

Highly oxygenated fullerenes by catalytic epoxidation of C₆₀ and single walled carbon nanotubes with methyltrioxorhenium–hydrogen peroxide

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Abstract

Highly oxygenated fullerenes, C₆₀O_n with 3 ≤ n ≤ 9, have been prepared by the Lewis base enhanced catalytic oxidation of C₆₀ with ReMeO₃/H₂O₂. Pyridine, pyrazole, and 2,2'-bipyridine decrease the activity of the catalyst, while 3-cyanopyridine or 4-bromopyrazole show significant enhancements even at low base:MTO ratios. Increasing the catalyst:C₆₀ ratio increases the yield as well as shifting the product distribution to higher oxygenated products, in contrast, increasing the H₂O₂ concentration or increasing the reaction temperature shifts the product distribution in the opposite manner. Epoxidation of single walled carbon nanotubes (SWNTs) is accomplished with ReMeO₃/H₂O₂/4-bromopyrazole. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

The oxidation of fullerenes, such as C₆₀, has been of increasing interest with regard to applications in photoelectric devices, biological systems, and possible remediation of fullerenes [1,2]. It has also been shown that C₆₀O will undergo a thermal polymerization [3,4], in an analogous manner to that of organic epoxides. The oxidation of C₆₀ to C₆₀O_n (n = 1, 2) may be accomplished by a range of methods, including, photooxidation [5,6], ozonolysis [7–10], and epoxidation [11,12]. With each of these methods, there is a limit to the isolable oxygenated product, C₆₀O_n with n < 3. The only exception involves passing C₆₀ through a corona discharge ionizer in the presence of oxygen allows for the detection of species formulated as [C₆₀O_n][−] (n ≤ 30), however, the products were only observed in the MS [13]. It has been postulated that the reason for the limited oxidation of C₆₀ may be due to the formation of an electron rich fullerene and subsequent lowering of the reactivity of each subsequent olefinic C=C bond [14,15]. In this regard, it would be expected that a suitable catalyst would offer a route to the synthesis of highly oxygenated fullerenes, C₆₀O_n (where n > 3).

To date reports of the catalytic oxidation of C₆₀ are limited, however, Murray and Iyanar reported [12] that C₆₀O might be formed in modest yields (up to 35% after 24 h at room temperature) by the catalytic oxidation of C₆₀ with the methyltrioxorhenium (MTO) hydrogen peroxide system. The MTO/H₂O₂ system had been previously shown to be an active catalyst for the epoxidation of olefins [16,17]. Although C₆₀O₂ and C₆₀O₃ could also be prepared (in up to 18% yield) with MTO/H₂O₂, a 20-fold excess of the MTO “catalyst” was required, as well as the use of urea–hydrogen peroxide as an additional oxidant. It would be desirable to have a catalyst system that allows for the synthesis of highly oxygenated fullerenes that does not require a large excess of catalyst or multi-step reactions.

It has previously been reported that for the epoxidation of olefins with MTO ring hydrolytic opening of the epoxide and the formation of diols is a detrimental side reaction that may be limited by the addition of nitrogen bases, e.g., pyridine [16,17]. However, the addition of bases also appeared to lower the catalytic activity significantly. Sharpless and co-workers [18] found that increasing the amount of pyridine (with a py:MTO ratio of 24 versus a ratio of 2 used previously) actually increased the overall yield. Subsequently, pyrazole was found to offer enhanced activation as compared to pyridine [19]. Other research groups have since promoted their own particular additive for increased activity and selectivity [20,21]. Given the potential of

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enhanced activity observed for epoxidation with the addition of selected nitrogen Lewis bases, we have investigated the use of nitrogen Lewis bases in order to promote the formation of $C_{60}O_n$ with $n > 3$. The addition of a nitrogen base to MTO/ H_2O_2 was originally aimed at reducing hydrolytic opening of the epoxide [18]. In the case of the epoxidation of C_{60} , hydrolytic ring opening is not an issue since the SN_2 reaction is precluded by the fullerene cage structure; however, the effectiveness of various additives in changing the product yield and distribution is significant.

