



4-1985

Reactivity of Some Nitrogen-Containing Compounds at Supercritical Water Conditions

David M. Tiffany

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

 Part of the Organic Chemistry Commons

Recommended Citation

Tiffany, David M., "Reactivity of Some Nitrogen-Containing Compounds at Supercritical Water Conditions" (1985). *Master's Theses*. 1473.

https://scholarworks.wmich.edu/masters_theses/1473

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.



REACTIVITY OF SOME NITROGEN-CONTAINING COMPOUNDS
AT SUPERCRITICAL WATER CONDITIONS

by

David M. Tiffany

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
April 1985

REACTIVITY OF SOME NITROGEN-CONTAINING COMPOUNDS
AT SUPERCRITICAL WATER CONDITIONS

David M. Tiffany, M.A.

Western Michigan University, 1985

The use of water at supercritical conditions to remove nitrogen from several nitrogen-containing compounds was studied with the purpose of exploring the use of supercritical water as a method of removing nitrogen from the extraction products of coal. Quinoline and isoquinoline were the primary model compounds used with benzonitrile and carbazole also being examined briefly. Reaction conditions varied in temperature (350-500°C), pressure (3500-5200 psi), and water density (0.170-0.426 g/cc). The major products formed by isoquinoline were benzene, toluene, ethylbenzene, and o-xylene as well as nonvolatile tar and char. Quinoline produced aniline and toluidine in addition to those obtained from isoquinoline. Most of the reacted nitrogen was converted to ammonia. The highest yield of total hydrocarbon formed from aromatic nitrogen compounds was 55 mole%, based on reactant consumed. An order of reactivity of benzonitrile isoquinoline quinoline carbazole was established. The position of the nitrogen relative to the homocyclic aromatic ring appeared to be a major factor affecting reactivity. The use of ZnCl_2 as a catalyst was found to improve reactivity.

ACKNOWLEDGEMENTS

An expression of gratitude to my research advisor, Dr. Thomas Houser, for his help and patience and to my committee members, Dr. Michael McCarville and Dr. Robert Nagler. A special thanks to Dr. Don Iffland for his help with the mass spectrometer.

In addition, I would like to recognize Doug Conran for his patient listening as I discussed various problems with him. Finally, I would like to thank Michele McLaughlin for her help with the typing and final format.

David M. Tiffany

INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.
2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of "sectioning" the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.

**University
Microfilms
International**

300 N. Zeeb Road
Ann Arbor, MI 48106

1325231

Tiffany, David Mark

**REACTIVITY OF SOME NITROGEN-CONTAINING COMPOUNDS AT
SUPERCRITICAL WATER CONDITIONS**

Western Michigan University

M.A. 1985

**University
Microfilms
International** 300 N. Zeeb Road, Ann Arbor, MI 48106

PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy.
Problems encountered with this document have been identified here with a check mark ✓.

1. Glossy photographs or pages _____
2. Colored illustrations, paper or print _____
3. Photographs with dark background _____
4. Illustrations are poor copy _____
5. Pages with black marks, not original copy _____
6. Print shows through as there is text on both sides of page _____
7. Indistinct, broken or small print on several pages ✓ _____
8. Print exceeds margin requirements _____
9. Tightly bound copy with print lost in spine _____
10. Computer printout pages with indistinct print _____
11. Page(s) _____ lacking when material received, and not available from school or author.
12. Page(s) _____ seem to be missing in numbering only as text follows.
13. Two pages numbered _____. Text follows.
14. Curling and wrinkled pages _____
15. Other _____

**University
Microfilms
International**

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
LIST OF TABLES	iv
LIST OF FIGURES	v
Chapter	
I. INTRODUCTION	1
Supercritical Fluids	1
Hydrodenitrogenation	5
II. EXPERIMENTAL	7
Apparatus	7
Procedure	9
Materials	17
III. RESULTS AND DISCUSSION	20
Isoquinoline	20
Quinoline	24
Miscellaneous Compounds	26
IV. CONCLUSIONS	29
APPENDICES	
A. Experimental Data	34
B. Steam Table	41
C. Calibration Data	43
D. Error Analysis	45
E. Computer Programs	49
REFERENCES	61

LIST OF TABLES

1.	Data for Benzene from Run IQ-37	18
2.	IQ-37 Averages for All Identified Compounds	19
3.	Reaction of Water with Isoquinone	21
4.	Reaction of Water with Quinoline	25
5.	Reaction of Water with Other Compounds	27
A1.	Average Retention Time	34
A2.	Elemental Analysis of Organic Component of Char	36
A3.	Reaction of Water with Isoquinoline	37
A4.	Reaction of Water with Quinoline	38
A5.	Reaction of Water with Other Compounds	39
B1.	Steam Table	41

LIST OF FIGURES

1.	Reactor	8
2.	Extraction Set-up	10
3.	Isoquinoline-Water Reaction	30
4.	Quinoline-Water Reaction	31

CHAPTER I

INTRODUCTION

The removal of nitrogen from several types of molecular structures under supercritical water (SCW) conditions was the focus of this work. The purpose was to use model, nitrogen-containing compounds to determine if SCW could be used to remove nitrogen from the organic components of coal and if so, to find the least severe conditions under which removal occurred. The choice of quinoline and isoquinoline as model compounds was based on Given's model of coal (1) which characterized coal as having most of the nitrogen being incorporated into heterocyclic, aromatic rings. Much of the work was exploratory in nature, requiring the development of new procedures and analyses.

Supercritical Fluids

Supercritical fluids are substances which are above their critical temperature and pressure and therefore exist as only one phase regardless of pressure. At or slightly above the critical point a fluid has several properties which make it of interest in extracting coal. The most important property exploited by supercritical fluid extracting (SFE) is the ability of a compressed supercritical fluid (SCF) to increase the solubility (volatility) of high molecular weight, low-volatility compounds present in coal. Thermodynamic analysis of binary systems shows that the solvent power of a fluid increases with density.

Experimental data for a naphthalene/ethylene system provided evidence for the linear relationship between the log of solubility versus density (2). Since the compressibility of a fluid increases dramatically at temperatures slightly above the critical point, the greatest solubility occurs at supercritical pressures slightly above the critical temperature. Under optimum conditions this increase may be by a factor as large as 10^4 (3).

A second important property of a SCF is its low viscosity and high diffusion coefficient. Supercritical fluids have a density of about one-third that of normal fluids. This gives them a density high enough to be a good solvent while still having a viscosity low enough to be able to penetrate porous structures easily.

The use of SFE in the liquefaction of coal has been of interest for more than ten years. The major advantage of SFE has been its ability to remove low-volatility organic material. At about 400°C thermal reactions occur from the rupture of weak bonds in the coal structure generating smaller fragments that can be extracted (2). These fragments have too low a volatility to be distilled at 400°C and if they remain in the coal matrix they may polymerize to form larger, non-volatile, molecular structures leading to chars. By using SFE the volatility of these fragments can be increased enough to allow them to be extracted when formed and thereby avoid the undesired reactions. Since the solubility in SFE is dependent on pressure and density, the extracted material can be easily precipitated out of the solvent by simply reducing the pressure. As stated earlier, the greatest solubility occurs near the critical point, therefore the best supercritical solvents will be those with a critical point near the desired extraction temperature

of about 400°C.

Much of the early work with SFE was done in Great Britain by the National Coal Board (4). Most of the studies used toluene as the supercritical solvent and focused on the influence of residence time, temperature, and pressure on the yield from the SFE of coal using bench scale and small pilot plant units. More recent work has examined other possible solvents including water and methanol. Vasílakos et al (5) studied the relationship between size of solvent molecules and their effectiveness as a SFE solvent. They found that in the case of n-paraffins the relation was highly linear. When they used other solvents such as toluene, water, methanol, and acetone they found that the functionality of the solvent affected the degree of extraction. As a non-polar solvent toluene was found to be slightly better than the n-paraffins. Among the polar solvents, acetone decomposed at the experimental conditions of 400°C and gave low extraction yields. Methanol was considered inferior to the aliphatic hydrocarbons as an extracting solvent because it gave lower yields at much higher extraction pressures (20.6% at 3610 psig compared with 21.2% at 1290 psig for n-nonane). Water, on the other hand, proved to be a very effective extraction solvent (34% at 3580 psig). Deshpande et al (6) found that supercritical water appeared to act as both a solvent and reactant in the conversion of coal to gases and liquids. They also found that the fraction of the coal that remained tetrahydrofuran insoluble (char) was greater at subcritical densities than at supercritical densities and that this char fraction further decreased with SCW density and reaction time.

There are several reasons that water is a good extraction solvent. First, it meets the criteria stated earlier of having a critical point near the desired extraction temperature of 400°C (374.2°C). Second, as a polar solvent, water can exert a stronger depolymerization action on the coal than a nonpolar solvent such as toluene (2). The third, and probably most important reason involves the nature of a binary supercritical fluid system. In a binary system a critical curve, which represents the boundary between one and two phases, exists between the critical points of the two pure components. It is therefore possible to have high-density, homogeneous fluid mixtures of organics and water at temperatures around 400°C and above 3500 psi. The solubility of organic materials in water is also affected by its dielectric constant which, near the critical point, is close to that of benzene. Therefore the solubility of the organic material increases. The high density and temperature of SCW produce an additional change which may become very significant. This change is an increase in the dissociation of the water molecules which may promote acid catalysis.

A desirable function which might be performed during coal processing is the removal of heteroatoms to yield a cleaner burning product relative to possible pollutant formation. This work focused on the removal of nitrogen, since studies have shown it to be the more difficult to remove than sulfur, both of which are present in most coal. For example, Rollman (8) found that when nitrogen was bonded either within or to an aromatic ring, saturation of the ring was necessary for the scission of the C-N bond to occur. This was not true for sulfur compounds,

Water was chosen as a possible supercritical solvent for the removal of nitrogen because of its reactivity with CN compounds. Patents held by U. Schindewolf (9) claimed that aqueous cyanide solutions can be hydrolyzed into ammonia and formate salts using pressurized steam at 160-200°C. The same workers also converted cyanide salts to carbonates, hydrogen, carbon monoxide, and ammonia by melting them and reacting them at 600 to 700°C with steam.

Hydrodenitrogenation

One of the major methods currently being studied for the removal of nitrogen from heterocyclic, aromatic compounds is hydrodenitrogenation (HDN). This method involves the use of hydrogen and a catalyst to selectively hydrogenate the heteroring and remove the nitrogen as ammonia. The general mechanism for HDN involved three steps: (a) ring saturation, (b) cracking of the heteroring, and (c) loss of nitrogen as ammonia. Much of the work with hydrodenitrogenation has been done by Satterfield et al (10-13). The work has involved the use of quinoline as a model compound and NiMo/Al₂O₃ catalysts. The reactions were run in a continuous flow microreactor at pressures of 500 and 1000 psig and temperatures of 330 and 420°C. The objective of these investigators was to study chemical equilibria among quinoline and its reaction products. Some of their major results include the following: (a) 5,6,7,8-tetrahydroquinoline is thermodynamically more stable than 1,2,3,4-tetrahydroquinoline although not necessarily favored kinetically, (b) the amount of hydrogen required for effective nitrogen removal caused substantial saturation of the quinoline to form decahydroquinoline,

- (c) the hydrogenation reactions were all reversible and reached an equilibrium while the denitrogenation reactions were irreversible, and
- (d) H_2S accelerated the overall HDN process while H_2O slightly inhibited it.

