

Catalytic epoxidation of C_{60} using $Mo(O)_2(acac)_2/tBuOOH^\dagger$ Cite this: *Dalton Trans.*, 2013, **42**, 2186Robin E. Anderson^{‡a} and Andrew R. Barron^{*a,b,c}Received 22nd October 2012,
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Highly oxygenated fullerenes, $C_{60}O_n$ with $1 \leq n \leq 13$, have been prepared by the $Mo(O)_2(acac)_2$ catalysed oxidation of C_{60} with $tBuOOH$. Increasing the catalyst : C_{60} ratio or increasing the reaction temperature increases the yield as well shifting the product distribution to higher oxygenated products, in contrast, increasing the $tBuOOH$ concentration shifts the product distribution in the opposite manner. The MALDI mass spectra of reactions containing the highest oxygenated products ($n > 5$) show additional peaks (not observed for C_{60} under the same MS conditions) due to the cage-opened products C_x ($x = 54, 56, 58$) along with their oxygenated derivatives, C_xO_n ($x = 54, 56, 58; n = 1-3$).

Introduction

Oxidized fullerenes, such as $C_{60}O_n$, have been shown undergo a thermal polymerization,¹ and have the potential as precursors to cage-opened fullerenes.² The formation of lower oxides $C_{60}O_n$ where $n < 3$ may be accomplished by photooxidation,³ ozonolysis,⁴ epoxidation,^{5,6} and oxidation.⁷ Higher oxides $n \leq 30$ were first reported for the reaction of C_{60} in a corona discharge ionizer in the presence of oxygen.⁸ More recently, copper catalyzed oxygenation with O_2 has been demonstrated in derivatives of C_{60} ,⁹ and a comprehensive review on C_{60} oxygenation recently appeared.¹⁰ We have previously reported that the Lewis base enhanced catalytic oxidation of C_{60} with $MeReO_3/H_2O_2$ results in the formation of higher oxygenated fullerenes, $C_{60}O_n$ with $3 \leq n \leq 10$.¹¹ However, it should be noted that in the absence of a suitable base (but with urea-hydrogen peroxide as an additional oxidant) $C_{60}O_2$ and $C_{60}O_3$ are only prepared with a 20-fold excess of the $MeReO_3$ catalyst.⁶ The $MeReO_3/H_2O_2$ /base system also enables the oxidation of carbon nanotubes.¹¹

The key reaction step for the $MeReO_3$ oxidation of C_{60} involves the formation of a metallocyclic intermediate, whose de-cyclisation results in epoxide formation.^{11,12} We were interested in whether an oxidation catalyst in which the olefinic $C=C$ unit (in this case C_{60}) reacts with a coordinated oxidant

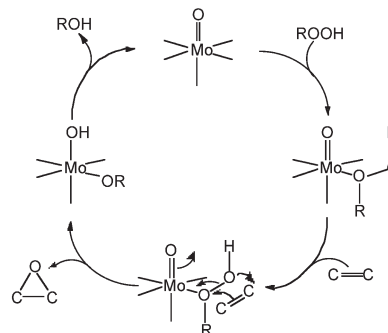
reacts in a different manner. The catalyst that we chose to investigate was $Mo(O)_2(acac)_2$, which is well known as a catalyst for olefin epoxidation in the presence of hydroperoxide, in particular $tBuOOH$ (Scheme 1).¹³

Gan *et al.*, have previously report the use of Fe^{III} and Ru^{III} salts as catalysts for the $tBuOOH$ oxidation and functionalization of C_{60} to yield $C_{60}(O)(OO^tBu)_4$.¹⁴ However, it is worth noting that these catalysts result in a radical reaction,¹⁵ whereas the $Mo(O)_2X_2L_2$ type catalysts, as exemplified by $Mo(O)_2(acac)_2$, are known to react by a non-radical concerted mechanism (Scheme 1),¹⁶ even with non-chelate ligands.¹⁷

Through a systematic investigation of all reaction variables, we have shown that this catalyst does produce as many as 13 epoxide groups per fullerene. The results of this study are reported herein.

