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Tetrahedron Letters 48 (2007) 8132–8137

Tetrahedron Letters

Solvent free mechanochemical oxygenation of fullerene under oxygen atmosphere

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Received 10 July 2007; revised 22 August 2007; accepted 18 September 2007
Available online 21 September 2007

Abstract—Oxygenation of fullerene took place under mechanical stressing by a simple vibration mill in an oxygen atmosphere at 1 atm. Milled products were mixtures of poly-oxidized fullerene, $C_{60}O_n$, containing C–O–C and C=O bonds. We observed a concurrent reaction as well, that is, polymerization of C_{60} and $C_{60}O$. The average number of oxygen, n, of the overall products obtained by milling for 5 h was 8.6 per molecule of C_{60}. We confirmed generation of singlet oxygen during the present mechanochemical reaction by an ESR spin trapping method. Trapping of $^1O_2$ was completely inhibited the oxygenation of fullerene. Formation of $^1O_2$ is attributed to the energy transfer from mechanically excited state of fullerene and plays a decisive role on the present oxygenation of fullerene under mechanical stressing in O_2. In contrast, no $^1O_2$ was observed by mechanically stressing the conventional photo-sensitizer, rosebengal. The difference in the behavior of C_{60} and rosebengal is interpreted in terms of molecular deformation, being much easier for a 3D molecule, C_{60}, than a planar molecule, in line with the concept of inverse Jahn–Teller effects.

1. Introduction

Oxidation or oxygenation of fullerene has widely been studied since the discovery of fullerene itself.[1] Many kinds of oxidants were used, for example, *m*-chloroperbenzoic acid,[1a] dimethyldioxirane,[1b] or ozone.[1c] Molecular oxygen was also used as an oxidant in well documented photo-oxidation of C_{60}.[2] Active species of the photo-oxidation is known to be singlet oxygen ($^1O_2$). Formation of $^1O_2$ is accomplished via energy transfer from photo-excited fullerene, serving as a photo-sensitizer. Fullerene is photo-excited to its singlet state and turns immediately to its triplet excited state via inter system crossing.[3] Energy transfer from excited triplet fullerene to ground state oxygen generates $^1O_2$. Fullerene is oxygenated to give fullerene epoxide ($C_{60}O$),[4] as a consequence of the interaction between $^1O_2$ and excited fullerene to form epoxy ring. When $^1O_2$ reacts with ground state fullerene, in contrast, oxygenation results in ketone groups.[5]

Mechanochemical reactions of molecular crystals are driven via unusual electron distribution due to molecular deformation.[6] These kinds of reactions were extensively studied in the fields of explosives under the concept of strain-induced reaction and coined as inverse Jahn–Teller effects.[7] Theoretical calculations on this effect were carried out,[6] and compared with photo-initiation mechanisms.[6,8] When the explosive molecules are strained, energy gap between HOMO and LUMO decreases due to the deformation of their molecular orbital. This induces an electron excitation to trigger the mechanical explosion.[6,8] Therefore, products of mechanically initiated decomposition differ from those of usual thermal decomposition. Rather, they are similar to those obtained from photolysis.[9] These differences in the reaction products are often observed in inorganic mechanochemical reactions.[10]

Recently, we demonstrated a theoretical calculation on anthracene, to have actually recognized a decrease of HOMO–LUMO band gap energy during hypothetical deformation of π plane of anthracene.[11] Orbitals of fullerene, typically HOMO and LUMO, are degenerated due to its highly symmetrical molecular structure.[12] Once the orbital degeneration is removed by photo-excitation, a molecule is deformed due to the change of its orbital distribution, that is, an excitation-induced strain. This is just opposite to strain-induced excitation,

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Keywords: Fullerene; Oxygenation; Mechanochemistry; Solid state reaction; Inverse Jahn–Teller effect.

