

The Response of High Temperature Catalytic  
Tetralin-Hydrogen Reaction to Free Radical Addition

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I. INTRODUCTION

The literature is ambiguous regarding the reaction products obtained when tetralin and hydrogen are reacted above 425°C in the presence of a catalyst. Yen et al. (1) reported that tetralin disproportionation occurs, at 455°C, and naphthalene and only one of the decalin isomers are formed. They also reported the presence of an unidentified product. Hooper et al. (2), with the aid of recent advances in chromatographic analysis, suggested that the compound identified as a decalin isomer could be methyl indan and attempted to show that tetralin disproportionation did not occur. However, they did not analyze any actual products from catalytic hydrotreatment of tetralin.

In this report, gas chromatographic analyses of the products from catalytic dehydrogenation of tetralin at 450°C are presented. These analyses served as the baseline for comparison of reactions in which dibenzyl was added to provide a source of free radicals similar to those produced during the initial stages of coal liquefaction.

II. EXPERIMENTAL

The experiments were carried out in a tubing bomb microreactor constructed from a six inch length of 316 seamless stainless steel, 1/2-inch O.D. tubing. One end of the microreactor was sealed with a 1/2-inch Gyrolok cap. The other end was connected to a 3 and 1/4-inch length of 316 seamless stainless steel, 1/4-inch O.D., tubing with a Gyrolok reducing union. A Nupro fine metering valve was connected to the other end of the 1/4-inch O.D. tubing.

The reaction temperature was maintained by immersing the microreactor in a fluidized sand bath which was equipped with a temperature controller and a thermocouple for monitoring the temperature. The microreactor was agitated in a vertical plane with a 1 and 1/2-inch stroke. An agitation rate of 860 rpm has been shown (3) to reduce mass transfer effects in the microreactor. Two steel ball agitators of 1/8-inch diameter were also added to the microreactor to ensure good end-to-end mixing during reaction.

At the end of the desired reaction time, the microreactor was quenched in water (20-25°C) to stop the reaction. The microreactor was then vented and its contents collected in a vial.

The reaction products were analyzed using a Varian 3700 gas chromatograph equipped with a CDS-111 integrator. Separation was accomplished with a 60-meter, 0.314 mm I.D., fused silica capillary column with a DB-5 bonded phase (0.25  $\mu$ m). To assist in the identification of the reaction products, some of the samples were analyzed with a gas chromatography-mass spectroscopy (GCMS) unit. A capillary column

was used for separation of the products. The composition of the other reaction experiments were then identified by comparison of the chromatograms with the chromatograms of the samples analyzed with GCMS.

### III. RESULTS AND DISCUSSION

Three reaction parameters were chosen for manipulation to investigate the tetralin-hydrogen reaction at a relatively high temperature (450°C). These parameters were:

- (1) addition of dibenzyl as a free radical precursor
- (2) catalyst addition
- (3) addition of gaseous hydrogen

Dibenzyl was selected as the free radical precursor. Dibenzyl cleaves at coal liquefaction conditions, producing benzyl free radicals. The primary reaction of dibenzyl is assumed to be thermal cracking followed by stabilization of the benzyl free radicals. Cronauer et al. (4) observed no increase in the rate of dibenzyl conversion with the addition of catalysts.

Table 1 presents the response of the product distribution to the addition of dibenzyl, and hence, the presence of free radicals. The principal products of the dibenzyl-tetralin-hydrogen reaction were benzene, toluene, methyl indan, and naphthalene. Very small amounts of ethyl benzene, butyl benzene, and trans-decalin were found in some experiments. Traces of cis-decalin and stilbene were also detected.

With the addition of dibenzyl, the most significant result was an increase in the formation of methyl indan, the isomer of tetralin. Approximately twenty percent of the tetralin was isomerized with the addition of dibenzyl, both with and without catalyst. Cronauer et al. (5) and McNeil et al. (6) have also reported an increase in the isomerization of tetralin with the addition of dibenzyl.

