Ozonolysis of [60]Fullerene

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Ozonolysis of [60]fullerene (C_{60}) generates a mixture of the oxidized products having ketone, ester, and epoxide functionalities; an intermediate in this reaction can also transfer an oxygen to aromatic compounds to give normal and NIH-shifted phenols.

Ozonolysis of olefins and aromatics is a complex reaction, and is generally accepted to proceed *via* formation of an unstable molozonide, 1,2,3-trioxolane, which opens into a carbonyl compound and a carbonyl oxide which, in turn, recombine to form a true ozonide, 1,2,4-trioxolane.[1–3] [60]Fullerene, C_{60}, contains thirty formal double bonds, and hence facile ozonolysis of [60]fullerene is expected. However, its spherical nature places stringent steric constraints on the conversion of the molozonide intermediate to the ozonide, and raises questions about the fate of the initial adduct. The carbonyl oxide generated during ozonolysis is also capable of transferring an atom of oxygen to an olefin and arenes.[4–7] We report here on the nature of the oxidation products of [60]fullerene and on the ability of the reaction intermediate to transfer an atom of oxygen to aromatic compounds.

McElvany *et al.*[8] have conducted a study of the ozonolysis of [60]fullerene, but the only products they reported were the curious fullerenes containing odd-number of carbons, C_{119}, C_{129}, and C_{139}. [60]Fullerene epoxides, $C_{60}O_n$ (n = 1–5), were recently reported by Chibante and Heyman[9] to be the products of exposing C_{60} in toluene to ozone for short periods of time. These epoxides are soluble in the reaction medium, toluene. In contrast to these findings, in our experience even brief exposure (5 min) led to formation of a precipitate.† Small amounts of [60]fullerene epoxide were detected along with unconverted [60]fullerene in the solution phase, but the bulk of the product, which precipitated out of the toluene, consisted of highly oxidized derivatives of [60]fullerene.

The elemental analysis of the precipitate from entry 1 of Table 1 (ppt. 1) shows that it is an outcome of extensive oxidation. Its carbon content is less than 50% and hydrogen is *ca.* 3%. If the remainder is presumed to be oxygen, the precipitate should contain 44 atoms of oxygen for every sixty atoms of carbon. If all the hydrogen in the precipitate is from water of hydration (3 wt. % H would account for 24 molecules of water), the precipitate still has 20 atoms of oxygen for every 60 of carbon. Similar consideration leads to ppt. 3 having at least 10 and ppt. 5 at least 4 atoms of oxygen for every 60 of carbon. The main reason for the varying degrees of oxidation is the amount of ozone passed and not the solvent or the temperature. The amount of ozone passed was varied by changing the restriction to flow through a by-pass. While the actual amount of ozone absorbed by the solutions was not determined, it was largest for ppt. 1 and least for ppt. 5.

IR spectra of these precipitates, taken as KBr pellets, show strong absorptions at 1725 cm^{-1} corresponding to carbonyl groups, and strong, broad bands at 3375 cm^{-1} corresponding to hydroxyl groups. These precipitates are generally quite hygroscopic, and the O–H groups shown by IR spectroscopy are likely to be hydrated forms of ketones or other carbonyl functionalities. In accord with the extent of oxidation, ppt. 1 and ppt. 3 are soluble in water and acetone, whereas ppt. 5 is insoluble in water and sparingly soluble in acetonitrile and THF.

The ^{13}C NMR of ppt. 1 taken in deuteriated DMSO shows a peak at δ 211 corresponding to a ketone functionality. In addition to the many peaks in the range δ 115–130, there were also a few in the range δ 95–105. These latter peaks are probably due to carbons in epoxide rings. The elemental analysis, IR, and NMR data of these oxidized products are similar to those reported by Taylor *et al.*[10] for the oxidation products obtained by exposing [60]fullerene solutions to ultraviolet light.

