



12-1985

Reactions of Supercritical Water with Quinolone and Related Compounds

Zhuangjie Li

Follow this and additional works at: https://scholarworks.wmich.edu/masters_theses

 Part of the Chemistry Commons

Recommended Citation

Li, Zhuangjie, "Reactions of Supercritical Water with Quinolone and Related Compounds" (1985). *Master's Theses*. 4367.

https://scholarworks.wmich.edu/masters_theses/4367

This Masters Thesis-Open Access is brought to you for free and open access by the Graduate College at ScholarWorks at WMU. It has been accepted for inclusion in Master's Theses by an authorized administrator of ScholarWorks at WMU. For more information, please contact wmu-scholarworks@wmich.edu.



REACTIONS OF SUPERCRITICAL WATER WITH QUINOLINE
AND RELATED COMPOUNDS

by

Zhuangjie Li

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Arts
Department of Chemistry

Western Michigan University
Kalamazoo, Michigan
December 1985

ACKNOWLEDGEMENTS

The author is grateful to Professor T.J. Houser under whom the research was completed, and to Professor M.E. McCarville for his help in the research.

Zhuangjie Li

REACTIONS OF SUPERCRITICAL WATER WITH QUINOLINE
AND RELATED COMPOUNDS

Zhuangjie Li, M.A.

Western Michigan University, 1985

One function which coal processing can perform is the removal of heteroatoms to yield a less polluting product. The removal of nitrogen atoms from the model compounds quinoline and aniline, which are believed to be representative of the nitrogen functional groups found in coal, was studied using supercritical water (SW) as the fluid. Water at these conditions serves as a reactant, helping to promote the rupture of the heterocyclic ring and in the removal of nitrogen attached to an aromatic ring. Heterocyclic ring rupture leads to the formation of several methylated products, methyl and dimethyl anilines, phenols and quinolines. The other volatile major products were aniline and phenol; in addition, small amounts of several aromatic hydrocarbons were found. The kinetics of the quinoline-SW reaction were examined in the temperature range of 400-500 C, using ZnCl_2 as a catalyst. With a constant loading of 0.2 g ZnCl_2 it was found that the reaction rate could be represented by an equation 1st-order in quinoline but including a constant that was proportional to the catalyst loading. The Arrhenius parameters for the apparent 1st-order constant are $\log A (\text{sec}^{-1}) = 3.5$ and $E = 27.0$ kcal/mole. The mechanistic implications of the data are discussed.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	ii
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
CHAPTER	
I. INTRODUCTION.....	1
Supercritical Fluids and Their Application to Coal Extraction.....	1
Hydrodenitrogenation.....	8
II. EXPERIMENTAL.....	11
Apparatus.....	11
Materials.....	15
Procedure.....	15
Calculations.....	21
III. RESULTS AND DISCUSSION.....	30
Quinoline Reaction.....	30
Products.....	30
Water Density Effect.....	34
Kinetic Results.....	36
Catalyst and Additive Effects.....	42
Comparison to Previous Work.....	45
Miscellaneous Compounds.....	47
IV. CONCLUSIONS.....	49
APPENDICES.....	51
A.....	51

Table of Contents - Continued

B.....	53
REFERENCES.....	55

LIST OF TABLES

1.	Quantitative Results From Run Q-42.....	25
2.	Hydrogen Balance Calculation Results.....	27
3.	Hydrogen Balances.....	32
4.	Reaction of Quinoline With Supercritical Water, Water Density Effect.....	35
5.	Reaction of Quinoline With Supercritical Water, Kinetic Data.....	37
6.	Reaction of Quinoline With Supercritical Water, Catalyst Effect.....	43
7.	Reaction of Quinoline in Supercritical Toluene, Effect of Added Dihydroanthracene.....	44
8.	Reaction of Aniline and DHA With Supercritical Water..	48

CHAPTER I

INTRODUCTION

The investigation of the removal of nitrogen atoms from some nitrogen-containing compounds at supercritical water (SW) conditions and the determination of kinetic properties of the quinoline/SW reaction are the goals of this work. By studying the reactions of several model compounds with SW, the possible use of this fluid to remove nitrogen from the organic components of coal was explored. Quinoline was chosen as the major model compound since Given's molecular structure of coal (1) is accepted widely as a reasonable working model for practical purposes, and the model characterizes coal as having most of the nitrogen incorporated into heterocyclic, aromatic rings. Much of the work, both with model compounds and with coal, is exploratory, requiring the development of new procedures and analyses before this new technique, the supercritical fluid extraction (SFE) of coal, can be applied in industry.

Supercritical Fluids and Their Application to Coal Extraction

A fluid can exist as a liquid below its critical temperature (T_c), but above this temperature the fluid will exist in the gaseous state regardless of its pressure. At temperatures below T_c a gas

can be liquified by increasing the pressure, however, at a temperature exceeding T_c the fluid cannot be liquified and is referred to as a "supercritical fluid" (SF).

Supercritical fluids have important properties which may be exploited for SFE of natural products. Starting with the virial equation of state of a pure gas:

$$PV/RT=1+B/V+C/V^2+\dots \quad (1)$$

where V is the molar volume, R the gas constant, and B, C, \dots the second, third, ... virial coefficients (which are functions of temperature only), Paul and Wise (2) developed an approximate equation to predict the enhanced solubility of a solute in a SF:

$$\ln \alpha = (V_s - 2B_{12})/V \quad (2)$$

where $\alpha = C_2/C_2^0$, a measure of enhanced solubility, C_2 is the molar concentration of component 2 in vapor, C_2^0 the concentration of solute vapor at its vapor pressure without solvent, V_s the molar volume of the component being extracted, V is the molar volume of the SF and B_{12} is the cross second virial coefficient between solvent and solute, which is determined empirically and is always negative. The theory of gas extraction concludes that higher values of α will be obtained if the critical temperature of the fluid is close to the extraction temperature, because B_{12} is then more negative, indicating that the volatility enhancement is the greatest at temperatures near the critical (2). The experimental determination of the vaporization of phenanthrene supported this conclusion. The concentration of phenanthrene showed a sharp increase

in the gas phase at the temperature of 313K and a pressure of 394 atm when ethane was used as the SF. Under favorable conditions the effect may be very large and an increase in volatility of up to a factor of 10^4 can be obtained (3). In addition, since there is a reciprocal relationship between V and P, by increasing the pressure the term $1/V$ can be increased, thus yielding a higher value of α (eq. 2). The system ethylene/naphthalene has been studied by Diepen and co-workers (2), and the plots of log solubility against the reciprocal of volume were essentially linear.

A SF also has some other physicochemical properties which are of fundamental importance for SFE. The study of the pressure dependence of the dielectric constant of CO_2 (4) and water (5) shows that it increases with pressure. This effect provides evidence for the flexibility of the solvent power of a SF for low-volatility compounds at elevated pressures. Finally, a SF has good transport properties, in particular low viscosity. The viscosity of squalene with a SF such as CO_2 decreases with rising pressure, and its diffusion coefficient becomes relatively high (4). This property makes a SF a good solvent having a low viscosity and a high mobility, which allows the transfer of materials readily through microporous structures.

Though the enhanced solvent power of a SF was known in the 19th century, it was not applied in the energy industry until the late 1950s when Zhuze reported that supercritical propane/propylene mixtures could be used in deasphalting petroleum residues (2). The

area of most interest in energy production has been that of SFE. The ability of SF to increase the volatility of heavy molecules formed from the processing of coal is of very practical importance and has been of great interest since 1975. The SFE of coal has been regarded as a potentially viable method for the extraction of liquid fuel constituents. Coal contains 25-30% hydrogen-bonded compounds, these bonds rupture during the thermal conversion of coal at about 400 C (6). The thermolysis of these weak bonds generates small reactive fragments within the coal, and the fragments cannot be well separated from the coal residue. Instead, these reactive intermediates can recombine with the residue, yielding undesirable refractory chars, reducing the efficiency of the extraction. The extraction can be improved by SFE because the fluid enables the rapid separation of coal fragments from residue, avoiding retrogressive char-forming reactions. As mentioned above, SFE exploits the capability of a compressed SF to enhance the volatility of the high molecular weight compounds, and since the solubility depends mainly on pressure, it is possible by simply lowering the temperature and pressure to precipitate the dissolved compounds out of the solvent, fractionating the coal into a solid and a viscous liquid. Both fractions are essentially free of the solvent.

The choice of the solvent becomes most important in SFE. First, in order to get the maximum miscibility, the T_c of the solvent must be in the vicinity of the extraction temperature. In the vaporization of phenanthrene at 40 C, it was found that carbon dioxide

($T_c=340$ K), ethane ($T_c=305$ K) and ethylene ($T_c=283$ K) have T_c s close to the vaporization temperature, and were effective solvents for the vaporization of phenanthrene, whereas solvents with low T_c s (such as methane $T_c=191$ K) are not effective (2). For coal extraction, the best extraction temperatures are found to be about 400 C. Therefore, various solvents such as toluene ($T_c=318$ C), methanol ($T_c=239$ C), and water ($T_c=374$ C) may be used for the SFE of coal. Second, in addition to being a solvent, it may be useful that the fluid function as a reactant or hydrogenation agent, etc., depending on the requirements of the extraction (7). Last, the solvent should be cheap and readily available.

The use of toluene as a SF for coal extraction was studied previously by the National Coal Board in Great Britain(3). The work was focused on the effects of temperature and pressure on the extraction yield and on the subsequent processing of the extraction products. The kinetics of the extraction process was also studied to determine the preferred operating conditions. More recent work has used a variety of solvents to determine their effect on the SFE of coal. Vasilakos, Dobbs, and Parisi (8), divided solvents into non-polar, polar and synergistic solvents for the SFE of coal and studied the relationship between the yield and type of solvent under the conditions of 400 C and pressures up to 5140 psi. For the non-polar solvents, the extraction yield increased with increasing molecular weight of the solvent (from pentane to dodecane), and toluene gave higher yields (36%) than n-paraffins (18-23%). With

regard to polar solvents, it was found that acetone decomposed at 400 C and gave the lowest yield in the extraction (7.3%), while methanol gave a yield (20.6%) which was slightly lower than that predicted theoretically. Water, on the other hand, displayed a large positive deviation from the predicted extraction yield. It was also noticed that for the supercritical water runs, after dropping to ambient conditions, the extract-containing liquid phase was an almost clear, strongly smelling solution with a small amount of precipitate, which was completely different from the black coal solutions obtained in the supercritical toluene runs. The studies of synergistic effects for a series of toluene/methanol and toluene/acetone mixtures revealed different consequences for these two solvent combinations. The former gave an extraction curve which passed through a maximum at a composition of about 70 mole% toluene (yield=37%) while the latter displayed an approximately linear dependence of increasing extraction yield in molar composition of toluene, indicating no synergism in the toluene/acetone system.