Results and discussion

Based upon literature precedent, a $C_{60}:tBuOOH:Mo(O)_2(acac)_2$ ratio of 1 : 1 : 0.002 was initially investigated.¹¹ However,



Scheme 1 Catalyst cycle for the molybdenum(vi) catalyzed epoxidation of olefins.

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even after reacting overnight at room temperature, no epoxidation was observed by mass spectrometry (MS), neither did increasing the amount of catalyst and peroxide to a ratio of 1 : 1.33 : 0.04. Although increasing the reaction temperature to 60 °C resulted in a low yield of the mono epoxide ($C_{60}O$) after 24 h. Further increasing the catalyst and peroxide concentrations to a ratio of 1 : 4 : 0.4 allowed for the formation of $C_{60}O_n$ ($n = 1-5$) after 12 h at 60 °C but only $n = 1-4$ after 24 h at room temperature. The reaction solution appears purple for lower oxides ($1 \leq n \leq 3$) and red for higher ones ($n > 3$). Based upon these initial results, it was evident that the concentrations of peroxide and catalyst were appropriate to achieve some level of epoxidation and unlike the $MeReO_3$ /base catalyst system heating the reaction is required. A summary of the various reaction conditions studied is shown in Table 1.

The epoxide products were characterised by MS, UV-visible and IR spectroscopy. We have previously shown that there exists a good correlation between the relative MS peak height and the molar fraction of each $C_{60}O_n$ species as determined by HPLC.¹¹ Thus, the relative yield of each epoxide (*i.e.*, $n = 1, 2, 3$, *etc.*) can be determined from the MS. A typical mass spectrum is shown in Fig. 1. The FT-IR spectra of samples of $C_{60}O_n$ (Fig. S1†) show bands 1260 (s, ring breathing), 1182 (m, fullerene cage), 950 (s, asymmetrical ring stretch), 796 (s), 527 (s, fullerene cage).³ The UV-visible spectrum of a sample of $C_{60}O_n$ (Fig. S2†) exhibits a new band at 444 nm and the decreased in the characteristic C_{60} band at 408 nm. There is also the increased absorbance at 486 nm. These observations are consistent with those of previous reported UV-visible spectra of $C_{60}O$.³ Furthermore, the 1H and ^{13}C NMR spectra of the products shows no evidence for tBu groups associated with $C_{60}(O)-(OO^tBu)_4$, or related compounds, observed by Gan *et al.*¹⁴

To explore the dependence of epoxide formations on temperature, a series of reactions were conducted with stirring at different temperatures. It was found that the number of epoxides per fullerene increases with increasing temperature up to

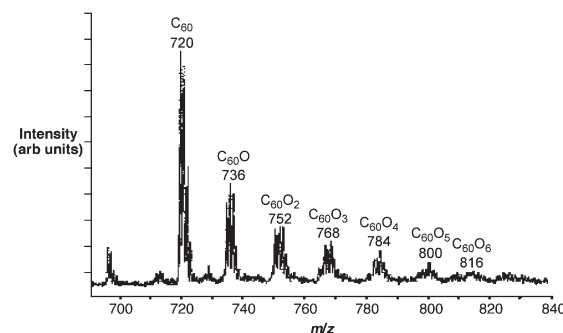


Fig. 1 Representative MALDI-TOF mass spectrum of $C_{60}O_n$ formed from the catalytic epoxidation of C_{60} at 60 °C using a $C_{60} : ^tBuOOH : Mo(O)_2(acac)_2$ ratio of 1 : 4 : 0.4.