Since the selective formation of 1,2,3,4-tetrahydroquinoline is kinetically controlled, Boucher et al (14) tried to improve the selectivity of the catalyst by using metallocphthalocyanines $[\text{M}(\text{PC})]$ because they have a more defined catalytic site than metal alumina catalysts. The results showed that the $\text{M}(\text{PC})$ were very selective hydrogenation catalysts but did not act as a denitrogenation catalyst.

CHAPTER II

EXPERIMENTAL

Apparatus

The equipment used in all the experiments can be divided into three groups: the reaction system, the extraction system, and the instruments used for analysis and data processing. The reaction system consisted of a stainless steel reaction vessel and a temperature regulated furnace. The reaction vessel was a cylinder, the internal volume of which was 47 ± 1.5 mL (See Figure 1). The lid was sealed using a copper gasket (id = 26mm, od = 35mm) and six, hex head, stainless steel bolts ($1/4"$ x 20 x 1"). The reactor was heated using two different methods. Early experiments used an electric furnace which was later replaced by a Tecam SBS-4 Fluidized Sandbath because the sandbath reduced the heat up time from 30 to 10 minutes. The electric furnace consisted of a 23 Ω resistance nichrome wire wrapped around a ceramic cylinder which was then surrounded with insulation. Power to the furnace was supplied by a 1 KVA variac. In both cases the heating was regulated by a chromel-alumel thermocouple connected to a Honeywell Temperature Controller, type K 200-1200°C, Model MS2. The temperature controller dial settings were calibrated and periodically checked using a thermocouple and a Leeds and Northrup model 8690-2 Millivolt Potentiometer.

Extraction and separations of the organic material from the water used a 60 mL separatory funnel, a 60 mm stemless gravity funnel, a 60

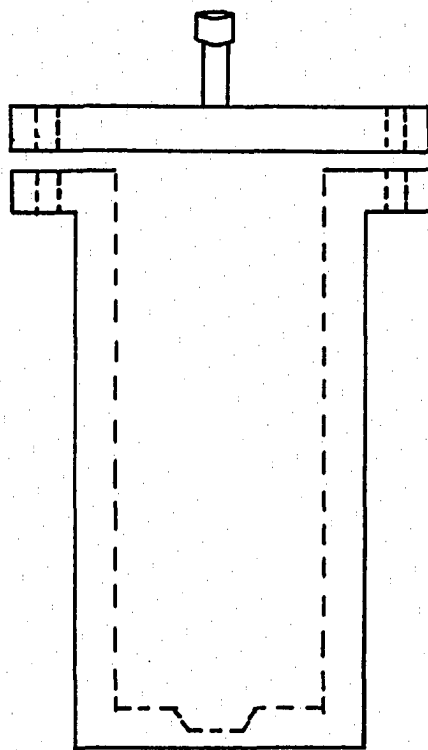
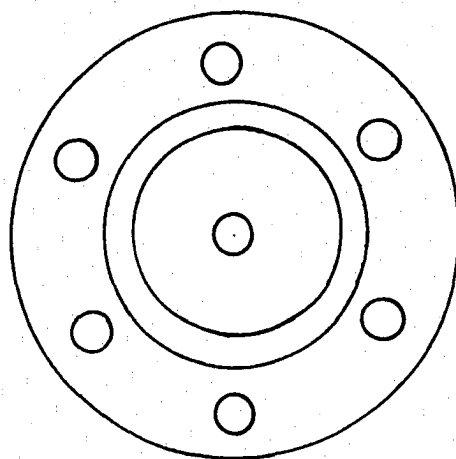


Figure 1. Reactor

mm short stem gravity funnel, and a 25 mL volumetric flask. The glassware was set up as shown in Figure 2.

Quantitative analyses were made with a F and M 720 Dual Column, Programmed Temperature Gas Chromatograph (G.C.) with a thermal conductivity detector. The general operating settings were: injector temperature 245°C, bridge current 150 ma, and detector temperature 245°C for isoquinoline experiments with an IQ# of 28 or less and 260°C for all other experiments. The temperature was raised when work began with quinoline due to the higher boiling point of some of its products. Both columns were 6' x 1/4" stainless steel tubing packed with 10% SE-30 on Chromosorb W. The carrier gas was helium and has a flow rate of about 10 cm³/7 sec (90 cm³/min) as measured by a bubble meter.

Qualitative analysis of the product mixture was performed on a DuPont 21-490B Gas Chromatograph-Mass Spectrometer (G.C.-M.S.). The G.C. used a 6' x 1/8" stainless steel column packed with 10% SE-30 on Chromosorb W and a flame ionization detector.

The ammonia analysis of the water in the reactor was accomplished with an Orion Research Ionalyzer, Model 407A, and a Model 95-10 ammonia electrode.

All calculations were done on a Hewlett-Packard HP-85 computer with the exception of the M.S. data which was converted to relative abundance spectra using a DEC-10 computer.

Procedure

The experimental procedures can be divided into four general areas: the reaction process which included the charging of the reactor, the

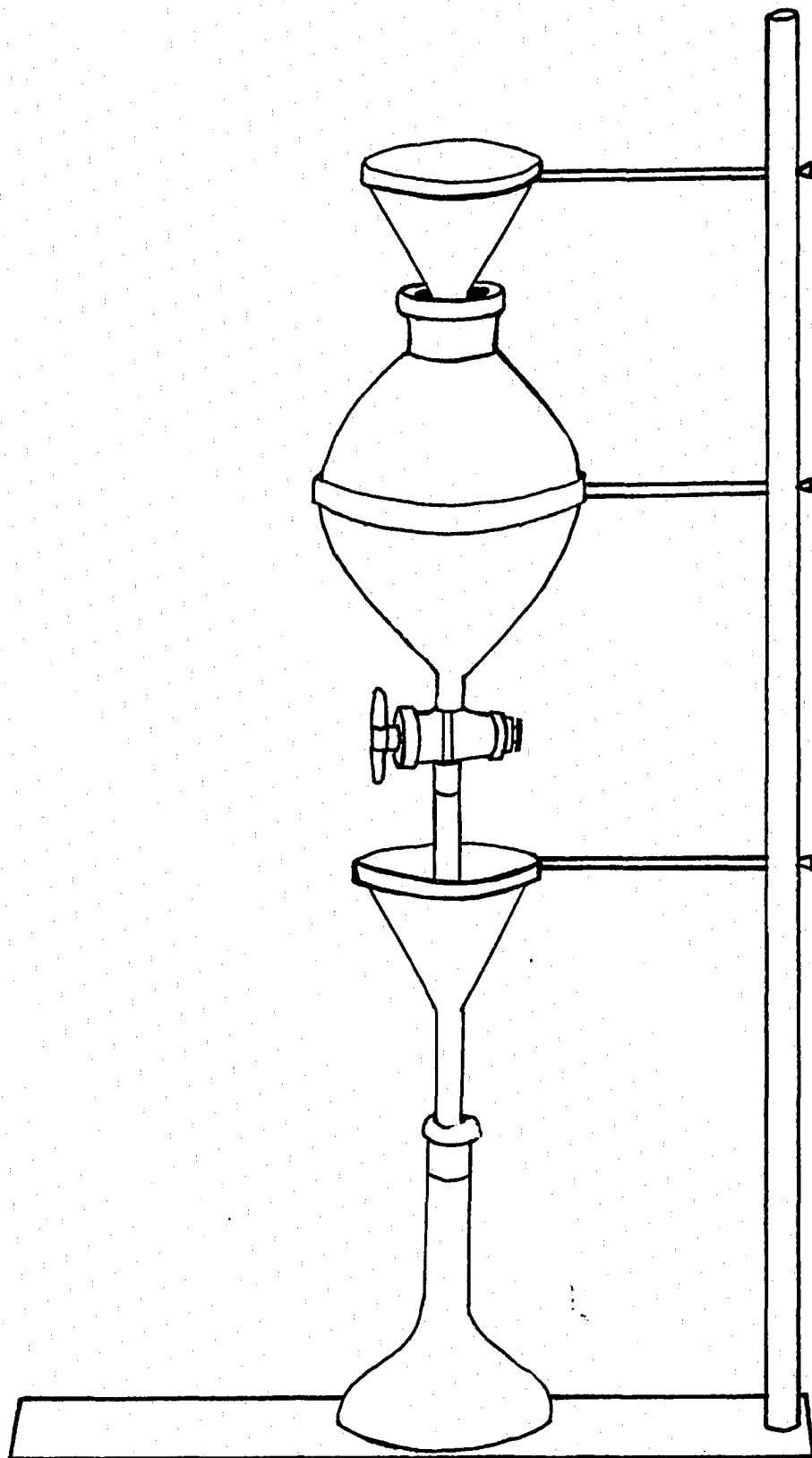


Figure 2. Extraction Set-up

reaction itself and the extraction of the reaction products; qualitative analysis of reaction products; and quantitative calibration of the gas chromatograph thermal conductivity detector; and quantitative analysis of products. The procedure for loading the reactor and extracting the products after the reaction was complete varied slightly as experimental technique improved and as some of the experimental parameters were varied.

Experiment IQ-38 (isoquinoline-38) is used as an example for describing a typical loading and extraction procedure for the quinoline and isoquinoline reactions. Major variations in the procedure are noted when they occur. A 2.0 mL pipet was calibrated and determined to deliver $2.172 \pm .009$ g (.0168 moles) of isoquinoline. It was then calibrated for quinoline and determined to deliver $2.176 \pm .009$ g (.0168 moles) quinoline. While this pipet was used to charge all liquid starting materials, it was calibrated only for quinoline and isoquinoline. For the other liquids the molar quantity was calculated using the compounds' density and molecular weight cited in the literature (15). After the 2.0 mL isoquinoline had been added, 8.0 mL water was added using a 10 mL graduated pipet calibrated in .01 mL units. If a hydrogen transfer agent or catalyst was to be used, it was added at this time. Liquids were added by pipet while solids were weighed to the nearest 0.01 gram and added. The reactor was purged with argon and the copper gasket inserted. The lid was bolted down as tightly as possible. The reactor was then suspended in the sandbath (or in the case of the early experiments, the furnace) for 96 hours. At the end of 96 hours the reactor was removed and allowed to cool on the bench top. It took

approximately 45 minutes to an hour to reach room temperature. If a quicker cooling time of about 15 to 30 minutes was desired, cool air was blown across the reactor while it was on the bench. When the reactor was opened, a note was made if any gas was vented.

To extract the material about 3 mL of distilled methylene chloride (CH_2Cl_2) was added to the reactor. If any char (insoluble solid products) was present in the reactor, a preweighed piece of glass wool was placed in the top funnel of the extraction set-up. The content of the reactor was poured through the top funnel into the separatory funnel. While pouring, additional CH_2Cl_2 was squirted into the reactor and poured into the funnel. The lip of the reactor was then washed with solvent and allowed to dry before the reactor was turned upright. The organic layer was separated from the aqueous layer and drained into a 25 mL volumetric flask. The reactor was then washed several times with small portions of solvent until the washes were colorless. These washes were also used to wash any soluble organics through the glass wool and to extract any products that might be in the aqueous layer. The 25 mL volumetric flask was finally filled to the mark with CH_2Cl_2 . The water was measured in a 10 mL graduated cylinder and the pH checked with pH paper. If the water layer was to be analyzed for ammonia it was saved in a stoppered test tube and analyzed within 24 hours to minimize loss of ammonia through vaporization. The char was collected by scraping the sides of the reactor and pouring the char into a weighing boat. The weights of the char in the boat and on the glass wool were added together for the final char weight.

