ADSORPTION AND KINETIC STUDIES OF QUINOLINE HYDRODENITROGENATION AND ITS INTERMEDIATE COMPOUNDS

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ABSTRACT

Removal of nitrogen containing aromatic compounds from hydrocarbon feedstocks in refinery operations is critical because of the poisonous nature of these compounds to the catalytic processes. Quinoline is frequently used as a model compound to study catalytic hydrodenitrogenation (HDN) of the nitrogen compounds.

Previous studies on this compound reported on the reaction network of quinoline and the modeling based solely on the kinetic data. Separate studies on the adsorption of quinoline or its intermediates on the HDN catalysts have not been done previously. In this work, separate studies of adsorption and kinetics of quinoline and its intermediates were performed. The experiments were conducted at the typical reaction conditions of 350 C and 10.34 MPa (1500 psig). Each individual intermediate compound in the reaction network was studied separately. The experiments were performed in a gradientless reactor with Berty internals. The reactor was operated in a closed system for the adsorption studies and in a continuous flow system for the kinetic studies.

The adsorption constants thus obtained indicated that different intermediate compounds have different adsorption characteristics which is contrary to previous thinking in the literature that most of the nitrogen compounds have similar adsorption strengths. The compound 1,2,3,4-tetrahydroquinoline (1-THQ) was found to have the highest adsorption strength. The individual rate parameter for each step in the reaction network was obtained from the kinetic data of each intermediate compound. The formation of decahydroquinoline was found to be favored over the formation of OPA from 1-THQ. The limiting step in overall HDN rate was the conversion of 1-THQ. This was assumed to be related to the strong adsorption of 1-THQ on the catalyst. Propylbenzene was found to convert readily to propylcyclohexane under reaction conditions. A new reaction network for quinoline HDN was obtained from combining all of this information which is slightly different from the existing network for quinoline HDN.

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CHAPTER I

INTRODUCTION

As the traditional sources of fossil fuels are depleted, search for alternative hydrocarbon sources increased as far back as several decades ago. One of the promising areas is the conversion of coal to liquid and gaseous hydrocarbons. Because of today's economics, heavier fractions of the petroleum crudes are being processed to maximize the yield. Both coal liquefaction products and the heavier crude fractions contain higher concentrations of contaminants than other petroleum sources.

Problem-causing contaminants are classified in four groups; sulfur compounds, nitrogen compounds, oxygen compounds, and metal compounds. All of these compounds have adverse effects in further processing of the fuels. Examples of the problems are the poisoning of the precious metal catalysts by sulfur in reforming and poisoning of the acidic sites by basic nitrogen compounds of the hydrocracking and fluid catalytic cracking catalysts. Among these contaminants, the nitrogen compounds are the hardest to remove. This is mainly because most of the compounds are in the form of heterocyclic aromatic compounds. There are several ways to remove these nitrogen compounds. One is hydrotreatment wherein these compounds are removed via hydrogenation and hydrogenolysis through processing the oils at high temperatures and moderate pressures in an hydrogen atmosphere. The other is the removal through an ion exchange process using the basic nature of these compounds in either liquid phase or solid phase. Several investigations have been reported on the attempts to remove these compounds through ion exchange operations as reported by Prudich and his coworkers (Prudich, et al., 1986; Marcelin, et al., 1986; and Cronauer, et al., 1986) and also by Charlesworth (1986). Choi and Dines (1984) also reported on using solid acids for extracting the nitrogen compounds from shale oils. However, the processes have not become economically feasible. Wilkinson (1983) reported on an acid washing process of Solvent Refined Coal (SRC) liquids. Although significant amounts of nitrogen compounds were removed through acid washing, final result indicated that the compounds removed are those most easily converted during the hydrotreatment. In the past, the majority of the hydrotreatment investigations have been on hydrodenitrogenation (HDN) of the oils and the model compounds. It has been reported that the derivatives of unsaturated cyclic compounds comprise the majority of the basic nitrogen compounds present in coal-derived liquids and shale oils (Winans, et al., 1980 and Burchill, et al., 1982). As a result, pyridine and quinoline have been used as the model compounds to represent the basic nitrogen compounds.

Most of the model compound studies have been performed using the model compounds as the feed with different limitations imposed upon the reaction systems. Through these studies the reaction path and the kinetics of the reactions have been well established. Hydrodesulfurization (HDS) of unsaturated cyclic sulfur compounds proceeds without complete ring saturation. The carbon-sulfur bonds are broken before the double bonds become saturated. However, hydrodenitrogenation (HDN) of cyclic nitrogen compounds requires complete saturation of the rings before the carbon-nitrogen bonds can be broken. This is an interesting phenomenon since the same catalysts can be used for both HDS and HDN processes and the same active sites are thought to be responsible. Understanding the nature of the difference can be a significant step toward developing better catalysts for HDN with less hydrogen consumption involved during the process.

This work is focused on understanding this difference through the study of individual intermediate compounds previously identified in the quinoline HDN process. It is hoped to show that the different intermediate compounds have different reaction characteristics and these characteristics can be used to correlate the HDN activity of the compounds. Nagai, et al., (1986) reported that the basicity of the nitrogen compounds seem to be important in the poisoning of the catalyst activity by different nitrogen compounds on hydrodesulfurization (HDS) of dibenzothiophene. They claimed that the adsorptivity of the nitrogen compounds could be correlated by their respective basicities and that the nitrogen compounds adsorbed onto the hydrogenation sites rather than hydrogenolysis site. Through a study of the individual intermediate compounds of quinoline HDN, it is hoped to obtain similar results or a comparable understanding of the HDN process. The objectives of this study are the following:

1. To develop a technique to directly measure the adsorption of each intermediate compound in the quinoline HDN network under the same reaction conditions used to determine the kinetics of the quinoline HDN.

2. To study the kinetics of quinoline HDN by using each intermediate compound as the feed and obtaining the individual reaction rates. Previous investigators have all studied the reaction mechanism of quinoline HDN using quinoline as the feed material. The reaction kinetics of all the intermediates will be studied by starting from the last product of the quinoline network to the initial reactant, i.e., quinoline.

CHAPTER II

LITERATURE REVIEW

Review of Chemistry of Hydrodenitrogenation

The literature review on the chemistry of quinoline hydrogenation has already been covered extensively by El-Bishtawi (1986). Only the studies pertinent to this work will be reviewed here. Most of the investigations on the chemistry of hydrodenitrogenation (HDN) have been performed using model compounds. However, some investigations have also been done with coal liquids and heavy crudes.

Hydrotreatment of Heavy Crudes

Nakamura, et al. (1982) reported that various catalysts were tried on the residual oils from Arabian light, Gach-Saran, and Shengli crudes. The prepared catalysts contained approximately 6% nickel oxide and 18% molybdenum oxide on various support materials. They tried to optimize the catalysts based on the acidity and the pore-size distribution. The silica-supported catalysts had poor HDN and HDS activity while alumina-supported catalysts had high HDN and HDS activity. When the HDN activity was compared to the acidity of aluminum-based catalysts, it was found that the catalysts with higher acidities had the lowest HDN activity. Alumina-boron supported catalysts had the best HDN activity. A suitable HDN catalyst should have the acid strength that would enable the nitrogen compounds to be adsorbed readily, and the ammonia to be desorbed easily from the active sites. After testing the catalysts with varying pore sizes, they concluded that the catalysts with smaller pore sizes had better HDN activities while the catalysts with larger pore sizes had lower activities. Furthermore, the large pore catalysts had a longer life because of less pore-mouth plugging due to demetallation. Also, the pore size was suggested to influence the HDS more strongly than HDN. When more than 60% of the nitrogen in the residual oils were removed, the yield of the lighter fractions from these oils were observed to have increased substantially.

Sivasubramanian and Crynes (1979) studied the denitrification of a raw anthracene oil. They studied the effects of the catalyst support materials on the HDN process. Various support materials were acquired commercially and the active metals were impregnated by the researchers. When the support materials were subjected to a steam treatment before impregnation of active metals, the HDN activities decreased at all temperatures studied. They reported that the HDN rate of the coal liquid decreased when the surface area decreased. However, the pore size of the catalyst did not affect the HDN rate.

Bhan (1983) studied the hydrotreatment of a SRC-I coal liquid with several Ni-Mo/alumina commercial catalysts. Two catalysts having different pore sizes and similar metal loadings were used to study the effect of the pore size on the hydrotreating process and the deactivation of the catalysts. He concluded that the HDN kinetics of the coal liquid followed a first-order model with respect to the nitrogen content. Furthermore, it was found that the smaller pore size resulted in a higher HDN activity because of the higher surface area. The smaller pore size resulted in a lower deactivation of the catalyst because the smaller pore size limited the access of large molecular species which were thought to be the coke precursors. This was in agreement with Nakamura, et al., (1982). High heteroatom content of the deposited residues indicated that a part of the initial deactivation was due to the adsorption of the heteroatom compounds which were thought to be basic in nature.

Guin, et al. (1986) studied the reduction of intraparticle diffusivity during the hydrotreatment of coal-derived liquids. The catalysts were Co-Mo/alumina (Harshaw 0402T) and Ni-Mo/alumina (Shell 324M). The catalysts were examined in fresh, used, regenerated and aged form. The aged catalysts were left in appropriate solvents for a length of time to simulate the contact time of the catalysts with the solvents during a typical hydrotreatment run. There were not any appreciable differences between fresh, regenerated and aged catalysts. Data for the used catalysts indicated a decreasing diffusivity with longer hydrotreatment time. This was determined to be due to the coke deposition in the pores. The porosity of the catalysts was found to have decreased by about half. The major contributor to the catalyst deactivation was the change in pore geometry. This was possibly due to the increases in the tortuosity resulting in the reduction of the effective diffusivity. The diffusivity values could be restored by using the oxidative regeneration.

Hirschon and Laine (1985) studied the effect of hydrogen sulfide on the HDN activity of a SRC-II middle distillate oil. A commercial Co-Mo/alumina catalyst (Harshaw HT-400) was used in their studies. The inclusion of hydrogen sulfide resulted in an improved HDN activity of the coal liquid. They suggested that the acidity of the hydrogen sulfide was a significant factor in the improvement of HDN activity. In fact, the addition of hydrogen sulfide resulted in a lower sulfur content in the product oil over the runs without any catalyst.

Harvey, et al. (1986) investigated the performance of various catalysts on the hydrotreatment of Rundle shale oil. The tested catalysts were Ni-Mo/alumina, Co-Mo/alumina, and Ni-W/alumina. Their results indicated that the Ni-Mo catalyst was the best at removing nitrogen from the shale oil. This catalyst also produced the lowest aromatic content of the product oil as a result of the efficiency of nickel for hydrogenation. However, the Ni-W catalyst lost its activity after 30 hours of operation. Since the pore-size distributions were similar for two catalysts, they attributed the poor performance of the Ni-W catalyst to an undetermined chemical characteristic. They also reported that the remaining nitrogen compounds were present in the forms of less basic benzo- and dibenzopyrroles in the produced oils. Even when the Ni-Mo catalyst was used, the nitrogen removal was insufficient for producing an acceptable middle-distillate fuel from the shale oil. However, enough of the nitrogen compounds were removed to consider the product of the HDN process to be used as a substitute crude oil.

Kaernbach, et al. (1987) studied the structural changes of coal oils during the HDN process. Products obtained from non-catalytic hydrogenation of coals were subjected to HDN with Co-Ni-Mo/Alumina catalysts. They reported that during the HDN process, the aromatic nuclei of some of the unsaturated compounds remained unchanged while the peripheral rings underwent hydrogenation. Yamada, et al. (1987) studied the effect of the hydrogen sulfide on HDN of a coal liquid from the SRC-II process. They reported that the HDN of the coal liquid was promoted by the addition of the hydrogen sulfide which also resulted in retardation of HDS activity.

Bhan, et al. (1987) investigated the hydrotreatment of a 650-1000 F distillate fraction of Wilmington (California) crude oil. This fraction was hydrotreated over a commercial Ni-Mo/alumina catalyst (Armak 840) using a trickle bed reactor. The nitrogen removal was observed to follow the first-order kinetics satisfactorily. At some of the more severe hydrotreating conditions, the hydrogen consumption increased without significant decreases in the polar species of the oils. Mochida, et al., (1985) used a two-stage HDN process to remove nitrogen compounds from a heavy distillate fraction of a coal liquid. The catalyst used was a commercial Ni-Mo/alumina (HDN-30). The study was carried out in a batch autoclave with 100 ml capacity. The first stage was used to extensively hydrogenate the nitrogen compounds at 350 C for 8 hours, and the second stage was used to break the C-N bonds of the compounds at 420 C for 3 hours. When compared to the products from a single stage HDN run at 420 C at 3 hours, the nitrogen removal was higher (34% versus 60%). When a heavy aromatic compound (pyrene or fluroranthene) was added, overall HDN activity increased from 89 to 100%. They also found that the selection of the solvents influenced the total amount of removed nitrogen compounds and the required amount of the hydrogen pressure. They argued that the solvent selection could influence the formation of coke if the solvent interfered with the formation of coke precursors, which would result in a slower catalyst deactivation due to coking.

Shabtai, et al. (1987) studied the HDN of a blend of SRC-II middle-heavy distillate with 1,10-phenanthroline and compared it with the HDN of a feed consisting of 1,10-phenanthroline in tetralin. Co-Mo and Ni-Mo catalysts were prepared by impregnation of an alumina support and the experiments were conducted in a Magnedash autoclave. The feed included CS_2 to maintain the sulfided states of the catalysts. The results indicated that the hydrogen consumption for the Co-Mo catalyst was lower than that for the Ni-Mo catalyst at temperatures of 300 and 325 C but was similar at 350 and 375 C. They found that it was easier to remove nitrogen from the SRC-II(MHD) than from 1,10-phenanthroline at 300 C, whereas the opposite occurred at 350 C. They attributed the results to the variety of nitrogen compounds present in the coal liquid. They found that insufficient selectivities exist for C-N hydrogenolysis compared to the ring hydrogenation for both Co-Mo and Ni-Mo catalysts. They stressed a need for the development of new sulfided catalysts possessing a better selectivity for hydrogenolysis of the C-N bond, instead of the ring hydrogenation, to minimize the hydrogen consumption during the HDN processing of heavy oils.

Katti, et al. (1986) reported on the results of hydroprocessing of a basic fraction from a SRC-II heavy distillate. They separated the synthetic crude, produced from the SRC-II hydroliquefaction of Powhatan No. 5 coal, into neutral, acidic and basic fractions. They further separated the basic fraction into three groups: strongly basic, weakly basic and very weakly basic. They reported that the strongly basic fraction contained nitrogen compounds in the forms of substituted benzoquinolines and quinolines with very few amines. The very weakly basic fraction contained the nitrogen compounds in the forms of carbazole and cabazole derivatives, but their identifications were considered very tentative. A commercial Ni-Mo/Alumina catalyst (American Cyanamid HDS-9A) was used in a crushed form for hydroprocessing the oils, and Alundum RR was used as a dilutant for the catalysts. A packed bed reactor was used at a high pressure and a constant temperature. When the crude fractions were subjected to hydroprocessing, only 40 percent of the nitrogen compounds were removed from the strongly basic fraction while almost complete removal was reported for the very weakly basic fraction. They concluded that a correlation between the basicity of the organo-nitrogen reactants and the HDN activity is possible. They claimed that a greater basic strength resulted in a lower HDN activity. Another possible influence from the basic strength was the differing hydrogen requirements for opening the nitrogen containing rings, since the less basic compounds were already partially hydrogenated.

Hydrotreatment of Model Compounds

The basic nitrogen compounds present in the liquid fossil fuels can be represented by pyridine, quinoline, acridine and derivatives of these compounds. Initial investigations of the HDN reactions using model compounds concentrated on pyridine and its derivatives. Pyridine is first hydrogenated to piperidine then the carbon-nitrogen bond is broken to form n-pentylamine, which dissociates into n-pentane and ammonia. McIlvried (1971) studied the HDN of pyridine and reported that ammonia was strongly adsorbed on the hydrogenation sites, while other nitrogen compounds adsorbed strongly on the hydrogenolysis sites. The rate-controlling step was the cleavage of C-N bond. Sonnemans, et al. (1973) reported the order of the adsorption as piperidine > pyridine > ammonia, with hydrogen adsorbing on separate sites. Later, they studied the reactions of piperidine and pentylamine (Sonnemans, et., 1974). Goudriaan, et al. (1973) reported that the presulfided catalyst performed 25-45% better than the oxidic catalyst in removing nitrogen from pyridine feed. Other studies were performed on the effect of thiophene on pyridine HDN by Satterfield, et al. (1975,1980) and Anabtawi (1980).

Earlier studies on quinoline HDN were reported by Horne and McAfee (1960), Flinn, et al. (1963), and Doelman and Vulgter (1963). They all reported finding 1,2,3,4,-tetrahydroquinoline (1-THQ) as the hydrogenated intermediate resulting in o-propylaniline and eventually in propylbenzene. Flinn found the HDN of quinoline to be first order with respect to quinoline concentration with the hydrogenation of quinoline being the rate controlling step. Doelman and Vulgter reported that at temperatures around 300 C, 1-THQ was the predominant product of quinoline hydrogenation while at temperatures above 350 C, 5,6,7,8-tetrahydroquinoline (5-THQ) was observed to form.

Cocchetto and Satterfield (1976) studied the chemical equilibrium of HDN reactions of various nitrogen compounds. Using the free energies of formation, the equilibrium constants were calculated for each suspected reaction step in the HDN of quinoline. For quinoline, the equilibrium constants for the ring saturation reactions were found to be unfavorable above 200 C, and all of the other reactions were favorable up to 500 C. They pointed out that if the hydrogenation step is the rate-limiting step, then the hydrogenated compounds will react as soon as they are formed and the equilibrium of this step will not affect the overall rate. However, if the hydrogenolysis step is the rate limiting, the hydrogenation step can reach equilibrium, and the thermodynamic of the first step will affect the overall rate.

Rollmann (1977) studied the hydrotreatment of various model compounds including HDS of dibenzothiophene, HDN of indole and quinoline, and HDO of alkylphenols. While the sulfur compounds were readily broken down without requiring a complete saturation of the aromatic rings, the nitrogen and oxygen compounds seemed to require a saturation of the aromatic rings attached to the heteroatom before a cleavage of the C-N or C-O bonds could occur. This conclusion was different from earlier works in which only the aromatic rings containing heteroatom were seen to undergo saturation.

Shih, et al. (1977) reported a comprehensive study of quinoline HDN. They reported that two paths can exist for the HDN of quinoline, through formation of either decahydroquinoline (DHQ) or 5-THQ. The hydrogenation of quinoline to 1-THQ was found to reach a thermodynamic equilibrium because similar ratios of 1-THQ to quinoline were observed in the products regardless of whether the feed contained quinoline or 1-THQ. Other hydrogenation steps were assumed to be irreversible because the results indicated that the reverse reactions were very slow compared to the formation of 1-THQ. The removal of nitrogen atom was assumed to be primarily through decahydroquinoline because a high concentration of propylcyclohexane (PCH) was observed in the product. The rate constants for the hydrogenolysis steps leading to the formation of PCH and propylbenzene (PBZ) were comparable to that of the hydrogenation step, and neither step was considered rate limiting. The reaction network and the individual reaction steps proposed by them are shown in Figure 1. The rate constants shown were obtained from assuming first-order kinetics for each step. Langmuir-Hinshelwood type models were used for each step to obtain the intrinsic kinetic rates. They assumed that hydrogen and nitrogen compounds adsorbed on the same sites and the nitrogen compounds had similar adsorption strengths. The hydrogenation steps were first order with respect to the hydrogen pressure and the hydrogenolysis steps showed lower-order dependency on the hydrogen pressure.

Satterfield, et al. (1978) studied the intermediate reactions of quinoline HDN in vapor phase on a commercial

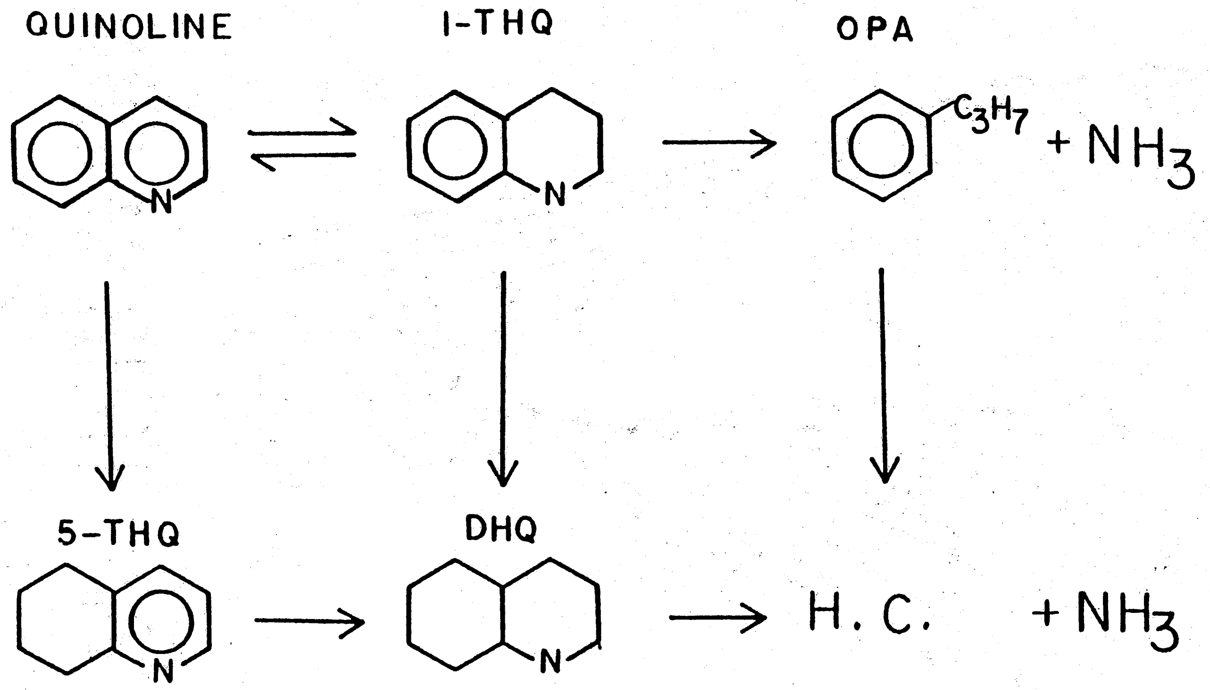


Figure 1. Quinoline Reaction Network of Shih

Ni-Mo/alumina catalyst (American Cyanamid, HDS-3A). The thermodynamic equilibrium was essentially reached between quinoline and 1-THQ at all of the conditions studied. The overall HDN activity was observed to be less than first order with respect to the quinoline concentration, which indicated a strong adsorption of reactants. They postulated that the reaction path between PBZ and PCH was unimportant. They basically agreed with the reaction network proposed by Shih, et al (1977).

Nelson and Levy (1979) discussed the quinoline HDN from a molecular level point of view. They argued that the high hydrogen requirement of quinoline HDN was consistent with the known chemistry of carbon-nitrogen bonds, for most of the amine degradations require the nitrogen atom to be quaternized before the reactions become feasible. The α and β carbon bonds attached to the nitrogen atom need to be completely saturated before nitrogen removal becomes possible. They also discussed the hydrogen sulfide enhancement observed by previous investigators. Hydrogen sulfide can enhance the break-up of the saturated rings by supplying the necessary proton normally supplied by the catalytic site because of the acidic nature of hydrogen sulfide. They postulated that even though high hydrogen consumption is unavoidable for HDN, the overall rate can be enhanced by using more acidic catalysts. They suggested that the addition of hydrogen sulfide may help the HDN of feedstocks containing high concentrations of nitrogen and low amounts of sulfur compounds because of acidity of hydrogen sulfide.

Cocchetto and Satterfield (1981) reported a slightly different reaction network for the quinoline HDN from previous studies as shown on Figure 2. The hydrogenation steps were found to be reversible. Therefore, the equilibrium among the hydrogenated compounds was studied and compared to the theoretical values reported earlier (Cocchetto and Satterfield, 1978). They reported that both the experimental and theoretical values agreed well with each other. Under most operating conditions, the formation of DHQ was favored thermodynamically. It was also reported that the hydrogenation and dehydrogenation steps were much faster than the hydrogenolysis step and reached equilibrium at most of the reaction conditions studied. In an accompanying paper, Satterfield and Cocchetto (1981) reported on HDN of quinoline and its intermediates. Quinoline and 1-THQ were seen to be most difficult to denitrogenate while DHQ was surprisingly easy to denitrogenate. Hydrocarbon products from OPA were very similar in make-up to the products from each individual heterocyclic nitrogen compound. The dominant product was propylcyclohexane (PCH). During catalyst deactivation, hydrogenation decreased by 60% while hydrogenolysis decreased by 20%. This indicated that different catalyst sites were responsible for the reactions. They reported that the quinoline HDN occurred primarily through the DHQ route. When the ratio of quinoline to 1-THQ was studied over longer contact times, it was found that the

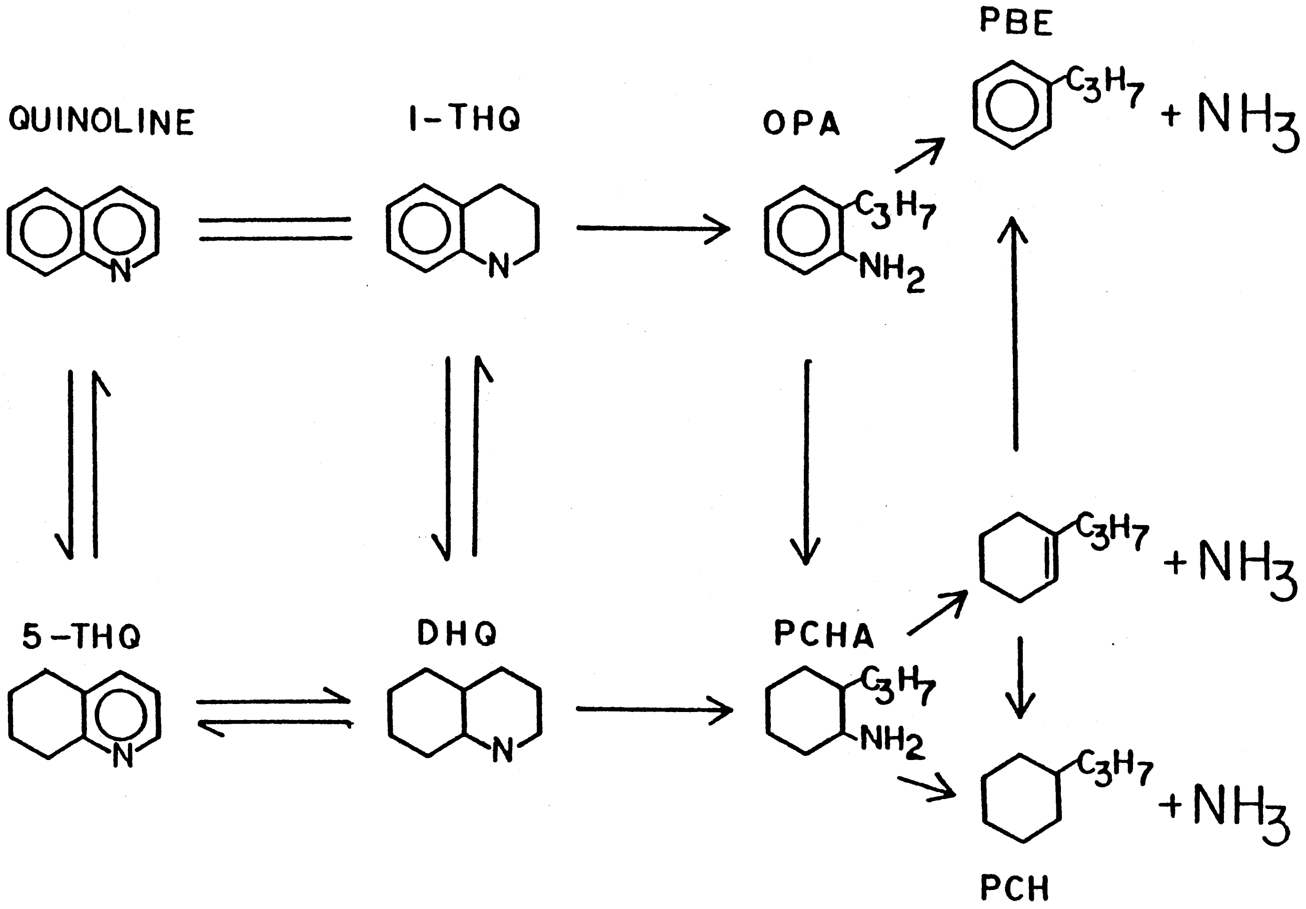


Figure 2. Quinoline Reaction Network of Cocchetto

ratio departed significantly from the equilibrium ratio reported earlier. They postulated that quinoline would be more weakly adsorbed than other intermediates. Since the catalytic sites were thought to be acidic, the less basic quinoline was thought to be prevented from adsorbing after initial hydrogenation and formation of intermediate compounds.

Satterfield and Gultekin (1981) studied the effect of hydrogen sulfide on the HDN of quinoline. Significant inhibition of the hydrogenation steps was observed while remarkable increases in the hydrogenolysis steps were seen. The net effect of the hydrogen sulfide was an increase in the total HDN rate. The hydrogenation of propylbenzene (PBZ) to PCH was inhibited, but HDN of quinoline resulted in a higher ratio of PCH to PBZ in the presence of hydrogen sulfide than in its absence. They reported that a primary limiting factor on the overall HDN rate was the strong adsorption of intermediate compounds containing secondary amines. Yang and Satterfield (1983) studied the effect of sulfiding procedure on the HDN of quinoline. They proposed that there were two types of sites available on the sulfided catalyst. Type I sites were sulfur vacancies associated with the molybdenum atom which facilitated the hydrogenation/dehydrogenation reactions and removed sulfur directly from the sulfur compounds. Type II sites were Bronsted acid sites either from promoter atoms or from support itself. These sites were responsible for hydrogenolysis, cracking and isomerization. They concluded further that a moderate sulfiding procedure was best for HDS reactions while complete sulfiding was best for HDN reactions.

Later, Satterfield and Yang (1983) studied the simultaneous reactions of HDN and hydrodeoxygenation (HDO) over a Ni-Mo/alumina catalyst. Quinoline was used as the nitrogen compound while benzofuran was used as the oxygen model compound. Quinoline was found to be an inhibitor of HDO reactions. They attributed this fact to the competitive adsorption of quinoline on HDO sites. The presence of oxygen compounds resulted in an enhancement of HDN reactions. They claimed that the formation of water from HDO reactions was the reason for the enhancement, and hydrogen bonding between a nitrogen compound and a hydroxyl group would increase the probability of adsorption of the nitrogen compound by shielding the nitrogen atom from poisoning the sites. They also postulated that the basic molecular structures of the reactant played a significant role and, the accessibility of a molecule to the catalyst surface was affected by its basicity.

Miller and Hineman (1984) tried to identify the reaction conditions when the HDN of quinoline was non-first order by using Co-Mo/alumina and Co-Mo/silica-alumina catalysts. They found that at 330 C, significant amounts of 1-THQ and DHQ were observed while PCH was the major hydrocarbon compound product, with PBZ being produced in a small amount. An initial feed concentration of quinoline of 100 ppm resulted in the first-order kinetics while a feed concentration of 9,659 ppm resulted in a non-first order kinetics. They assumed that all of the nitrogen compounds in the reaction network have similar adsorption constants, and the adsorption constants for all of the nitrogen compounds were lumped into a single constant in a Langmuir-Hinshelwood type kinetic modeling. They reported that the acidic sites of the supports could play an important role in hydrogenolysis of the C-N bond.

Satterfield and Yang (1984) studied the HDN of quinoline in a liquid carrier and compared the results to their vapor-phase experiments reported earlier. The HDN reaction rate was found to be independent of the feed concentration of quinoline for both phases. At the same temperatures and pressures, the product distributions from both phases were similar. Classifying the nitrogen compounds into aromatic amines (AA), secondary amines (SA) and ammonia for adsorption purposes resulted in a good data fit for Langmuir-Hinshelwood type model. They reported the ratios of 6.1 for K(SA)/K(AA) and 0.65 for K(NH3)/K(AA). They were essentially same as the ratios found by Sonnemans, et al. (1973) who reported values of 6.1 and 0.23 for K(piperidine)/K(pyridine) and K(NH3)/K(pyridine).

In the accompanying paper to the previous one, Yang and Satterfield (1984) studied the effect of hydrogen sulfide on the liquid phase HDN of quinoline. The results were similar to those of the vapor phase. In addition, tetralin was used at two different concentrations to investigate the effect of a hydrogen donor solvent on the HDN reaction rate. It was found that because tetralin can adsorb in significant amounts, the rates of the hydrogenation steps were reduced.