Even when there was no dibenzyl present, some isomerization of tetralin was observed (i.e., 5.7 wt% and 7.9 wt% methyl indan was formed with and without catalyst present, respectively). Isomerization of tetralin has been reported at temperatures as low as 350°C in a nitrogen atmosphere (2). Penninger and Slotboom (7,8) heated tetralin with hydrogen in the absence of catalyst at pressures of 10 to 100 atm and temperatures of 460 to 560°C. Methyl indan was reported among the principal products. They proposed that the dehydrogenation of tetralin to naphthalene provided the hydrogen atoms (i.e. free radicals) to initiate the isomerization reaction.

The formation of benzyl free radicals from dibenzyl is a thermal process. Thus, the use of catalysts was not intended to change the amount of dibenzyl converted; instead it was felt that its addition would alter the product distribution, i.e., mainly the relative amounts of tetralin isomerization and dehydrogenation products. The rate of formation of the tetralin isomer, methyl indan, changed slightly with the addition of presulfided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. However, the rate of tetralin dehydrogenation to from naphthalene increased significantly with the addition of catalyst. This increase was even more pronounced when no dibenzyl was added; the amount of naphthalene formation increased from 1.3 wt% to 13.0 wt% with the addition of catalyst. When dibenzyl was present, the amount of naphthalene formation increased only from 6.6 wt% to 9.8 wt% with the addition of catalyst.

For the product analyses given in Table 1, only a small amount of trans-decalin was observed, and that was when catalyst was present. No significant amount of cis-decalin was observed in any of the products analyzed. For the reaction

conditions used here then (450°C, etc.), catalyst addition caused an increase in the rate of dehydrogenation of the tetralin rather than an increase in that of hydrogenation.

The third reaction parameter which was studied was the addition of gaseous hydrogen. Vernon (9) has shown that molecular hydrogen can react directly with the benzyl free radical to yield toluene. Shah and Cronauer (10), however, have demonstrated that the benzyl free radicals have a distinct preference for combined hydrogen over molecular hydrogen under reaction conditions similar to those used in this work. They reported that this preference is enhanced if the concentration of hydroaromatics is high. The molecular hydrogen was believed to provide hydrogen for "rehydrogenation" of depleted hydrogen donor solvent. In this work, tetralin serves as the hydrogen donor, and a primary objective of the study was to evaluate the response of the rehydrogenation rate of the tetralin versus that of isomerization to the addition of gaseous hydrogen.

Two extremes of reactor atmosphere were used: a hydrogen atmosphere (800 psig at room temperature) and an inert nitrogen atmosphere (300 psig at room temperature). The product distributions for each case are presented in Table 2. The conversion of dibenzyl was approximately the same in each case. The rate of isomerization of tetralin to form methyl indan was lower in the nitrogen atmosphere. This result suggests that molecular hydrogen can participate in the reaction mechanism for tetralin isomerization. However, this participation may be indirect. In a hydrogen atmosphere the dehydrogenation rate for tetralin should be lower than that in a nitrogen atmosphere. As a result, more tetralin should be available for isomerization. A more direct role of the hydrogen could be that the benzyl radicals react with the molecular hydrogen to produce hydrogen atoms, then these atoms could participate directly in the tetralin isomerization reactions (8,9).

The rate of tetralin dehydrogenation was higher than that of isomerization with an inert nitrogen reaction atmosphere (Table 2). The opposite was true with a hydrogen atmosphere.

The reaction of tetralin in the presence of both dibenzyl and hydrogen was used as a baseline system for comparison. The increase in the amount of tetralin dehydrogenation that occurred, when no hydrogen was initially present, relative to that obtained with this baseline system was determined. The increase observed when no dibenzyl was present was also determined. These responses are compared in Table 3. Apparently the increase in the rate of tetralin dehydrogenation, in response to the absence of hydrogen, was much higher than it was in response to the absence of dibenzyl.