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doi:10.1016/j.tetlet.2007.09.101

mentioned above.[13] This theory is known as a Jahn–Teller effect of the molecules. Therefore, when similar removal of degeneracy takes place in fullerene via a mechanochemical route, we may directly expect to reduce HOMO–LUMO band gap energy to generate exited states. In this context, we anticipate excitation of fullerene through molecular distortion via mechanical stressing to initiate chemical reactions.

Dimerization of fullerene was known to be one of the few examples of organic mechanochemical reactions, yielding dumbbell shaped dimer of fullerene, connected with two carbon–carbon bonds.[14] Mechanochemical dimerization of fullerene was promoted by adding alkali metal salts or electron donor molecules.[15] Therefore, the mechanism of dimerization was understood as a reaction starting from anion or radical anion of fullerene. In addition, the dimerization was also reported to take place without any addition of the catalyst, and similar polymerization was observed by photo-irradiation.[14] Therefore, we presume that mechanochemical dimerization would also occur through the mechanically excited fullerene, similar to the photo-reaction.

Polymerization of $C_{60}O$ is known to take place in a solid state, by calcining at above 473 K.[16] Due to instability of the epoxy ring on fullerene, this reaction is initiated by thermal cleavage of the epoxy ring, and takes place through radical additions. Via a mechanical route, similar bond cleavage of the epoxy ring would also occur as a result of molecular deformation.

For these reasons, we chose self-sensitizing oxidation or oxygenation of fullerene under mechanical stress by molecular oxygen as a model reaction in order to demonstrate a new organic reaction pathway. By determining active species of oxygen, we try to focus into the mechanisms of the present reaction system. We also examined possibility of two kinds of polymerization processes during mechanical stressing, that is, through C_{60} and $C_{60}O$.

2. Experimental

2.1. Materials

Fullerene [C_{60}] (Nanom Purple®) was used as purchased from Frontier Carbon Corp. Fullerene epoxide ($C_{60}O$ FX-011) was purchased from Flox Corp. Toluene used for HPLC analysis was supplied from Nacalaitesque, Inc. Carbondisulfide and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were purchased from Tokyo Kasei Kogyo Co., Ltd, and 2,2,6,6-tetramethyl-4-piperidone (4-oxo-TEMP) was supplied from Sigma–Aldrich. All the reagents were used without particular pretreatment.

2.2. Mechanochemical oxidation of fullerene

A 500 mg of crystalline powder of fullerene was put into an agate or a stainless steel vessel of the vibrational mill together with a single ball made of either agate (170 g) or stainless steel (507 g). The mill was equipped with a 12 mm thickness PTFE cover, to which an oxygen filled balloon was attached to keep the atmosphere constant at 1 atm oxygen, and to shield daylight.[26] Milling operation was carried out at 298 K with an amplitude 2.0 mm, and a frequency of 50 Hz. Detailed conditions of milling were given elsewhere.[17] After milling for 1–5 h, the product mixture was collected. Unreacted fullerene and soluble fullerene oxides were dissolved in toluene to determine the reaction conversion and yield of $C_{60}O$ by HPLC analysis with a Buckyprep column (Nacalaitesque, Inc.). Toluene was used as a mobile phase at 1 ml/min, at room temperature.

For infrared spectroscopy and elemental analyses, the product was washed with CS_2 and centrifuged until HPLC peak of unreacted fullerene in the supernatant disappeared. IR spectra were obtained from a conventional KBr disk method (IR, FTS-175, BIO RAD).

2.3. ESR spin trapping of $^1O_2$ with photo-irradiation

A 50 mg of physical mixture containing equimolar amount of 4-oxo-TEMP and fullerene [C_{60}] or rosebengal was put into an ESR tube, under oxygen atmosphere. After irradiation with a black light UV lamp (356 nm) for 5 h, we carried out ESR measurements (JEOL JES-RE3X).