Because experiments have indicated that water may be a very effective extraction solvent, more attention is being paid to it. Recently Deshpande, Holder, Bishop, Gopal, and Wender (9), did some work on the SFE of coal using water. They concluded that SW appears to act as both solvent and reactant in the conversions of coal to gases and liquids. They found that subcritical densities resulted in a higher percentage of tetrahydrofuran insolubles (THFI) than did supercritical densities, and the THFI, which was an undesirable

product, approached a constant value at a longer reaction time. They also concluded that a high water density could reduce the extraction time, and heating the ambient coal in a stepwise fashion could prevent retrogressive reactions. What is more, it was found that the product water had a high acidity, assumed to be due to dissolved H_2S . This indicates that one of the significant advantages of SFE of coal with water may be the removal of heteroatoms.

As a supercritical extractant, in addition to cost and availability, water has several advantages over toluene. To begin with, the T_c for water is 374 C, while for toluene it is 319 C. Since the coal extraction is carried out at about 400 C, the volatility enhancement of water will then be greater than that of toluene. In addition, the size of the water molecule is smaller than that of toluene, making the penetration of the micropore structure of coal easier by water than by toluene. Moreover, being both polar and hydrogen bonding, water exerts a stronger dissociating or depolymerizing action on coal than toluene during extraction, thus increasing the rate of extraction. Finally, water is highly reactive with cyanide wastes to form ammonia (10), and it appears to be able to extract sulfur atoms present in the coal, removing them in the form of hydrogen sulfide (9). One of the desirable functions which could be performed during coal processing is the removal of heteroatoms to yield a cleaner product, so that environmental pollution could be reduced when the products derived from coal are used. A study has shown that sulfur is easier to remove than

nitrogen, because the saturation of the heterocyclic ring is necessary during conventional hydrodenitrogenation for the rupture of the C-N bond, but this is not necessary for the rupture of the C-S bond (11).

The present study has focused primarily on the removal of nitrogen from quinoline. That quinoline is used as the major model compound for denitrogenation studies is based on the fact that the quinoline type structure is considered one of the most difficult to convert to hydrocarbons and ammonia (12-14).

Hydrodenitrogenation

As one of the important methods to remove nitrogen from the nitrogen-containing organic compounds, hydrodenitrogenation (HDN) has been studied for more than twenty years. The studies included the exploration of the effectiveness of HDN for a group of nitrogen compounds (14), the reaction network of the HDN of quinoline (13,15), the chemical equilibria among quinolines and their reaction products during HDN (12), and the effect of catalysts and other compounds on the HDN of quinoline (16,17). Studies of various heterocyclic nitrogen compounds show that there are three steps for the HDN mechanism. First, the saturation of heterocyclic ring with hydrogen (hydrogenation); second, the hydrogenolysis of the C-N bond to open the heterocyclic ring; and third, the conversion of resulting aliphatic or aromatic amine intermediates to hydrocarbons and ammonia. The results of the study of quinoline HDN gives

further information as follows:

(1) The initial ring saturation reactions are reversible and the reactions approach equilibrium, while the denitrogenation reactions are irreversible.

(2) The rates of various steps in HDN reactions obey first-order or pseudo-first-order kinetics.

(3) Denitrogenation of quinoline occurs primarily through the hydrogenolysis of 1,2,3,4-tetrahydroquinoline-decahydroquinoline, though kinetically, the 5,6,7,8-tetrahydroquinoline-decahydroquinoline route is favored, and propylcyclohexane is always the major product.

(4) Hydrogen sulfide has a positive effect on the rate of HDN of quinoline while water has a slightly negative effect on this rate.

(5) Hydrogenation is retarded by the adjacent, puckered cyclohexane ring or piperidine ring.

The conventional catalyst used in HDN is $\text{NiMo}/\text{Al}_2\text{O}_3$, which allows the hydrogenation of quinoline to occur on both rings to form 1,2,3,4-tetrahydroquinoline and 5,6,7,8-tetrahydroquinoline as reaction intermediates. In order to control the selective formation of tetrahydroquinoline, Boucher, et al (16) used metallophthalocyanines (MPC) as catalysts to improve the selectivity of the catalyst, because they provide a well-defined catalytic site. It was found that MPC are active in hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline in the range of temperatures from 300 to

400 C, and at hydrogen pressures from 1000 to 3000 psi, but they are not denitrogenation catalysts.

Although HDN has been proven to be an effective way for the removal of nitrogen from quinoline, it is not an economical method because of the requirement of a large quantity of hydrogen. On the other hand, SW has also been shown to be successful in nitrogen removal, and no hydrogen needs to be added in the reaction. Unfortunately, very little work has been done on this subject. The lack of information about the quinoline/SW reaction indicates that further study of the kinetic properties of the reaction is required, which is one of the tasks of this work.

CHAPTER II

EXPERIMENTAL

Apparatus

The equipment used in all experiments may be divided into three groups: the reaction system, the extraction system, and the analysis system. The reaction system includes a reactor, a furnace for heating the reactor, and controller for setting different temperatures. The reactor is a cylindrical vessel made of stainless steel. The internal height of the vessel is 73.2 mm, and the internal diameter of the reactor is 28.2 mm. The top of the reactor was a removable, flanged lid which was sealed with six, hex head, stainless steel bolts (1/4"*20*1"). The combination of lid and reactor gave an internal volume of $47.0 \pm 0.5 \text{ cm}^3$. Between the lid and the reactor body a copper gasket is used which serves to seal the system, which prevented leaking during reaction. There is a hole passing through both flanges of the lid and the reactor for thermocouple insertion (Figure 1). The reactor does not have a vent for gas collection or a pressure gauge. The furnace is a Tecam SBS-4 fluidized sandbath with the heating element in the bottom. The fine sand is fluidized by air blowing up from the bottom. The power to the furnace is supplied by a 1 KVA variac. The heating is

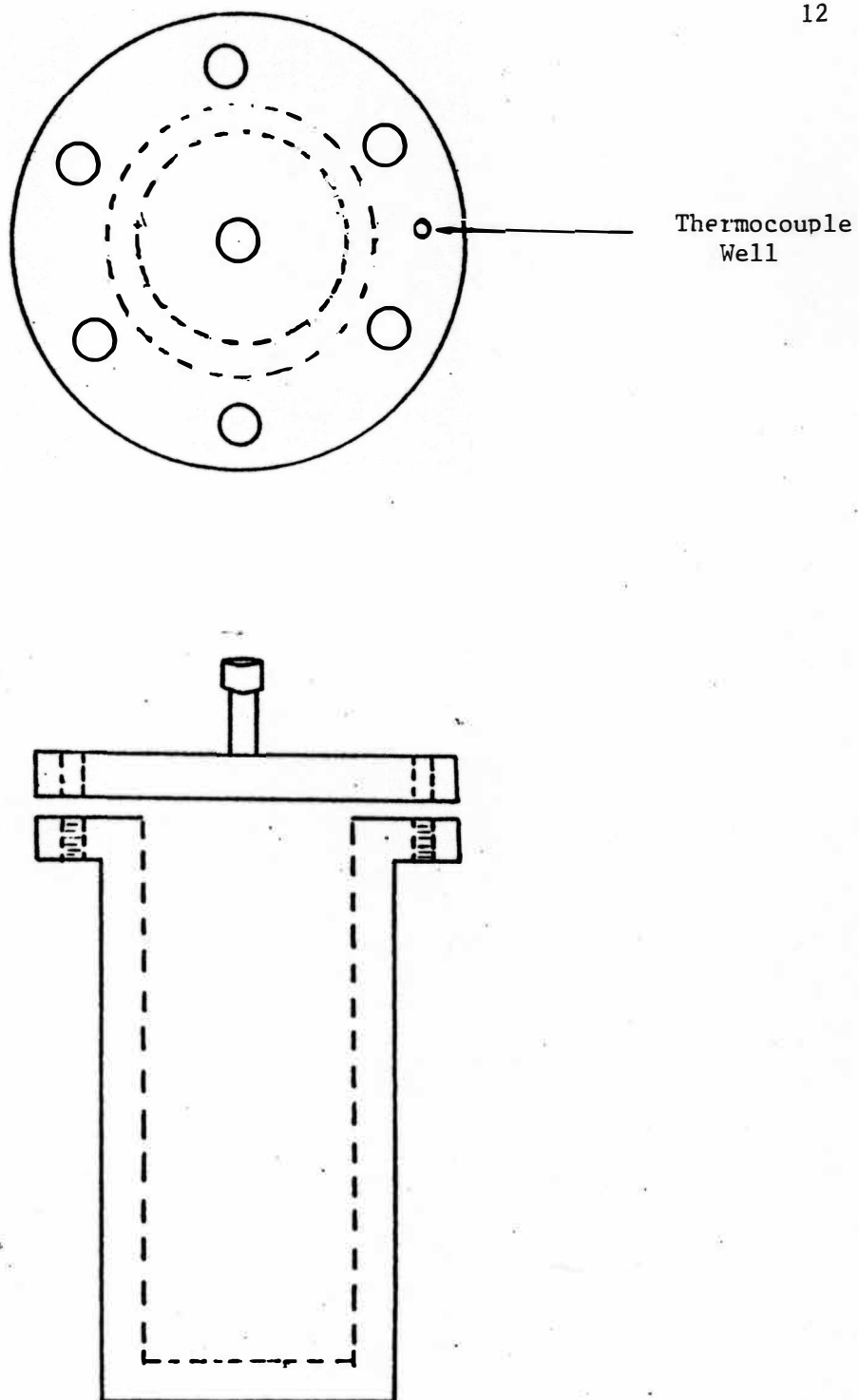


Figure 1. Reactor

regulated by a chromel-alumel thermocouple connected to a Honeywell Temperature Controller, type K 200-1200 C, Model MS2. The temperature controller dial settings are calibrated and frequently checked using a thermocouple and a Leeds and Northrup Model 8690-2 millivolt potentiometer.

The separations and extractions of the organic material from water for all experiments were carried out using a 60 mm stemless gravity funnel, a 60 mL separatory funnel, a 60 mm short stem gravity funnel, and either a 25 mL or 50 mL volumetric flask depending on the amount of solvent to be used. The glassware was set up as shown in Figure 2.

