

Synthesis of Fullerene Oxide by Fullerene [C₇₀] and Various Amine N-Oxides under Ultrasonic Irradiation

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초음파 조건에서 여러가지 아민 N-옥시드와 풀러렌[C₇₀]을 이용한 풀러렌 산화물의 합성

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ABSTRACT : Fullerene oxides were synthesized by fullerene [C₇₀] and several amine N-oxides such as 3-picoline N-oxide, pyridine N-oxide hydrate, quinoline N-oxide, and isoquinoline N-oxide under ultrasonic condition at 25~43 °C. The reactivity of fullerene [C₇₀] with various amine N-oxides under ultrasonic irradiation showed the same in all of the proceeding experiments; 3-picoline N-oxide ≈ pyridine N-oxide hydrate ≈ quinoline N-oxide ≈ isoquinoline N-oxide. The MALDI-TOF MS, UV-vis spectrophotometer and HPLC analysis confirmed that the products of fullerene oxidation are [C₇₀(O)_n] (n=1).

요 약 : 풀러렌[C₇₀]을 3-picoline N-oxide, pyridine N-oxide hydrate, quinoline N-oxide, isoquinoline N-oxide의 여러가지 아민 N-옥시드를 사용하여 25~43 °C, 초음파 조건에서 반응시켜 풀러렌 산화물을 합성 하였다. 동일한 초음파 조건에서 여러가지 아민 N-옥시드에 대한 풀러렌 [C₇₀]의 반응성은 3-picoline N-oxide ≈ pyridine N-oxide hydrate ≈ quinoline N-oxide ≈ isoquinoline N-oxide 처럼 동일하게 나타났다. MALDI -TOF MS, UV-vis 그리고 HPLC를 사용하여 생성된 풀러렌 산화물을 분석한 결과 [C₇₀(O)_n] (n=1)임을 알 수 있었다.

Keywords : fullerene oxide, amine N-oxide, ultrasonic irradiation, MALDI-TOF MS.

I . Introductio

Since the discovery of fullerene by Kroto et al. in 1985,¹ the research in this area has become one of the most popular topics in pure and applied physics, chemistry, and materials science,^{2,3} and fullerene oxides have attracted much attention.⁴ A

variety of synthetic methods⁵⁻¹⁰ are at hand to introduce the epoxide functionality to fullerenes. Also, fullerene oxides show an interesting reaction behavior both with themselves and in reactions with pure fullerenes. In contrast to C₆₀, fewer investigations have been conducted on the synthesis of C₇₀.¹¹ The oxidation of C₇₀ is more difficult compared with that of C₆₀.¹² The conceded difficulty is revealed to be the availability of fewer reactive

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double bond present in C_{70} as compared with C_{60} .¹³ Fullerene oxidation has been shown to produce $C_{70}O_1, C_{70}O_2$ which have an epoxide structure, and also higher oxides.^{14,15} Many chemical reagents have been used for the deoxygenation of amine N-oxide, including chemicals such as low valent titanium.¹⁶⁻¹⁸

The Cp_2TiCl_2/In system had been used as an efficient reagent for deoxygenation of amine N-oxide into amine.¹⁹ Deoxygenation of aromatic amine N-oxide is a very valuable transformation in organic synthesis,²⁰⁻²¹ that is to say, oxidation of olefin compounds.²² The epoxidation of alkene by various aromatic amine N-oxide compound occurred.²² Deoxygenation of aromatic amine N-oxides has received considerable attention as this reaction is a key step in the synthesis of cyclic derivatives in many procedures.²³ The ultrasonic process was applied to the synthesis and oxidation of C_{60} .^{24,27} We have been employed ultrasonic irradiation for the deoxygenation of amine-N-oxides reacting with fullerene[C_{70}]. This process has been shown to reduce aromatic amine N-oxides into various aromatic amine when they reacted with fullerene[C_{70}] under ultrasonic irradiation. We found that the oxidation of fullerene[C_{70}] can be produced by the reduction of the aromatic N-oxides under ultrasonic irradiation. Acoustic waves in liquids (at ultrasonic frequencies) are known to cause chemical reaction either in homogeneous or in heterogeneous systems.²⁴⁻²⁶ The chemical reactions are promoted by cavitation of liquids caused by ultrasonic waves traveling in the liquid. Cavitation here implies the formation of microbubbles in the sonicated liquids which implode generating high pressures and temperatures in their surroundings.²⁴⁻²⁶ An alternative theory explains chemical reaction caused by ultrasound by advocating electric discharge inside the collapsing cavitation bubble.²⁴⁻²⁶ Until now the oxidation of fullerene [C_{70}] by ultrasonic irradiation with various amine N-oxide has not been studied. We are now reporting that the reaction of C_{70} by ultrasonic irradiation with various amine N-oxides such as 3-picoline N-oxide, pyridine N-oxide

hydrate, quinoline N-oxide, and isoquinoline N-oxide under ultrasonic irradiation at 25~43 °C causes the oxidation of fullerene [$C_{70}(O)_n$] ($n=1$).

