

## ISOTOPIC STUDIES OF THERMALLY INDUCED REACTIONS OF

## COAL AND COAL-LIKE STRUCTURES

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We recently (2) reported that under conditions of coal conversion (tetralin, 400°) several diarylalkanes undergo carbon-carbon cleavage, and that the scission of carbon-carbon bonds must therefore be considered as an important process in asphaltene formation. We also reported (2) that vitrinite (from Illinois No. 6 coal) was a "better hydrogen transfer agent" than tetralin itself for the hydrogenolysis of 1,1,2-triphenylethane to diphenylmethane and toluene. We have now extended these studies to establish a) that vitrinite is indeed a better hydrogen donor than tetralin toward several organic structures; b) that tetralin, in addition to its function as a hydrogen donor, can undergo certain other reactions with coal and with coal-like structures which involve both carbon-carbon bond formation and bond cleavage.

A Comparison of Tetralin and Vitrinite as H-Donors

When 1,2-diphenyl-1-p-tolyethane is heated at 400° (either in glass capillaries or in stainless steel tubes) with an excess of tetralin, the major products are toluene and phenyl-p-tolylmethane. The same products are obtained when 1,2-diphenyl-1-p-tolyethane is heated at 400° in the presence of an excess of vitrinite (handpicked from Illinois No. 6 coal). Given in Table I is a comparison of the

Table I

A Comparison of Tetralin and Illinois  
No. 6 Vitrinite as Hydrogen Donors

Reactants	Conditions	Percent Reaction
1,2-Diphenyl-1-p-tolyethane	400°, 5 min <sup>a</sup> tetralin	2%
"	400°, 30 min <sup>b</sup> tetralin	94%
"	400°, 5 min <sup>a</sup> vitrinite	50%
1,3-diphenylpropane	400°, 30 min <sup>b</sup> tetralin	23%
"	400°, 30 min <sup>b</sup> tetralin & vitrinite	43%
"	400°, 30 min <sup>b</sup> vitrinite	65%

a) The oven was at 400°, but the warm-up time is 15 minutes, thus the actual temperature was considerably less than 400°.

b) 30 min included warm-up time.

extent reaction — as determined by g.c. analysis of the products — after various contact times with tetralin or with vitrinite.

Another diarylalkane which is easily decomposed in the presence of excess tetralin or excess vitrinite is 1,3-diphenylpropane. The major products in both cases are toluene and ethylbenzene, although a multiplicity of minor products are produced. Also given in Table I are comparisons of the extent reaction of 1,3-diphenylpropane (400° for 30 minutes) a) with excess tetralin; b) with excess tetralin and vitrinite; and c) with excess vitrinite. The extent reaction in each case was estimated from the g.c. trace.

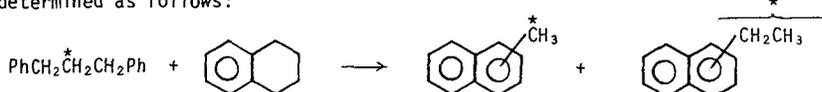
Since the reactions were monitored by g.c., which would detect neither nonvolatile polymeric material, nor high molecular weight products of reaction with vitrinite, it is possible that the vitrinite is acting not as a hydrogen donor, but merely as a catalyst, and that the source of the hydrogen for the hydrogenolyses comes from the 1,2-diphenyl-1-*p*-tolylethane or from the 1,3-diphenylpropane. To circumvent this problem, we heated benzophenone to 400° for one hour a) in the presence of excess tetralin, and b) in the presence of excess vitrinite. The major products are diphenylmethane and water, with traces of toluene and benzene. The reaction in tetralin proceeded to the extent of only 12%, whereas in the presence of vitrinite 35% reaction had occurred.

#### Reactions of Tetralin other than Hydrogen Donation

V. F. Raaen (3) showed recently that tetralin-1-<sup>14</sup>C reacts with Wyodak coal at 400° (1 hour) to the extent that the pyridine-insoluble residue contains chemically bound carbon-14 equivalent to 5% tetralin by weight. Further, when the residue was reheated in normal tetralin (400°, one hour) the reisolated solvent contained no measurable amount of either tetralin-<sup>14</sup>C or of naphthalene-<sup>14</sup>C. There were, however, traces of labeled alkylated naphthalenes, which were identified by g.c. retention times as 1- and 2-substituted methyl- and ethylnaphthalenes. These products undoubtedly arise as a result of free radical intermediates. We therefore investigated the possibility that methyl- or ethylnaphthalenes could be produced by the reaction of tetralin with structures containing aromatic moieties separated by two or more methylene groups, or with aryl alkyl ethers. Both types of structure (4,5) are known to be present in different kinds and ranks of coal.