Qualitative analyses of the product mixtures were performed on a Dupont 21-490B Gas Chromatograph-Mass Spectrometer (GC-MS). The GC uses a 6" \times 1/8" stainless steel column packed with 10% SE-30 on Chromosorb W (kieselguhr) and a flame ionization detector. All quantitative analyses of the volatile products were made with an F and M 720 Dual Column, Programmed Temperature Gas Chromatograph with a thermal conductivity detector. For all experiments, the general operating conditions were: injector temperature 245 C, detector temperature 260 C and bridge current 150 ma. Both columns are 6" \times 1/4" stainless steel tubes packed with 10% SE-30 on chromosorb W. Helium was used as the carrier gas, which had a flow rate of about 90 cm³/min. The measurement of the flow rate was made by means of a bubble meter with the meter reading 10 cm³/7 sec.

An Orion 407A/L Specific Ion Meter and a Model 95-10 ammonia

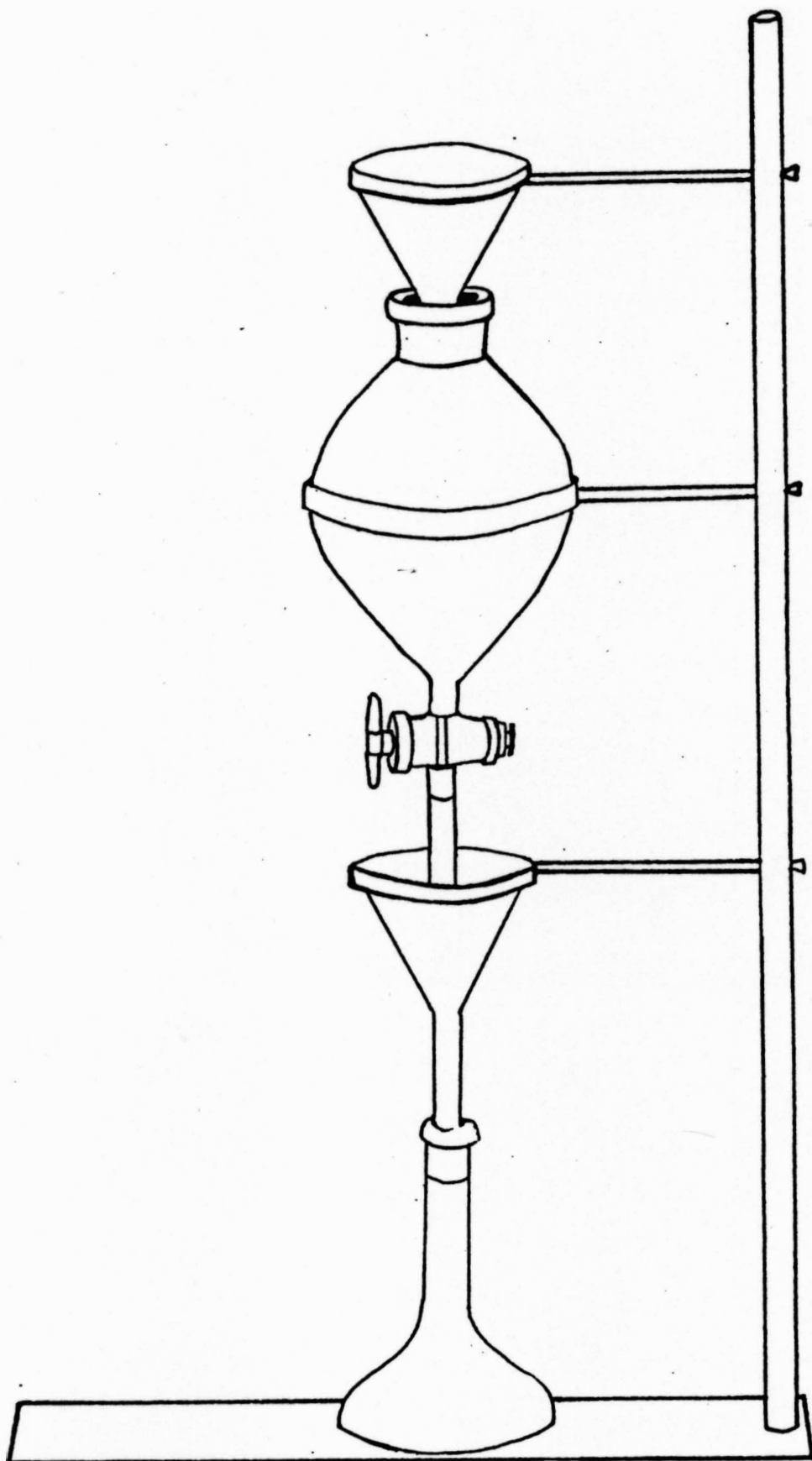


Figure 2. Extraction Set-Up

electrode were used for the ammonia analyses of the water collected after the reaction. The concentration of NH_3 was measured in moles per liter.

The sample weighings were performed using a Mettler H10 balance, for which $P_{\text{max}}=160$ g and $d=\pm 0.0001$ g. All calculations were made using a solar cell scientific calculator, Sharp EL-5106. For plotting straight lines a least squares program was employed in a microcomputer to calculate the slope and intercept.

Materials

Reagent grade quinoline and aniline were vacuum distilled. Commercial 9,10-dihydroanthracene (DHA) with a purity of 97% was used directly. The compounds used for calibrating the GC are either analytical or spectral grade. In all cases the purity is high enough to show only one peak when a 2 μL sample of straight compound is injected into gas chromatograph. The ZnCl_2 catalyst was used off the shelf after drying. Methylene chloride (CH_2Cl_2) was used as an extraction solvent and had a little benzene as its only impurity, which was taken into account during analysis.

Procedure

The experimental procedures for all the experiments can be divided into five parts: (a) loading the reactor and the reaction itself, (b) product separation and collection, (c) qualitative analysis of the product mixture, (d) quantitative analysis of the

products, and (e) the final treatment of the samples. The quinoline run number 42 (Q-42) will be used as an example showing a typical loading and extraction procedure for this reaction.

A 2.00 mL pipet, which was calibrated, transferred 2.188 ± 0.001 g (.01694 mole) quinoline into the reactor. This pipet then was labeled and used only for delivering quinoline to avoid any contamination. In the calibration of other liquid compounds, another 2 mL pipet was used, and their molar quantity was calculated using the compound's density given in the literature (18) and the molecular weight. After the addition of quinoline, 10 mL of water was added using a 10 mL graduated pipet calibrated in 0.1 mL units. Then the preweighted catalyst, ZnCl_2 , was added as the experiment required. For every reactor loading all liquids were added by pipet while solids were weighed to the nearest 0.001 gram and added. The reactor was flushed with argon and the gasket inserted. The bolts were lubricated with an oil/molybdenum disulfide mixture then the lid was bolted as tightly as possible. The reactor was suspended in the sandbath which had reached the desired temperature; it required about 15 minutes to heat the reactor to the reaction temperature. At the end of the reaction time (6 hours for Q-42), the reactor was removed from the sandbath and allowed to cool on the bench top. The cooling normally took from 60 minutes to 90 minutes to reach room temperature. When a quicker cooling time of about 15 minutes was needed, cool air was blown against the reactor while it was on the bench.

When the reactor was opened, a note would be made if any gas escaped, and the reactor was checked for leaking. If the amount of water in the reactor remained essentially the same after reaction as before, there apparently was no leaking and the experiment could be continued. Otherwise the run was abandoned, the reactor was cleaned up, reloaded and placed back into the furnace again.

The glassware was set up for extraction. To extract the material, whenever ZnCl_2 was used or any solid was found in the reactor, a piece of glass wool was placed on the stemless funnel to filter the solution. The lid and the gasket were first rinsed with a small amount of methylene chloride and the liquid was collected as part of the product mixture. The contents of the reactor were poured through the wool into the top funnel then into the separatory funnel. The reactor then was rinsed several times with small portions of CH_2Cl_2 to wash the material attached to the interior of the reactor, until the washes were colorless. Finally, any CH_2Cl_2 soluble organics on the glass wool were also washed so that any products that might be trapped on the wool were extracted. In the separatory funnel the organic product solution was separated from the top water layer. The organic layer was then collected by draining into a 25 mL volumetric flask which was filled to the mark with CH_2Cl_2 and labeled. The water was drained into a 10 mL graduated cylinder for recovered volume measurement and then taken to the Ionalyzer for ammonia analysis immediately, so that the ammonia loss through vaporization could be minimized. The solid in

the reactor (char) was collected by scraping the inner surface of the reactor and pouring the contents into a 100 mL beaker for possible further analysis.

The ammonia analysis of the water layer was carried out using the Ionalyzer which was calibrated according to the procedure given in the instruction manual (19). Standard ammonium chloride solutions had been made and were used for calibration. The sample water was prepared by diluting the reaction water to 1000 mL. The electrode was then placed in 100 mL of diluted sample and about 1.0 mL of 10 M NaOH was added. The reading from the Ionalyzer gave directly the concentration of ammonia in the water solution, which could be converted into the number of moles of ammonia.

The qualitative analyses were done using the GC/MS procedure in only a few experiments to identify the products formed in the quinoline reaction. In a preliminary experiment, an 8 microliter (uL) sample of product was injected into the F and M GC to find the relative retention times of the products to be analyzed, then a 5 uL sample of the organic layer was injected into the GC/MS. The column conditions were: initial temperature 60 C, program temperature 4 C/minute, final temperature 175 C. Mass spectra were obtained at several different locations of each chromatographic peak. Because of the complexity of the product mixture, the acidic components were separated from the others by extracting with aqueous base, the extract was reacidified and extracted with CH_2Cl_2 , then this solution and the original organic layer were examined by GC/MS. By

the comparison of the mass spectra with the standard mass spectra given in the literature (20), the identification of the compounds in the product mixture was made. The identities of the compounds were then confirmed using GC by spiking the reaction product mixture with known compounds.

Based on the GC principle that the quantity of a compound in the solution is proportional to the peak area under the GC curve of that compound, quantitative measurement of the quinoline reaction products was possible. The quantitative analyses for this work began with calibrating the GC response, the procedure for determining a calibration factor will be described using quinoline. A typical calibration standard solution was prepared by adding 0.5 mL quinoline to CH_2Cl_2 to a total volume of 25 mL in a volumetric flask. However, to reduce the total number of injections needed to calibrate the instrument for several compounds, quinoline was added with other standard compounds such as 0.5 mL toluene, 0.5 mL aniline, and 0.5 mL 2-methyl quinoline to make a mixture of standards. All volumes were measured by pipet, and the standard solutions were prepared using 0.5 mL, 1.0 mL, 2.0 mL, and 4.0 mL of compound per 25 mL solution for each known compound. For the compounds found in smaller quantities in the reaction mixture, such as toluene, ethylbenzene, and xylene, standard solutions using 0.1 mL, 0.2 mL, 0.4 mL, and 0.5 mL were also prepared. A minimum of three 8 μL samples were injected into the F and M GC. The column conditions for running the calibration and reaction samples are given below,

and there were no changes during the analyses of the product mixtures: the initial temperature was 70 C, the programmed temperature rate for the first 7 minutes was 5 C/minute, then the rate was increased to 20 C/minute until the final temperature of 260 C was reached. The temperature was then held at this point until all the compounds had been eluted. Higher attenuation settings were used to avoid going off the scale when there were high concentrations of a compound in the solution.