II. Experimental

Fullerene [C_{70}] used in this work was 99.9% from Tokyo Chemical Inc (TCI). All solvents and chemical reagents were from Aldrich, Fluka, Daejung Chemicals. 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 conditions: Model number: Shiseido nano-space SI-2; Column: Cosmosil 5 μ PBB (250 X 4.6 mm) made by phenomenex^R; Detector: 330 nm; Flow rate: 1.0 ml/min; Mobile phase: toluene/hexane is at the ratio of 6:4(v/v); Injection volume 20.00 μ l; Pump pressure: 5.0MPa. The electronic absorption spectra were obtained by UV-visible spectrophotometer (Shimadzu UV-1601 PC).

1. The reaction of fullerene [C_{70}] by ultrasonic irradiation with 3-picoline N-oxide.

The solution of C_{70} (20 mg, 0.024 mmol) which was dissolved in 50 ml of tetrahydrofuran, reacted by ultrasonic irradiation with 3-picoline N-oxide (52.4 mg, 0.48 mmol) for 24 hr in air at 25-43 °C. The resulting solution was evaporated and then the remaining solid was obtained as a mixture of fullerene oxide.

2. The reaction of fullerene [C_{70}] by ultrasonic irradiation with pyridine N-oxide hydrate.

The solution of C_{70} (20 mg, 0.024 mmol) which

was dissolved in 50 ml of tetrahydrofuran, reacted by ultrasonic irradiation with pyridine N-oxide hydrate (45.7 mg, 0.48 mmol) for 24 hr in air at 25-43 °C. The resulting solution was evaporated and then the remaining solid was obtained as a mixture of fullerene oxide.

3. The reaction of fullerene [C₇₀] by ultrasonic irradiation with quinoline N-oxide.

The solution of C₇₀ (20 mg, 0.024 mmol) which was dissolved in 50 ml of tetrahydrofuran, reacted by ultrasonic irradiation with quinoline N-oxide (69.7 mg, 0.48 mmol) for 24hr in air at 25-43 °C. The resulting solution was evaporated and then the remaining solid was obtained as a mixture of fullerene oxide.

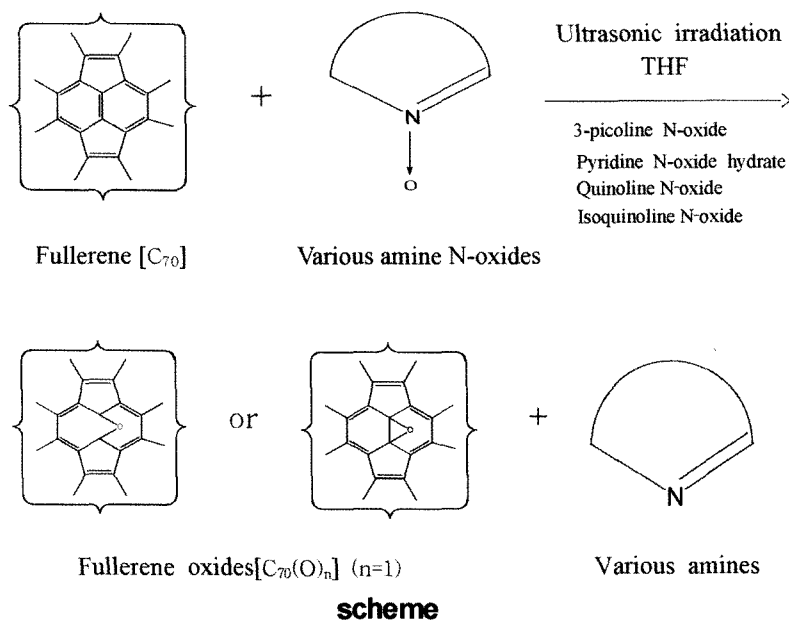
4. The reaction of fullerene [C₇₀] by ultrasonic irradiation with isoquinoline N-oxide.

