

SYNTHESIS OF FULLERENE C₇₀ FROM C₆₀ BY GASEOUS CARBON INSERTIONS INTO CC BONDS

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Abstract

We report the synthesis of fullerene C₇₀ from C₆₀ by gaseous carbon insertion into CC bonds. Gaseous carbon atoms “jump” into CC bonds without cleavage of the overall molecular structure and without the significant occurrence of side reactions. The carbon insertion reactions, known for linear carbon chains, are simple, clean, efficient, and require only :C and a CC bond. As an extension of the carbon insertion reactions into CC bonds, we have formed fullerene C₇₀ from C₆₀ by insertion of carbon atoms produced by the photolysis of C₃O₂. The reactions were made at 800~1000°C. A significant amount of C₇₀ was formed with negligible side products and was confirmed by HPLC and TOF-MS spectrometries. In this reaction system, carbon carbenes :CCO were the only chemically active species which were known to jump into CC bonds spontaneously and C₇₀ has been formed without the occurrence of side reactions, implying the carbon insertion reactions should have occurred without cleavage of the C₆₀ structure. A possible reaction mechanism of the C₇₀ formation from C₆₀ was presented.

1. Introduction

Carbon insertion is a “humorous” reaction: gaseous carbon atoms of the :C, :CCO or C₃O₂ species (carbon carbenes) “jump” into previously existing CC bonds without cleavage of the overall molecular structure and without the significant occurrence of side reactions [1,2,8-15,19]. More than ten years ago, Ogata *et al.* [14,15] resumed the study on the carbon insertion reaction into CC bond, intrigued by Endo’s development of the pulsed-discharge-nozzle FTMW spectrometer. As was expected, a series of carbon monoxides C_nO ($n = 2 \sim 9$) had been simultaneously synthesized by creating an electrical discharge in a sample of tricarbon dioxide C₃O₂. The fact that the relative abundance of C_nO ($n = 2 \sim 9$) (Fig.1) and C_mO⁺ ($m = 2 \sim 5$) ions [19] were similar means they were formed by the carbene insertion reaction. We report here the preparation of fullerene C₇₀ from fullerene C₆₀ by the carbon insertion reactions.

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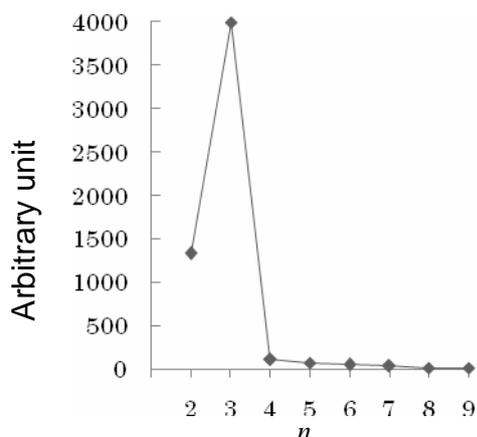


Figure 1. Relative abundances of the C_nO ($n=2\sim 9$) synthesized by the discharge of C_3O_2 . The abundance of C_2O is lower than that of C_3O , because C_2O was consumed by the further carbon insertion reactions.

2. Experimental

2.1 Materials

Fullerene C_{60} (> 99.5%) and fullerene C_{70} (> 98.0%) were purchased from Matsubo Co. HPLC measurements showed that the fullerene C_{60} contained ca. 0.0421% of fullerene C_{70} and the fullerene C_{70} contained ca. 5.83% of fullerene C_{60} (see section 3.2). Tricarbon dioxide was prepared by dehydration of malonic acid.

2.2 Methods

The apparatus used for the photochemical reaction of C_3O_2 with C_{60} is shown in Fig. 2; it is essentially the same as those used in ordinary work [5-10], except that it was heated to 1100 °C. The hollowed quartz tube is 50 mm in diameter and 600 mm long (Vidrex). UV light from a medium-pressure mercury lamp (Ushio, UM-452) radiated from the inside of the quartz reaction tube. The reaction tube was connected to a container filled with pure C_3O_2 or C_3O_2 diluted with helium or argon gas at a total pressure of 0.2 ~ 1.0 bar. C_{60} samples of 30 ~ 200 mg were located on the