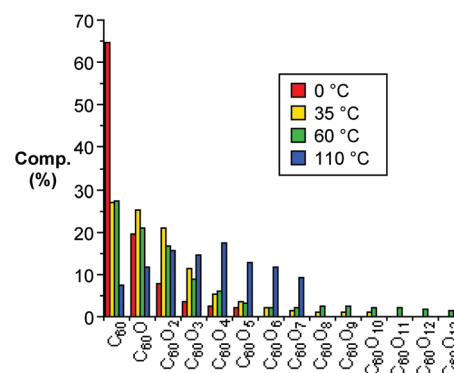


Fig. 2 Plot of the relative composition of the extent of epoxidation (n) for $C_{60}O_n$ as a function of reaction temperature (°C) using a $C_{60} : ^tBuOOH : Mo(O)_2(acac)_2$ ratio of 1 : 4 : 0.4.

60 °C, after which the number of epoxides per fullerene possible lessens (Fig. 2). This suggests that either conversion of $C_{60}O_n$ ($n > 8$) to other products occurs or there is a redistribution of products. The first involves the epoxidation of C_{60} . The second reaction involves the subsequent reactions of $C_{60}O_n$. As can be seen from the above data, the maximum number of epoxides groups produced from these experiments was $n = 13$. While stirring at 60 °C produced the greatest number of epoxides per fullerene, refluxing temperature produces a higher concentration of epoxides in the sample.

To investigate the dependence of epoxide formation on reaction time, a solution was prepared using a $C_{60} : ^tBuOOH : Mo(O)_2(acac)_2$ molar ratio of 1 : 4 : 0.4. Samples were removed from the reaction mixture at $t = 0, 2, 4, 8, 12, 24$, and 72 hours and analysed by MS. There was a clear dependence of epoxide formation on time of reflux up to 4 hours (Fig. 3), after which time no additional epoxidation was detected by MS. In fact it appears as if the percentage of unreacted C_{60} increases, see below.

By varying catalyst concentration it was observed that the number of epoxides/fullerene increases with increasing concentration (Fig. 4). Above a $C_{60} : ^tBuOOH : Mo(O)_2(acac)_2$ molar ratio of 1 : 4 : 0.4, however, there is no apparent increase in efficacy of the catalyst. It is interesting to note that in the

Table 1 Summary of various reaction conditions for the oxidation of C_{60} to $C_{60}O_n$ ^a

$MoO_2(acac)_2$ (mg)	tBuOOH (mL)	Temp (°C)	Time (h)	Max n^b
20	3	60	12	5
20	3	RT	48	4
20	3	110	0	2
20	3	110	2	7
20	3	110	4	7
20	3	110	24	6
10	3	110	24	5
40	3	110	24	7
100	3	110	24	0
100	15	RT	24	6
20	0	RT	24	0
20	6	RT	24	6
20	15	RT	24	2
20	3	0	24	5
20	3	35	24	10
20	3	60	24	13

^a All reactions used 100 mg C_{60} in 50 mL toluene. ^b Observed by MS.

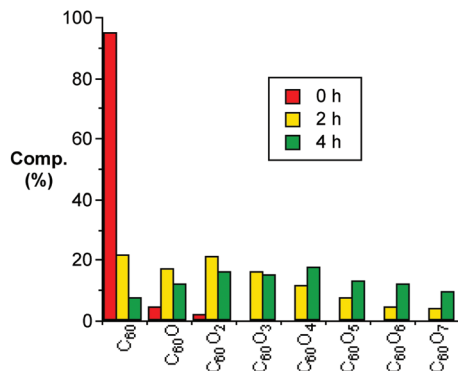


Fig. 3 Plot of data showing epoxide formation (n) as a function of reaction time (at 110 °C using a C_{60} : t BuOOH:Mo(O) $_2$ (acac) $_2$ ratio of 1:4:0.4) taking relative abundance into account. Relative abundance was calculated by measuring the heights of all of the peaks and calculating each peak's height as a percentage of the total.