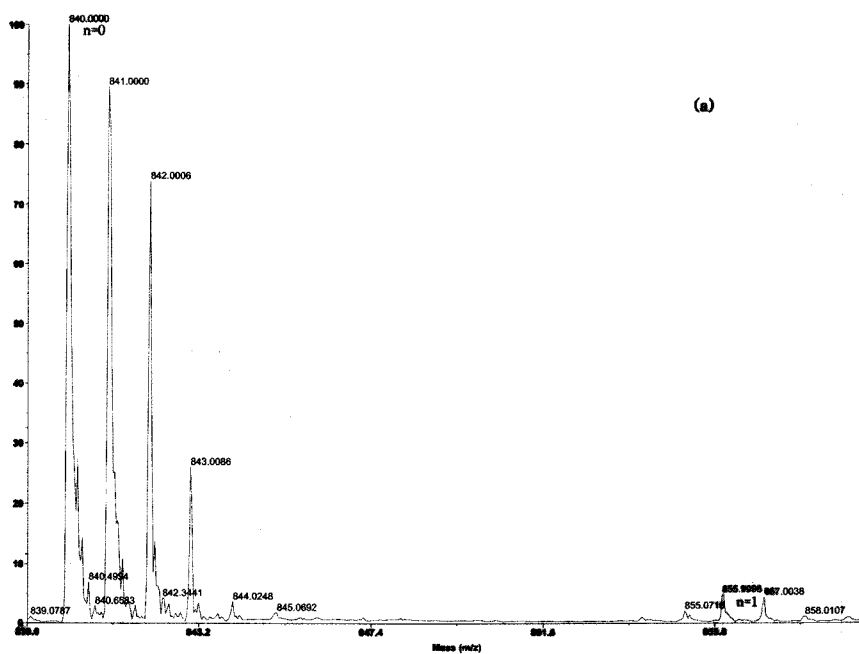
The solution of C₇₀ (20 mg, 0.024 mmol) which was dissolved in 50 ml of tetrahydrofuran, reacted

by ultrasonic irradiation with isoquinoline N-oxide (69.7 mg, 0.48 mmol) for 24hr in air at 25-43 °C. The resulting solution was evaporated and then the remaining solid was obtained as a mixture of fullerene oxide.

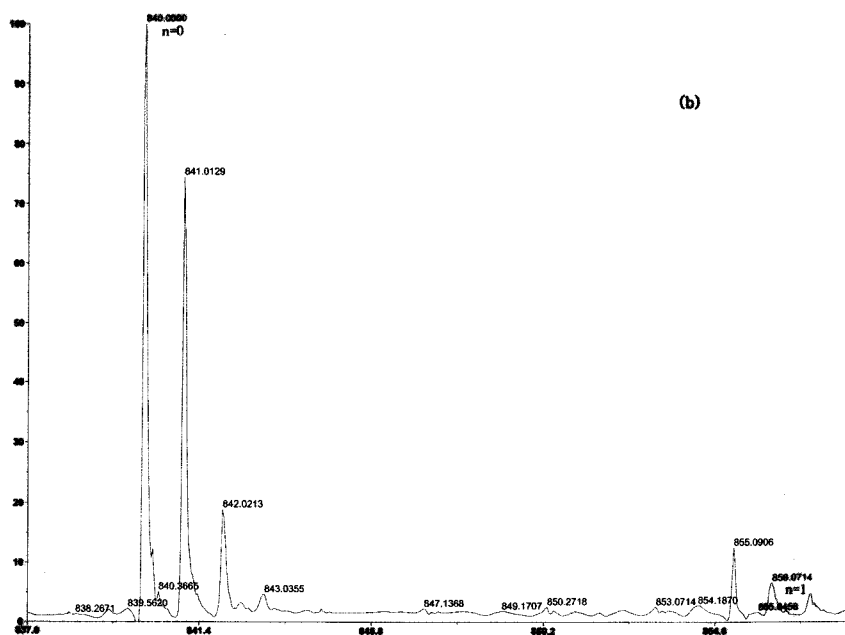
III. Results and discussion

The MALDI-TOF MS, UV-vis spectra, and HPLC analysis revealed that the products were fullerene oxide [C₇₀(O)_n] (n=1). The reactivity of fullerene [C₇₀] under ultrasonic irradiation was the same in all of the proceeding experiments; 3-picoline N-oxide ≈ pyridine N-oxide hydrate ≈ quinoline N-oxide ≈ isoquinoline N-oxide. The MALDI-TOF MS analysis in the Figure 1 shows the formation fullerene oxide observed at m/z = 840(C₇₀), 856(C₇₀O₁) in the MALDI-TOF MS spectrum. The reaction of C₇₀ various amine N-oxides in a refluxing solvent did not result in the production of [C₇₀(O)_n] (n=1) when the ultrasonic irradiation was not used. The oxidation of fullerene [C₇₀] with ultrasonic irradiation in the absence of