To obtain a carbon, hydrogen, nitrogen, and oxygen elemental

analysis of the char, it was ground, weighed, dried to remove any volatiles trapped in it, and reweighed. The dried char was soaked in concentrated HCl to remove any metal oxides. The soaked char was collected on a preweighed sintered crucible (30 mL-30F) and washed several times with water to remove the acid. It was then dried, weighed and sent for elemental analysis.

The tar (products soluble in CH_2Cl_2 but not gas chromatographable) was analyzed in a 15 mL sample of IQ-38 by evaporating the CH_2Cl_2 on a steam bath. It was then weighed and the isoquinoline was removed by gently heating the tar in a crucible over a Meeker burner. A control of pure isoquinoline was also heated in a crucible to establish that the isoquinoline did not leave any residue due to decomposition or charring. The residue from the tar was then reweighed. The percent weight tar was calculated in the following manner:

$$\frac{\text{Tar in sample} * \text{Total Solution}}{\text{Sample Volume}} = \text{Total Tar in Solution}$$

$$\frac{0.0769 \text{ g} * 25 \text{ mL}}{15 \text{ mL}} = 0.128 \text{ g}$$

$$\frac{\text{Total Tar in Solution}}{\text{Weight Starting Isoquinoline}} = \% \text{ Weight Tar}$$

$$\frac{0.128 \text{ g}}{2.172 \text{ g} * 100} = 5.9\%$$

To determine the amount of CH_2Cl_2 insolubles in the tar residue formed during the heating, the tar residue was extracted with CH_2Cl_2 and then filtered. The insoluble residue was then weighed.

Water solution was analyzed for ammonia using the Ionalyzer which was calibrated according to the procedure given in the operation manual (16). A sample was prepared by diluting 1.0 mL of reaction water to 100 mL.

The electrode was then placed in 50 mL of diluted sample and 0.5 mL of 10 M NaOH was added. The concentration was read from the Ionalyzer.

The results of experiment IQ-36 are described as a sample calculation.

Water recovered: 7.2 mL Concentration NH_3 in sample: $8.6 \times 10^{-3} \text{ M}$

Concentration NH_3 in IQ-36: $8.6 \times 10^{-3} \text{ M} \times 100 \text{ mL}/1 \text{ mL} = 8.6 \times 10^{-1} \text{ M}$

Mole NH_3 produced in IQ-36: $8.6 \times 10^{-1} \text{ M} \times 0.0072 \text{ L} = 6.19 \times 10^{-3} \text{ moles}$

Moles isoquinoline converted in IQ-36: $.0168 \text{ moles} \times 59.5\%/100 = .01000$

Percent NH_3 of nitrogen in products: $.00619/.01000 \times 100 = 62\%$

Qualitative analysis was done using mass spectrometry in only a few experiments. Q-10 was used to determine the products formed by quinoline. The organic material was separated from the aqueous layer by extraction with CH_2Cl_2 . Any char or high molecular weight tars were removed by washing the product through a short silica gel column with CH_2Cl_2 . The eluted material was then concentrated by blowing air over the solution. This was done to remove the solvent while retaining the more volatile products. A comparison of gas chromatograms before and after evaporation showed that all the major products had been retained plus the appearance of some additional minor peaks due to their increase in concentration. About a 3 μL sample of product was injected on the F and M G.C. to establish the retention times of the products to be analysed. A sample was then injected on to the G.C.-M.S. The column conditions were: (a) initial temperature 60°C , (b) program for $4^\circ\text{C}/\text{min}$, and (c) final temperature 175°C . Mass spectrometer sweeps of each peak were made at several different parts of each peak. The ion peaks of each mass spectrum were measured and converted to relative heights with the assistance of the DEC-10 computer and the programs of MASSP.PRg and

CHM;GPPLCC. The mass spectra were compared to mass spectra in the literature for identification of the compounds (17). The identities of the compounds were then confirmed by spiking a reaction product with known compounds.

The procedure for calibrating the G.C. detector response is described using aniline. A typical aniline calibration standard solution was prepared by adding 0.5 mL aniline along with 0.05 mL toluene, 0.1 mL ethylbenzene, 1.0 mL toluidene, and 0.5 mL 4-methylquinoline to distilled CH_2Cl_2 in a 25 mL volumetric flask. Mixtures of standards were used to reduce the number of total injections needed to calibrate the instrument. Volumes of 0.05 mL or less were measured with a 50 μL syringe, all other volumes were measured by pipet. Calibration standards were prepared at 0.05, 0.1, 0.5, and 1.0 mL compound per 25 mL solution for each identified compound. Since quinoline and isoquinoline were found in larger quantities in the reaction mixture than 1.0 mL, standard solutions using 1.5 and 2.0 mL were also prepared for these compounds. The total volume of added material for each solution was 1.5 to 3.0 mL. A minimum of five 8 μL samples were injected into the F and M G.C. Column conditions were the same as those used in analysing the product mixture. The initial temperature was 70°C with a program rate of 5°C/min. for 7 minutes. The program rate was then increased to 20°C/minute until the final temperature of 250°C was reached. The temperature was then held at 250°C until all the compounds has been eluted.

The peak areas were determined by multiplying the height of the peaks by the width at one-half the peak height. The height was measured in millimeters to ± 1.0 mm while the width was measured to ± 0.2 mm. To reduce error due to the narrow peak width, the width was carefully

defined as the distance between the outside edges of the ink line. The measured area was then multiplied by the G.C. attenuation to give the attenuated area which was directly proportional to the compound's concentration.

A program on the HP-85 called "CALIB4" (see Appendix E) was used to calculate the attenuated area per microliter of sample injected.

The calculation for aniline as an example:

Attenuated area for 8 μ L 1.0 mL aniline/25 mL solution:
 $113 \text{ mm} \times 4.0 \text{ mm} \times 4 = 1808 \text{ mm}^2$

Attenuated area per microliter:
 $1808 \text{ mm}^2 / 8 = 226 \text{ mm}^2 / \mu\text{L}$

Average attenuated area/ μ L:
 1 mL aniline/25 mL solution
 $\frac{226+236+244+232+232}{5} = 234 \text{ mm}^2 / \mu\text{L}$

The final response factor was defined as the attenuated area/ μ L for 1.0 mL standard in 25 mL of solution. It was calculated by performing a least squares linear regression of all the individual response factors. The slope of the linear regression was used as the response factor.

Quantitative analyses of products were accomplished as described for the calibration experiments using an 8 μ L sample of the products in 25 mL of solution. The mole percent of known products formed as a percentage of the original amount of starting material and the amount of starting material converted were calculated using a program for the HP-85 called "%CONV5" (See Appendix E). Those products which were not identified by mass spectrometer were recorded in terms of attenuated area/ μ L.

A sample calculation using the results of the IQ-37 experiment and in detail, the benzene determination is as follows:

Sample size = 8.0 μL
 Initial isoquinoline = 0.0168 moles = 2.172 g/129.15 g/mole
 Properties of benzene: density = 0.879; molecular weight = 78.11
 Conversion factor = $\frac{298 \text{ attenuated area}/\mu\text{L sample}}{\text{mL compound}/25 \text{ mL solution}}$

Attenuated area/ μL = height x width x attenuation/ μL :
 (51 mm x 2 mm x 1)/8.0 μL = 12.73 $\text{mm}^2/\mu\text{L}$

Moles compound = [(atten. area/ L / conversion factor) x density]

Molecular weight:
 [(12.78/298) x 0.879]/78.11 = 4.82×10^{-4}

Percent yield = moles compound/moles initial isoquinoline x 100:
 0.000482/0.0168 x 100 = 2.8%

Materials

The isoquinoline and quinoline were reagent grade which was vacuum distilled. Compounds used for calibrating the G.C. were either analytical or spectral grade. In all cases the purity was high enough to show only one peak when a 2 μL sample of straight compound was injected into the G.C. The AlCl_3 and ZnCl_2 were off the shelf.

Table 1

Data for Benzene from Run IQ-37

Trial	Height	Width	Atten	Atten Area	$\frac{\text{Atten area}}{\mu\text{L}}$	mL	gr	moles $\times 10^{-4}$	% Yield
1	51	2.0	1	102	12.75	0.0428	0.0376	4.82	2.8
2	60	2.0	1	120	15.00	0.0503	0.0568	6.44	3.8
3	68	2.0	1	136	17.00	0.0570	0.0501	6.42	3.8
4	75	2.0	1	150	18.75	0.0629	0.0553	7.08	4.2
5	69	2.0	1	138	17.25	0.0579	0.0509	6.51	3.8
Average:					16.15	0.0542	0.0476	6.10	3.6

Table 2

IQ-37 Averages for All Identified Compounds

Compound Name	% Yield	% Reactant Recovered	$\frac{\% \text{ Yield}}{\% \text{ Reactant}}$
Toluene	11.0	-	14.0
o-Xylene	4.0	-	5.1
Ethylbenzene	3.7	-	4.7
Benzene	3.6	-	4.6
Isoquinoline	-	21.5	-

Total product recovered:
 $11.0 + 4.0 + 3.7 + 3.6 = 22.3\%$

Total material recovered = total product + isoquinoline recovered:
 $22.3 + 21.5 = 43.8$

Percent isoquinoline converted = $100 - \text{isoquinoline recovered}$:
 $100 - 21.5 = 78.5\%$

Percent of product identified = $\text{products recovered} / \text{isoquinoline converted}$:
 $22.3 / 78.5 = 28.4\%$

Weight percent char = $\text{weight char} / \text{weight initial isoquinoline}$:
 $0.239 \text{ g} / 2.172 \text{ g} \times 100 = 11.1\%$

CHAPTER III

RESULTS AND DISCUSSION

Isoquinoline

The extent of reaction of isoquinoline at supercritical or near supercritical water conditions, as shown in Table 3, was significant in producing alkylbenzenes, low volatility tar and char. The extent of reaction was affected by time, temperature and addition of a catalyst. While the effects of pressure or water density and hydrogenation agents were also studied, the results of those experiments were more ambiguous. The amount of alkylbenzene products along with the ammonia analysis showed that significant nitrogen removal was possible using supercritical water.

The alkylbenzenes were identified as o-xylene, ethylbenzene, and toluene. Benzene was also found at 450°C and above. The char was defined as the solid, CH_2Cl_2 insoluble material which coated the inside wall of the reactor. An elemental analysis of a char sample (see Appendix A, Table A2) produced in a reaction at 500°C gave an atom ratio of $\text{C}_{22.2} \text{H}_{10.5} \text{O}_{0.6}$. This is a significantly lower nitrogen content than the reactant. The tar was defined as the remaining organic material and was characterized as a dark brown, CH_2Cl_2 soluble material. No qualitative analysis was done on the tar except to remove the solvent and inject a sample on the G.C. The result was a complex mixture of compounds many of which had retention times greater than isoquinoline.