El-Bishtawi (1986) studied the HDN of quinoline, acridine and a mixture of the two compounds. An autoclave batch reactor was employed to study the reaction. A commercial Ni-Mo/alumina catalyst (American Cyanamid HDS-9A) was used throughout the study. Experimental temperatures ranged from 357 to 390 C at 10.4 MPa (1500 psig). Increasing temperature resulted in increased conversion. However, the equilibrium conversion was not affected by temperature. Increasing temperature also increased the formation of 5-THQ and decreased the formation of 1-THQ. It was found that the pseudo-first order model did not fit well for total nitrogen removal rate during HDN of quinoline and quinoline-acridine mixture. The model derived by considering different adsorption sites for hydrogen and nitrogen compounds gave the best fit of the experimental data. Quinoline HDN was influenced by the presence of acridine and its HDN products. Presence of acridine shifted intermediate products from 1-THQ to 5-THQ with increased hydrogenation of 1-THQ to DHQ. Acridine HDN was also decreased by the presence of quinoline. All of the paths in the reaction network of acridine were affected in varying degrees. The reaction network proposed by El-Bishtawi for quinoline HDN is presented in Figure 3. The differences between this model and the networks proposed by

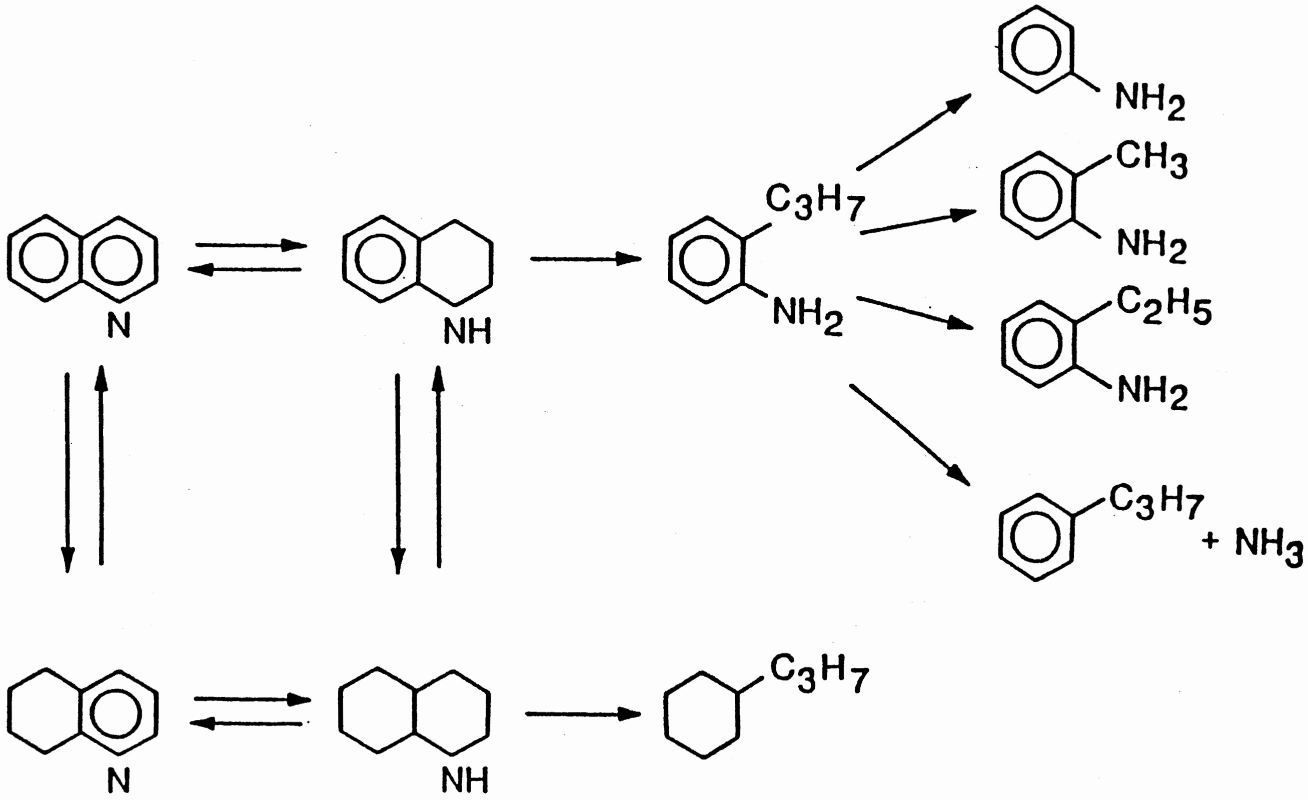


Figure 3. Quinoline Reaction Network of El-Bishtawi

previous investigators (Figures 1 and 2) are that once OPA is formed from 1-THQ, only various aniline and benzene compounds are formed, and that PCH exclusively forms from DHQ.

Fish, et al. (1986) reported on a 50% nickel-oxide loaded catalyst for a selective HDN of quinoline. They reported that when 1-THQ was used as the feed, products from direct hydrogenolysis compounds, such as propylbenzene, predominated while some amounts of quinoline and 5-THQ were also formed. When the OPA was used as the feed, no hydrogenation took place and only the products from cleavage of C-N bond were detected. They theorized that the N-atom could have inhibited the hydrogenation of aromatic ring and C-C bond cleavage. Dehydrogenation to quinoline from 1-THQ seemed to compete with C-N bond cleavage.

Stohl (1987) studied deactivation of a commercial Ni-Mo/alumina catalyst (Shell 324M) with various intermediates of quinoline HDN. Two time durations of 5 minutes and 120 minutes were used to study the time effect. After 5 minutes, the hydrogenated products caused a deactivation of the catalysts comparable to that due to quinoline. After 120 minutes, 1-THQ caused significantly less deactivation than other two-ring nitrogen compounds. There were not much differences in the deactivations of the catalyst whether the samples were taken after 5 minutes or 120 minutes. It indicated that the deactivation due to quinoline and its intermediates were rapid. The basic nature of the nitrogen compounds was seen to be responsible for the immediate poisoning of the catalytic sites. Curtis and Cahela (1987) investigated the HDN activity of various transition metal sulfides. Molybdenum sulfide and ruthenium sulfide were seen to rival the activity of commercial catalysts. Aboul-Gheit (1987) studied the influence of acidity of the catalyst support on HDN reaction of quinoline and indole. The data indicated that the stronger acidity of the catalyst enhances the quinoline HDN more than the indole HDN because the quinoline HDN has the hydrocracking step as the rate-limiting step, while indole HDN has the hydrogenation step as the rate-limiting step. Hirschon, et al. (1987) studied the HDN of quinoline with ruthenium-promoted Co-Mo/alumina catalysts. They reported that the catalyst gave five-fold increase over traditional catalystsin the selectivity for the aromatic hydrocarbon products .

Thormodsen, et al. (1987) studied the selective reduction of various heterocyclic compounds by transition metal complexes. They studied the hydrogenation of quinoline through the use of deuterium and found that the 1-2 Carbon-Nitrogen bond was first reversibly hydrogenated, followed by the irreversible hydrogenation of 3-4 C-C bond. When various catalysts were tried for cleavage of C-N bond in 1-THQ, highly loaded Ni/Silica catalysts were found to be the most active. Malakani, et al., (1987) studied the HDN of 7,8-benzoquinoline with a commercial Ni-Mo/alumina catalyst. They found that the hydrogenation of the compound was a step-by-step process initially involving the hydrogenation of the heterocyclic ring, and that the presence of hydrogen sulfide favored C-N bond cleavage while inhibiting hydrogenation. One of the requirements before cleavage of C-N bond was that the adjoining ring to the hetero-ring be saturated.

Basicities of Heteroatom Compounds

Many of the catalyst surface studies performed recently have confirmed that the active sites for HDN reactions contain both Bronsted and Lewis acidic sites. Promoter atoms such as cobalt and nickel seemed to produce acidic sites in varying strengths. It follows then that the basic nature of the nitrogen compounds might play a significant role in the reaction mechanism. Nagai, et al. (1986) studied the poisoning effect of nitrogen compounds on dibenzothiophene HDS with sulfided Ni-Mo catalysts. Nitrogen compounds were found to be strong and effective poisons for the hydrogenation but not for desulfurization. They proposed the existence of different sites for hydrogenation and desulfurization and claimed that the nitrogen compounds poisoned only the hydrogenation site. They used gas phase basicity of the nitrogen compounds to correlate the poisoning effects of the compounds. They found that the adsorption constants did not correlate well with pKa values, which are the traditional measure of the compound basicity. When the gas phase basicity was used, the adsorption constants were found to correlate well with it. They attributed this to the fact that the gas phase basicity is a measure of the intrinsic basicity while the pKa values are influenced by solvation effects in aqueous solutions. Their data are reproduced in Figure 4.

The most familiar approach to comparing or estimating the strengths of basic nitrogen compounds is to use the dissociation constants or pKa values. The pKa is defined as the log of dissociation constant for the following reaction.

$$B + H^+ \rightleftarrows BH^+ \qquad (1)$$

where B denotes the basic compound and BH^+ the protonated compound. The reported values are usually evaluated in aqueous solutions from measuring concentrations of each species in the solvent.

Recent investigators have suggested that pKa could be a misleading indicator of the basicity if the environment around the molecules in question is non-aqueous. More appropriate measurements suggested the gas phase basicity (GB) or proton affinity (PA). Both of these quantities are defined in terms of the reaction (1).

The gas phase basicity is defined as the negative of the free energy change associated with this reaction, while the proton affinity is the negative of the corresponding enthalpy change. There are relatively few compounds where direct measurement of the values has been done. The majority of the proton affinities are based on measurements of equilibrium constants of gas-phase proton transfer reactions:

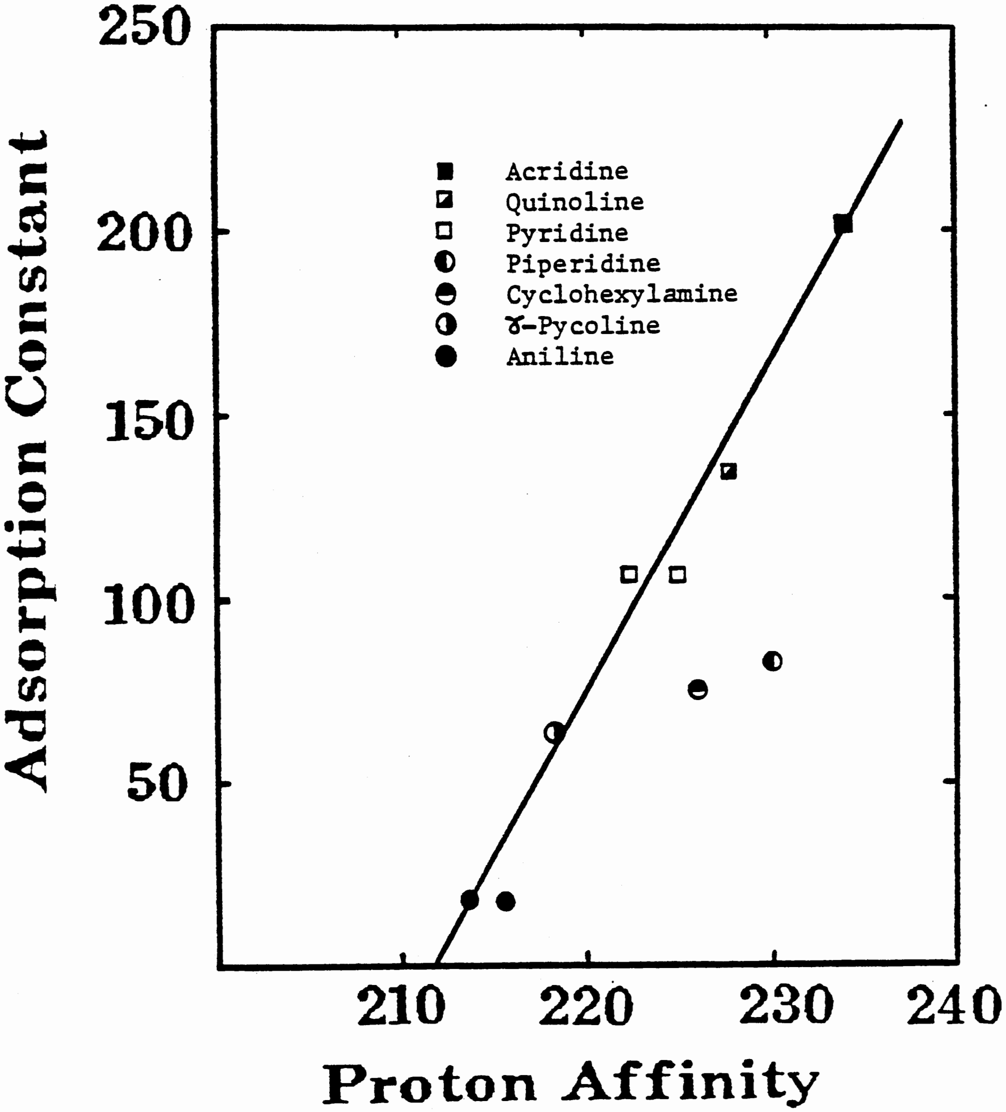


Figure 4. Plot of Adsorption Constants Against Basicity

$$MH^+ + N \rightleftharpoons NH^+ + M \qquad (2)$$

The equilibrium constants from this reaction can be used to obtain the Gibbs free energy of the reaction, which gives the relative gas phase basicity of compounds M and N. If GB value for one of the compounds is known, then the value for the other compounds can be estimated. The techniques currently available in estimating the PA or GB values are a pulsed electron beam ion cyclotron resonance (ICR) spectrometer, high-pressure mass spectrometer, and flowing afterglow technique. Lias, et al. (1984) have published extensive compilation of these values. Table I presents the PA values taken from their work, along with available pKa values, for the intermediate compounds identified in quinoline HDN reaction network. For 1-THQ and DHQ, the PA values are not available and must be estimated. The estimation procedure is described in Appendix A.

Surface Studies of Catalysts

From the previous section, it is clear that molybdenum-based catalysts have been found to be excellent for hydrotreatment of residual oils and coal liquids, especially if promoted by cobalt or nickel. Further it was found that sulfiding these catalysts have resulted in a higher activity. Many of the recent investigations have been focused on understanding the catalyst surfaces and the structures responsible for the catalytic activity. The instruments used

TABLE I

LIST OF BASICITY VALUES

Compound	Proton Affinity	pKa
Quinoline	226.5	4.9
1,2,3,4-tetrahydroquinoline	231.5 *	5.0
5,6,7,8-tetrahydroquinoline	227.7	6.7
Decahydroquinoline	233.3 *	11.3
o-Propylaniline	217.2	4.4

* - estimated from the homolog series analysis

have been Laser Raman Spectroscopy (LRS), ultraviolet spectroscopy (UV), X-ray photoelectron spectroscopy (XPS), high-resolution and analytical electron microscopy (HREM and AEM). More recently, Mossbauer emission spectroscopy (MES) and extended X-ray adsorption fine structure (EXAFS) have been employed for more detailed study of the catalyst surface.

Topsoe, et al., (1986) reviewed the recent research on hydrodesulfurization catalysts. Their review mainly focused on supported or unsupported Co-Mo catalysts. Sulfur vacancies were seen to be responsible for HDS activity. The vacancies at the edge of the molybdenum sulfide clusters were found to have a higher activity. When cobalt was used as a promoter, it was present in a cobalt-molybdenum sulfide structure similar to MoS_2, which was termed Co-Mo-S phase. EXAFS studies confirmed that the Mo atoms in Co-Mo-S had a MoS_2 like structure. The promotion of the cobalt in cobalt-molybdenum catalysts was proportional to the concentration of Co present in the Co-Mo-S structure.

Even though studies on HDS catalysts gave valuable insight into the nature of hydrotreating catalysts, the sites for HDN catalysts may have different nature. Portefaix, et al. (1986) studied HDS, HDN and hydrogenation using an unsupported molybdenum sulfide catalyst. They claimed that HDN reactions were different from HDS or hydrogenation and the HDN reactions took place on sites which are made up of a large number of atoms and probably are dependent on their environment.

Schrader and Cheng (1983,a) studied the structure of a Cobalt-Molybdenum catalyst by using laser Raman spectroscopy with pyridine adsorption. They concluded that the molybdenum oxide species formed aggregated or polymeric species on the surface of the aluminum oxide support. The aggregates were responsible for the Bronsted acidity sites. With the addition of cobalt, the acidity was altered by creating a new site having an acidity intermediate between Bronsted and Lewis acidity. The same authors (1983,b) also reported on the in-situ study of sulfiding the Mo/alumina catalyst using laser Raman spectroscopy. When the catalysts were sulfided for longer than two hours at 400 C, molybdenum sulfide was relatively stable and was not degraded upon contacting with oxygen. When the catalysts were sulfided for less than two hours, the sulfides began to break down; and when the sulfiding was only done for five minutes, complete destruction of the sulfides was seen. At lower temperatures, reduced molybdenum, oxysulfides and sulfides were observed. Based on their findings, they suggested that incomplete covering of the alumina surface accounted for the Lewis acid sites, and the molybdenum sulfides existed in the forms of islands or rafts. Incomplete sulfiding of the molybdenum due to the interference of the support (alumina) resulted in strong Bronsted acidic sites.

Suarez, et al., (1983) studied the acidic properties of Mo/alumina for different extents of reduction using infrared and thermal gravimetric studies of adsorbed pyridine. They detected the presence of both Lewis acid sites and Bronsted acid sites. Only Lewis acid sites were found on the alumina surface. When the catalyst was reduced with hydrogen, the total acidity increased to a maximum and then decreased as the reduction was continued. At a high level of reduction, the Bronsted acid sites were completely eliminated and Lewis sites decreased.

Knozinger and Jeziorowski (1981) characterized Ni-Mo/alumina catalysts by using optical, Raman, and ion scattering spectroscopy. They reported that molybdenum existed as a monolayer on the support surface and nickel was found both in the surface layer and in the support network. The ratio of nickel in the surface and in the support depended on the sequence of the impregnation of the metals. When MoO_3 was detected, the catalytic activity dropped significantly.

Harris and Chianelli (1986) studied the promoting effect of the first row transition metals on the HDS activity of molybdenum sulfide. They claimed that the promoting effect comes from electronic factors and not from physical factors. The active sites were upgraded instead of creating more sites. Only Co and Ni atoms were found to promote while Cu poisoned the catalytic activity. They also claimed that Co or Ni have the ability to reduce Mo while Cu has the ability to oxidize Mo. They furthermore stated that HDS of sulfur compounds were facilitated by the bonding of the sulfur atom to a sulfur vacancy, which resulted in the weakening of the C-S bonds. This may explain the fact that the aromatic rings can be broken before the ring undergoes a complete saturation.

Hayden and Dumesic (1986) studied the structures of molybdenum oxide and sulfide, supported on thin films of alumina, by using X-ray photoelectron spectroscopy and scanning transmission electron microscopy. They found that Mo atoms were highly dispersed initially when impregnated at low concentrations. As the concentration was increased, bulky MoO_3 crystallites were formed. As the sulfiding proceeded, destruction of MoO_3 was observed. Molybdenum sulfides were formed in clusters and bonded to the support through Mo-O-Al linkages. The higher activity for HDS after high sulfiding temperatures was explained by less steric hindrance of bulky sulfur-containing aromatics in reaching the active sites at the edge planes.

Adsorption Studies

The Langmuir-Hinshelwood (L-H) model is used most commonly to correlate the reaction rate data of catalytic reactions. The model originated from the Langmuir theory of activated adsorption on active surfaces and the application of this theory by Hinshelwood to a large number of reactions. The model was extended and popularized by Hougan and Watson. The Langmuir theory of adsorption resulted in the following equation for equilibrium between a solution and a surface.

$$\theta = \frac{K_A C_A}{(1 + K_A C_A)} \qquad (3)$$

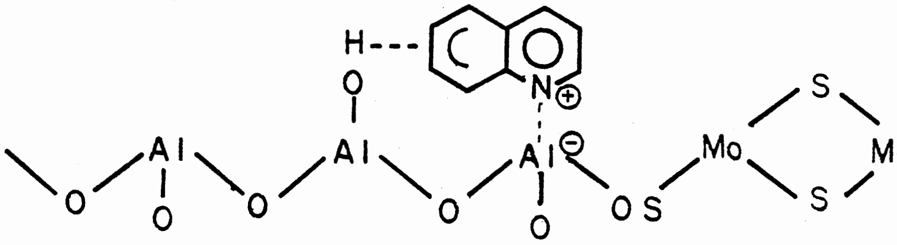
If Compound A is converted to Compound B through a reversible first order catalytic reaction and if surface reaction is the rate controlling step, L-H kinetic modeling results in the following equation (Lee, 1986).

$$-r_A = k(C_A - C_B/K)/(1 + K_A C_A + K_B C_B)$$

Various other formulations have been obtained for other types of reactions and for whether adsorption or desorption process is the rate controlling step. Kabel and Johanson (1962) confirmed the validity of this approach using vapor-phase dehydration of ethanol. They measured the adsorption constants separately and then compared them to the adsorption constants obtained from the L-H kinetics.

The rate data from a reacting system are used to obtain the L-H kinetic parameters by simply curve fitting the data to the assumed model. Individual separation of adsorption coefficients and the kinetic parameters requires dynamic measurements. Ahn, et al. (1985) reported on a dynamic method for a slurry reactor using a pulsed technique and applying Laplace transformations to solve the governing equations. They were successful in elucidating individual constants for the catalytic oxidation of sulfur dioxide in aqueous slurries of activated carbon. However, this type of experiments requires a system capable of measuring the in-situ concentrations of reacting species and products in response to the pulsed inlet of the reacting species.

Bandyopadhyay, et al., (1985) studied quinoline adsorption on calcined and sulfided Mo/alumina catalyst with Fourier Transform-Infrared/Photoacoustic (FT-IR/PA) spectroscopy. Both Lewis and Bronsted acid sites were observed on the oxide catalyst while only Lewis acid sites were observed on the sulfided catalyst. An interaction between hydroxyl groups on the alumina surface and delocalized pi-electrons from non-nitrogen aromatic ring was found to exist on both forms of the catalyst. This may indicate a binding of the aromatic ring to the surface of the catalyst. The following picture is the proposed binding picture of the quinoline adsorption.



Combined with the previous finding that the edge sites on molybdenum sulfide complexes on alumina surfaces are the most active in HDS or HDN, the above picture may be an accurate representation of the quinoline adsorption.

Ledoux, et al., (1982) studied both HDN and adsorption of substituted pyridine and of piperidine on a Mo/alumina catalyst. They postulated that two types of adsorption occur for aromatic nitrogen compounds, horizontal or vertical. If the compound adsorbs horizontally onto the catalyst surface, cyclic and even aromatic hydrocarbons are formed. If the compound adsorbs vertically onto the surface, then the dealkylation of the compound or hydrogenation and denitrogenation results in the formation of linear hydrocarbons. They also postulated that two types of molybdenum molecules existed where one accepts the nitrogen molecules and the other accepts hydrogen molecules in dissociative adsorption.

Summary of Literature Review

In summary, It is clear that there are fundamental differences reported between HDN and HDS mechanisms. Nitrogen compounds are more difficult to process and require higher consumption of hydrogen. Generally, a Ni-Mo/alumina type of catalyst is superior for HDN over other types such as Co-Mo/alumina or Ni-W/alumina. This was shown to be true in the studies of process fluids such as a coal liquid and in the studies involving model compounds. Hydrogen sulfide or other types of sulfur compounds seemed to promote HDN of nitrogen compounds. The acidity of the sulfur compounds may involve them as potential proton donors to initiate the break up of the saturated nitrogen compounds, which indicates that HDN of nitrogen compounds may be affected by changes in acid-base relationships.

For a coal liquid fraction, it was reported that a greater basic strength resulted in a lower HDN activity. Less basic quinoline seemed to be more weakly adsorbed than other intermediate compounds. Different intermediate compounds resulted in different deactivation of a Ni-Mo catalyst. Other investigations reporting on the effect of catalyst acidity indicated that the acidity played a significant role in the selectivity of the catalyst. Others also reported on possible surface mechanisms for adsorption of quinoline and other nitrogen compounds on the catalyst surfaces.

All of the studies seemed to suggest that different nitrogen compounds behave differently, due to acid-base relationship or other physical mechanisms. However, none of the investigations studied adsorption and kinetic behavior of quinoline HDN separately. Separate studies on the adsorption and the kinetic behavior of individual intermediate compounds may result in a better understanding of HDN mechanisms for nitrogen compounds and aid us in formulating more efficient HDN process.

In this work, a gradientless reactor will be used to study the adsorption of each individual compounds on a commercial catalyst. The individual compounds will also be used to study the reactivity of each step in quinoline HDN.

CHAPTER III

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Experimental Equipment

The experimental setup consists of three major systems: a reactor, liquid and gas feed systems, and a product separation and sampling system. Figure 5 shows a schematic diagram of the experimental setup for this project. Williams (1987) first designed, constructed and operated this system. Others (Tscheikuna (1988); Seapan and Crynes (1988)) reported their analyses of the operating methods and the performance of the reactor system.

The reactor is an autoclave reactor with Berty-type internals. It was purchased from Autoclave Engineers along with the drive mechanism (Magnedrive) and the temperature controller (Beckman). The reactor is made of stainless steel with an internal diameter of 76.4 mm and a total volume of 300 ml. The internals of the reactor are shown in Figure 6. The Berty type internals will circulate a reaction mixture at a high recycle ratio without necessitating any movement of the catalyst bed. As a result, the temperature of the catalyst bed along with the fluid phase temperature can be accurately measured.

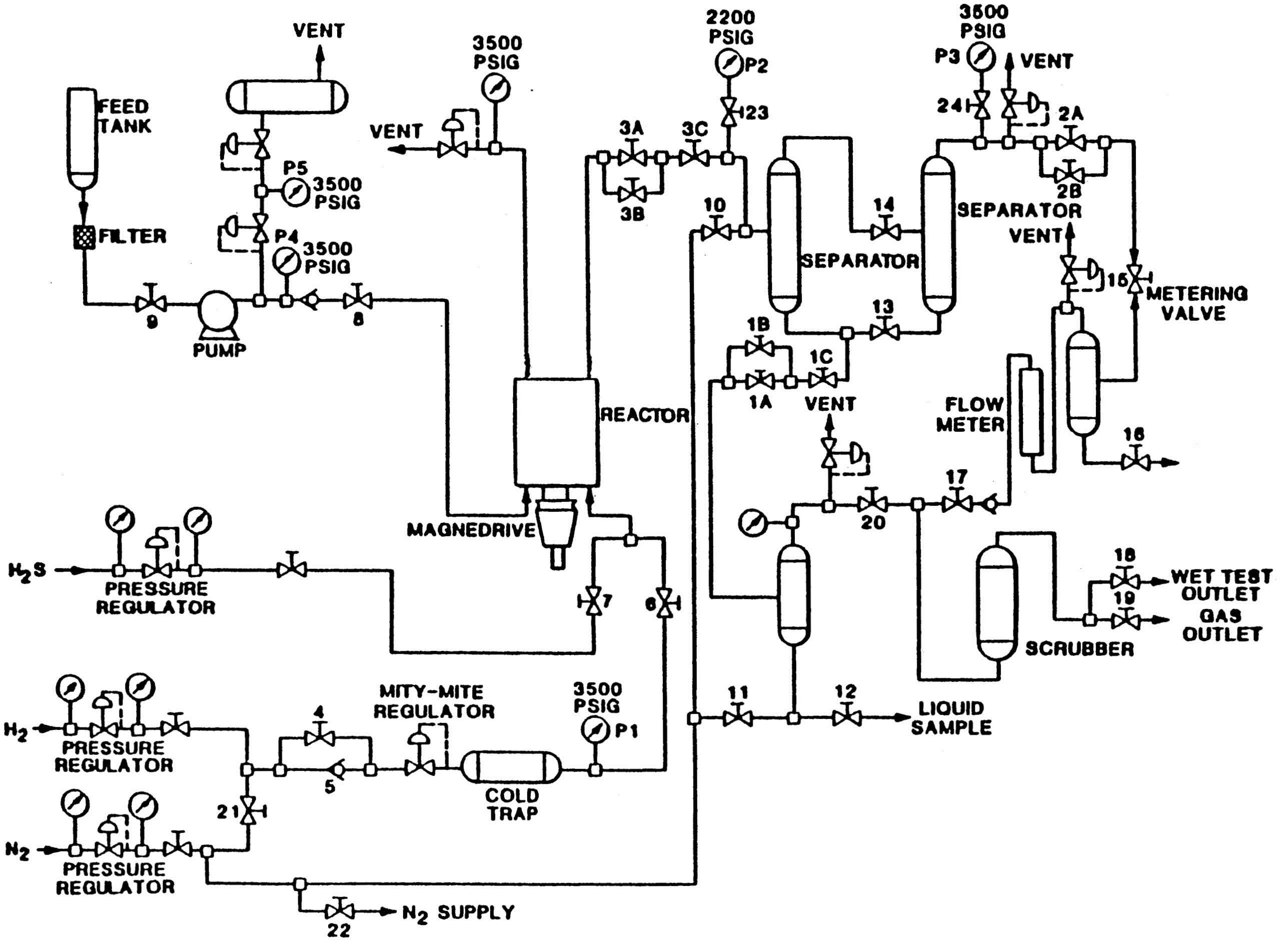


Figure 5. Schematic Flow Diagram of the Experimental System

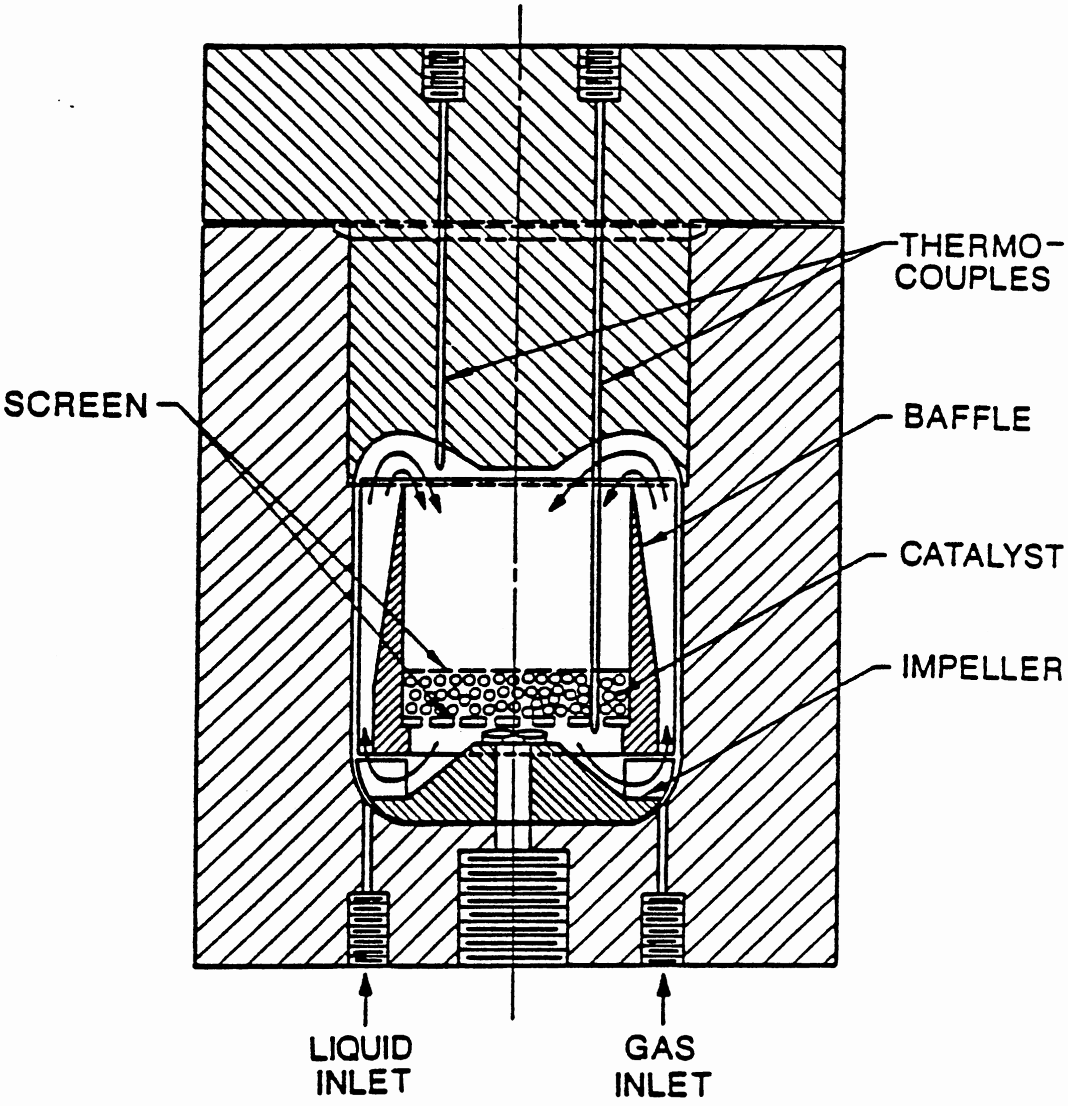


Figure 6. Schematic Diagram of the Berty Reactor Internals

Liquid and gas are fed into the bottom of the reactor where they are mixed with the recirculating fluid. With the Magnedrive spinning the impeller at a relatively high speed, the mixed fluid is forced up the annular space between the catalyst basket and the reactor wall. The fluid is then directed to the center of the catalyst basket by the reactor cap which is shaped like the outside of a doughnut. The mixture then flows down through the catalyst basket before mixing with the new gas and liquid feedstreams. The rotation of the impeller is actuated by an external Magnedrive system. The reactor is heated by three heating elements and the elements are controlled concurrently by a temperature controller. The temperature of the reactor is monitored by two thermocouples, one for the fluid phase and the other for the catalyst bed. A small amount of the circulating mixture flows out through a port at the top of the reactor to a product cylinder in which the liquid and the gas separate. Any entrained liquid in the gas stream is separated in the second separation cylinder. The gases from the second separation cylinder are throttled to 240 kPa (20 psig) and any condensed liquid is collected in the third separation cylinder. The exit gas flow rate is measured by a rotameter. The gases are then scrubbed with a sodium hydroxide solution and are vented to the atmosphere.

Liquid feed is pumped from the feed tank to the reactor by a Milton Roy positive displacement pump. The pump rate can be controlled by varying the amount of displacement per stroke. Two check valves located before the pump inlet and after the pump outlet prevent any backward flow. A relief valve between the reactor and the pump allows the reactor pressure to be contained even if the pump is shut down for any reason. It also allows a gradual building up of the pump pressure during the initial start up of the liquid feed. The feed tank is a graduated cylinder so that the liquid feed rate can be monitored constantly. The gas feed is controlled by adjusting a pressure regulator between the gas supply tank and the reactor.

