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**REACTIVITIES OF SOME AROMATIC COMPOUNDS
AT SUPERCRITICAL WATER CONDITIONS**

by

Chun-Cheng Tsao

**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
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REACTIVITIES OF SOME AROMATIC COMPOUNDS AT SUPERCRITICAL WATER CONDITIONS

Chun-Cheng Tsao, M.A.

Western Michigan University, 1991

The goals of this study are the removal of nitrogen from the extraction products of coal by Supercritical Water and the development of an understanding of the reactions leading to this removal. Six model compounds with structures similar to the intermediates of the coal liquefaction processes were studied. Benzylamine generated toluene through hydrogen abstraction after the C-N bond rupture. To a lesser extent, the oxidation of the benzylic carbon took place leading to benzene formation. Both reaction pathways occurred with equal probability for benzylidenebenzylamine, producing comparable yields of benzene and toluene. Benzaldehyde generated benzene through the oxidation/decarboxylation sequence. Benzyl alcohol formed toluene as the major product while benzoic acid produced benzene. The low yield of benzene in the bibenzyl study reveals that the C-N bond is essential for the oxidation of benzylic carbon. Kinetic data of the benzaldehyde-Supercritical Water reaction show a second order process with an inhibition by the product.

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Last, my deepest gratitude and appreciation are extended to my wife, Tsui-yun, for her love, support, sacrifice and encouragement needed to bring this study to completion.

Chun-Cheng Tsao

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
LIST OF TABLES	v
LIST OF FIGURES	vi
CHAPTER	
I. INTRODUCTION	1
Supercritical Fluid Extraction	2
Application of SFE to Coal Extraction	6
Supercritical Water for Coal Extraction	7
Studies of Model Compounds at SW Conditions.	8
II. EXPERIMENTAL METHOD	12
Apparatus	12
Materials	14
Procedure	15
Calculations	18
III. RESULTS AND DISCUSSION	23
Benzylamine-SW Reaction	23
Benzylidenebenzylamine-SW Reaction	26
Benzaldehyde-SW Reaction	29
Benzoic Acid-SW Reaction	33
Benzyl Alcohol-SW Reaction	35
Bibenzyl-SW Reaction	37
Kinetic Study of the Benzaldehyde-SW Reaction	40

Table of Contents--Continued

CHAPTER

IV. CONCLUSIONS	47
REFERENCES	53
APPENDICES	
A. Average Retention Times and Calibration Factors	55
B. Program of Product Distribution Calculation	58
C. Abbreviations and Structures of Some Organic Compounds.....	68

LIST OF TABLES

1. Data and Quantitative Results of Toluene From Run BBA-3	21
2. Quantitative Results From Run BBA-3	22
3. Benzylamine Pyrolysis Result	24
4. Reaction of Benzylamine With SW	25
5. Reaction of Benzylidenebenzylamine With SW.....	28
6. Benzaldehyde Pyrolysis Results	30
7. Reaction of Benzaldehyde With SW	31
8. Reaction of Benzaldehyde With SW and Additives	32
9. Reaction of Benzoic Acid With SW	34
10. Reaction of Benzyl Alcohol With SW	36
11. Reaction of Bibenzyl With SW	38
12. Reaction of Bibenzyl With SW and Additives	39
13. Kinetic Data of the Benzaldehyde-SW Reaction at 380 ^o C	42
14. Kinetic Data of the Benzaldehyde-SW Reaction at 400 ^o C	43
15. Kinetic Data of the Benzaldehyde-SW Reaction at 425 ^o C	45
16. Average Retention Times and Calibration Factors	56
17. Abbreviations and Structures of Some Organic Compounds	69

LIST OF FIGURES

1. Density Diagram in the Vicinity of the Critical Point	3
2. Isoquinoline-Water Reaction Scheme	10
3. Reactor	13
4. Benzylamine-SW Reaction Scheme	48
5. Benzylidenebenzylamine-SW Reaction Scheme	50
6. Benzaldehyde-SW Reaction Scheme	51

CHAPTER I

INTRODUCTION

The use of Supercritical Water (SW) in coal extraction to obtain more versatile fluid products has attracted significant interest recently. In addition to acting as a solvent, SW participates actively in the decomposition of many organic compounds leading to different mechanisms than those observed at other conditions (1). The objectives of this study are to investigate the reactivities and reaction mechanisms of SW with some organic compounds which contain functional groups that are thought to be present in coal or to be formed during SW extraction of coal, and to study the kinetic behavior of benzaldehyde which is thought to represent one of the important intermediates formed during SW extraction process. The choice of benzylamine, benzylidenebenzylamine, benzyl alcohol, benzaldehyde, and benzoic acid as model compounds was based on the report (2) that they exist as, or are similar to, intermediates in the SW reaction with isoquinoline, a major model compound used to represent fuel-nitrogen in the coal structure. A detailed mechanism study of the isoquinoline system will help to understand the behavior of heteroatom removal from organic compounds at SW conditions. In addition, bibenzyl was selected to study because it contains an aliphatic linkage between two aromatic rings, and, through breaking the C-C bond, lower molecular weight products can be produced which is one of the important functions of fossil fuel processing. It is acknowledged that much of the work can be improved through a better understanding of the basic chemistry of SW.

Supercritical Fluid Extraction

Supercritical fluids are substances that are heated above their critical temperatures and pressures. When a compound's temperature is below the critical temperature (T_C), liquid and gaseous states can be transformed reversibly by either increasing or decreasing pressures. At temperatures above T_C a continuous "fluid" exists regardless of the pressure. One uniform phase of such a fluid is the most important feature of a supercritical fluid.

When a supercritical fluid is used as an extraction solvent, it is possible to separate a multicomponent mixture by capitalizing on both the differences in component volatilities, which is the feature of distillation, and the differences in the specific interactions between the mixture components and the supercritical fluid solvent, which is a feature of liquid extraction. So, this method, supercritical fluid extraction (SFE), combines many advantages of distillation with those of extraction.

The technique of SFE has many industrial applications, such as the extraction of oleoresin (3), the separation of solid aromatic isomers (4), and the removal of lower-molecular-weight constituents from coal at high temperature (5). A compressed supercritical fluid possesses several properties which make it interesting for the coal liquefaction process. The most important one is the ability to enhance the solubilities of high molecular weight, low volatility species in, or formed during the processing of, coal.