Each peak was carefully measured for both peak height and the width at one-half the peak height. The product of peak height and the width gave a measured peak area. The height was measured in millimeters to ± 1.0 mm, while the width was measured to ± 0.2 mm. To reduce the error due to the narrow peak width, the width was carefully defined as the distance between the outside edges of the ink line. The attenuated peak area was obtained by multiplying the measured area by the GC attenuation and the attenuated peak area was used for the response factor calculation. The response factors were checked periodically, especially for quinoline, so that the analyses could be as accurate as possible. There were differences in the factors from the more concentrated solutions and those from the more dilute solutions for some compounds such as toluene when used as the SF, thus a plot of the response factor vs. concentration was made and used to reduce the factor error. By using the response factors, the mole percents of known products formed, based on the initial moles and on the converted moles, were calculated. A sample

calculation will be given in a later section.

After quantitative analysis, the sample was poured into an evaporating dish, and the dish was placed in a paraffin oil bath, which was heated gently to 110 C for 24 hours. The solution was changed into tar after complete evaporation of volatiles. The mass of the tar was then determined, redissolved with CH_2Cl_2 and stored for checking. Several pure compounds such as quinoline, 2-methylquinoline, and toluene were also heated individually in the dish to confirm that there was no residue left from the reactant or volatile products because of decomposing or charring.

The solids from the reactor and glass wool were ground and treated with about 50 mL dilute HCl to remove any metal oxides from the char. Then it was washed several times on a piece of filter paper to remove the acid. The solid was then dried and its mass determined to 0.01 g. To obtain carbon, hydrogen, nitrogen, and oxygen analyses of both tar and char, samples Q-61 and Q-78 were completely dried and sent out for elemental analysis.

Calculations

The unit for the response factor was defined as the attenuated area/uL sample*mole in 25 mL of solution, and the calculation procedure for quinoline serves as an example.

Properties of quinoline: density = 1.094 g/mL, M.W. = 129.15 g/mole

Attenuated area for 8 uL of a 1.0 mL quinoline/25 mL solution:

$$\text{height} \times \text{width} \times \text{attenuation} = 130 \pm 1 \text{ mm} \times 1.9 \text{ mm} \times 8 = 1976 \pm 210 \text{ mm}^2$$

Attenuated area per microliter:

$$1976 \text{ mm}^2 / 8 \text{ uL} = 247 \pm 26 \text{ mm}^2 / \text{uL}$$

Average attenuated area per microliter (3 injections):

$$(247 + 237 + 239) / 3 = 241 \pm 4 \text{ (mm}^2 / \text{uL)}$$

Thus, the attenuated area per microliter solution per mL quinoline:

$$241 \text{ mm}^2 / \text{uL} / 1.0 \text{ mL} = 241 \text{ mm}^2 / (\text{uL} \times \text{mL})$$

The propagated error appears much larger than the statistical error due to the relatively large uncertainty in the narrow widths.

The attenuated area per microliter solution per gram quinoline:

$$241 \text{ mm}^2 / \text{uL} \times \text{mL} / (1.094 \text{ g/mL}) = 220 \text{ mm}^2 / (\text{uL} \times \text{g})$$

The attenuated area per microliter solution per mole quinoline:

$$(220 \pm 4 \text{ mm}^2 / \text{uL} \times \text{g}) \times 129.15 \text{ g/mole} = 28450 \pm 500 \text{ mm}^2 / (\text{uL} \times \text{mole})$$

The final response factor was calculated by averaging all the individual response factors from different concentrations, and used as the response factor for further calculations:

$$(27880 + 28010 + 28450 + 29340) / 4 = 28420 \pm 480 \text{ mm}^2 / (\text{uL} \times \text{mole})$$

A list of response factors used in this work is in Appendix A of this thesis.

In quantitative calculations for all of the reactions, nitrogen removal, or denitrogenation, is defined as the moles of ammonia formed/mole of the reacted nitrogen compound $\times 100$, and product yields in percents are calculated on the same basis.

A sample calculation using the results of the experiment Q-42 and showing in detail the product distribution is as follows:

Reaction condition: quinoline (Q) = 2 mL, H₂O = 10 mL, ZnCl₂ = 0.2 g, temperature = 450 C, time = 12 hours

Sample size in injection = 8.0 μ L.

Initial Q = (2.000 mL*1.094 g/mL)/129.15 g/mole = 0.01694 mole

Response factor of Q = 28420 \pm 480 mm²/ μ L/mole in 25 mL solution

Attenuated area per microliter Q = height*width*attenuation/ μ L

$$(106 \text{ mm} * 2.00 \text{ mm} * 8) / 8 \text{ uL} = 212 \text{ mm}^2 / \mu\text{L}$$

The average attenuated area per microliter (3 runs):

$$(212 + 202 + 210) / 3 = 208 \pm 4 \text{ (mm}^2 / \mu\text{L)}$$

The moles of the compound recovered = attenuated area/ μ L/-
response factor:

$$208 \pm 4 \text{ mm}^2 / \mu\text{L} / (28240 \pm 480 \text{ mm}^2 / \mu\text{L} / \text{mole}) = 7.31 \pm .19 \times 10^{-3} \text{ mole}$$

% of Q recovered = (mole of Q recovered/mole of initial Q)*100%

$$7.31 \times 10^{-3} / 1.694 \times 10^{-2} * 100\% = 43.2 \pm 1.1\%$$

% of Q reacted = 100% - % of Q recovered:

$$100 - 43.2\% = 56.8 \pm 1.1\% = 57\%$$

For toluene, response factor = 28440 \pm 600 mm²/ L/mole

The average attenuated area = 19 \pm 2 mm²

The average attenuated are per μ L = 19 mm²/8 μ L = 2.4 \pm .3 mm²/ μ L

The moles of toluene formed = 2.4/28440 = 8.4 \pm 1.1 $\times 10^{-5}$ (mole)

Percent yield based on initial Q [% (BI)] = (mole of compound
formed/initial mole of Q)*100% =:

$$[8.4 \times 10^{-5} / 1.69 \times 10^{-2}] * 100\% = 0.5 \pm .1\%$$

Percent yield based on %mole of Q reacted $[\% (BR)] = [\% (BI)/\%$
of Q reacted] $*100\% =$

$$(0.5\%/57\%)*100\% = 0.9 \pm 2\%$$

In exactly the same way the yield for each known compound in the product mixture was calculated for % (BI) and % (BR). For some minor compounds which were not identified (thus response factors were not available) the percent yield was estimated based on the response factor of a compound with a molecular weight close to that of the unidentified compound. For example, the response factor of quinaldine is $36070 \text{ mm}^2/\mu\text{L}\cdot\text{mole}$, and the average attenuated peak area is 285 mm^2 , thus

$$\% (BI) = 285/8/36070/0.01694*100\% = 5.8\%$$

$$\% (BR) = (5.8\%/57\%)*100\% = 10.2\%$$

The molecular weight of other methylquinolines is the same as quinaldine, and their average peak area is 34 mm^2 , thus the percent yield for it was estimated as follows: $\% (BI) = (\text{average attenuated area of unknown}/\text{average attenuated area of quinaldine})*\% (BI)\text{quin-aldine} =$

$$(34/285)*5.8 = 0.7\%$$

similarly,

$$\% (BR) = (\% BI/\% \text{ reacted})*100 = 0.7/0.57 = 1.2\%$$

Table 1 is an example of the volatile organic compounds formed in run Q-42.

Table 1
Quantitative Results From Run Q-42

Compound	Average Attenuated Area	% (BI)	% (BR)
Quinoline	1664	43	57
Toluene	19	0.5	0.9
Ethylbenzene	20	0.5	0.9
Xylene	18	0.5	0.9
Aniline	75	2.6	4.6
Phenol	226	8.2	14.4
Mixture 1	145	(3.6)	(6.3)
Mixture 2	69	(1.7)	(3.0)
Isoquinoline	9	0.3	0.5
Quinaldine	285	5.8	10.2
Mixture 3	151	(3.0)	(5.3)
Methylquinoline	34	(0.7)	(1.2)

The values in parentheses were the ones estimated. The values for mixtures were estimated assuming an average response factor for the components, and mixture 1 includes indane, cresols, methylindane, and toluidine; mixture 2 includes xylenols, xylidines, and naphthalene; mixture 3 includes other methylquinolines and dimethylquinolines.

The mass of Q reacted = initial mass of Q*percent reacted Q =

$$2 \text{ mL} \cdot 1.094 \text{ g/mL} \cdot 57\% = 1.25 \text{ g}$$

Percent of reacted Q forming volatile product:

$$0.9\% + 0.9\% + 0.9\% + 4.6\% + 14.4\% + 6.3\% + 3.0\% + 0.5\% + 10.1\% + 5.3\% + 1.2\% = 48.1\%$$

The mass of reactant forming volatile product = fraction total volatile product*mass of Q reacted =

$$1.25 \text{ g} \cdot .481 = 0.60 \text{ g}$$

The mass of char = 0.12 g

The mass of tar = 0.49 g

Total reacted mass recovered = mass forming volatile product + mass of char + mass of tar =

$$0.60 \text{ g} + 0.12 \text{ g} + 0.49 \text{ g} = 1.21 \text{ g}$$

The reading on the Ionalyzer gave directly the concentration of NH_3 in the sample water for Q-42, which was 2.2×10^{-3} M. Since the water was diluted to 1000 mL, the number of moles of NH_3 in the water was the same as the reading. Thus, the percent yield of ammonia (BI) = (mole of NH_3 /mole of initial Q)*100% = $[2.2 \times 10^{-3} \text{ mole} / 1.694 \times 10^{-2}] \cdot 100\% = 13\%$. The percent nitrogen from converted Q appearing as ammonia in the products (BR) = $(13\%/57\%) \cdot 100\% = 23\%$.

The hydrogen balance for the reaction was calculated as follows: mole of H reacted = fraction of Q reacted*moles of initial Q*number of H in Q =

$$.57 \cdot .01694 \cdot 7 = 6.76 \times 10^{-2} \text{ (moles)}$$

The moles of H for each known compound was calculated using the following formula: mole of H of a compound = $[\%(\text{BR})/100] \cdot \text{fraction of Q reacted} \cdot \text{initial mole of Q} \cdot \text{number of H in the compound}$.