Experimental Procedure

Catalyst Preparation Procedure

The catalyst used for this project is an American Cynamid HDN 60 Trilobe catalyst. This catalyst is formulated mainly for hydrodenitrogenation and is a Ni-Mo/Alumina type catalyst. The shape of the catalyst is specially arranged as a trilobe cylinder to give a higher surface area per gram of the catalyst and higher effectiveness factor. The properties of the catalyst are presented in Table II. The catalyst preparation procedure in the reactor is outlined below.

1. The catalyst was loaded into the reactor before the assembly of the parts. The reactor was tested for a pressure leak after complete assembly.

2. Heating of the reactor was started. When the

TABLE II

PROPERTIES OF CATALYST (HDN-60)

Chemical Composition, wt %	
Molybdenum (MoO_3)	22
Nickel (NiO)	3
Sodium (Na_2O)	0.03
Sulfate (So_4)	0.3
Alumina	balance

Physical Properties	
Average diameter, mm	1.6
Average length, mm	4.0
* Surface area, m^2/g	155.0 (195)
* Pore volume, ml/g	0.4 (0.42)

* The values in parenthesis are from our laboratory measurement

reactor temperature reached 200 C, nitrogen gas was added at 300 psig and at approximately 400 ml/min.

3. When the reactor temperature reached 300 C, the temperature was held constant for at least one hour to complete calcination. The reactor was then cooled to 250 C.

4. When the reactor temperature reached 250 C, hydrogen sulfide was started at 551 kPa (80 psig) at 400 ml/min and the reactor was heated again.

5. When the reactor temperature reached 350 C, the temperature was held for two hours to complete the sulfidation of the catalyst.

6. The reactor was then flushed with nitrogen gas three or four times. The catalyst was ready for the run.

The steps one through three are commonly referred to as the calcination procedure and four through six are commonly referred as the presulfiding procedure. In calcination, the water molecules are driven off the surface of the catalyst which results in the creation of acidic sites. The sulfiding procedure converts molybdenum oxides into molybdenum sulfides. As was noted in chapter 2, transition metal sulfides are known to be much more effective for hydrotreatment than oxides.

Adsorption Study Procedure

After the catalysts were prepared, the pressure in the reactor was increased to approximately 8.96 MPa (1300 psig) with nitrogen gas. The reactor was then closed in completely except for the liquid feed line. The liquid feed line was then flushed with n-hexadecane (n-16) to avoid any contamination from the previous run. Next, pure n-16 was pumped into the reactor at a high flow rate until exactly 100 ml of the solvent was in the reactor. For the duration of the pumping, the reactor pressure was monitored closely to avoid an excessive build up inside the reactor. The reactor pressure was lowered several times through the top of the reactor using the product line as it bacame necessary. After pumping was stopped, the Magnedrive was turned on, its speed was increased to 1500 rpm, and the liquid line was closed. The following procedure was used for the remainder of an adsorption experiment.

1. The fluid was circulated inside the reactor for one hour before a sample was taken. The sample was taken by opening the product line for a few seconds and then by closing back.

2. The liquid line was opened and a measured amount of n-16 containing the desired nitrogen compound with a known concentration was pumped into the reactor.

3. Steps one and two were repeated until the end of the run so that each time, the adsorption equilibrium of a higher concentration could be measured.

A known amount of the liquid was injected and the exact amount of the product was measured every hour; consequently, the concentration of the nitrogen compound could be estimated with reasonable confidence. A liquid feed containing a high concentration of the nitrogen compound was injected into the reactor at every sampling time which initially contained only the solvent; as a result, the concentration of the compound inside the reactor could be increased continuously. Ten to twelve adsorption samples were taken for each nitrogen compound. Appendix B contains a detailed sample-taking procedure.

Kinetics Experiment Procedure

The procedures described by Williams (1987) and Tscheikuna (1988) were followed closely. The major difference between the adsorption experimental procedure and the kinetic experimental procedure was that while the adsorption experiments were conducted in a semi-batch mode, the kinetic experiments were conducted in a continuous flow mode. The liquid and the hydrogen gas were continuously fed into the reactor while the product continuously flowed out of the reactor. The product was collected in the separation tanks as described earlier in this chapter. The product tank was periodically emptied and the amount of sample measured. A part or whole of the product was then kept for a gas chromatographic analysis. The kinetic experiments were conducted at 10.4 MPa (1500 psig) and at 350 C (662 F). Three different feed rates were used for each nitrogen compound. The Magnedrive speed was kept constant at 1500 rpm. Previous investigators (Tscheikuna, 1988; Seapan and Crynes, 1988) have found that the recirculation ratio was adequately high at this speed, in which one may assume a perfectly mixed reactor model for the rate calculations. The sample taking procedure is described in Appendix B. The step by step procedure in the reactor operations can be found in detail in Williams and Tscheikuna's works.

Analytical Methods

Catalyst Analysis

The catalyst from each run was extracted in a Soxhlet extraction unit with tetrahydrofuran for 24 hours to remove any compounds trapped in the pores of the catalyst. The extracted catalyst was then dried for 24 hours in a vented hood before being analyzed for the coke content. The coke content was obtained by measuring the change in the weight of the extracted catalyst as a result of the burning of the catalyst at 550 C (1022 F) for 60 hours in a temperature controlled oven.

The surface area, the pore volume, and the pore size distribution were measured using a QuantaChrome Autoscan 60 Porosimeter. These analyses were performed before and after decoking the catalyst samples. The instrument consists of an Autoscan porosimeter, micro-computer data acquisition and reduction system, and the filling apparatus. The data acquisition system has a complete Z80 micro-computer with the control program in ROM, and the data are stored in RAM. The filling apparatus consists of a sample cell, a vacuum pump and a stainless steel sheath. This porosimeter uses mercury penetration method to measure the pore volume and the surface area. This method is based on the fact that mercury has a significant surface tension and does not wet the catalyst surface. The catalyst sample is gradually pressured to 416 MPA (60,000 psig), and the amounts of mercury forced into the catalyst pores are measured at different pressures. The pressure at a data point can be corresponded to a pore radius. The surface area, pore volume, pore size distribution, and pore volume distribution can all be calculated from these data.

Product Analysis

The product samples were analyzed by using a Hewlett Packard Model 5890A Gas Chromatograph, equipped with a 60 m DB-1 capillary column and a thermal conductivity detector. The output of the detector was integrated and recorded by a Hewlett Packard Integrator Model 3392A. The chromatograph was programmed to obtain maximum separations between peaks in a reasonable time period. Initially, the column temperature was held at 60 C for two minutes; then the temperature was increased at 8 C/min rate until 200 C was reached. The column was then held at this temperature for at least 9 minutes. Approximately 0.1 microliter of the liquid sample was injected into the GC through an injection port, which was held at 225 C to vaporize the injected sample. The vaporized sample was then mixed with the helium carrier gas.

The compounds were identified by comparing the retention times of the unknown peaks with those of the standard compounds. Table III gives the listing of the retention times for different compounds along with the response factors. The response factors can be used to estimate the weight concentrations of the compounds in the sample. They were obtained by using known concentrations of each compound. The samples were analyzed no later than 24 hours after the collection, more often immediately after an experimental run; as a result, the errors resulting from the storage of liquid samples were avoided. The precision of GC analysis is discussed in Appendix C.

Characteristics of Reactants

All the gases were obtained from Sooner Supply, a local supplier affliated with Union Carbide. The nitrogen and the hydrogen were delivered at 99 % purity and were used without any further purification. Hydrogen sulfide was received in a diluted form, in which 95 % was hydrogen and 5 % was hydrogen sulfide. The compounds used in this study are listed along with the suppliers and their purity levels in Table IV. All of the chemicals were used as received. The feed concentrations of each compound were different and the concentrations used are listed in Table V along with the densities of the feed mixture. The densities were calculated using the reported densities of the compounds and the feed concentrations.

TABLE III

RETENTION TIMES AND RESPONSE FACTORS

Compounds	Retention time (min)	Response factors
Benzene	4.92	1.00
Cyclohexane	5.09	1.00
Propylcyclohexane	10.60	1.10
	11.08	
Propylbenzene	11.17	1.19
Aniline	11.48	1.00
Methylaniline	13.93	1.00
Ethylaniline	15.81	1.33
Decahydroquinoline	16.11	1.38
5,6,7,8-tetrahydro-quinoline	17.43	1.39
Propylaniline	17.60	1.29
Quinoline	17.85	1.48
1,2,3,4-tetrahydro-quinoline	19.52	1.40
n-Hexadecane	27.40	1.00

TABLE IV

LIST OF NITROGEN COMPOUND INVESTIGATED

Compound	Supplier	Purity, %
Quinoline	Alfa	99
1,2,3,4-Tetrahydroquinoline	Aldrich	98
5,6,7,8-Tetrahydroquinoline	Aldrich	97
Decahydroquinoline	Alfa	98
o-Propylaniline	Aldrich	97
o-Ethylaniline	Aldrich	98
Propylbenzene	Aldrich	98
Propylcyclohexane	Alfa	97
Hexadecane	Alfa	99
Dodecane	Alfa	99

TABLE V

FEED CONCENTRATIONS USED

Compound	Concentration (wt %)	Solution Density (g/ml)
Quinoline	10	0.797
1,2,3,4-Tetrahydroquinoline	10	0.795
5,6,7,8-Tetrahydroquinoline	5	0.783
Decahydroquinoline	2	0.776
o-Propylaniline	2	0.776
Propylbenzene	5	0.777
Propylcyclohexane	2	0.774

CHAPTER IV

EXPERIMENTAL RESULTS

Adsorption and kinetic studies were conducted using intermediate compounds, identified during the previous studies of quinoline HDN. The nitrogen compounds are listed in Table IV. Initially, the adsorption and kinetic studies were to be conducted during the same runs, but because of logistical problems encountered, the experiments were performed separately. The experimental runs are listed in Table VI by the compounds. The solvent was initially selected to be dodecane, but because the dodecane peak overlapped some of the nitrogen compound peaks during the gas chromatographic analyses, n-hexadecane was used as the solvent. The experimental conditions were held constant throughout this study and are listed in Table VII. The pressure and the temperature used in all of the experiments were 10.4 MPa (1500 psig) and 350 C (662 F) respectively. The amount of catalyst used per run was 20 grams. For the kinetic runs, the liquid feed rate was varied to obtain different residence time in the reactor.

Results from Adsorption Studies

During the adsorption study of quinoline, no side

TABALE VI

LIST OF EXPERIMENTAL CONDITIONS FOR DIFFERENT FEED

Run no.	Feed Compound	Solvent	Liquid Flow Rate (ml/hr)	Experimental Comments
Feed - Quinoline				
QA-3	Quinoline	Dodecane	30	Kinetic
QA-4	Quinoline	Hexadecane	32.6	"
OA-5	Quinoline	Hexadecane	53.8	"
QA-6	Quinoline	Hexadecane	91.2	"
QA-7	Quinoline	Hexadecane	n/a	Adsorption
QA-8	Quinoline	Hexadecane	n/a	Adsorption
Feed - 1,2,3,4 Tetrahydroquinoline (1-THQ)				
1THQ-2	1-THQ	Dodecane	30	Kinetic
1THQ-3	1-THQ	Dodecane	53	"
1THQ-4	1-THQ	Dodecane	43.4	"
1THQ-5	1-THQ	Hexadecane	30.0	Contaminated feed., Kinetic
1THQ-6	1-THQ	Hexadecane	34.6	Kinetic
1THQ-7	1-THQ	Hexadecane	63.0	"
1THQ-8	1-THQ	Hexadecane	94.0	"
1THQ-9	1-THQ	Hexadecane	n/a	Adsorption
1THQ-10	1-THQ	Hexadecane	n/a	"

TABLE VI (Continued)

Run no.	Feed Compound	Solvent	Liquid Flow Rate (ml/hr)	Experimental Comments
Feed - 5,6,7,8 Tetrahydroquinoline (5-THQ)				
5THQ-1	5-THQ	Hexadecane	28.5	Kinetic
5THQ-2	5-THQ	Hexadecane	62.7	"
5THQ-3	5-THQ	Hexadecane	96.7	"
5THQ-4	5-THQ	Hexadecane	n/a	Adsorption
Feed - Decahydroquinoline (DHQ)				
DHQ-1	DHQ	Hexadecane	27.3	Kinetic
DHQ-2	DHQ	Hexadecane	98.0	"
DHQ-4	DHQ	Hexadecane	n/a	Adsorption
Feed - o-Propylaniline (OPA)				
OPA-1	OPA	Hexadecane	31.0	Kinetic
OPA-2	OPA	Hexadecane	59.0	"
OPA-3	OPA	Hexadecane	93.3	"
OPA-4	OPA	Hexadecane	n/a	Adsorption
Feed - o-Ethylaniline (OEA)				
OEA-1	OEA	Dodecane	33.5	Kinetic
OEA-2	OEA	Dodecane	56.3	"
Feed - Propylbenzene (PBZ)				
PBZ-1	P-Benzene	Hexadecane	32.6	Kinetic
PBZ-2	P-Benzene	Hexadecane	60.0	"
PBZ-3	P-Benzene	Hexadecane	95.5	"

TABLE VI (Continued)

Run no.	Feed Compound	Solvent	Liquid Flow Rate (ml/hr)	Experimental Comments
Feed - Propylcyclohexane				
PCH-1	PCH	Hexadecane	25.0	Kinetic
Other miscellanious runs				
P-2	none	Dodecane	30	no catalyst
P-3	none	Dodecane	30	Catalyst
HEX-1	none	Hexadecane	33.2	"
HEX-2	none	Hexadecane	27.5	"
HEX-3	none	Hexadecane	59.3	"

TABLE VII

COMMON EXPERIMENTAL CONDITIONS

Variable	Value
Pressure	10.34 MPa (1500 psig)
Temperature	360 C (680 F)
Magnedrive speed	1500 rpm
Gas flow rate	400 ml/min
Amount of Catalyst	20 grams
Type of catalyst	HDN-60

products were observed. Since the adsorption study was done under a nitrogen atmosphere, quinoline was not expected to undergo any hydrogenation. The amounts of quinoline adsorbed are shown in Figure 7 against the quinoline concentration in the fluid. It can be seen that the adsorption curve can be approximated by a Langmuir-type adsorption model. The adsorption data for OPA are shown in Figure 8. A Langmuir type model can also describe the OPA data. Since OPA also requires hydrogen before undergoing any further reaction, it did not produce any side compounds. The experimental errors for each instrument used in the studies are included in Appendix C. The cumulative error for calculating an adsorbed amount was estimated to be ±4%.

When 1-THQ was used as the feed component in the adsorption study, the other compounds in the reaction network were observed in the product. Even though the experiment was conducted under the inert nitrogen atmosphere, 1-THQ acted as a hydrogen doner by self-generating hydrogen from dehydrogenation to quinoline. The produced hydrogen was then used for further hydrogenation of 1-THQ to DHQ or for hydrogenolysis to produce OPA, PBZ, and PCH. Figure 9 presents the percentage of each individual compound present in the fluid phase against the total amount of nitrogen compounds present in the fluid phase. It can be seen that even though the feed was pure 1-THQ, high levels of quinoline and 5-THQ existed in the fluid along with a significant amount of OPA. However, a very minimal amount of DHQ was observed.

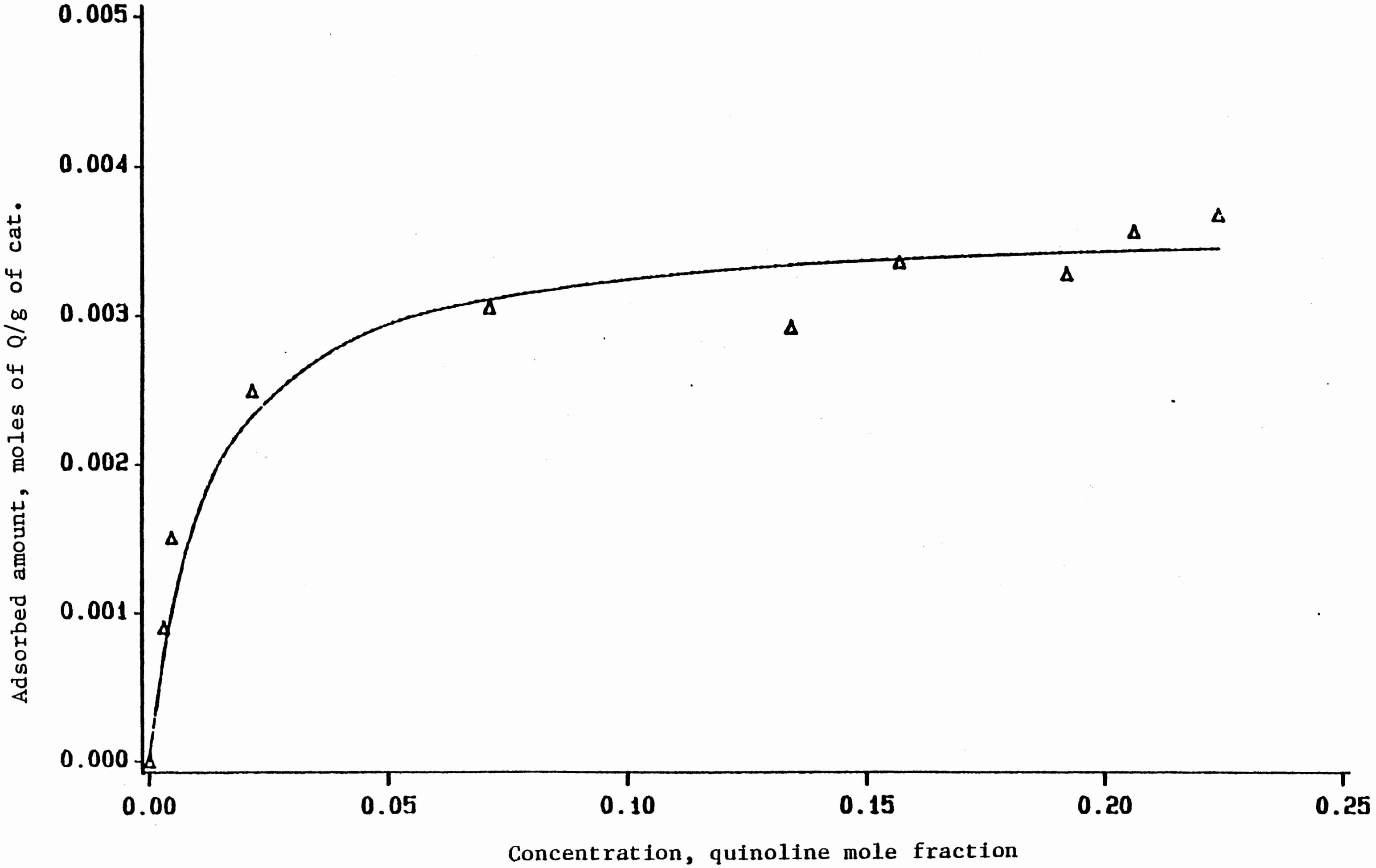


Figure 7. Quinoline Adsorption Isotherm at 350 C
(Run QA-7)

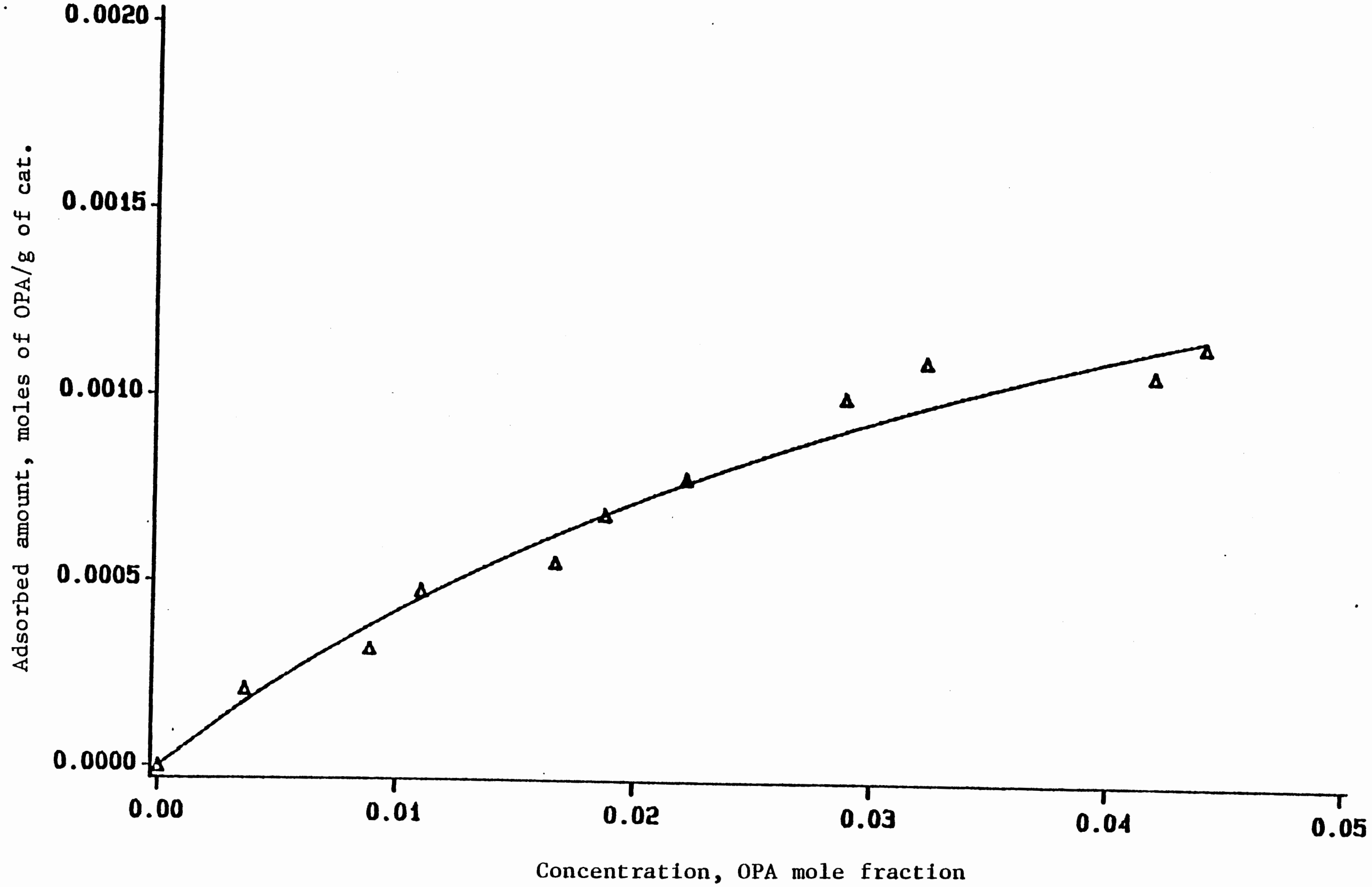


Figure 8. OPA Adsorption Isotherm at 350 C
(Run OPA-4)

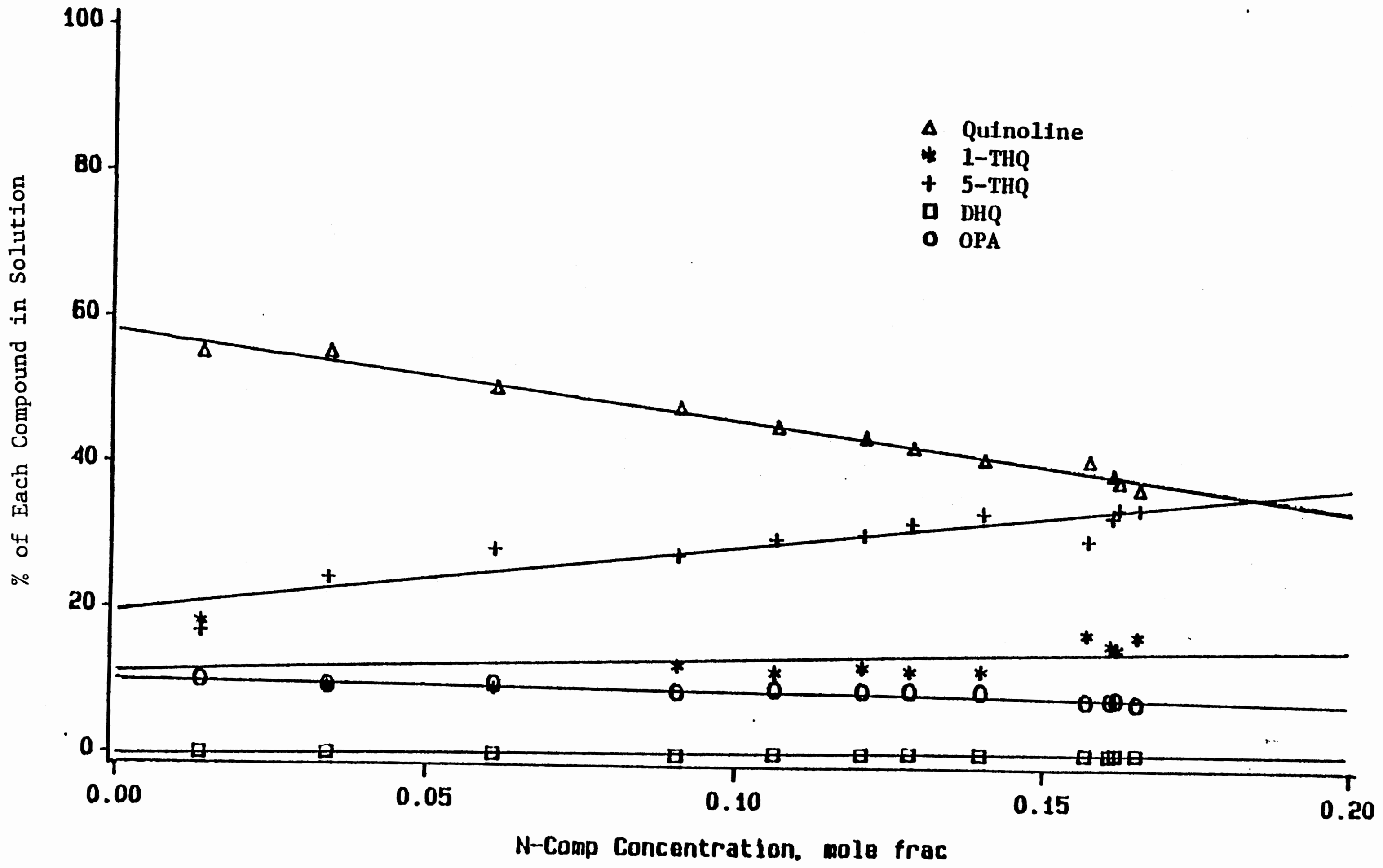


Figure 9. Composition of Compounds Present for Adsorption Run with 1-THQ Feed

A high level of quinoline is not suprising, since the reaction step between quinoline and 1-THQ is reversible and the absence of hydrogen would favor the formation of quinoline from 1-THQ. This in turn produces enough hydrogen for the hydrogenolysis of the rest of 1-THQ to proceed to produce OPA. 5-THQ can be produced through the hydrogenation of quinoline or dehydrogenation of DHQ. The low levels of DHQ observed indicate either that DHQ is a very reactive compound or that the conversion of 1-THQ to DHQ is very slow. Considering the results from previous investigations of quinoline HDN, it is more likely that DHQ is a very reactive compound, leading to the formation of either 5-THQ or PCH.

Because of the existence of various compounds in the fluid phase for 1-THQ adsorption experiment, there is a competitive adsorption between the compounds onto the catalytic surface. When a material balance is performed around the reactor, only the total adsorbed amount of nitrogen compounds can be calculated. The adsorption of individual components can only be determined after some manipulations of the adsorption equation, which will be discussed in next chapter. Figure 10 presents the total amount of adsorption plotted against the total concentration of nitrogen compounds present in the fluid phase. Two separate runs were conducted to determine the repeatability of the experiments. As can be seen on this figure, a good reproduction of the results was obtained. There appears to be three distinct regions of adsorption on this plot. The initial region

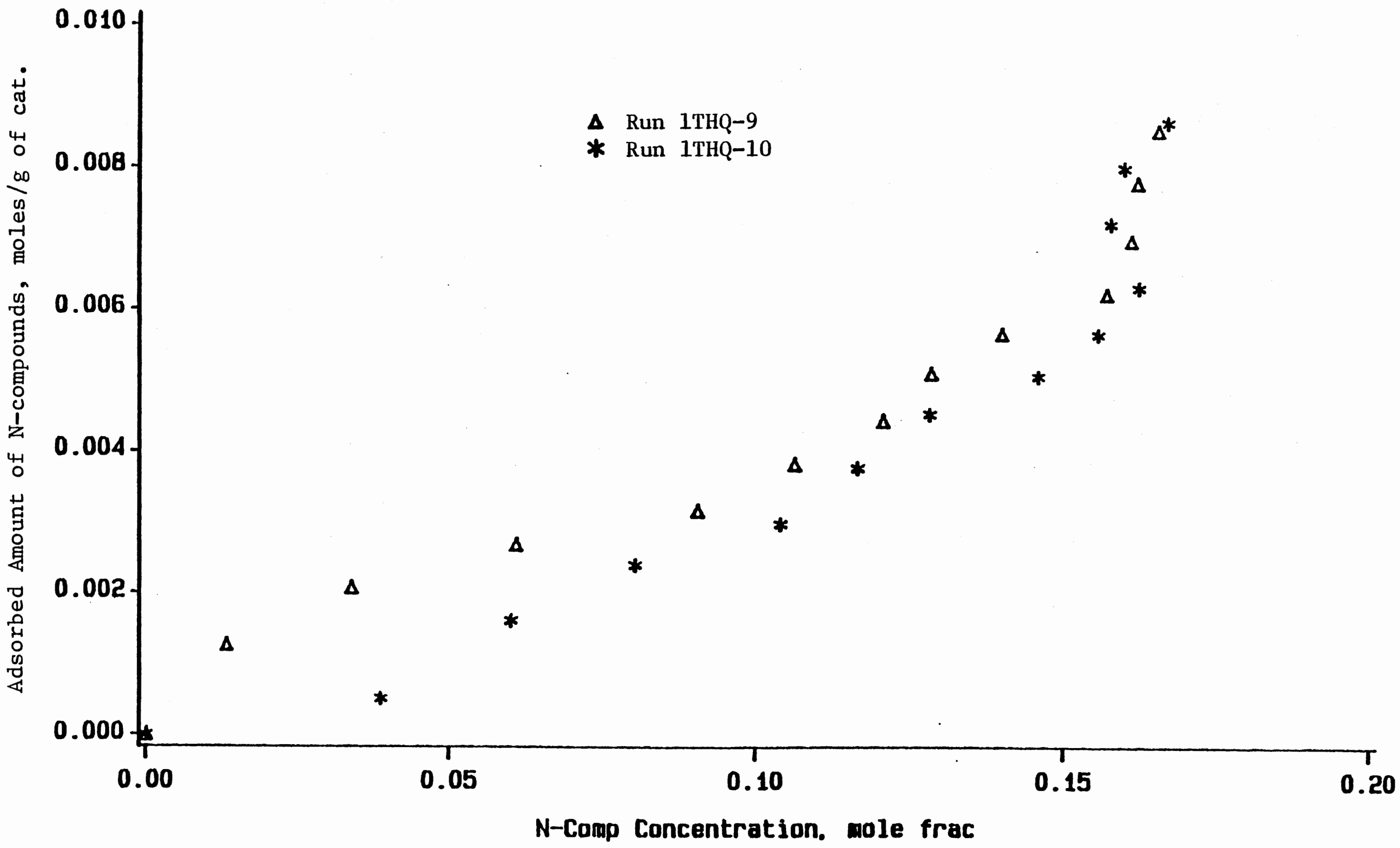


Figure 10. Reproducibility of the Adsorption of THQ

seems to follow Langmuir type adsorption. However when the concentration increased past a certain point, there was a sharp increase in the adsorption contrary to typical Langmuir type adsorption. It is theorized that further adsorption past this transition point was occurring either as a multiple layer adsorption or at the sites unavailable at lower concentrations. Indeed, the transition point matched closely with the calculated monolayer coverage for quinoline, which was estimated to be 0.00395 mol/g.

