

Chemical Structures and Reactivities of Coal
as an Organic Natural Product

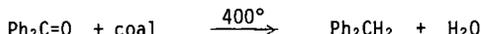
Clair J. Collins, Hans-Peter Hombach, Ben M. Benjamin

W. H. Roark, Brian Maxwell, and Vernon F. Raaen (1)

Contribution from the Chemistry Division
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

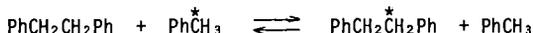
A. The Role of Tetralin in the Pott-Broche Process

It has recently been demonstrated (2) that several bituminous coals and lignites are better hydrogen donors than tetralin, a donor which has been employed, since its use in the Pott-Broche process (3), as the coal chemists' "standard." The better hydrogen-donating abilities of these various coals were tested toward several reactions (4), but that used as the model was the reduction, in a closed tube at 400°, of benzophenone to diphenylmethane:

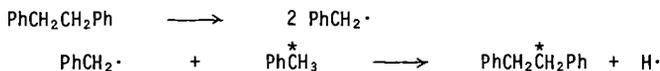


These results naturally raise the question of the role of tetralin, or of the recycle oil used in its place, during many of the solvent-refined coal processes — particularly since the solid product of such processes often contains no more hydrogen than the original coal (5). Neavel (6) examined the liquefaction of coal in tetralin and other solvents, using kinetic techniques, and found that donor and nondonor solvents appear to be equally capable in dispersing the coal after 5 minutes at temperatures of 400-570°C. Upon prolonged heating in nondonor solvents, the free radicals which form in the coal are thought to polymerize to higher molecular weight materials, whereas in the presence of tetralin, these radicals can be trapped by transfer of hydrogen.

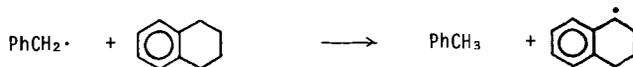
In order to test some of these concepts we carried out several experiments with carbon-14-labeled compounds. In one of these bibenzyl and toluene-¹⁴C were heated at 400° for one hour. There was intermolecular transfer of hydrogen with formation of toluene and other products, but the reisolated bibenzyl had undergone (to a small extent) an exchange reaction with toluene as shown by the fact that the reisolated bibenzyl contained carbon-14:



This exchange reaction must take place through a free-radical mechanism, possibly as follows:



When the two components — bibenzyl and toluene-¹⁴C — were heated in the presence of tetralin, however, there was no exchange between the two as shown by the fact that the reisolated bibenzyl was completely devoid of carbon-14. The reason must lie in the ready ability of tetralin to trap the benzyl radicals before they can react with toluene:



In several other reactions carried out with Illinois No. 6 coal and labeled substrate (e.g. α -naphthol- α - ^{14}C), the mixtures were heated for up to one hour in closed tubes at 400° , and benzene was used as a vehicle to ease material transfer. To our surprise, significant quantities of unlabeled biphenyl were discernible upon subsequent work-up. Although the yields were not determined, sufficient biphenyl was formed in one case to allow its isolation and identification by nmr. Through some as yet unexplained mechanism, a phenyl radical must have been produced, which then reacted with another benzene molecule to form biphenyl:



The presence of tetralin, however, inhibits biphenyl formation.

In an effort to determine whether tetralin does more than act as a radical scavenger during Pott-Broche-like processes, we prepared tetralin-1- ^{14}C (7) and heated it (1.933 g, 15.82 C; per mole) for one hour with 3.06 g of vitrain (from Illinois No. 6 coal). The product was extracted with pyridine, and the residue was treated with THF, plus a mixture of nonradioactive tetralin and naphthalene. The residue still contained carbon-14 which, on a tetralin basis represents 2.6-2.8% by weight of the residue. The pyridine soluble fraction also contained carbon-14 representing 1.6% by weight of that fraction (on a tetralin basis). Thus the tetralin- ^{14}C appears to have undergone a chemical reaction with the coal. We have previously reported (4) that tetralin and Illinois No. 6 coal when heated at 400° yield α - and β -methyl-naphthalenes, in which the methyl groups undoubtedly have their origin in the coal.

The role of tetralin during coal conversion, therefore, is 1) to act as a dispersion vehicle; 2) to supply hydrogen radicals, when needed, to trap coal radicals, and 3) in a very minor way to undergo intermolecular reaction with the coal through making and breaking of C-C (and possibly other) bonds.

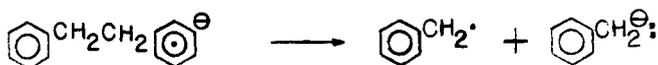
B. Reductions of Coal

Two chemical reactions for solubilizing coals have received much attention in recent years, these are 1) the Friedel Crafts reaction (8-19) and 2) reductions, either with lithium in suitable solvents (20-26), or electrolytically with lithium salts in ethylenediamine (27-32). Part of the interest in these reactions is undoubtedly due to the fact that they can be carried out at low temperatures.