Thus,

$$\text{moles of H of toluene} = .009 \cdot .57 \cdot .01694 \cdot 8 = 7.0 \times 10^{-4} \text{ (moles)}.$$

For the mixtures, the average H number calculated from the compounds

in the mixture was used. The mass of H in the char was calculated by multiplying the mass of the char by the fraction H in the char, which was an average value based on the element analyses of two samples. The mass of H in the tar was also calculated in a similar way. Table 2 is a sample list showing the hydrogen balance calculation results for run Q-42.

Table 2
Hydrogen Balance Calculation Results

Compound	Number of H (or% H)	mole of Hx10 ³
Toluene	8	.7
Ethylbenzene	10	.9
Xylene	10	.9
Aniline	7	3.1
Phenol	6	8.3
Mixture 1	9	5.5
Mixture 2	10	2.9
Isoquinoline	7	.3
Quinaldine	9	8.8
Mixture 3	11	5.6
Methylquinoline	9	1.0
Char	2.7	3.2
Tar	4.6	22.5
NH ₃	3	6.7
Total		70.4

The ratio of H in the product to that reacted = $70.4 \times 10^{-3} / 67.6 \times 10^{-3} = 104\%$

% of reacted H/% product recovered = $104/96 = 108$.

The difference between moles of H reacted and that of the product:

$$\Delta(H) = 70.5 \times 10^{-3} - 67.6 \times 10^{-3} = 2.9 \times 10^{-3}$$

The rate constant for each experiment was calculated assuming the quinoline reaction followed first-order kinetics. Subsequently the data proved this assumption to be valid. Thus,

$$-d[Q]/dt = k[Q] \quad (3)$$

where $[Q]$ is the concentration of quinoline, t is the reaction time in seconds and k is the rate constant in sec^{-1} . The integration of equation (3) gives:

$$-\ln [Q] = kt + C \quad (4)$$

where C is an integration constant. At $t = 0$, $[Q] = [Q]_0$ therefore,

$$-\ln [Q]_0 = C \quad (5)$$

Substituting (5) into (4) and rearranging gives

$$\ln ([Q]_0/[Q]) = kt \quad (6)$$

Let x be the fraction of quinoline reacted, then

$$[Q] = [Q]_0(1-x) \quad (7)$$

Substitute (7) into (6):

$$\ln [1/(1-x)] = kt \quad (8)$$

For Q-42, $x = 0.57$, and the time for the reaction was 12 hours, or $t = 12 \text{ hours} = 12 \text{ hours} \times 3600 \text{ seconds/hour} = 4.32 \times 10^4 \text{ seconds}$. The rate constant for the reaction can then be calculated using equation (8):

$$\ln [1/(1-0.57 \pm 0.01)] = k \cdot 43200$$

and

$$k = 1.95 \pm 0.05 \times 10^{-5} \text{ sec}^{-1}$$

Using the Arrhenius law (21):

$$k = Ae^{(-E/RT)} \quad (9)$$

where R is the gas constant (1.987 cal/K mole), T is the absolute temperature in K, E the activation energy and A is the frequency factor (sec^{-1}), it is possible to calculate E for the quinoline reaction. Taking logarithms of both sides of equation (9):

$$\ln k = \ln A - E/RT \quad (10)$$

If the Arrhenius law applies to the quinoline reaction, a plot of $\ln k$ versus $1/T$ will be a straight line, and the slope (which has the unit of K) will be $-E/R$. Thus the E can be given by the product of R and $-\text{slope}$. For the quinoline reaction with 0.2g ZnCl_2 the average rate constants at each temperature were:

Temperature	$k \times 10^6 (\text{sec}^{-1})$
673	5.9 ± 1.0
723	19.3 ± 1.7
773	$81. \pm 11$

A plot of $\ln k$ versus $1/T$ was made by performing a least squares linear regression, and the slope and the intercept of the plot were -13601 ± 1290 K and 8.10 ± 1.79 , respectively. Therefore,

$$\begin{aligned} E &= -\text{slope} \cdot R = -(-13601 \cdot 1.987) \\ &= 27025 \pm 2565 \text{ (cal/mole)} = 27.0 \pm 2.6 \text{ Kcal/mole,} \end{aligned}$$

and

$$\ln A = 8.10, A = 3300/\text{sec.}^{-1}$$

CHAPTER III

RESULTS AND DISCUSSION

Quinoline Reaction

The extent of the quinoline reaction was significant at SW conditions and produced volatile organic compounds, low volatility tar and char. The extent of reaction varies with time, temperature, water density and catalyst concentration, but not with quinoline concentration. The analyses of volatile organic compounds and ammonia showed that some nitrogen removal was possible under SW conditions, and by controlling the reaction conditions, it is possible to control the extent of the reaction, and to some degree the distribution of volatile organic products.

Products

The reaction of quinoline at SW conditions yields three kinds of products: volatile organic compounds, a low volatility tar and a char. The volatile organic compounds are defined as the compounds vaporizing in the GC when heated up to 260 C, including benzene, toluene, ethylbenzene, xylenes, aniline, phenol, indane, cresols, methylindanes, toluidines, xylins, xylidines, naphthalene, iso-quinoline, methylquinolines, and dimethylquinolines. Among them

aniline, phenol, methylquinoline, and dimethylquinoline isomers, as well as mixture 1 in total (including indane, cresols, methylindane, toluidine) are products formed in significant quantities (See Table 5).

The char is defined as the organic solid, CH_2Cl_2 insoluble, material, some of which coated the inside wall of the reactor. Elemental analyses of chars (see Table 5, Q-60 and Q-78) produced at 450 C gave atom ratios of $\text{C}_{10.8}\text{H}_{4.8}\text{N}_{1.00}\text{O}_{0.5}$ at 81% reaction and $\text{C}_{8.6}\text{H}_{5.4}\text{N}_{1.0}\text{O}_{0.3}$ at 17% reaction, which indicates a somewhat lower nitrogen content than the reactant ($\text{C}_9\text{H}_7\text{N}$) at higher extents of reaction. When the char was treated with HCl to remove the metal ions, it was found that some white solid in the char dissolved, and a little gas was given off. It appears that some carbon was oxidizing to form carbonate in the reaction, which produced ZnCO_3 on cooling. The tar is defined as the nonvolatile organic material remaining in the organic solvent and is characterized as a dark brown, CH_2Cl_2 soluble substance. Elemental analyses of the tars from Q-60 and Q-78 gave atom ratios of $\text{C}_{10.6}\text{H}_{7.9}\text{N}_{1.0}\text{O}_{0.5}$ at 17% reaction and $\text{C}_{12.6}\text{H}_{9.5}\text{N}_{1.0}\text{O}_{0.4}$ at 81% reaction which have lower nitrogen contents than the chars, and more nitrogen is removed at higher extents of reaction. There was also a little material retained at the entrance of the GC column on the glass wool plug. No GC-MS analysis was done on this because the material could not be collected in significant quantities to make an acceptable sample for the GC-MS instrument.

The hydrogen balances for several experiments were calculated and the results are summarized in Table 3.

Table 3
Hydrogen Balances

Temperature (C)	400	450	450	450	500	500
% Q Reacted	42	40	57	81	75	62
H Reacted $\times 10^2$	4.98	4.74	6.76	9.61	8.89	7.35
H in Product $\times 10^2$	5.60	6.08	7.04	9.42	10.63	6.84
(H) $\times 10^2$.62	1.34	.28	-.19	1.74	-.51
% of Reacted H	112	128	104	98	120	93
%Reacted H/ %Prod Recovered	1.00	1.06	1.08	1.22	1.25	1.25
Run Number	Q-69	Q-58	Q-42	Q-78	Q-81	Q-82

The H in products included those from organic volatile products, char, and tar as well as ammonia. The results show that the amounts of H in the non-gaseous products were more than that of the reacted quinoline in many experiments. In addition, some product hydrogen was probably lost in the gaseous products that could not be measured. A ratio of the % of reacted H to the total products recovered compensates for variations in yields and more reliably shows that the hydrogen in the products exceeds that from the reacted quinoline. It is obvious that the extra hydrogen must come from water. This further validates the assumption that SW acts as an oxidizing agent in the quinoline-SW reaction.

