Synthesis of fullerene oxides[$C_{70}(O)_n$](n=1~3 or n=1) under microwave irradiation

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Abstract : Synthesis of fullerene oxides[$C_{70}(O)_n$] (n=1~3 or n=1) by fullerene [C_{70}] and several oxidants such as 3-chloroperoxy benzoic acid, chromium(VI) oxide, benzoyl peroxide, trichloroisocyanuric acid take place under microwave irradiation. The MALDI-TOF MS, UV-visible spectra and HPLC analysis confirmed that the products of fullerene oxidation are [$C_{70}(O)_n$] (n=1~3 or n=1).

Keyword : A.Fullerene oxides [$C_{70}(O)_n$] (n=1~3 or n=1); B.Several oxidants; C. Microwave irradiation; D.MALDI-TOF MS

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Introduction

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], fullerene oxides have attracted much attention[4]. A variety of synthetic methods [5-10] 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 C_{60}, fewer investigations have been conducted on the synthesis of C_{70}[11]. The oxidation of C_{70} is more difficult compared with that of C_{60}[12].The conceded difficulty is revealed to be the availability of fewer reactive double bond present in C_{70} as compared with C_{60}[13].Fullerene oxidation has been shown to produce $C_{70}O_1$ and $C_{70}O_2$ which have an epoxide structure, and also higher oxides[14,15].

The first stable C_{70} monoxide,$C_{70}O$ was isolated by Diederich's group[16].The fullerene oxides $C_{70}(O)_n$ (n=1~3) are interesting precursors to the formation of other fullerene - based materials or starting materials for the formation of odd-numbered fullerene derivative species[17]. Van Cleempoel et al.[18], have reported that $C_{70}O$ and higher C_{70} oxides in toluene solution oxidize further upon standing by the addition of one oxygen atom to each oxide[15]. C_{70} can also be oxidized with various oxidants under microwave irradiation. Microwave irradiated reactions have been extensively studied and they have been proven to be a useful synthetic techniques for a variety of chemical reactions[19]. The reactions under microwave irradiation sometimes proceed faster than conventional heating reactions[20]. Also, one point of merit of the microwave irradiated reaction is its solvent free condition[21].

Microwave-assisted solvent free reactions have been widely investigated in chemical synthesis[22]. Amorphous carbon and graphite, in their powdered form, irradiated at 2.45 GHz, reach very high temperatures[23].Many reactions have been accelerated by the use of microwave irradiation [24]. Thus, the microwave assisted process will be of interest to many chemists who work with fullerene chemistry. The very rapid

rise of temperature of reactants by microwave irradiation favors some reaction pathways over others and thus leads to selectivity and hence cleaner products[25].This methodology is expected to be applicable to the simple and efficient preparation of fullerene oxides under microwave irradiation. In this paper, we report a novel, simple, and efficient method for the preparation of fullerene oxides, with the formation of [$C_{70}(O)_n$] (n=1~3 or n=1) by the reaction of fullerene[C_{70}] with several kind of oxidants, such as 3-chloroperoxy benzoic acid, chromium(VI) oxide, benzoyl peroxide, and trichloroisocyanuric acid under microwave irradiation.

Experimental

The fullerene[C_{70}] used in this work was 99.0% purity from Tokyo Chemical Inc(TCI).The oxidants used were 3-chloroperoxy benzoic acid (Fluka,99.0%), chromium(VI) oxide (Aldrich,97.0%), benzoyl peroxide (Fluka,99.0%) and trichloro-isocyanuric acid (Aldrich, 99.0%).The microwave irradiation of all the samples was conducted in multimode with continuous heating at full power by a domestic oven (2450 MHz,700W).

All 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: Cosmosil 5μPBB (250 X 4.6mm) made by Phenomenex Detector: 330 nm; Flow rate: 1.0ml/min; Mobile phase: Toluene and hexane(6:4, v/v); Injection volumn 10.00 μℓ , Pump pressure: 1,000 psi. The electronic absorption spectra was obtained by shimadzu UV-1601 PC UV-visible spectrophotometer.