2. Experimental

2.1. Materials and characterization

All reagents and solvents were ACS reagent grade or better and used as received. C_{60} (C-Sixty Inc.), pyridine, pyrazole, 2,2'-bipyridine, 3-cyanopyridine, 4-bromopyrazole, (Aldrich), and $MeReO_3$ (MTO) (Strem Chemical) were used as received. Triphenylphosphine (Aldrich) was recrystallized from EtOH [22]. The Smalley Lab at Rice University donated SWNTs.

High-performance liquid chromatography was obtained using a Waters Alliance 2690 chromatographic system. A photodiode array (model 996) detector was used to gather chromatograms and ultra-violet visible spectra (UV-vis). Chromatographic and UV-vis resolutions were 1.0 s and 1.2 nm, respectively. Typical injection volumes were 100 μ L. A Cosmosil[®] 5PBB (4.6 i.d. \times 250 mm) column with toluene as the mobile phase at a flow rate of 1 mL/min was used for all separations. Column temperature was held constant at 30 °C. Mass spectra were recorded on a Bruker BIFLEX[™] III MALDI-TOF (matrix sulfur) mass spectrometer operating with positive polarity and an electron beam of 19 kV. UV-vis spectra were recorded on a Cary 5000 UV-vis-NIR spectrophotometer using water or ethanol as a blank. IR spectra (4000–400 cm^{-1}) were recorded on a Thermo Nicolet Nexus 670 FTIR spectrometer by evaporating a toluene solution onto a KBr plate to form a thin film. Raman spectra were recorded on a Renishaw Ramanscope with a Renishaw Raman Microscope using 633 nm HeNe laser operating at 50 W. Raman samples were prepared by evaporating a methylene chloride suspension of dried deoxygenated SWNTs on a glass slide.

2.2. Typical preparation of $C_{60}(O)_n$

In a typical oxidation reaction, MTO (52.0 mg, 0.209 mmol) was dissolved in toluene (10 mL). H_2O_2 (30% aqueous, 14 mL) was added, and the solution turned yellow. 4-Bromopyrazole (61 mg, 0.415 mmol) was then added. C_{60} (100 mg, 0.139 mmol) dissolved in toluene (40 mL) was then added to start the reaction. The reaction was allowed to stir at room temperature for 24 h. After 24 h, the solution was red-brown in color. The aqueous layer was separated from the toluene layer and discarded. The organic layer was treated with MnO_2 , filtered, treated with $NaSO_4$, and filtered again. UV-vis: 423, 486, and 592 nm. IR (cm^{-1}): 1261 (s, ring breathing), 1182 (m, fullerene cage), 950 (s, asymmetrical ring stretch), 796 (s), 527 (s, fullerene cage).

2.3. Epoxidation of SWNTs

MTO (75 mg, 0.301 mmol) was dissolved in CH_2Cl_2 (10 mL). H_2O_2 (30% aqueous, 10 mL) was added, and the solution turned yellow. 4-Bromopyrazole (200 mg, 0.681 mmol) was then added. SWNTs (67.7 mg) suspended in CH_2Cl_2 (50 mL) were then added to start the reaction. The reaction was stirred at room temperature, overnight. When the reaction was completed, the solid tubes were filtered over a PTFE membrane (0.2 μ m), centrifuged at 4000 rpm for 15 min., and washed with fresh CH_2Cl_2 (3×35 mL).

3. Results and discussion

We have investigated the relative catalyst activity using pyridine, pyrazole, 2,2'-bipyridine, 3-cyanopyridine and 4-bromopyrazole. The effect of the appropriate nitrogen bases was investigated using a base:MTO ratio of 2 and 10. The results are summarized in Table 1.

The epoxide reaction products, $C_{60}O_n$, have been characterized by MS, FT-IR, and UV-vis spectroscopy, while the product distributions were determined by HPLC and MS. The FT-IR spectra of samples of $C_{60}O_n$ show bands 1260, 950, and 796 cm^{-1} , consistent with previous studies [5]. The UV-vis spectrum of a sample of $C_{60}O_n$ exhibits a new band at 423 nm and the loss of the characteristic C_{60} band at 408 nm. There is also the increased absorbance at 486 nm and decreased absorbance at 592 nm. These observations are consistent with those of previous reported UV-vis spectra of $C_{60}O$ [5]. A representative HPLC chromatogram and the MS for the same sample are shown in Fig. 1. A plot of the fraction of each $C_{60}O_n$ determined by HPLC as compared to the relative MS peak intensity for the same species (Fig. 2), suggests that at the product distribution observed from the MALDI-TOF-MS is due to the formation of specific $C_{60}O_n$ species rather than fragmentation products from higher oxides.