It has been determined that the solvent power of a supercritical fluid can be related to the solvent density in the critical region (6), as will be illustrated by equation 1 to be discussed later. Figure 1 represents the variation of the reduced density (ρ_R) as a function of reduced pressure (P_R) and reduced temperature (T_R) in the vicinity of the critical point. The reduced density of the solvent can change from about 0.1,

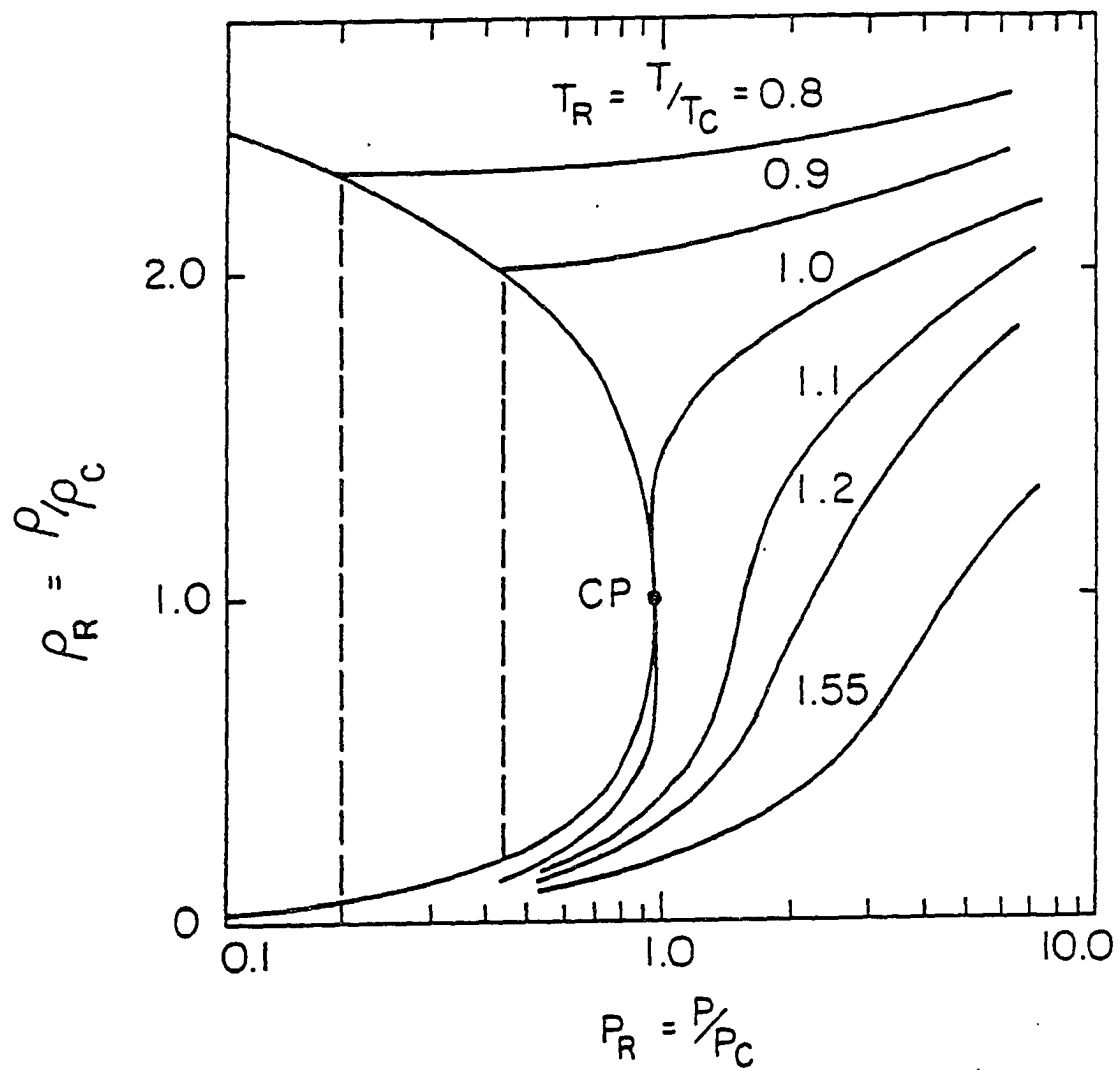


Figure 1. Density Diagram in the Vicinity of the Critical Point.

a gas-like density, to about 2.5, a liquid-like density. When the reduced densities increase from gas-like to liquid-like, certain solvent powers appear gradually. In the cases of constant temperature processes, the higher the pressures, the larger the reduced densities and, therefore, the solvent powers. However, as the reduced temperature is increased, such as to 1.55, the liquidlike density can be matched only when the reduced pressure is elevated to about 10. This indicates that for a supercritical fluid, both pressure and temperature can be used to control the solvent density and, hence, the solvent power.

Thermodynamic analysis (7) provides a semiquantitative treatment of SFE which is described by the following relationship for solids dissolving in compressed gases:

$$\ln \alpha = (V_s - 2B_{12}) / V \quad (1)$$

where $\alpha = C_2 / C_2^0$, a measure of enhanced solubility, C_2 and C_2^0 represent the molar concentrations of solute in the vapor state with and without the presence of solvent respectively, V_s and V are the molar volumes of solute and solvent in the fluid state respectively, and B_{12} is the cross-virial coefficient which represents the interactions between the molecules of solvent 1 and solute 2. The greater the interaction the more negative the value of B_{12} and the greater the enhancement in solubility. Using eqn.(1) and the characteristic behavior of B_{12} (5), two general conclusions can be made:

1. Higher values of α will be obtained when the extraction temperature approaches the critical temperature of the fluid (8) because the term $-2B_{12}$ in eqn.(1) also increases. Therefore the solvent power can be enhanced either by decreasing the extraction temperature, if a given supercritical fluid is used, or by using a fluid with higher T_c , if the extraction temperature is fixed. The importance of the critical temperature of the extractant is illustrated by Gangoli and Thodos (7). The solubilities

of phenanthrene in several supercritical fluids were examined at the conditions of $T = 40^{\circ}\text{C}$ and $P = 40\text{ MN / m}^2$. They reported that ethane ($T_c = 32^{\circ}\text{C}$) was found to have the largest solvent power followed by carbon dioxide ($T_c = 31^{\circ}\text{C}$), ethylene ($T_c = 10^{\circ}\text{C}$), carbon tetrafluoride ($T_c = -51^{\circ}\text{C}$), methane ($T_c = -82^{\circ}\text{C}$) and nitrogen ($T_c = -147^{\circ}\text{C}$).

2. The only term in eqn.(1) which is related to pressure is V . Since the volume is inversely related to pressure, the value of α can be continuously adjusted by controlling the pressure. Under favorable conditions, the enhanced solubility of the solute may be as large as a factor of 10^4 (9). Gangoli and Thodos reported that the Russian scientists Tskhanskaya et al. (7) have studied ethylene/naphthalene system at the temperatures of 12°C and 45°C . Their results gave plots of log solubility against the reciprocal of volume that were essentially linear which supports this theoretical consideration.

In addition to its unique ability to enhance solubility, a supercritical fluid possesses certain other physicochemical properties that add to its utility as a solvent, e.g., it exhibits gaslike transport properties even though it possesses a liquidlike density. Literature data (10) show that in either a single or binary phase system, supercritical fluids exhibit relatively low viscosities as well as diffusion coefficients that are considerably higher than the usual values for liquids. This property, combined with zero surface tension (11), allows facile penetration into microporous materials.