Mass spectrometric analysis of negative ions of ppts. 1, 3, and 5 using desorption chemical ionization with NH_3 reagent gas did not show any peak above m/z 720 (corresponding to [60]fullerene). Mass spectrometry of ppts. 1 and 3 using laser desorption photoionization (Surface Analysis by Laser Ionization, SALI) also did not show peaks higher than m/z 720. The absence of high-mass peaks in these spectra is probably due to difficulties in the desorption of highly polar molecules. However, SALI of ppt. 5, showed peaks with strong signals corresponding to $C_{60}O$ (m/z 736), $C_{60}O_2$ (752), $C_{60}O_3$ (768), $C_{60}O_4$ (784), and $C_{60}O_5$ (800), and a weak signal due to $C_{60}O_6$ (816) (Fig. 1). Signals corresponding to $C_{58}O_2$ (m/z 728), $C_{58}O$ (712), C_{58} (696), C_{56} (672), C_{54} (648), and C_{52} (624) were also seen. Independent tests show that the set of C_{2n} signals are not fragmentation products of C_{60}; they are most likely due to fragmentation of $C_{60}O_x$ during the SALI experiment. Non-aqueous reverse phase HPLC analysis of ppt. 5 on a C-18 column showed that it is a mixture of at least six different components.

Ozonolysis of [60]fullerene **1** in toluene **2** was accompanied by formation of isomeric cresols, *o*-cresol **3**, *m*-cresol **4**, and *p*-

Table 1 Experimental conditions and products from ozonolysis of [60]fullerene

Entry	[60]Fullerene mg (mmol)	Solvent (T/°C)	Yield of oxidized products[a]/ 10^2 mmol (%)	
1	60 mg (8.33×10^{-2})	Toluene (−78)	*o*-Cresol	5.8 (70)
			m/*p*-Cresols[j]	5.6 (67)
			Total cresols	11.4 (137)
2	Control of Entry 1[b]	Toluene (−78)	*o*-Cresol	1.8
			m/*p*-Cresols	1.7
			Total cresols	3.5 (30% of Entry 1)
3[c]	50 mg (6.94×10^{-2})	TCE[d] (−35)	2,5-Xylol[k]	1.89 (27)
			2,4-Xylol[f]	1.26 (18)
			Total xylols	3.15 (45)
4[c]	Control of Entry 3[b]	TCE[d] (−35)	2,5-Xylol	0.486 (25% of entry 3)
			2,4-Xylol[e]	0.181 (10% of Entry 3)
			Total xylols	0.667 (21% of Entry 3)
5[g]	50 mg (6.94×10^{-2})	Decalins (−78)	[f,h,l]	
6[g]	Control of Entry 5[b]	Decalins (−78)	[f,h,l]	

[a] Percentage yield of products is based on amount of C_{60} used. [b] C_{60} not added in the control experiments. [c] Added arene = *p*-xylene. [d] 1,1,2,2-Tetra- chloroethane. [e] NIH-shifted product. [f] Naphthalene precipitated upon cooling. [g] Added arene = naphthalene. [h] Naphthols not formed. [j] Elemental analysis of oxidised C_{60} (%): C 48.55, H 3.25. [k] C 61.00, H 2.60. [l] C 71.55, H 340.

cresol **5**, in 137% yield based on the amount of C_{60} used. In a control experiment where **1** was not used, ozonolysis of **2** afforded only about a third of the cresols produced in the reaction where **1** was used. The nature of this oxygen transfer was further probed by conducting the reaction in two nonaromatic solvents, 1,1,2,2-tetrachloroethane and decalins, both of which have high solubility for **1**.[11] Ozonolysis of **1** in 1,1,2,2-tetrachloroethane at −35 °C in the presence of *p*-xylene **8** produced 2,5-xylol **10** and 2,4-xylol **11** in 27 and 18% yields, respectively (Scheme 1). In the absence of **1**, ozonolysis of **8** produced only about one-fourth of **10** and a tenth of **11** as compared with the experiment where **1** was used. Ozonolysis of **1** in decalins (*cis* and *trans* mixture) at −78 °C in the presence of naphthalene did not produce either of the naphthols, however, naphthalene precipitated out when the solution was cooled to −78 °C.