Table 3
Reaction of Water with Isoquinoline^a

	350	400						450						500			
Temperature (c)	350																
Pressure (psi)	2400	3640	3640	3870	3870	3870	3870	3580	4680	4680 ^c	4680 ^c	4680 ^d	4680	5200	4680	4680	
Density (g/cc)	0.170	0.170	0.170	0.213	0.213	0.213	0.213	0.106	0.170	0.170	0.170	0.170	0.170	0.170	0.213	0.128	0.128
Time (hour)	72	48	48	48	96	96	144	48	48	48	48	96	120	48	24	48	
Catalyst (g)	ZnCl ₂ 0.08	-	ZnCl ₂ 0.05	-	-	ZnCl ₂ 0.05	-	-	-	Tet	DA	-	-	-	-	-	-
IQ number	34	20/21	33	23	22	30	24	27/31	26	18	36	38	25/32	28	37	39	
% converted	33.8	24.3/13.5	54.2	30.5	49.9	57.1	50.7	55.2/46.1	42.2	93.2	58.7	82.6	80.3/89.7	81.5	78.5	61.3	
% of Converted Identified	2.3	14.3/23.0	20.8	36.3	38.0	39.6	44.3	42.8/24.3	54.5	46.8	30.6	55.3	46.5/40.8	40.9	28.4	41.5	
Products (% of Converted Reactants) ^b																	
Benzene	0	0/0	0	0	0	0.4	0	2.0/0.5	1.1	2.5	0	2.7	4.5/3.5	3.0	4.6	4.4	
Toluene	0	4.0/7.3	6.2	10.4	8.8	10.5	14.1	20.5/12.1	23.6	10.8	8.8	23.4	22.3/20.2	20.8	14.0	19.8	
Ethylbenzene	0.5	5.3/8.2	7.5	12.8	15.3	13.0	16.5	13.8/6.0	16.7	13.8	13.3	18.9	11.7/10.9	9.8	4.7	8.5	
o-Xylene	1.7	4.9/7.4	7.0	13.0	14.0	15.7	13.7	6.4/5.6	13.6	6.4	8.4	10.4	7.9/6.2	7.3	5.1	8.8	
Ammonia	-	-/-	-	-	-	-	-	-/-	-	-	63	-	-	-	-	73	
% Water Recovered	-	-/98.8	92.5	98.0	98.0	-	98.0	96.0/84.0	98.8	98.8	90.0	-	98.8/67.5	90.0	-	86.7	
Char	0	0/0	10.5	6.2	12.6	13.2	12.7	21.9/-	12.6	10.7	18.8	15.7	18.0/13/4	10.0	14.5 ^e	16.5	

^aAn experiment run at 450 C for 48 hours with no water gave greater than 90% reactant recovered and no products by GC or char

^bYields of compounds are given as mole %, char as weight %. The remainder of the sample is tar and a few minor products-very small peaks which may be aniline and toluidene were found but not measured.

^cThese experiments were with added tetralin and dihydroanthracene. The extents of reaction are believed reliable but product distributions are more uncertain because of consumption of hydrogen transfer agents.

^dAn analysis of the tar gave 5.9% isoquinoline free tar. When this was added to the rest of the products 76% of the converted material was accounted for,

^eElemental analysis of this tar gave the atom ratio C_{22.2}H_{10.5}N_{1.0}O_{0.62}.

(or quinoline). There was also evidence that some of the material was being retained at the beginning of the G.C. column in the glass wool plug. No G.C-M.S analysis was done because the non-volatiles could not be removed sufficiently to make the sample acceptable for the G.C-M.S instrument.

The effect of temperature was studied at constant pressure and at constant density. At 400°C, 0.170 g/cc H₂O, 3640 psi and 48 hours, the average degree of conversion was 18%. When the temperature was increased to 450°C at the same density of 0.170, the degree of conversion was 42%. When the temperature was raised to 450°C at a pressure of 3580 psi the degree of conversion was essentially the same at 50%. The relationship between time and degree of conversion is not yet clear. The degree of conversion increases with time at shorter reaction times but appears to level off at about 96 hours. The inconsistency in the degree of conversion for the two different times at 500°C cannot be explained.

The effect of pressure is also not yet certain. In two cases, one at 400°C with a pressure increase of 3640 to 3870 psi and one at 450°C with a pressure increase of 4680 to 5200, the pressure increases caused an increase in conversion. However, in one case at 450°C with a pressure increase of 3580 to 4680 the increase pressure caused a slight decrease in conversion.

The amount of benzene and alkylbenzenes formed showed significant nitrogen removal. It ranged from 15 to 55 mole % of isoquinoline converted with an average of 38%.

Addition of ZnCl₂ as a catalyst improved the degree of conversion but did not appear to affect the selectivity toward the alkylbenzene

products. The results from addition of the hydrogenation agent, tetralin, produced a conversion of 93%. This was significantly higher than the 42% conversion found in the reaction without tetralin. The product distribution, however, could not be determined accurately for this reaction because of interference by tetralin's decomposition products, toluene and ethylbenzene. The 59% conversion produced by the addition of 9,10-dihydroanthracene was also an improvement. However, the selectivity toward alkylbenzenes appeared to be slightly less.

Ammonia analyses of the water in two of the isoquinoline reactions showed 60 to 75 percent of the nitrogen from reacted isoquinoline was converted to ammonia.

An experiment at the subcritical conditions of 350°C and 2400 psi using ZnCl_2 catalyst and having a reaction time of 72 hours converted 34% of the reactant with only 2.7% of the product found as alkylbenzenes. In comparison a supercritical reaction at 400°C and 3640 psi using ZnCl_2 and a reaction time of 48 hours consumed 54% of the reactant with 20.9% converted to alkylbenzenes. This showed a marked increase in the amount of alkylbenzenes produced at supercritical vs subcritical conditions.

One other experiment of importance was a thermal reaction run at 450°C for 48 hours without water. In this reaction over 90 percent of the isoquinoline was recovered and no products were detected by G.C. or as char. When water was introduced at the same temperature and reaction time, the amount of conversion ranged from 42% at 4680 psi to 81% at 5200 psi.

Several duplicate experiments were done to determine the reproducibility of the extent of conversion and the distribution of products. In

all three cases the difference between the two runs was about ten percentage points. This was the same regardless of the amount of conversion. There was also significant variation in the amount of identified product as a % of converted reactant. The most likely source for this variation was the extraction procedure where small losses of the concentrated product material could significantly affect the final results.

Quinoline

The results of the reaction of quinoline at supercritical water conditions are presented in Table 4. These results showed several differences between quinoline and isoquinoline. The quinoline is significantly less reactive and required a catalyst at temperatures of less than 500°C for a large extent of reaction. Two catalysts were used, AlCl_3 and ZnCl_2 . The ZnCl_2 was found to be the better catalyst for purposes of valuable product formation, since the AlCl_3 produced almost twice as much char (13.3%) as the ZnCl_2 (5.9%).

The product distribution for quinoline was significantly different than that from isoquinoline. The average yield of identifiable products was much lower at only 17% and included large amounts of aniline and toluidine. Small amounts of quinaldine were also found. There was also significantly less o-xylene produced by quinoline than by isoquinoline. An elemental analysis of one quinoline char gave an atom ratio of $\text{C}_{12.3}\text{H}_{5.3}\text{N}_{10.5}\text{O}$. While this char was lower in nitrogen than the original quinoline, its nitrogen content was higher than the char from the isoquinoline. Two ammonia analyses of reactions at 400°C gave yields of 96 and 115%. These appear high considering the amount of char and tar

Table 4
Reaction of Water with Quinoline

Temperature (C)	400				450								500
Pressure (psi)	3870	4664	4020	4020	4680	4680	5200	5200 ^a	5200	5200	5200	5200 ^a	5650
Density (g/cc)	0.213	0.426	0.255	0.255	0.170	0.170	0.213	0.213	0.213	0.213	0.213	0.213	0.170
Time (hours)	48	48	48	48	48	48	24	48	48	48	48	48	48
Catalyst (g)	ZnCl ₂ 0.05		AlCl ₃ 0.05	ZnCl ₂ 0.05		ZnCl ₂ 0.10	ZnCl ₂ 0.01			ZnCl ₂ 0.05	ZnCl ₂ 0.05	ZnCl ₂ 0.08	
Q#	7	15	12	11	1	2	3	5	8	4	6	13	16
% Converted	22.4	27.2	60.0	53.2	28.2	81.0	14.8	9.2	5.2	78.9	55.6	54.5	70.0
% of Converted Identified	11.8	0.8	2.6	2.9	15.3	14.2	21.0	48.8	36.4	13.4	17.3	18.1	23.2
Products (% of Converted Reactants) ^b													
Benzene	0.0	0.8	0.0	0.0	0.0	0.8	0.0	0.0	0.0	0.9	0.4	0.4	4.0
Toluene	0.9	0.0	0.0	0.0	3.5	2.5	2.7	8.6	11.3	2.5	2.5	1.5	5.5
Ethylbenzene	2.5	0.0	0.0	0.0	2.0	0.9	3.7	8.0	10.6	0.9	1.3	1.4	1.8
o-Xylene	2.7	0.0	0.0	0.0	0.7	0.5	4.0	4.3	3.7	0.5	1.1	0.9	0.3
Aniline	2.4	0.0	1.4	1.5	3.8	6.0	5.4	23.6	0.0	6.2	8.3	9.2	8.3
Toluidene	3.3	0.0	1.2	1.4	5.3	3.4	5.0	4.1	10.6	2.4	3.7	4.8	3.3
Ammonia	-	-	96	115	-	-	-	-	-	-	-	-	-
Char	7.2	13.6	13.3	5.9	0.0	6.1	0.0	0.0	0.0	-	16.6	-	27.0 ^c

^aThe normal charge of quinoline was halved to 1.0 mL in experiment Q-5 and doubled in experiment Q-13

^bYields of compounds are given as mole %, char as weight %. The remainder of the sample is tar or minor products. Quinaldine was found but not measured.

Elemental analysis of this char gave the atom ratio C_{12.3}H_{5.3}N_{1.0}O_{0.5}.

produced in these reactions. This suggests a problem with the ammonia analysis which will be studied in future work. In addition an elemental analysis of the tar is needed to account for all the nitrogen.

Miscellaneous Compounds

Several other compounds were examined at supercritical water conditions, the results of which are summarized in Table 5. Benzonitrile and carbazole were reacted at supercritical conditions to study the reactivity of a nitrile and a non-aromatic nitrogen bonded between two aromatic rings. Tetralin and 9,10-dihydroanthracene, when used as hydrogenating agents, were found to react and were therefore examined to determine their product distribution. Since aniline and ethylbenzene were products of quinoline and isoquinoline respectively, these were reacted to determine if they produced secondary products.

The benzonitrile was the most reactive of the nitrogen compounds producing only benzene in a yield of over 95%. This is a substantially different product distribution from the polymer formation which would be predicted if the reaction was only a pyrolysis. The product mixture showed no discoloration indicating the nitrile was cleanly hydrolyzed followed by decarboxylation. The carbazole was the least reactive with no indication of reaction and no measurable products formed. The tetralin reacted completely, producing about 50% naphthalene and significant amounts of alkylbenzenes. The dihydroanthracene was much less reactive producing anthracene and several other products in smaller amounts and with retention times less than anthracene.

An experiment using aniline as the starting material gave uncertain

Table 5
Reaction of Water with Other Compounds

Compound	Benzonitrile	Ethylbenzene	Tetralin	DA ^b	Carbazole ^c	Aniline ^d
Temperature (C)	400	450	450	450	450	450
Pressure (psi)	3640	5200	5200	5200	5200	5200
Density (g/cc)	0.170	0.213	0.213	0.213	0.213	0.213
Time (hour)	24	48	48	48	48	48
Catalyst (g)			ZnCl ₂ 0.05	:	ZnCl ₂ 0.05	ZnCl ₂ 0.05
% Reacted	100	10	100	100	>50	<15
Products ^a						
Benzene	95	22	1.5	1.5	0	0
Toluene	-	78	10	7.0	0	0
Ethylbenzene	-	-	13	8.9	0	0
Naphthalene	-	-	52	45	0	0
Anthracene	-	-	-	-	ε	0
Ammonia	-	-	-	-	-	66
						59

^aMole % of consumed reactant. No char found for any reactant.