1.The reaction of fullerene[C_{70}] with 3-chloroperoxy benzoic acid by microwave irradiation.

The fullerene[C_{70}](20mg, 0.024mol) and 3-chloroperoxy benzoic acid(41.4mg, 0.240mol) were prepared by grinding with a mortar and pestle until the mixture was visually homogeneous. A powdered mixture of the fullerene[C_{70}] and 3-chloroperoxy benzoic acid was poured into a 50ml round bottom flask. The flask was placed into the microwave oven and was irradiated microwave for 20 minutes. The resulting solid was obtained as a mixture of fullerene oxides.

2. The reaction of fullerene[C_{70}] with chromium(VI)oxide by microwave irradiation.

The fullerene[C_{70}](20mg, 0.024mol) and chromium(VI)oxide(24.0mg, 0.240mol) were prepared by grinding with a mortar and pestle until the mixture was visually homogeneous. A powdered mixture of the fullerene[C_{70}] and chromium(VI)oxide was poured into a 50ml round bottom flask. The flask was placed into the microwave oven and was irradiated microwave for 20 minutes. The resulting solid was obtained as a mixture of fullerene oxides.

3. The reaction of fullerene[C_{70}] with benzoyl peroxide by microwave irradiation.

The fullerene[C_{70}](20mg, 0.024mol) and benzoyl peroxide (58.0mg, 0.240mol) were prepared by grinding with a mortar and pestle until the mixture was visually

homogeneous. A powdered mixture of the fullerene[C_{70}] and benzoyl peroxide was poured into a 50ml round bottom flask. The flask was placed into the microwave oven and was irradiated microwave for 20 minutes. The resulting solid was obtained as a mixture of fullerene oxides.

4.The reaction of fullerene[C_{70}] with trichloroisocyanuric acid by microwave irradiation.

The fullerene[C_{70}](20mg, 0.024mol) and trichloroisocyanuric acid(56.0mg, 0.240mol) were prepared by grinding with a mortar and pestle until the mixture was visually homogeneous. A powdered mixture of the fullerene[C_{70}] and trichloroisocyanuric acid was poured into a 50ml round bottom flask. The flask was placed into the microwave oven and was irradiated microwave for 20 minutes. The resulting solid was obtained as a mixture of fullerene oxides.

Results and Discussion

The microwave irradiating process is applied to the synthesis of fullerene oxides by the reaction of fullerene[C_{70}] with several kind of oxidants such as 3-chloroperoxy benzoic acid, chromium(VI)oxide, benzoyl peroxide, trichloroisocyanuric acid and gives rise to the oxidation of fullerene[C_{70}] with the formation of [$C_{70}(O)_n$] (n=1~ 3 or n=1). For many chemical syntheses, the development of microwave assisted solvent-free procedures has led to enhanced yields and reaction rates, compared to conventional heating. In some cases, the use of graphite as a support has considerably increased reaction rates, due to strong coupling of graphite with microwave by a conduction process that generates high temperature gradients.

The MALDI-TOF MS spectra and HPLC profile revealed the oxidation of fullerene[C_{70}] by microwave irradiation in the presence of various oxidants such as 3-chloroperoxy benzoic acid(Fluka, 99.0%),chromium(VI) oxide(Aldrich, 97.0%), benzoyl peroxide(Fluka, 99.0%), trichloroisocyanuric acid(Aldrich, 99.0%). The reactivity of fullerenes[C_{70}] under microwave irradiation conditions, was increased in the order of 3-chloroperoxy benzoic acid (Fluka, 99.0%) first, chromium(VI) oxide(Aldrich, 97.0%) second, with trichloroisocyanuric acid and benzoyl peroxide(Fluka, 99.0%) last. The differences between various oxidation reactions with and without microwave irradiation are as follows: the reaction time is shortened due to high pressure and temperature under microwave conditions. Epoxidation mediated by microwave irradiation 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 [$C_{70}(O)_n$](n= 1~3 or n=1).