The last interesting property of a supercritical fluid is the pressure dependence of dielectric constant. A study of CO_2 (10) has shown that dielectric constant increased with pressure. For water at critical point, the dielectric constant is about 2.5, which is close to that of benzene (12). As the pressure increases to 600 atm., the dielectric constant increases to about 12.5 which is similar to that of pyridine. Thus, a

variation of pressure may shift the solvent characteristics significantly.

Application of SFE to Coal Extraction

The properties of gas-like diffusivity and viscosity, zero surface tension, and liquid-like density combined with the pressure-dependent solvent power and dielectric constant of a supercritical fluid have recently increased industrial interest in the technique of SFE, although it has been known since 1879 (11). The application of SFE in the liquefaction of coal has been of interest for about 15 years. Its ability to enhance the volatility (solubility) of heavy molecules from coal is the major advantage of SFE.

Generally, three types of chemical processes are of concern during the thermal conversion of coal (13). Primary reactions involve thermolysis of weak bonds at about 400° C, generating smaller reactive fragments and reactive sites within the coal residua. Then these reactive intermediates can undergo two kinds of secondary reactions which are (a) stabilization to produce tar (liquids of low volatility) and light gases and (b) recombination to produce refractory char (nonvolatile solids). Usually, the small fragments formed in the primary reactions are not sufficiently volatile to distill at 400° C. If the temperature is increased the retrogressive combinations predominate and only a small amount of the coal distills as tar, reducing the efficiency of the extraction. However, SFE offers a means to recover those small fragments by increasing their volatilities when formed and thereby avoids the undesired reactions. Besides, as mentioned above, the solvent power is pressure dependent. It is possible to precipitate the extracted materials out of the solvent by simply reducing the pressure. Thus, a solid residue and a viscous liquid are fractionated and both are essentially free of the solvent.

The selection of the solvent is the most important point when the liquefaction process of coal is performed using the technique of SFE. Water was found to be an excellent extractant when the following fundamental considerations are made:

1. Critical temperature: As mentioned above, extract volatility enhancement is greater when extraction is carried out near the fluid critical temperature. For coal extraction, the best extraction temperatures are found to be about 400^o C. Thus, some candidates such as water ($T_C = 374^o$ C) and toluene ($T_C = 318^o$ C) can be considered to be used for coal extraction.

2. Reactivity: In addition to being a solvent, some degree of participation in the reaction may be useful for the whole process, such as being a reactant, catalyst, or hydrogenation reagent, etc., depending on the requirements of the extraction. According to the report from Deshpande et al. (1), supercritical water (SW) was found to act as both solvent and reactant in the conversion of coal to gases and liquids. In addition, water shows a high reactivity with cyanide wastes to form ammonia (14) and appears to be able to extract sulfur atoms by the formation of hydrogen sulfide (1). These special properties make the coal liquefaction products more environmentally acceptable.

3. Molecular polarity: Polar solvents tend to exert a stronger depolymerizing action on coal than nonpolar ones and also to increase the extraction rate (7). Vasilakos et al. have studied the relationship between some specific physical and chemical characteristics of supercritical solvents and their effectiveness as SFE solvents (15). They found that among those nonpolar solvents being examined, toluene gave the highest extraction yield (27.6% at 1440 psi and 36.0% at 5140 psi), and that n-paraffins showed a linear relationship between molecular weight (72-170 g/mole) and extraction yield (18-23% at 1290-2032 psi). In the group of polar

solvents, they found that the functionality of the solvent affected the yields and the properties of coal extracts and that water acted as the best solvent with a extraction yield much higher than the predicted value (34% at 3580 psi). Methanol gave a yield (20.6% at 3610 psi) which was slightly lower than that predicted theoretically, while acetone decomposed at the extraction temperature (400^o C) and gave a low yield (7.3% at 3840 psi). A comparison of toluene and water yields shows that water was an even better supercritical solvent than toluene for coal extraction, affecting high extraction yields at moderately high pressures. Besides, when returned to ambient conditions, the extract-containing aqueous phase of the water runs were almost clean with a minimal amount of organic material, while the solutions were essentially black in the toluene runs.

4. Cost and availability: From the viewpoint of economics, water should be the best solvent.

5. Others: The size of the water molecule is smaller than that of toluene and other common solvents, making water penetration into the microporous structure of coal easier. The dielectric constant of SW near the critical point, as indicated above, is close to that of benzene. Therefore, the solubility of the organic material is increased at SW conditions.

Studies of Model Compounds at SW Conditions

During coal processing, two important functions might be performed: (1) the removal of heteroatoms to yield environmentally more acceptable products, and (2) the formation of lower molecular weight products. Because nitrogen and sulfur are the two major sources of pollution from the coal, and sulfur was found to be easier to remove than nitrogen (16), the removal of nitrogen from the coal structure is the primary concern of this work. Thus model compounds containing heterocyclic nitrogen, such as quinoline, isoquinoline and other related compounds, were chosen

to examine their reactivities at SW conditions (14). The results of these previous studies gave the following information:

1. The heterocycles studied are more reactive and react by different mechanisms in the presence of SW than when undergoing inert pyrolysis.
2. The two quinolines react by very different mechanisms. Isoquinoline appears to undergo simple C-N bond rupture followed by hydrolysis and decarboxylation. Therefore, ethylbenzene, o-xylene and the products of further side chain elimination, toluene and benzene, are present as the major products. The proposed reaction pathway is shown in Figure 2. Quinoline appears to be more inert than isoquinoline at SW conditions and there is a pronounced preference for the 1-2 bond rupture which does not allow the hydrolysis-decarboxylation sequence to occur because the nitrogen is bonded to the aromatic ring which leads to aniline and phenol type products. Thus, the mechanism becomes more complicated than that of the isoquinoline reaction.
3. About 60 - 70% of the nitrogen from the consumed quinoline, isoquinoline and aniline is removed in the water layer as ammonia.
4. The presence of oxygen in the char indicates that many C-N bonds are broken followed by the oxidation of carbon atoms by water, thus providing hydrogen for other products.
5. Acid catalysts, such as ZnCl_2 , can promote the reactivities of the two quinolines and aniline and the hydrogen transfer agent, dihydroanthracene (DHA), increases the reactivity of both quinolines.
6. Nitrile structures hydrolyse and decarboxylate to form hydrocarbons, NH_3 and CO_2 .
7. Aromatic amines can undergo substitution of the NH_2 group by OH to