2.4. ESR spin trapping of $^1O_2$ or superoxide and peroxide radicals under mechanical stressing

A 0.7 mmol of 4-oxo-TEMP (109 mg for $^1O_2$ trapping) or DEMPO (78.6 mg for superoxide or peroxide radical trapping) and fullerene (500 mg) or rosebengal (498 mg) were milled under the same condition for 5 h. A 50 mg of the milled powder was collected and put into the ESR tube, and immediately subjected to ESR measurements.[26]

2.5. Mechanochemical polymerization of fullerene epoxide or fullerene

A 50 mg of fullerene epoxide ($C_{60}O$) or 500 mg of fullerene was milled under Ar atmosphere for 5 h, in the same reactor used for oxygenation. Milled powders were collected and dissolved in toluene and supernatant solution was subjected to HPLC analysis (Develosil C30 RPFULLERENE column, toluene/acetonitrile = 30:70, 335 nm detection). For infrared spectroscopy, collected powder was washed with CS_2 and carried out by a conventional KBr disk method.

3. Results and discussion

In Figure 1, we observe two types of IR peaks from the mechanochemically obtained product. The peak at around 1000 cm^{-1} is assigned to C–O–C and at 1600 cm^{-1} to C=O. Both peaks are similar to those in the prolonged ozonation product of fullerene in a solution .[18] The apparent composition of the product was $C_{60}O_{8.6}$, according to an elemental analysis. HPLC analysis of supernatant solution used to remove unreacted

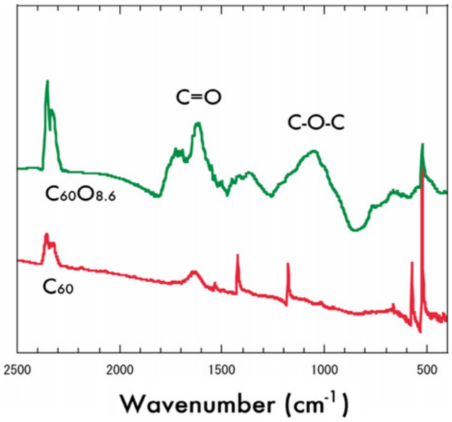


Figure 1. IR spectra of fullerene oxide [$C_{60}O_{8.6}$] (agate reactor, 2 mm amplitude, frequency 50 Hz, reaction time 5 h), and fullerene [C_{60}].

fullerene revealed co-existence of a small amount of $C_{60}O$ (see Fig. S1 in Supplementary data). The reaction conversion, yield of $C_{60}O$, and the average number of obtained fullerene oxides for various reaction periods and conditions are summarized in Table 1. The reaction conversion and the average number of poly-oxidized fullerene were increased with increasing the milling time, amplitude and ball density.

We subsequently tried to determine the active oxygen species of the reaction out of the candidate species, $^1O_2$, superoxide or hydroxyl radicals. To detect $^1O_2$, we used an ESR spin trapping method with 4-oxo-TEMP, an excellent $^1O_2$ spin trapping reagent to give the adduct, 4-oxo-TEMPO free radical.[19,20] We added 4-oxo-TEMP to an equimolar amount with fullerene in the intact mixture. We then milled the mixture under the same condition to compare with photochemical reaction. As shown in Figure 2, we observed ESR peaks assigned to 4-oxo-TEMPO free radical, for both photo-irradiated (Fig. 2b) and mechanically stressed (Fig. 2c) samples. These results unequivocally indicate that $^1O_2$ is generated during the present mechanochemical oxygenation process. Furthermore, oxygenation of fullerene was completely inhibited by adding 4-oxo-TEMP. This implies that fullerene is not oxygenating itself directly under mechanical stressing from oxygen and fullerene at their ground states. Thermal oxidation of C_{60} actually needs temperatures as high as 493 K.[21] Bulk temperature during milling operation was kept at around room temperature. As for the local temperature, we examined that it does not exceed the melting point of menthol, 322 K.[17] Therefore, thermal reaction could not take place under the present reaction condition. Furthermore, possibility of C_{60} cage rapture and the formation of dangling radicals during mechanical stressing is to be excluded either, since we observe 100% recovery of C_{60} by trapping $^1O_2$. Molecular dynamic simulation of C_{60} collision with diamond surface indicated that the threshold energy of C_{60} cage rapture is about 200 eV.[22] This value is orders of magnitude higher than the excitation energy of fullerene, 1.6 eV.[3]