For baseline comparison, the addition of aqueous H_2O_2 to a toluene solution of C_{60} results in essentially unreacted C_{60} with traces of $C_{60}O$, $C_{60}O_2$, and $C_{60}O_3$ being detected by MS only. Under our conditions, although unreacted C_{60} is observed with the addition of 5% MTO, there is significant formation of $C_{60}O$ and $C_{60}O_2$, with decreasing amounts of $C_{60}O_3$ through $C_{60}O_6$ being detected by HPLC and MS, see Table 1. These yields are identical to those reported by Murray and Iyanar for the reaction carried out in benzene over 24 h.

The addition of 2,2'-bipyridine essentially shuts down the catalytic activity of the MTO (Table 1). Increasing the 2,2'-bipyridine:MTO ratio further decreases the activity of the catalyst. This is in contrast to prior studies that suggest 2,2'-bipyridine to be a suitable additive [23]. Prior reports [16,17] suggest that a pyridine:MTO ratio of 2 should lower the epoxidation yield as compared to no Lewis base additive, this is also observed in the present system (Table 1). However, unlike the results reported by Sharpless and co-workers [10] the use of an excess of pyridine does not increase product yield, but further reduces the conversion of C_{60} to $C_{60}O_n$. The overall yield appears insensitive to the concentration of pyrazole, but at the

Table 1
Product distribution from the oxidation of C₆₀ with MTO/H₂O₂/Lewis base^a

| Lewis base (mmol) | C ₆₀ | C ₆₀ O | C ₆₀ O ₂ | C ₆₀ O ₃ | C ₆₀ O ₄ | C ₆₀ O ₅ | C ₆₀ O ₆ | C ₆₀ O ₇ | C ₆₀ O ₈ | C ₆₀ O ₉ | C _n O _y | Yield (%) |
|--------------------------------------|-----------------|-------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|-------------------------------|-----------|
| – | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| – | 47.2 | 34.8 | 12.6 | 3.5 | 0.9 | 0.5 | 0.1 | 0 | 0 | 0 | 0 | 52.8 |
| Pyridine (0.497) | 60.1 | 22.8 | 12.1 | 3.5 | 1.3 | 0 | 0 | 0 | 0 | 0 | 0 | 39.9 |
| Pyridine (0.993) | 71.3 | 14.1 | 9.4 | 3.8 | 1.2 | 0 | 0 | 0 | 0 | 0 | 0 | 28.6 |
| 2,2'-Bipyridine (0.416) | 94.4 | 5.5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5.0 |
| 2,2'-Bipyridine (0.896) | 86.1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 13.8 | 0 |
| Pyrazole (0.411) | 50.6 | 28.8 | 13.2 | 5.1 | 1.6 | 0.4 | 0 | 0 | 0 | 0 | 0 | 49.3 |
| Pyrazole (0.881) | 51.6 | 22.2 | 1.2 | 6.3 | 3.7 | 1.92 | 1.8 | 0 | 0 | 0 | 0 | 48.3 |
| 4-Bromopyrazole (0.386) | 2.2 | 6.3 | 6.8 | 21.6 | 22.8 | 17.1 | 10.2 | 5.5 | 3.3 | 2.2 | 1.6 | 96.1 |
| 4-Bromopyrazole (0.386) ^b | 0.2 | 0.6 | 1.4 | 6.1 | 14.6 | 20.6 | 21.9 | 15.1 | 6.5 | 4.5 | 8.2 | 91.5 |
| 4-Bromopyrazole (0.386) ^c | 12.2 | 28.2 | 20.5 | 19.6 | 11.6 | 4. | 2.1 | 1.1 | 0 | 0 | 0 | 87.7 |
| 4-Bromopyrazole (0.392) ^d | 2.5 | 8.4 | 2.6 | 24.2 | 14.1 | 10.2 | 6.1 | 2.9 | 2.1 | 0 | 2.2 | 95.1 |
| 4-Bromopyrazole (0.386) ^e | 5.4 | 10.1 | 13.6 | 22.4 | 16.1 | 9.6 | 7.6 | 4.1 | 1.9 | 1.4 | 7.5 | 86.9 |
| 3-Cyanopyridine (0.413) | 0.8 | 4.2 | 17.2 | 30.5 | 23.9 | 11.3 | 5.2 | 2.7 | 1.3 | 0 | 2.4 | 96.6 |

^a [MTO] = 0.209 mmol, [H₂O₂] = 173 mmol, in toluene at room temperature.

