Reactions of Three Double Ring Heteroaromatic Model Coal Compounds in Excess Tetralin

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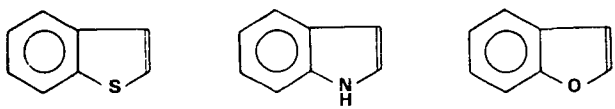
INTRODUCTION

The liquefaction of coal is one of the ways needed for extending liquid fuel supplies. In order to better utilize these resources through modelling and optimization of processes, a fundamental understanding about the nature of the chemical and physical changes taking place is necessary. One of the major processes now under development involves a donor solvent to help transfer hydrogen to the coal. Recently more and more effort has been devoted to the understanding of the chemistry of reactions between the solvent and model coal compounds which contain structural similarities to coal moieties (1,2,3,4,5,6,7).

This study investigates the reaction rates of three heteroaromatic compounds; benzothiophene (I), indole (II), and benzofuran (III), in excess tetralin.



(I) (II) (III)

Temperatures from 400 to 450°C are used with a pressure of 1500 psig in a batch microreactor without hydrogen gas. The reactions of tetralin in the absence of acceptor compounds have also been examined. The major reactions for all of the systems have been modelled as first or second order reactions which give rise to a coupled nonlinear system of equations which is solved numerically.

EXPERIMENTAL

The batch microreactor system is depicted in Figure 1. The reactor is a 9/16 inch tee made of 316 stainless steel by Autoclave Engineers. To this are fitted reducers which allow the use of 1/8 inch tubing for inlet and exit lines. The actual lines to the reactor are 1/16 inch O.D. tubing with an I.D. of 0.005 inches. Pieces of 1/8 inch tubing are fitted over the 1/16 inch tubing at the ends to couple them to the aforementioned reducers, and the inlet and exit valves. The reactor volume is 4.1 milliliters. A fluidized bed sandbath with an external controller maintains the reactor temperature to within ± 0.5°C of the desired value. The reactor remains in the bath at all times and is charged from a manually operated piston displacement pump. The operating pressure for all experiments is 1500 psig which is sufficiently high to suppress vaporization of reaction products. The pressure is generated by the pump, rather than by gas pressure. The basic procedure to charge a sample to the reactor is to first evacuate the reactor through valves C and B (Figure 1). Then, after valve C is closed, the reactor is charged with the appropriate volume of fluid from the pump sufficient to achieve a pressure of 1500 psig after thermal equilibrium is reached. The temperature initially drops 30 to 35°C upon charging, but recovers to within about 3°C in about one minute. After the temperature has recovered and the operating pressure reached, valve D is shut. At the end of the reaction period the sample is discharged through valve E from which it expands and condenses into a trap. After the sample has cooled, a nitrogen

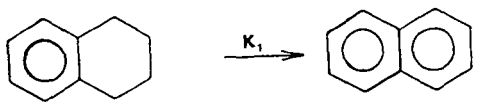
purge displaces the sample into a sample vial. The reactor is evacuated and is then ready for another sample.

The chemicals used in this study were all purchased from Aldrich Chemical Company. The purity of all reactants was at least 99%. Tetralin was redistilled to 99.8 percent purity with naphthalene the only observed impurity.

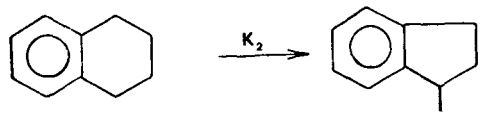
Analyses are made by gas liquid chromatography. A Hewlett Packard 5710A G.C. with thermal conductivity detector is used. Two types of liquid phases are used, Apiezon L for a boiling point separation and Bentone 34 for a π bond separation, both supported on chromasorb W packing. Quantification of the samples is accomplished with a Columbia Scientific CSI-208 digital integrator. Further details of this work are available elsewhere (6).