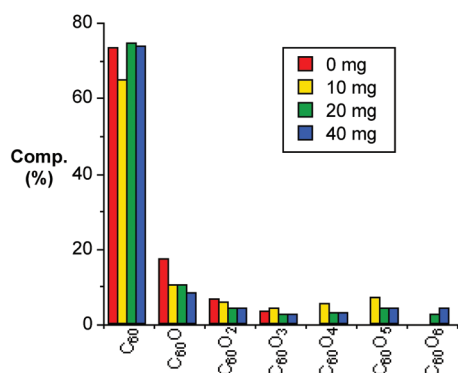


Fig. 4 Plot of the dependence of relative abundance of epoxides, $C_{60}O_n$, on Mo(O) $_2$ (acac) $_2$ concentration (mg/50 mL toluene) for reactions at 110 °C for 24 hours.

absence of catalyst a small amount of oxidation appears to occur. As noted previously, the reaction of C_{60} with t BuOOH has been investigated,¹⁸ and the reaction in the absence of catalyst (and in the dark) appears to result in minimal oxidation (see 0 mg data in Fig. 4).

Increased t BuOOH concentration initially increases the average number of epoxides per C_{60} (Fig. 5). However, above a C_{60} : t BuOOH:Mo(O) $_2$ (acac) $_2$ molar ratio of 1:8:0.4 there appears to be a bias towards lower epoxides, smaller value of n (see 6 mL data in Fig. 5) but with higher concentrations. This appears to support the notion that the oxidation of pre-oxidized compounds is slower than that of those with lower functionality.¹¹ Once a ratio of 1:20:0.4 is used the product yield is increased but the product distribution appears to behave in a similar manner to the reaction of C_{60} with t BuOOH in the absence of catalyst (*i.e.*, similar to the 0 mL data in Fig. 5).¹⁸

Based upon the above results the single phase Mo(O) $_2$ (acac) $_2$ / t BuOOH catalyst system appears to behave in a different manner to that of the epoxidation with the two-phase MeReO $_3$ /H $_2$ O $_2$. We have previously shown¹¹ that in the latter continued oxidation of C_{60} results in the formation of a greater

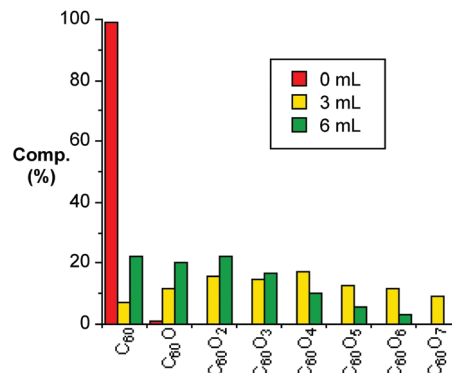


Fig. 5 Plot of the dependence of relative abundance of epoxides, $C_{60}O_n$, on t BuOOH concentration (mL/50 mL toluene) for reactions at 110 °C for 24 hours.

fraction of higher oxides (up to $n = 10$). In contrast, although the present catalyst results in higher epoxides (up to 13 have been detected), the yields are very low. Furthermore, increased reaction time or reagent appears to result in increased yields of the moderate epoxide products ($1 \leq n \leq 6$) rather than continued conversion to higher epoxide ($n > 6$). It is possible that in the present case these higher epoxides are reacting further or decomposing or reacting further (see below). In the absence of a secondary reaction, there are two possible explanations for the lower activity.

It has been previously postulated that limited oxidation of C_{60} may be due to the formation of the electron rich fullerene, which causes a subsequent lowering of the reactivity of each consecutive C=C bond towards oxidation.¹⁹ This effect would be increasingly important when the activity of the oxidation is lowered. Whereas the MeReO $_3$ oxidation involves the direct reaction of the oxide ligand with the C=C bond, the Mo(O) $_2$ (acac) $_2$ / t BuOOH catalyst involves the reaction of the C=C bond with the activated epoxide of the molybdenum-peroxide complex (see Scheme 1).