Figure 3 is a schematic of the reaction sequence for the

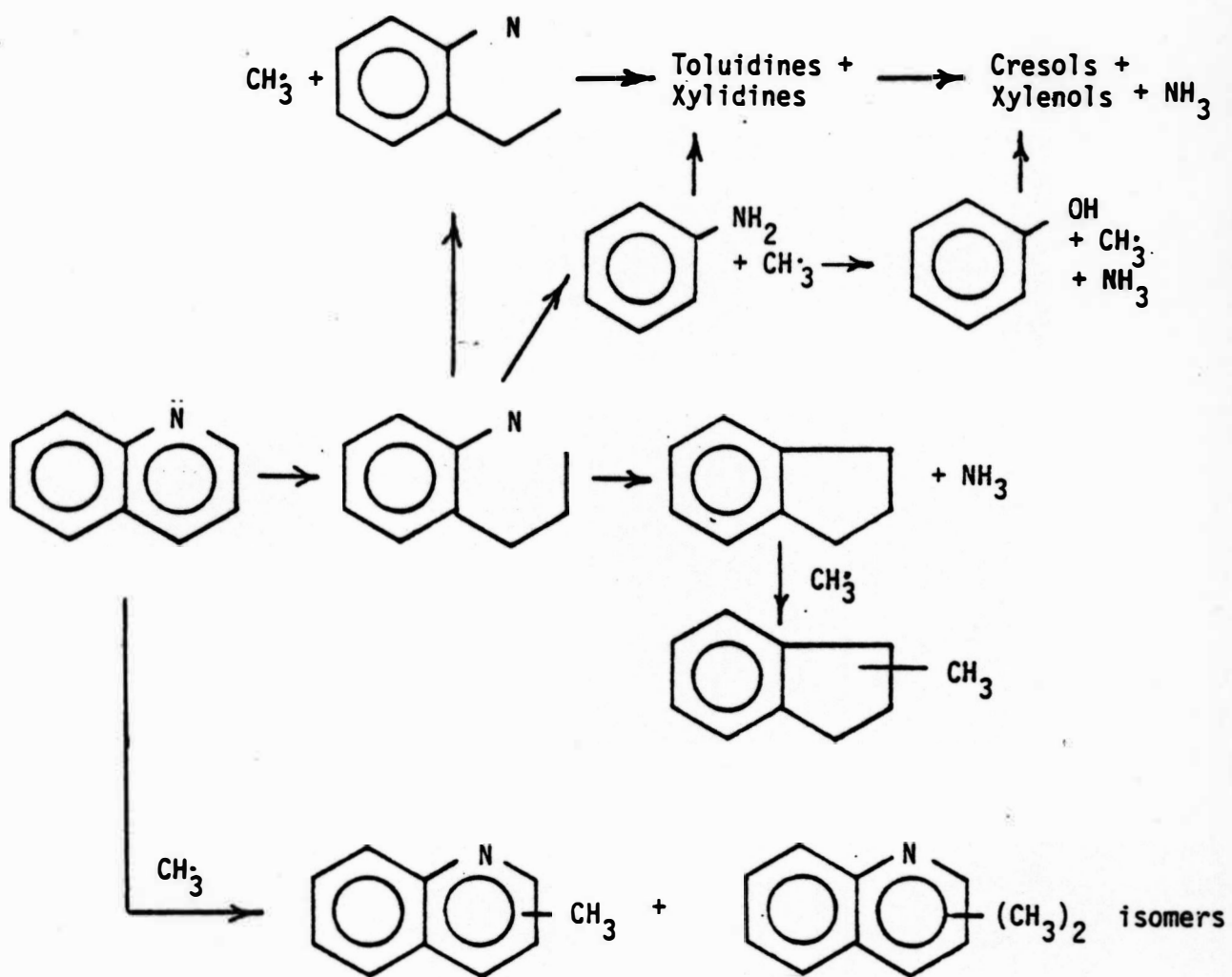


Figure 3. Quinoline - Water Reaction Schematic

formation of the known products. The intermediate formed after the initial C-N bond scission is thought to play an important role in the reaction. Its further scission provides active carbon for various products. Some minor products are not considered in the scheme, i.e. the one ring hydrocarbons, naphthalene and isoquinoline. The isoquinoline may be formed by the migration of N in the intermediate from positions 1 to 2 (22), naphthalene may be formed from either a methylindane rearrangement or a methyl-indane reaction, and the one ring hydrocarbons may result from reacted isoquinoline.

Water Density Effect

The effect of water density on the quinoline reaction is summarized in Table 4. The pressure effect on the degree of conversion and product distribution is relatively small at water densities of .213 g/mL and .255 g/mL. These results were confirmed by several sets of data obtained later, thus these conditions were used for most experiments, although some used only .170 g/mL at 500 C because of the high pressure obtained with a higher loading of water. However, too small amounts of water caused higher extents of reaction and more undesirable char to form. It is believed that this is because when smaller amounts of water are used it takes more time to establish the supercritical condition, and during this period the reactant has undergone decomposition and reforming to char and other polymeric products, as found by others (9).

Table 4
Reaction of Quinoline with Supercritical Water
Water Density Effect^a

Water (mL)	6	8	10	12	6	8	10	12
Density (g/cc)	.128	.170	.213	.255	.128	.170	.213	.255
Pressure (psi)	3990	4680	5200	5640	3990	4680	5200	5640
ZnCl ₂ (g)	.2	.2	.2	.2	.1	.1	.1	.1
% Reaction	88	64	57	48	42	32	30	24
Mass Reacted (g)	1.92	1.40	1.24	1.06	0.92	0.71	0.66	0.53
Total Volatile Product (%)	37	48	49	41	48	45	50	56
Mass Volatile Product (g)	0.71	0.67	0.61	0.43	0.44	0.32	0.33	0.53
Mass of Char (g)	0.72	0.35	0.12	0.06	0.33	0.02	0.03	0.04
Mass of Tar (g)	0.15	0.26	0.49	0.46	0.23	0.33	0.42	0.38
Total Products Mass (g) ^b	1.58	1.28	1.22	0.95	1.00	0.67	0.78	0.71
% NH ₃ ^c	19	21	23	27	21	21	26	32
Run Number	Q-44	Q-43	Q-42	Q-41	Q-48	Q-47	Q-46	Q-45

^a Other conditions for all of these experiments were time 12 hours, temperature 450 C, and 2 mL quinoline.

^b Total product mass is calculated as the quinoline necessary to form those products, some mass was lost as gaseous products not measured.

^c The ammonia yield was calculated based on the fraction reacted.

Kinetic Results

The results of the different initial quinoline concentrations at three temperatures are summarized in Table 5. The consistency of the results indicates that changing the concentration of quinoline had little effect on the extent of the reaction, the nitrogen removal efficiency and the distribution of the products. This consistency justifies the application of first-order kinetics to the quinoline-water reaction. The product yields for 0.5 mL quinoline reaction are not very reliable because of the difficulty of measuring the small peak areas in the chromatogram. The insensitivity of the GC to very small amounts probably contributes to the low yield in some experiments.

The effect of time on the quinoline reaction with SW is summarized in Table 5 also. Using first-order kinetics the rate constant for each reaction condition was calculated. The rate constants show a somewhat larger variation at 400 than at 450 C, but no trends are evident at these temperatures. The data showed a general rising trend of % NH_3 with time for the reaction at all temperatures, ranging from 20% to 72%, but again with a large scatter. Lastly, it is interesting to note that phenol yields increase with time, while those of quinaldine decrease at the two higher temperatures, indicating that longer time favors the substitution of $-\text{NH}_x$ by $-\text{OH}$. In other words, longer time favors nitrogen removal from quinoline and its products.

Temperature affects the extent of the reaction, varies the

Table 5
Reaction of Quinoline with Supercritical Water^a
Kinetic Data
400 C

Water (mL)	10	10	10	10	12	12	12	12	10	10
Quinoline (mL)	2	2	2	2	2	2	2	2	1	4
Time (hour)	6	12	24	48	6	12	24	48	24	24
% Reaction	12	21	42	58	8	24	51	52	45	43
Mass Reacted (g)	.27	.46	.92	1.27	.18	.53	1.11	1.13	.49	1.87
Volatile Products ^b										
Benzene	0	0	0	0	0	0	0	0	0	0
Toluene	0	0	.4	.5	0	0	.4	.5	.3	.4
Ethylbenzene	0	0	.4	.4	0	0	.4	.4	.4	.5
Xylene	2	0	.4	.5	0	1	.4	.5	0	.5
Aniline	2.7	1.0	3.7	3.7	0	1.0	3.0	3.2	.9	4.4
Phenol	0	0	4.6	10.8	0	0	6.8	11.3	2.3	3.0
Mixture 1 ^d	6.8	2.0	5.0	10.8	2.9	2.2	3.4	8.3	3.0	5.3
Mixture 2 ^e	0	0	3.6	2.6	0	0	2.0	2.0	.9	2.3
Isoquinoline	0	0	0	0	0	0	0	0	0	0
Quinaldine	9.6	3.6	8.7	11.3	6.5	4.2	8.2	11.9	4.3	10.9
Mixture 3 ^f	0	0	7.2	8.6	0	0	4.2	8.0	2.9	7.3
Methylquinoline	0	0	1.4	2.4	0	0	1.2	1.0	0	1.0
Total Vol. Prod.	21	7	36	51	10	8	30	47	15	36
Mass Vol. Prod. (g)	.06	.03	.33	.64	.02	.04	.33	.53	.07	.65
Mass of Char (g)	.30	.18	.34	.29	.06	.23	.05	.11	.13	.17
Mass of Tar (g)	.40	.31	.38	.42	.24	.28	.39	.50	.22	1.01
Total Mass (g) ^c	.76	.52	1.04	1.35	.32	.55	.76	1.13	.42	1.83
% NH ₃	32	20	33	38	31	24	34	46	31	28
Rate Const. x 10 ⁶ /sec	6.13	5.43	6.28	5.02	3.86	6.44	8.21	4.21	6.88	6.44
Run Number	Q-72	Q-73	Q-69	Q-75	Q-68	Q-71	Q-70	Q-74	Q-77	Q-76

Table 5 (Continued)
450 C

Water (mL)	10	10	10	10	12	12	12	12	10	10	12	12	12
Quinoline (mL)	2	2	2	2	2	2	2	2	1	4	.5	1	4
Time (hour)	3	6	12	24	3	6	12	24	6	6	6	6	6
% Reaction	20	38	57	81	17	40	48	81	50	30	35	36	34
Mass Reacted (g)	.44	.84	1.24	1.77	.38	.88	1.06	1.77	.33	1.31	.19	.40	1.49
Volatile Products													
Benzene	0	0	0	0	0	0	0	0	0	0	0	0	0
Toluene	1.4	1.1	.9	.7	1.2	.8	.7	.7	.7	.6	0	.6	1.3
Ethylbenzene	1.0	1.0	.9	.6	1.7	.8	1.0	.3	1.4	1.2	.7	.7	0
Xylene	2.0	1.3	.9	.5	3.4	1.0	1.0	.6	1.6	1.0	2.0	1.7	1.3
Aniline	2.5	7.0	4.6	2.7	6.2	5.7	4.0	2.7	2.9	4.2	0	1.7	9.8
Phenol	0	10.4	14.4	15.3	4.6	9.2	10.0	15.7	4.0	2.0	4.4	4.8	8.0
Mixture 1	5.0	6.0	6.3	9.3	9.3	9.4	5.0	6.7	4.3	8.0	0	4.5	13.0
Mixture 2	2.5	4.0	3.0	1.6	5.2	4.3	3.0	1.2	4.0	6.0	0	1.9	7.7
Isoquinoline	0	0	0	0	0	0	0	0	0	0	0	0	0
Quinaldine	8.6	15.7	10.1	6.4	14.5	12.8	10.9	7.8	7.4	11.4	3.5	6.1	.8
Mixture 3	1.4	7.8	5.3	4.5	1.2	6.3	5.0	4.5	1.4	9.0	0	2.0	8.6
Methylquinoline	1.4	1.3	1.2	1.4	0	1.3	0	.9	0	1.0	0	0	1.0
Total Vol. Prod.	26	56	48	43	47	52	41	41	28	44	11	24	69
Mass Vol. Prod. (g)	.11	.47	.60	.76	.18	.46	.43	.73	.09	.58	.02	.10	1.03
Mass of Char (g)	.26	.26	.12	.21	.21	.24	.06	.15	.14	.34	.05	.12	.10
Mass of Tar (g)	.28	.50	.49	.35	.34	.40	.46	.51	.20	.73	.10	.22	1.05
Total Mass (g)	.65	1.23	1.21	1.32	.73	1.10	.95	1.39	.43	1.65	.17	.44	2.18
% NH ₃	21	32	23	47	41	32	27	48	25	39	31	28	39
Rate Const. x 10 ⁵ /sec	2.10	2.24	1.94	1.92	1.74	2.36	1.52	1.92	1.68	1.66	1.98	2.08	1.89
Run Number	Q-61	Q-59	Q-42	Q-79	Q-60	Q-58	Q-41	Q-78	Q-65	Q-63	Q-66	Q-64	Q-62