^b [MTO] = 0.418 mmol.

^c [H₂O₂] = 350 mmol.

^d No light.

^e At 75 °C.

higher pyrazole:MTO ratios the yield of C₆₀O₅ and C₆₀O₆ are increased.

The addition of 3-cyanopyridine or 4-bromopyrazole has a significant effect on both the activity and product distribution even at low base:MTO ratios. The effectiveness of both 3-cyanopyridine and 4-bromopyrazole at the low base:MTO ratio is surprising in light of prior results that suggest that they should hinder catalysis [16,17]. We propose that in the present case the ligands stabilize the catalyst allowing for a moderation in the reaction with the highly reactive C₆₀. Both 3-cyanopyridine and

4-bromopyrazole show a small amount (<8% total yield) of what appears to be a cage-open oxidation product.

As would be expected, increasing the catalyst:C₆₀ ratio increases the yield as well as shifting the product distribution to being centered about C₆₀O₆ rather than C₆₀O₄. By contrast, increasing the H₂O₂ concentration results in a significant decrease in the overall yield and a shift in the product distribution maximum from C₆₀O₄ to C₆₀O. Increasing the reaction temperature to 75 °C decreases both the product yield and shifts the product distribution to be centered about C₆₀O₃, see Table 1. Increasing the temperature also has a detrimental effect on the product yield by the formation of a greater amount of decomposition products.

Creegan et al. have reported that the oxidation of C₆₀ to C₆₀O may be accomplished by photooxidation [5]. In addition, it has been reported that C₆₀ is itself a source of singlet oxygen in the presence of O₂ under photolysis conditions [24]. In order to determine if the MTO catalyzed oxidation is affected by light,

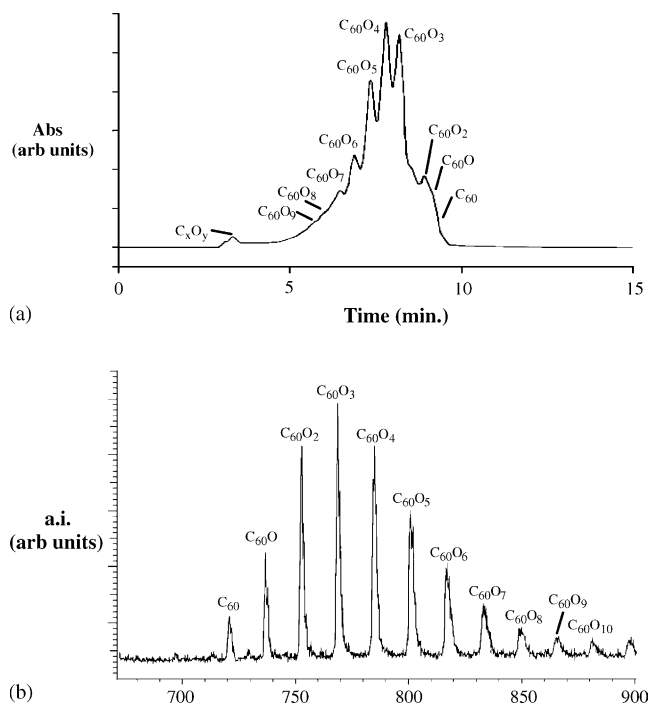


Fig. 1. Representative (a) HPLC chromatogram and (b) MALDI-TOF-MS for C₆₀O_n products from the oxidation of C₆₀ by MTO/H₂O₂ in the presence of 4-bromopyrazole.