When 5-THQ and DHQ were used as the initial compound fed to the reactor for the adsorption experiment, the obtained results were similar to those of the 1-THQ experiments. Figures 11 and 12 present the levels of all intermediate compounds for 5-THQ and DHQ adsorption experiments. It can be seen that the quinoline exists in the largest amount at lower total N-compound concentrations. However, with total concentration increasing, the quinoline fraction decreased while 5-THQ fraction increased. The OPA and 1-THQ fractions remained approximately constant with increasing concentration of the total N-compounds. Figures 13 and 14 present the adsorption data from 5-THQ and DHQ adsorption experiments respectively. It can be seen that the adsorption behaviors of 5-THQ and DHQ are not similar to those of 1-THQ as observed in Figure 11. When the adsorption levels are compared, the range of nitrogen concentration for 5-THQ and DHQ is substantially lower than that of 1-THQ experiments. The adsorption levels were sufficiently low so that

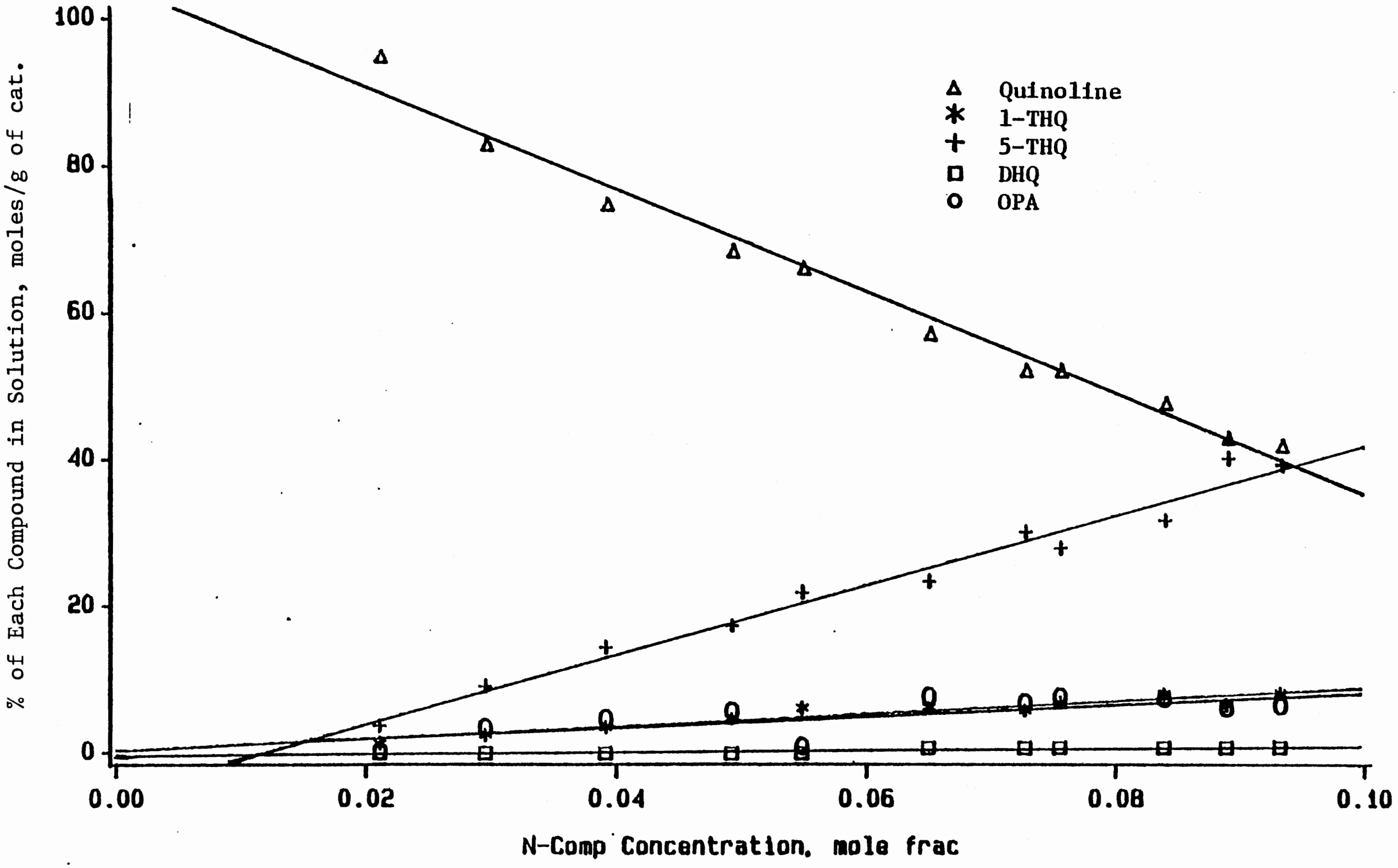


Figure 11. Composition of Compounds Present for Adsorption Run with 5-THQ Feed

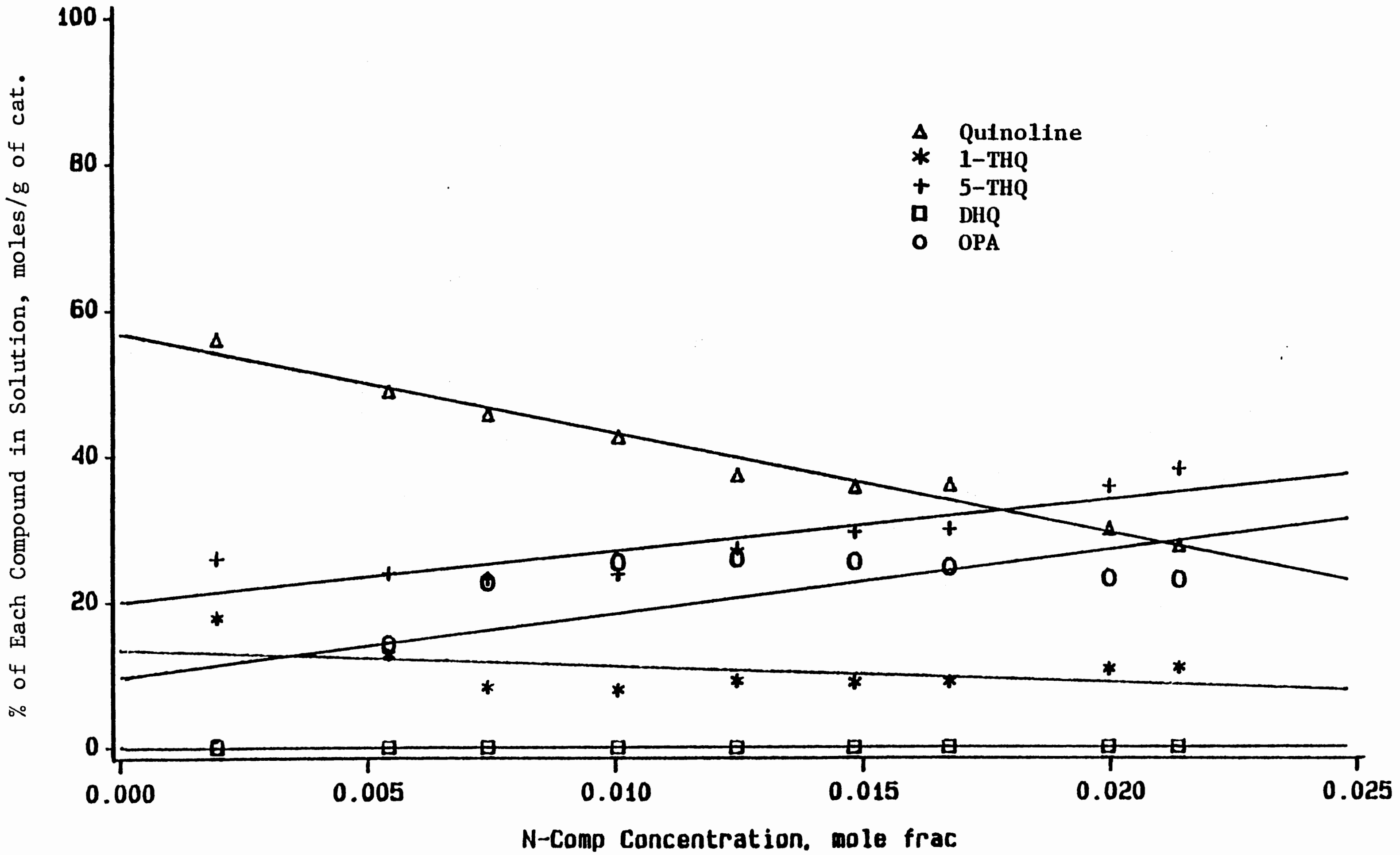


Figure 12. Composition of Compounds Present for Adsorption Run with DHQ Feed

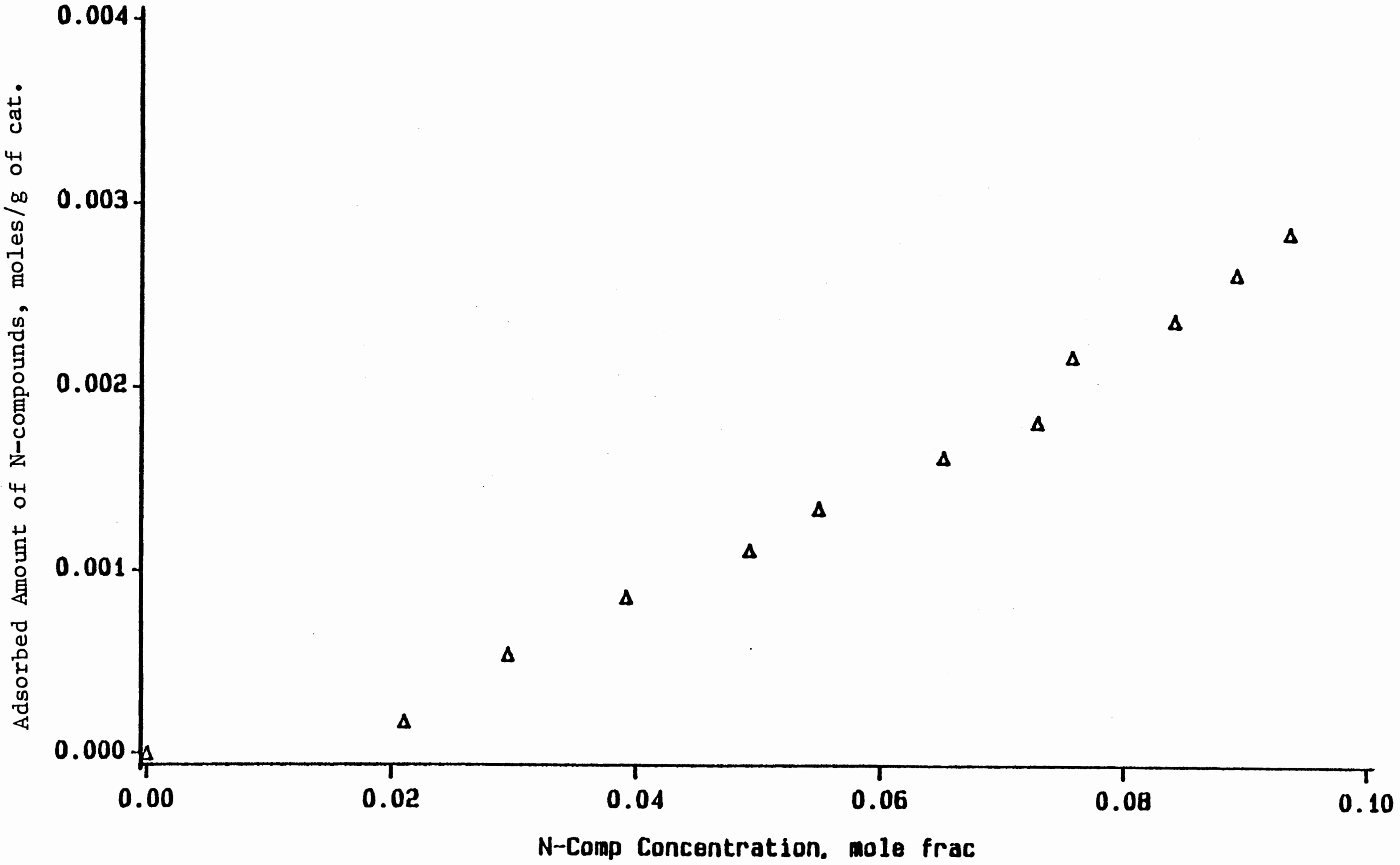


Figure 13. Adsorbed Amounts of Nitrogen Compounds
for 5-THQ Feed (Run 5THQ-4)

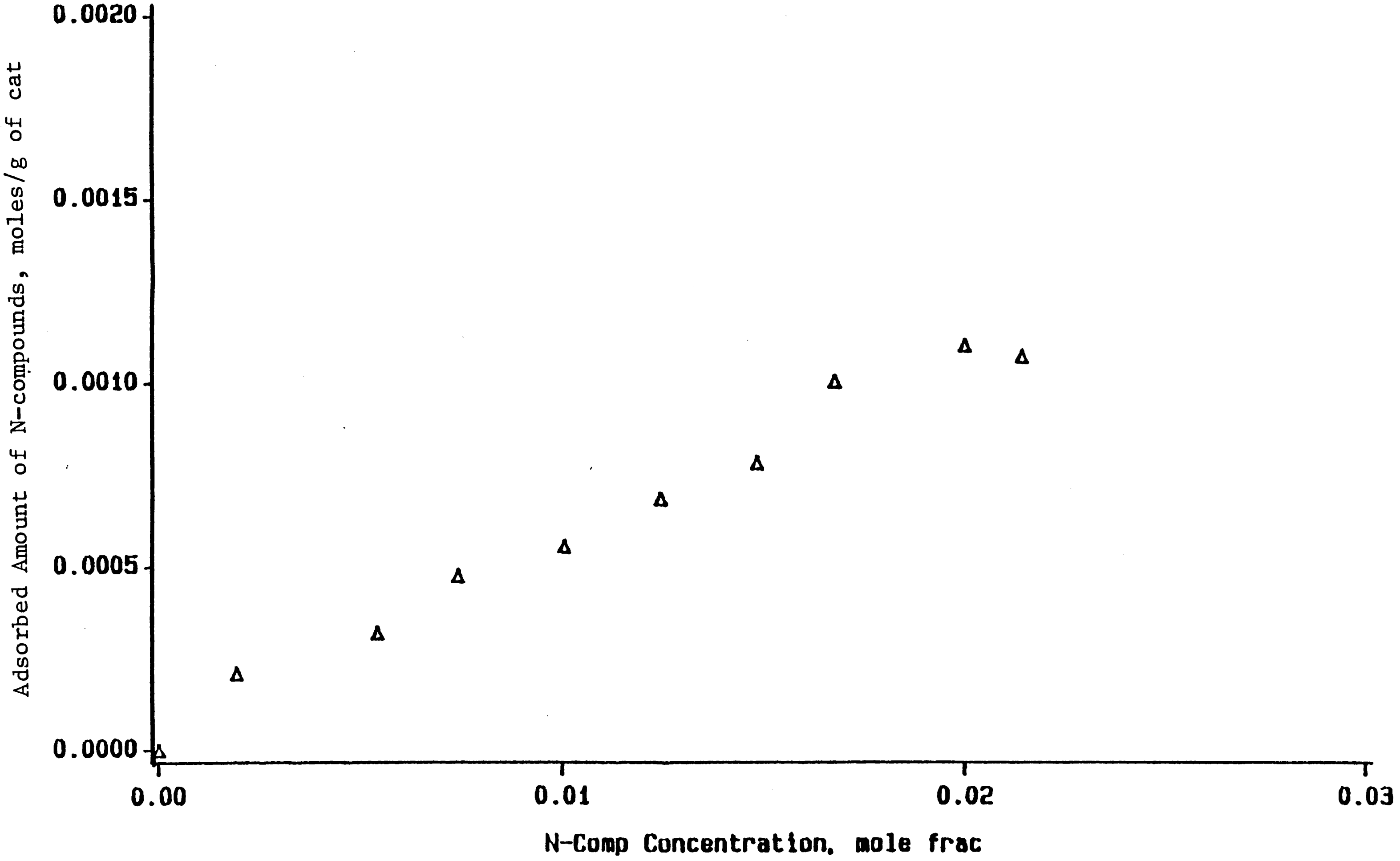


Figure 14. Adsorbed Amounts of Nitrogen Compounds for DHQ Feed (Run DHQ-4)

the adsorption of 5-THQ and DHQ was limited to a monolayer coverage only.

Results from Kinetic Experiments

The results of the kinetic runs are presented in Table VIII. For each experiment, the reactor was operated until the concentrations of the individual compounds stabilized. Three flow rates were used for each feed compound except for DHQ, in which two flow rates were used. When quinoline was used, all of the intermediate compounds were detected in significant quantities. When 1-THQ was studied as the feed compound, very low levels of quinoline were detected. This was expected since the kinetic runs were operated in hydrogen atmosphere and the reverse reaction to quinoline was heavily unfavored. The levels of OPA were also seen to be low. This was attributed to the reactivity of OPA to other compounds. This was confirmed by the runs with OPA as the feed. Even when OPA was in the feed, outlet levels of OPA were very low. When 5-THQ was used, no significant amount of quinoline was detected as expected, but 1-THQ and OPA were also not detected for these runs. This was unexpected since 1-THQ runs produced significant amounts of 5-THQ. This seemed to indicate that once quinoline hydrogenates into 5-THQ, the HDN route proceeds through DHQ to PCH. This was confirmed by the results from the runs with DHQ as the feed. No 1-THQ or OPA was detected in the DHQ runs which indicated that DHQ proceeded to form PCH. However, signifi-

TABLE VIII

PRODUCT CONCENTRATIONS FROM KINETIC RUNS

FEED: QUINOLINE

Run number	QA-4	QA-5	QA-6
Initial Conc. (mole fraction)	0.1731	0.1763	0.1723
Feed Rate (moles/hr)	0.1361	0.2244	0.3808
Quinoline	1.01 E-3	1.37 E-3	1.77 E-3
1-THQ	8.52 E-3	1.29 E-2	2.24 E-2
5-THQ	5.43 E-4	8.26 E-4	1.45 E-3
DHQ	1.46 E-2	1.56 E-2	2.26 E-2
OPA	6.11 E-4	1.37 E-3	2.29 E-3
PCH	9.19 E-2	8.11 E-2	8.22 E-2
PBZ	5.62 E-3	4.45 E-3	5.20 E-3

TABLE VIII (Continued)

FEED: 1-THQ

Run number	1THQ-6	1THQ-7	1THQ-8
Initial Conc. (mole fraction)	0.1695	0.1668	0.1654
Feed Rate (moles/hr)	0.1460	0.2593	0.3869
Quinoline	3.35 E-4	7.56 E-4	7.99 E-4
1-THQ	4.68 E-3	1.74 E-2	3.47 E-2
5-THQ	3.56 E-4	1.22 E-3	1.74 E-3
DHQ	7.10 E-3	1.80 E-2	4.44 E-2
OPA	3.62 E-4	2.00 E-3	1.75 E-3
PCH	1.26 E-1	9.59 E-2	2.32 E-2
PBZ	5.69 E-3	5.03 E-3	1.74 E-3

TABLE VIII (Continued)

FEED: 5-THQ

Run number	5THQ-1	5THQ-2	5THQ-3
Initial Conc. (mole fraction)	0.0913	0.1001	0.0866
Feed Rate (moles/hr)	0.1080	0.2348	0.3622
Quinoline	0.00	0.00	0.00
1-THQ	0.00	0.00	0.00
5-THQ	7.31 E-4	2.16 E-3	3.91 E-3
DHQ	2.11 E-3	6.81 E-3	8.71 E-3
OPA	0.00	0.00	0.00
PCH	6.58 E-2	6.27 E-2	5.41 E-2
PBZ	1.68 E-3	2.04 E-3	2.39 E-3

TABLE VIII (Continued)

FEED: DHQ

Run number	DHQ-1	DHQ-2
Initial Conc. (mole fraction)	0.0337	0.0328
Feed Rate (moles/hr)	0.0961	0.3458
Quinoline	0.00	0.00
1-THQ	0.00	0.00
5-THQ	0.00	0.00
DHQ	4.08 E-4	6.32 E-4
OPA	0.00	0.00
PCH	2.34 E-2	2.76 E-2
PBZ	3.94 E-4	6.45 E-4

TABLE VIII (Continued)

FEED: OPA

Run number	OPA-1	OPA-2	OPA-3
Initial Conc. (mole fraction)	0.0352	0.0357	0.0336
Feed Rate (moles/hr)	0.1096	0.2252	0.3299
Quinoline	0.00	0.00	0.00
1-THQ	0.00	0.00	0.00
5-THQ	0.00	0.00	0.00
DHQ	0.00	0.00	0.00
OPA	4.32 E-4	1.26 E-3	1.28 E-3
PCH	3.20 E-2	2.90 E-2	2.87 E-2
PBZ	9.43 E-4	2.31 E-3	1.72 E-3

TABLE VIII (Continued)

FEED: PBZ

Run number	PBZ-1	PBZ-2	PBZ-3
Initial Conc. (mole fraction)	0.0947	0.0947	0.0947
Feed Rate (moles/hr)	0.1133	0.2085	0.3595
Quinoline	0.00	0.00	0.00
1-THQ	0.00	0.00	0.00
5-THQ	0.00	0.00	0.00
DHQ	0.00	0.00	0.00
OPA	0.00	0.00	0.00
PCH	7.17 E-2	7.16 E-2	5.27 E-2
PBZ	1.40 E-2	1.92 E-2	2.85 E-2

cant amounts of PBZ were detected. This was contradictory to previous investigators since El-Bishtawi and others had indicated that PBZ only forms from OPA under hydrogen atmosphere. Later runs with OPA and PBZ indicated that the path between PBZ and PCH is fully reversible and PBZ can form from PCH. As expected, PCH and PBZ were the only products detected when DHQ was the feed compound. When OPA was used, PCH was also formed, which indicated that PBZ proceeds to hydrogenate to form PCH at the reactor conditions studied.

The concentrations of major compounds versus reaction time were plotted as shown in Figures 15 through 31. PCH was the dominating product for all of the runs regardless of the feed compound. On Figures 16 and 17, it can be seen that 1-THQ and 5-THQ start forming at the same time with DHQ appearing some time later. This indicates that 1-THQ and 5-THQ will form independently from quinoline and neither one is a product of the other. The delayed formation of DHQ indicates that it is a product of 1-THQ and/or 5-THQ and does not form directly from quinoline. On the same figures, it can be seen that the formation of OPA proceeds that of PCH. This indicates that the formation of PCH will involve longer path or slower steps. It can be also seen that as the PCH levels increase, 1-THQ levels are sustained while 5-THQ levels drop. These facts lead us to believe that the formation of PCH mainly proceeds through 1-THQ instead of 5-THQ. The discussion of the reaction path and the calculation of the rate constants will be presented in next chap-

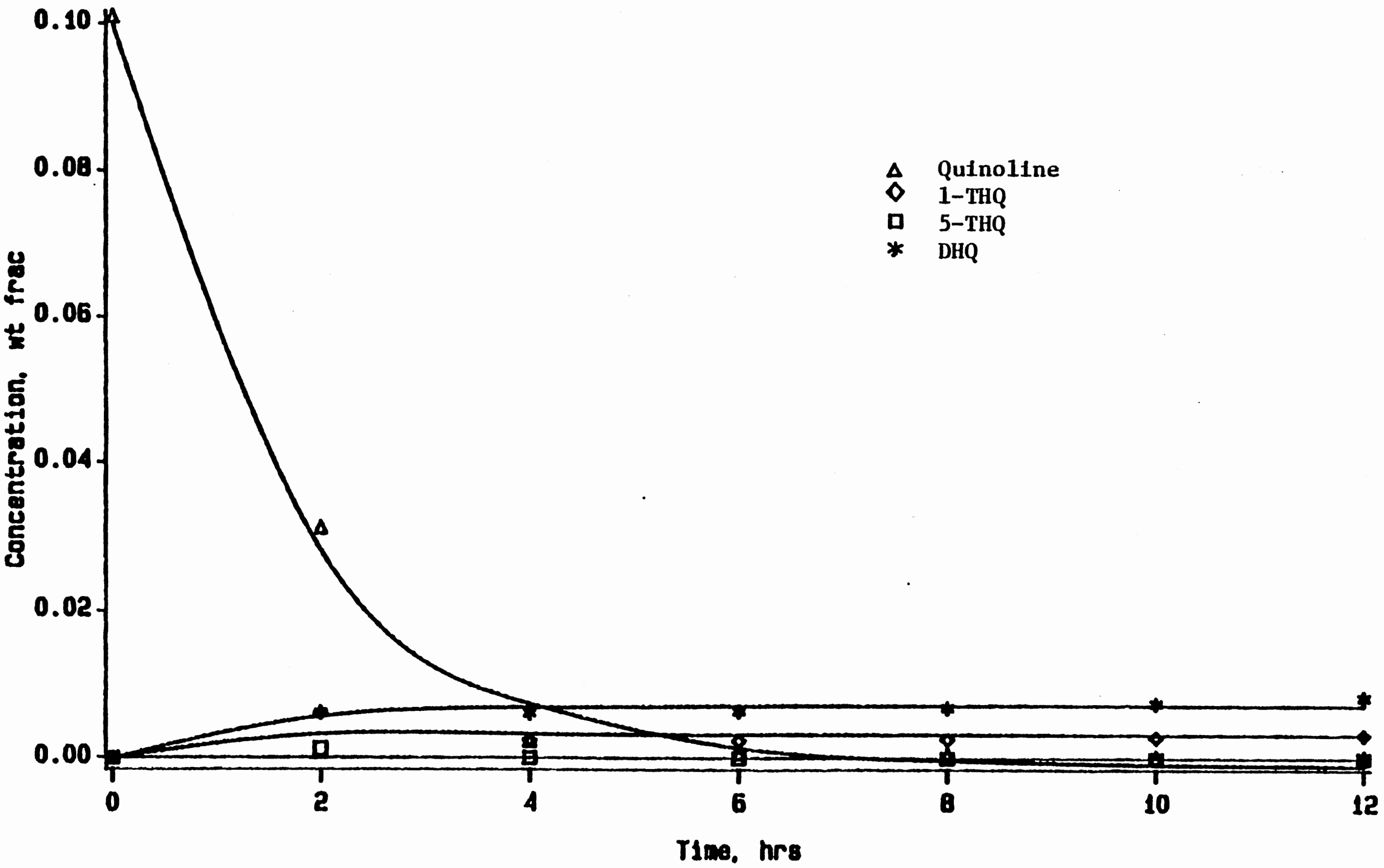


Figure 15(a). HDN Products of Quinoline Feed
(32.6 ml/hr, Run QA-4)

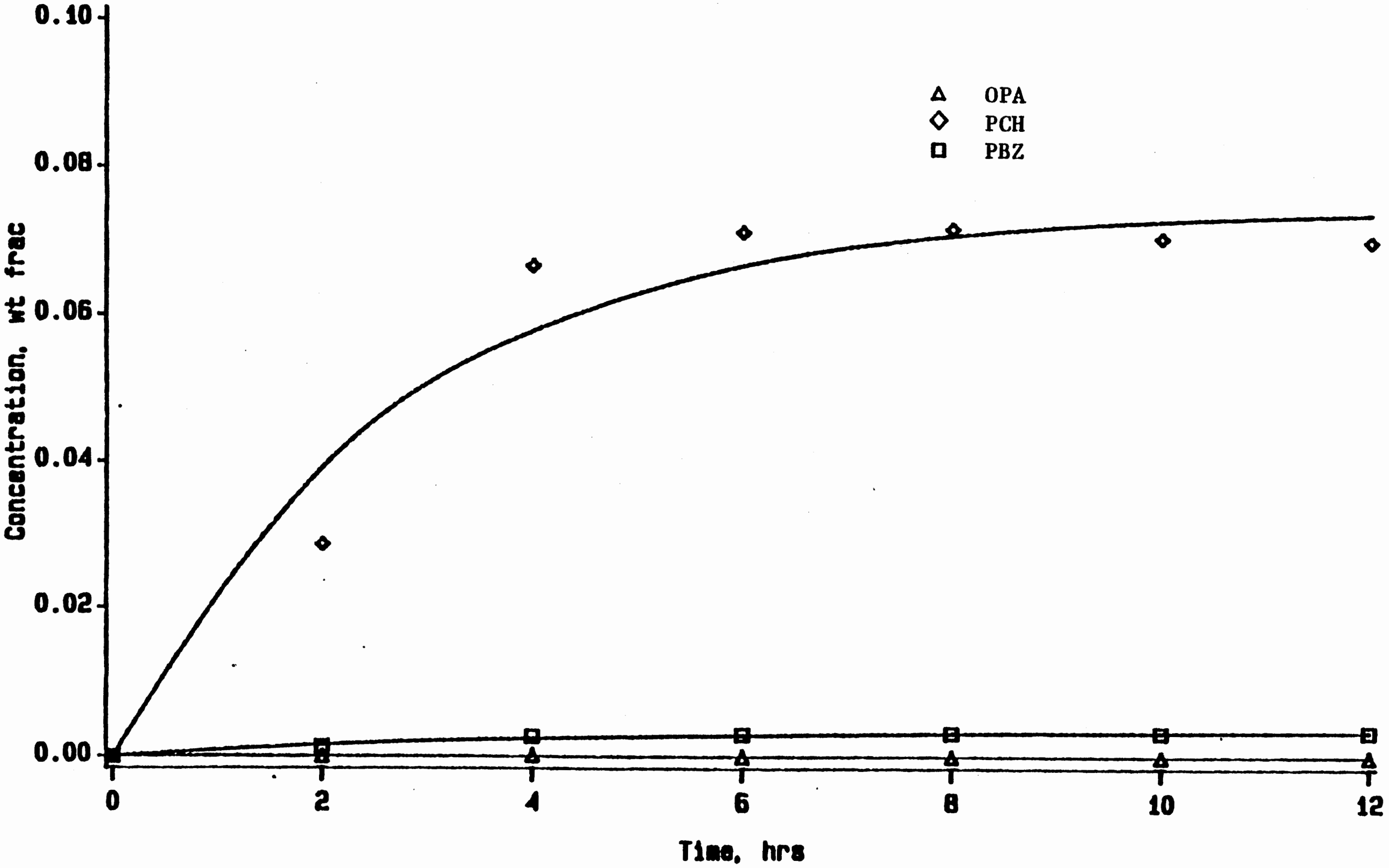


Figure 15(b). HDN Products of Quinoline Feed
(32.6 ml/hr, Run QA-4)

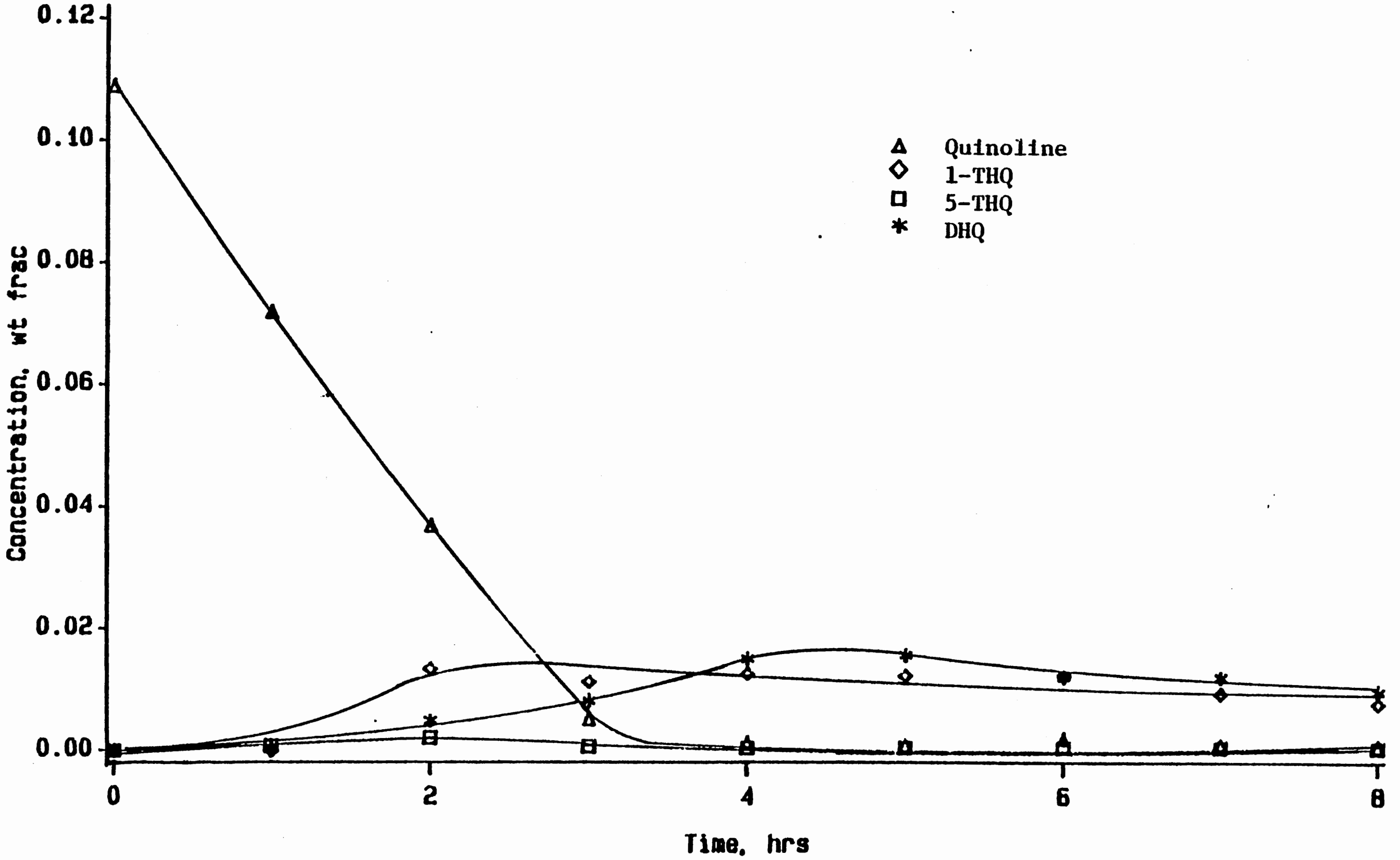


Figure 16(a). HDN Products of Quinoline Feed (53.7 ml/hr, Run QA-5)