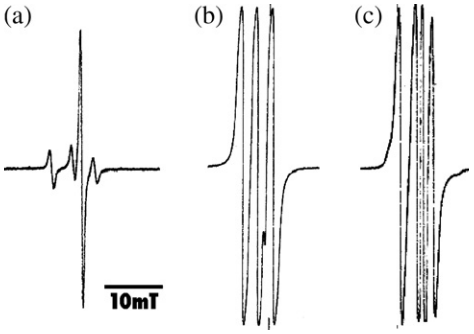


Figure 2. ESR spin trapping of $^1O_2$ in the case of fullerene with 4-oxo-TEMP. (a) Physical mixture of fullerene and 4-oxo-TEMP. (b) Photo-irradiated sample. (c) Mechanically stressed sample. Triplet signals were assigned to 4-oxo-TEMPO free radical. Singlet signal, typically shown in (a) was assigned to oxygen adsorbed on fullerene.[25]

An alternative of active oxygen-containing species for fullerene oxygenation is superoxide or hydroxyl radical. We therefore tried to detect these kinds of active oxygen species during the mechanochemical reaction with ESR by using a spin-trapping reagent, DMPO, which scavenges both radical species.[20] We observed neither superoxide nor hydroxyl radical during mechanical stressing (see Fig. S3 in Supplementary data).

We tried the same $^1O_2$ trapping method by replacing fullerene with a conventional photo-sensitizer of planar molecule, rosebengal.[23] We observed generation of $^1O_2$ by photo-irradiation, but not by milling (see Fig. S2 in Supplementary data). We also examined the possibility of direct excitation of molecular oxygen by mechanical stressing, by milling 4-oxo-TEMP independently in an oxygen atmosphere. However, no $^1O_2$ was detected.

These results reveal that $^1O_2$ generated during milling fullerene under oxygen atmosphere is the sole active

Table 1. Results of mechanochemical oxidation

Materials of a milling ball	Reaction time (h)	Conversions (%)	Yields of $C_{60}O$[a] (%)	Average number of oxygen, n, in fullerene oxide $C_{60}O_n$[b] (n=)
Agate	1	11	0	—
Agate	3	25	1.7	1.4
Agate	5	68	1.5	8.6
Stainless	1	48	2	2.9
Stainless	3	98	0	11.5
Stainless	5	>99	0	12.4

[a] Reaction conversion and yield of $C_{60}O$ were determined by HPLC.

[b] The average number of oxygen, n, in $C_{60}O_n$ was determined by elemental analysis.

oxygen species in the present mechanochemical reaction. Generally, the formation of $^1O_2$ requires energy transfer from excited state of sensitizer to oxygen in a ground state.[3,23] Therefore, our observation of $^1O_2$ generation during mechanochemical processing without irradiation suggests the existence of mechanically excited sensitizer in the system. From our experimental results, generation of $^1O_2$ occurs with the co-existence of fullerene, but not of rosebengal. Therefore, we reasonably presume that the present mechanical excitation is a phenomenon characteristic of the system containing fullerene.

A critical difference between rosebengal and fullerene is in their molecular structure. Fullerene molecules are 3-dimensional and highly symmetrical. Their molecular orbitals are, therefore, highly degenerated.[12] Once mechanical stress is applied to fullerene, degeneration of the molecular orbital can easily be removed as a consequence of molecular deformation and associated breakage of the molecular symmetry.[24] At this stage, a number of new split energy levels would be generated, leading to the reduction of HOMO–LUMO energy gap. In a manner similar to the mechanical excitation triggering the explosion, the reduction of the energy gap may result in the excitation of fullerene through an inverse Jahn–Teller effect.[6,8] Although there are no critical evidences about the states of deformation, it is reasonable to anticipate that fullerene is deformed more easily due to its sphericity than planer rosebengal.[24] Therefore, we attribute the $^1O_2$ generation in the system containing fullerene to the inverse Jahn–Teller effects.