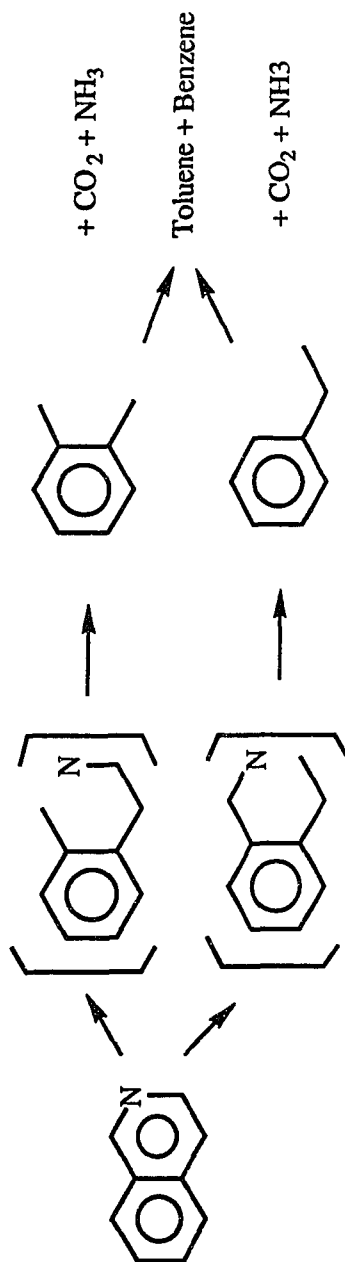


Figure 2. Isoquinoline-Water Reaction.

form phenolics and NH_3 .

Basically, the current study is an extension of the study of isoquinoline-SW reaction. Therefore, benzylamine (BA) was first chosen to study because it was assumed to be representative of the intermediate structure formed after the initial bond rupture in the heterocycle. Since benzyldenebenzylamine (BBA), benzaldehyde, benzyl alcohol and benzoic acid were found (or assumed) to be intermediates in the BA-SW reaction, they were studied in this work. Finally, as indicated in the introduction section, bibenzyl was also studied briefly due to the interest in the behavior of a saturated carbon linkage in a SW environment.

CHAPTER II

EXPERIMENTAL METHOD

Apparatus

Three groups of equipment were used in all the experiments: the reaction, extraction, and product analysis systems.

The reaction system consisted of a stainless steel, batch reactor, a fluidized sand furnace, a temperature controller, and a temperature measuring device. The reactor was a cylindrical vessel with internal height 73.2 mm and internal diameter of 28.2 mm (Figure 3). The lid was sealed using six, hex head, stainless steel bolts (1/4" x 20 x 1"). A copper gasket (id = 26 mm, od = 35 mm) was used between the lid and the reactor to prevent leaking under high pressure conditions. The total internal volume of the sealed reactor was $47.0 \pm 0.5 \text{ cm}^3$. A hole which passed through the lid and the flange of the reactor was designed so that the thermocouple can be inserted into the proper position. The reactor was not equipped for the collection of gaseous products and for pressure measurement. The furnace was a Tecam SBS-4 fluidized sandbath with air blowing from the bottom. The reaction temperatures were controlled by a chromel-alumel thermocouple connected to a custom made temperature controller. Reaction temperatures were frequently checked using a thermocouple with one end embedded in the reactor's flange, the other end connected to a Honeywell Millivolt Model 2732 Potentiometer.

The extracting system for all the experiments included a 125 mL separatory funnel, a 60 mm gravity funnel, a 60 mm short stem gravity funnel, and a 25, 50 or 100 mL volumetric flask depending on the amount of solvent to be used.

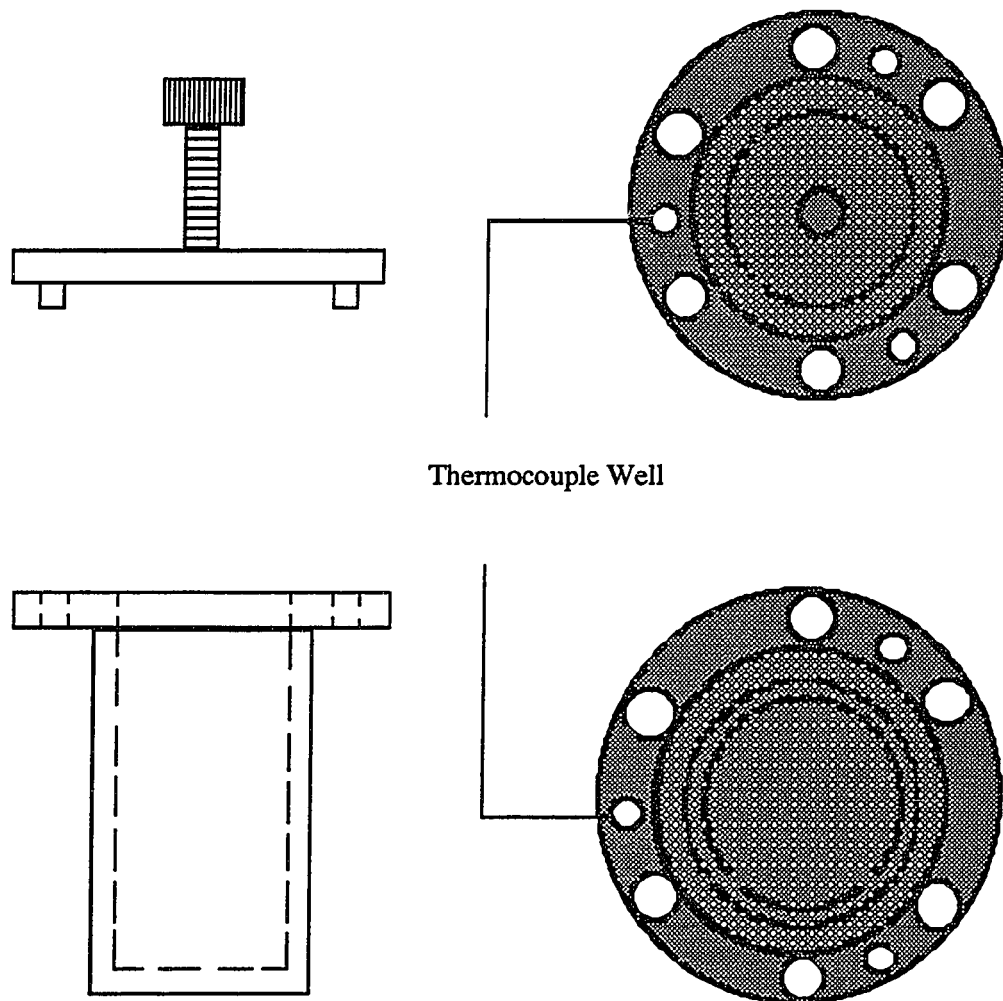


Figure 3. Reactor.