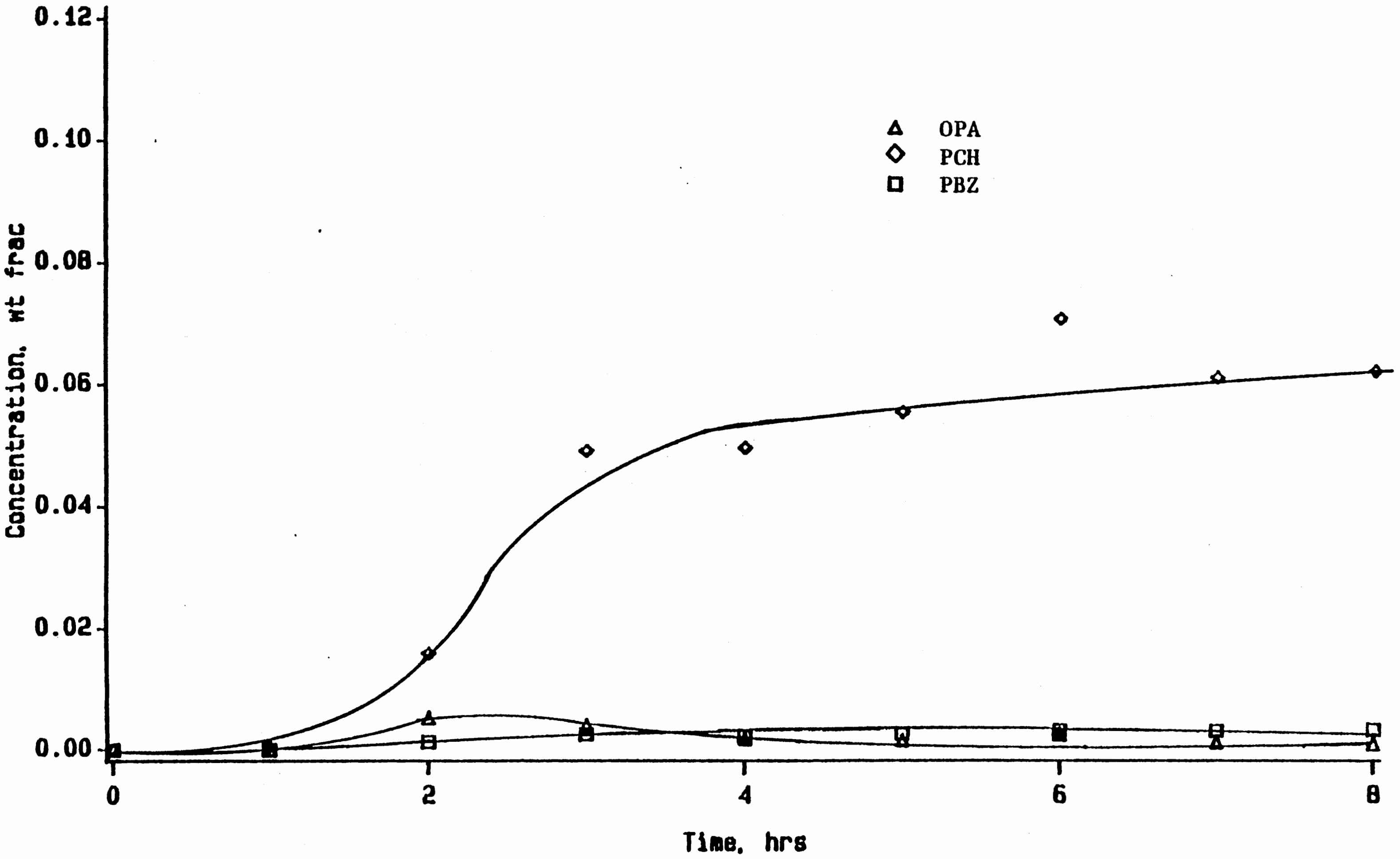


Figure 16(b). HDN Products of Quinoline Feed
(53.7 ml/hr, Run QA-5)

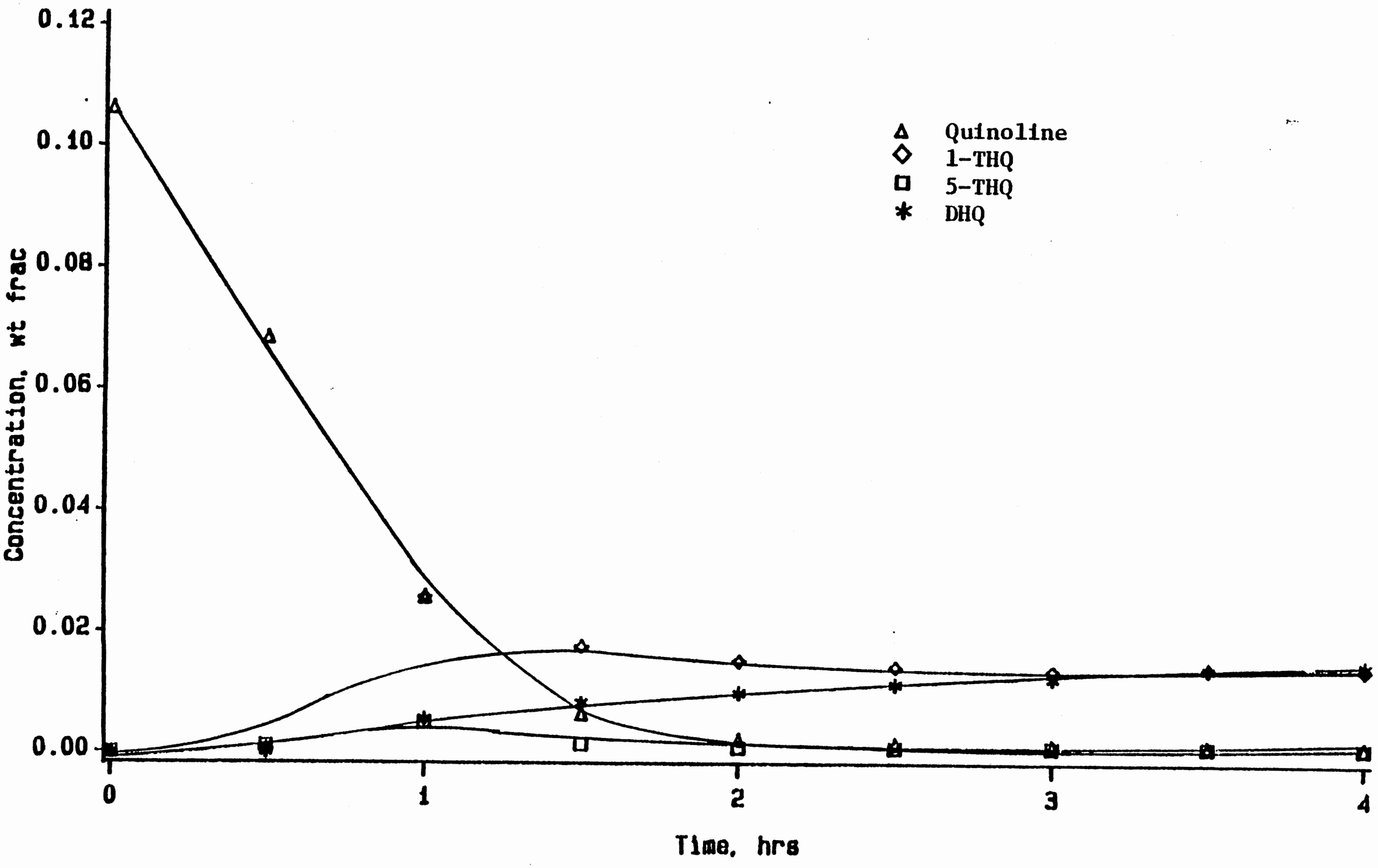


Figure 17(a). HDN Products of Quinoline Feed
(91.2 ml/hr, Run QA-6)

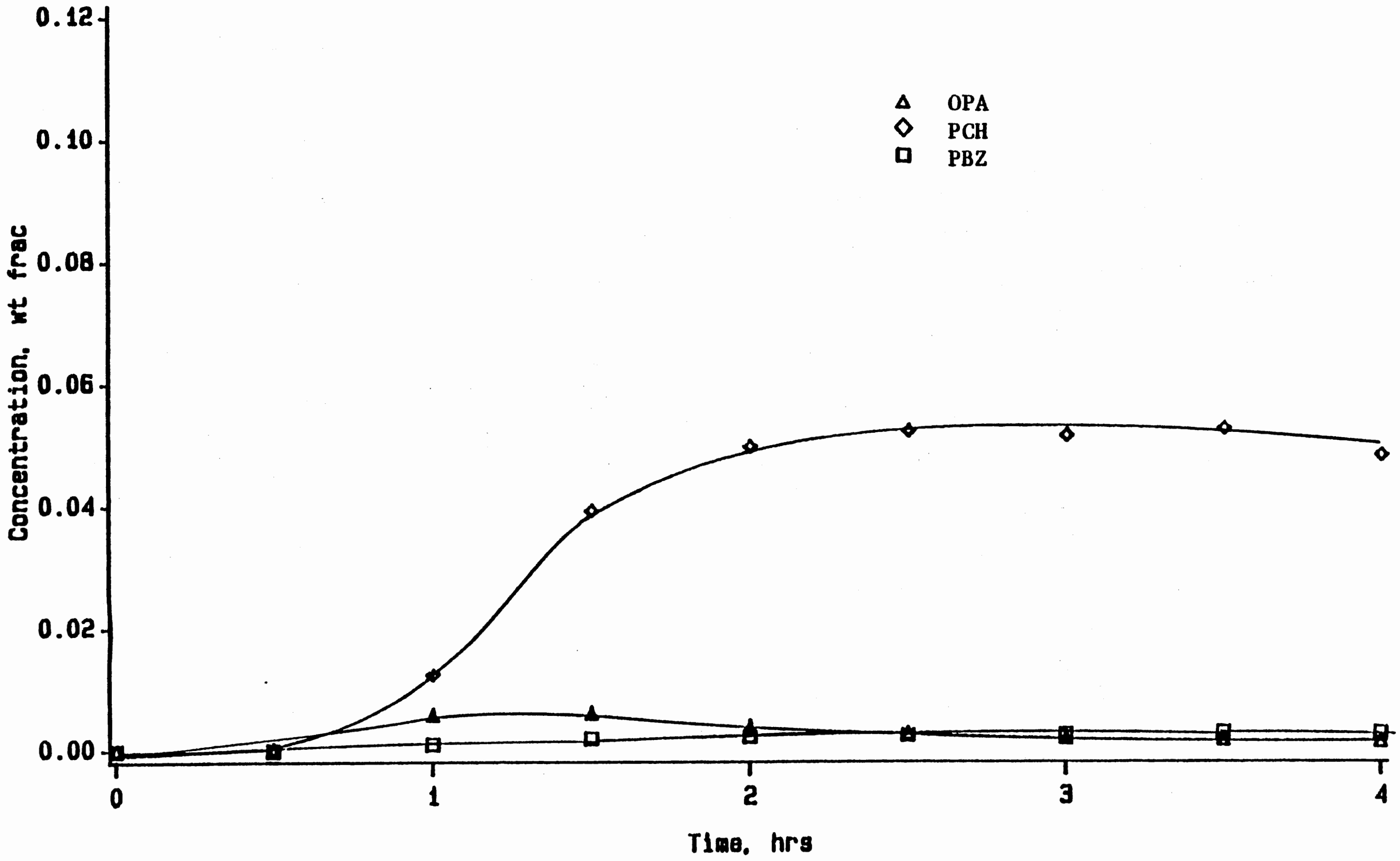


Figure 17(b). HDN Products of Quinoline Feed
(91.2 ml/hr, Run QA-6)

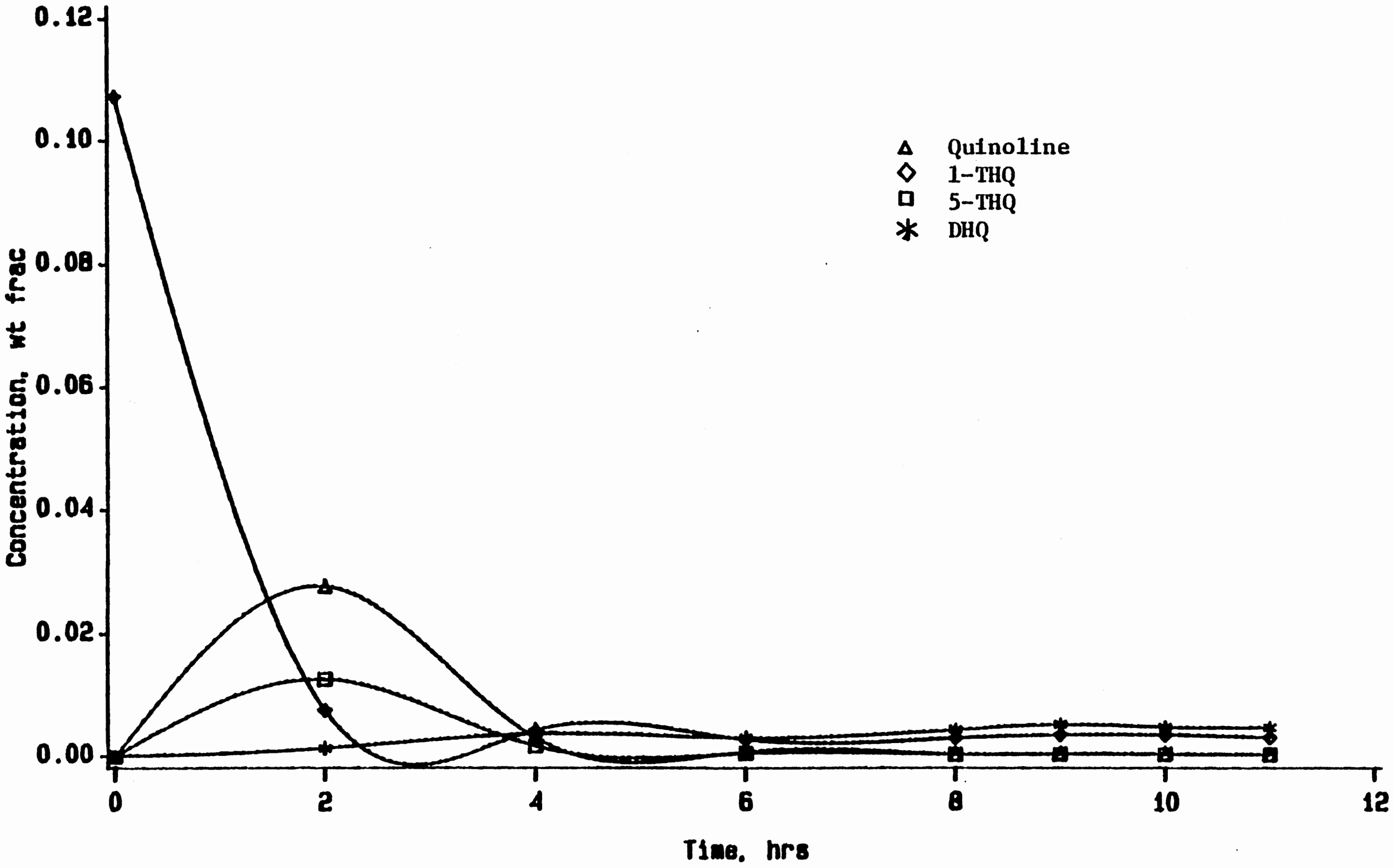


Figure 18(a). HDN Products of 1-THQ Feed
(34.6 ml/hr, Run 1THQ-6)

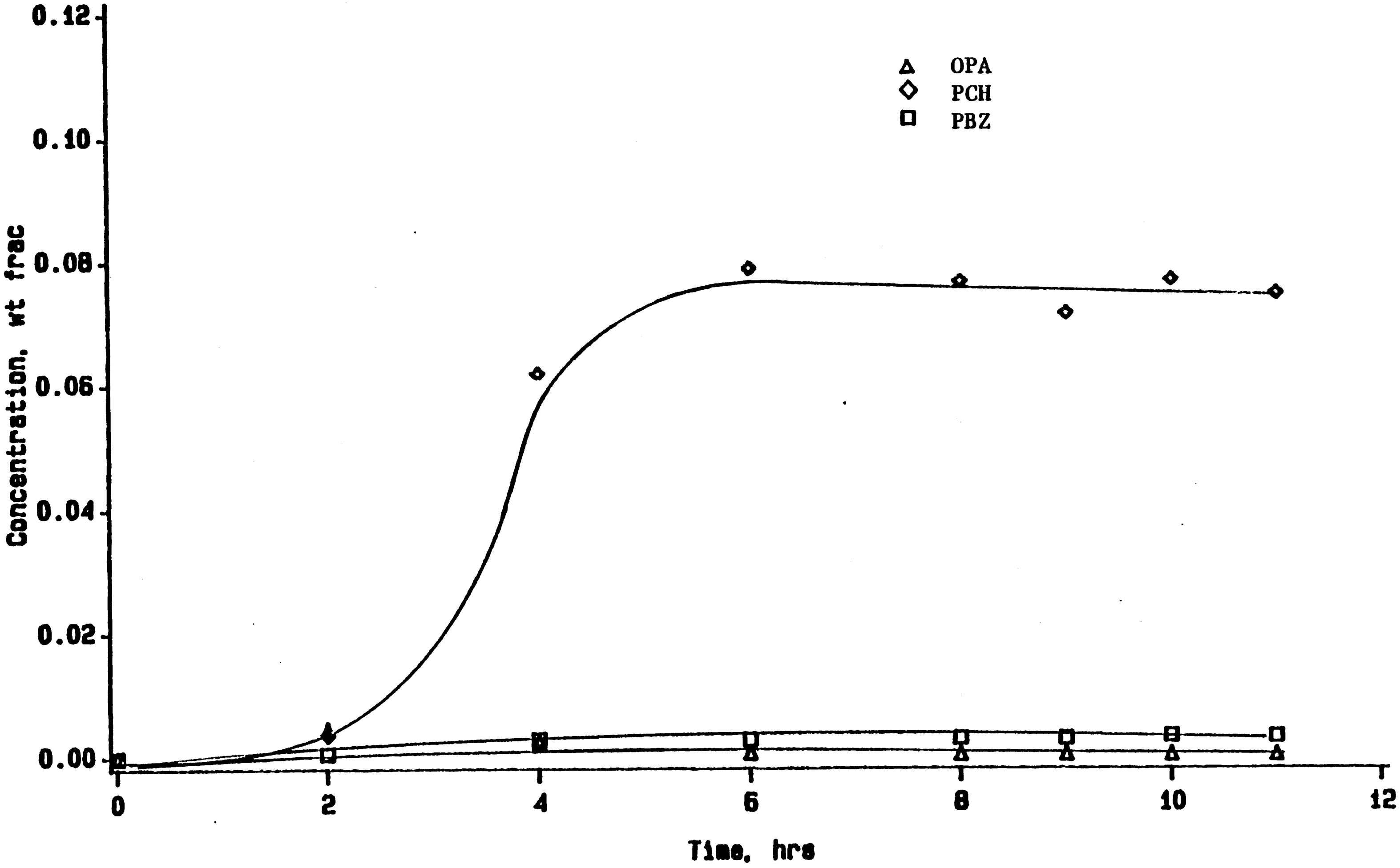


Figure 18(b). HDN Products of 1-THQ Feed
(34.6 ml/hr, Run 1THQ-6)

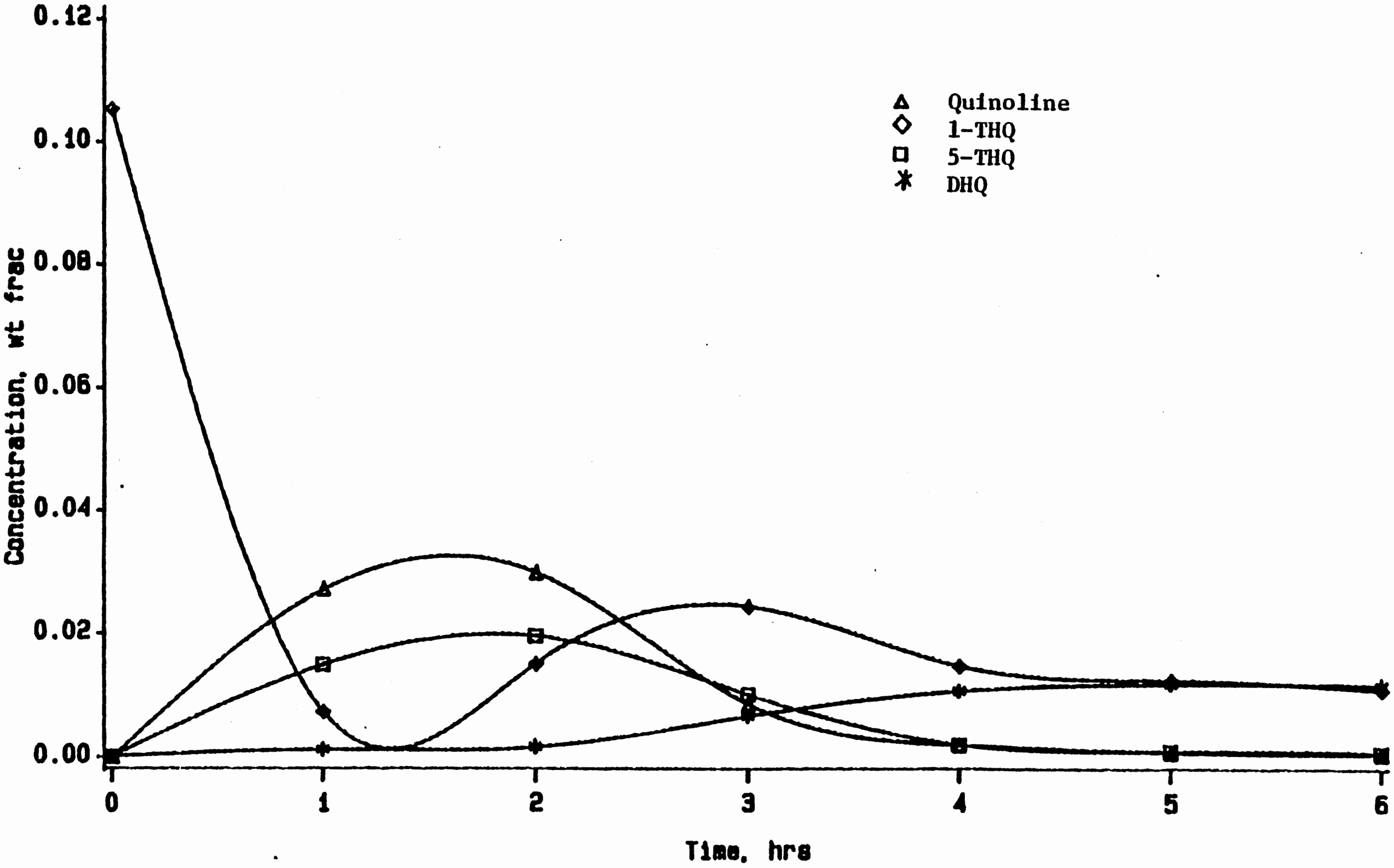


Figure 19(a). HDN Products of 1-THQ Feed
(63.0 ml/hr, Run 1THQ-7)

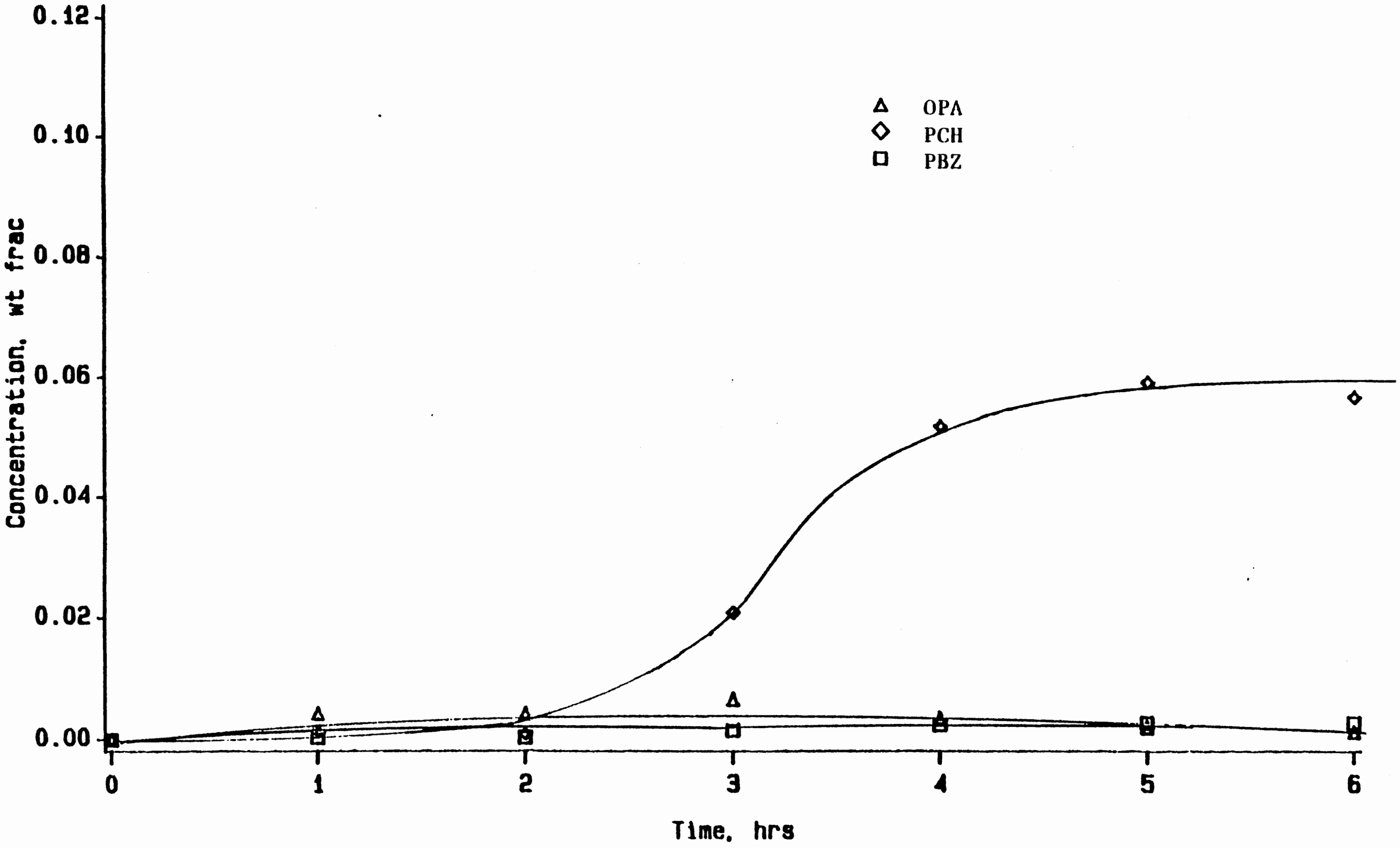


Figure 19(b). HDN Products of 1-THQ Feed
(63.0 ml/hr, Run 1THQ-7)

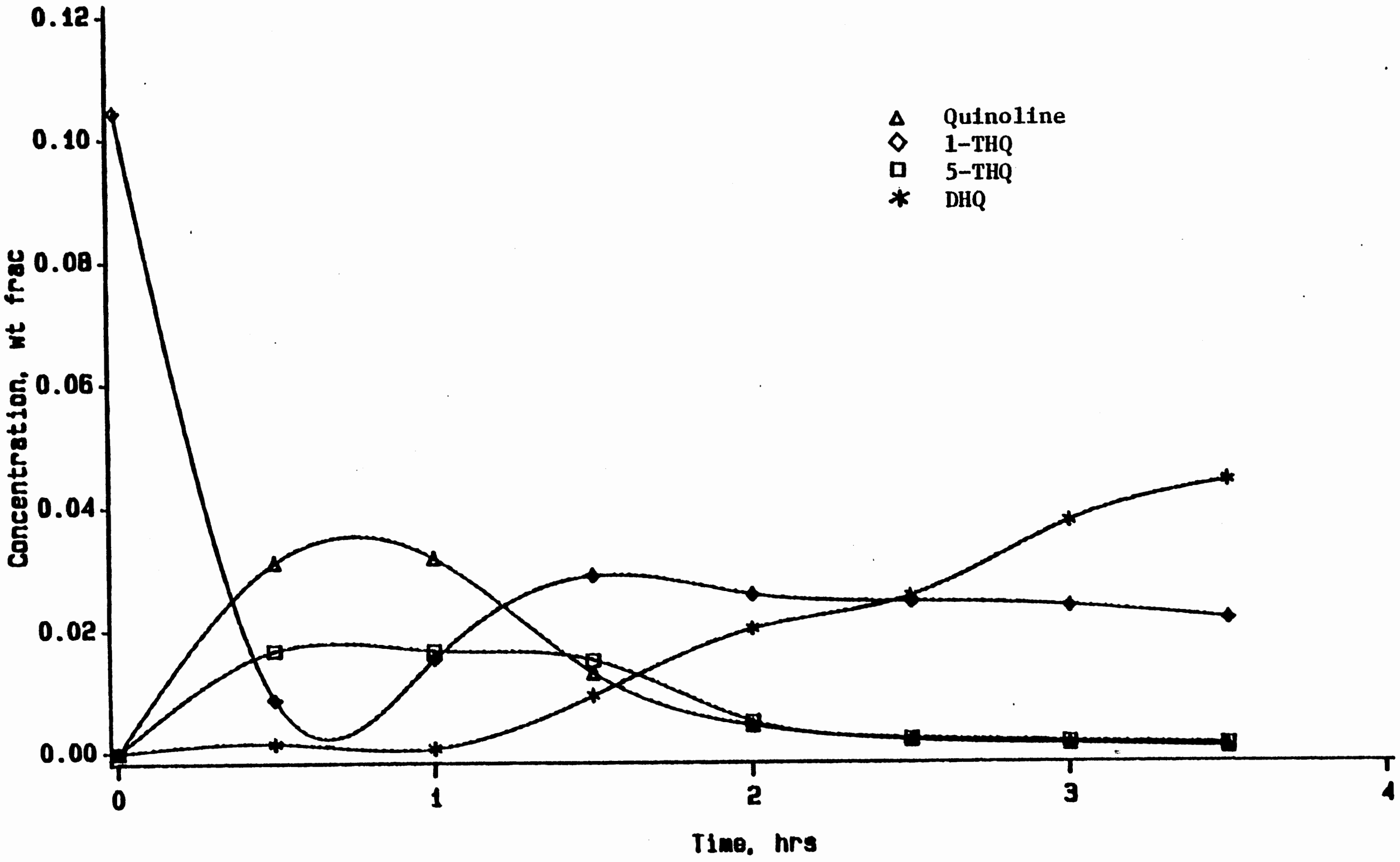


Figure 20(a). HDN Products of 1-THQ Feed
(94.0 ml/hr, Run 1THQ-8)

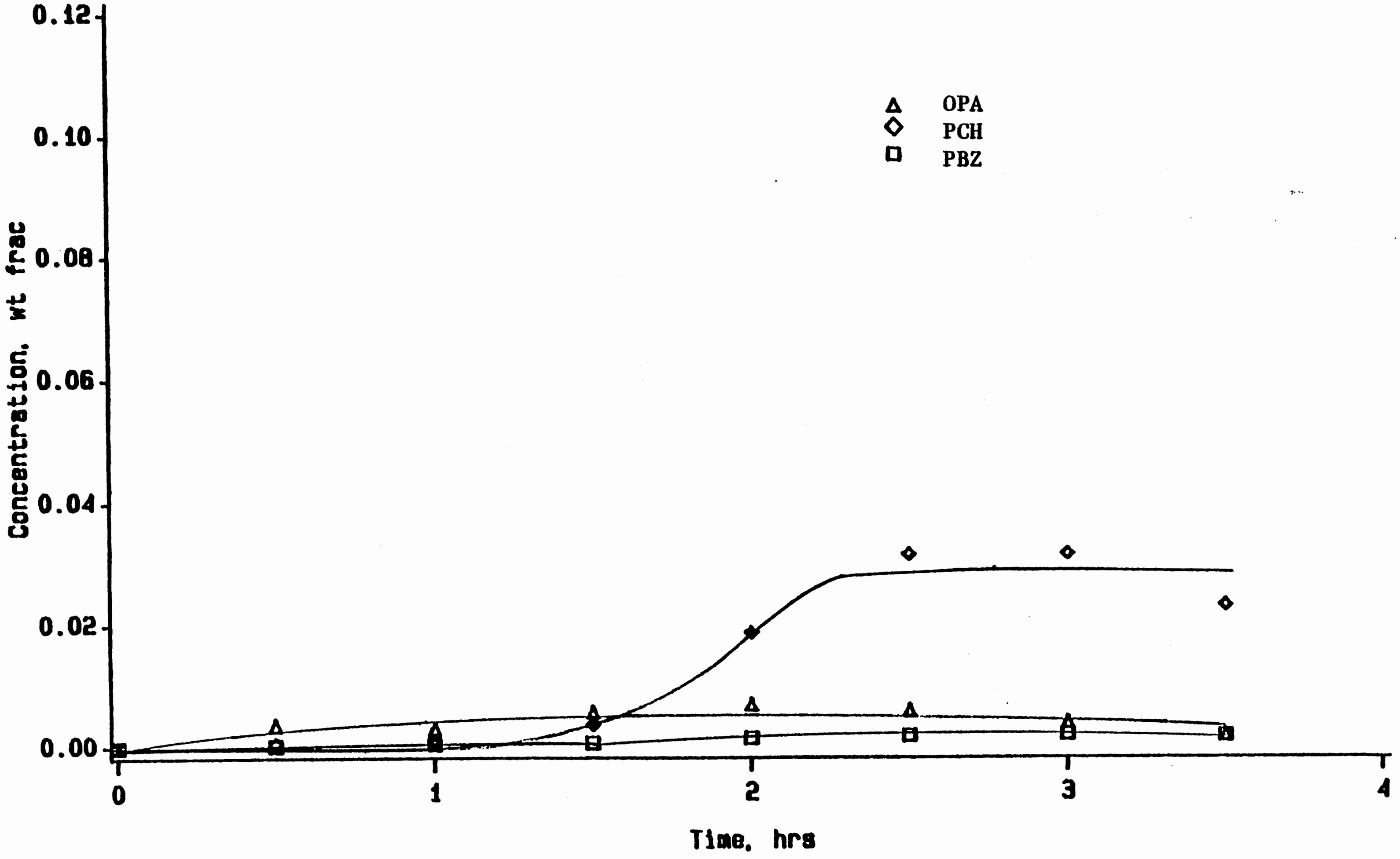


Figure 20(b). HDN Products of 1-THQ Feed
(94.0 ml/hr, Run 1THQ-8)