In the present mechanochemical oxygenation reaction, the conversion of fullerene increased with increasing reaction time or by increasing intensity of mechanical stressing. On the other hand, yield of the $C_{60}O$ shows its maximum with decreased milling intensity or at shorter reaction time (Table 1). If direct polymerization through C_{60} or $C_{60}O$ occured, they could reduce the yield of $C_{60}O$. We, therefore, further examined possibilities of these two different types of polymerization processes.

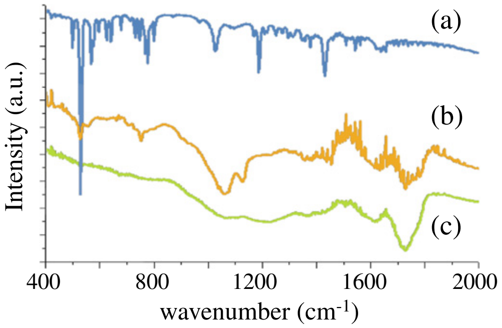
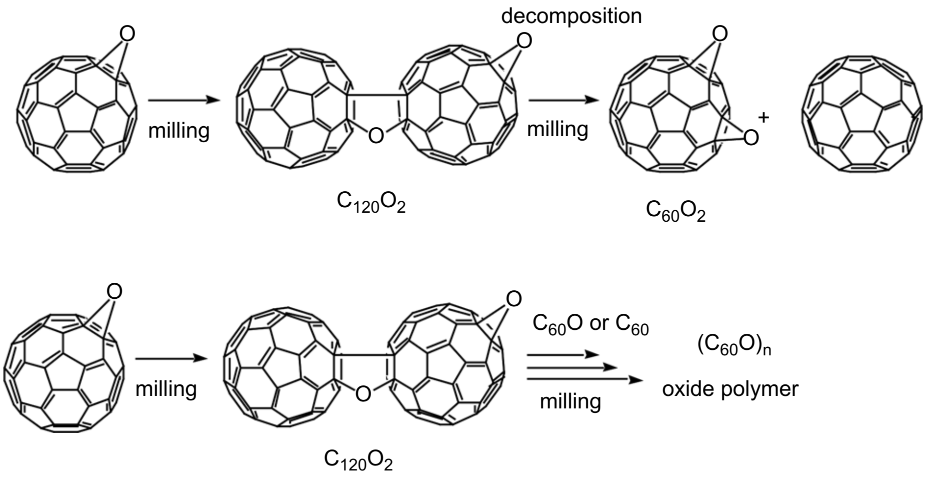


Figure 3. FT-IR spectra of polymerized $C_{60}O$. (a) $C_{60}O$. (b) $C_{60}O$ milled in Ar atmosphere for 3 h. (c) The product of mechanochemical oxygenation.

As a result of mechanical stressing of $C_{60}O$ under Ar atmosphere, insoluble polymeric species were obtained. Their IR spectra are shown in Figure 3. We observe two types of peaks assigned to the carbon–oxygen bonds, that is, C–O–C type absorption at around 1000 cm^{-1} and C=O type absorption at around 1600 cm^{-1}, similar to the product of mechanochemical oxygenation of C_{60} in O_2. HPLC analysis of the supernatant solution obtained during washing process reveals that the co-existence of higher epoxides, $C_{60}O_n$, ($2 \leqslant n \leqslant 5$) and bare fullerene, as minor products (see Fig. S5 in Supplementary data). This demonstrates that the polymerization of $C_{60}O$ also occurs by mechanical stressing. Furthermore, co-existence of un-substituted fullerene and higher epoxides, both being actually observed, would be explained by reversible reaction as described in Scheme 1.