The most intense peak was at m/z=840 in the MALDI-TOF MS spectrum which is due to the unreacted fullerene[C_{70}] and the fragmentation of fullerene oxide [$C_{70}(O)_n$] (n= 1~3 or n=1). HPLC analysis reported in Table 1, shows the formation of [$C_{70}(O)_n$](n= 1~3 or n=1). The HPLC chromatogram is for the most oxidated fullerene oxides of fullerene [C_{70}], among various oxidants under microwave irradiated conditions was 3-chloroperoxy benzoic acid, which showed C_{70}(22.62 min), $C_{70}O_1$(21.70 min), $C_{70}O_2$(21.27 min), $C_{70}O_3$(20.02 min) at different retention times respectively.

Table 1. The MALDI-TOF MS and HPLC analysis of [$C_{70}(O)_n$] (n=1~3 or n=1) produced by microwave irradiation for 20mins

Various oxidants	Fullerene	Formation of $C_{70}(O)_n$ (n=1 ~ 3 or n=1)	Mass unit (m/z)	Retention times, (min)
3-chloroperoxy benzoic acid	C_{70}	$C_{70}O_3$	888	20.02
	C_{70}	$C_{70}O_2$	872	21.27
	C_{70}	$C_{70}O_1$	856	21.70
	C_{70}	C_{70}	840	22.62
Chromium(Ⅵ) oxide	C_{70}	$C_{70}O_2$	872	21.44
	C_{70}	C_{70} O_1	856	21.75
	C_{70}	C_{70}	840	22.65
Trichloro isocyanuirc acid	C_{70}	C_{70} O_1	856	21.72
	C_{70}	C_{70}	840	22.63
Benzoyl peroxide	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 5μPBB (250 X 4.6mm) made by Phenomenex; Detector: 330nm; Flow rate: 1.0ml/min; Mobile phase: Toluene/Hexane is at the ratio of 6:4(v/v); Injection volumn 20.00 μℓ; Pump pressure: 5.0MPa.

Electronic absorption bands (λ_{max}) of [$C_{70}(O)_n$](n= 1~3 or n=1), in benzene were observed at 277, 306, 330, 358, 383, and 453nm in [$C_{70}O_n$], (n=1~3) and at 278, 311, 334, 364, 383, and 471nm in [$C_{70}O_n$](n=1). This electronic absorption spectrum of the oxidation of fullerene[C_{70}], by microwave irradiation with various oxidants, is not similar to that of pure C_{70} as the number of oxygen atom increases. This indicates that the multiepoxide of fullerene[C_{70}] perturbs the molecular orbital in pure C_{70}, while the monoepoxide of fullerene[C_{70}] does not seriously perturb the molecular orbital in pure C_{70}. The reaction of fullerene[C_{70}] by microwave irradiation with various oxidants may proceed by nucleophilic attack of various oxidants on the 6-6bond in the fullerene[C_{70}], followed by the heterolytic cleavage of the O-O bond.

The consensus mechanism for fullerene oxidation by microwave irradiation with various oxidants involves oxygen atom transfer to the fullerene[C_{70}]. It is suggested that the fullerene epoxides [$C_{70}(O)_n$](n= 1~3 or n=1) may be used as oxygen transfer materials. Also, the fullerene oxides, [$C_{70}(O)_n$](n= 1~3 or n=1) are interesting starting materials for the formation of other fullerene-based entities.

Conclusions

By the HPLC profile, UV-visible and MALDI-TOF MS spectra of products, which were obtained by microwave irradiation oxidation reaction, we have confirmed that [$C_{70}(O)_n$](n= 1~3 or n=1) was formed in the reaction of C_{70} by microwave irradiation with 3-chloroperoxy benzoic acid(Fluka, 99.0%),chromium(VI)oxide(Aldrich, 97.0%), benzoyl peroxide(Fluka, 99.0%), trichloroisocyanuric acid (Aldrich, 99.0%). The

epoxidation of olefin by the multiepoxides of fullerene, [$C_{70}(O)_n$](n= 1~3 or n=1) is presently under investigation.