Since in a general Mo(O) $_2$ L $_2$ / t BuOOH system, the function of the molybdenum catalyst is to increase the electrophilicity of the co-ordinated hydroperoxide, the activity of the catalyst is increased with increasing Lewis acidity of the molybdenum centre. Thus, the use of electron withdrawing ligands (such as acac) is found to increase the activity of the catalyst. This has been found to be true for Mo(O) $_2$ (acac) $_2$.^{13,20} However, under epoxidation conditions the ligand originally present is rapidly replaced by substrate molecules, in this case C_{60} (and its oxygenated derivatives and t BuOOH). The steric bulk of the C_{60} and its lower electron withdrawing nature as a ligand²¹ means that the activity of the catalyst would be expected to decrease with age: as is observed.

In attempting to detect higher oxygenates in the MS, higher laser intensity resulted in the observation of a series of fragmentation species (Fig. 6). We note that these peaks are generally not observed with lower energies. Furthermore, at high laser intensity essentially only the cage-opened products are observed. For example, Fig. 7 is the MALDI MS of the same sample as shown in Fig. 1, but with increased laser intensity.

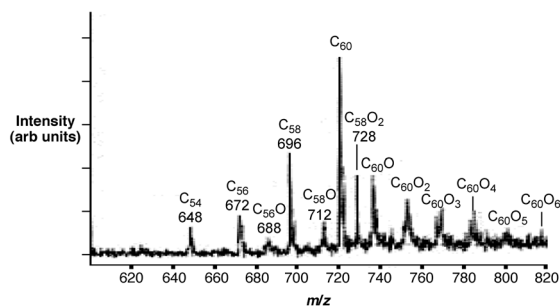


Fig. 6 MALDI-TOF mass spectrum of epoxidated sample showing open-cage fullerene fragmentation species from the catalytic epoxidation of C_{60} at 110 °C using a C_{60} : t BuOOH:Mo(O) $_2$ (acac) $_2$ ratio of 1:4:0.4 for 24 hours.

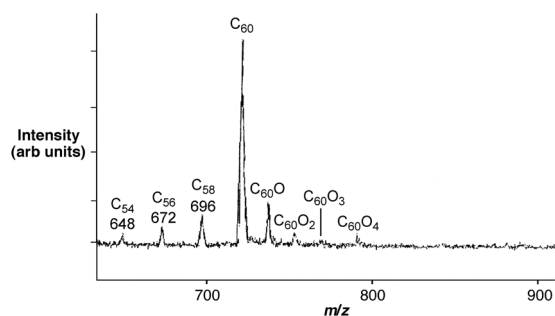


Fig. 7 MALDI-TOF mass spectrum of $C_{60}O_n$ formed from the catalytic epoxidation of C_{60} at 60 °C using a C_{60} : t BuOOH:Mo(O) $_2$ (acac) $_2$ ratio of 1:4:0.4, as shown in Fig. 1 but with collected using an increased laser intensity.

Thus, it appears that the laser source of the MALDI MS effectively decomposes the peroxide and produce the cage opened species in the gas phase. The new peaks can be assigned to the removal of 2, 4, or 6 carbon atoms from the fullerene cage, *i.e.*, C_{58} , C_{56} , and C_{54} , respectively. In addition, their oxygenated products are observed C_xO_n ($x = 58, 56, 54$; $n = 1, 2$). HPLC of reaction mixtures were not successful in separation of the cage-opened products, suggesting that they are most likely the result of fragmentation (along with CO_2) from highly oxygenated products.

Using high-resolution reverse geometry mass spectrometry, the ions C_{58}^+ and C_{56}^+ have been previously observed,²² and their structures calculated.²³ Scheier *et al.*, have proposed that C_{58}^+ is formed from the decomposition of the di-cation of C_{60} .²⁴ However, in the present case no C_{58}^+ ion is observed in the MS of C_{60} without epoxidation. Oxygenated species such as $C_{58}O^-$ have been observed during the reaction of molecular oxygen clusters with laser-ablated (308 nm) hot fullerenes in a molecular beam/time-of-flight mass spectrometer.²⁵ There is precedent for the formation of fragmentation products from oxygenated fullerenes. For example, C_{58}^- has also been observed from the laser desorption mass spectra of thin films of pure $C_{60}O$.²⁶ In the MS of $C_{60}O_2$, a signal corresponding to $C_{58}O_2$ was observed as a minor peak,²⁷ while dioxafullerene $C_{58}O_2$ was selectively generated in the gas phase under MALDI-TOF conditions.²⁸ The tri-oxy species, $C_{58}O_3$, was proposed from ESR measurements and all-electron density functional