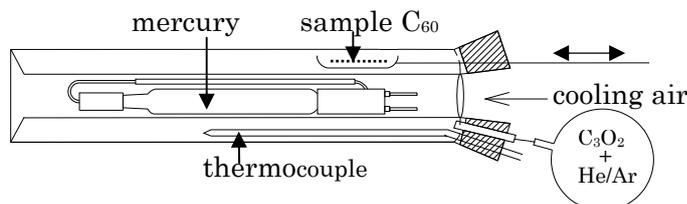


Figure 2. The carbon carbene insertion reaction tube. The central part of the reaction tube is placed in the electric furnace. The samples in the reaction tube are irradiated with UV light from a medium-pressure mercury lamp located within an air-cooling tube. The thermocouple thermometer measures the temperature of the samples.

slidable boat inside the tube. The central part of the reaction tube was placed in an electric furnace (Asahi Rika, ARF-50K(M)) and heated to a temperature between 800 and 1,100 °C. The temperature of the reactants was measured using a thermocouple thermometer inserted into the reaction vessel. Reaction products such as fullerene C_{70} at the bottom and on the wall of the tube were analyzed by time-of-flight mass spectroscopy (TOF-MS) and high performance liquid chromatography (HPLC).

The TOF-MS spectrometer used was a Bruker AutoFLEX at the Institute for Genetic Research and Biotechnology, Shizuoka University. HPLC was performed using a JASCO Gulliver series at the Faculty of Science, Shizuoka University. The column dimensions were $4.6 \phi \times 250$ mm, with a sample load of 200 μ L, and it was packed with COSMIL BuckyPrep-M. The eluent was toluene, at a flow rate of 1 mL/min. Absorbance was recorded at $\lambda = 300$ nm. The samples were dissolved in o-xylene and subjected to ultrasonic vibration and filtration. The amount of dissolved sample was calculated based on the weight of the sample and residual amounts.

Results and discussions

3.1 Analysis of the reaction of C_3O_2 with C_{60}

Typically, 50 mg of fullerene C_{60} (> 99.5%) in a sample boat was placed inside the reaction tube and 200 ml of C_3O_2 in a container was connected to the tube. The quartz tube was heated to 1000 $^{\circ}$ C and irradiated with UV light, and then the C_{60} and C_3O_2 were brought together at the center of the reaction tube. The reaction was subjected to this temperature for a few minutes. The products and materials inside the tube were extracted with o-xylene and were analyzed by TOF-MS and HPLC. The TOF-MS spectra of the reaction products and the starting material fullerene C_{60} are shown in Fig. 3. C_{70} contamination in the starting material resulted in a weak peak in the TOF-MS spectrum. The reaction produced C_{70} efficiently and almost exclusively. Almost all of the other reactions attempted also produced fullerene C_{70} . HPLC spectra of the C_{60} starting material, the reaction products without C_3O_2 , and the reaction products using C_3O_2 are shown in Figs. 4a, 4b, and 4c, respectively. The product with a retention time of 10.33 min was

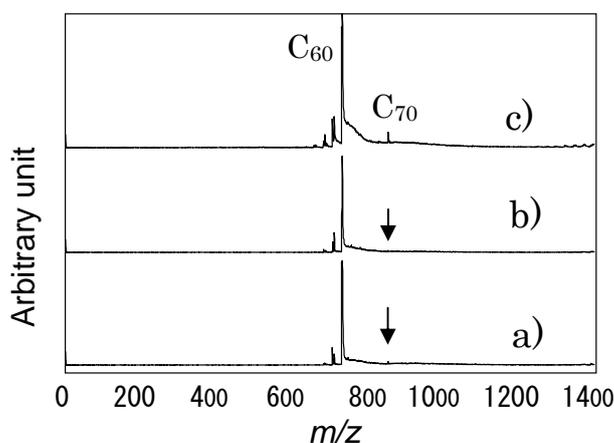


Figure 3. TOF-MS spectra for the carbon insertion reactions. Spectrum for a) the material before the reaction and b) after the reaction in absence of C_3O_2 , and c) after the carbon insertion reaction. Spectrum c) shows the peak corresponding to C_{70} ($m/z = 840$).