Product analyses included identification using a Gas Chromatograph-Mass Spectrometer and quantitative determination of product distributions using a Gas Chromatograph. The GC-MS unit consisted of a Hewlett Packard Model 5890 GC, which included and used a 12 m x 0.2 mm x 0.33 μ m capillary column packed with HP-1 (crosslinked methyl silicone gum), and a Hewlett Packard Model 5970 Mass Selective Detector. The determinations of product distributions were accomplished by using a Varian Model 3700 GC which used a 50 cm x 1/8" column packed with 5% OV-101 (liquid methyl silicone) on chromosorb G-HP (100/120), a thermal conductivity detector, a Bristol 64A-1PH760-51 Recorder, and a Varian CDS111L Chromatograph Data System. The general operating settings of GC in all the experiments were: flow rate of carrier gas, He, 30 cm³/min, detector temperature 260^o C, injector temperature 240^o C, and filament current 180 ma.

For the earlier research, calculations were made using a Casio Fx-4000p Calculator. A self-designed software, using PASCAL language, and a personal computer were used for all the later calculations. Straight line plotting was accomplished by using a least squares program from the VAX System.

Materials

Either certified grade or reagent grade benzylamine, benzylidenebenzylamine, benzoic acid, benzaldehyde, benzyl alcohol and bibenzyl were used for reactions. The compounds used for calibrating the GC were either analytical or spectral grade. In all cases, the purities of the calibrating compounds were high enough to give only one peak when a 3 μ L sample of undiluted compound was injected. 2M and 6M NH₃ were prepared from reagent grade concentrated NH₃. ZnCl₂, Al and 9,10-dihydroanthracene (DHA) were off the shelf. Certified grade methylene chloride, which was used for the extraction and dilution solvent, contained a little

benzene that was taken into account during analysis. Water for the reaction is tap distilled water.

Procedure

Generally the experimental procedures contained five steps: (1) charging of the reactor, (2) reaction at the desired conditions, (3) product separation and collection, (4) qualitative analysis of reaction products, and (5) calibration of the GC and quantitative analysis of products.

Two milliliter of liquid starting materials, such as benzylamine, benzylidenebenzylamine, benzyl alcohol and benzaldehyde, were transferred into the reactor using a 2.00 mL pipet which had been calibrated and determined to deliver 1.9626 ± 0.0002 g (18.316 mmole) of benzylamine, 2.0760 ± 0.0002 g (10.631 mmole) of benzylidenebenzylamine, 2.0826 ± 0.0002 g (19.258 mmole) of benzyl alcohol and 2.0860 ± 0.0002 g (19.655 mmole) of Benzaldehyde. If solid starting materials were used, such as bibenzyl and benzoic acid, approximately 2 grams were weighed and transferred into the reactor. After the addition of the organic reactant, 10.0 mL water was added using a 10 mL graduated pipet calibrated in 0.1 mL units. Some experiments used 10.0 mL 2M or 6M NH_3 instead of 10.0 mL water to produce the same water pressure and an additional NH_3 environment. If a hydrogen transfer agent or catalyst was needed, it was added at this time. Then the reactor was purged with high purity grade argon and the copper gasket inserted. Finally, the reactor was bolted closed as tightly as possible.

After the thermocouple was bound to the reactor, the reactor was suspended in the fluidized sandbath furnace for the required reaction time. Usually 10 minutes were required to heat the reactor to the desired reaction temperature. The reactors' temperatures were checked frequently with the potentiometer during the reaction.

Following reaction, the reactor was removed and allowed to cool on the bench top; about one hour was needed for the hot reactor to reach room temperature.

When the reactor was opened, a note was made if any gas was vented. If a solid species was present in the reactor, a piece of glass wool was placed on the stemless funnel to filter the solution. To start the extraction the lid and the gasket were rinsed with a small amount of methylene chloride. The washing liquid was then collected as part of the product mixture. The contents of the reactor were poured through the glass wool into the separatory funnel. The organic layer was separated from the aqueous layer and drained into a 25 mL (or 50 mL, if more solvent was needed) volumetric flask. The reactor was then rinsed several times with small amounts of solvent until the washes were colorless. These washes were also used to wash soluble organic materials through the glass wool and to extract organic products that might be in the water layer. Then the washes were added to the flask and mixed with the organic layer. Finally additional solvent was added to fill the flask to the mark and the flask capped and labeled. The remaining water was collected for recovered volume measurement using a 10 mL graduated cylinder. If the amount of recovered water remained essentially the same as the initial amount, then apparently leaking did not occur. Otherwise, the reaction was invalid, and the same run would be performed again.

Qualitative analyses using GC-MS were done only when a new starting material or a new catalyst was used. Pyrolysis reactions gave different product distributions which also needed GC-MS to identify the products. Before performing GC-MS analysis a preliminary gas chromatogram was obtained to establish the relative retention times of the products to be analyzed. Some compounds which were not identified with certainty by GC-MS can be confirmed using GC by mixing the product mixture with known compounds. But some products were reported as an isomer of a

probable structure as deduced from the molecular weight and MS fragmentation pattern.

Quantitative analyses included calibration of the GC detector response, measurement of the reaction product mixture peak areas and calculation of product yields and percent reaction. The calibration solutions were mixtures of possible products with different retention times. The amount of standard compound used for calibration was dependent on the approximate amount found in the product mixture. The procedure for calibration is described using bibenzyl. A typical bibenzyl calibration standard solution was prepared by adding about 1 gram of bibenzyl along with about 1 gram of toluene, 0.05 gram of ethylbenzene, 0.1 gram of diphenylmethane, 0.3 gram of stilbene, and 0.2 gram of phenanthrene to methylene chloride to a total volume of 25 mL in a volumetric flask. All the masses of standard compounds were determined to a ± 0.0002 g uncertainty. Different amounts of standard compounds in 25 mL CH_2Cl_2 were used to calibrate each known compound. Then the calibration factors (attenuated area/ $\mu\text{L} \times \text{mmole}$) used for yield calculations were determined by either taking the average of individual calibrating factors from different concentrations or making a plot of calibration factor vs. concentration, depending on the relationship between the calibration factor and concentration. Three injections were necessary for each solution to obtain an average value, and 3 μL was used for each injection. The column conditions for calibration were the same as those used in running the reaction sample, and programmed as follows: the initial temperature was 45 $^\circ$ C for 1 minute, then the temperature increased at a rate of 10 $^\circ$ C/min. for three minutes, then the rate was changed to 15 $^\circ$ C/min. until the final temperature of 300 $^\circ$ C was reached. The temperature was then kept 300 $^\circ$ C until all the compounds were eluted. The determinations of peak areas and retention times were accomplished by the integrator. The calibration factor was

defined as the attenuated area/1 μL injection solution/1 mmole compound in 25 mL of solution.

Determinations of product mixtures were accomplished as described in the calibration procedure using 3 μL injections of the product solutions. The attenuated areas per μL sample and the calibration factors were used to calculate the mole numbers of the known products. The mole percent yields of products were calculated based on the moles of reactant converted and on the moles of product formed. Some components which could not be separated completely were reported as a total yield of mixture using an average calibration factor. Some compounds, especially for the higher molecular weight minor products, could not be identified with certainty, thus, their yields were calculated using an estimated calibration factor. All the calculations were accomplished utilizing a personal computer and a program called "R DATA" (see Appendix B). A sample calculation including the determination of a calibration factor will be given in the following section.