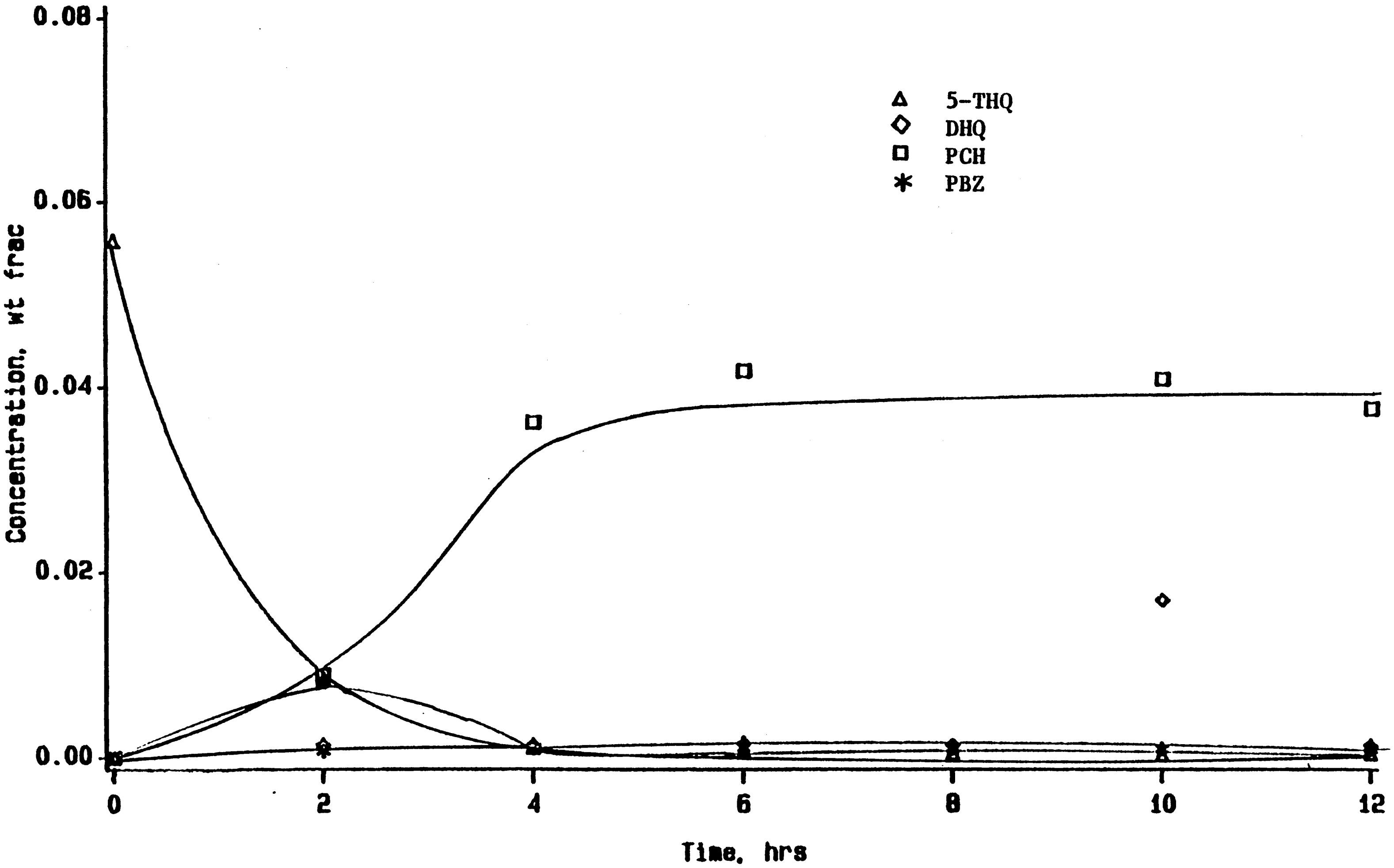


Figure 21. HDN Products of 5-THQ Feed
(28.5 ml/hr, Run 5THQ-1)

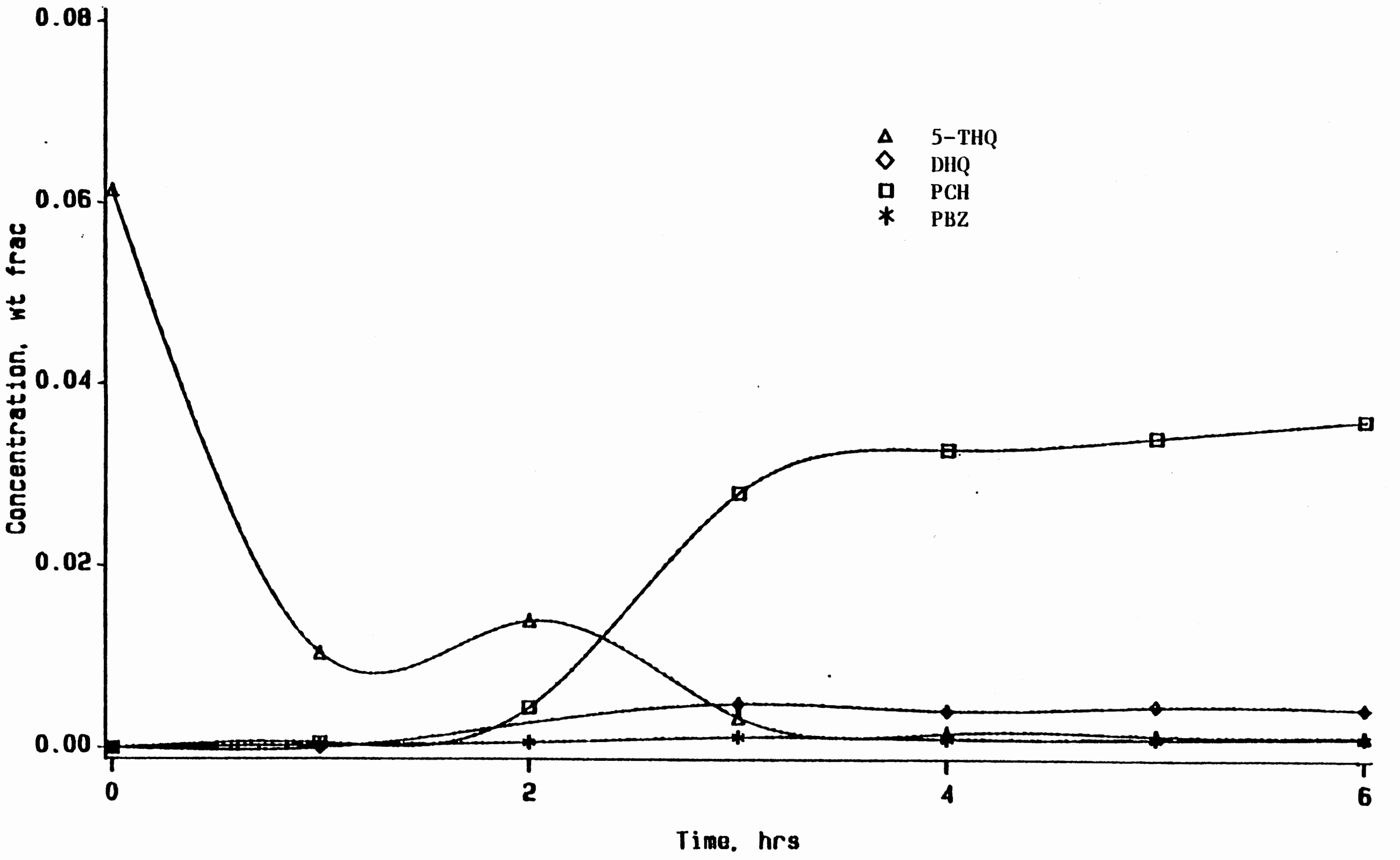


Figure 22. HDN Products of 5-THQ Feed
(62.7 ml/hr, Run 5THQ-2)

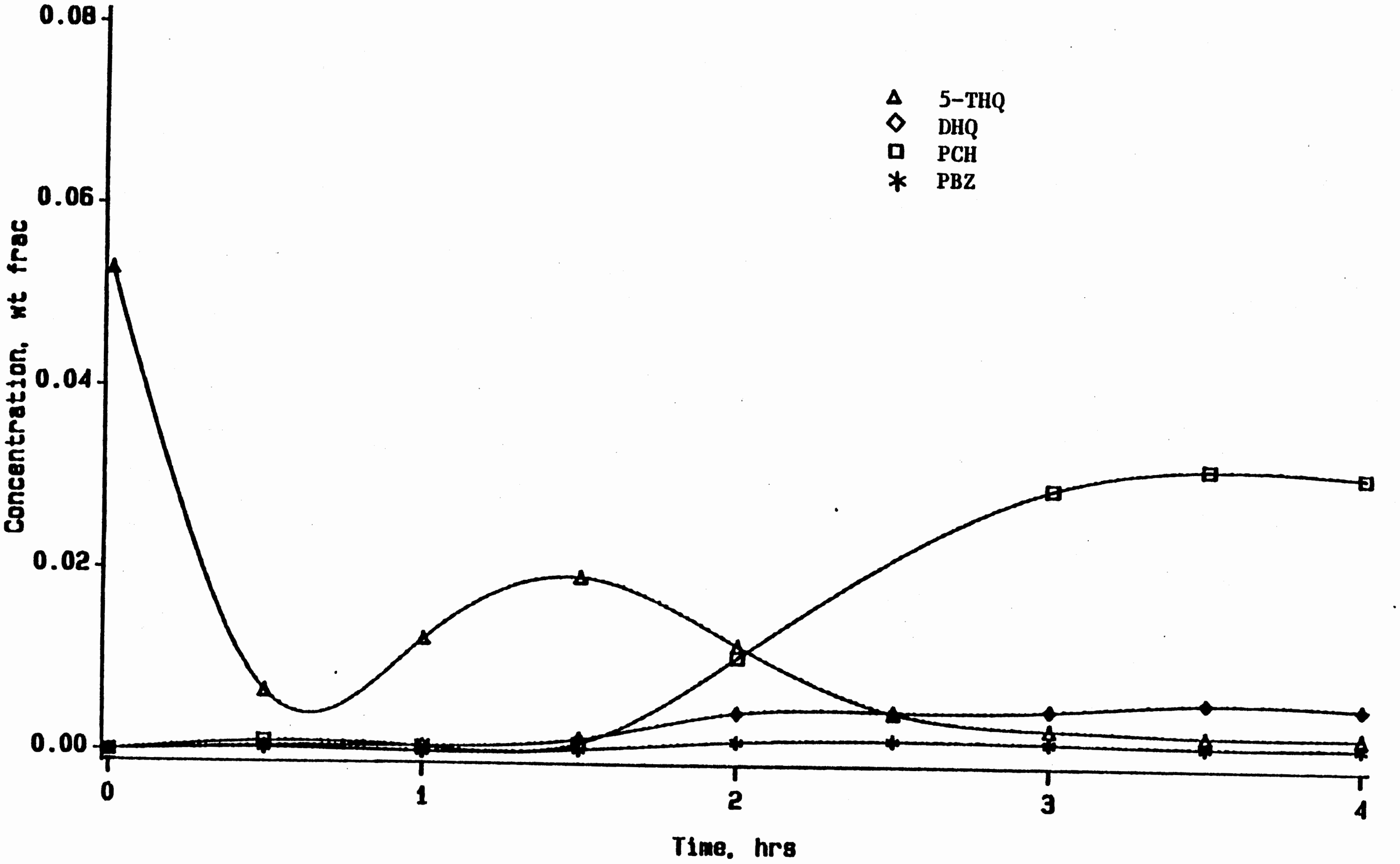


Figure 23. HDN Products of 5-THQ Feed
(96.7 ml/hr, Run 5THQ-3)

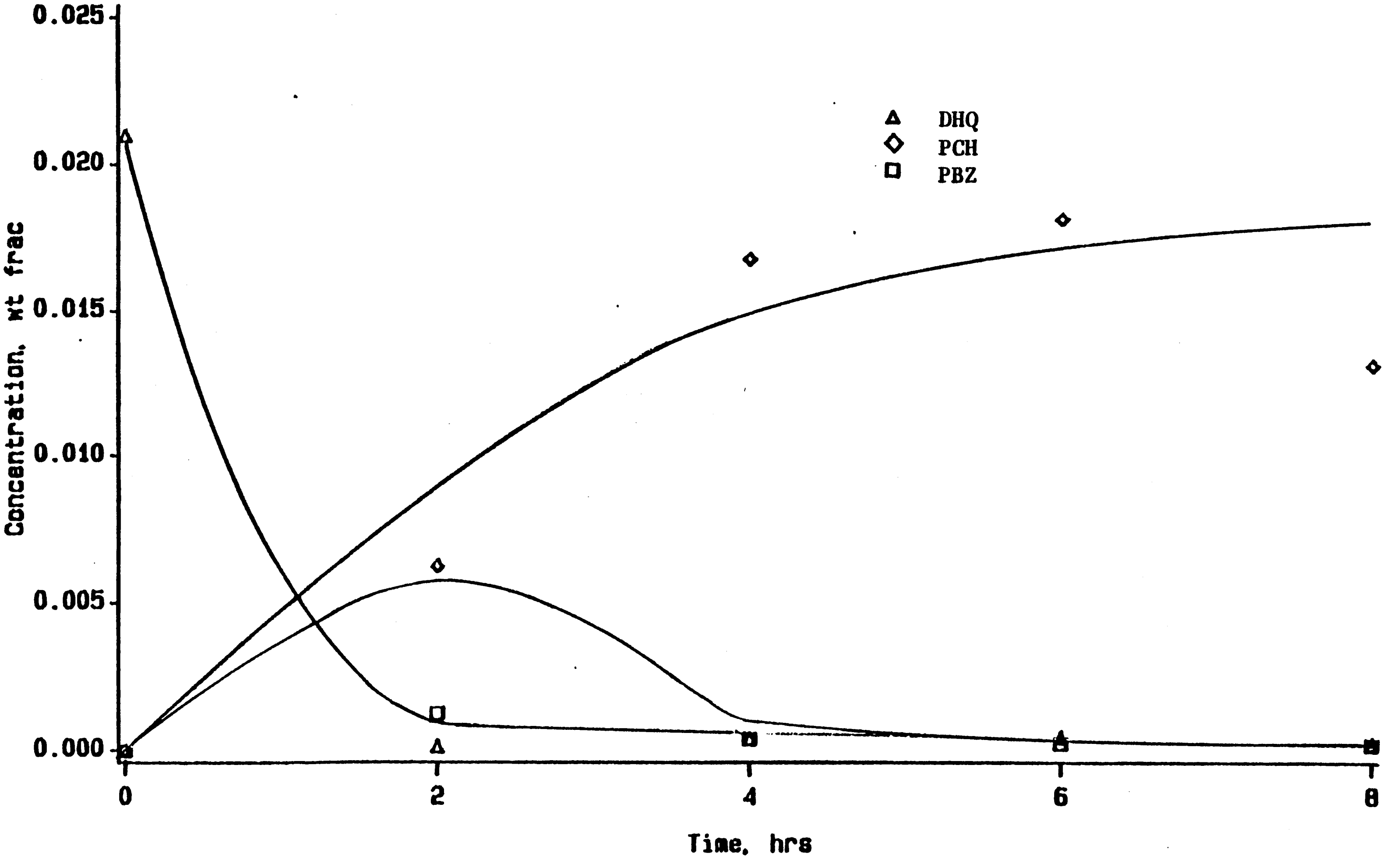


Figure 24. HDN Products of DHQ Feed
(27.25 ml/hr, Run DHQ-1)

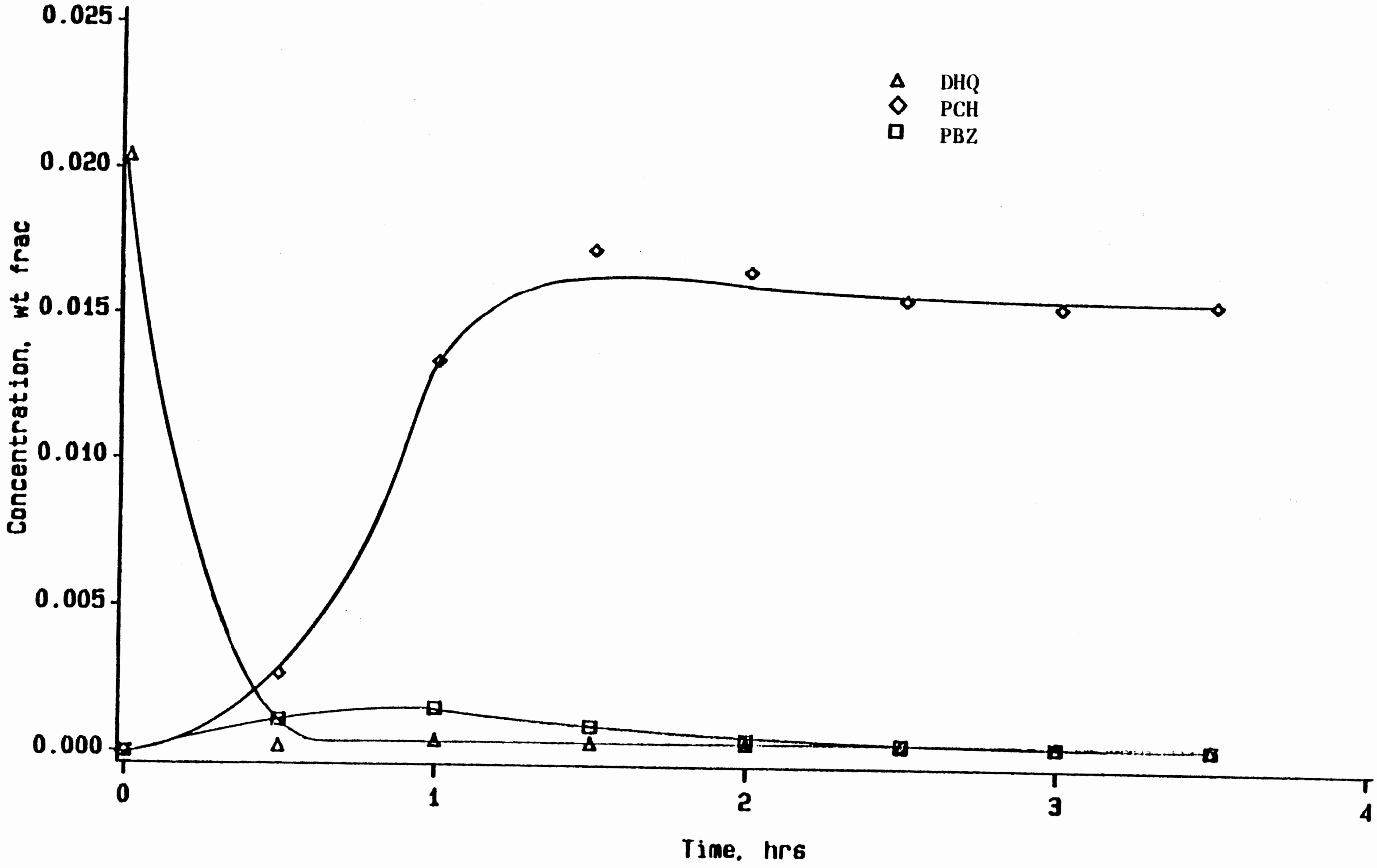


Figure 25. HDN Products of DHQ Feed
(98.0 ml/hr, Run DHQ-2)

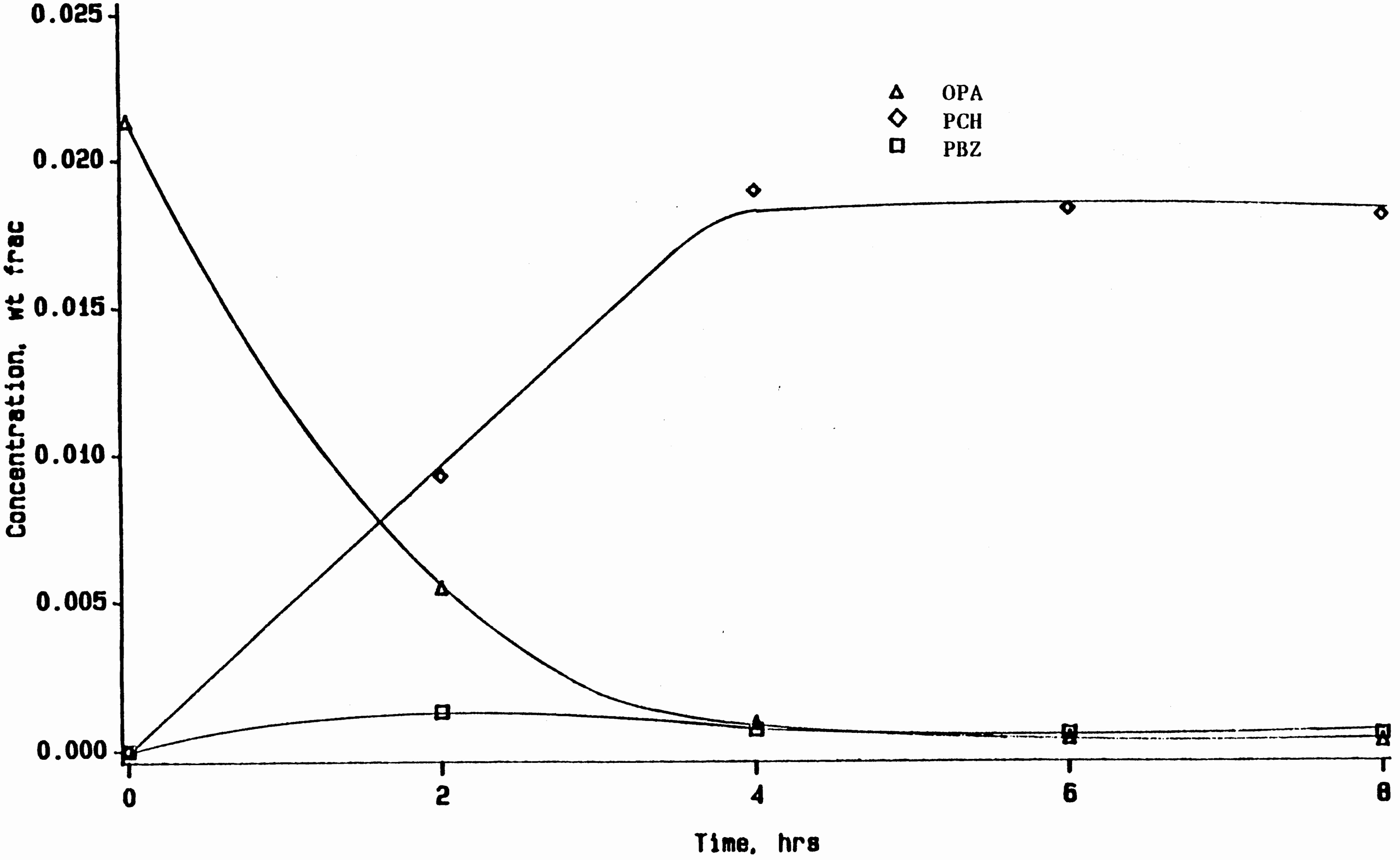


Figure 26. HDN Products of OPA Feed
(31.0 ml/hr, Run OPA-1)

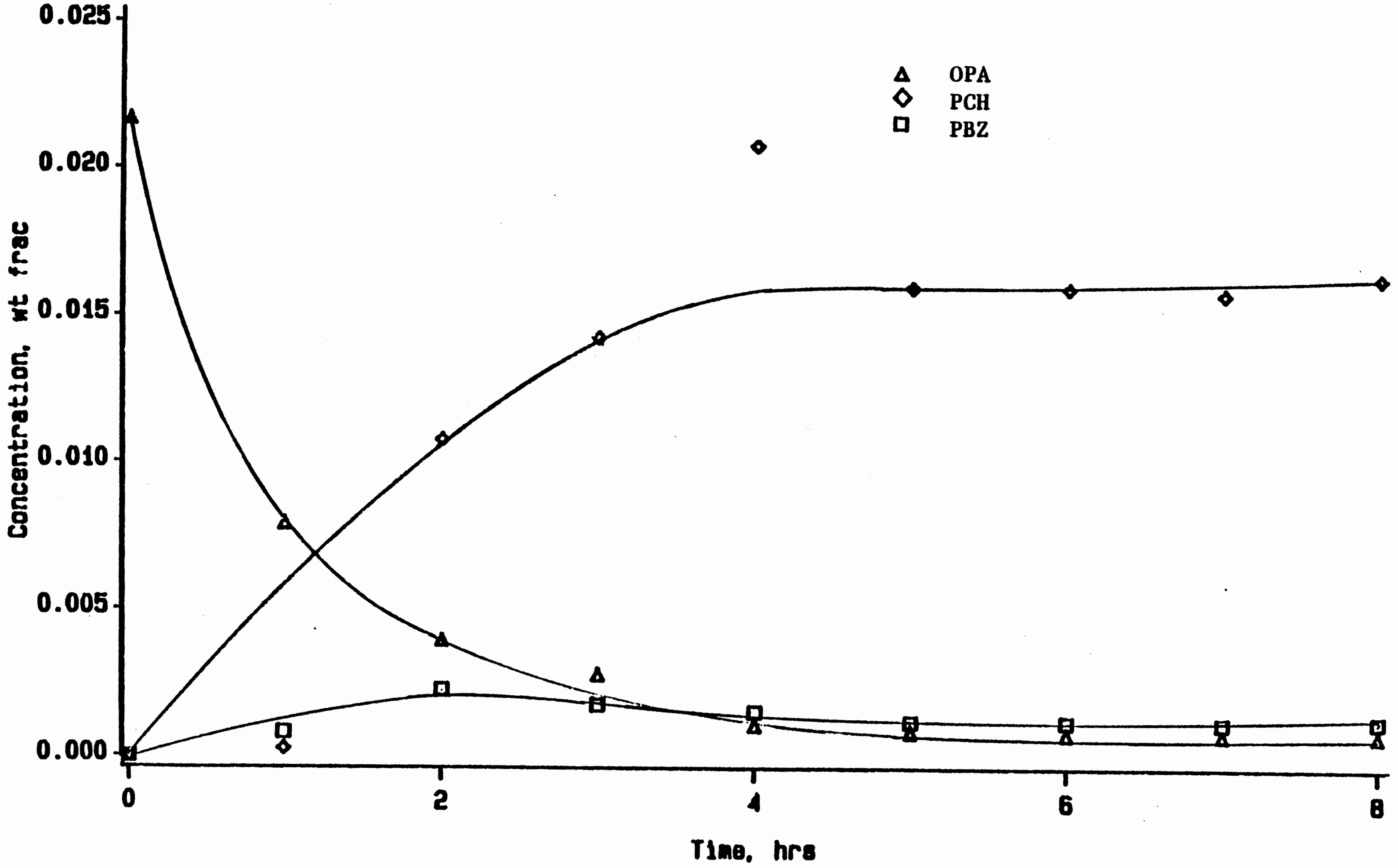


Figure 27. HDN Products of OPA Feed
(59.0 ml/hr, Run OPA-2)

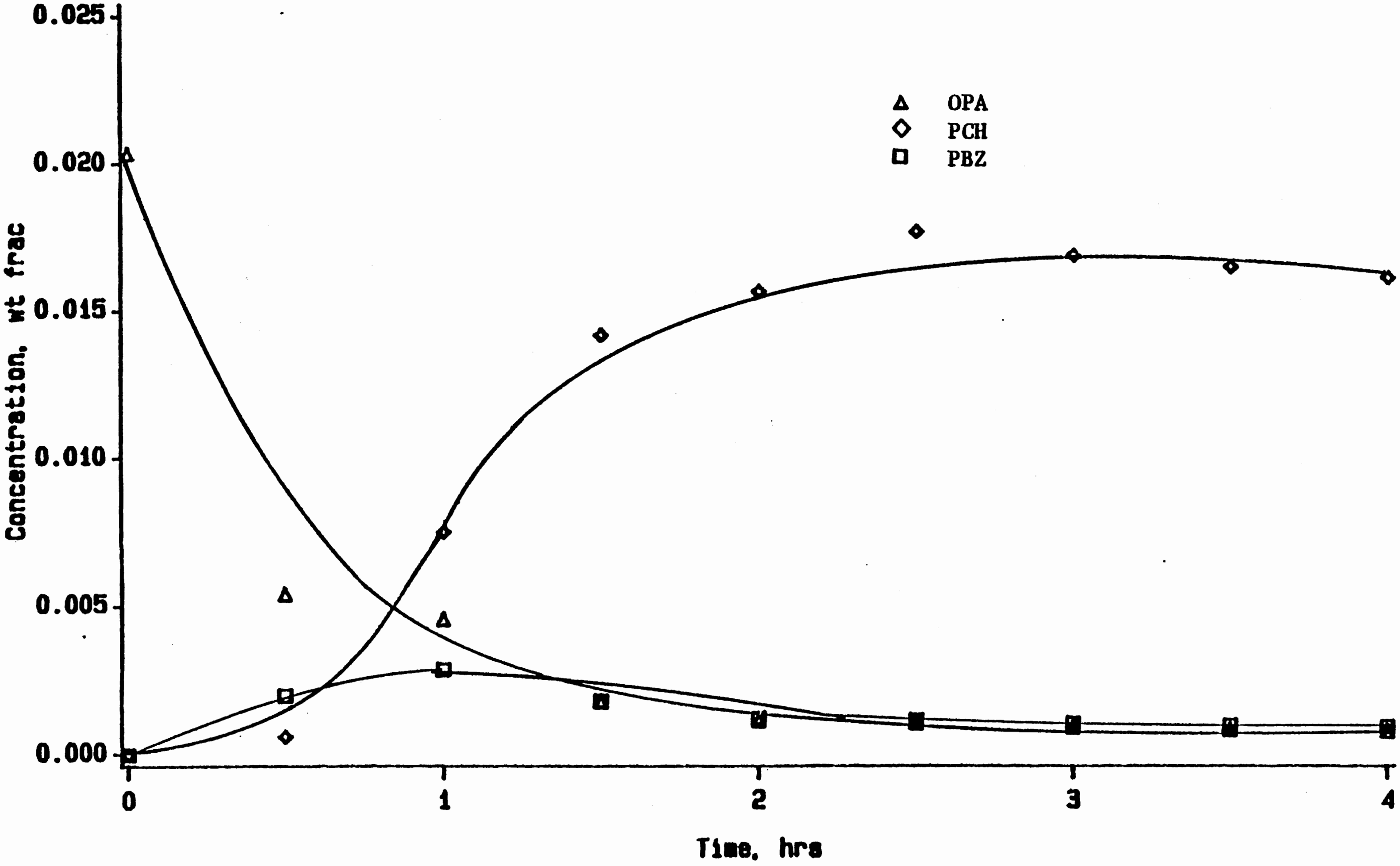


Figure 28. HDN Products of OPA Feed
(93.3 ml/hr, Run OPA-3)

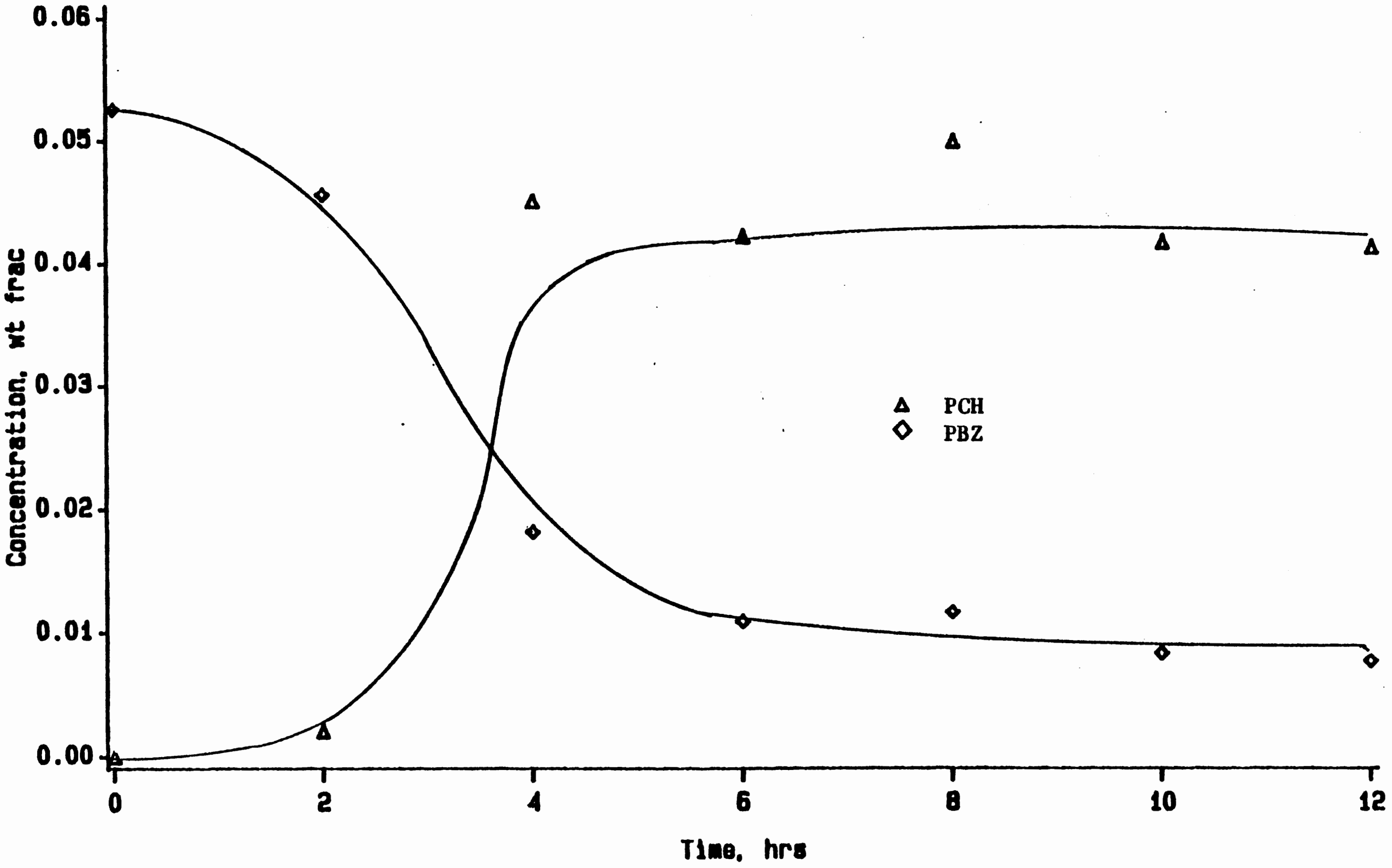


Figure 29. HDN Products of PBZ Feed
(32.6 ml/hr, Run PBZ-1)

