보닐 착물 $M(CO)_6$ ($M=Cr, Mo, W$)을 반응시켜 풀러렌 산화물 $[C_{70}O_n]$ ($n=1\sim 2$)을 합성하였다. 동일한 초음파 조건에서 풀러렌 $[C_{70}]$ 과 여러 가지 금속 헥사카르보닐 착물 $M(CO)_6$ ($M=Cr, Mo, W$)의 반응성은 $Mo(CO)_6 > W(CO)_6 > Cr(CO)_6$ 순으로 증가함을 나타냈다. MALDI-TOF-MS, UV-visible 스펙트럼과 HPLC를 사용하여 분석한 결과 초음파화학 반응의 생성물은 $[C_{70}O_n]$ ($n=1\sim 2$)임을 알 수 있었다.

Keywords : sonochemical synthesis, fullerene oxides, metal hexacarbonyl complexes, MALDI-TOF-MS, air atmosphere

I. Introduction

Recently, sonochemical reactions have been proven to be a useful synthetic technique to generate novel material with desirable properties.¹ Ultrasonic synthesis of fullerene derivatives has attracted considerable attention in materials science and solid-state chemistry.² Power of ultrasound provides one

of the most exciting way to synthesize nanomaterials of fullerene derivatives for research and industry.³

The chemical effects of ultrasound arise from acoustic cavitation : formation, growth, and implosive collapse of bubbles in liquid.^{2,4} The implosive collapse of bubble generates localized hot spots through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. The conditions formed in these hot spots have been experimentally determined, with transient

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temperatures of ~ 5000 K, pressure of 1800 atm, and cooling rates in excess of 10^{10} K/s.^{2,4} These extreme conditions attained during bubble collapse have been exploited to decompose the metal-carbonyl bonds and generate metals,^{1b,c} and metal oxides.^{1e}

The oxidation of fullerenes $[C_{60}, C_{70}]$ has been the subject of many researchers over the last decades.^{5,6} Metal hexacarbonyl complexes $M(CO)_6$ ($M=Cr, Mo, W$) were the original material to make several metal oxides (MoO_3, WO_3, CrO_3) which used as catalyst to synthesize fullerene oxides in air atmosphere under ultrasonic irradiation.

The most stable oxides of molybdenum are MoO_2 and MoO_3 , where the oxidation states of Mo are tetravalent and hexavalent, respectively.²

The presence of several metal oxides (MoO_3, WO_3, CrO_3 or MoO_2, WO_2, CrO_2) may promote the formation of fullerene $[C_{60}]$ oxides in air atmosphere under ultrasonic irradiation.⁶

Herein, we report the fullerene oxides, $[C_{70}O_n]$ ($n=1-2$) prepared by ultrasonic irradiation of $M(CO)_6$ ($M=Cr, Mo, W$) and fullerene $[C_{70}]$ in hexane under air atmosphere.

II. Experimental

Fullerene $[C_{70}]$ used in this work had 99.9% at purity and obtained from Tokyo Chemical Inc (TCI). Metal hexacarbonyl complexes $M(CO)_6$ ($M=Cr, Mo, W$) were purchased from Aldrich. Hexane was purchased from Daejung Chemical Company. The ultrasonic irradiation of all samples was conducted in continuous 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 was performed with a Shiseido nanospace SI-2 model. Column used was a Cosmosil 5 μ PBB (250 X 4.6

mm) made by Phenomenex. UV-Detector was used at 330 nm. The flow rate was 1.0 ml/min during the mobile phase for toluene/hexane at the ratio of 6:4(v/v). The injection volume was 20.00 μ l at a pump pressure of 5.0 MPa. The electronic absorption spectra was obtained by UV-visible spectrophotometer (Shimadzu UV-1601 PC).

1. The reaction of fullerene $[C_{70}]$ by ultrasonication in air atmosphere with chromium hexacarbonyl

The solution of C_{70} (20 mg, 0.024 mmol) which was dissolved in 50 ml of hexane was reacted by ultrasonication with chromium hexacarbonyl (161.1 mg, 0.732 mmol) for 24 h in air at 25–43 °C. The resulting solution was evaporated and then the remaining solid was obtained as a mixture of fullerene $[C_{70}]$ oxides.