Calculations

The calculation procedure for determining calibration factors is demonstrated using an example of benzylidenbenzylamine.

The first standard solution contained 0.0508 g (0.260 mmole) benzylidenbenzylamine in a 25 mL solution. The attenuated area read from the integrator for an injection of 2.95 μL of this solution was 41642 units which was translated into 4.1642 units by dividing by 10,000 for convenience.

Attenuated area per microliter (AA / μL):

$$4.1642 \text{ units} / 2.95 \mu\text{L} = 1.412 \text{ units} / \mu\text{L}$$

Calibration factor (attenuated area per microliter solution per millimole benzylidenbenzylamine):

$$(1.412 \text{ units} / \mu\text{L}) / 0.260 \text{ mmole} = 5.431 \text{ units} / (\mu\text{L} \times \text{mmole})$$

Average calibration factor of three injections:

$$(5.431 + 5.322 + 5.372) / 3 = 5.375 \text{ units} / (\mu\text{L} \times \text{mmole})$$

The final calibration factor (CF) used for further calculations was calculated by averaging all the individual calibration factors (the \pm values are average deviations) from other standard solutions with different benzylidenebenzylamine concentrations (0.260, 0.530, 0.925, 1.279 and 1.954 mmole in 25 mL solutions):

$$(5.375 + 5.411 + 5.346 + 5.238 + 5.428) / 5 = 5.360 \pm 0.054 \text{ units} / (\mu\text{L} \times \text{mmole})$$

The product yields in percents are generally defined as (moles of products formed/mole of reactant consumed) \times 100%. A sample procedure in calculating percent reaction and product yield using run BBA-3 is shown.

The reaction conditions were: 2 mL benzylidenebenzylamine (calibrated to be 10.631 mmoles) mixed with 10 mL water at 400^o C for 6 hours. The first injection of a 25 mL sample solution was 3.00 μL , and gave 1.6100 units of attenuated area.

Thus, the attenuated area per microliter solution:

$$1.6100 \text{ units} / 3.00 \mu\text{L} = 0.537 \text{ unit} / \mu\text{L}$$

The mmoles of the compound recovered = (AA / μL) / CF

$$(0.537 \text{ unit} / \mu\text{L}) / (5.360 \text{ units} / \mu\text{L} \times \text{mmole}) = 0.100 \text{ mmole}$$

The mmoles of BBA reacted = mmoles of initial BBA - mmoles of BBA recovered

$$10.631 - 0.100 = 10.531 \text{ mmoles}$$

% of BBA reacted = (mmole of BBA reacted / mmole of initial BBA) \times 100%

$$(10.531 / 10.631) \times 100\% = 99.06\%$$

Average of % reaction of 3 injections:

$$(99.06 + 98.49 + 98.59) / 3 = 98.71 \pm 0.23\%$$

Benzene, one of the reaction products in run BBA-3, has a CF = 2.586. In the

first injection of 3.00 μL benzene gave an AA = 57.0251 units of which 0.2300 units was contributed by benzene impurity of a 25 mL CH_2Cl_2 solution. Thus, the attenuated area per microliter solution:

$$(57.0251 - 0.2300) / 3.00 = 18.932 \text{ units} / \mu\text{L}$$

The mmoles of benzene formed:

$$(18.932 \text{ units} / \mu\text{L}) / (2.586 \text{ units} / \mu\text{L} \times \text{mmole}) = 7.321 \text{ mmoles}$$

According to the proposed BBA-SW reaction mechanism, one BBA molecule produces only one benzene molecule. Thus, the percent yield of benzene =

$$(\text{mmole of benzene} / \text{mmole of BBA reacted}) \times 100\%$$

$$(7.321 / 10.531) \times 100\% = 69.52\%$$

Average of benzene yields of 3 injections:

$$(69.52 + 70.28 + 70.60) / 3 = 70.13 \pm 0.41\%$$

The yields of other known compounds in the product mixture were calculated in exactly the same way as illustrated above. For some minor compounds which were not identified by GC-MS the percent yields were calculated based on the estimated calibration factors. For example, in the run BBA-3, the calibration factor of diphenylmethane isomer (probably phenyltoluene) was estimated to be 4.343, same as that of diphenylmethane. The high molecular weight, unidentified compounds which appeared at the end of chromatogram of run BBA-3 had molecular weights of 230-309, and were assigned to have a calibration factor of 5.200 according to the trend as molecular weights increased, see the Appendix, Table 16. Besides, the yields of these high molecular weight products were calculated as double of mmoles of products formed/mmole of reactant consumed because they were found to be 3 (or more)-ring structures while BBA contains only two benzene rings. Tables 1 and 2 show the product yield calculation results in run BBA-3.

Table 1
Data and Quantitative Results of Toluene From Run BBA-3

Injection #	R.T. ^a	R.R.T. ^b	Volume(μL)	A.Area	AA/μL	CF(AA/μLxmmole)	mmole	yield(%) ^c
1	1.07	0.10	3.0	56.658	18.887	3.208	5.887	55.90
2	1.06	0.10	3.0	56.681	18.894	3.208	5.890	55.93
3	1.07	0.10	3.0	57.612	19.204	3.208	5.986	56.84
Average	1.07	0.10			18.995		5.921	56.22±0.41

^a Retention time (R.T.) with unit of minute.

^b Relative retention time (R.R.T.) = R.T. of toluene / R.T. of BBA recovered.

^c Yield of toluene = (mmoles of toluene / mmoles of BBA reacted) x 100%.

Table 2
Quantitative Results From Run BBA-3^a

Compound	R.T.			R.R.T.			AA/ μ L	CF	mmoles	% Recovered	% Yield
Benzene	0.42			0.04			19.053	2.586	7.367	-	70.13
Toluene	1.07			0.10			18.993	3.208	5.921	-	56.22
Benzaldehyde	3.19			0.30			2.257	3.215	0.703	-	6.68
Benzylalcohol	4.42			0.42			0.183	3.593	0.050	-	0.47
Biphenyl	7.96			0.75			3.323	4.294	0.770	-	7.34
Diphenylmethane and isomers	8.13	8.37	8.86	0.76	0.78	0.83	3.230 ^b	4.343 ^c	0.770	-	7.12
Bibenzyl	9.10			0.85			1.047	4.958	0.210	-	2.00
Fluorene	9.53			0.89			0.290	4.727	0.063	-	0.60
Benzophenone	9.81			0.92			0.577	4.912	0.120	-	1.14
Benzophenylketone	10.52			0.99			0.967	5.000 ^c	0.193	-	1.84
Benzylidenebenzylamine	10.66			1.00			0.730	5.360	0.137	1.29	-
High M.W. mixture ^d	>10.66			>1.00			2.110	5.200 ^c	0.403	-	7.69

^a All values shown are average of three trials.