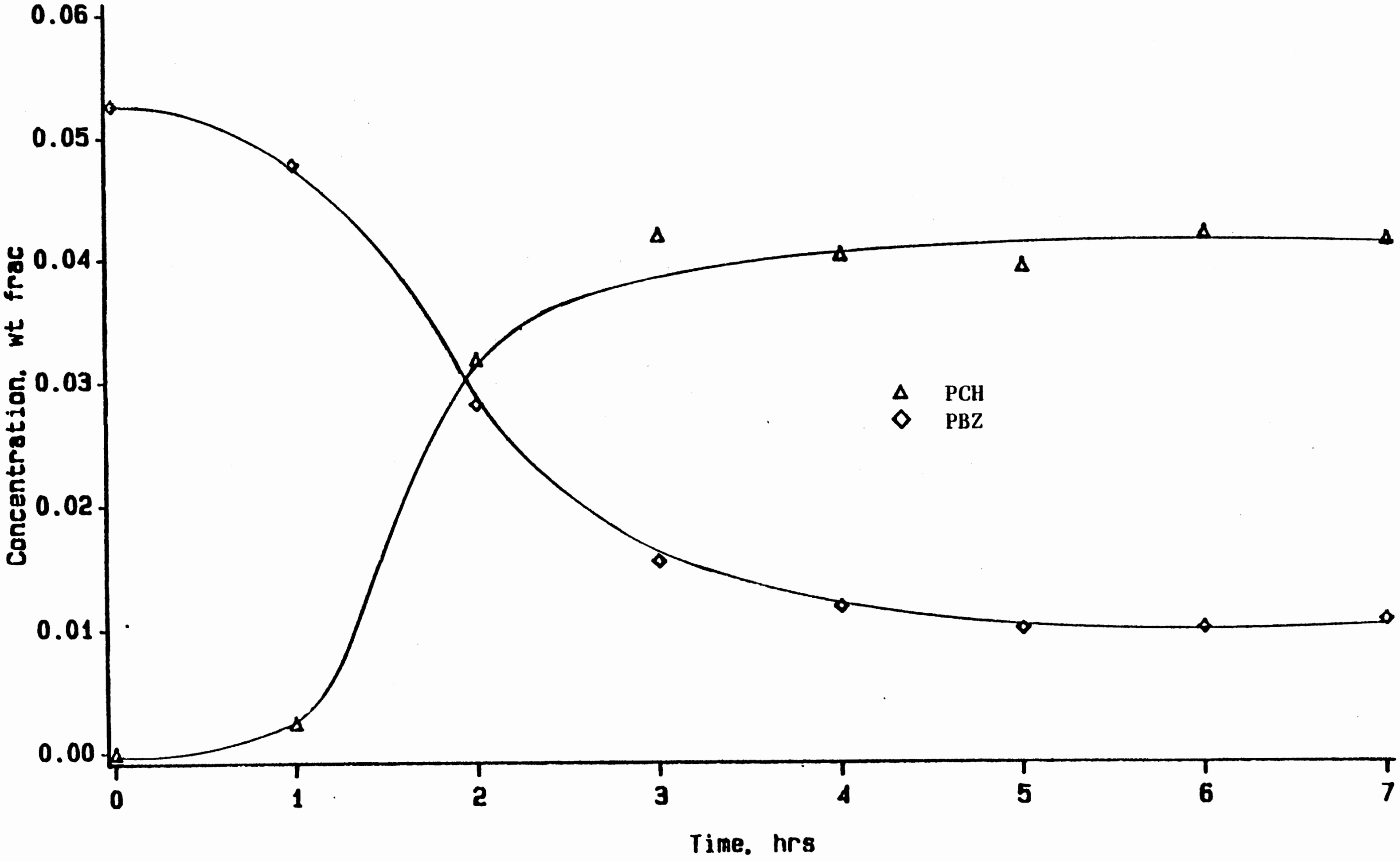


Figure 30. HDN Products of PBZ Feed
(60.0 ml/hr, Run PBZ-2)

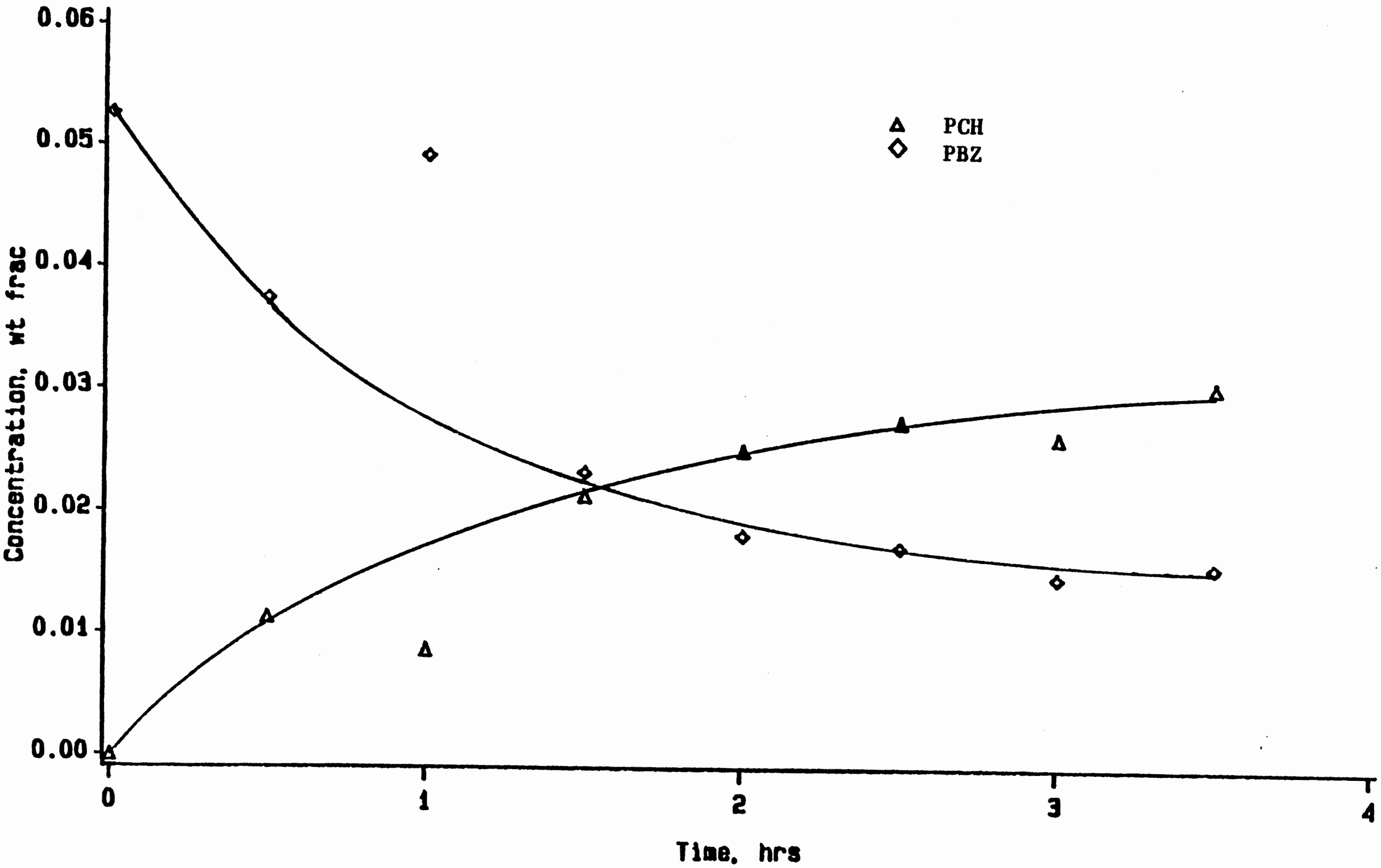


Figure 31. HDN Products of PBZ Feed
(95.5 ml/hr, Run PBZ-3)

ter. The estimation of experimental errors is included as part of Appendix C. The greatest error in calculating concentrations comes from GC analysis. The errors for obtaining flow rates and reaction rates were estimated to be 5.0% and 5.5% respectively.

Analyses of Coke Laydown on Catalyst

The amounts of coke on the surfaces of the used catalysts were analyzed as discussed in the previous chapter. Table IX presents the data by the feed compounds used for each run. It can be generally seen that the amount of coke did not vary much when the nitrogen compounds were used as the feed compound except when DHQ was used. The coking levels from DHQ runs were comparable to those from PCH and PBZ runs. DHQ molecules could be adsorbing at lower amounts than other nitrogen compounds to account for the lower level of coking. Indeed, when the adsorption constants were estimated from the adsorption data, as will be discussed in the next chapter, this was found to be the case. The adsorption constant for DHQ was 0.1 while the values for other nitrogen compounds ranged from 9.0 to 80.

Analyses of Catalyst Characteristics

The measured surface area and pore volume for fresh catalyst did not vary much from the numbers supplied to us by the vendor. The surface area and the pore volumes of the used catalysts were measured both before decoking and after

TABALE IX

LIST OF COKE ANALYSIS

Run no.	Feed Compound	Analysis #1	Analysis #2	Analysis #3	Average
		(% of coke on catalysts)			
Feed - Quinoline					
QA-3	Quinoline	28.0	26.00	25.84	26.61
QA-4	Quinoline	13.8	12.84	13.02	13.22
OA-5	Quinoline	15.6	14.63	14.66	14.96
QA-6	Quinoline	12.7	12.44	13.28	12.78
QA-7	Quinoline	14.08	13.12	14.47	13.89
QA-8	Quinoline	13.48	13.23	13.98	13.56
Feed - 1,2,3,4 Tetrahydroquinoline					
1THQ-2	1-THQ	15.1	14.27	14.39	14.59
1THQ-3	1-THQ	13.4	12.93	12.73	13.02
1THQ-4	1-THQ	17.62	16.58	17.80	17.33
1THQ-5	1-THQ	14.0	13.06	13.42	13.49
1THQ-6	1-THQ	11.48	11.1	12.18	11.59
1THQ-7	1-THQ	13.82	13.37	14.35	13.85
1THQ-8	1-THQ	15.24	14.82	16.22	15.42
1THQ-9	1-THQ	13.47	12.98	14.04	13.50

TABLE IX (Continued)

Run no.	Feed Compound	Analysis #1	Analysis #2	Analysis #3	Average
		(% of coke on catalysts)			
Feed - 5,6,7,8 Tetrahydroquinoline					
5THQ-1	5-THQ	12.4	11.97	11.99	12.12
5THQ-2	5-THQ	13.76	13.26	14.56	13.86
5THQ-3	5-THQ	14.22	14.13	14.92	14.42
5THQ-4	5-THQ	14.37	14.06	15.41	14.61
Feed - Decahydroquinoline					
DHQ-1	DHQ	12.8	12.32	12.50	12.54
DHQ-2	DHQ	12.0	10.93	11.02	11.32
DHQ-4	DHQ	11.98	11.52	12.82	12.11
Feed - o-Propylaniline					
OPA-1	OPA	13.6	12.49	12.64	12.91
OPA-2	OPA	13.9	13.21	13.10	13.4
OPA-3	OPA	12.2	12.16	12.2	12.19
OPA-4	OPA	12.9	12.53	13.55	12.99
Feed - o-Ethylaniline					
OEA-1	OEA	15.5	14.44	14.52	14.82
OEA-2	OEA	12.41	11.85	13.08	12.45
Feed - Propylbenzene					
PBZ-1	P-Benzene	12.2	11.38	11.51	11.70

TABLE IX (Continued)

Run no.	Feed Compound	Analysis #1	Analysis #2	Analysis #3	Average
PBZ-2	P-Benzene	11.70	11.3	12.39	11.80
PBZ-3	P-Benzene	12.3	11.72	11.50	11.84
Feed - Propylcyclohexane					
PCH-1	P-Cyclohex	11.0	9.84	10.03	10.29
Other miscellanious runs					
HEX-1	none	12.1	10.76	10.82	11.23
HEX-2	none	13.6	14.30	14.13	14.01
HEX-3	none	11.1	10.82	10.60	10.84

decoking, and the results are presented in Table X. The measurements marked HDN 60(1)-(3) are the values for the fresh catalyst. The surface area of the used catalyst as measured before decoking decreased somewhat from the value of the fresh catalysts but not to any great extent. The pore volume decreased significantly, which indicated the pore mouth plugging by the coking materials. When the catalysts were analyzed after decoking, even though the pore volume was regained to that for the fresh catalysts, the surface area decreased sharply to two thirds of the original catalysts. The process of decoking apparently changed the catalyst pore shape by increasing the average diameter of the pores, which would result in the decrease of the surface area while the pore volume remained constant. Thess data negate the possibility of regenerating hydrotreatment catalysts by simply decoking the catalysts. Some other non-destructive ways need to be found.

TABLE X

SURFACE ANALYSIS OF CATALYSTS

Run no.	Before decoking		After decoking	
	Pore Vol. (ml/g)	Surf. Area (m^2/g)	Pore Vol. (ml/g)	Surf. Area (m^2/g)
Fresh Catalyst				
HDN-60 (1)	0.41	195		
HDN-60 (2)	0.43	202		
HDN-60 (3)	0.41	196		
Feed - Quinoline				
QA-3	0.22	123	0.39	108
QA-4	0.31	165	0.38	135
OA-5	0.26	156	0.43	116
QA-6	0.29	160	0.41	118
QA-7	0.24	140	0.42	115
QA-8	0.27	158	0.41	161
Feed - 1,2,3,4 Tetrahydroquinoline				
1THQ-2	0.30	153	0.40	134
1THQ-3	0.33	175	0.42	141
1THQ-4	0.24	142	0.41	164
1THQ-5	0.29	169	0.42	116
1THQ-6	0.31	164	0.41	164
1THQ-7	0.26	137	0.41	160

TABLE X (Continued)

Run no.	Before decoking		After decoking	
	Pore Vol. (ml/g)	Surf. Area (m^2/g)	Pore Vol. (ml/g)	Surf. Area (m^2/g)
1THQ-8	0.28	149	0.38	166
1THQ-9	0.27	152	0.39	162
Feed - 5,6,7,8 Tetrahydroquinoline				
5THQ-1	0.33	174	0.41	114
5THQ-2	0.28	146	0.40	165
5THQ-3	0.26	147	0.41	121
5THQ-4	0.28	158	0.40	111
Feed - Decahydroquinoline				
DHQ-1	0.31	161	0.41	123
DHQ-2	0.32	163	0.41	112
DHQ-4	0.29	158	0.42	159
Feed - o-Propylaniline				
OPA-1	0.31	174	0.42	134
OPA-2	0.31	157	0.40	144
OPA-3	0.31	164	0.42	115
OPA-4	0.31	166	0.40	120
Feed - o-Ethylaniline				
OEA-1	0.31	155	0.41	109
OEA-2	0.32	173	0.44	184

TABLE X (Continued)

Run no.	Before decoking Pore Vol. (ml/g)	Surf. Area (m^2/g)	After decoking Pore Vol. (ml/g)	Surf. Area (m^2/g)
Feed - Propylbenzene				
PBZ-1	0.32	167	0.43	132
PBZ-2	0.33	172	0.41	166
PBZ-3	0.29	174	0.42	136
Feed - Propylcyclohexane				
PCH-1	0.33	172	0.41	115
Feed - n-Hexadecane (solvent)				
HEX-1	0.33	174	0.41	120
HEX-2	0.33	161	0.41	116
HEX-3	0.33	171	0.41	115

CHAPTER V

DISCUSSION OF RESULTS

Evaluation of the experimental data and interpretation of the results have been performed by formulating mathematical models for the adsorption and for the reaction network. The adsorption data were of two types as discussed in the previous chapter. Quinoline and OPA resulted in single component adsorption behavior while the hydrogenated compounds resulted in multicomponent adsorption behavior. The reaction rate data were analyzed by formulating a linear system of equations. This was possible only because the adsorption constants were estimated separately and the type of the reactor used in this work resulted in the direct measurement of the reaction rate of each individual component. The reaction network of quinoline HDN will be discussed first; then the results from the analyses of the adsorption and the kinetic data will be reported.

Reaction Network of Quinoline HDN

Many of the previous investigators of quinoline HDN have published varying reaction networks for this reaction. The most recent one has been by El-Bishtawi (1986), whose model was introduced earlier in Figure 3, Chapter 2. There are general agreements among the investigators on the existence of the major intermediate compounds in quinoline HDN. However, several different major paths of quinoline HDN have been reported along with different minor by-products by various investigators. The reaction network formulated from this study is shown in Figure 32. Investigators generally agree on the existence of 1-THQ, 5-THQ, DHQ, OPA, PBZ and PCH. From the data obtained in this study, it was observed that quinoline was more easily converted to 1-THQ than 5-THQ. In fact, it was first thought that the step between quinoline and 5-THQ did not exist and 5-THQ was produced from the dehydrogenation of DHQ. But when 5-THQ was used for the adsorption studies, the formation of quinoline from the dehydrogenation of 5-THQ was detected which, proved the existence of the step between quinoline and 5-THQ. Also 5-THQ proceeded to form DHQ, which in turn formed PCH.

When 1-THQ is formed, it can either undergo hydrogenation to form DHQ or undergo hydrogenolysis of the saturated ring to form OPA, which subsequently proceeds to form PBZ after denitrogenation. The reaction network discussed so far is generally agreed upon by all of the previous investigators. From this study, the rate for the reversible step between 1-THQ and DHQ is so low that this step is considered to be irreversible as indicated in Figure 32. This reaction network differs from El-Bishtawi's in another respect. No matter which nitrogen compound was used as the feed compound, PBZ and PCH were both detected. This leads us to

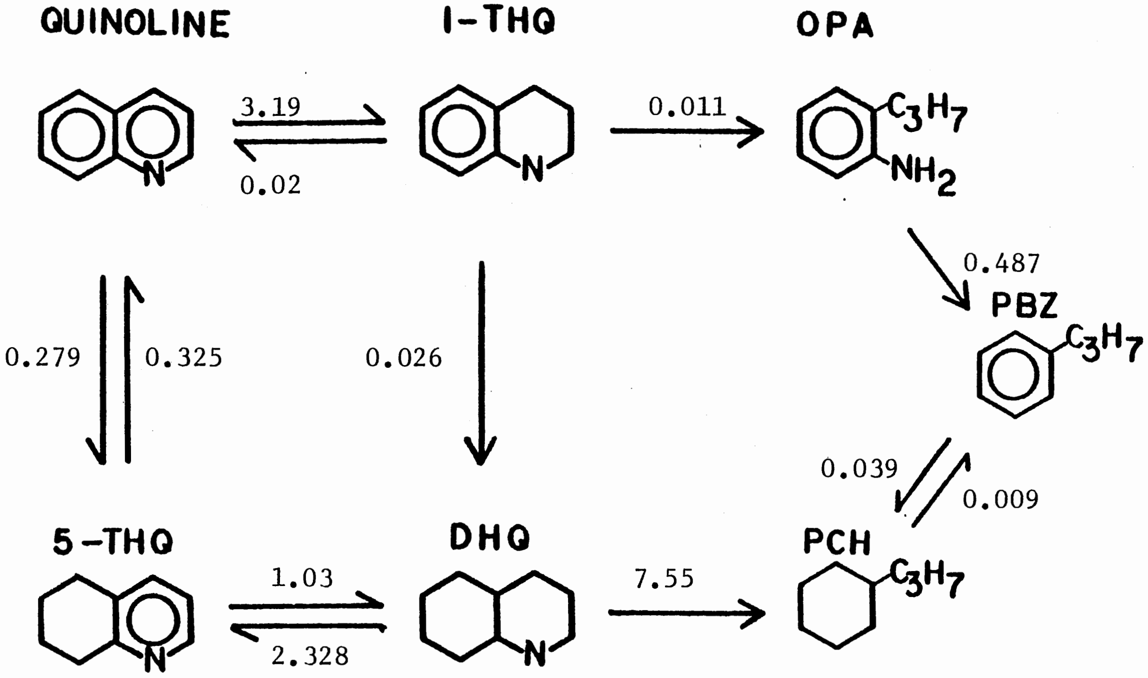


Figure 32. Proposed Quinoline HDN Network

believe that these two compounds readily convert to each other and the only limiting factor seems to be the thermodynamic equilibrium. Even when PBZ was used as the feed compound, the conversion of PBZ to PCH reached 84%. The step between PBZ and PCH cannot be ignored as was done by El-Bishtawi, Satterfield, and others. El-Bishtawi included in his reaction network some of the minor products: o-ethylaniline, o-methylaniline, and aniline. In this work, the produced concentrations of the minor products were so low that the formation of these compounds would not be of any significance in a continuous flow situation such as this work. Hence it was decided to ignore the steps leading to the formation of these minor products in this reaction network.

Discussion of Adsorption Model

A typical catalytic reaction model assumes Langmuir-Hinshelwood type with one of the reaction steps as being the rate controlling. As the name implies, Langmuir type adsorption is assumed for the adsorption of the reacting species onto the catalyst surface. Among all the assumptions involved with this model, the major ones are the monolayer adsorption, whether physical adsorption or chemisorption, and the equal strength of the sites. Then the following equation can be developed for single adsorbing species.

$$\theta = \frac{K_A C_A}{(1 + K_A C_A)} \qquad (3)$$

The adsorption constants for quinoline and OPA were calculated from this equation. To evaluate the adsorption constants from the experimental data for different concentrations of individual components, a least squares method needs to be used. The General Linear Model procedure available on SAS package was used to estimate the adsorption constants.

When the fluid phase contains multiple components competing for the same types of sites, the above equation cannot be used. If the number of available sites remains constant and can be estimated, then the following equation can be obtained after some derivation as will be discussed below.

$$\frac{\theta}{(1 - \theta)} = \sum_{i=1}^{n} K_i C_i \qquad (5)$$

where;

θ = fraction of covered sites

K_i = adsorption constant of component i

C_i = concentration of component i

If all of the intermediate nitrogen compounds are assumed to adsorb onto the same type of sites, then a competition between the compounds will occur and the amount adsorbed for individual compound will be determined by the strength of the adsorption of that compound. If the adsorption constants for the individual compounds do not vary with concentrations, then a straightforward model can be derived from assuming the Langmuir type of adsorption for each individual compound.

If there are n number of compounds competing for the same type of sites, then following equations can be set up:

$$r_{ads,1} = k_{ads,1}C_1(1-\theta) \tag{6.1}$$

$$r_{dsp,1} = k_{dsp,1}\theta W_1 \tag{7.1}$$

$$\vdots$$

$$r_{ads,n} = k_{ads,n}C_n(1-\theta) \tag{6.n}$$

$$r_{dsp,1} = k_{dsp,n}\theta W_n \tag{7.n}$$

where, $r_{ads,i}$ = adsorption rate of compound i

$r_{dsp,i}$ = desorption rate of compound i

$k_{ads,i}$ = rate constant for adsorption of i

$k_{dsp,i}$ = rate constant for desorption of i

C_i = concentration of i in fluid

W_i = fraction of i among total adosrbed molecules

When the adsorption reaches equilibrium,

$$r_{ads,1} = r_{dsp,1} \tag{8.1}$$

$$\vdots$$

$$r_{ads,n} = r_{dsp,n} \tag{8.n}$$

Then at equilibrium,

$$k_{ads,1}C_1(1-\theta) = k_{dsp,1}\theta W_1 \qquad (9.1)$$

$$\vdots$$

$$k_{ads,n}C_n(1-\theta) = k_{dsp,n}\theta W_n \qquad (9.n)$$

Solving for W_i's from these equations,

$$\frac{K_1C_1(1-\theta)}{\theta} = W_1 \qquad (10.1)$$

$$\vdots$$

$$\frac{K_nC_n(1-\theta)}{\theta} = W_n \qquad (10.n)$$

where, $K_i = k_{ads,i}/k_{dsp,i}$

We also know that if the compounds are competing for the same types of sites:

$$W_1 + W_2 + \cdot\cdot\cdot\cdot + W_n = 1 \qquad (11)$$

Then,

$$\frac{K_1C_1(1-\theta)}{\theta} + \cdot\cdot\cdot\cdot + \frac{K_nC_n(1-\theta)}{\theta} = 1 \qquad (12)$$

Finally by factoring out the site terms,

$$\frac{\theta}{(1-\theta)} = K_1C_1 + \cdot\cdot\cdot + K_nC_n \qquad (13)$$

The above derivation contains a major assumption in addition to traditional Langmuir assumptions. It is assumed that the active adsorption sites are available in equal amounts to every individual compound. There are arguments for and against this assumption. There have been several investigations that have indicated that hydrogenation and hydrogenolysis sites are different. It is also known that there are both Bronsted and Lewis acid sites available on Ni-Mo catalysts, such as the one used in this project. However, the adsorption of nitrogen molecules seems to occur because of the basic nature of the molecules. If it can be assumed that the acid sites are available in equal probability to all of the nitrogen compounds, then the strength of individual adsorption will determine the amount of adsorption for the individual nitrogen compound.

When 1-THQ, 5-THQ, and DHQ were used as the feed compound in the adsorption experiments, multiple component systems developed while being equilibrated inside the reactor, as was discussed in previous chapter. This system resulted in a competitive adsorption situation described earlier. The multiple component data obtained from these runs were then analyzed using equation (5) to estimate the adsorption constants of 1-THQ, 5-THQ, and DHQ. The adsorption constants thus obtained for all of the nitrogen compounds are shown in Table XI. It can be seen that 1-THQ has the highest adsorption value and DHQ has the lowest value. This was unexpected because DHQ has the highest basicity value

TABLE XI

ADSORPTION CONSTANTS

Temperature	350 C
Pressure	10.34 MPa (1500 psi)
Catalyst	HDN-60
Compound	Adsorption Constant (mole fraction $^{-1}$)
Quinoline	18.3 ± 7.3
1,2.3.4-Tetrahydroquinoline	81.0 ± 11.4
5,6,7,8-Tetrahydroquinoline	3.4 ± 4.5
Decahydroquinoline	0.1 ± 3.2
o-Propylaniline	20.0 ± 3.6

while 1-THQ has an intermediate value as reported in Table I. The lower adsorptivity of DHQ was also confirmed from the coking results. There were lower amounts of coke deposited on the catalyst surface when DHQ was the feed compound, compared to when other nitrogen compounds were the feed compounds. In fact, the coking resulting from DHQ is comparable to those for PBZ and PCH. The standard deviations are also listed in Table XI. From these numbers it can be seen that the value for DHQ is also the least accurate one. This inaccuracy resulted from the fact that the outlet concentrations of DHQ were very low and the estimated adsorption varied significantly. When the values were plotted along with the ones reported by Nagai, et al., the values from this work did not correlate well with those of Nagai, et al. One of the major differences between the values was that the literature values were all obtained from fitting the data into kinetic models while the adsorption constants from this work were directly measured at the reaction conditions. From these values, 1-THQ appears to be the most poisonous compound of all of the intermediate compounds existing in the reaction network of quinoline HDN. It is shown in next section that the conversion of 1-THQ has the slowest rate among all the steps involved in quinoline HDN.

The adsorption constants were then used to predict the levels of adsorption and were compared with the actual data. Figure 33 presents the comparison for the runs with 1-THQ as

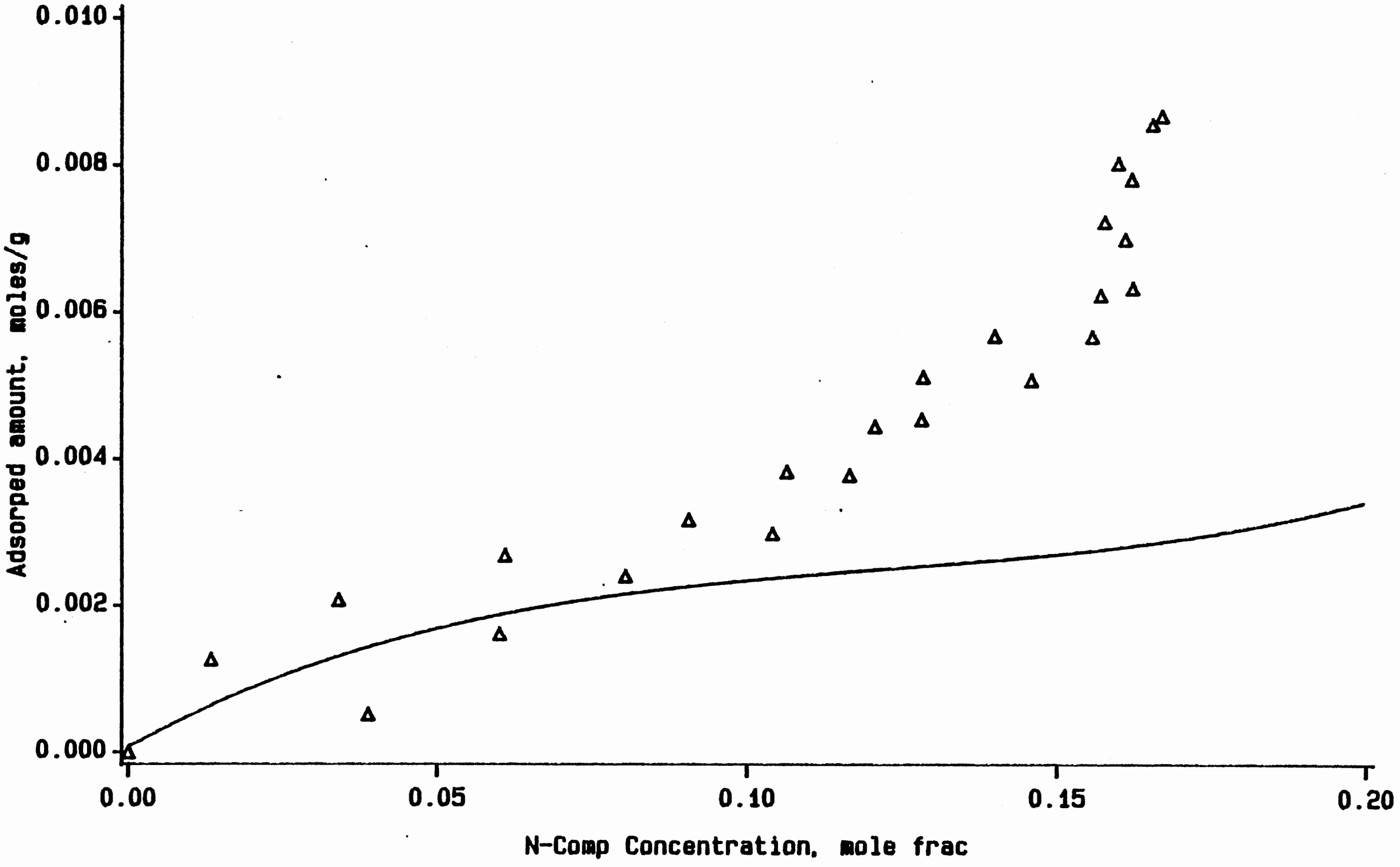


Figure 33. Comparison of Calculated and Actual Adsorption for 1-THQ Feed

the feed. It can be observed that the predicted adsorptions are substantially lower than the actual data at higher fluid concentrations. This occurs because the predictions are based on monolayer adsorption while a case can be made for multiple adsorption at higher concentrations. Figure 34 presents the comparison for the run with 5-THQ as the feed compound. The predictions are slightly higher at lower concentrations and lower at higher concentrations than the actual data. Figure 35 presents the comparison for the run with DHQ as the feed compound. It can be seen that the predictions agree very well with the actual data. It should be noted that the concentrations studied were smaller for this run than for 1-THQ or 5-THQ. It is expected that the actual concentrations of nitrogen compounds in coal liquid or shale oils are lower than these. Hence the adosrption constants obtained in this study could be applied with some confidence.

Discussion of Kinetic Modeling

One of the advantages of using the continuously stirred tank reactor (CSTR) to study a reaction system is that the reaction rate can be directly measured. In turn, the estimation of the rate constants can be performed easily without solving a series of differential equations as would be the case if the reactor is a batch or a plug flow type. The reaction rate of a compound in a CSTR reactor can be calculated from the following equation.