RESULTS AND DISCUSSION

Tetralin. We have studied the decomposition of tetralin by itself in order to establish "baseline" reaction rates. Temperatures of 400 and 450°C have been used. The two major reactions are:



1)



2)

At 450°C a small amount of indan is also observed along with trace amounts of benzene, toluene, and ethylbenzene. These products are as expected from the literature (5). Reactions 1 and 2 are modelled as first order in tetralin. The rate constants and activation energies are listed in Table 1. Figures 2, 3 and 4 show the data (points) with the curves generated by the models:

$$\frac{d[TET]}{dt} = -(K_1+k_2)[TET] \qquad 3)$$

$$\frac{d[NAPTH]}{dt} = k_1[TET] \qquad 4)$$

$$\frac{d[MEI]}{dt} - k_2[TET] \qquad 5)$$

where: [TET] = mole fraction tetralin

[NAPTH] = mole fraction naphthalene

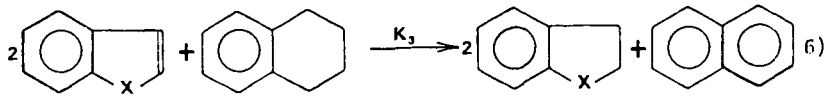
[MEI] = mole fraction methylindan

It can be seen that the model fits the data well. A zero order model was found to give a worse fit of the data.

Benzothiophene in tetralin. Benzothiophene with an initial mole fraction of 0.10 in tetralin was reacted at 400, 425, and 450°C. The major product was dihydrobenzothiophene. At 450°C toluene and ethylbenzene appeared in small amounts. These two products appeared in equimolar amounts with a rate that increased with time, indicative of a secondary product. They reached a concentration of 0.63 mole

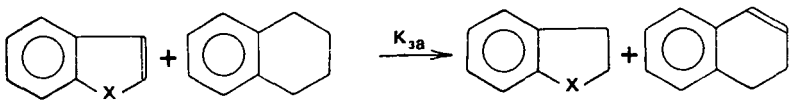
percent at the maximum reaction time of 120 minutes. Benjamin et.al. (1) also found toluene and ethylbenzene as well as benzene as products from benzothiophene reacted in excess tetralin at 400°C for 18 hours. It thus appears that benzothiophene desulfurized thermally.

Based on the observed reactions of benzothiophene the proposed model is:

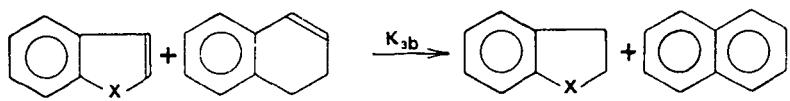


6)

The stoichiometry requires that two moles of benzothiophene react with one mole of tetralin in order to balance the hydrogen. This is written as a net reaction. We have made the steady state assumption for dihydronaphthalene to simplify the rate expression from the reactions:



7)



8)

Dihydronaphthalene is observed in very small amounts (<0.05 mole percent) throughout all of the reactions. This implies that k_{3a} is rate determining and is what is determined as k_3 from reaction 6. The rate equations for reactions 1, 2 and 6 are:

$$\frac{d[ACCEPT]}{dt} = -2k_3[ACCEPT][TET] \qquad 9)$$

$$\frac{d[TET]}{dt} = -\{k_1+k_2+k_3[ACCEPT]\}[TET] \qquad 10)$$

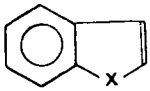
$$\frac{d[NAPTH]}{dt} = \{k_1+k_3[ACCEPT]\}[TET] \qquad 11)$$

where: [ACCEPT] = mole fraction of acceptor

Here [ACCEPT] is used to represent the acceptor species concentration generally since the same model is used for the indole reactions to be described subsequently. Reaction 2 is not altered so equation 5 remains unchanged. For convenience, concentrations are expressed in mole fractions. The units of all rate constants are then inverse minutes. The use of mole fractions requires the assumption of a constant molar volume for the reaction mixture. The system of equations 5,9,10, and 11 are coupled and nonlinear. A computer program (6) utilizing a Marquardt optimization scheme was used for parameter estimation. The results for the benzothiophene reaction system are shown in Figures 5 through 8 where the curves represent the model and the points represent the data. It can be seen that the data is well represented by the model at all three temperatures. The rate constants and activation energies are given in Table 2. A comparative discussion of the rates and activation energies between the different reacting systems is postponed until all of the results have been presented. We do point out now that k_1 and k_2 are always determined from the data of the particular reaction system rather than being held constant at the values determined for tetralin.