Involvement of **1** in the hydroxylation of **2** and **8** is clearly indicated as only a fraction of the hydroxylated products are formed by the reaction of ozone with **2** and **8** alone. The intermediate carbonyl oxide **7** produced by the breakdown of the initial molozonide **6** of **1** as shown in Scheme 1 is most likely responsible for hydroxylation of **8**. Carbonyl oxides generated from non-ozonolysis sources have been shown to hydroxylate aromatic compounds *via* arene oxides, and have been shown to be electrophilic in nature.[5,12–16] Accordingly, in Scheme 1, **7** is shown with a formal positive charge to indicate its electrophilic nature. The reaction of **7** with **8** in Scheme 1 is shown to produce an arene oxide **9** which then isomerizes to **10** and **11**. The formation of **11** requires a 1,2-migration of a methyl group. This type of hydroxylation-induced 1,2-methyl migration has been termed the NIH shift in the enzyme catalyzed hydroxylation of aromatic compounds, and is generally interpreted as indicating arene oxide intermediates in these reactions.[17,18] Formation of **11**, the NIH shift product, strongly suggests the formation of the arene oxide **9** which, in turn, suggests **7** as the causative agent for an oxygen atom transfer.

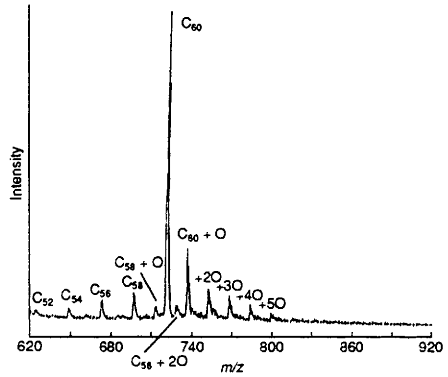
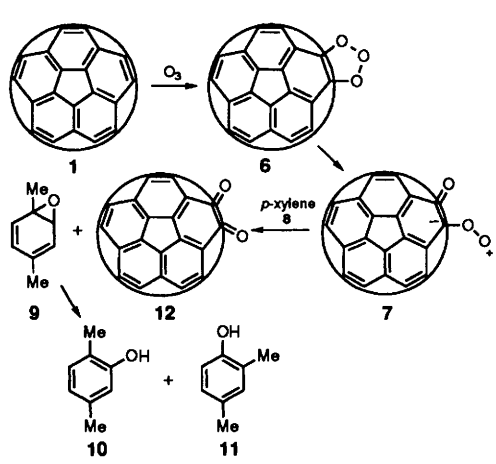


Fig. 1 SALI Spectrum of ppt. 5



Scheme 1 Ozonolysis of [60]fullerene in the presence of *p*-xylene

The foregoing discussion suggests that ozonolysis of C_{60} double bonds generate intermediates (most likely carbonyl oxides) which are capable of epoxidation of aromatic solvents (to finally generate hydroxylated products, including the NIH shift product), and another C_{60} molecule. The oxidation occurs at various double bonds of the C_{60} ball generating a mixture of the oxidized products. These products have ketone functionality, and may have ester and epoxide functionalities. The hydroxyl groups in these precipitates are present due to interaction of water with the oxidized products and are responsible for solubility in water. Quantitative ozonolysis, separation, and analysis of the products are in progress.

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Footnote

† Formation of precipitates in ozonolysis experiments was observed with freshly purified [60]fullerene and with samples that had been exposed to lab environment (light, oxygen *etc.*) over periods extending several months. Thus, the absence of any 'visible change' in the experiments by McElvany *et al.*[8] does not appear to be due to differences in sample history, which was raised as a reasonable possibility by one of the referees.

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