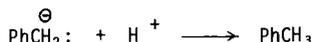
The chemical changes affected during coal reductions are usually considered to be breakage of ether and thioether linkages, as well as reduction of aromatic nuclei. Alkyl groups are not affected (33). The Birch-Hückel reaction (34) of aromatic rings to cyclic olefins is well known. It was recently reported (35) that the use of NaK in mixed ethers as a coal reductant cleaves the alkyl linking groups (e.g. $-\text{CH}_2-\text{CH}_2-$) between aromatic moieties, and results in an increase in the number of methyl groups in the reduced product. Oxidation studies (36, 37) have indicated a high frequency of ethylene connecting links in some bituminous coals, as shown by the isolation of large quantities of succinic acid. We therefore carried out the reduction of three model compounds under the conditions reported (37) by Hombach and Niemann, using glycol ethers as the solvent. The compounds chosen were diphenylmethane, bibenzyl, and 1,3-diphenylpropane. Of the three compounds, diphenylmethane exhibited some, and bibenzyl exhibited considerable C-C splitting in only 20 minutes, whereas 1,3-diphenylpropane was stable except for traces of toluene and ethylbenzene (when quenched with propanol-2). The results can be illustrated for bibenzyl, which was added to the solution (37) of "solvated electrons." The mixture was stirred for 20 minutes, then $^{14}\text{CH}_3\text{I}$ was added to the reaction mixture, followed by water and then pentane. The pentane solution was washed, dried, and subjected to g.c. analyses with an apparatus fitted with a carbon-14 radioactivity monitor (38). The

results are shown in Fig. 1. The products were separated on a preparative g.c. column (39) and identified through their nmr spectra.

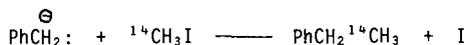
Thus, to the methods previously employed for breaking bonds in coal molecules and thereby lowering their molecular weights, must now be added the use of "solvated-electrons" for breaking -CH₂-CH₂- linkages. The mechanism for cleavage of bibenzyl must be approximately as follows



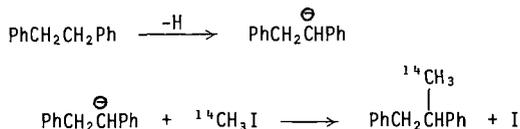
Toluene results by donation of a proton to a benzyl carbanion from the solvent:



The carbon-14-labeled ethylbenzene is formed by reaction of the benzyl carbanion with ¹⁴CH₃I:



The other product, 1,2-diphenylpropane is formed in the conventional manner:



References

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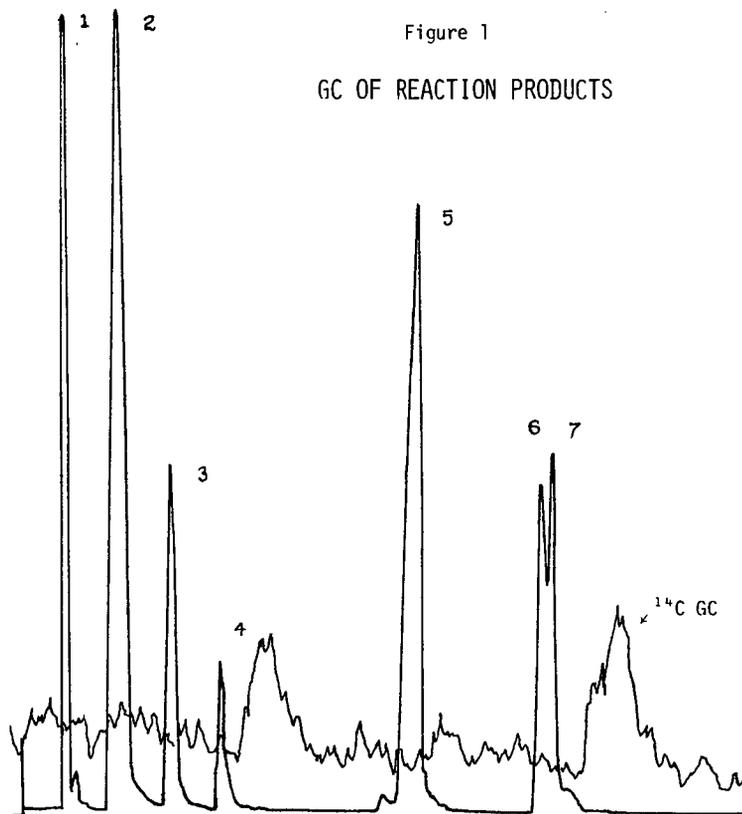


Figure 1
GC OF REACTION PRODUCTS

- 1 pentane
- 2 1,2-dimethoxyethane
- 3 toluene
- 4 ethylbenzene
- 5 2,5,8,11-tetra-oxadodecane
- 6 1,2-diphenylethane
- 7 1,2-diphenylpropane