Indole in tetralin. Indole was reacted in tetralin with an initial indole mole fraction of 0.128. The reaction was run at 425 and 450°C. The major product was indoline (2,3-dihydroindole). At 450°C small amounts of o-ethylaniline and o-methylaniline (o-toluidine) were observed. Figure 9 shows the indole concentration versus time at the two temperatures. The model again fits the data well, and the model also represents the tetralin, naphthalene, and methylindan concentrations well at both temperatures. The rate constants and activation energies are given in Table 3.

Benzofuran in tetralin. The initial mole fraction of benzofuran in tetralin was 0.10. The reactions were run at 400 and 450°C. The reaction was very fast at 450°C with a half life of 25 minutes. Unlike the previous two acceptors, the hydrogenated acceptor, 2,3-dihydrobenzofuran, was not observed. At 450°C the major products were o-ethylphenol and o-methylphenol (o-cresol). At 400°C, however, only small amounts of these two products were observed. Since dihydrobenzofuran was not observed it was not clear whether it was an unstable intermediate or whether the reaction proceeded through another chemical route. An experiment was conducted with 5 mole percent dihydrobenzofuran in excess tetralin at 425°C to help elucidate the pathway. The same products (alkylphenols) were formed, and the rate was comparable to that of the reaction of benzofuran (eg; not instantaneously). An additional note is that benzofuran was formed from the dihydrobenzofuran. Thus it seems that the reaction of benzofuran is different from its sulfur and nitrogen analogs. It was found that the model used for the previous two acceptor compounds represented poorly the benzofuran concentration at 400°C, but not so poorly at 450°C. At both temperatures the model fittings of methylindan, naphthalene and tetralin were good. Evidently a non-hydrogen transferring reaction is dominant at 400°C. To account for this different reaction a first order decomposition model is used:



$$\xrightarrow{K_4} \text{PRODUCTS} \qquad 12)$$

The kinetic equation is then:

$$\frac{d[\text{Benzofuran}]}{dt} = -k_4[\text{Benzofuran}] \qquad 13)$$

Equations 3,4, and 5 are then used for tetralin, naphthalene and methylindan concentrations respectively. Table 4 shows the values for k_1, k_2, and k_4 along with the activation energies. Figure 10 shows the predicted benzofuran concentration for reaction 12 and the data. The fit of the data is good, much better at 400°C than for the hydrogen transfer model and no worse at 450°C. The predictions for tetralin, naphthalene, and methylindan are also as good for this model as with the hydrogen transfer model at both temperatures.

Comparative discussion. Figure 11 summarizes the result of the acceptor reaction models. It can be seen that benzothiophene and indole react at similar rates while benzofuran reacts at a significantly higher rate. The activation energies range from 30.0 to 51.2 kcal/gmole with benzothiophene exhibiting the largest temperature effect, with indole and benzofuran considerably less.

The end products of the three reactions indicate that only benzothiophene loses its heteroatom, producing alkylbenzenes. Indole and benzofuran produce the corresponding anilines and phenols. The products of the benzothiophene reaction and the stability of anilines and phenols under the type of reaction conditions as in this study is confirmed by the literature (1).

The kinetics of reaction 4 (production of naphthalene via tetralin decomposition that is not due to acceptor reactions) is summarized in Figure 12. The activation energy for this reaction with no acceptor present is 27.9 kcal/gmole, lower than in any of the acceptor systems. The rates are also lowest for the non-acceptor system,

by a significant amount. The benzothiophene and indole systems have similar rates with activation energies of 38.7 and 60.1 kcal/gmole, respectively. Originally it was planned to not optimize the rate constants for reactions 1 and 2, but to keep them constant at the values determined from the non-acceptor tetralin decomposition run. The variation in the rate has been observed previously (2) with changes in acceptor or solvent components, and we also noted changes in the methylindan rates, despite its model independence from the acceptor reaction. The values of k_1's and E_a's are in the range of values previously reported for reaction 4 (2) except that the E_a = 60.1 kcal/gmole for indole is significantly higher.