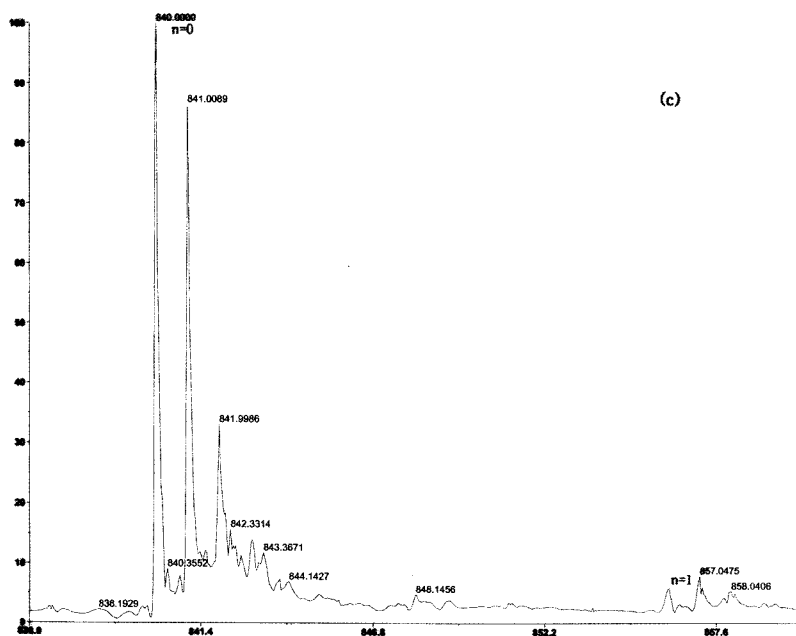




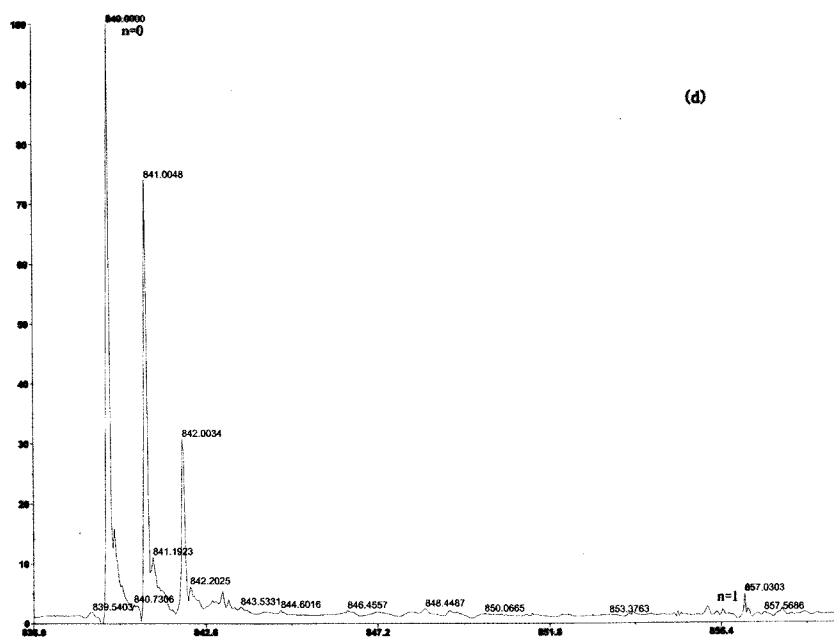
(a) The mixture reacted with 3-picoline N-oxide, $n=0,1$ by ultrasonic irradiation shows the presence of C_{70} , $C_{70}O_1$;



(b) the mixture reacted with pyridine N-oxide hydrate, $n=0,1$ by ultrasonic irradiation shows the presence of C_{70} , $C_{70}O_1$;



(c) the mixture reacted with quinoline N-oxide, n=0,1 by ultrasonic irradiation shows the presence of C₇₀, C₇₀O₁;



(d) the mixture reacted with isoquinoline N-oxide, n=0,1 by ultrasonic irradiation shows the presence of C₇₀, C₇₀O₁.

Figure 1. MALDI-TOF MS spectra of C₇₀(O)_n (n=1).

the various amine N-oxides did not occur therefore, it seems that the various amine N-oxides are essential as oxygen transfer material in the production of $[C_{70}(O)_n]$ ($n=1$) by ultrasonic irradiation.

Epoxidation mediated by sonication with various amine N-oxides is efficient for both electron rich olefins and fullerenes.