^b Summation of three isomers.

^c Estimated values.

^d Mixture includes compounds with molecular weights 230, 244, 256, 258, 270, 271, 272, 281, 284, 287, 296, and 309. Their quantities are summarized together.

CHAPTER III

RESULTS AND DISCUSSION

Benzylamine-SW Reaction

Benzylamine was found to be relatively reactive as was benzonitrile (14). In both the pyrolysis and reaction with SW, benzylamine was consumed quantitatively at the mildest condition used without a catalyst. The % yields reported in the data tables are generally based on (moles product formed/mole reactant consumed) x 100. However, when two or more moles of reactant are required for one mole of product, the yields are multiplied by the number of moles needed. For example, biphenyl or bibenzyl yields from benzylamine, benzaldehyde, etc. are 2 x moles product x 100/mole reactant consumed. The yields from benzylidenebenzylamine may exceed 100% since more than one mole of product can be formed from one mole of reactant. Thus, these values are primarily intended to show product distributions. Tables 3 and 4 summarize the results of the benzylamine reaction, without and with water respectively, at 400° C as well as selected literature data (2). The results of this work and the previous data were consistent except that NH₃ was not measured in this work. There is a significant difference between the products from the pyrolysis and those from the SW reaction. The major products generated by pyrolysis were toluene, benzonitrile, bibenzyl, stilbene and smaller amounts of high molecular weight compounds, while SW reaction produced more toluene with a yield of about 40-49% and much less, or negligible amounts of the other major products found in the pyrolysis. In addition, the SW reaction produced benzene, which reached a yield of 20-30% at longer reaction times, and the intermediate products benzaldehyde, benzyl

Table 3
Benzylamine Pyrolysis Result^a

Volatile products ^b	% yield
Toluene	26.9
Benzonitrile	9.5
Diphenylmethane	1.2
Bibenzyl	18.1
Stilbene	11.7
High M.W. products (total) ^c	17.8

^a Reaction condition was 400° C for 1 hour and extent of reaction was 100%.

^b In addition to those listed some products with very small quantities (each less than 0.5%) were observed by the GC-MS. According to the molecular weights, they are assumed to be xylenes, xylidines, benzyltoluene, phenanthrene, methylphenanthrene, triphenylpropene and diphenylmethylene indene.

^c The total yield of these more abundant products is calculated from estimated calibration factors. It is assumed from the molecular weights that they consist of methylcarbazole, diphenylmethylene indole, triphenylimidazole and tetraphenylpyrrole.

Table 4
Reaction of Benzylamine With SW^a

	Run			
	BA-1			BA-2
Temperature (° C)	400	400	400	400
Time (hour)	1	1	3	6
H ₂ O pressure (psi)	3870	3870	3870	3870
% Reaction	100	100	100	100
Volatile products (% yield)				
Ammonia	-	66	101	-
Benzene	10.7	11	22	19.9
Toluene	43.0	48	49	40.6
Benzaldehyde	17.5	13.5	4.7	6.5
Benzyl alcohol	5.6	2.0	1.4	2.0
Benzamide	0.7	-	-	0.3
Biphenyl	1.9	1.0	2.8	5.0
M.W. 168 isomers ^b	4.4	1.8	4.4	7.6
Bibenzyl	2.4	2.0	1.4	2.5
Benzylidenebenzylamine	6.4	9.5	3.5	2.5
Minor products (total)	6.5 ^c	0.6 ^d	0.8 ^d	4.5 ^c

^a The 2nd and 3rd reactions with the measurement of NH₃ are adopted from literature (2) for comparison.

^b These may be diphenylmethane and/or phenyltoluene isomers.

^c Consists of fluorene, benzophenone, benzyltoluene, benzylphenylketone and other unidentified high molecular weight products. Yields are calculated using estimated calibration factors.

^d Consists of small amounts of fluorene, benzophenone, stilbene and dihydro-phenanthrene.

alcohol and benzyldenebenzylamine (BBA), which all disappeared concurrently at longer reaction times. The rest of the SW reaction products were primarily two or three ring species, the yields of some of which, such as biphenyl and diphenylmethane, also increased at longer reaction times.

Since toluene and benzene were the major products at the longer times in the benzylamine-SW reaction, it is believed that there are at least two major mechanistic pathways occurring. One is through the simple breakage of the C-N bond to form the benzyl radical which can dimerize to bibenzyl or capture an H atom to form toluene which restrict further reaction. The amine radical is converted to ammonia. The alternate pathway involves the formation of an imine intermediate (to be discussed later) and the oxidation of the benzylic carbon followed by decarboxylation to produce benzene. Because of the decrease with reaction time in the yields of benzaldehyde, benzyl alcohol and BBA, these are assumed to be the intermediates during the oxidation process. The latter pathway requires an environment of water as evidenced by the absence of benzene, benzaldehyde, benzyl alcohol and BBA in the pyrolysis, therefore, water is considered to be a source of hydrogen according to the reaction:

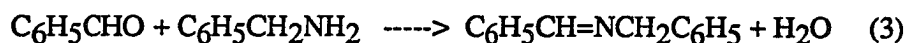


It is interesting to note that the rate constant determined by the toluene carrier technique (17) and very low pressure technique (18) for the initial reaction of benzylamine to form benzyl and amino radicals indicated a half life of over 6,000 hours at 400° C. By comparing this half life with the much faster pyrolysis or SW reaction, it indicates that a chain mechanism may occur in the absence of inhibitors.

Benzyldenebenzylamine-SW Reaction

Since BBA was found to be an intermediate in the benzylamine-SW reaction, the reactivity of BBA was studied at SW conditions. In the benzylamine-SW reaction,

benzaldehyde is found to be an important intermediate with relatively high yields, therefore, the formation of BBA is probably via the dehydration reaction of benzaldehyde and benzylamine, which is a common reaction for imine preparation.



BBA was very reactive at SW conditions, reacting over 95% at 400° C for one hour without any additive. The resulting solution was yellow and clear, thus no tar or char was formed. Table 5 lists the results which are summarized as follows:

1. The yields of benzene and toluene are comparable, and increase with reaction time.
2. Benzaldehyde, the major intermediate, and benzyl alcohol show decreasing yields with reaction time.
3. Other products formed from the phenyl radical, such as biphenyl and diphenylmethane, also show increasing yields with reaction time. Because BBA produces a large quantity of benzaldehyde in the initial reaction with water, reaction (3) must be somewhat reversible. With the supporting evidence which will be given in the following sections, benzaldehyde appears as an intermediate for the formation of benzene and other products formed from phenyl radicals. It also appears that benzyl alcohol is probably produced by the reduction of benzaldehyde and consumed to contribute partially to the yield of toluene, the evidence for which also will be given in the following sections.