theory computations from the heating of C_{60} intercalated by oxygen, *i.e.*, $O_2@C_{60}$.²⁹ Finally, collision induced dissociation of $C_{60}O_n^-$ ($n = 2-4$) in the gas phase yielded $C_{60-x}O_{n-x}^-$, and in particular $C_{59}O^-$.³⁰ It is interesting to note, however, that we do not observe the $C_{59}O$ fragment.

Our observation of $C_{56}O$, $C_{56}O_2$, $C_{54}O$, and $C_{54}O_2$ (along with the previously reported C_{58} , $C_{58}O$, $C_{58}O_2$, $C_{58}O_3$, C_{56} , and C_{54}) as fragmentation products from mixtures of highly oxygenated fullerenes, $C_{60}O_n$ ($n > 5$), in combination with prior reports,¹⁸⁻²¹ suggests that the thermal and/or ionization induced reduction (presumably *via* loss of CO or CO_2) is a facile pathway to a wide range of cage-opened and doped fullerenes. Furthermore, this cage opening process may be related to the oxidative cutting of carbon nanotubes,³¹ and to the oxidation of multiwalled carbon nanotube to give nano-ribbons of graphene.³²

Conclusions

Fullerenes have been epoxidized *via* transition metal catalysis. More epoxides per fullerene ($n = 13$) have been produced by this method than previously reported, but with very low yields. In addition, the catalyst shows low general activity and in particular limited catalytic turnover. This is in agreement with a recent study that compared the reactivity of Mo(O) $_2$ X $_2$ L $_2$ complexes with t BuOOH with that of the MeReO $_3$ /H $_2$ O $_2$, and showed the latter to have a greater activity.³³ It has been proposed that such an effect may be as a result of the substitution of the initial spectator ligands.²⁰ However, a recent study of the antioxidant effects of water-soluble fullerene derivatives has shown their activity is altered by the extent and identity of the substituents, suggesting that the reactivity of $C_{60}O_n$ may decrease with increase in the value of n .¹⁹ Finally, the MALDI-MS of the highly oxygenated samples, using a high laser intensity, offers a route to the observation of a much wider range of oxygenated open-cage fullerenes than previously enabled.

Experimental

C_{60} (99.5%) was obtained from MER corp. (Tucson, AZ). Mo(O) $_2$ (acac) $_2$ (99%, Alfa Aesar), anhydrous t BuOOH (5.5 M in decane, Fluka), and toluene- d_8 (99.5%, Cambridge Isotope Laboratories, Inc.) were used as purchased.

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 UV-visible spectra. High Performance 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 $^{-1}$ was used for all separations. Column temperature was held constant at 30 °C. The samples analysed were used as produced from the

reaction without work-up. Mass spectra were recorded on a Bruker BIFLEX™ III MALDI-TOF (with a sulphur matrix) mass spectrometer operating with positive polarity and an electron beam of 19 kV. The solutions were in toluene with a sulphur matrix. UV-visible 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.

Oxidation of C₆₀ with Mo(O)₂(acac)₂/^tBuOOH

In a typical reaction, C₆₀ (100 mg, 0.14 mmol) was dissolved in dry degassed toluene (50 mL). This solution was syringed into a flask containing Mo(O)₂(acac)₂ (1.0 mg, 0.003 mmol) under N₂. ^tBuOOH (0.75 mL, 0.14 mmol) was added and the solution was stirred at room temperature overnight. Alternative reaction conditions are listed in Table 1.

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