2. The reaction of fullerene $[C_{70}]$ by ultrasonication in air atmosphere with molybdenum hexacarbonyl

The solution of C_{70} (20 mg, 0.024 mmol) which was dissolved in 50 ml of hexane was reacted by ultrasonication with molybdenum hexacarbonyl (180.0 mg, 0.732 mmol) for 24 h in air at 25–43 °C. The resulting solution was evaporated and then the remaining solid was obtained as a mixture of fullerene $[C_{70}]$ oxides.

3. The reaction of fullerene $[C_{70}]$ by ultrasonication in air atmosphere with tungsten hexacarbonyl

The solution of C_{70} (20 mg, 0.024 mmol) which was dissolved in 50 ml of hexane was reacted by ultrasonication with tungsten hexacarbonyl (257.6 mg, 0.732 mmol) for 24 h in air at 25–43 °C. The resulting solution was evaporated and then the remaining solid was obtained as a mixture of fullerene $[C_{70}]$ oxides.

III. Results and discussion

The sonochemical processing applied to the synthesis of fullerene oxides by the reaction of fullerene[C₇₀] with metal hexacarbonyl complexes M(CO)₆ (M=Cr, Mo, W) which gives rise to the oxidation of fullerene[C₇₀] with the formation of [C₇₀O_n] (n=1~2). Spill-over of activated oxygen has been proposed by Delmon and his coworkers in explaining synergetic effects of physical mixtures of metal oxides in selective oxidation reactions.⁶⁻⁸

According to the donor/acceptor scale Delmon proposed, carbon has to be a strong acceptor of spill-over oxygen.⁶ Therefore, fullerene[C₇₀] may be act to be a strong acceptor of spill-over oxygen. The spill-over of activated oxygen is related to catalytic formation of fullerene oxides[C₇₀O_n] (n=1~2) because catalytic formation of several oxygen complexes is proposed to be related to spill-over of activated oxygen.⁶

For many chemical synthesis, ultrasonic reaction has led to enhanced reaction rates compared to conventional heating. The MALDI-TOF-MS spectra and HPLC profile revealed the oxidation of fullerene[C₇₀] by ultrasonic irradiation in the presence of metal hexacarbonyl complexes M(CO)₆ (M=Cr, Mo, W) under air atmosphere. The reactivity of fullerene [C₇₀] with the metal hexacarbonyl com-

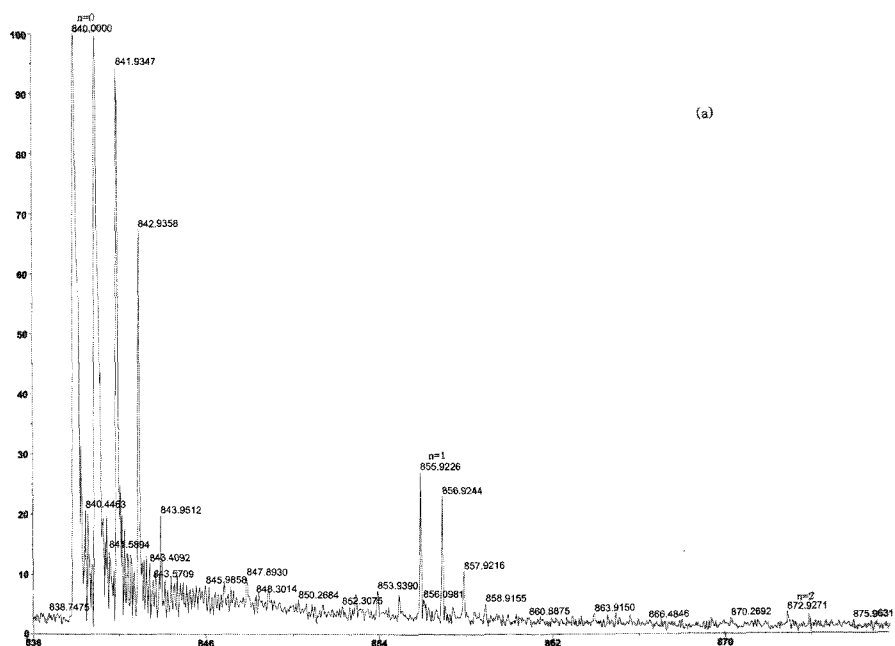
plexes M(CO)₆ (M=Cr, Mo, W) under ultrasonic irradiation increased in the order of Mo(CO)₆>W(CO)₆>Cr(CO)₆.