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References

[1] Kroto H.W, Health J.R, O'Brien S.C, Curl R.F, Smalley R.F. Nature 1985; 318:162-163.
[2] Kratschmer W, Lamb L.D, Fostiropowlos K, Huffman D.R. Nature 1990;347:354-358.
[3] Wang B.C, Wang H.W, Tso H.C, Chen T.L, Chou Y.M. J.Mol.struct. (Theochem) 2002;581:177-186.
[4] Al-Jafari M.S, Barrow M.P, Taylor R, Drewello T. Int.J.Mass Spectrom. 1999;184:L1-L4.
[5] Creegan K.M ,Robbins J.L, Robbins W.K, Millar J.M, Sherwood R.D, Tindall P.J Cox D.M, Smith A.B, McCau-ley J.P, Jones D.R, Gallagher R.T. J. Am. Chem. Soc. 1992;114:1103-1105.
[6] Heymann D, Chibante L.P.F. Rec. Trav. Chim. 1993;112:531-534.
[7] Heymann D, Chibante L.P.F, Rec. Trav. Chim. 1993;112:639-642.
[8] Malhotra R, Kumar S, Satyam A. J. Chem. Soc., Chem.Commun.1994:1339-1340.
[9] Deng J.P, Mou C.Y, Han C.C, Fullerene Sci. Technol. 1997;5:1033-1044.
[10] Balch A.L, Costa D.A, Noll B.C, and Olmstead M.M. J. Am. Chem. Soc. 1995;117:8926-8932.
[11] Blank V.D, Kulnitskiy B.A, Zhigalina O.M. Carbon 2000;38:2051-2054.
[12] Ko W.K, Baek K.N. Phys. Solid State. 2002; 44:424-426.
[13] Nisha J.A, Premila M, Sridharan V, Sundar C.S, Radhakrishnan T.S. Carbon. 1998;36:637-639.
[14] Penn S.G, Costa D.A, Balch A.L, Lebrilla C.B. Int. J. Mass Spectrom. Ion processes 1997;169:371-386.
[15] Ko W.B, Baek K.N. ultrasonics 2002;39(10):729-733.
[16] Derich F, Ettl R, Rubin Y, whetten R, Baek R.L, Alvazez M, Anz S, sensharma D, Wudl F, Khemani K.C, Koch A. Science 1991;252:548-551.
[17] Wang B.C, Chen L, Lee K.J, Cheng C.Y. J.Mol. Struct.(Theochem) 1999;469:127-134.
[18] Van Cleempoel A, Gijbels R, Van den Heuvel H, Claeys M. Proc. Electrochem, Soc. 1997;14:783.
[19] (a) Perreux, L.; Loupy, A. Tetrahedron 2001;57:9199-9223 (b) Lidstrom, P.; Tierney, J.; Wathey, B.; Westman. Tetrahedron 2001; 57: 9225-9283.
[20] Richard N.G, Microwaves in organic synthesis, 1st Ed.; Andre Loupy Eds.;Wiley-VCH Verlag Gmb H & Co.KGaA, Weinheim. 2002:115.
[21] Vincent Bailliez, Renata M. de Figueiredo, Alain Olesker, Jeannine Cleophax, Synthesis. 2003; 7:1015.
[22] Loupy A, Petit A, Hamelin J, Texier-Boulet F, Jacquault P, Mathe D. Synthesis 1998; 2:1213
[23] Andre L, Julien M,and Jacquse D,Microwaves in organic synthesis,1stEd.;

Andre Loupy Eds.;Wiley-VCH Verlag GmbH & Co.KGaA, Weinheim. 2002: 219.
[24] Bose, A. K.; Banik, B. K.; Mathur, C.; Wagle, D. R.; Manhas. M. S. Tetrahedron 2000;56:5603-5619.
[25] Manhas. M. S.; Banik, B. K.; Mathur, A.; Vincent, J. E.:Bose, A. K. Tetrahedron 2000;56: 5587-5601.