When no hydrogen was present there was about an 8.4 wt.% decrease from the baseline value (19.9 wt.%) in the amount of tetralin that isomerized to form methyl indan (Table 4). Similarly, when no dibenzyl was present, the amount of tetralin converted to methyl indan decreased by about 12.0 wt.% below the baseline value.

A number of compounds such as tetrahydroquinoline (THQ) have been shown to have a higher hydrogen donor reactivity than that of tetralin (12). A crude measure of the relative reactivity of the tetralin for donating hydrogen to the benzyl radicals was made by determining the decrease in the extent of tetralin dehydrogenation that occurred in response to the addition of either quinoline or phenanthridine. Quinoline and phenanthridine are basic nitrogen-containing aromatic compounds similar to those found in coal-derived liquids. These compounds have a relatively high adsorptivity. As a result, these compounds adsorb preferentially onto the catalyst surface and are hydrogenated in preference to compounds like naphthalene (i.e., the dehydrogenated tetralin product) which have a lower relative adsorptivity (13). The hydrogenated products of these compounds (eg. THQ) are excellent hydrogen donors.

McNeil et al. (6) measured the response of tetralin dehydrogenation and isomerization in the presence of dibenzyl to the addition of different polynuclear aromatic compounds (e.g. phenanthrene, pyrene). They observed an insignificant response to occur in the tetralin isomerization. However, a significant decrease in the tetralin dehydrogenation occurred in response to the addition of certain aromatics. In an earlier work (11), this decrease in tetralin dehydrogenation was observed to vary directly with the number of condensed rings in the aromatic compound added.

The response of tetralin isomerization to the addition of either quinoline or phenanthridine is shown in Figure 1. The presence of quinoline or phenanthridine had a significant influence on the extent of tetralin isomerization that occurred. However, as shown in Figure 2, the addition of either quinoline or phenanthridine caused only a slight decrease in the amount of tetralin dehydrogenation (14.2 wt.% versus 6.6 and 10.4 wt%). The relative insensitivity of the tetralin dehydrogenation to the addition of these basic nitrogen-containing compounds is somewhat surprising. Earlier it was shown that the presence of a catalyst caused a significant increase in tetralin dehydrogenation (Table 1). Preferential adsorption of the quinoline or phenanthridine on the catalyst should inhibit dehydrogenation. It appears, however, that these compounds act more to quench the benzyl radicals and thereby inhibit tetralin isomerization without significantly inhibiting dehydrogenation of the tetralin.

#### IV. SUMMARY OF RESULTS

The principal products of the high temperature, catalytic reaction of tetralin in the presence of dibenzyl and gaseous hydrogen were found to be naphthalene and methyl indan. A small amount of trans-decalin was observed to be formed. The isomerization of tetralin increased with the addition of dibenzyl, a free radical precursor. The addition of a presulfided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst had a small effect on tetralin isomerization and dehydrogenation in the presence of dibenzyl. However, in the absence of dibenzyl, catalyst addition had a significant effect on tetralin dehydrogenation.

Tetralin dehydrogenation increased significantly when an inert nitrogen atmosphere rather than a hydrogen atmosphere was used.

Tetralin isomerization decreased significantly with the addition of either quinoline or phenanthridine; whereas tetralin dehydrogenation decreased only slightly with the addition of either of these compounds.

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Table 1  
Response in Product Distribution to Addition of Dibenzyl,  
with and without Catalyst Present

Initial Dibenzyl (wt%)	Catalyst (ppm)	Product Distribution, wt%					
		Tetralin	Naphthalene	Methyl Indan	Benzene	Toluene	Dibenzyl
0	0	92.9	1.3	5.7	--	--	--
20	0	56.9	6.6	16.4	0.6	11.4	8.0
0	1000	71.2	13.0	7.9	--	--	--
20	1000	54.3	9.8	15.9	0.6	10.4	8.8