The difference between various oxidation reaction with and without ultrasonic irradiation is as follows; the reaction time is shorten due to high pressure and temperature under ultrasonic irradiation. They have taken time more than 3 days to get same results without ultrasonic irradiation. Epoxidation mediated by ultrasonic irradiation in air atmosphere with various metal hexacarbonyl complexes is efficient for both electron-rich olefins and fullerene. The MALDI-TOF-MS and HPLC analysis data reported in Table 1 show the formation of [C₇₀O_n] (n=1~2). The MALDI-TOF-MS analysis reported in the Figure 1 shows the formation of [C₇₀O_n](n=1~2) observed at m/z 840(C₇₀),856(C₇₀O₁),872(C₇₀O₂) in the MALDI-TOF-MS spectrum. The most intense peak was at m/z=840 in the MALDI-TOF-MS spectrum in Figure 1 (a)~(c) which is due to the unreacted fullerene[C₇₀] and the fragmentation of fullerene oxides [C₇₀O_n](n=1~2). The HPLC analysis data in Table 1 for the oxidation of fullerene[C₇₀] in air atmosphere under ultrasonic irradiation with metal hexacarbonyl complexes M(CO)₆ (M=Cr, Mo, W) showed C₇₀, C₇₀O₁, C₇₀O₂ at different retention times, respectively.

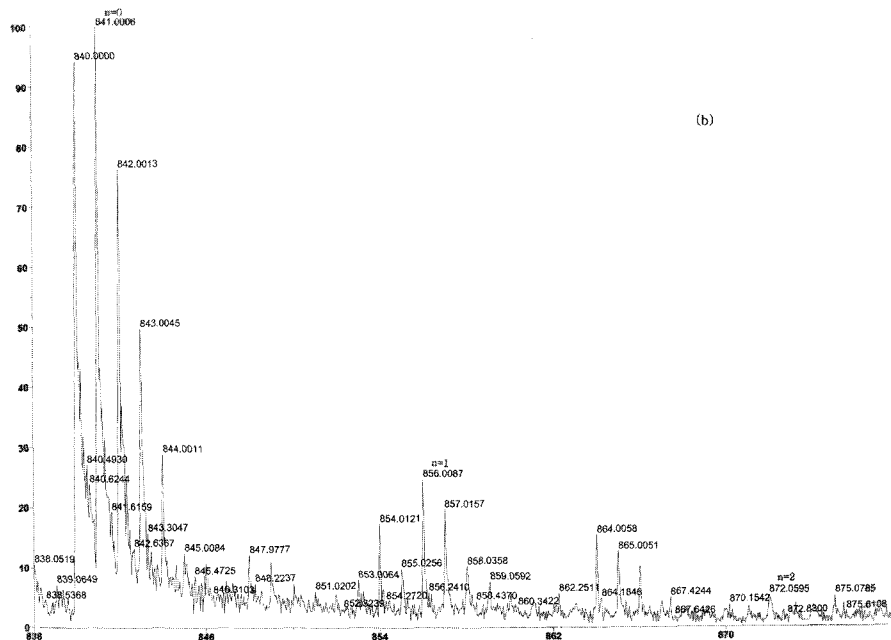
The mechanism for the MoO₃ catalyzed carbon

Table 1. The MALDI-TOF-MS and HPLC Analysis of [C₇₀O_n] (n=1~2) Produced by Ultrasonic Irradiation in Air Atmosphere for 24 h

