Approaches to chemical functionalization of fullerenes[*]

R. Malhotra[a], A. Satyam[a], S. Kumar[b], S. C. Narang[a], D. S. Tse[a], R. S. Ruoff[a], and
D. C. Lorents[a]

[a]Chemistry and Molecular Physics Laboratories, SRI International (ACTA), 333 Ravenswood
Avenue, Menlo Park, CA 94025, USA

[b]Governors State University, University Park, IL 60466

Oxygenation, hydrogenation, and carboxylation of fullerenes is described to illustrate three general
approaches for functionalizing fullerenes: cycloadditions, radical additions, and reaction of
electrophiles with anions. Oxygenation was attempted by ozonolysis, which proceeds by initial
cycloaddition of O_3 followed by rearrangements. A mixture of products having ketone, hydroxyl,
and epoxy functionalities is obtained. An intermediate in the ozonolysis was shown to transfer
oxygen to aromatic substrates to produce phenols and induce the NIH shift. Hydrogenations were
effected by several methods: transfer hydrogenations with hydroaromatics, direct hydrogenation,
and catalytic hydrogenations. Most highly hydrogenated C_{60} was achieved with 9,10-dihydro-
phenanthrene. Carboxylation of fullerenes was attempted by treating polyanions of C_{60}, obtained by
treating C_{60} with Na in tetrahydrofuran (THF) solvent, with ethyl chloroformate. NMR and IR data
support the formation of $C_{60}(COOEt)_n$ product.

1. OXYGENATION

The reaction of ozone with alkenes[1] and to
some extent with aromatic compounds is well
known,[2] and leads to carbonyl products. The
mechanism of ozonolysis is quite complex,
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] Buckminsterfullerene, C_{60},
with a soccer ball structure, contains 30 formal
double bonds arranged in twenty benzene like
hexagonal faces. Hence facile ozonolysis of
C_{60} is expected. However, the spherical nature
of C_{60} places severe steric constraints on the
conversion of the molozonide intermediate to
the ozonide. Thus an additional motivation

for the study was to determine the fate of the
molozonide intermediate.

Ozonolysis of C_{60} in toluene at -78°C
produced oxidized C_{60} products with carbonyl,
epoxide, and hydroxyl functionalities. In
addition, the reactions were accompanied by
formation of isomeric cresols. Control experi-
ments showed that in the absence of C_{60} the
yield of cresols was less than a third of that in
its presence. We also studied the ozonolysis in
two nonaromatic solvents, 1,1,2,2,-tetra-
chloroethane (TCE) and decalins, with added
aromatics as O-acceptors. Ozonolysis of C_{60}
in TCE at -35°C in the presence of p-xylene
produced 2,5-xylol and 2,4-xylol in 27% and
18% yields respectively. In a control
experiment where C_{60} was not used,
ozonolysis of p-xylene produced only about

one-fourth of 2,5-xylol and a tenth of 2,4-xylol as compared with the experiment where C_{60} was used.

The involvement of C_{60} in the hydroxylation of toluene and p-xylene is indicated by the fact that only a fraction of the hydroxylated products are formed by the reaction of ozone with toluene and p-xylene alone. The formation of 2,4-xylol requires migration of a methyl group, an NIH shift, and indicates that intermediate responsible for oxygen transfer is electrophilic in nature. Based on previous work by Murray and coworkers,[4,5] we suggest that the likely intermediate is a carbonyl oxide produced by the break down of the initial molozonide of C_{60} for hydroxylation of p-xylene.

In these C_{60}-ozonolysis experiments, the oxidized C_{60} precipitated out of the reaction solution. The IR spectra taken as KBr pellets of these precipitates show a strong absorption at 1725 cm^{-1} corresponding to carbonyl groups, and strong and broad bands at 3375 cm^{-1} corresponding to hydroxyl groups. These precipitates are quite hygroscopic, and the O-H groups shown in IR are likely to be hydrated forms of ketones or other carbonyl functionalities. The elemental analysis of the precipitates showed that they are an outcome of extensive oxidation of C_{60}.