Table 5 (Continued)
500 C

Water (mL)	10	10	10	10	10	10	10
Quinoline (mL)	1	2	4	.5	1	2	4
Time (hour)	3	3	3	6	6	6	6
% Reaction	65	62	69	79	79	75	79
Mass Reacted (g)	.71	1.36	3.02	.43	.86	1.64	3.47
Volatile Products							
Benzene	1	.2	0	0	0	.4	.7
Toluene	.6	.9	.8	.7	.7	1.7	1.7
Ethylbenzene	.2	.5	.4	0	.2	.7	.6
Xylene	.4	.5	.3	0	.4	.5	.2
Aniline	2.6	5.8	6.0	0	1.5	2.6	4.1
Phenol	14.9	13.7	8.6	12.8	17.8	28.2	14.5
Mixture 1	2	3.7	3	.6	2.5	7.8	2.9
Mixture 2	1	1	1	0	.6	4.8	1.2
Isoquinoline	1.6	1	1	.5	1.1	0	.9
Quinaldine	3.4	5	5	1.6	1.9	4.8	1.8
Mixture 3	2	3.1	4	0	1.5	4.0	1.5
Methylquinoline	0	0	0	0	0	.6	0
Total Vol. Prod.	30	35	30	16	28	56	30
Mass Vol. Prod. (g)	.21	.48	.9	.07	.24	.92	1.04
Mass of Char (g)	.02	.09	.46	.10	.14	.29	1.08
Mass of Tar (g)	.22	.43	.93	.13	.17	.37	.92
Total Mass (g)	.45	1.00	2.29	.30	.55	1.58	3.04
%NH ₃	42	56	43	60	65	72	68
Rate Const.x10 ⁵ /sec	9.7	9.0	10.8	7.2	7.2	6.4	7.2
Run Number	Q-89	Q-82	Q-88	Q-90	Q-92	Q-81	Q-91

^a All experiments used 0.2 g ZnCl₂ catalyst.

^b The values for volatile products are % yields based on % of quinoline reacted.

- ^c Total product mass is calculated as the quinoline necessary to form those products, some mass was lost in gaseous products not measured.
- ^d The values for mixtures were estimated assuming an average response factor for the components. Mixture 1 consists of indane, cresols, toluidine, and methylindanes.
- ^e Mixture 2 consists of xylinsols, xylindenes, and a little naphthalene.
- ^f Mixture 3 consists of other methylquinoline isomers and dimethylquinoline isomers.
- ^g The element analysis of both char and tar for Q-78 have the atom ratio of $C_{10.8}H_{4.8}N_{1.0}O_{0.5}$ and $C_{12.6}H_{9.5}N_{1.0}O_{0.4}$, respectively. The atom ratio in both char and tar for Q-60 were $C_{8.6}H_{5.4}N_{1.0}O_{0.3}$ and $C_{10.6}H_{7.9}N_{1.0}O_{0.5}$, respectively.

efficiency of nitrogen removal, and changes the distribution of the products. The conversion rate increases with temperature, and based on the first-order kinetics, the average rate constants are:

T (K)	k(1/sec) x 10 ⁶
673	5.9±1.0
723	19.3±1.7
773	81. ±11.

Using the Arrhenius law, the activation energy for the quinoline reaction was calculated, and the average activation energy was 27.0±2.6 Kcal/mole, which is about one fourth of the C-C bond energy (117.2 Kcal/mole) and C-N bond energy (106.5 Kcal/mole) in heterocyclic rings(23). In general, nitrogen removal efficiency is increased with temperature. It was noted that at 500 C a higher % NH₃ could be reached at shorter times and comparable extents of reaction than those at lower temperatures, indicating that high temperatures favor the removal of nitrogen from quinoline. The results also show the temperature effect on the product distribution. As the temperature increases from 400 to 500 C, the yields of non-nitrogen-containing compounds in the product mixture increased, ranging from 6% to 44%. In addition, it was found that phenol yields increase with temperature, indicating higher temperatures favor substitution of NH_x by -OH. Quinaldine yields were less at high temperatures, indicating that at high temperature, instead of the combination with methyl radical to form quinaldine the reactant undergoes more C-N bond scission to generate several intermediates.

Moreover, high temperature makes C-C bonds more reactive since benzene was found as a product only at 500 C. Finally, isoquinoline was also formed only at 450 and 500 C, in yields ranging from 0.5 to 2%. This provides evidence that the intermediates possess diradical nitrene character and undergo C-to-N migration to form the precursors of isoquinoline (22).

Catalyst and Additive Effects

The effect of the ZnCl_2 catalyst on the quinoline reaction is summarized in Table 6. Zinc chloride is assumed to act as a protic acid at SW conditions as in the hydrocracking of aromatic structures (24), and its addition increases the rate of the reaction but does not appear to affect the total yields of the volatile products based on extent of reaction. The first-order rate constant was proportional to the mass of zinc chloride, thus the 2nd-order constants were calculated by dividing the 1st-order constants by the mass of zinc chloride. Compared with the run without catalyst (Q-96 and Q-59 in Table 7), it can be seen that ZnCl_2 is an effective catalyst in the quinoline reaction with SW. However, the mass of char also increases with the amount of catalyst, which was undesirable. The catalyst also affects the nitrogen removal in the quinoline-SW reaction. In general, the NH_3 formation increases with the addition of ZnCl_2 , ranging from 23 to 50%, but the ammonia yields seem to level off at about 45% when 0.4 or more of catalyst was used.

Table 7 summarizes the results of experiments with toluene or

Table 6
Reaction of Quinoline with Supercritical Water
Catalyst Effect^a

Water (mL)	10	10	10	10	12	12	12	12	10	10	10	12	12	12
ZnCl ₂ (g)	.1	.2	.4	.8	.1	.2	.4	.8	.2	.4	.8	.2	.4	.8
Time (hour)	12	12	12	12	12	12	12	12	6	6	6	6	6	6
% Reaction	30	57	79	94	24	48	70	90	38	63	86	40	59	80
Mass Reacted (g)	.66	1.24	1.73	2.06	.53	1.06	1.54	1.97	.84	1.38	1.88	.88	1.30	1.75
Total Vol. Prod.	50	49	56	52	56	41	48	72	58	68	63	51	46	49
Mass Vol. Prod. (g)	.33	.61	.97	1.07	.29	.43	.74	1.42	.49	.94	1.19	.44	.60	.86
Mass of Char (g)	.03	.12	.45	.75	.04	.06	.14	.50	.26	.33	.82	.24	.26	.40
Mass of Tar (g)	.42	.49	.36	.24	.38	.46	.50	.35	.50	.47	.36	.40	.59	.73
Total Mass (g)	.78	1.22	1.78	2.06	.71	.95	1.38	2.27	1.25	1.74	2.37	1.08	1.45	1.99
% NH ₃	26	23	47	43	32	27	46	50	32	47	45	32	36	42
Rate Const.														
1st-Order x 10 ⁵ /sec	.84	1.94	3.58	6.36	.64	1.52	2.79	5.26	2.24	4.58	9.00	2.36	4.16	7.36
2nd-Order x 10 ^{5b}	8.4	9.7	9.0	7.9	6.4	7.6	7.0	6.7	11.2	11.5	11.3	11.8	10.4	9.3
Run Number	Q-46	Q-42	Q-50	Q-55	Q-45	Q-41	Q-49	Q-54	Q-59	Q-53	Q-56	Q-58	Q-52	Q-57

^a Footnotes on yields are the same as Table 4, all experiments were at 450 C and with 2 mL of quinoline.

^b The 2nd-order constants were calculated by dividing the 1st-order constant by the weight of catalyst, and the units are (sec.g)⁻¹.

Table 7
Reaction of Quinoline in Supercritical Toluene^a
Effect of Added Dihydroanthracene

Water (mL)	0	0	0	0	10	10	10	10
Toluene (mL)	0	15	15	10	0	0	0	0
DHA (g)	0	0	0	0	0	0	1	1
ZnCl ₂ (g)	0	0	0	0	0	.2	0	.2
Time ² (hour)	12	12	12	12	6	6	6	6
% Reaction	10	18	20	22	17	38	32	80
Mole of Benz. $\times 10^3$	0	1.0	1.4	.67	0	0	0	0
Mole of Tolu. $\times 10^2$	0	12.9	13.1	9.0	0	0	0	0
Mass of Char (g)	0	0	0	0	0	.26	0	0
Mass of Tar (g)	-	-	-	-	-	.50	-	-
% NH ₃ ^b	-	-	-	-	6	32	11	40
Run Number	Q-94	Q-95	Q-98	Q-100	Q-96	O-59	O-97	O-99

^a The temperatures were 450 C and all experiments used 2 mL of quinoline. The experiments were incomplete in terms of complete product analyses since only conversions were being compared.

^b The ammonia yield was calculated based on the quinoline reacted, it could not be determined for the toluene experiments since it is not soluble in the solvent and was lost on opening the reactor.

9,10-dihydroanthracene (DHA) added. The addition of the hydrogenation agent, DHA, showed a significant increase in conversion, up about a factor of 2 (compare Q-97 to Q-96 and Q-99 to Q-59). This indicates that the presence of hydrogen speeds the decomposition of quinoline, probably either by prereduction, thus weakening the bonds in the ring, or by stabilizing intermediates by the formation of reduced products. The quinoline reaction using toluene as the SF at 450 C was studied briefly also. The results showed less conversion with toluene than those with SW and ZnCl_2 (Q-100 and Q-59, Table 7). This confirms the suggestion that water with catalyst works better than toluene as a SF in the quinoline reaction. It was thought that ZnCl_2 would not be effective as a catalyst in toluene. One final experiment without a SF shows very little reaction at 450 C (Q-94).

Comparison to Previous Work

Early work on the isoquinoline and quinoline reactions with SW has been reported (25). The comparison of those results with this work shows several differences between quinoline and isoquinoline:

(1) The mechanism for the quinoline reaction seems to be more complex than that for the isoquinoline reaction, since more compounds were found in the product mixture from the former.

(2) No substitution of $-\text{NH}_x$ by $-\text{OH}$ occurred in the isoquinoline reaction because no OH species were found in the volatile products.

(3) The selectivity of ring rupture in isoquinoline showed no

preference for the 1-2 bond vs. the 2-3 bond, but in the case of quinoline the rupture of bonds favored the 1-2 bond over the 1-9 bond, since large amounts of phenol and aniline were found in the product.

With regard to the quinoline study, the largest discrepancy is observed for the ammonia yield. The current results showed an upper limit below 500 C of about 50% for the ammonia yields, whereas the previous results gave much higher values.

