

The oxidation of fullerenes (C_{60} and C_{70}) with various oxidants by ultrasonication

© Weon-Bae Ko, Kyung-Nam Baek

Department of Chemistry, Sahmyook University,
139-742 Seoul, Korea

E-mail: kowb@syu.ac.kr

The reaction of C_{60} by ultrasonication with various oxidants such as 3-chloroperoxy benzoic acid (Fluka 99%), 4-methyl morpholine N-oxide (Aldrich 97%), chromium (VI) oxide (Aldrich 99.9%), and oxone[®] monopersulfate compound, at room temperature causes the oxidation of fullerenes. The FAB-MS spectra and HPLC profile confirmed that the products of fullerene oxidation are $[C_{60}(O)_n]$ ($n = 1\sim 3$ or $n = 1$). C_{70} also reacted by ultrasonication with various oxidants but the reaction rate of C_{70} was slower than that of C_{60} .

This work was supported by Sahmyook University funding in Korea.

The $[C_{60}(O)_n]$ ($n = 1\sim 3$) has been obtained by a number of oxidation processes in solution. These include the photooxygenation of C_{60} [1,2], the electrochemical oxidation of C_{60} , the addition of dimethyldioxirane to C_{60} [3], the ozonolysis of C_{60} [4,5], and the ultrasound induced oxidation of C_{60} [6]. The fullerene monooxide, $C_{60}O$, has shown to have an epoxide structure in which the oxygen atom is positioned over a 6 : 6 ring junction [2,7,8].

Acoustic waves in liquids (at ultrasonic frequencies) are known to cause chemical reaction either in homogeneous or in heterogeneous systems [8,9]. 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 [8,9]. We are now reporting that the reaction of C_{60} and C_{70} by ultrasonication with various oxidants such as 3-chloroperoxy benzoic acid, 4-methyl morpholine N-oxide, chromium (VI) oxide, and oxone[®] monopersulfate compound, at room temperature generates the oxidation of fullerenes, $[C_{60}(O)_n]$ ($n = 1\sim 3$ or $n = 1$) and $[C_{70}(O)_n]$ ($N = 1\sim 2$ or $n = 1$).

1. Experimental

Fullerenes (C_{60} and C_{70}) used in this work were Golden grade from Hoechst, and Southern chemical group Inc. All solvents and chemical reagents were from Aldrich and Fluka.

1) The reaction of fullerenes (C_{60} and C_{70}) by ultrasonication with 3-chloroperoxy benzoic acid. The solutions of C_{60} (20 mg, 0.028 mmol) and C_{70} (20 mg, 0.024 mmol) which were dissolved in 60 ml of benzene, reacted by ultrasonication with 3-chloroperoxy benzoic acid (96 mg, 0.56 mmol) at C_{60} and 3-chloroperoxy benzoic acid (82.8 mg, 0.48 mmol) at C_{70} for 5 hrs in air at room temperature. Each resulting solution was evaporated and then the remaining solid material was washed with methanol to remove excess 3-chloroperoxy benzoic acid and was dried in the vacuum oven.

2) The reaction of fullerenes (C_{60} and C_{70}) by ultrasonication with 4-methyl morpholine N-oxide. The solutions of C_{60} (20 mg, 0.028 mmol) and C_{70} (20 mg, 0.024 mmol) which were dissolved in 50 ml of benzene, reacted by ultrasonication with 4-methyl morpholine N-oxide (32.5 mg, 0.280 mmol) at C_{60} and 4-methyl morpholine N-oxide (28.1 mg, 0.240 mmol) at C_{70} dissolved in 10 ml of benzene for 5 hrs in air at room temperature. Each resulting solution was evaporated and then the remaining solid material was obtained as a mixture of fullerene oxidation products.

3) The reaction of fullerenes (C_{60} and C_{70}) by ultrasonication with chromium (VI) oxide. The solutions of C_{60} (20 mg, 0.028 mmol) and C_{70} (20 mg, 0.023 mmol) which were dissolved in 60 ml of carbon disulfide, reacted by ultrasonication with chromium (VI) oxide (28.0 mg, 0.280 mmol) at C_{60} and chromium (VI) oxide (23.0 mg, 0.230 mmol) at C_{70} dissolved in 10 ml of acetone for 5 hrs in air at room temperature. Each resulting solution was evaporated and then the remaining solid material was obtained as a mixture of fullerene oxidation products.