The most intense peak was at $m/z=840$ in the MALDI-TOF MS spectrum (Figure 1. a-d) which is due to the unreacted C_{70} and the fragmentation of $[C_{70}(O)_n]$ ($n=1$). HPLC analysis reported in Table.1 shows the formation of $[C_{70}(O)_n]$ ($n=1$). HPLC analysis data in Table.1 for the oxidation of fullerene $[C_{70}]$ by ultrasonic irradiation with various amine N-oxides show C_{70} , $C_{70}O$ at different retention times respectively.

Electronic absorption bands (λ_{max}) of $[C_{70}(O)_n]$ ($n=1$) in benzene were observed at 278, 311,334, 364, 383, and 471 nm. This electronic absorption spectrum of the oxidation of fullerene $[C_{70}]$ by ultrasonic irradiation with various amine N-oxides is not similar to that of pure C_{70} , as the number of oxygen atoms increase. This indicates that the multiperoxide of fullerene $[C_{70}]$ perturbs the π molecular orbital in pure C_{70} , while the monooxide of fullerene $[C_{70}]$ does not seriously perturbs the π molecular orbital in pure C_{70} . The reaction of

fullerene $[C_{70}]$ by ultrasonic irradiation with various amine N-oxides may proceed by a nucleophilic attack of various amine N-oxides to a 6-6 bond in the fullerene, followed by the heterolytic cleavage of the O-O bond. The consensus mechanism for fullerene oxidation by ultrasonic irradiation with various amine N-oxides involve oxygen atom transfer to the fullerene $[C_{70}]$. In conclusion, we have identified the $[C_{70}(O)_n]$ ($n=1$) formed in the reaction of C_{70} by ultrasonic irradiation with 3-picoline N-oxide, pyridine N-oxide hydrate, quinoline N-oxide, and isoquinoline N-oxide in air at 25~45°C. It is suggested that the fullerene epoxide $[C_{70}(O)_n]$ ($n=1$) may be used as oxygen transfer materials. Also, the fullerene epoxide, $[C_{70}(O)_n]$ ($n=1$) are interesting starting materials for the formation of other fullerene-based entities.

IV. Conclusions

We have investigated the oxidation of fullerene $[C_{70}]$ by ultrasonic irradiation with various amine N-oxides such as 3-picoline N-oxide, pyridine N-oxide hydrate, quinoline N-oxide, and isoquinoline N-oxide. These reactions are of the ultrasound induced chemical oxidation type. Ultrasonic treatment may enhance or promote chemical reactions

Table 1. The MALDI-TOF MS and HPLC analysis of $[C_{70}(O)_n]$ ($n=1$) produced by ultrasonic irradiation with various amine N-oxides for 24h.

Various amine N-Oxide	Fullerene	Formation of $C_{70}(O)_n(n=1)$	Mass unit(m/z)	Retention time, (min)
3-picoline N-oxide	C_{70}	$C_{70}O_1$	856	21.70
	C_{70}	C_{70}	840	22.62
Pyridine N-oxide hydrate	C_{70}	$C_{70}O_1$	856	21.75
	C_{70}	C_{70}	840	22.65
Quinoline N-oxide	C_{70}	$C_{70}O_1$	856	21.72
	C_{70}	C_{70}	840	22.63
Isoquinoline N-oxide	C_{70}	$C_{70}O_1$	856	21.71
	C_{70}	C_{70}	840	22.61

Note : MALDI-TOF MS (Voyager-DE STR) analysis conditions: the matrix was a cyano-4-hydroxy cinnamic acid. HPLC analysis conditions: model number; Shiseido nanospace SI-2; column; Cosmosil 5 μ PBB (250 \times 4.6 mm) made by phenomenex; detector; 330 nm; flow rate; 1.0 ml/min; mobile phase; toluene/hexane is at the ratio of 6:4(v/v); Injection volume; 20.00 μ l; Pump pressure; 5.0 MPa.

by the cavitation enhance oxidation of fullerene[C₇₀] with various amine N-oxides under ultrasonic irradiation. The sonochemical oxidation reaction was detected by HPLC analysis, UV-vis and MALDI-TOF MS spectra. By the HPLC analysis, UV-vis and MALDI-TOF MS spectra of products which were obtained by sonochemical oxidation reactions, we have identified the [C₇₀(O)_n](n=1) formed in the reaction of C₇₀ by ultrasonic irradiation with 3-picoline N-oxide, pyridine N-oxide hydrate, quinoline N-oxide, and isoquinoline N-oxide in air at 25~43 °C. The epoxidation of olefin by the multiperoxide of fullerene, [C₇₀(O)_n](n=1) is presently under investigation.

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