identified as fullerene C_{70} by comparison with the spectrum of a commercial sample of C_{70} . HPLC measurements data for C_{60} , C_{70} and the reaction products with and without C_3O_2 are shown in Table 1. The relationship between the absorbance (μ V \times s) and the sample weight (mg) was calculated from the analytical curve for C_{60} and C_{70} . The C_{60} starting material (> 99.5%) was found to contain traces of C_{70} at ca. 0.0421(8)% (see Fig. 4a). After the insertion reaction, the absolute amount of C_{70} was found to have increased from 0.0421(8) g to 0.209(4) g per 100 g of reactant (see Fig. 4a, 4c). The amount of fullerene C_{70} in the reaction products had increased five times more than the amount of C_{70} contained in the reactant C_{60} . We have repeated the synthetic experiments more than ten times with these

conditions; we usually gained fullerene C_{70} from C_{60} at least five to two times more than that contaminated in the starting material. To confirm that fullerene C_{70} was produced by the carbon carbene insertions originated from C_3O_2 , the same reactions were attempted in the absence of C_3O_2 , and were found not to produce C_{70} but to degrade from 0.0421(8) g to 0.0351(9) g per 100 g of reactant (Fig. 4b). It is evident from the error margins that the fullerene C_{70} was produced by the reactions and that the inserted carbon came from C_3O_2 because the amount of C_{70} in the product of the reaction without C_3O_2 did not increase but decreased by ca. 20%. The production of almost pure fullerene C_{70} (Fig. 4c) without significant occurrence of side reactions means the reactions have proceeded without cleavage of the overall molecular structure of C_{60} , which is the characteristic of the carbon carbene insertion reactions. The formation of fullerene C_{70} from C_{60} by the carbon carbene insertion reactions via photochemical reaction of tricarbon dioxide was thus confirmed.

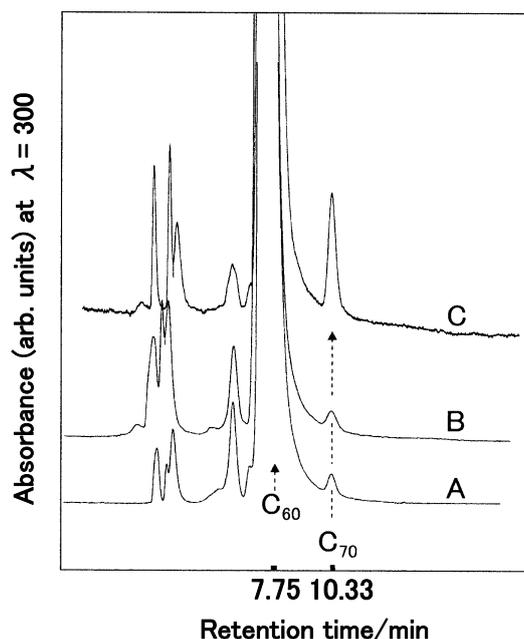


Figure 4. HPLC spectra of carbon carbene insertion reactions. a) Starting material; b) after the reaction without C_3O_2 ; c) after the reaction with C_3O_2 . The retention times for C_{60} and C_{70} are 7.75 and 10.33 min, respectively. Spectrum a) exhibits a small peak corresponding to fullerene C_{70} of ca. 0.0421 g in the starting material 100g. Spectrum c) shows the reaction products, with C_{70} at ca. 0.209 g per 100g of reactant.

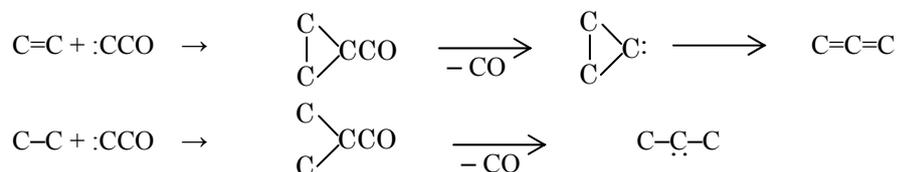
Table 1. HPLC measurements data for the carbon insertion reactions.