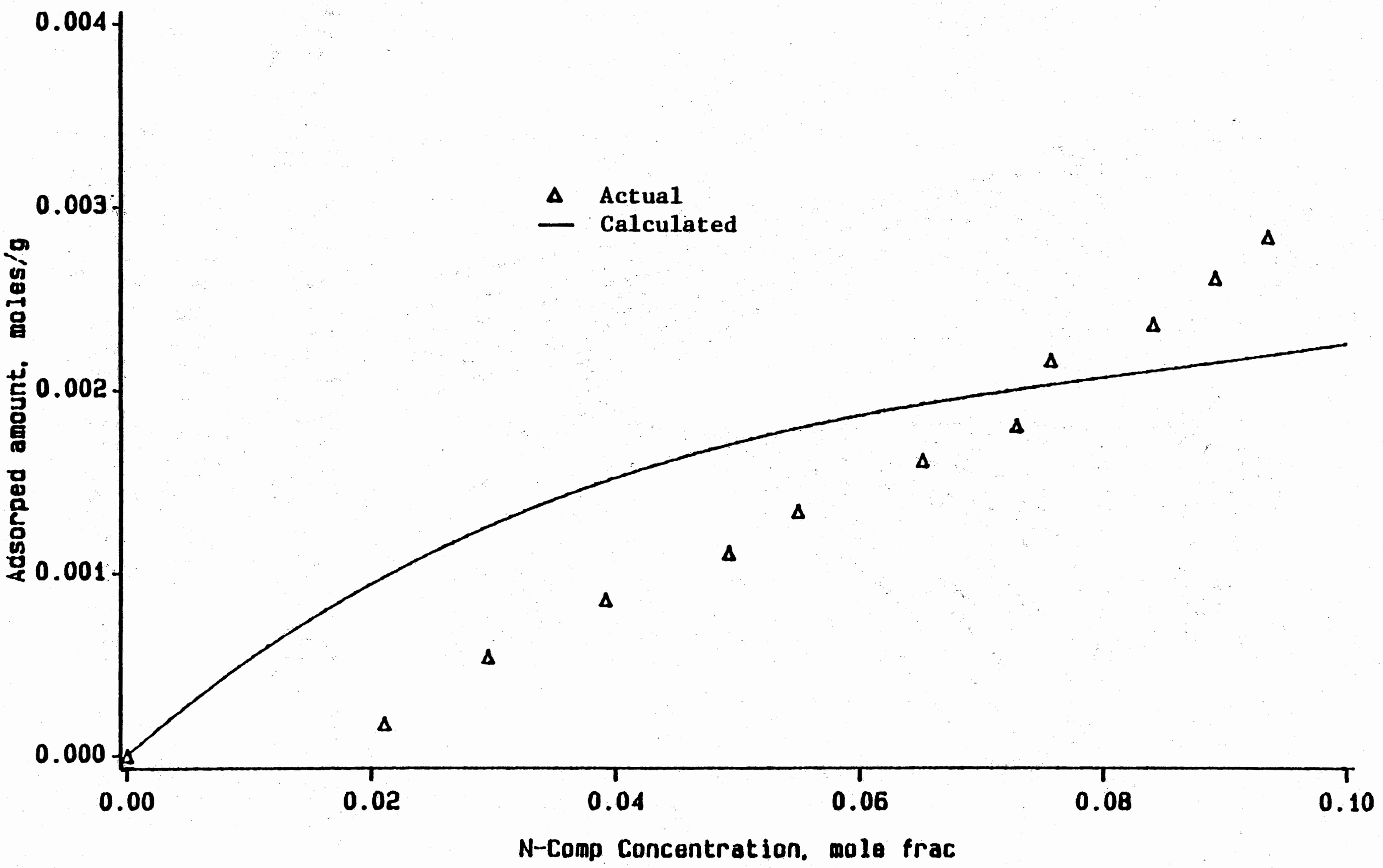


Figure 34. Comparison of Calculated and Actual Adsorption for 5-THQ Feed

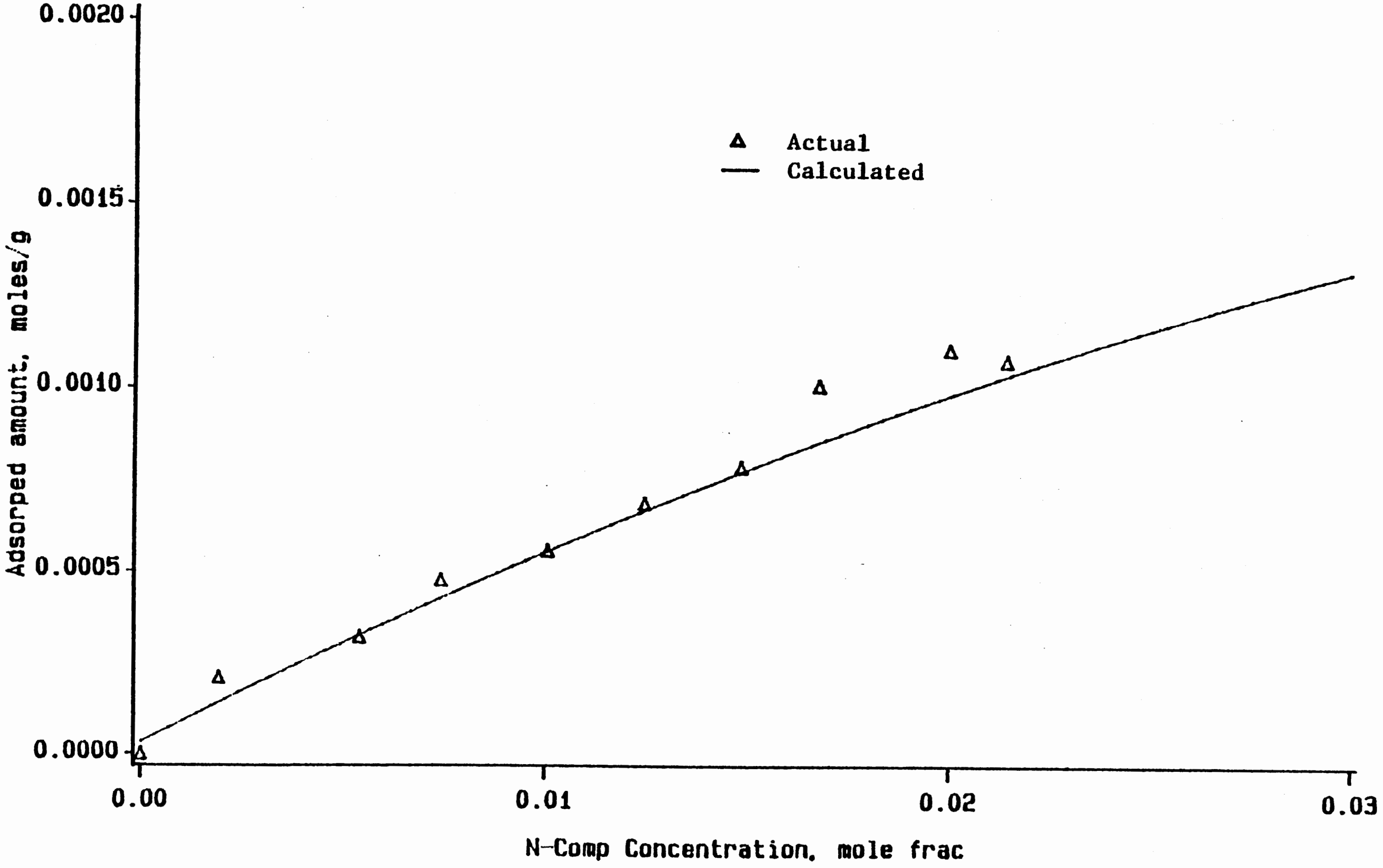


Figure 35. Comparison of Calculated and Actual Adsorption for DHQ Feed

$$r_i = \frac{F_o(C_{i,in} - C_{i,out})}{W} \qquad (14)$$

This equation was shown to be a good approximation for the reactor used in this work by a previous investigator (Tsheikuna, 1988) if the stirrer speed is above 1000 rpm. Since the stirrer speed was always held at 1500 rpm, this equation was used to estimate the reaction rates of individual compounds.

If a material balance is set up around the reactor for each individual compound, another equation involving rate constants can be obtained. The following equations were formulated for each intermediate compound in the network:

$$r_A/C_S = k_{AB}K_AC_A - k_{BA}K_BC_B + k_{AC}K_AC_A - k_{CA}K_CC_C \qquad (15)$$

$$r_B/C_S = (k_{BE} + k_{BD} + k_{CA})K_BC_B - k_{AB}K_AC_A - k_{DB}K_DC_D \qquad (16)$$

$$r_C/C_S = (k_{CD} + k_{CA})K_CC_C - k_{AC}K_AC_A - k_{DC}K_DC_D \qquad (17)$$

$$r_D/C_S = (k_{DB} + k_{DC} + k_{DG})K_DC_D - k_{CD}K_CC_C - k_{BD}K_BC_B \qquad (18)$$

$$r_E/C_S = k_{EF}K_EC_E - k_{BE}K_BC_B \qquad (19)$$

$$r_F/C_S = k_{FG}C_F - k_{EF}K_EC_E - k_{GF}C_G \qquad (20)$$

$$r_G/C_S = k_{GF}C_G - k_{DG}K_DC_D - k_{FG}C_F \qquad (21)$$

where, subscripts A, B, C, D, E, F, and G refer to quinoline, 1-THQ, 5-THQ, DHQ, OPA, PBZ, and PCH respectively.

For an experimental run with a compound, The rate of disappearance of the feed compound can be easily calculated from inlet and outlet concentrations using equation 14, and the rate of formation of other individual compounds can be calculated from outlet concentrations. Combined with the adsorption constants obtained earlier, the above equations were used to formulate the following linear problem:

$$C_{nm} * x_m = R_n \tag{22}$$

where, C is a matrix with n x m dimensions with appropriate concentration terms as its elements. The subscript n refers to the number of rate constants to be solved, and the subscript m refers to the number of rate data available for all of the individual compounds. The x vector is composed of the rate constants to be solved. The R vector contains the reaction rates for all of the compounds. Formulations of the elements in the matrices are presented in Appendix D.

There was a total of seventeen kinetic runs with various intermediate compounds. From all of the material balance equations around each component of the reaction network, 119 total equations were obtained. There were thirteen rate constants to be solved. Since this was obviously an overly determined system, a least squares technique had to be used to obtain the best solution. There are several different techniques available to solve this system. Among these, Householder and Givens methods (Golub and Van

Loan, 1983) were used and compared with each other. When the results from the two methods were compared, an agreement to four significant digits was obtained. The obtained rate constants are listed in Table XII along with standard deviations. Figure 32 also presents the reaction network with the rate constant values. It can be seen that the formation of 1-THQ from quinoline is favored over the formation of 5-THQ. This result is generally supported by previous investigators. Satterfield, et al., (1981) indicated that the step between quinoline and 1-THQ was so fast that an equilibrium existed at reaction conditions. However, the results of this study indicate that even though the rate constant for this step is an order of magnitude higher than the formation of 5-THQ, the formation of 1-THQ is not the fastest in the reaction network. As a result, it is unlikely that the formation of 1-THQ could have reached equilibrium.

The reaction step between 1-THQ and DHQ was unexpectedly slow and also the reversible rate was seen to be nonexistent. However, the formation of DHQ was twice as fast as when compared to the rate of formation of OPA. Because of this, the majority of 1-THQ proceeded to DHQ once they were formed from quinoline. The formation of DHQ from 5-THQ was fast compared to the formation of 5-THQ from quinoline. This was why very low levels of 5-THQ were detected, compared to those of 1-THQ.

The denitrogenation rate of DHQ was very fast. In fact this step was the fastest rate of all the steps involved in

TABLE XII

CALCULATED RATE CONSTANTS

Variable	Value
k_{AB}	3.190 ±0.049
k_{BA}	0.020 ±0.120
k_{AC}	0.279 ±0.065
k_{CA}	0.325 ±0.008
k_{BE}	0.011 ±0.059
k_{BD}	0.026 ±0.081
k_{CD}	1.030 ±0.008
k_{DC}	2.328 ±0.017
k_{DG}	7.550 ±0.027
k_{EF}	0.487 ±0.069
k_{FG}	0.039 ±0.010
k_{GF}	0.009 ±0.043

the HDN of quinoline. Combined with the fact that the reversible reaction from DHQ to 1-THQ was very slow, the formation of 5-THQ from quinoline led to the formation of PCH only. This was why when 5-THQ was used as the feed compound, neither 1-THQ nor OPA could be detected. Similarly when DHQ was used as the feed compound, no other compounds except for PCH and PBZ were detected.

The fact that PBZ was present in the product even when DHQ was the feed compound is very interesting. In fact, for any feed material, PBZ was detected in substantial quantities. This proves beyond any doubt that PBZ can be formed from PCH even under hydrogen atmosphere. As expected, the rate of formation of PCH from PBZ was larger than the reverse rate. Existence of this path can be substantiated by the fact that when OPA and PBZ were used as the feed compounds, PCH was still the dominant product. This result contradicted with the findings of El-Bishtawi (1986), who suggested that there is no reaction path between PBZ and PCH during HDN of quinoline. When DHQ was used as the feed product, significant levels of PBZ were detected, indicating that the step between PCH and PBZ was reversible.

To determine if any of the intermediate compounds interfered with other reaction paths in the reaction network, the reaction rates were analyzed in several ways. The reaction rates for PBZ to PCH and PCH to PBZ were determined using only the data for the runs with PBZ as the feed. Then the reaction rates were determined again by adding the rate data from the run with OPA as the feed. Thus a partial determination could be made if OPA interfered with the hydrogenation of PBZ to PCH. Similarly, the runs with DHQ feed, 5-THQ feed, and 1-THQ feed were added successively to determine the rate constants of other steps. The rate constants thus obtained are presented in Table XIII. It can be seen that overall, the nitrogen compounds did not affect the reaction rate of PCH to PBZ or the reverse one. However, the reaction rate of DHQ to PCH seem to be affected by the addition of 5-THQ and 1-THQ. No definite conclusions could be made for the other reaction rates.

The results from this work were compared with the previously published data. Table XIV presents this comparison. Shih, et al., (1977) did not evaluate some of the reverse rate constants because of their assumption of irreversibility of the steps. Different catalysts and preparation techniques were used between different sets of data. To have a meaningful comparison between the numbers, each set of numbers was normalized by the rate constant for the formation of DHQ from 1-THQ. These results differed from those reported in the earlier works for several constants but compared well in the magnitude of the other constants. One of the difference was that the fastest step from earlier works was the formation of 1-THQ from quinoline. Even though the rate constant for this step from this work was not the fastest one, it was still substantially greater than most of the other steps. More importantly, the slowest step among

TABLE XIII

INTERMEDIATE RATE CONSTANTS

Rate Constant	Feed Compounds				
	PBZ	OPA PBZ	DHQ OPA PBZ	5-THQ DHQ OPA PBZ	1-THQ 5-THQ DHQ OPA PBZ
k_{BE}	-	-	-	-	0.01
k_{BD}	-	-	-	-	0.03
k_{CD}	-	-	-	0.73	1.34
k_{DC}	-	-	-	8.37	4.65
k_{DG}	-	-	66.88	12.87	6.66
k_{EF}	-	0.212	0.24	-	0.36
k_{FG}	0.031	0.026	0.038	0.044	0.039
k_{GF}	0.005	0.003	0.007	0.010	0.009

TABLE XIV

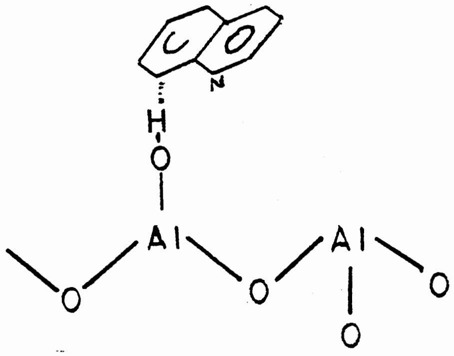
COMPARISON OF RATE CONSTANTS

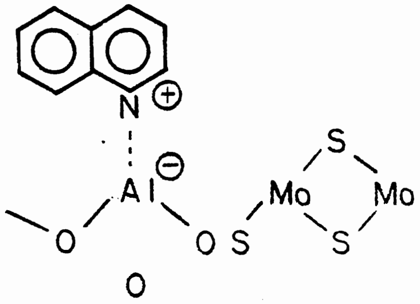
Variable	This work	Shih (1977)	Cocchetto (1981)	Yang (1983)
k_{AB}	122.7	*	70.0	337.3
k_{BA}	0.8	*	12.0	45.0
k_{AC}	10.7	8.7	22.5	40.0
k_{CA}	12.5	*	0.9	1.8
k_{BE}	0.4	0.4	0.8	2.3
k_{BD}	1.0	1.0	1.0	1.0
k_{CD}	39.6	4.3	36.3	40.0
k_{DC}	89.5	*	2.6	7.5
k_{DG}	290.4	10.7	1.5	3.7
k_{EF}	18.7	0.2	6.5	17.5

* The author did not evaluate these values

all of the forward reactions was still the formation of DHQ from 1-THQ. Other intermediate steps were comparable to the results from this work.

To explain the favoring of DHQ formation over that of OPA, one can go back to the two types of adsorption proposed by Ledoux, et al., (1982) who proposed that there were two types of adsorption by nitrogen compounds onto the surface of the catalyst, horizontal and vertical. Similarly to their pyridine adsorption models, the following model is proposed for the adsorption of quinoline.





The horizontal adsorption occurs through π bond while the vertical adsorption occurs through the nitrogen atom. The horizontal adsorption can result in the hydrogenation of the aromatic ring while the vertical adsorption can result in hydrogenation of the nitrogen side or in breakage of the nitrogen bond. If quinoline adsorbs onto the acidic sites, 1-THQ is likely to be formed, and if quinoline adsorbs through π bond, 5-THQ will be formed. The π bond (horizontal) adsorption requires a larger surface area and also the acid-base bonding is stronger than the adsorption through π bond. Because of this 1-THQ is preferentially formed over 5-THQ. The 1-THQ molecules will have hard time adsorbing onto acidic sites because of the hindrance from hydrogen molecules attached to the nitrogen containing ring. Hence the molecules will tend to adsorb through the benzene ring and produce DHQ. But the production of DHQ is not expected to be too much favored since 1-THQ will try to adsorb onto acidic sites. Once 1-THQ adsorbs onto the acidic sites, production of OPA will result. From the rate constants it is seen that the formation of DHQ is only twice as fast as the formation of OPA.

To minimize the hydrogen consumption during quinoline HDN, the elimination of benzene ring adsorption may be necessary to inhibit further hydrogenation of 1-THQ to DHQ. The commercial catalyst used in this study and other available catalysts all fail in this respect. If the hydrogenation step of 1-THQ to DHQ can be inhibited, then the hydrogen consumption can be minimized and the hydrogen consumption of HDN reactions will become comparable to that of the HDS of sulfur compounds. Further, the products of OPA need to be controlled so that the formation of PBZ will be favored over the generation of PCH. Elimination of benzene adsorption sites will also control the formation of PCH from PBZ. If the reaction is left alone to proceed to PCH, the same amount of hydrogen will be consumed as the route through DHQ. Recently, Hudson (1986) filed a patent on a catalytic system which will perform as described obove. The catalyst is said to be made up of an alkaline-earth metal promoted iron on alumina surface. The key catalyst preparation step seems to be the activation of the iron molecules by ammonia and hydrogen. This appears to be similar to presulfiding the HDS catalysts. Our own laboratory has investigated using molybdenum nitride as a HDN catalyst (Noh, 1988). The catalyst showed a very selective behavior of producing 1-THQ from quinoline without producing any other by-products. Even though molybdenum nitride did not have hydrogenolysis capability to remove nitrogen atom, further development of this catalyst, such as impregnating onto an acidic function group or combining with other HDN catalysts (i.e., HDN-60), may lead to a better performance than the presently available commercial HDN catalysts.

In summary, the major route of the quinoline HDN is the formation of DHQ through 1-THQ followed by hydrogenolysis of DHQ to form PCH. Significant amounts of OPA are also formed directly from 1-THQ. PBZ is produced from OPA after denitrogenation and most of the PBZ hydrogenate to form PCH. Among all of the nitrogen compounds, 1-THQ dominates the adsorption onto the catalytic surface. Because of the strong adsorption of 1-THQ, the conversion of this compound is the rate-limiting step among all of the steps involved in quinoline HDN. The step of converting DHQ to PCH was several orders of magnitude larger than the other steps in the reaction path. This means that DHQ proceeds to PCH as soon as it is formed from either 1-THQ or 5-THQ.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

In this investigation, the HDN of quinoline was used as a model for denitrification reactions of fuel oils. The reaction was studied in detail by using the intermediate compounds identified previously by other investigators. The reaction network was refined and the separate studies of adsorption and reaction kinetics were conducted. From this work, following conclusions were obtained:

1. A method was developed to use the autoclave reactor with Berty internals for adsorption studies. This method allowed estimation of the adsorption constants at the reaction conditions. Most of the adsorption studies were performed under idealistic conditions such as at atmospheric pressure and/or in vapor phase even if the reaction occurs in liquid phase. Most of the studies also employed single pellet for their work. The real reactor conditions could affect these idealistic estimations.

2. A competitive adsorption model was developed and utilized to obtain individual adsorption constants of the intermediate compounds in quinoline HDN. This technique will be especially valuable in estimating adsorption constants of any reaction where many intermediates form during

the course of the reaction. However, this technique requires an important assumption that all of the intermediate compounds have a similar access to the active sites. This may or may not hold true for other reactions; however, for the reactions considered in this study, this assumption is applicable because of the similar size and make-up of the compounds.

3. A technique which utilized the simplicity of CSTR reactors was developed to obtain the individual rate constants for complicated reactions, in which many intermediates are formed. A definite advantage of CSTR is that individual reaction rates can be directly measured while the mass balance results in an algebraic equation instead of a differential equation. For quinoline HDN, the resulting linear system was solved using a least square method.

4. Among the intermediates in quinoline HDN, 1-THQ was observed to have the highest adsorption constant while DHQ was found to have the lowest adsorption constant. When the adsorption constants were compared with the compound basicity as a previous investigator had done, no correlation could be found which was contrary to the previous findings.

5. For quinoline HDN, the primary route seemed to be through the formation of 1-THQ, its further hydrogenation to DHQ, and then the breakage of the nitrogen containing ring of DHQ to form PCH. The route through OPA from 1-THQ was found to be substantially lower in activity than the route through DHQ. The route through 5-THQ was found to be unim-

portant in overall quinoline HDN. However, once 5-THQ was formed, only PCH formed through DHQ from 5-THQ. This was because the reverse reaction from DHQ to 1-THQ was found to be nonexistent.

6. There is an important step between PBZ and PCH contrary to the results reported by previous investigators. Because of the existence of this step, the final product of quinoline HDN can be PCH even if the reaction is forced to go through OPA instead of through DHQ. If a minimal consumption of hydrogen is to be achieved, then any proposed catalyst will have to select the route through OPA and block further hydrogenation of PBZ to PCH.

7. For quinoline HDN, it was determined that the rate-limiting step in quinoline HDN is the further processing of 1-THQ. This is consistent with the fact that 1-THQ has the highest adsorption constant among all of the intermediate compounds. Because of the strong adsorption, 1-THQ is hardest to break up on the catalyst surface.

Following recommendations are proposed to further the findings obtained in this work:

1. An investigation should be performed to elucidate why 1-THQ has such a high adsorption constant compared to the other intermediate compounds. Some type of correlations with chemical or physical characteristics are desired for the adsorption constants obtained in this work. This type of work will help in understanding the nature of the adsorption of the intermediate compounds in quinoline HDN.

Already it is proven in this work that the basicity of the compounds is not a good correlating characteristic contrary to a previous investigation.

2. The technique developed in this work for adsorption studies needs to be refined. A better sample-handling method is required for better accuracy. Present technique could introduce large errors due to the large size of sample collectors. A preferable technique is an on-line capability of analyzing the outlet products. This would eliminate the possible errors in handling, storing, and transporting the samples from the reactor lab to the analytical lab.

3. A study should be conducted to find the ideal catalyst which would have the selectivity for producing OPA instead of DHQ and have the capability to block hydrogenation of PBZ to PCH. A present work with molybdenum nitride should be investigated further, possibly combining molybdenum nitride with an existing commercial catalyst.

4. The technique developed in this work using CSTR reactors should be utilized to study other complex catalytic reactions. The technique would be especially useful for those reactions involving many intermediates or side reactions because of the advantages already mentioned.

5. For further understanding of quinoline HDN, a study on the poisoning effect of intermediate compounds will add considerably to present knowledge. By determining which intermediate compound has the highest inhibiting or promoting effect, a further understanding as to the effect of the

adsorption constants of the intermediate compounds can be obtained. From the results of this work, 1-THQ will have the highest inhibiting effect on overall HDN of quinoline or any other nitrogen compound. Similarly, any intermediate compound found to have a promoting effect can be tried on HDN of other compounds or in coal liquids.

6. Similar intermediate studies of other nitrogen compounds are recommended for a better understanding of HDN of nitrogen compounds. From this work, it is shown that a better understanding of reaction network and the role of adsorption of intermediate compounds can be obtained.

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APPENDIXES

APPENDIX A

ESTIMATION OF PA VALUES

An extensive compilation of proton affinity values has been published by Lias, et. al., (1984). However, there are still many compounds not yet evaluated including 1-THQ and DHQ, two of the intermediate compounds used in this study. To estimate PA values for these compounds, an approach based upon a similarity to pyridine homologue series can be used. The following table lists the known values of proton affinity for the compounds of interest in this work:

Compound	PA
Pyridine	220.8
Quinoline	226.5
Acridine	231.9
Piperidine	226.4
5-THQ	227.7

Two different routes are used to estimate the proton affinity of 1-THQ.

a. To estimate the value of 1-THQ, it was recognized that it has a similar relationship to quinoline that piperidine has with pyridine. The difference between piperidine and pyridine is 5.6. If this value is added to the value for quinoline, an estimate of 232.1 is obtained.

b. Also 1-THQ has a similar relationship to piperidine as pyridine, quinoline, and acridine have in common, namely that a benzyl group is successively added. The difference between pyridine and quinoline is 5.7, and that between quinoline and acridine is 5.4. If the average value of 5.5 is added to piperidine, then an estimate of 232.0 is obtained.

These two routes result in PA values that are very close to each other, 232.1 versus 232.0.

To estimate the value for DHQ, it was recognized that it has a similar relationship with piperidine as 5-THQ has with pyridine. The difference between 5-THQ and pyridine is 6.9. If this value is added to the value for piperidine, then a value of 233.3 is obtained.

APPENDIX B

SAMPLING PROCEDURE

Adsorption runs

1. Make sure all of the valves are closed before taking a sample. Then pressurize the sample bombs to 1000 psig (500 psig below the reactor pressure).

2. Quickly open fully the valves between the reactor and the sample bombs for a few seconds. (Normally a drop of 200 psi in the reactor will be sufficient for obtaining enough samples for analysis).

3. After closing the valves between the reactor and the sample bombs, open the valve between the liquid feed pump and the reactor. The reactor pressure will hold because of the back pressure regulator located between the manual valve and the pump. Then start the liquid feed pump. Monitor the pressure until the pressure of the pump builds up to the reactor pressure and the back pressure valve opens.

4. Monitor the liquid level to pump the correct amount of the liquid into the reactor. Also monitor the reactor pressure closely to avoid overpressurizing the reactor.

5. Once the desired amount of liquid is pumped in, shut the pump and close the manual valve between the reactor

and the liquid feed pump.

6. Double-check that all of the valves are closed before proceeding to the next step.

7. Release the separated liquid into the bottom sample bomb. (It should be empty).

8. After all of the liquid drains into the bottom bomb, close the valve between the top sample bombs and the bottom one. Then pressurize the sample section to equal the reactor pressure and to avoid leakage of reactor contents into the sample line.

9. Release the liquid in the bottom bomb to the sample jar. Open the valve slowly (a large pressure differential exists between the bomb and the jar). Even though some liquid will flow out first, the flowing gas may splash the liquid drops if allowed to flow too fast.

Kinetic run

Because the kinetic runs are continuous flow experiments, the sample taking needs to be performed relatively fast. The procedure should be well practiced before attempting this.

1. Close the valve between the reactor and the sample bombs.

2. Open the valve between the top sample bombs and the bottom one. The bottom one should be empty initially and there should be a quick transfer of collected samples between the sample bombs.

3. Close the valve after the transfer is complete.

4. Pressurize the top sample bombs to the operating pressure of the reactor.

5. Open the valve between the reactor and the sample bombs.

6. Monitor the pressures and the flow rates to make sure that unusual upsets to the system have not occurred.

7. Release the contents of the bottom sample bomb to the sample jar.

8. After the transfer is complete, the valve should be closed for next sample taking.

APPENDIX C

EXPERIMENTAL ERROR ANALYSES

Any experimental measuring device will have certain uncertainties associated with it. Most of the uncertainties for our equipment have been determined through the calibrations or through repeated experiments.

The accuracy of the gas chromatograph analyses was checked periodically throughout the experiments. This was done simply by injecting the same liquid samples three times successively, and then selected peaks were compared to each other in terms of the compositions calculated. Table C-1 presents an example of such analysis. This was an adsorption run and the sample was taken after one hour. The calculated OPA and PBZ concentrations were very close to each other.

TABLE XV

AN EXAMPLE OF ACCURACY OF THE GC ANALYSIS

Compound	Concentration (wt. frac.)	Deviation (from avg.)
OPA	0.003903	-1.5 %
	0.004017	+1.3 %
	0.003973	+0.2 %
PBZ	0.002434	+1.4 %
	0.002392	-0.4 %
	0.002378	-1.0 %

It can be seen that the maximum deviation from the average was 1.5 percent. For all of the GC analyses that were checked, this figure was not exceeded.

All of the GC analyses data that were gathered are available from this investigator or Dr. Mayis Seapan of the School of Chemical Engineering at Oklahoma State University.

The temperature probes were calibrated against a standard and were found to be accurate within 1 degree through the most of the ranges. The pressure gauges were determined to have an accuracy of ±20 psi. The accuracy of reading the liquid level of the liquid feed tank was estimated to be ±1 ml. The time was read to ±1 min. The weighting scale had an accuracy of ±0.01g.

An example of the experimental error analyses is the calculation for the flow rate. To calculate the liquid flow rate, the readings were taken before the liquid pump was started and after the pump was stopped. Then the flow rate was calculated as:

feed rate = (second reading - first reading)/time

The lowest flow rate measured was 30 ml/hr. Then following procedure can be used to estimate the accuracy of the flow rate.

The accumulative error was estimated as:

1. Accumulation through subtraction

$$\delta_t = \sqrt{\delta_1^2 + \delta_2^2}$$

Then,

$$\delta_t = \sqrt{1^2 + 1^2}$$

$$= 1.4$$

2. Accumulation through division

$$\frac{\delta_t}{x} = \sqrt{\left|\frac{\delta_1}{x_1}\right|^2 + \left(\frac{\delta_2}{x_2}\right)^2}$$

Then,

$$\frac{\delta_t}{x} = \sqrt{\left(\frac{1.4}{30}\right)^2 + \left(\frac{1}{60}\right)^2}$$

$$= 0.05 \quad \text{or } 5.0\ \%$$

Hence, for a calculated flow rate of 30 ml/hr, the experimental accuracy was ±5%.

The calculation for reaction rate is as follows:

$$r_i = \frac{F_o(C_{i,in} - C_{i,out})}{W}$$

There are one subtraction, multiplication, and division each in this calculation. The subtraction can be considered same as the addition and the division can be considered same as the multiplication when estimating the error. Hence there are one addition and two multiplications in this operation. After performing a similar analysis to the calculations for the flow rate, ±5.5% was obtained for the accuracy of the flow rate.

APPENDIX D

FORMULATION OF KINETIC RATE MATRIX

The individual reaction rate constants were calculated from the experimental data after performing the material balance for individual intermediate compound for each run. For an intermediate compound, a material balance would be the sum of what was inputted into the reactor and the production from the other compounds minus the consumption to produce the other compounds. For any catalytic reaction where A reacts to form B, and if the surface reaction is assumed to be controlling, following reaction rate equation can be formulated:

$$-r_A = k_{AB}C_{AS} - k_{-AB}C_{BS}$$

Where, k_{AB} = forward reaction rate constant

k_{-AB} = backward reaction rate constant

C_{AS} = Concentration of Adsorbed A species

C_{BS} = Concentration of adsorbed B species

If the adsorption of A and B species are assumed to be in equilibrium with the available sites, then it can be shown that following relations hold:

$$C_{AS} = K_A C_S C_A$$

$$C_{BS} = K_B C_S C_B$$

where, K_A = Adsorption constant for A species

K_B = Adsorption constant for B species

C_S = Concentration of vacant sites

C_A = Concentration of A species in fluid phase

C_B = Concentration of B species in fluid phase

Combining the equations following one can be obtained:

$$-r_A = k_{AB} C_S C_A - k_{-AB} C_S C_B$$

For quinoline HDN, various intermediate compounds are formed before the denitrogenation occurs. To evaluate each individual rate constant, a similar approach was taken with little modification to allow for the fact that several different steps could be associated with a single compound. For simplicity, quinoline, 1-THQ, 5-THQ, DHQ, OPA, PBZ, and PCH were assigned A, B, C, D, E, F, and G respectively. If it is assumed that the surface reaction is rate controlling for all of the steps in quinoline HDN, then the equations developed so far can be extended.

For quinoline:

$$-r_A = k_{AB} K_A C_A C_S - k_{BA} K_B C_B C_S$$
$$+ k_{AC} K_A C_A C_S - k_{CA} K_C C_C C_S$$

Rearranging,

$$-r_A = (k_{AB} + k_{AC})K_AC_AC_S - k_{BA}K_BC_BC_S - k_{CA}K_CC_CC_S$$

For 1-THQ:

$$-r_B = (k_{BE} + k_{CD} + k_{BA})K_BC_BC_S - k_{AB}K_AC_AC_S$$
$$- k_{DB}K_DC_DC_S$$

For 5-THQ:

$$-r_C = (k_{CD} + k_{CA})K_CC_CC_S - k_{AC}K_AC_AC_S - k_{DC}K_DC_DC_S$$

For DHQ:

$$-r_D = (k_{DB} + k_{DC} + k_{DG})K_DC_DC_S - k_{CD}K_CC_CC_S$$
$$- k_{BD}K_BC_BC_S$$

For OPA:

$$-r_E = k_{EF}K_EC_EC_S - k_{BE}K_BC_BC_S$$

For PBZ:

$$-r_F = k_{FG}C_F - k_{EF}K_EC_EC_S - k_{GF}C_G$$

The reactor used for this work allows one to estimate the reaction rate directly from following:

$$-r_A = \frac{F_i(C_{A,i} - C_{A,o})}{W}$$

To solve for the rate constants, following matrix was formulated from above equations:

$$C_{nm} * x_m = R_n$$

The elements of each matrix would be as following:

$$C_{nm} = \quad K_A C_A \quad -K_B C_B \quad K_A C_A \quad -K_C C_C \quad 0 \; .... \; 0$$

$$\vdots$$

Concentration terms associated with a rate constant in D1 to D6.

$$x_m = [k_{AB}\ k_{BA}\ k_{AC}\ k_{CA}\ k_{BE}\ k_{BD}\ k_{DB}\ k_{CD}\ k_{DC}\ k_{DG}\ k_{EF}\ k_{FG}\ k_{GF}]^{-1}$$

$$R_n = [\text{ all of the associated reaction rate }]^{-1}$$

VITA

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Doctor of Philosophy

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