Figure 13 summarizes the results of the reaction producing methylindan. The rate constants are very similar to those in (2) again, although with less variation than those of (2). The activation energies range from 46.9 kcal/gmole for tetralin decomposition, to 57.0 kcal/gmole for benzothiophene. The activation energies are significantly higher in this study than in (2). As previously noted, the variation in k's is evidently due to the effect of the acceptor. Possibly the acceptor acts as an "initiator" by enhancing hydrogen abstraction from the solvent. Once the tetralin free radical is formed it can give up another hydrogen to form dihydronaphthalene or rearrange to form a more stable methylindan free radical and then accept a hydrogen atom back.

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Table 1. Rate Constants and Activation Energies for Tetralin Blank Run

	400°C	450°C	E_a(Kcal/gmole)
$k_1(min^{-1})$	2.89×10^{-5}	1.23×10^{-4}	27.9
$k_2(min^{-1})$	5.66×10^{-5}	6.46×10^{-4}	46.9

Table 2. Rate Constants and Activation Energies for Benzothiophene Run

	400°C	425°C	450°C	E_a(Kcal/gmole)
$k_1(min^{-1})$	2.79×10^{-6}	1.41×10^{-4}	3.70×10^{-4}	38.7
$k_2(min^{-1})$	7.00×10^{-5}	3.86×10^{-4}	1.34×10^{-3}	57.0
$k_3(min^{-1})$	1.991×10^{-4}	7.4×10^{-4}	2.81×10^{-3}	51.2

Table 3. Rate Constants and Activation Energies for Indole Run

	425°C	450°C	E_a(Kcal/gmole)
$k_1(min^{-1})$	1.17×10^{-4}	5.18×10^{-4}	60.1
$k_2(min^{-1})$	3.84×10^{-4}	1.44×10^{-3}	53.4
$k_3(min^{-1})$	1.08×10^{-3}	2.43×10^{-3}	32.7

Table 4. Rate Constants and Activation Energies for Benzofuran Run

	400°C	450°C	E_a(Kcal/gmole)
$k_1(min^{-1})$	1.64×10^{-4}	1.55×10^{-3}	43.6
$k_2(min^{-1})$	1.24×10^{-4}	1.82×10^{-3}	52.2
$k_4(min^{-1})$	5.93×10^{-3}	2.78×10^{-2}	30.0