^bThe dihydroanthracene chromatogram showed about six products, all having longer retention times than naphthalene but shorter than anthracene, which was by far the largest in size. (The ε symbol indicates a large but unmeasured amount.)

^cCarbazole appeared close to zero% reacted.

^dDue to chromatogram anomalies, the extents of these reactions are uncertain. The only significant organic product identified was in small amounts. This indicates a small product peak. A second, large peak with a long retention time was found but not identified.

results. Two major peaks were found near the retention time of aniline. These peaks, however, could not be resolved on the G.C-M.S and therefore positive peak assignments could not be made. The aniline did show some benzene present as a product. The ethylbenzene was only slightly reactive and produced a clean product solution containing only benzene and toluene.

CHAPTER IV

CONCLUSIONS

The significant production of hydrocarbons and ammonia from nitrogen-containing compounds shows that supercritical water can be an effective reactant in the removal of nitrogen from some types of organic compounds. The effectiveness of this removal varied with molecular structure and temperature. Acidic catalysts also increased reactivity, e.g., ZnCl_2 was found to be effective. Based on the extent of reaction, the order of reactivity was found to be benzonitrile > isoquinoline > quinoline > carbazole. The reactivity of aniline could not be determined as accurately as the other compounds but it clearly falls between the extremes of benzonitrile and carbazole. One can conclude from these results that the position and bonding of the nitrogen in a molecule has a major effect on the ease of its removal.

While not enough information has been obtained to present a detailed mechanism, Figures 3 and 4 show a general reaction pathway for the known products. The carbon adjacent to the nitrogen appears to play a critical role in nitrogen removal. In every case where nitrogen was removed, as in the case of the nitrile or heterocyclic ring, one or more carbon atoms external to the benzenoid aromatic ring were lost. This was true even when the nitrogen was not removed. The absence of such a carbon in carbazole and aniline may explain why carbazole is so unreactive and aniline does not appear to decompose to benzene and ammonia.

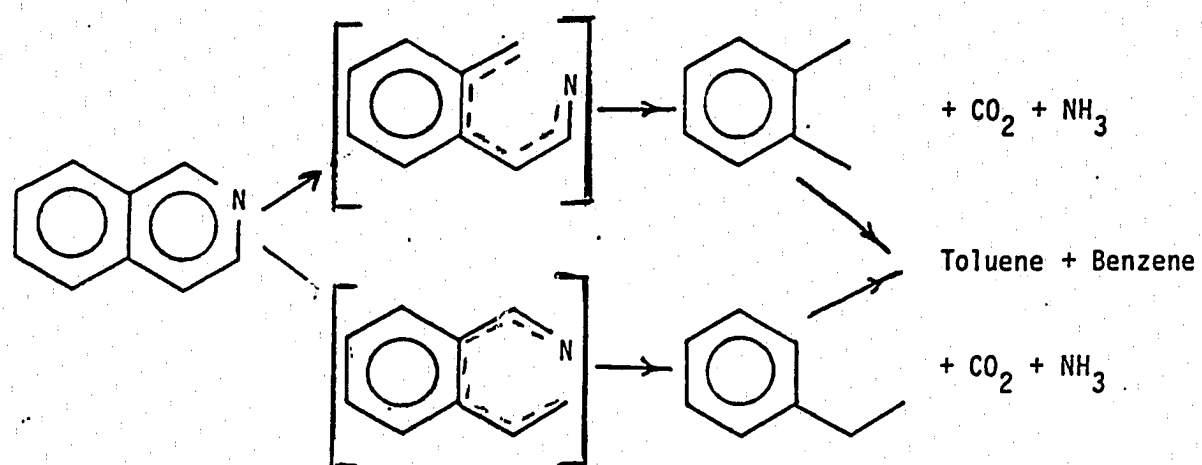


Figure 3. Isoquinoline-Water Reaction

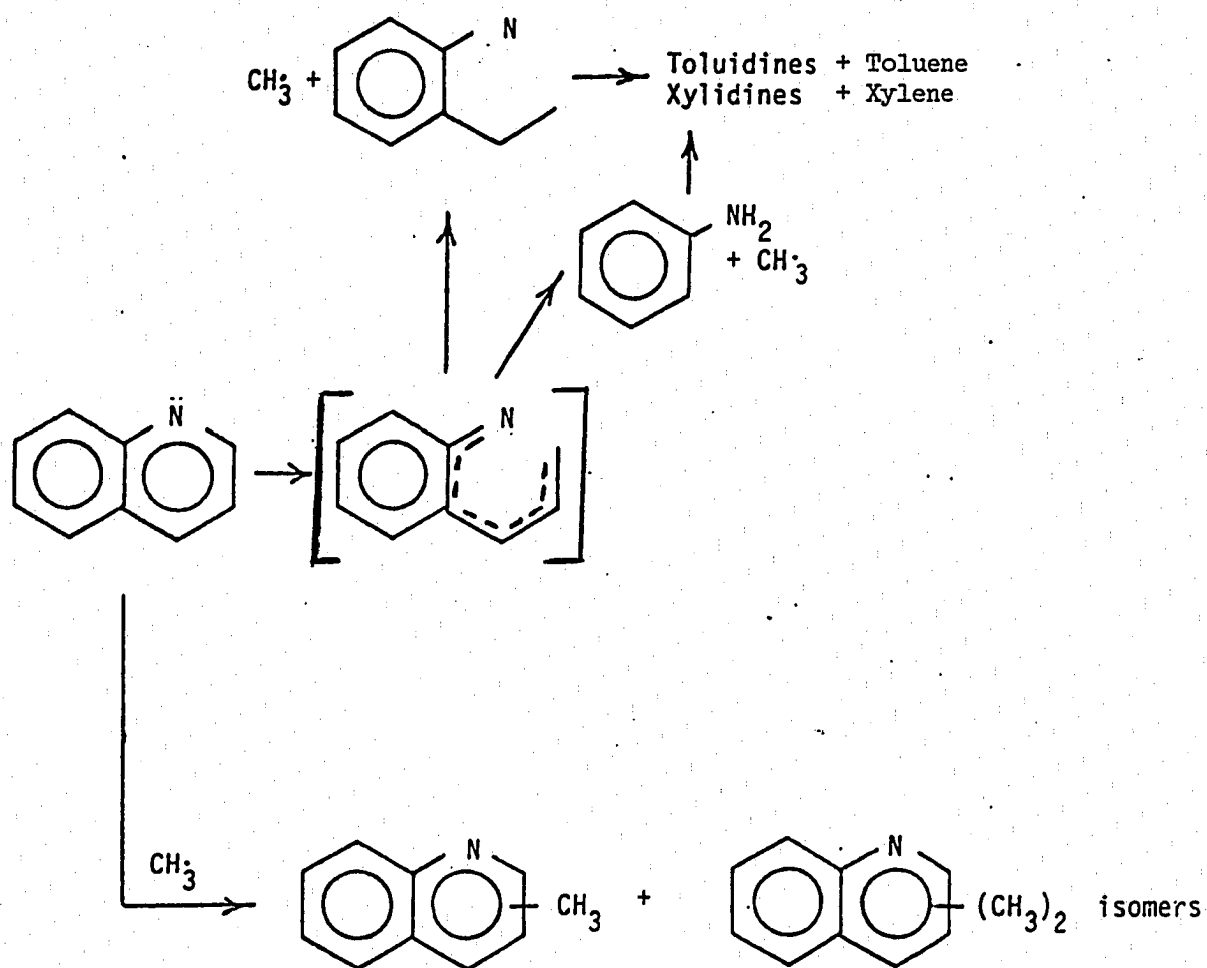


Figure 4. Quinoline-Water Reaction

The selectivity of the ring rupture in isoquinoline showed no preference for the 1-2 bond versus the 2-3 bond, as shown by the essentially equal molar amounts of ethylbenzene and o-xylene formed, particularly at the lowest temperature. In the case of quinoline the rupture of bonds favored the 1-2 bond over the 1-8a bond. Since neither the 1-2 or 2-3 bond in isoquinoline nor the 1-2 bond in quinoline was attached to the homocyclic aromatic ring, their reactivity would be expected to be about the same. However the 1-8a bond in quinoline was attached to the homocyclic ring and therefore could account for the difference in reactivity of quinoline and isoquinoline.

The initial alkylbenzenes formed are also reactive under supercritical conditions. The presence of toluene and benzene in the product mixtures from both the heterocyclic compounds and from ethylbenzene demonstrated that carbons could be lost from the alkyl side chain until only the benzene ring was left.

In the case of quinoline, the presence of quinaldine, o-xylene, and possibly some polysubstituted quinolines indicates that the carbon lost from the alkyl side chain is a reactive species capable of aromatic substitution reactions. The presence of a GC peak on the isoquinoline chromatogram with an analogous retention time to the quinaldine peak in the quinoline chromatogram suggests that methyl substitution on the isoquinoline ring may also be occurring. The identity of this peak, however, could not be confirmed by M.S. due to its low concentrations.

When the removal of nitrogen by SCW is compared to HDN, one significant observation can be made. Neither method showed any evidence of the homocyclic ring rupturing. However, HDN did require a substantial amount

of the homocyclic rings to be hydrogenated before significant nitrogen removal occurred. Since use of SCW is not a hydrogenation process, the homocyclic ring is left unaffected. This enables the SCW method to produce a product mixture with a higher degree of unsaturation.

APPENDIX A
Experimental Data

Experimental Data

Table A1
Average Retention Time^a

Known Compounds	Retention Time (min)
Benzene	1.5 ± 0.2^b
Toluene	3.1 ± 0.6
Ethylbenzene	5.5 ± 0.6
o-Xylene	6.3 ± 0.7
Aniline	9 ± 2^c
Tolidine	10 ± 2^c
Quinoline	13 ± 2^c
Isoquinoline	13.0 ± 0.6
Unknown Compounds	
Isoquinoline experiments	
Unknown #1	9.0 ± 0.4
Unknown #2	10.0 ± 0.4
Unknown #3	14.0 ± 0.6

^aRetention times were relative to the air peak and were for injections at standard G.C. operating conditions.

^bThe variation given in the retention time is one standard deviation.

^cThe G.C. temperature program was adjusted slightly for some of the quinoline experiments to maximize the separation of the more complex mixture of unknowns found after o-xylene. These adjustments caused a larger variation in the retention time of some of the higher retention times.