4) The reaction of fullerenes (C_{60} and C_{70}) by ultrasonication with oxone[®] monopersulfate compound. The solutions of C_{60} (20 mg, 0.028 mmol) and C_{70} (20 mg, 0.023 mmol) which were dissolved in 60 ml of benzene, reacted by ultrasonication with oxone[®] monopersulfate compound (170.7 mg, 0.280 mmol) at C_{60} and oxone[®] monopersulfate compound (146.0 mg, 0.238 mmol) at C_{70} dissolved in 1 ml of H_2O and 10 ml of methanol (99%). 18-crown-6 (5 mg, 0.019 mmol) was added and reacted for 5 hrs in air with the solution at room temperature. Each resulting solution was evaporated and then the remaining solid material was obtained as a mixture of fullerene oxidation products.

2. Results and Discussion

The FAB-MS spectra and HPLC profile revealed that the oxidation of fullerenes (C_{60} and C_{70}) by ultrasonication in the presence of various oxidants such as

The FAB-MS and HPLC analysis of $C_{60}(O)_n$ ($n = 1 \sim 3$ or $n = 1$) and $[C_{70}(O)_n]$ ($n = 1 \sim 2$ or $n = 1$) produced by ultrasonication with various oxidants for 5 hrs

Oxidants	Fullerenes	Formation of $C_{60}(O)_n$ ($n = 1 \sim 3$ or $n = 1$) and $C_{70}(O)_n$ ($n = 1 \sim 2$ or $n = 1$)	Mass unit (m/z)	Retention times, min
3-Chloroperoxy benzoic acid	C_{60}	$C_{60}O_3$	779	6.67
	C_{60}	$C_{60}O_2$	753	9.00
	C_{60}	$C_{60}O_1$	737	12.72
	C_{60}	C_{60}	721	17.11
	C_{70}	$C_{70}O_2$	873	14.23
	C_{70}	$C_{70}O_1$	857	20.57
	C_{70}	C_{70}	841	28.07
4-Methyl morpholine N-oxide	C_{60}	$C_{60}O_3$	779	6.68
	C_{60}	$C_{60}O_2$	753	9.01
	C_{60}	$C_{60}O_1$	737	12.73
	C_{60}	C_{60}	721	17.14
	C_{70}	$C_{70}O_2$	873	14.18
	C_{70}	$C_{70}O_1$	857	20.06
Chromium (VI) oxide	C_{70}	C_{70}	841	28.14
	C_{60}	$C_{60}O_1$	737	12.70
	C_{60}	C_{60}	721	17.17
Oxone [⊖] monopersulfate	C_{70}	$C_{70}O_1$	857	20.09
	C_{70}	C_{70}	841	28.14
	C_{60}	$C_{60}O_1$	737	12.67
Oxone [⊖] monopersulfate	C_{60}	C_{60}	721	17.08
	C_{70}	$C_{70}O_1$	857	20.57
	C_{70}	C_{70}	841	28.07

FAB-MS analysis conditions: acceleration voltage was 10 kV. FAB source was CSI ionized in 20 kV, and the matrix was nitrobenzyl alcohol. 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: 10.00ml; Pump pressure: 1.000 psi.

3-chloroperoxy benzoic acid, 4-methyl morpholine N-oxide, chromium (VI) oxide, and oxone[⊖] monopersulfate compound was $[C_{60}(O)_n]$, ($n = 1 \sim 3$ or $n = 1$) and $[C_{70}(O)_n]$ ($n = 1 \sim 2$ or $n = 1$). 4-Methyl morpholine N-oxide is not well known as other powerful oxidants for their reactivity under mild conditions. The differences between various oxidation with and without ultrasonication are as follows. Firstly, the reaction time is being shortened due to high pressure and temperature under the condition of ultrasonication. Secondly, the reactions of C_{60} and C_{70} with 4-methyl morpholine N-oxide produce $[C_{60}(O)_n]$ ($n = 1 \sim 3$) and $[C_{70}(O)_n]$ ($n = 1 \sim 2$) by ultrasonication, not through a thermal reaction.