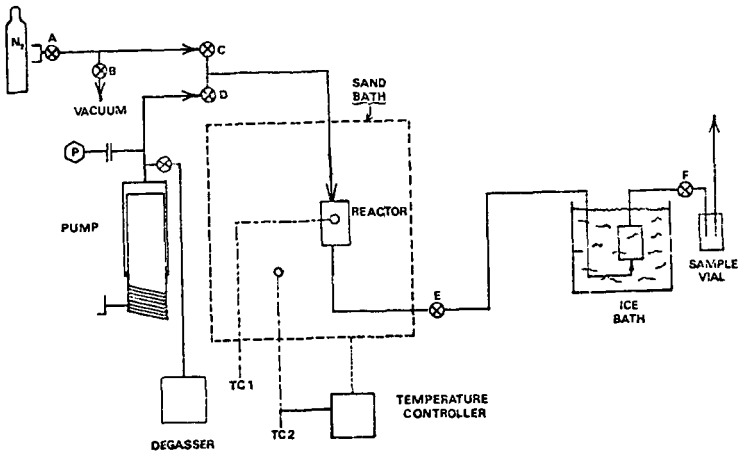

Figure 1. Experimental Microreactor System

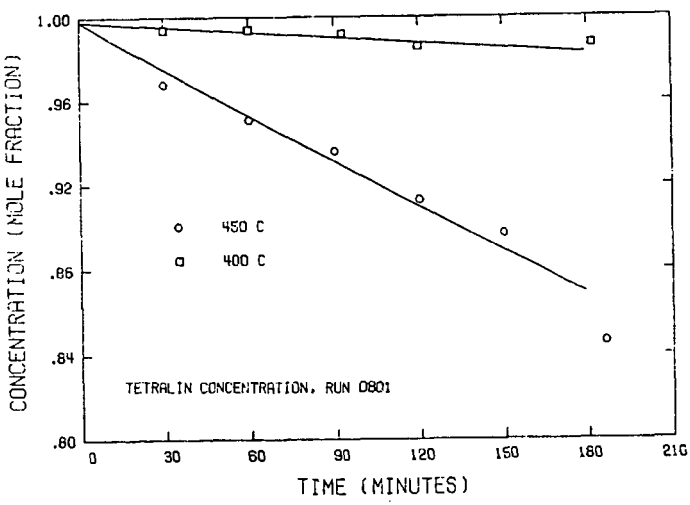

Figure 2. Tetralin Composition in Tetralin Blank Run

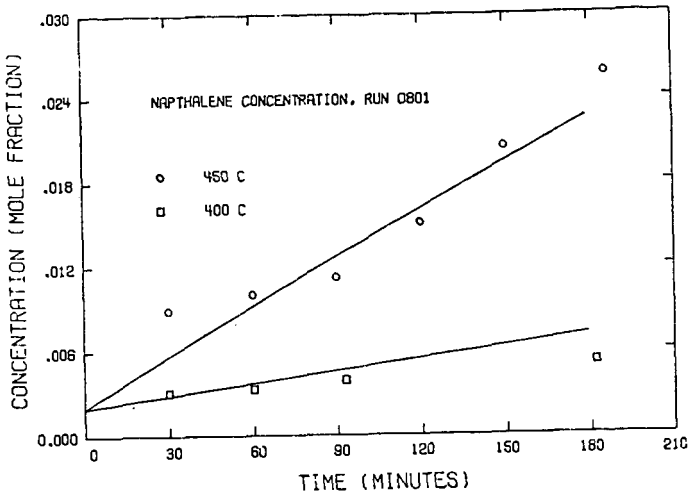

Figure 3. Naphthalene Composition in Tetralin Blank Run

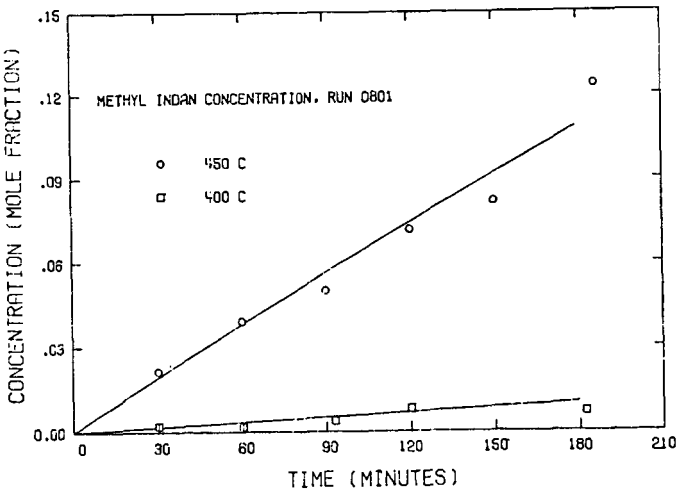

Figure 4. Methylindan Composition in Tetralin Blank Run

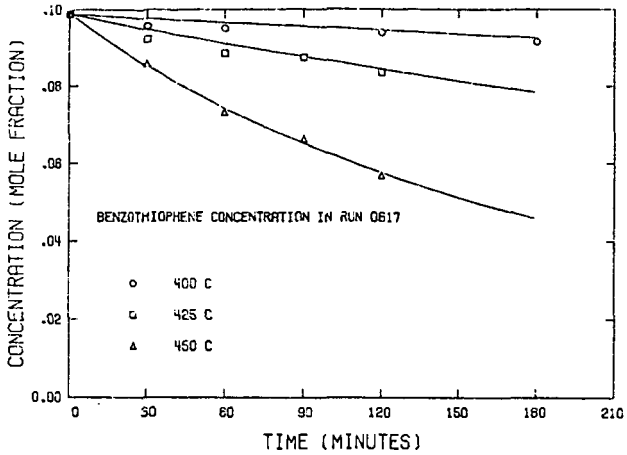