We also examined the possibility of direct polymerization through a mechanically excited state of fullerene by milling fullerene under Ar atmosphere. As shown in Figure 4, we obtained insoluble products characterized to the oligomers of the fullerene.[14b] Reaction conversion reached to 30% by stressing in a stainless steel reactor for 5 h.



Scheme 1. Reversible mechanochemical polymerization of $C_{60}O$.

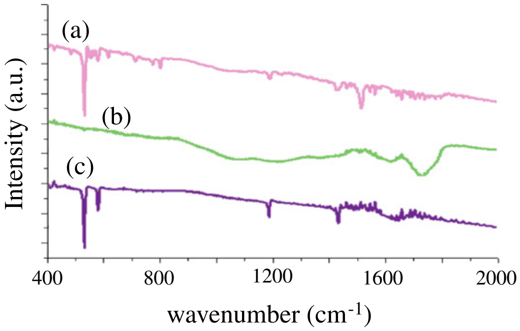


Figure 4. FT-IR spectra of polymerized C_{60}. (a) C_{60} milled in Ar atmosphere for 5 h. (b) The product of mechanochemical oxygenation. (c) Fullerene.

In contrast, milling fullerene with 4-oxo-TEMP under an oxygen atmosphere did not produce any oxides nor polymerized product, even after 5h milling in stainless reactor with 2.0 mm amplitude. As described before, inhibition of the oxygenation could be understood as a result of trapping $^1O_2$. At the same time, relaxation of the mechanically excited fullerene occurs through energy transfer to oxygen molecules. This could inhibit the polymerization of fullerene through its excited state. Therefore, we suspect that the working mechanism for the present mechanochemical polymerization of fullerene could also be explained by mechanical excitation of fullerene through an inverse Jahn–Teller effect.

We therefore reasonably suggest that the main reason for the reduction of the $C_{60}O$ yield is a mechanochemical polymerization of $C_{60}O$ itself. Insoluble oxidative products in mechanochemical oxygenation would be generated through polymerization of $C_{60}O$, as a result of reaction with singlet oxygen (Scheme 1).

4. Summary

We demonstrated the novel mechanochemical oxygenation of fullerene under oxygen atmosphere. Products comprise poly-oxygenated species of fullerene with a small amount of $C_{60}O$ epoxide. During the mechanochemical reaction, we observed generation of singlet oxygen by an ESR spin trapping method. Oxygenation of fullerene was completely inhibited by trapping singlet oxygen. This indicates that mechanochemical oxygenation requires singlet oxygen as an excited species, similar to the case of photochemical oxygenation.

Under mechanical stressing, we observed two kinds of polymerization processes, namely through C_{60} and $C_{60}O$, respectively. Polymerization of C_{60} totally inhibited under oxygen atmosphere. It was most probably due to energy transfer from excited fullerene to oxygen molecule. Thus, we conclude that the products of present mechanochemical oxygenation are the complex mixture of polymerized species originated from fullerene oxide $C_{60}O$, generated via a reaction with singlet oxygen.

Acknowledgments

The authors are indebted to Dr. Yusuke Tajima (RIKEN, Flox Corporation) for assistance with LC–MS analysis, providing fullerene epoxide, and helpful discussions. This work was supported by Grant-in-Aid for the 21st Century COE program ‘KEIO Life Conjugate Chemistry’.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.09.101.

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26. Exposure from daylight was avoided during both milling operation and ESR measurements. Furthermore, to ensure the certainty of the ESR trapping method, we carried out several control experiment. We tried same ESR trapping experiment with C_{60} and 4-oxo-TEMP in Ar atmosphere (Fig. S4 in Supplementary data). Even after exposure to O_2 atmosphere for 5 h, there was no significant change from a signal from physical mixture of fullerene and 4-oxo-TEMP (Fig. 2a).