Reaction Mixture: 5.0g dibenzyl and tetralin  
 Catalyst Loading: 1000 g of total metal in presulfided CoMo/Al<sub>2</sub>O<sub>3</sub> per 10<sup>6</sup> g of tetralin.  
 Reaction Conditions: Temperature = 450°C  
 Initial H<sub>2</sub> Pressure = 800 psig at 25°C  
 Time = 60 minutes  
 Agitation Rate = 860 rpm  
 Reactor = Tubing Bomb Microreactor

Table 2  
Comparison Between Product Distribution in a Hydrogen Atmosphere  
with That in a Nitrogen Atmosphere

Atmosphere	Product Distribution, Weight %					
	Tetralin	Naphthalene	Methyl Indan	Benzene	Toluene	Dibenzyl
H <sub>2</sub>	54.3	9.8	15.9	0.6	10.4	8.8
N <sub>2</sub>	47.0	23.6	9.2	0.3	9.8	9.8

Reaction Mixture: 5.0 g 20 wt% dibenzyl in tetralin  
 1000 g metal in presulfided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst per 10<sup>6</sup> of tetralin  
 Reaction Conditions: Temperature = 450°C  
 Initial Pressure = 800 psig H<sub>2</sub>, or 300 psig N<sub>2</sub>, at 25°C  
 Time = 60 minutes  
 Agitation Rate = 860 rpm  
 Reactor = Tubing Bomb Microreactor

Table 3

Comparison Between the Change in the Weight Percent  
of the Tetralin Dehydrogenated with No Dibenzyl  
Present and That with No Hydrogen Gas Present

Change from Baseline Conditions*	Increase in Amount of Tetralin Dehydrogenated ( $\Delta$ Wt.%)
No Dibenzyl Present	0.7
No Hydrogen Present	17.5

## \*Baseline Reaction Conditions:

Reaction Mixture: 5.0g of 20 wt.% dibenzyl in tetralin  
Catalyst Loading: 1000 g of total metal in presulfided CoMo/Al<sub>2</sub>O<sub>3</sub> per  
10<sup>6</sup> g of tetralin  
Reaction Conditions: Temperature = 450°C  
Initial H<sub>2</sub> Pressure = 800 psig at 25°C  
Time = 60 minutes  
Agitation Rate = 860 rpm  
Reactor = Tubing Bomb Microreactor

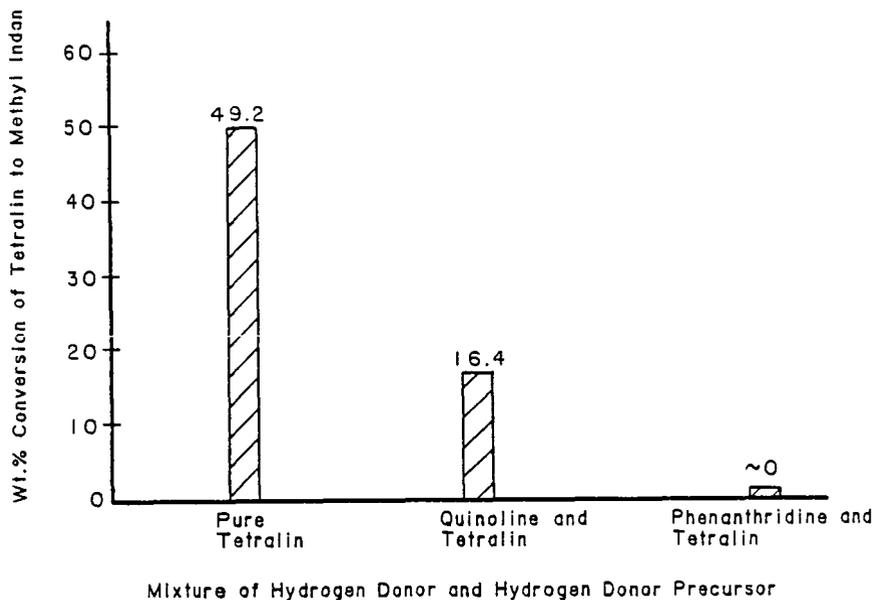
Table 4

Comparison Between the Change in the Weight Percent  
of the Tetralin Isomerized with No Dibenzyl  
Present and That with No Hydrogen Gas Present