In both quinoline HDN and quinoline-SW reactions hydrocarbons and ammonia were formed though from different intermediates. Both methods may be essentially described by first-order kinetics. However, HDN requires hydrogenation of both rings before the removal of the nitrogen atom takes place, yielding propylcyclohexane as a major product, while the later requires no hydrogen, and the homocyclic ring remained intact and aromatic when the heterocyclic ring was ruptured during the reaction, yielding various substituted benzenes. The carbon is only oxidized in the quinoline-SW reaction. Finally, quinoline denitrogenation in HDN is more sensitive to temperature than that in the quinoline-SW reaction, since nitrogen removal increased from only 6% at 330 C to 42% at 375 C and was 100% at 420 C in HDN (13), while the quinoline-SW reaction showed nitrogen removal increased from 32% at 400 C to 72% at 500 C.

Miscellaneous Compounds

The reactivity of aniline and DHA with SW were briefly examined

and the results are summarized in Table 8. Only two significant products were formed from aniline and phenol was by far the dominant one, providing evidence that probably the phenol derivatives are produced from aniline derivatives in the quinoline-SW reaction. The conversion became higher in the presence of zinc chloride compared to former work without a catalyst. The ammonia yields are about 2/3 of the reacted aniline.

Because 9,10-dihydroanthracene, when used as a hydrogenating agent, was found to react with SW (25), it was examined to determine its product distribution. Over 90% of the DHA reacted, about half of which formed anthracene, several other products were also found in small amounts with retention times less than that of anthracene. The mass spectra of these products were consistent with two ring hydrocarbons.

Table 8
Reaction of Aniline and DHA with Supercritical Water^a

ZnCl ₂ (g)	.2	.2	0	0	0
Aniline (mL)	2	2	0	0	0
DHA (g)	0	0	2	1	2
Time (hour)	24	6	48	48	48
% Reaction	77	75	98	92	94
Volatile Products ^b					
Diphenylamine	5.4	4.6	0	0	0
Phenol	57	64	0	0	0
Anthracene	0	0	40	60	56
Others (Total) ^c	0	0	5	8	10
% NH ₃	92	67	-	-	-
Run Number	An-5	AN-6	DHA-4	DHA-5	DHA-7

^a Reaction conditions were: 10 mL of water at 450 C.

^b The values for volatile products were based on % of starting material reacted.

^c This mixture gave GC-MS consistent with isomers of methylnaphthalene, dimethylnaphthalene, benzyltoluene and phenyltoluene, all in small amounts.

CHAPTER IV

CONCLUSIONS

That many nitrogen-free products and ammonia are generated from nitrogen-containing compounds at SW conditions shows that water can be an effective SF for the removal of nitrogen from some types of organic compounds. The effectiveness of this removal and extent of the reaction vary with temperature and time as well as catalyst concentration. The quinoline-SW reaction can be approximately described by first-order kinetics. Since no pyridine or pyridine derivatives are found in the quinoline product mixtures, the ring rupture of quinoline shows a preference for the heterocyclic ring, and the products show that the rupture of the 1-2 bond is preferred to that of the 1-9 bond. Acidic catalysts such as zinc chloride can increase the reactivity of quinoline and aniline with SW, and in particular aids in the removal of nitrogen.

The substituted benzenes initially formed are also reactive under SW conditions. The presence of benzene, toluene, and ethylbenzene in the product mixture from quinoline demonstrates that carbons can be lost from the alkyl side chain until only the benzene ring is left, depending on the severity of the reaction conditions.

The presence of methylquinolines, xylenes, and dimethylquinolines indicates that the carbon lost from the alkyl side chain

is a reactive species capable of aromatic substitution reactions. Some of the carbons are apparently oxidized during the reaction, thus providing hydrogen for other products. Aromatic amines undergo substitution of the -NH_2 group by -OH to form phenolics and ammonia. The time dependence of the yields indicates that methylquinolines are formed early in the sequence, i.e., the first volatile product to be formed, whereas, the phenolics are formed later in the sequence.

Though the unstable intermediates have not been isolated, Figure 3 (p. 33) provides an assumed scheme for the quinoline reaction, which describes the formation of most of the identified products.

Appendix A

Table 1A
Average Retention Time, Relative Retention Time and Response Factor

Compound	R.T. (min) ^a	R.R.T. ^a	Response Factor ^b
Benzene	1.8±0.2 ^c	.136	26450
Toluene	3.9±0.3	.295	28440 ^d
Ethylbenzene	6.4±0.4	.485	32020
o-Xylene	7.5±0.5	.568	29310
Aniline	9.3±0.3	.705	21390
Phenol	9.5±0.3	.720	20280
Mixture 1 ^e	11.0±0.5	.833	(30000)
Mixture 2 ^f	12.2±0.5	.924	(30000)
Quinoline	13.2±0.3	1.000	28420
Isoquinoline	13.7±0.2	1.038	26730
2-Methylquinoline	14.1±0.3	1.068	36070
Mixture 3 ^g	14.5±0.3	1.098	(36070)
Unknown (M.W. 143)	15.5±0.5	1.175	(36070)

^aR.T. were retention times relative to the air peak and were for injections at standard G.C. operating conditions, R.R.T. were relative retention times based on the R.T. of quinoline.

^bThe response factor is the average factor from different concentrations and its unit is mm²/μL/mole in a 25 mL solution. Those values in parenthesis are estimated.

^cThe variation given in the retention time is one average deviation.

^dThis response factor was obtained from low concentration standard solutions.

^eMixture 1 includes indane, cresols, methylindane, and toluidine. The factors for mixtures are either an average response factor for the components or the same response factor as the one with a similar molecular weight.

^fMixture 2 includes xylenols, xylidines, and naphthalene.

^gMixture 3 includes methylquinolines and dimethylquinolines.

Appendix B

Steam Table^a

Water Volume (mL)	12.0	10.0	8.0	6.0
Density (g/cc) ^b	.255	.213	.170	.128
Temperature (C)	Pressure (psi)			
382	3460	3400	3280	3040
399	4020	3870	3640	3260
416	4560	4320	4000	3480
432	5100	4760	4340	3770
449	5640	5200	4680	3990
465	6170	5630	5010	4200
482	6450	6060	5300	4420
499	7110	6480	5650	4640
527	8120	6960	6180	5076
554	8770	7690	6700	5370
582	9570	8410	7110	5730
610	10440	9140	7690	6090

^aThis is a summary of the pressure values (Ref: Keenan, J.H., Keyes, F.G., Hill, P.G. & Moore, J.G. Thermodynamic properties of water including steam tables. New York: John Wiley & Sons, 1969.

^bThe density of steam was calculated using 47 mL for the reactor volume.

REFERENCES

1. Given, P.H. The distribution of hydrogen in coals and its relation to coal structure. Fuel, 1960, 39, 147.
2. Paul, P.F.M. & Wise, W.S. The principles of gas extraction. M & B Monographs CE/5, Mills and Boon, London, 1971, 20-25.
3. Whitehead, J.C. & Williams, D.F. Solvent extraction of coal by supercritical gases. J. Inst.Fuel, 1975, 182.
4. Schneider, G.M. Physicochemical principles of extraction with supercritical gases. Angew. Chem. Int. Ed. Engl., 1978, 17, 716.
5. Frank, E.U. Supercritical water. Endeavour, 1968, 27, 101.
6. Gangoli, N. & Thodos, G. Liquid fuels and chemical feedstocks from coal by supercritical gas extraction. Ind. Eng. Chem. Prod. Res. Dev., 1977, 16, 208.
7. Stenberg, V.I., Hei, R.D., Sweeny, P.G., Nowok, J. & Willson, W.G. Novel liquefaction solvent: H_2O-H_2S . Preprints, Div. Fuel Chem., Amer. Chem. Soc. 1984, 29(5), 63.
8. Vasilakos, N.P., Dobbs, J.M. & Parisi, A.S. Solvent effects in supercritical extraction of coal. Preprint, Div. Fuel Chem., 1983, Am. Chem. Soc., 28(4), 212.
9. Deshpande, G.V., Holder, G.D., Bishop, A.A., Gopal, J. & Wender, I. Extraction of coal using supercritical water. Fuel, 1984, 63, 956.
10. Chementator, Dec. 25, 1972/Chem. Eng., 20.
11. Rollman, L.D. Catalytic hydrogenation of model nitrogen, sulfur and oxygen compounds. J. Catalysis, 1977, 46, 243.
12. Cocchetto, J.F. & Satterfield, C.N. Chemical equilibria among quinoline and its reaction products in hydrodenitrogenation. Ind. Eng. Chem. Process Des. Dev., 1981, 20, 49.
13. Satterfield, C.N. & Cocchetto, J.F. Reaction network and kinetics of the vapor-phase catalytic hydrodenitrogenation of quinoline. Ind. Eng. Chem. Process Des.Dev., 1981, 20, 53.
14. Flinn, R.A., Larson, D.A. & Beuther, H. How easy is hydrodenitrogenation? Hydrocarbon Processing & Petroleum Refiner, 1963, 42, 129.

15. Stern, E.W. Reaction networks in catalytic hydrodenitrogenation. J. Catalysis, 1979, 57, 390.
16. Boucher, L.J., Holy, N.L. & Davis, B.H. Coal liquid upgrading using metallophthalocyanine catalysts: Hydrogenation of the model compound quinoline. New Approaches in Coal Chemistry, ACS Symposium Series 169, Am. Chem. Soc., 1981, 319.
17. Satterfield, C.N. & Gultekin, S. Effect of hydrogen sulfide on the catalytic hydrodenitrogenation of quinoline. Ind. Eng. Process Des.Dev., 1981, 20, 62.
18. Handbook of chemistry and physics (63rd ed.). CRC Press, Inc., Boca Raton, FL: 1982.
19. Operation Manual Orion Research Ionalyzer, p. 12.
20. Stenhagen, E., Abrahamsson, S. & McLafferty, F.W. Registry of mass spectral data. John Wiley & Sons, New York, 1974.
21. Laidler, K.J. & Meiser, J. Physical chemistry, Benjamin/Cummings Publishing Co., Menlo Park, CA, 1982, 365.
22. Patterson, J.M., Issidorides, C.H., Papadopoulos, E.P. & Smith, W.T., Jr. The thermal interconversion of quinoline and isoquinoline. Tetrahedron Letters, 1970, 15, 1247.
23. Houser, T.J., McCarville, M.E. & Biftu, T. Kinetics of the thermal decomposition of pyridine in a flow system. Intl. J. Chem. Kinetics, 1980, 12, 555.
24. Salim, S.S. & Bell, A.T. Effects of Lewis acid catalysts on the hydrogenation and cracking of three-ring aromatic and hydro-aromatic structures related to coal. Fuel, 1984, 63, 469.
25. Tiffany, D.M., Houser, T.J., McCarville, M.E. & Houghton, M.E. Reactivity of some nitrogen-containing compounds at supercritical water conditions. Preprints, Div. Fuel Chem., Am. Chem. Soc., 1984, 29(5), 56.