Table A2

Elemental Analysis of Organic Component of Char (Weight Percent)

Element	Isoquinoline	Quinoline
Carbon	88.59	84.09
Hydrogen	3.49	3.04
Nitrogen	4.62	8.01
Oxygen	3.30	4.86

Table A3

Reaction of Water with Isoquinoline
Average Attenuated area/ μL ($\text{mm}^2/\mu\text{L}$)

IQ#	Temp ($^{\circ}\text{C}$)	Pressure (psi)	Density (g/cc)	Time (hr)	Catalyst	Benz. (g)	Tolu. (g)	Etbenz. (g)	o-Xyl. (g)	Isoquin. (g)	Char (g)	mL	
												Water	Ammonia
												Recov	(M)
34	350	2400	0.170	72	-	-	0	0	1	396	0	-	-
20	400	3640	0.170	48	-	-	0	5	7	453	0	-	-
21	400	3640	0.170	48	-	-	0	5	6	518	0	7.9	-
33	400	3640	0.170	48	ZnCl ₂	0.05	0	17	22	274	0.123	7.4	-
23	400	3870	0.213	48	-	-	0	16	21	416	0.040	9.8	-
22	400	3870	0.213	96	-	-	0	22	41	300	0.136	9.8	-
30	400	3870	0.213	96	ZnCl ₂	0.05	0	30	40	257	0.162	-	-
24	400	3870	0.213	144	-	-	0	36	45	295	0.137	9.8	-
27	450	3580	0.106	48	-	-	5	57	41	268	0.261	4.8	-
31	450	3580	0.106	48	-	-	1	28	15	323	-	4.2	-
26	450	4680	0.170	48	-	-	2	50	38	346	0.114	7.9	-
18	450	4680	0.170	48	Tet	1.25	16	77	101	41	0.215	7.9	-
36	450	4680	0.170	48	DA	0.50	0	26	42	247	0.235	7.2	0.86
38	450	4680	0.170	96	-	-	10	97	84	104	0.288	-	-
25	450	4680	0.170	120	-	-	16	90	51	118	0.314	7.9	-
32	450	4680	0.170	120	-	-	14	91	53	61	0.261	5.4	-
28	450	5200	0.213	48	-	-	11	85	43	111	0.175	9.0	-
37	500	4680	0.128	24	-	-	15	55	20	129	0.239	-	-
39	500	4680	0.128	48	.	.	12	61	28	232	0.219	5.2	1.45

Table A4

Reaction of Water with Quinoline
Average Attenuated area/ μL ($\text{mm}^2/\mu\text{L}$)

Q#	Temp (°C)	Pres. (psi)	Density (g/cc)	Time (hr)	Catalyst	(g)	Benz.	Tolu.	Ethbez.	o-xyl.	Anil.	Tolid.	Quin.	Char (g)	Water Recov (mL)	Ammonia
7	400	3870	0.213	48	ZnCl ₂	0.05	0	1	3	3	2	4	453	0.034	-	-
15	400	4664	0.426	48	-		1	0	0	0	0	0	424	0	-	-
12	400	4020	0.255	48	AlCl ₃	0.05	0	0	0	0	3	4	233	0.171	8.0	1.2
11	400	4020	0.255	48	ZnCl ₂	0.05	0	0	0	0	3	4	273	0.067	8.5	1.2
1	450	4680	0.170	48	-		0	5	3	1	4	8	419	0	5.3	-
2	450	4680	0.170	48	ZnCl ₂	0.10	3	10	4	2	18	15	111	0.107	-	-
3	450	5200	0.213	24	ZnCl ₂	0.01	0	2	3	3	3	4	497	0	9.2	-
5	450	5200	0.213	48	-		1	2	2	1	4	1	265	0	8.0	-
8	450	5200	0.213	48	-		0	3	3	1	0	3	553	0	-	-
4	450	5200	0.213	48	ZnCl ₂	0.05	3	10	4	2	18	10	123	-	-	-
6	450	5200	0.213	48	ZnCl ₂	0.05	1	7	4	3	17	11	259	0.197	-	-
13	450	5200	0.213	48	ZnCl ₂	0.05	2	8	8	5	37	28	531	-	-	-
16	500	5650	0.170	48	-		11	17	6	1	19	11	222	0.363	-	-

Table A5

Reaction of Water With Other Compounds
Average Attenuated area/ μL ($\text{mm}^2/\mu\text{L}$)

Compound	Benzonitrile	Ethylbenzene	Tetralin	DA ^a	Carbazole ^b	Aniline ^c
Temperature (C)	400	450	450	450	450	450
Pressure (psi)	3640	5200	5200	5200	5200	5200
Density (g/cc)	0.170	0.213	0.213	0.213	0.213	0.213
Time (hour)	24	48	48	48	48	48
Catalyst (g)	-	-	ZnCl ₂ 0.05	-	ZnCl ₂ 0.05	-
Benzene	381	12	5	5	0	s
Toluene	-	41	39	28	0	0
Ethylbenzene	-	470	54	37	0	0
Tetralin	-	-	0	0	-	-
Aniline	-	-	-	-	-	379
Naphthalene	-	-	314	211	0	-
9,10-dihydro-anthracene	-	-	-	-	d	-
Anthracene	-	-	-	-	e	-
Carbazole	-	-	-	-	1.7 g ^f	-
Ammonia (moles x 10 ⁻³)	-	-	-	-	-	2.6

^aThe dihydroanthracene chromatogram showed about six products, all having longer retention times than naphthalene but shorter than anthracene which was by far the largest.

^bCarbazole appeared close to zero% reacted.

^cDue to chromatogram anomalies, the extents of these reactions are more uncertain. The only significant organic product identified was in small amounts. The s indicates small product peak. A second, large peak was found but not identified.

^dNo quantitative measure of 9,10-dihydroanthracene was made. However, it can be stated with some certainty that over 50% reacted since the anthracene peak was greater than the 9,10-dihydroanthracene peak.

^e A large but unmeasured amount was found.

^f Carbazole was insoluble in CH_2Cl_2 . Therefore the recovered carbazole was based on the amount of solid collected and weighed.

APPENDIX B
Steam Table

Steam Table

Table B1

Steam Table^a

Density (g/cc)	0.255	0.213	0.170	0.106
V _s (ft ³ /lb)	0.0621	0.0745	0.0932	0.1490
Water volume ^b (mL)	12.0	10.0	8.0	5.0
<u>Temperature^c</u>	<u>Pressure (psi)</u>			
382	3460	3400	3280	-
399	4020	3870	3640	-
416	4560	4320	4000	3200
432	5100	4760	4340	3390
449	5640	5200	4680	3580
465	6170	5630	5010	3770
482	-	6060	5300	3950
499	-	6480	5650	4130
527	-	-	6180	4420
554	-	-	6700	4790
582	-	-	-	5000
610	-	-	-	5290

^aThis is a summary of the pressure values found in Keenan, J.H., F.G. Keyes, P.G. Hill & J.G. Moore, Thermodynamic Properties of Water Including Steam Tables, New York: John Wiley & Sons, 1969.

^bThe volume needed for an experiment was calculated using the following formula: [density of steam]*46 mL/1.0 g/mL = [volume liquid water]

^cThe temperatures are the centigrade equivalents of the fahrenheit used in the reference.

APPENDIX C
Calibration Data

Table C1
Calibration Data

Compound	Response Factor at Given Concentration of Standard Compound ^b						Final Response Factor ^a
	0.05 ^c	0.10	0.50	1.00	1.50	2.00	
Benzene	12	-	140	-	423	604	298
Toluene	14	29	133	274	411	-	281
Ethylbenzene	14	28	116	259	-	-	262
o-Xylene	12	26	117	239	378	-	248
Aniline	15	26	154	234	-	-	241
Toluidine	17	32	124	306	494	-	298
Quinoline	-	31	158	306	430	585	294
Isoquinoline	-	34	-	-	430	625	301
Tetralin	-	-	158	-	-	-	316 ^d

^aThe response factors are defined in units of attenuated area/ μ L per mL standard/ 25 mL solution and are calculated from the slopes of a least square treatment of all the G.C. data for a particular compound.

^bThe response factors for each concentration are stated as the average of all the G.C. data at a given concentration for a particular compound.

^cThese concentrations are expressed as mL standard per 25 mL solution.

^dThe tetralin response factor was calculated from only the one concentration of standard.

APPENDIX D

Error Analysis

Error Analysis

The uncertainties in the individual measurements and their effect on the final results were analyzed in the following ways:

(1) The volume of the reactor, which was used to determine the density, and from the density the pressure for a given charge of water, was determined by weighing the amount of dibutylphthalate needed to fill the reactor. The weight could be determined to ± 0.1 g. However, an additional uncertainty was introduced by the small volume in the lid. This volume was estimated at $1.0 \text{ mL} \pm 0.5 \text{ mL}$.

(2) The pipets were calibrated by averaging the weight of five samples measured with the pipet. The average deviation in weights was ± 0.009 g for both quinoline and isoquinoline.

(3) The amount of water was measured to ± 0.01 mL. The uncertainty in water addition was therefore $12.0 \text{ mL} \pm .08\%$ at the highest density and $5.0 \pm 0.2\%$ at the lowest density.

(4) The error in the char had to be estimated because the transfer from the reactor was not quantitative. Based on the range of weights collected, the error was estimated at 10.05 mg.

(5) The uncertainty in the ammonia value was based on the error in water recovered, sample dilution and the meter reading. The water for the example stated in the text was 7.2 ± 0.1 mL. The sample of water analyzed was $1.0 \text{ mL} \pm .001$ and diluted to $100 \text{ mL} \pm 0.1$. The meter reading was 8.6 ± 0.1 . This gave an error of $62\% \pm 2\%$.

(6) The response factor was calculated by taking the slope of the line of average attenuated area versus mL of standard in 25 mL solution.

The error was the 95% Confidence Limit of the slope of the line as calculated by the DEC-10 computer program CHM;GPPLCC. The following table lists the standard errors:

Compound	Response Factor	95% Confidence Limit
Benzene	298	9
Toluene	281	8
Ethylbenzene	262	8
o-Xylene	248	9
Aniline	241	16
Toluidine	298	16
Quinoline	294	10
Isoquinoline	301	12
Tetralin	316	25 ^a
Naphthalene	318	22 ^a

^aThe tetralin and naphthalene response factors were based on only one calibration standard and therefore the error was calculated as the 95% confidence limit for the average of injections for the single concentration.

(7) The error for the isoquinoline and quinoline results was based on the 95% confidence limit of the average attenuated area/ μ L for each reaction and carried through the calculations using standard error analysis. The error analysis of the benzene in IQ-37 is given as an example (18):

$$\begin{aligned} &\text{Average attenuated area}/\mu\text{L:} \\ &(12.75 + 15.00 + 17.00 + 18.75 + 17.25)/5 = 15.55 \end{aligned}$$

$$\begin{aligned} &\text{Sum of (atten area}/\mu\text{L} - \text{avg. atten area}/\mu\text{L})^2: \\ &(-2.8)^2 + (1.45)^2 + (-.55)^2 + (3.2)^2 + (1.7)^2 = 23.38 \end{aligned}$$

$$\begin{aligned} &\text{Square root of [Sum/(total samples - 1)]}: \\ &\sqrt{23.38/4} = 2.418 \end{aligned}$$

$$\begin{aligned} &\text{Square root} * t\text{-distribution/square of total samples:} \\ &2.418 * 2.571/5^2 = 0.25 \end{aligned}$$

$$\begin{aligned} &\text{Final average and error:} \\ &15.55 \pm 0.25 \end{aligned}$$

$$\begin{aligned} &\text{Percent error:} \\ &0.25/15.55 * 100 = 1.6 \% \end{aligned}$$

The only significant error associated with the conversion of the attenuated area to percent yield is the error associated with the response factor.