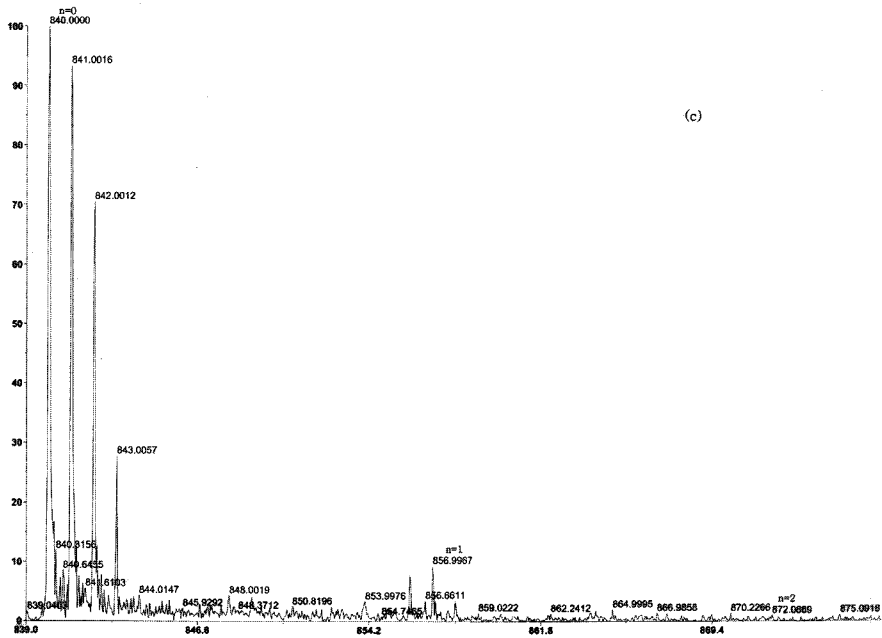
Metal hexacarbonyl complexes	Fullerene	Formation of C ₇₀ (O) _n (n=1~2)	Mass unit (m/z)	Retention times (min)
Chromium hexacarbonyl	C ₇₀	C ₇₀ O ₂	872	21.37
		C ₇₀ O ₁	856	21.70
		C ₇₀	840	22.62
Molybdenum hexacarbonyl	C ₇₀	C ₇₀ O ₂	872	21.44
		C ₇₀ O ₁	856	21.75
		C ₇₀	840	22.65
Tungsten hexacarbonyl	C ₇₀	C ₇₀ O ₂	872	21.44
		C ₇₀ O ₁	856	21.72
		C ₇₀	840	22.63



(a) The reaction of fullerene $[C_{70}]$ with chromium hexacarbonyl, $n=0, 1, 2$ by ultrasonication in air atmosphere shows the presence of $C_{70}, C_{70}O_1, C_{70}O_2$.



(b) The reaction of fullerene $[C_{70}]$ with molybdenum hexacarbonyl, $n=0, 1, 2$ by ultrasonication in air atmosphere shows the presence of $C_{70}, C_{70}O_1, C_{70}O_2$.



(c)

(c) The reaction of fullerene [C_{70}] with tungsten hexacarbonyl, $n=0, 1, 2$ by ultrasonication in air atmosphere shows the presence of C_{70} , $C_{70}O_1$, $C_{70}O_2$.

Figure 1. MALDI-TOF-MS spectra of $C_{70}O_n$ ($n=1\sim 2$).

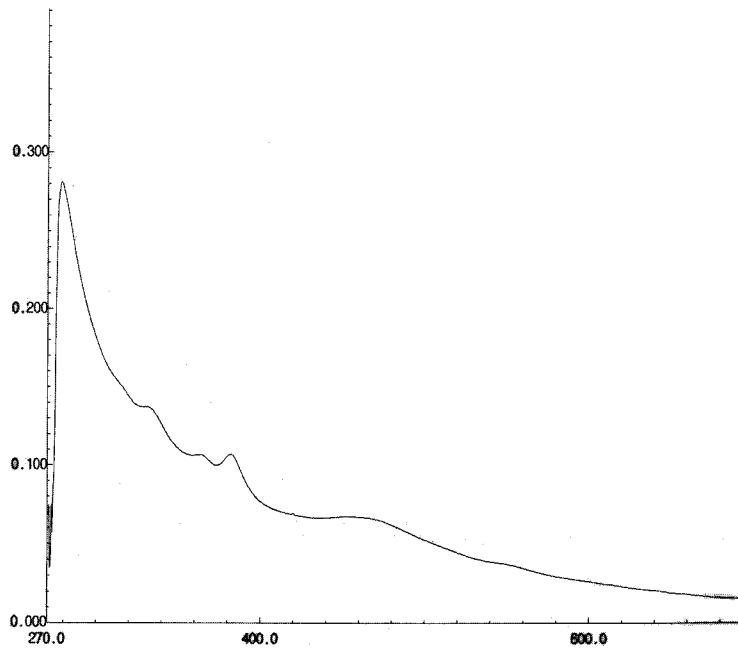
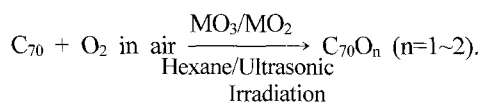
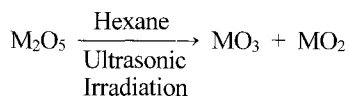
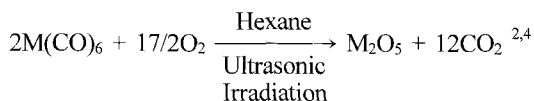