Figure 5. Benzothiophene Composition in Benzothiophene Run

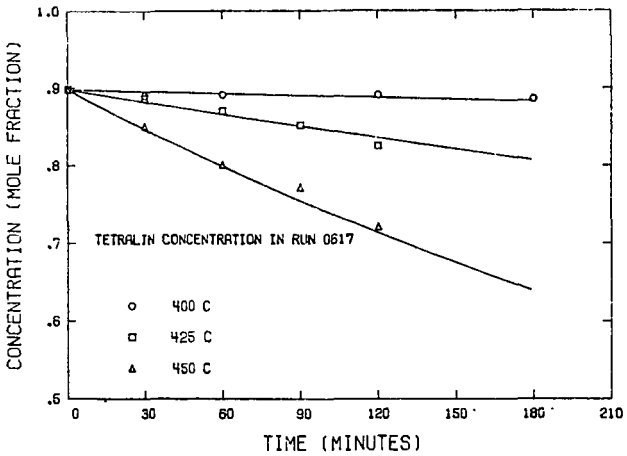

Figure 6. Tetralin Composition in Benzothiophene Run

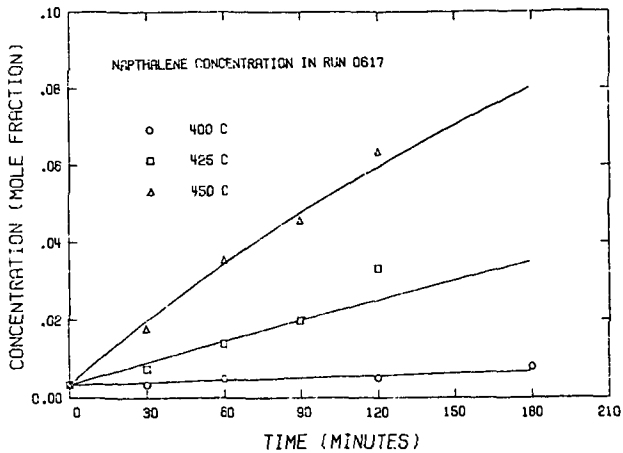

Figure 7. Naphthalene Composition in Benzothiophene Run

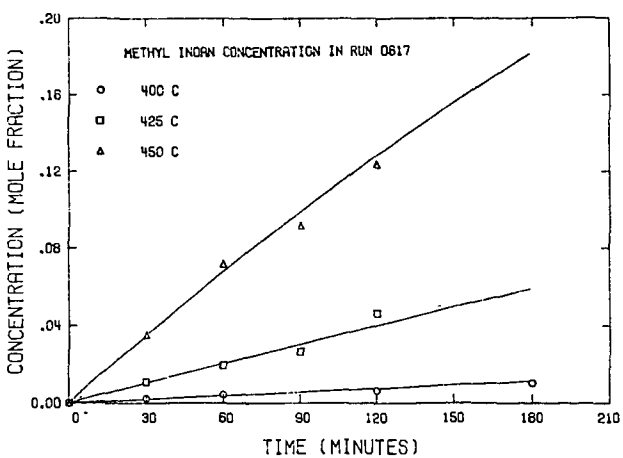

Figure 8. Methylindan Composition in Benzothiophene Run

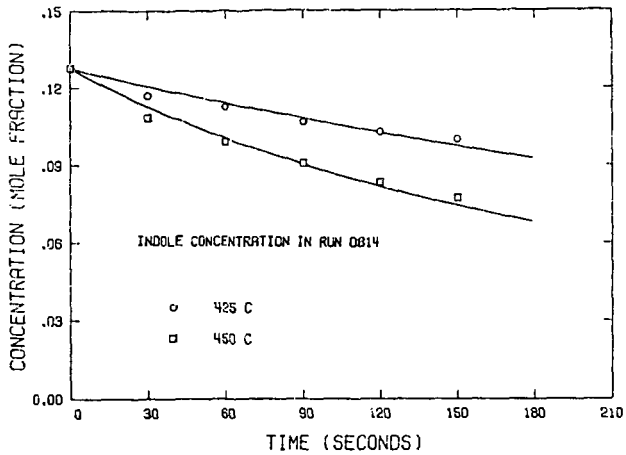

Figure 9. Indole Composition in Indole Run