Percent error of response factor:
 $9/298 \times 100 = 3.0\%$

Percent error of moles isoquinoline:
 $0.009/2.175 \times 100 = 0.4\%$

Total percent error for % yield:
 $1.6 + 3.0 + 0.4 = 5.0\%$

Error for % yield:
 $4.7\% \times 5.0/100 = 0.2\%$
or $4.7 \pm 0.2\%$

APPENDIX E
Computer Programs

Computer Programs

```

10 DISP "CALIB4"
20 DISP
30 DISP
40 DIM D$(32)
50 PRINT
60 DISP "COMPOUND PEAK NUMBER"
70 DISP "1=BENZENE      2=TOLUENE"
80 DISP "3=ETHYLBENZENE 4=O-XYLENE"
90 DISP "5=ANILINE      6=TOLUIDINE"
100 DISP "7=ISOQUINOLINE 8=QUINOLINE"
110 DISP "9=METHYLQUINOLINE 10=0-THER"
120 DISP "GIVE COMPOUND NUMBER"
130 INPUT N
140 ON N GOTO 150,190,230,270,310,350,390,430,470,510
150 A$="BENZENE"
160 M=78.11 ! MOLECULAR WEIGHT
170 D=.879 ! DENSITY
180 GOTO 580
190 A$="TOLUENE"
200 M=92.13 ! MOLECULAR WEIGHT
210 D=.866 ! DENSITY
220 GOTO 580
230 A$="ETHYLBENZENE"
240 M=106.16 ! MOLECULAR WEIGHT
250 D=.867 ! DENSITY
260 GOTO 580
270 A$="O-XYLENE"
280 M=106.16 ! MOLECULAR WEIGHT
290 D=.88 ! DENSITY
300 GOTO 580
310 A$="ANILINE"
320 M=93.12
330 D=1.022
340 GOTO 580
350 A$="TOLUIDINE"
360 M=107.15
370 D=.999
380 GOTO 580
390 A$="ISOQUINOLINE"
400 M=129.15
410 D=1.091
420 GOTO 580
430 A$="QUINOLINE"
440 M=129.15
450 D=1.095
460 GOTO 580
470 A$="METHYLQUINOLINE"
480 M=143.18
490 D=1.086
500 GOTO 580
510 DISP "COMPOUND NAME"
520 INPUT A$
530 DISP "MOLECULAR WEIGHT"

```

```

540 INPUT M
550 DISP "DENSITY"
560 INPUT D
570 GOTO 580
580 DISP "NUMBER OF DIFFERENT CO
NCENTRATION OF ";A$
590 INPUT R1
600 FOR I=1 TO R1
610 DISP "CONC.#";I;"  cpd.mL/25
mL"
620 INPUT C
630 IF C>25 THEN BEEP
640 IF C>25 THEN 610
650 DISP "NAME AND DATE OF VIAL
FOR CONC. ";C;" mL ";A$
660 INPUT D$
670 C1=C*D/M/.025 ! C1=MOL CONC
680 DISP "INTERNAL STANDARD (Y/N
)"
690 INPUT Y2$
700 IF Y2$="N" EXOR Y2$="Y" THEN
710 ELSE 680
710 DISP " NUMBER OF DIFFERENT S
AMPLE SIZES AT";C;"mL/25mL"
720 INPUT R2
730 DIM P1$(40)
740 DIM P2$(40)
750 DIM P3$(40)
760 DIM P4$(40)
770 PRINT
780 PRINT " Rt=RETENTION TIME"
790 PRINT " H=HEIGHT mm"
800 PRINT " W=WIDTH mm"
810 PRINT " A=ATTENUATION"
820 PRINT " Ar=AREA mm^2"
830 PRINT " AA=ATTENUATION"
840 PRINT "AA/μL=ATTENUATED AREA
/μL"
850 PRINT
860 PRINT D$
880 FOR J=1 TO R2
890 DISP "SAMPLE SIZE #";J;" IN
μL"
900 INPUT S
910 F2=0 ! INITIALIZE F2
920 Z7=0
930 Z1=0
940 DISP "NUMBER OF RUNS AT";S;"
μL"
950 INPUT R3
960 PRINT
970 PRINT C;"mL";" ";A$
980 PRINT "CONCENTRATION
";C1;"M"
990 PRINT "SAMPLE SIZE";" ";S;"
μL"
1000 P1$="7X,A,6X,2A"
1010 P2$="X,A,3X,A,3X,A,2X,2A,4X
,2A,3X,5A"
1020 P3$="6X,2D,5X,2D,0,X,3A"

```

```

1030 P4$="3D,X,D.O,X,2D,X,3D,2X,
4D,2X,3D,2D"
1040 PRINT USING P1$ ; "#","Rt"
1050 PRINT USING P2$ ; "H","W","A",
"R","Ar","AA","AA/μL"
1060 FOR K=1 TO R3
1070 DISP "RUN #";K,"HEIGHT, WID
TH,ATTENUATION"
1080 INPUT H,W,A
1090 DISP "RETENTION TIME RUN#"
;K
1100 INPUT T(K)
1110 IF Y2$="N" THEN 1150
1120 DISP "INTERN. STAND. PEAK H
EIGHT,ATTENUATION"
1130 INPUT H2,A2
1140 Y2(K)=H2*A2
1150 X=H*W ! X=AREA
1160 Y(K)=X*A ! Y=ATTEN AREA
1170 Z(K)=Y(K)/S ! Z=ATTEN AREA/
μL
1180 Z5(K)=Z(K)^2
1190 Z7=Z7+Z5(K)
1200 Z1=Z1+Z(K) ! SUM OF Z(K)
1210 IF Y2$="N" THEN 1250
1220 F1(K)=Y(K)/Y2(K) ! F1=I.S./
CPD.ATTEN AREA
1230 F2=F2+F1(K)
1240 IF K=R3 THEN F3=F2/K
1250 PRINT USING P3$ ; K,T(K),"m
in"
1260 PRINT USING P4$ ; H,W,A,X,Y
(K),Z(K)
1270 IF Y2$="N" THEN 1310
1280 PRINT "INTERN. STAND. HEIGH
T",H2
1290 PRINT "INTERN. STAND. ATTEN
",A2
1300 PRINT "INTERN. STAND./";A$,
F1(K)
1310 PRINT
1320 NEXT K
1330 Z2=Z1/R3 ! AVG ATTEN/μL
1340 S5=SQR((Z7-Z1^2/R3)/(R3-1))
1350 N1=R3-1
1360 ASSIGN# 1 TO "95tDIS"
1370 READ# 1,N1 ; T1
1380 C9=S5*T1/SQR(R3)
1390 C8=C9/Z2*100
1400 Z3=Z2/C ! AVG ATTEN/μL/mL
1410 Z4=.002/C+C8/100 ! .002=PIP
ET ERROR
1420 Z5=Z4*100 ! % ERROR AVG. AT
TEN AREA/μL/mL cpd IN 25 mL
CH2CL2
1430 Z6=Z4*Z3 ! ABSOLUTE ERROR
1440 F3=F2/R3
1450 PRINT "FOR ";R3;" RUNS"
1460 PRINT "AVG. ATTEN AREA/μL"
1470 PRINT "Z4="+OP+"C8"

```

```
1480 PRINT Z2;"+or-";C8;"%"
1490 PRINT
1500 IF Y2$="N" THEN 1530
1510 PRINT "AVG.INTERN STAND/" A
    $,F3
1520 PRINT
1530 PRINT "AVG ATTEN/ $\mu$ L/mL"
1540 PRINT Z3;"+OR-";Z5;"%"
1550 PRINT Z3;"+OR-";Z6
1560 PRINT
1570 NEXT J
1580 NEXT I
1590 DISP "LAST RUN COMPLETED DO
    YOU WISH TO RUN ANOTHER C
    OMPOUND? (Y/N)"
1600 BEEP
1610 INPUT C$
1620 IF C$="Y" THEN 60
1630 IF C$="N" THEN 1640 ELSE 15
    90
1640 DISP " END PROGRAM"
1650 END
```

```

10 DISP "%CONVS"
20 DISP
30 DISP
40 M2=.0167
50 GOTO 620
60 C2#="BENZENE"
70 D1=.879
80 M1=78.11
90 F1=232.1
100 GOTO 910
110 C2#="TOLUENE"
120 D1=.866 ! DENSITY
130 M1=92.13 ! MOL. WT.
140 F1=288.8 ! CONVERSION FACTOR
150 GOTO 910
160 C2#="ETHYLBENZENE"
170 D1=.867
180 M1=106.5
190 F1=255.8
200 GOTO 910
210 C2#="O-XYLENE"
220 D1=.88
230 M1=106.16
240 F1=256.3
250 GOTO 910
260 C2#="ANILINE"
270 D1=1.022
280 M1=93.12
290 F1=240.9
300 GOTO 910
310 C2#="TOLUIDINE"
320 D1=.999
330 M1=107.15
340 F1=297.7
350 GOTO 910
360 C2#="1-QUINOLINE"
370 D1=1.091
380 M1=129.15
390 F1=296.4
400 GOTO 910
410 C2#="QUINOLINE"
420 D1=1.093
430 M1=129.15
440 F1=299.5
450 GOTO 910
460 C2#="METHYLQUINOLINE"
470 D1=1.086
480 M1=143.18
490 F1=332
500 GOTO 910
510 DISP "NAME OF NEW COMPOUND"
520 INPUT C2#
530 DISP "DENSITY OF COMPOUND"
540 INPUT D1
550 DISP "MOLECULAR WEIGHT"
560 INPUT M1
570 DISP "CONVERSION FACTOR"
580 INPUT F1
590
600 C2#="UNKNOWN"

```

```

610 GOTO 910
620 DISP "TITLE OF REACTION"
630 DIM C1$(32)
640 INPUT C1$
650 DISP "NUMBER OF SAMPLES OF")
    C1$
660 INPUT S2
670 DISP "REACTION CONDITION (T
    EMP., mL WATER, TIME IN HOURS
    , PSI)"
680 INPUT T3, W1, T4, P9
690 Z=0
700 DISP "NUMBER OF PEAKS IN REA
    CTION P<10"
710 INPUT P1
720 IF P1>10 THEN 700
730 FOR K=1 TO S2
740 DISP "SIZE IN  $\mu$ L OF SAMPLE")
    K: "INJECTED"
750 INPUT S1
760 FOR I=1 TO P1 ! BEGIN INDIVI
    DUAL PEAK CALC. LOOP
770 DISP "THIS REACTION HAS ";P1
    " PEAKS"
780 DISP "1= BENZENE          2=TOLU
    ENE"
790 DISP "3=ETHYLBENZENE    4=O-XY
    LENE"
800 DISP "5=ANILINE         6=TOLU
    IDINE"
810 DISP "7=ISOQUINOLINE    8=QUIN
    OLINE"
820 DISP "9=METHYL "INOLINE"
830 DISP "10=OTHER          11=UNK
    NOWN"
840 DISP "NAME OF COMPOUND FOR P
    EAK#"; I
850 INPUT N
860 IF N>11 THEN BE$P
870 IF N>11 THEN 840
880 IF N=7 THEN Z=I
890 IF N=8 THEN Z=I
900 ON N GOTO 60,110,160,210,260
    ,310,360,410,460,510,600
910 DISP "RETENTION TIME OF PEAK
    #"; I
920 INPUT T1(I)
930 ON I GOTO 940,960,980,1000,1
    020,1040,1060,1080,1100,1120
940 B1$=C2$
950 GOTO 1140
960 B2$=C2$
970 GOTO 1140
980 B3$=C2$
990 GOTO 1140
1000 B4$=C2$
1010 GOTO 1140
1020 B5$=C2$
1030 GOTO 1140
1040 B6$=C2$