Analyte	Reactant /mg	Injected/ solution /(μ L/mL)	Absorbance / μ V s		weight/mg ^a			Resid ^b /mg	C_{70}/C_{60}	Abs. C_{70} ^c /g
			C_{60}	C_{70}	C_{60}	C_{70}	Total			
Material C_{60}	50.75	50/25.0	17205378	8021	50.75	0.0214	50.771	0.0	0.0421	0.0421(8)
Material C_{70}	39.86	50/100	19775	459699	2.324	37.536	39.860	0.0	16.15	94.1(23)
Products using C_3O_2 ^d	47.0	20/27.2	4408806	13595	35.372	0.0985	35.471	17.0	0.276	0.209(4)
Products without C_3O_2 ^e	38.57	100/35.7	18280216	7111	38.553	0.0135	38.567	0.0	0.0351	0.0351(9)

^a Amounts of C_{60} and C_{70} in the products. ^b Unresolved residuals. ^c Amount of C_{70} in the products par 100g of reactant. Figures in parentheses are errors in units of last significant figure. ^d Products of the carbon insertion reaction using C_3O_2 . ^e Products of the experiment without C_3O_2 .

3.2 Reaction Mechanism

In our experiment, in which UV irradiation of tricarbon dioxide is carried out using a medium-pressure mercury lamp, the energy produced is not sufficient to cause direct dissociation of the carbon carbene species $:C$, but it can produce carbonyl carbene $:CCO$ via the reaction $C_3O_2 + h\nu \rightarrow :CCO + CO$. The carbonyl carbene species $:CCO$ inserts into a CC bond in C_{60} , and then dissociates with the loss of a carbon monoxide molecule [1,16].



The result is that carbon carbene $:C$ is inserted into a CC bonds of C_{60} . Insertion of ten carbon atoms, followed by rearrangement and annealing, leads to fullerene C_{70} . Figure 5 shows three-dimensional models and Schlegel diagrams of fullerene C_{60} and C_{70} for the simplest case in which ten carbon carbenes are inserted at the equator of the C_{60} molecule. Carbon insertions into other CC bonds may result in the same product after rearrangements and annealing. At a basic level, this reaction mechanism corresponds to the diagram used by Professor Curl in his Nobel Prize lecture to explain the relationship between the structures of C_{70} and C_{60} (Fig. 14 in Ref. [3]); The carbon carbene insertion reactions in our experiment, however, involve no cleavage of CC bonds in the C_{60} molecule. The maintenance of the overall structure of the system without cleavage of chemical bonds is a characteristic aspect of this reaction, resulting in a low activation energy and a reduction in possible side-reactions.

The reaction mechanisms of the fullerene formation have been investigated with various methods [4,5-7,17,18]. The gas phase reaction of C_{60} with carbon atoms [19] showed that there is no preference for clusters containing an even number of carbon atoms and the TOF mass spectrum of the clusters exhibited the dominant C_{70} peak after the laser irradiations. These suggest the reaction of the C_1 insertions rather than the C_2 and the C_{70} formation later by the annealing. The presented reaction mechanism for the carbon insertion reaction is consistent with these results.

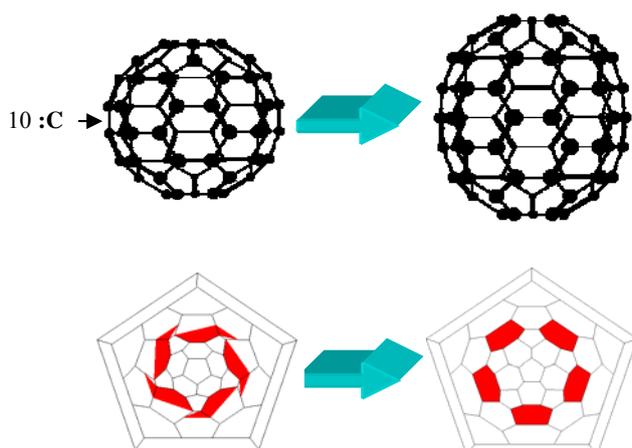


Figure 5. Reaction mechanism for conversion of fullerene C_{60} to fullerene C_{70} . Schlegel diagrams are shown for the carbon carbene insertion reactions. Ten carbon atoms are inserted into the CC bonds at the equator of fullerene C_{60} , followed by annealing and rearrangement to form fullerene C_{70} . No cleavage of the CC bonds in C_{60} occurs during the reaction, which prevents the occurrence of side-reactions.