We heated several diarylalkanes and aryl alkyl or aralkyl ethers to 400° in tetralin for varying periods of time. Many of these reactions yielded measurable quantities of methyl- and ethylnaphthalenes in addition to other products. Typical are the reactions of 1,3-diphenylpropane and of phenetole, both of which were investigated with carbon-14-labeled species. The products were analyzed a) by gas chromatography combined with radioactivity monitoring of carbon-14-labeled products; b) by gas chromatography equipped with mass spectrographic analyzers (5); and c) by isolation of specific products using preparative g.c. (6) followed by nmr analysis (Varian XL-100 Spectrometer). Given in Tables II and III are the major products obtained — together with appropriate yields — from the reactions of 1,3-diphenylpropane and phenetole, respectively, with tetralin.

The 1- and 2-methylnaphthalenes were isolated and identified by nmr analysis. Their genesis from the reaction of 1,3-diphenylpropane-2-<sup>14</sup>C (<sup>14</sup>C=\*) and tetralin was determined as follows:



The mixture of ethylnaphthalenes was identified by g.c. retention times and radioactivity assay by means of the g.c. radioactivity monitor. Traces of methylindane

Table II  
Major Products and Yields Obtained<sup>a</sup> on Heating 1,3-Diphenyl-  
propane with Tetralin One Hour at 400°

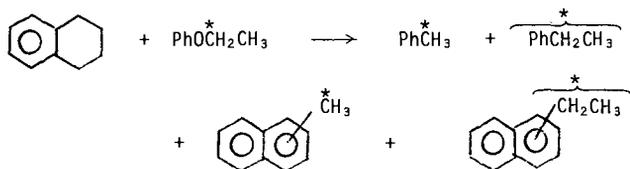
Toluene	28%
Ethylbenzene	19
1- and 2-(2-Phenylethyl) tetralins	8
1,4-Diphenylbutane	5
1- and 2-Methylnaphthalenes	3
Styrene	1.5
1,3-Diphenylpropene	1.5
Methyldihydronaphthalenes	}
1,2-Diphenylethane	
1- and 2-(2-Phenylethyl) naphthalenes	
Other	

<sup>a</sup>Based on 1,3-diphenylpropane consumed.

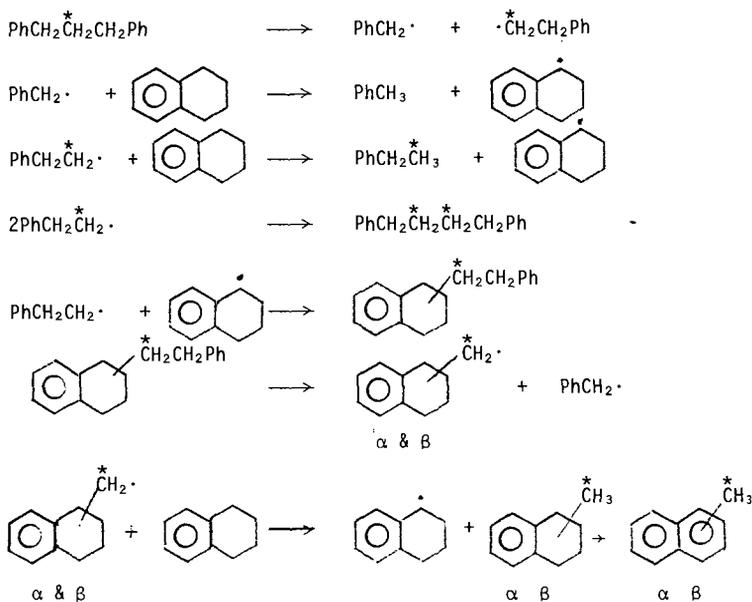
Table III  
Major Products and Yields Obtained on Heating Phenetole  
with Tetralin Eighteen Hours at 400°

Phenol	37%
Methylnaphthalenes	13
Toluene	7
Ethylbenzene	7
Ethyl naphthalenes	7
Methyltetralins	4
Ethylphenol	3
Ethyltetralins	3
Ethylmethylbenzene	}
Methylindane	
Butylbenzene	

and of butylbenzene were always present after reactants were heated with tetralin. That these latter two products were derived from tetralin was demonstrated by the fact that they contained carbon-14 when tetralin-<sup>14</sup>C was used in the reaction. In like manner, labeled phenetole and tetralin were subjected to the conditions of reaction with the following results:



It is clear from the isotopic labeling experiments that tetralin has entered into the reaction both with 1,3-diphenylpropane and with phenetole. The results are nicely accommodated by the postulation of radical intermediates. A possible mechanism for the reaction of 1,3-diphenylpropane is indicated:



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#### References

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