```

```

1050 GOTO 1140
1060 B7$=C2$
1070 GOTO 1140
1080 B8$=C2$
1090 GOTO 1140
1100 B9$=C2$
1110 GOTO 1140
1120 B0$=C2$
1130 GOTO 1140
1140 DISP "HEIGHT, WIDTH, ATTENU
      ATION OF",C2$," PEAK"
1150 INPUT H1(K,I),W1(K,I),A0(K,
      I)
1160 A1(K,I)=H1(K,I)*W1(K,I) ! A
      1=AREA
1170 A2(K,I)=A1(K,I)*A0(K,I) ! A
      2=ATTEN AREA
1180 A3(K,I)=A2(K,I)/S1 ! A3=A.A
      1
1190 IF C2$="UNKNOWN" THEN Y1(K,
      I)=0
1200 IF C2$="UNKNOWN" THEN G1(K,
      I)=0
1210 IF C2$="UNKNOWN" THEN 1260
1220 L1(K,I)=A3(K,I)/F1 ! mL Pro
      d/25mL
1230 G1(K,I)=L1(K,I)*D1 ! G1=GRA
      MS PROD/25mL
1240 M3(K,I)=G1(K,I)/M1 ! MOLE:
      CONVERTED
1250 Y1(K,I)=M3(K,I)/M2*100 ! %
      YIELD,2mL IQ
1260 NEXT I
1270 PRINT S1;"μL SAMPLE OF ",C1
      $;"#";K
1280 DIM Q3$(40)
1290 Q3$="5A,3D,A,2X,4A,2D,2A,2X
      ,5A,3D,3A"
1300 PRINT USING Q3$ ; "TEMP=",T
      3,"C","H2O=",W1,"mL","TIME=
      ",T4,"HRS"
1310 PRINT "      PSI=",P9
1320 DIM U1$(40)
1330 U1$="5A,X,6A,X,5A,X,6A,X,5A
      "
1340 PRINT USING U1$ ; "PEAK#","
      HEIGHT","WIDTH","ATTEN. ","A
      A/μL"
1350 PRINT
1360 DIM U2$(40)
1370 U2$="X,2D,4X,3D,3X,2D,D,5X,
      2D,4X,3D"
1380 FOR I=1 TO P1
1390 PRINT USING U2$ ; I,H1(K,
      I),W1(K,I),A0(K,I),A3(K,I)
1400 NEXT I
1410 PRINT
1420 DIM Q4$(40)
1430 Q4$="5A,4X,4A,4X,15A"
1440 PRINT "      Q4$="PEAK#","

```

```

1450 DIM Q5$(40)
1460 Q5$="X,20,3X,14A,3X,20,3X,3A"
1470 FOR I=1 TO P1
1480 GOSUB 1500
1490 GOTO 1720
1500 ON I GOTO 1510,1530,1550,1570,1590,1610,1630,1650,1670,1690
1510 C2$=B1$
1520 GOTO 1700
1530 C2$=B2$
1540 GOTO 1700
1550 C2$=B3$
1560 GOTO 1700
1570 C2$=B4$
1580 GOTO 1700
1590 C2$=B5$
1600 GOTO 1700
1610 C2$=B6$
1620 GOTO 1700
1630 C2$=B7$
1640 GOTO 1700
1650 C2$=B8$
1660 GOTO 1700
1670 C2$=B9$
1680 GOTO 1700
1690 C2$=B0$
1700 IF C2$="UNKNOWN" THEN I1(I)=2 ELSE I1(I)=1
1710 RETURN
1720 PRINT USING Q5$ ; I,C2$,T1(I), "min"
1730 NEXT I
1740 PRINT
1750 DIM Q1$(32)
1760 Q1$="5A,2X,3A,3X,3A,5X,3A,5X,2A"
1770 PRINT USING Q1$ ; "PEAK#","mL","gr","mol","%Y"
1780 DIM Q2$(40)
1790 DIM Q6$(40)
1800 FOR I=1 TO P1
1810 IF I1(I)=1 THEN 1830
1820 IF I1(I)=2 THEN 1860
1830 Q2$="X,00,3X,D.00,2X,D.00,2X,D.00E,X,00,D"
1840 PRINT USING Q2$ ; I,L1(K,I),G1(K,I),M3(K,I),Y1(K,I)
1850 GOTO 1890
1860 Q6$="X,20,3X,14A,40,7A"
1870 PRINT USING Q6$ ; I,"ATTEN AREA/ $\mu$ L=",A3(K,I),"mm2/ $\mu$ L"
1880 GOTO 1890
1890 NEXT I
1900 PRINT
1910 PRINT
1920 DISP "DO YOU WANT THIS UN TO COUNT IN THE AVERAGE Y

```

```

1930 INPUT A1$
1940 IF A1$="Y" THEN 1960
1950 IF A1$="N" THEN 740
1960 NEXT K
1970 FOR L=1 TO 3
1980 FOR K=1 TO S2
1990 FOR I=1 TO P1
2000 ON L GOTO 2010,2030,2050
2010 X(K,I)=A3(K,I)
2020 GOTO 2060
2030 X(K,I)=G1(K,I)
2040 GOTO 2060
2050 X(K,I)=Y1(K,I)
2060 NEXT I
2070 NEXT K
2080 GOSUB 2750
2090 FOR I=1 TO P1
2100 ON L GOTO 2110,2130,2150
2110 C1(I)=C9(I)
2120 GOTO 2160
2130 C2(I)=C9(I)
2140 GOTO 2160
2150 C3(I)=C9(I)
2160 ON L GOTO 2170,2190,2210
2170 A5(I)=X1(I) ! A5=AVG A.A/μL
2180 GOTO 2220
2190 G2(I)=X1(I) ! G2=AVG GRAMS
2200 GOTO 2220
2210 Y2(I)=X1(I) ! Y2=AVG %YIELD
2220 NEXT I
2230 NEXT L
2240 Y3=0
2250 FOR I=1 TO P1
2260 Y3=Y3+Y2(I) ! TOTAL MATERIA
L RECOVERED
2270 NEXT I
2280 I=Z
2290 Y4=Y3-Y2(I) ! TOTAL PROD. I
NDENTIFIED
2300 Y5=100-Y2(I) ! MATERIAL CON
VERTED
2310 Y6=Y4/Y5*100 ! % PROD IDEN.
2320 FOR I=1 TO P1
2330 IF I=Z THEN 2350
2340 Y7(I)=Y2(I)/Y4*100 ! % PROD
OF TOTAL PROD
2350 NEXT I
2360 DIM Q7$(40)
2370 DIM Q8$(40)
2380 DIM Q9$(40)
2390 DIM Q0$(40)
2400 Q7$="5A,2X,4A,3X,18A"
2410 Q8$="X,2D,2X,12A,2X,3D, A,2
D"
2420 Q9$="5A,3X,9A,3X,11A"
2430 Q0$="X,2D,3X,D,2D,4A,.2
,2D,D,4A,2D,D"
2440 PRINT "AFTER ";S2;" SAMPLES
2440 PRINT "BI = Q7$ ; "PEAK#","
      "Q8$ ; "PEAK#"; "Q9$ ; "PEAK#"; "Q0$ ; "PEAK#"/μL"

```

```

2450 FOR I=1 TO P1
2460 GOSUB 17
2470 PRINT USING Q9$ ; I,C2$,P
      I),"or-";C1(I)
2480 NEXT I
2490 PRINT
2500 PRINT USING Q9$ ; "PEAK#"
      AVG.GRAMS","AVG. %YIELD"
2510 FOR I=1 TO P1
2520 PRINT USING Q0$ ; I,G2(
      +or-";C2(I),Y2(I),"or-
      (I)
2530 NEXT I
2540 PRINT "TOTAL PRODUCT RECO
      RED"
2550 PRINT " ";Y4
2560 PRINT "TOTAL MATERIAL RE
      ERED"
2570 PRINT " ";Y3
2580 PRINT "% OF START MAT.CONVE
      RTED"
2590 PRINT " ";Y5
2600 PRINT "% CONVERTED MAT. IN
      EN."
2610 PRINT " ";Y6
2620 DIM Z1$(40)
2630 DIM Z2$(40)
2640 Z1$="5A,4X,4A,5X,10A"
2650 Z2$="X,2D,2X,15A,5X,3D,C"
2660 PRINT USING Z1$ ; "PEAK#","
      NAME","% OF PROD"
2670 FOR I=1 TO P1
2680 GOSUB 1500
2690 IF I=Z THEN 2710
2700 PRINT USING Z2$ ; I,C2$,Y2(
      I)
2710 NEXT I
2720 PRINT
2730 PRINT
2740 END
2750 ASSIGN# 1 TO "95tDIS"
2760 FOR I=1 TO P1
2770 X0=0
2780 FOR K=1 TO S2
2790 IF X(K,I)=0 THEN 2890
2800 IF X(K,I)=0 THEN 2890
2810 X0=X0+X(K,I) ! X0=SUM OF
2820 NEXT K
2830 X1(I)=X0/S2 ! X1= MEAN X
2840 X3=0
2850 FOR K=1 TO S2
2860 X2(K,I)=(X(K,I)-X1(I))^2
2870 X3=X3+X2(K,I) ! X3=SUM X2^2
2880 GOTO 2920
2890 K=S2
2900 NEXT K
2910 GOTO 2980
2920 NEXT I
2930 S=SOP(X3/(S2-1))
2940 N2= S2-1

```

```
2950 READ# 1,N2 ; T
2960 C9(I)=S*T/SQR(S2)
2970 GOTO 3000
2980 X1(I)=0
2990 C9(I)=0
3000 NEXT I
3010 RETURN
```

REFERENCES

1. Berkowitz, N. An introduction to coal technology. New York: Academic Press, 1979.
2. Gangoli, N. & Thodos, G. Liquid fuels and chemical feedstocks from coal by supercritical gas extraction. Ind. Eng. Chem. Prod. Res. Dev., 1977, 16, 208.
3. Whitehead, J.C. & Williams, D.F. Solvent extraction of coal by supercritical gases. J. Inst. Fuel., 1975, 182.
4. Whitehead, J.C. Development of a process for the supercritical gas extraction of coal. 88th AIChE National Meeting, Philadelphia, June 1980.
5. Vasilakos, N.P., Dobbs, J.M. & Parisi, A.S. Solvent effects in supercritical extraction of coal. Preprint Div. Fuel Chem., 1983, 28(4), 212
6. Deshpande, G.V., Holder, G.D., Bishop, A.A., Gopal, J. & Wender, I. Extraction of coal using supercritical water. Fuel, 1984, 63, 956.
7. Franck, E.U. Supercritical water. Endeavour, 1968, 27(101), 55.
8. Rollman, L.D. Catalytic hydrogenation of model nitrogen, sulfur and oxygen compounds. J. Catalysis, 1977, 46, 243.
9. Chementator, Dec. 25, 1972/Chem. Eng.; 20.
10. Cocchetto, J.F. & Satterfield, C.N. Chemical equilibria among quinoline and its reaction products in hydrodenitrogenation. Ind. Eng. Chem. Proc. Res. Dev., 1979, 20, 49.
11. Satterfield, C.N. & Cocchetto, J.F. Reaction network and kinetics of the vapor-phase catalytic hydrodenitrogenation of quinoline. Ind. Eng. Chem. Proc. Res. Dev., 1979, 20, 53.
12. Satterfield, C.N. & Gulatekin, S. Effect of hydrogen sulfide on the catalytic hydrodenitrogenation of quinoline. Ind. Eng. Chem. Proc. Res. Dev., 1979, 20, 62
13. Satterfield, C.N., Modell, M.M., Hites, R.A. & Declerck, C.J. Intermediate reaction in the catalytic hydrodenitrogenation of quinoline. Ind. Eng. Chem. Proc. Res. Dev., 1978, 17, 141.

14. 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, 1981, 319.
15. Lange, N.A. (Ed.). Handbook of chemistry. Sandusky, OH: Handbook Publishers, Inc., 1956.
16. Orion Research, Orion research instruction manual ammonia electrode model 95-10, Form IM95-10/8750, 1978.
17. Stenhagen, E., Abrahamson, S. & McLafferty, F (Eds.). Registry of mass spectra data. New York: John Wiley & Sons, 1974.
18. Peters, D.G., Hayes, J.M. & Hieftje, G.M. A brief introduction to modern chemical analysis. Philadelphia: W.B. Saunders Co., 1976.