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Hydrogen-Transfer Reactions Catalyzed by Fullerenes

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In previous work on the mechanisms of bond cleavage reactions during coal liquefaction and pyrolysis, we have drawn attention to the cleavage of bonds that are too strong to undergo simple thermolysis.^{1,2} Cleavage of such bonds (e.g., C_{aryl}-C_{alkyl} bonds with typical bond dissociation energies on the order of 90 kcal/mol) under coal liquefaction conditions (400 °C, several hours) results from transfer of a hydrogen atom to the ipso position followed by rapid scission of the C_{aryl}-C_{alkyl} bond in the cyclohexadienyl radical. Alternatively, strong bonds can also be formed by the reverse process of alkyl radical addition followed by the usually rate-limiting H-atom removal from the cyclohexadienyl intermediate. Consideration of the various pathways for engendering such reactions leads to the recognition of the importance of H-acceptor species in addition to the H-donor species in the reaction medium. Species that function very well in this regard are polycyclic aromatic hydrocarbons with extended π -systems. One particular PAH known to be very effective in promoting H-transfer reactions is fluoranthene. Viewed from this perspective, C₆₀ and other fullerenes, which have several fluoranthene subunits, appear as good candidates for facilitating H-transfer reactions. We report here results that bear out this expectation both for bond-formation and bond-cleavage reactions. To the best of our knowledge, this is the first demonstration of fullerenes acting as catalysts.

We first observed the catalytic effect of fullerenes in bond-formation reactions in our attempts to extract fullerenes from the raw arc-generated soot at high temperatures. The soot was obtained by the procedure of Haufler et al.,³ and we typically obtained about 12-14% fullerenes upon Soxhlet extraction with toluene.⁴ Other researchers have reported higher yields of fullerenes with high-boiling alkylbenzene solvents.⁵⁻⁷ However, in our experience, Soxhlet extraction of the soot with solvents like mesitylene and 1,4-diethylbenzene gave a tarry product. The tarry product was analyzed by field ion-

ization mass spectrometry and by SALI,^{8,9} a technique in which the sample is desorbed with an infrared laser (1.06 μ m) and the neutrals in the resultant plume are ionized using single-photon ionization (118 nm). These mass spectrometric analyses showed the presence of solvent dimers, trimers, and higher oligomers. In addition, there were satellite peaks corresponding to these oligomers with either more or fewer methyl substituents, which indicates the formation of transalkylated products. The peaks due to these solvent artifacts dominated over any of the fullerene peaks.

Formation of oligomers is also possible with toluene, although because its boiling point is only 110 °C these artifacts are not seen in the usual Soxhlet extractions. Lamb et al. have reported extraction of giant fullerenes using toluene in a tubing bomb at temperatures in excess of 230 °C.⁶ No absolute yields were reported in that study, which focused on the nature and distribution of giant fullerenes. We conducted similar high temperature extraction of a preextracted soot using a high-pressure flow cell. For most of the duration of this extraction the cell temperature was around 250 °C. A deeply colored effluent was obtained suggesting additional fullerenes were being solubilized by this treatment. The fractions were analyzed for their fullerene content by HPLC, which showed C₆₀, C₇₀, and higher fullerenes with a C₆₀ to C₇₀ weight ratio of 1.0:1.3. Interestingly enough, when the temperature was raised to near 300 °C, the color intensity of the effluent decreased, indicating a reduction in fullerene content, but the color intensified again upon reducing the temperature to about 250 °C.

The yield of this high-temperature extract from 5.0 g of soot was about 350 mg. Exhaustive Soxhlet extraction with toluene had previously yielded about 520 mg of fullerenes. Thus, it might appear that the high-temperature extraction provided an additional 70% of fullerenes. However, the C₆₀ and C₇₀ content of the high-temperature extract as determined by HPLC was only ~50 mg. An additional peak in the chromatogram corresponding to bibenzyl was also observed. Using a standard sample of bibenzyl, we calibrated the HPLC and determined the amount of bibenzyl in the extract to be 270 mg. The SALI spectrum of this product shows peaks at *m/e* 182 and 164 corresponding to bibenzyl and a coupling product formed with the loss of a methylene unit, respectively. Thus, solvent artifacts comprise over 80% of the higher temperature extract.

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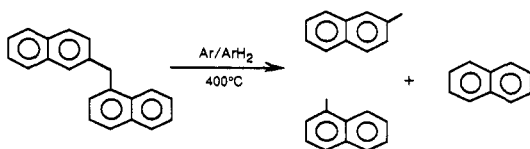
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Scheme I. Cleavage of 1,2'-Dinaphthylmethane in Aromatic/Hydroaromatic Solvents Leading to Naphthalene and Either 2- or 1-Methylnaphthalene Depending on Whether H Was Transferred to the 1- or the 2-Position