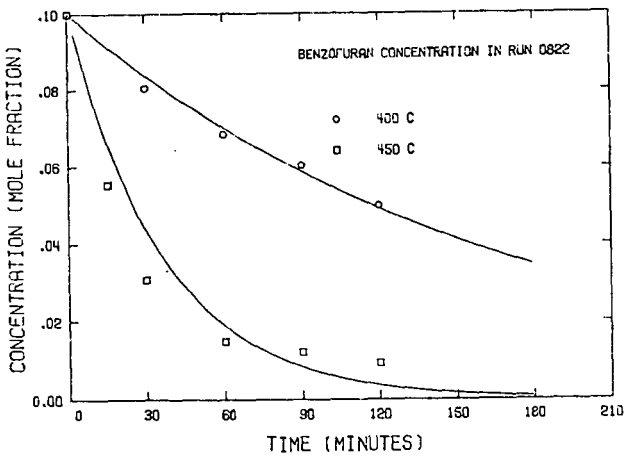

Figure 10. Benzofuran Composition in Benzofuran Run

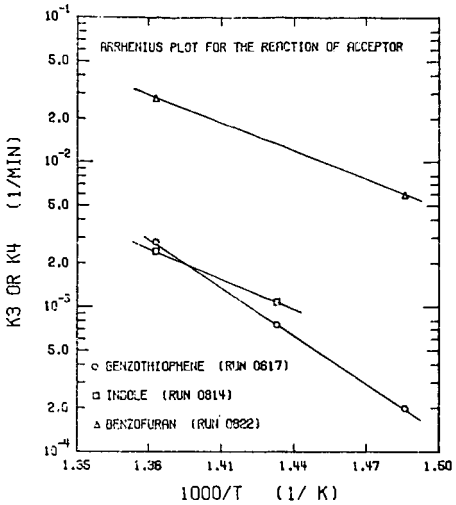

Figure 11. Arrhenius Plot for Acceptor Reaction Model

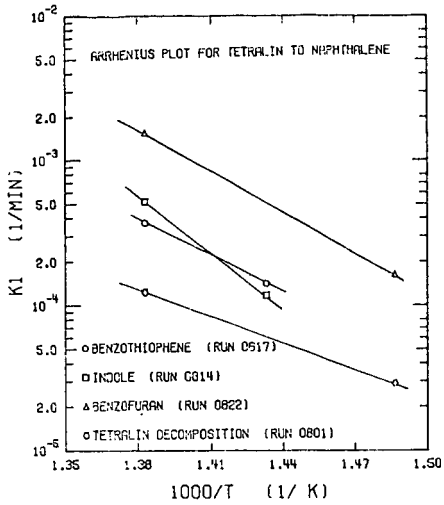

Figure 12. Arrhenius Plot for Reaction of Tetralin to Naphthalene

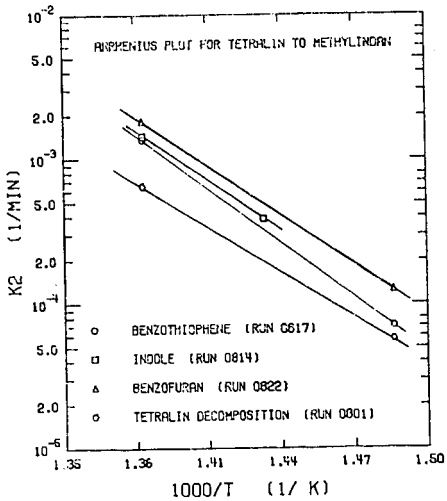

Figure 13. Arrhenius Plot for Reaction of Tetralin to Methylindan