Change from Baseline Conditions*	Decrease in Amount of Tetralin Isomerized ( $\Delta$ Wt.%)
No Dibenzyl Present	12.0
No Hydrogen Present	8.4

## \*Baseline Reaction Conditions:

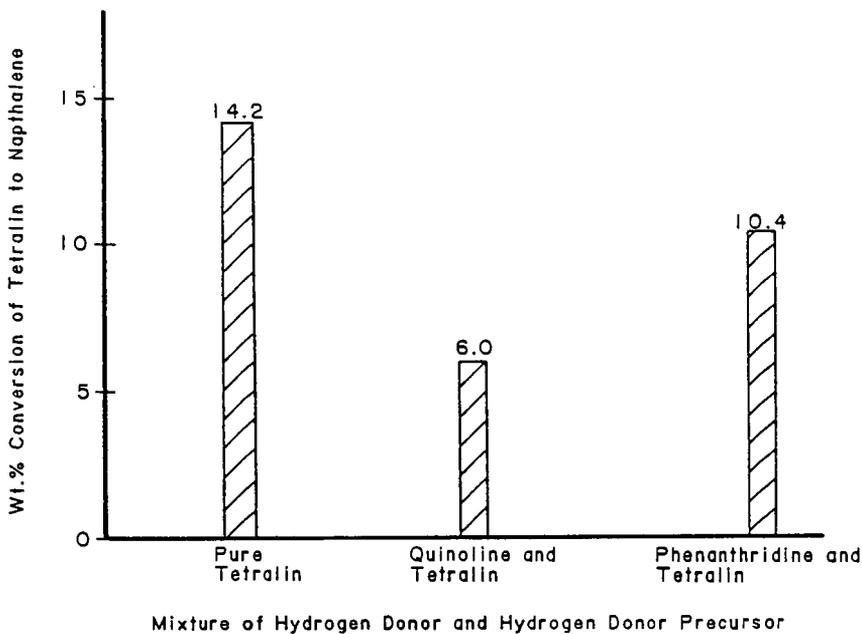
Reaction Mixture: 5.0g of 20 wt.% dibenzyl in tetralin  
Catalyst Loading: 1000 g of total metal in presulfided CoMo/Al<sub>2</sub>O<sub>3</sub> per  
10<sup>6</sup> g of tetralin  
Reaction Conditions: Temperature = 450°C  
Initial H<sub>2</sub> Pressure = 800 psig at 25°C  
Time = 60 minutes  
Agitation Rate = 860 rpm  
Reactor = Tubing Bomb Microreactor



Reaction Mixture: 2.0 g 50 wt% dibenzyl in tetralin or 1:1 wt. ratio of tetralin to quinoline or phenanthridine  
 1000 g of Mo per  $10^6$  g of tetralin and quinoline or phenanthridine mixture

Reaction Conditions: Temperature = 450°C  
 Initial H<sub>2</sub> Pressure = 800 psig at 25°C  
 Time = 60 minutes  
 Agitation Rate = 860 rpm  
 Reactor = Tubing Bomb Micro-reactor

Figure 1. Response of Tetralin Isomerization to the addition of either Quinoline or Phenanthridine



Reaction Mixture: 2.0 g 50 wt% dibenzyl in tetralin or 1:1 wt. ratio of tetralin to quinoline or phenanthridine  
 1000 g Mo per  $10^6$  g of tetralin and quinoline or phenanthridine mixture

Reaction Conditions: Temperature = 450°C  
 Initial H<sub>2</sub> Pressure = 800 psig at 25°C  
 Time = 60 minutes  
 Agitation Rate = 860 rpm  
 Reactor = Tubing Bomb Micro-reactor

Figure 2. Response of Tetralin Dehydrogenation to the addition of either Quinoline or Phenanthridine