These products also tended to be hydrophilic and in many cases water soluble. The ^{13}C NMR of one of the products in deuterated DMSO shows a peak at 211 ppm corresponding to a ketone functionality, and peaks at 157 ppm, 163 ppm, and peaks between 163-166 ppm. These peaks may arise from ester functionality, β carbons of α,β-unsaturated carbonyl systems, and/or an alkene carbon attached to an epoxide ring. The NMR also shows peaks between 115-129 ppm corresponding to aromatic and alkene functionalities.

2. HYDROGENATION

2.1. Transfer Hydrogenation by Hydroaromatics

We have previously reported on the ability of fullerenes to transfer hydrogen atoms from hydroaromatics to alkyl-aromatic substrates, such as 1,2'dinaphth-ylmethane, resulting in cleavage of strong C_{ar}-C_{al} bonds.[6] In these reactions, we also noted that the hydroaromatic component was extensively dehydrogenated. The extent of dehydrogenation was greater than that needed by the stoichiometry of the cleavage reaction. Examination of the products by laser desorption postioniztion mass spectrometry (SALI) showed that in each case C_{60} was hydrogenated to give $C_{60}H_x$ with x ranging between 2 and 36 depending on the hydroaromatic. The most potent reducing hydroaromatic, 9,10-dihydrophenanthrene, showed no intensity for peaks due to C_{60}. There is gradual increase in the signal intensity for peaks with increasing x, and then a precipitous drop in intensity beyond x = 36. Similar results were recently reported by Rüchardt et al.[7] The profile strongly suggests a barrier to reduction beyond $C_{60}H_{36}$. It is interesting to note that initial Birch reduction of C_{60} by Haufler et al. also resulted in a species characterized as $C_{60}H_{36}$.[8]

2.2. Direct Thermal Hydrogenation

In view of the facile reaction of fullerenes with hydroaromatics, we wondered if C_{60} would be likewise hydrogenated by molecular hydrogen. Experiments were conducted in which C_{60} and 1000 psi H_2 (cold) were heated to 400°C for 2 h in stainless steel microreactors with quartz liners. The product of direct hydrogenation without solvent was analyzed by SALI and found to contain $C_{60}H_x$ with x in the range of 0 to 16. HPLC analysis showed the presence of unconverted C_{60} along with some materials with very long retention times possibly corresponding to dimers and trimers.

2.3. Catalytic Hydrogenation

We also studied catalytic hydrogenation of C_{60} two catalysts: (a) Pd on carbon, and (b) an ultrafine ruthenium catalyst[9] generated in situ. Hydrogenation with Pd catalyst was conducted at room temperature with 50 psi H_2 was conducted in a Parr reactor for 24 h by

dissolving C_{60} in toluene. The hydrogenation conditions are mild enough such that toluene would not be hydrogenated by Pd. In the case of hydrogenation with finely divided Ruthenium catalyst, which is very potent and would hydrogenate even benzene, the reaction was conducted in decalin as a solvent. In all these runs, there was no C_{60} left as evidenced by HPLC or NMR. Thus, conversion was 100%. Mass spectrometry (SALI) showed the product was a mixture of variously hydrogenated C_{60}, and also showed a peak due to C_{60} itself, which we suspect was a result of decomposition during mass spectrometric analysis.

3. CARBOXYLATION

Polyanions of C_{60} were first produced by sonicating a suspension of C_{60} and Na in tetrahydrofuran (THF).[10] The anions were then treated with the following reagents: (1) CO_2 followed by CH_3I; (2) ethyl chloroformate, $ClCO_2C_2H_5$; and (3) CS_2 followed by CH_3I. Only treatment with ethylchloroformate produced carboxylated C_{60} derivatives (ethyl esters). The formation of ester group was indicated by IR and NMR spectroscopy. We could not get any good mass spectral data. Carboxyl groups were also successfully introduced by cycloaddition reaction with ethyl diazocarboxylate.

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