Conclusions

1. Fullerene C₇₀ was prepared from C₆₀ by gaseous carbon carbene insertions into CC bonds with negligible side products.
2. The fact that the chemically active species in the reaction system are carbonyl carbene :CCO only means C₇₀ was formed by the carbon insertion reactions.
3. The presented reaction mechanism by the C₁ insertions rather than the C₂ is consistent with that of the gas phase reaction of C₆₀ with carbon atoms.
4. The carbon insertion reactions are simple, clean, and efficient. It would be useful for fullerene syntheses.

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References

- [1] Bayes KD. 1962. The photolysis of carbon suboxide. I. Reaction with ethylene. *J. Am. Chem. Soc.* 84:4077-4080.
- [2] Bortolini O, Pandolfo L, Tomaselli C, Traldi P. 1999. Ion-molecular chemistry of carbon suboxide in an ion-trap mass spectrometer. *Int. J. Mass Spectrom.* 190/191:171-179.
- [3] Curl RF. 1997. Dawn of the fullerene: Conjecture and experiment (Nobel Lecture). *Angew. Chem. Int. Ed. Engl.* 36:1566-1576.
- [4] Dresselhaus MS, Dresselhaus G, Eklund PC. 1996. *Science of Fullerenes and Carbon Nanotubes*. Pages 143-168 Academic Press, New York, USA.
- [5] Homann K-H. 1998. Fullerene and soot formation— New pathways to large particles in flames. *Angew. Chem. Int. Ed.* 37:2434-2451.
- [6] Irle S, Zheng G, Wang Z, Morokuma K. 2006. The C₆₀ formation puzzle “solved”: QM/MD simulations reveal the shrinking hot giant road of the dynamic fullerene self-assembly mechanism. *J. Phys. Chem. B* 110:14531-14545.
- [7] Lee I-H, Kim H, Lee Y. 2004. Dynamic pathway model for the formation of C₆₀. *J. Chem. Phys.* 120:4672-4676.
- [8] Ogata T. 1982. Photochemical synthesis of allene derivatives and microwave spectrum of 1,1-difluoroallene. *The Reports of the Faculty of Liberal Arts, Shizuoka University (Sciences)*, 18:29-36.
- [9] Ogata T, Yoshikawa M, Fujii K. 1985. Microwave spectrum and dipole moment of fluoroallene. *Chem. Lett.* 1797-1798.
- [10] Ogata T, Ando B. 1986. Microwave spectrum, dipole moments, and structure of trifluoroallene. *J. Mol. Spectrosc.* 118:70-75.
- [11] Ogata T, Fujii K, Yoshikawa M, Hirota F. 1987. Microwave spectra and substitution structure of fluoroallene. *J. Am. Chem. Soc.* 109:7639-7641.
- [12] Ogata 1990. T. Microwave spectrum, nuclear quadrupole coupling constants for chlorine, and structure of 1-chloro-1-fluoroallene. *J. Mol. Spectrosc.* 139:253-258.

- [13] Ogata T. 1992. Microwave spectra and substitution structure of methylallene. *J. Phys. Chem.* 96, 2089-2091.
- [14] Ogata T, Ohshima Y, Endo Y. 1995. Rotational spectra and structures of carbon monoxides, C₅O, C₇O, and C₉O. *J. Am. Chem. Soc.* 117:3593-3598.
- [15] Ohshima Y, Endo Y, Ogata T. 1995. Fourier-transform microwave spectroscopy of triplet carbon monoxides, C₂O, C₄O, C₆O, and C₈O. *J. Chem. Phys.* 102:1493-1500.
- [16] Okabe H. 1978. *Photochemistry of Small Molecules*. Pages 319-323. Wiley-Interscience, New York, USA.
- [17] Ozawa M, Goto H, Kusunoki M, Osawa E. 2002. Continuously growing spiral carbon nanoparticles as the intermediates in the formation of fullerenes and nanooxions. *J. Phys. Chem. B* 106:7135-7138.
- [18] Pellarin M, Cottancin E, Lerme L, Vialle JL, Broyer M. 2002. Coating and polymerization of C₆₀ with carbon: A gas phase photodissociation study. *J. Chem. Phys.* 117:3088-3097.
- [19] Schildcrout SM, Franklin JL. 1970. High pressure mass spectra and ion chemistry of carbon suboxide. *J. Am. Chem. Soc.* 92:251-253.