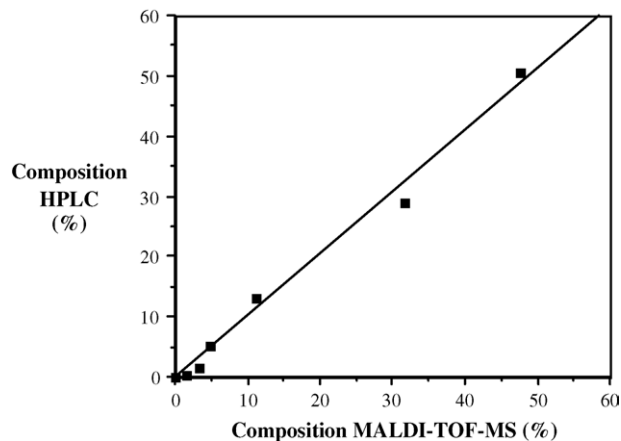


Fig. 2. A plot of the mole fraction of each C₆₀O_n determined by HPLC as compared to the relative MS peak intensity for a sample from the same oxidation reaction ($R = 0.992$).

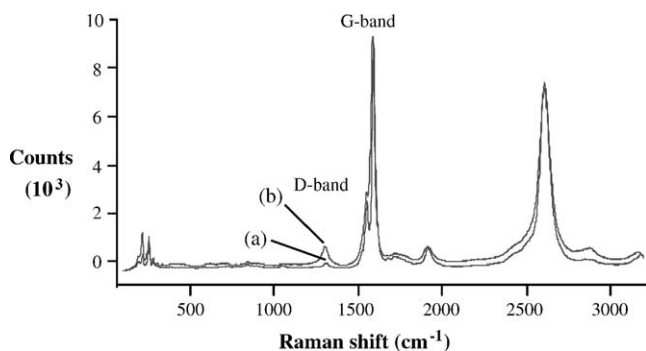


Fig. 3. Raman spectra of SWNTs before (a) and after (b) epoxidation with MTO/H₂O₂/4-bromopyrazole showing the increase in the disorder (D) band associated with sidewall functionalization.

the reaction in the presence of 4-bromopyrazole was studied in both light and dark. Based upon both HPLC and MS analysis there is essentially no change in the yield although there is a shift in the product distribution maximum from C₆₀O₄ to C₆₀O₂. Thus, it would appear that photochemical oxidation is not a component of the formation of C₆₀O_n under the present conditions. However, while the catalyst activity is unaffected by light, the reactivity of C₆₀O_n appears enhanced since oxidation of C₆₀O_n in preference to C₆₀ can account for the shift in the product distribution.

Since SWNTs are just “elongated” fullerenes, it is possible that this reaction would occur when SWNTs were used as the substrate. However, it should be noted that the reactivity of C₆₀ would be expected to be significantly higher than that of a SWNT since the majority of the latter (i.e., the side wall) is composed of fused [6,6] rings, whereas the former contains more reactive [5,6] ring junctions. Oxidation of a CH₂Cl₂ suspension of SF₆ “cleaned” HiPCo SWNTs with MTO/H₂O₂/4-bromopyrazole at 25 °C for 24 h results in an increase in the dispersion of the SWNTs in EtOH. More importantly, the Raman spectrum of the SWNTs after oxidation shows a significant increase in the disorder (D) mode (1350 cm⁻¹) as compared to tangential G mode (1500–1600 cm⁻¹). The tangential mode (G mode) is associated with tangential displacement C–C bond stretching motions in the 1500–1600 cm⁻¹ range (Fig. 3). The D, or disorder mode, observed at 1290–1330 cm⁻¹ depending on Raman excitation laser wavelength, represents conversion of C from sp² to an sp³ hybridization state, which breaks the symmetry of the graphite plane [25]. Spectroscopic and TGA analysis of the oxygenated SWNTs is identical to those formed from direct epoxidation or ozonolysis [26].

In conclusion, we have demonstrated that the addition of 4-bromopyrazole or 3-cyanopyridine allows for the formation of highly oxygenated fullerenes in relatively high yield with minimum side-product formation. Initial results indicate that the MTO/4-bromopyrazole/H₂O₂ oxidation of SWNTs is equal to or better than that of ozone or organic oxidation reagents, such as dimethyldioxarane.

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