Figure 2. UV-visible spectrum of fullerene oxides [$C_{70}O_n$] ($n=1\sim 2$).

oxidation was proposed by Silva and Lobo.⁹ Sonochemical reaction of fullerene [C₇₀] and metal hexacarbonyl complexes M(CO)₆ (M=Cr, Mo, W) under air atmosphere



Considering the presented result of the oxidation studies, and data published in the literature, the promotion of the formation of surface oxygen complexes on the surface of carbon material by the presence of MoO₃, might be explained by spill-over of activated oxygen.⁶

Electronic absorption bands(λ_{max}) of [C₇₀O_n](n=1~2) in benzene were observed at 277, 306, 330, 358, 383 and 453 nm in the mixture of [C₇₀O_n](n=1~2)(in figure 2). Due to the breaking of the conjugated 6-6 ring junction by addition of oxygen in the fullerene[C₇₀], the band of electronic absorption moved into blue shift.^{5b} By the additional breaking of the carbon-carbon double bond on fullerene[C₇₀], the wave length of absorption bands changed and became lower in the UV-visible spectrum. This electronic absorption spectrum of the oxidation of fullerene[C₇₀] by ultrasonic irradiation in air atmosphere with various metal hexacarbonyl complexes M(CO)₆ (M=Cr, Mo, W) is not similar to that of pure C₇₀ as the number of oxygen atom increase. This indicates that the multi-epoxide of fullerene[C₇₀] perturbs the π molecular orbital in pure C₇₀. The reaction of fullerene[C₇₀] by ultrasonic irradiation with various oxidants may proceed by nucleophilic attack of various oxidants on the 6-6 bond (6-6 ring junction) in the fullerene[C₇₀],

followed by the heterolytic cleavage of the O-O bond. The consensus mechanism for fullerene oxidation by ultrasonic irradiation in air atmosphere with various metal hexacarbonyl complexes involves oxygen atom transfer to the fullerene[C₇₀]. It is suggested that the fullerene epoxides in the mixture of [C₇₀O_n](n=1~2) may be used as oxygen transfer materials. Fullerene oxides [C₇₀O_n](n=1~2) appear attractive from a synthetic point of view as intermediates for further, more selective derivatisation.

The epoxide is one of the most versatile functionalities and provide easy access to further modification. Moreover, fullerene oxides show a rich chemistry in reactions both with fullerenes and with themselves. Epoxide of fullerene is a useful compound to synthesize some other fullerene derivatives such as alcohol, thiol, carboxylate, nitrate and so on from a ring opening reaction. Therefore, we synthesized fullerene oxides [C₇₀(O)_n](n=1~2) under ultrasonic irradiation. Also, the fullerene oxides, in the mixture of [C₇₀O_n](n=1~2) are interesting starting materials for the formation of other fullerene-based entities.

IV. Conclusions

We have confirmed that the mixture of [C₇₀O_n](n=1~2) was formed in the reaction of C₇₀ by ultrasonic irradiation with metal hexacarbonyl complexes M(CO)₆ (M=Cr, Mo, W) under air atmosphere by MALDI-TOF-MS, UV-visible spectra and HPLC analysis. These reaction are one of sonochemical oxidation type of fullerene[C₇₀] with oxygen in air atmosphere using metal hexacarbonyl complexes M(CO)₆ (M=Cr, Mo, W). The reactivity of fullerene[C₇₀] with several metal hexacarbonyl complexes M(CO)₆ (M=Cr, Mo, W) under same ultrasonic condition increased in the order of Mo(CO)₆>W(CO)₆>Cr(CO)₆. The epoxidation of olefin by the multi-epoxides of fullerene, in the mixture of [C₇₀O_n](n=1~2) is presently under investigation.

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