Epoxidation mediated by ultrasonication with various oxidants is efficient for both electron-rich olefins and fullerenes. FAB-MS and HPLC analysis reported in table shows the formation of $[C_{60}(O)_n]$ ($n = 1 \sim 3$ or $n = 1$) and $[C_{70}(O)_n]$ ($n = 1 \sim 2$ or $n = 1$).

Comparing C_{60} and C_{70} , the reactivity of C_{70} by ultrasonication with various oxidants looks lower than that of C_{60} under the same conditions. This reactivity difference

probably results from the symmetry of their structures. The oxidation of fullerenes (C_{60} and C_{70}) by ultrasonication may proceed by a nucleophilic attack of oxidants to a 6–6 bond, followed by the heterolytic cleavage of the O–O bond. The consensus mechanism for fullerene oxidation by ultrasonication with various oxidants involve oxygen atom transfer to the fullerenes (C_{60} and C_{70}).

It is suggested that the fullerene epoxide $[C_{60}(O)_n]$ ($n = 1 \sim 3$ or $n = 1$) and $[C_{70}(O)_n]$ ($n = 1 \sim 2$ or $n = 1$) may be used as oxygen transfer materials. Also, the fullerene epoxide, $[C_{60}(O)_n]$ ($n = 1 \sim 3$ or $n = 1$) and $[C_{70}(O)_n]$ ($n = 1 \sim 2$ or $n = 1$) are interesting starting materials for the formation of other fullerene-based entities.

In conclusion, by the HPLC profile and FAB-MS spectra, we have identified the $[C_{60}(O)_n]$ ($n = 1 \sim 3$ or $n = 1$) and $[C_{70}(O)_n]$ ($n = 1 \sim 2$ or $n = 1$) formed in the reaction of C_{60} and C_{70} by ultrasonication with 3-chloroperoxy benzoic acid, 4-methyl morpholine N-oxide, chromium (VI) oxide, and oxone[⊖] monopersulfate compound at room temperature. We observed that the reaction rate of C_{70} was slower than that of C_{60} . This may have resulted from the lower symmetry

of C₇₀ in their structures. The epoxidation of olefin by the multiperoxide of fullerene, [C₆₀(O)_n] ($n = 1 \sim 3$ or $n = 1$) and [C₇₀(O)_n] ($n = 1 \sim 2$ or $n = 1$) is presently under investigation.

We thank to Dr. J.J. Seo at the Korea Basic Sciences Institute Seoul for obtaining the FAB-MS spectra.

References

- [1] J.M. Wood, B. Kahr, S.H. Hake II, L. Dejarne, R.G. Cooks, D. Ben-Amotz. *J. Am. Chem. Soc.* **113**, 5907 (1991).
- [2] K.M. Creggan, W.K. Robbins, J.M. Millar, R.D. Sherwood, P.J. Tindall, D.M. Cox, A.B. Smith III, J.P. Mc Cauley Jr., D.R. Jones, R.T. Gallagher. *J. Am. Chem. Soc.* **114**, 1103 (1992); J.M. Millar, K.M. Creggan, J.L. Robbins, W.K. Robbins, R.D. Sherwood, P.J. Tindall, D.M. Cox. *Synth. Met.* **59**, 317 (1993).
- [3] W.A. Kalsbeck, H.H. Thorp. *J. Electroanal. Chem.* **314**, 363 (1991).
- [4] Y. Elemen, S.K. Silverman, C. Sheu, M. Kao, C.S. Foote, M.M. Alvarez, R.L. Whetten. *Angew. Chem. Int. Ed. Engl.* **31**, 351 (1992).
- [5] D. Heymann, L.P.F. Chibante. *Chem. Phys. Lett.* **207**, 339 (1993).
- [6] A.L. Balch, D.A. Costa, J.W. Lee, B.C. Noll, M.M. Olmstead. *Inorg. Chem.* **32**, 2071 (1994).
- [7] T.J. Mason, J.P. Lorimer. *Sonochemistry: Theory, Applications, and Uses of Ultrasound in Chemistry*. Ellis Horwood Ltd, Chichester (1988).
- [8] K.S. Suslick. *Ultrasound. Its Chemical, Physical and Biological Effects* / Ed. VCH publ., Weinheim (1989).
- [9] F. Cataldo, D. Heymann. *Fullerene Sci. Technol.* **7**, 752 (1999).