To determine if these coupling reactions were due to closed-shell fullerenes themselves or due to the carbonaceous soot that might have dangling bonds, we heated a solution of 100 mg of C_{60} in 50 mL of mesitylene to reflux (bp 163 °C) under argon for 24 h. The solution was then distilled to remove mesitylene and 220 mg of a deep red colored residue was obtained. HPLC analysis of this residue showed many peaks in addition to a relatively small one due to C_{60} . The UV spectra of these peaks recorded on the photodiode array detector were similar to that of bibenzyl with a single maximum around 250 nm, although none of the peaks had a retention time that corresponded to bibenzyl itself. The SALI spectrum of the product showed clear evidence for extensive coupling and transmethylation reactions, and also peaks corresponding to adducts of C_{60} with one, two, and three mesitylene residues and their transmethylated derivatives. Semiquantitative estimates of yields based on HPLC and SALI data show that more than 90% of the initial C_{60} is recovered unconverted; the remaining is transformed into adducts with mesitylene. The molar yield of mesitylene coupling products (dimers and trimers only) is at least 7 times the initial molar concentration of C_{60} . Therefore, we can say that C_{60} is acting like a catalyst in these bond-forming reactions.

We investigated the effect of C_{60} in facilitating bond-cleavage reactions using a reaction system we have previously used, namely cleavage of 1,1'-dinaphthylmethane in equimolar mixtures of three pairs of aromatic/hydroaromatic compounds: (i) anthracene/9,10-dihydroanthracene, (ii) pyrene/4,5-dihdropyrene, and (iii) phenanthrene/9,10-dihydrophenanthrene (Scheme I). Reactions were typically conducted in 3 mm i.d. fused silica ampules with about 300 mg of the arene/hydroarene solvent and about 30 mg of 1,2'-dinaphthylmethane. In runs with C_{60} , about 30 mg of chromatographically purified C_{60} was also taken in the ampule. The ampules were evacuated, sealed, and placed in a stainless steel pressure vessel, before immersion in a molten-salt bath set at 400 °C. After about 1 h, the ampule was removed and the amounts of naphthalene and methylnaphthalenes were determined by gas chromatography. Conversion of 1,2'-dinaphthylmethane under these conditions is only a few percent, and for comparison between runs, defined first-order rate constants for cleavage were derived from the conversion data. Addition of C_{60} to the anthracene system increased the rate constant from 4.4×10^{-6} to $10.8 \times 10^{-6} \text{ s}^{-1}$. Increased conversion was also observed in pyrene and phenanthrene systems; from 8.6×10^{-6} to $11.3 \times 10^{-6} \text{ s}^{-1}$ in pyrene, and from 4.2×10^{-6} to $6.5 \times 10^{-6} \text{ s}^{-1}$ in phenanthrene.

We also examined the changes in the ratio of 2-methylnaphthalene to 1-methylnaphthalene as a result of addition of C_{60} . This ratio reflects the selectivity with which hydrogen is transferred to the 1- and 2-positions,

respectively. When hydrogenolysis takes place by addition of free H atoms, the selectivity at 400 °C is expected to be quite low (~ 1.5). However, if the H atom is transferred from a bound species, the selectivity can be much higher. In previous studies,^{1,2} we found the selectivity of DNM cleavage to range from about 2 to 7 depending upon the solvent system. Replicate experiments showed that these measurements were reproducible to within 15%. In the present study, we found modest increases in selectivity in the anthracene and pyrene systems; from 4.8 to 5.4 and from 4.0 to 4.4, respectively. In both these systems, most of the cleavage takes place through bimolecular H transfers. In the phenanthrene system, where a large fraction of the cleavage results from addition of free H atoms, the selectivity in the control case was 2.9, but upon addition of C_{60} it increased to 4.6. Higher reactivity in the face of higher selectivity indicates that the increase in number of H-carriers more than compensates for the increased selectivity of those generated from C_{60} . Moreover, since the background reaction (i.e., without C_{60}) contributed to about half of the net cleavage, the selectivity of the C_{60} -catalyzed path alone is even greater than that observed for the total reaction. These results are consistent with C_{60} "abstracting" a hydrogen from the dihydroaromatics or the corresponding hydroaryl radicals, and then transferring the hydrogen in a bimolecular step to DNM. As yet, it is not clear whether the species transferring the hydrogen to DNM is a $C_{60}H_x$ -radical ($x = \text{odd}$) or a closed-shell species.

The addition of C_{60} also affected the extent of dehydrogenation of the hydroaromatic. For example, the aromatic to hydroaromatic ratio at the end of the control run with phenanthrene/hydrophenanthrene was 1.3, but in the run with C_{60} this ratio was 33. SALI analysis showed that C_{60} had been converted to variously hydrogenated derivatives. Upon prolonged heating (ca. 7 h), the hydrogenated C_{60} derivatives reverted to C_{60} . Thus, in the end C_{60} catalyzed the dehydrogenation of at least 20 times its molar amount of dihydrophenanthrene.

The coupling, bond-cleavage, and dehydrogenation reactions clearly demonstrate the ability of fullerenes to shuttle H atoms in alkylaromatics and thereby cause both bond-cleavage and coupling reactions. Together, these reactions suggest the possible use of fullerenes in hydrocracking and re-forming operations. The results also serve to caution against the use of high-temperature extraction of fullerenes from soot with alkylaromatic solvents.

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Supplementary Material Available: HPLC and SALI spectrum of toluene extract and residue after heating mesitylene with C_{60} under argon (7 pages). Ordering information is given on any current masthead page.