The rest of Table 5 shows that additional NH_3 has no apparent effect on the reactivity and product distribution. However, the addition of a hydrogen transfer agent, dihydroanthracene (DHA), increases the rate of formation of toluene significantly at the expense of benzene and other products derived from benzaldehyde. This observation suggests that the following reaction predominates when DHA is added,

Table 5

Reaction of Benzylidenebenzylamine With SW

	Run					
	BBA-1	BBA-2	BBA-3	BBA-4	BBA-5	BBA-6 ^a
Temperature (° C)	400	400	400	400	400	400
Time (hour)	1	3	6	9	3	3
Added NH ₃ (M)	0	0	0	0	6	6
Added DHA (g)	0	0	0	0	0	2.0
H ₂ O pressure (psi)	3870	3870	3870	3870	3870	3870
% Reaction	96.4	97.6	98.7	99.9	98.0	98.4
Volatile products (% yield) ^b						
Benzene	43.9	57.4	70.1	68.5	55.3	22.1
Toluene	48.2	52.1	56.4	57.2	57.3	108.1
Benzaldehyde	43.3	21.9	6.7	4.1	6.2	-
Benzyl alcohol	5.7	4.7	0.4	0.2	0.7	-
Benzamide	1.2	0.8	0	0	1.1	-
Biphenyl	4.1	6.4	7.3	7.2	4.2	-
M.W. 168 isomers ^c	3.9	5.5	7.1	7.4	4.5	-
Bibenzyl	2.7	2.6	2.0	1.9	3.4	-
Fluorene	0.1	0.4	0.6	0.8	0.4	-
Benzophenone	1.3	1.9	1.1	0.9	1.4	-
Mixture ^d	4.2	3.8	1.8	1.4	1.5	-
High M.W. products (total) ^e	6.1	5.6	7.7	7.8	15.4	-

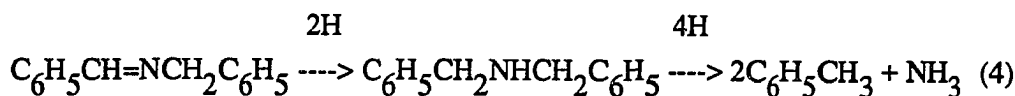
^a Only % reacted and yields of benzene and toluene are calculated because DHA reacts and decomposes in SW (12).

^b These values are intended to illustrate a product distribution. Since more than one mole of product can be formed from a mole of reactant, these yields may exceed 100%.

^c This may be diphenylmethane and/or phenyltoluene isomers.

^d Consists of substances with molecular weights of 182 (benzophenone or bibenzyl isomers), 194, 195 and 196 (phenylbenzyl ketone). Yields are calculated with an estimated calibration factor of 5.000.

^e Consists of triphenylimidazole (MW = 296), dimethylpyrene (MW = 230) and other substances with molecular weights above 200. An estimated calibration factor of 5.200 is used for yield calculations.



where the rupture of both single C-N bonds results in a high yield of toluene. Therefore, the overall results indicate that the breakage of the single C-N bond of the BBA molecule is primarily responsible for the formation of toluene while the other half of BBA molecule, which contains the unsaturated C-N bond, undergoes hydrolysis, the reverse of reaction (3), and subsequently produces phenyl radical products through the intermediate, benzaldehyde.

Benzaldehyde-SW Reaction

Benzaldehyde is thought to be an important intermediate in the formation of benzene in the benzylamine-SW reaction, thus its behavior in SW was studied. The temperatures used were 380, 400, 425 and 450° C. The resulting solutions were clear and had no tar or char. The experimental results including pyrolysis are listed in Tables 6, 7 and 8. Basically there is no apparent difference between the reactions with and without water except that pyrolyses show a little higher rate and that the SW reaction gives somewhat higher benzyl alcohol and lower biphenyl yields. Therefore, SW does not seem to have much effect on the benzaldehyde pyrolysis. Benzene is the most abundant product, while benzoic acid, which is believed to be a precursor of the formation of benzene, is the second major product. The reduction product from benzaldehyde, benzyl alcohol, and the product which it forms, toluene, are the next most abundant products. Again, other substances formed from phenyl radicals and benzyl radicals are also observed in small amounts. Because isoquinoline and benzylamine produced a large quantity of NH₃ in the SW reactions (14, 2), NH₃ is added in the benzaldehyde-SW reaction to generate a similar environment. The results show that NH₃ enhances the extents of reaction remarkably as well as the

Table 6
Benzaldehyde Pyrolysis Results^a

	Time (hour)	
	1	6
% Reaction	29.3	76.5
Volatile products (% yield)		
Benzene	70.0	54.4
Toluene	6.7	7.3
Ethylbenzene	0	2.0
Benzyl alcohol	1.7	0
Benzoic Acid	10.2	6.9
Biphenyl	11.0	14.2
M.W. 168 isomers ^b	6.4	9.0
Mixture (total) ^c	18.8	7.8
High M.W. products (total) ^d	0.8	2.5

^a Both experiments are at 400° C.

^b This may be diphenylmethane and/or phenyltoluene isomers.

^c Consists of species with molecular weights of 166 (fluorene), 180 (stilbene), 182 (bibenzyl and benzophenone etc.) and 196 (phenylbenzyl ketone). Yields are calculated using estimated calibration factors.

^d Consists of species with molecular weights over 200. Yields are calculated using an estimated calibration factor of 5.200.

Table 7
Reaction of Benzaldehyde With SW

	Run ^a									
	BAD-1	BAD-2	BAD-3	BAD-4	BAD-5	BAD-6	BAD-7	BAD-8	BAD-9	BAD-10
Temperature (° C)	400	400	400	400	400	400	400	400	380	425
Time (hour)	1	2	3	4	5	6	7	8	3	3
H ₂ O pressure (psi)	3870	3870	3870	3870	3870	3870	3870	3870	3400	4570
% Reaction	24.9	33.0	42.9	46.9	55.0	55.5	61.5	64.3	23.4	72.1
Volatile products (% yield)										
Benzene	35.7	40.5	54.4	55.5	51.4	50.4	47.3	53.8	29.7	56.3
Toluene	5.9	4.0	7.3	6.1	6.2	4.7	2.6	4.7	5.2	4.4
Benzyl alcohol	6.8	9.8	7.8	8.8	10.5	9.2	12.3	11.7	11.8	3.1
Benzoic acid	13.7	10.8	8.3	8.1	9.0	7.4	9.4	7.2	17.9	3.1
Biphenyl	3.4	4.3	5.4	5.4	6.1	5.7	6.6	7.9	2.2	9.7
M.W. 168 isomers ^b	1.9	1.1	2.7	2.4	1.3	2.7	2.4	2.5	0.9	4.0
Mixture (total) ^c	9.8	8.8	9.6	5.9	7.5	8.0	6.9	7.4	8.3	5.7
High M.W. products (total) ^d	0.4	0	1.6	2.3	1.4	1.6	2.1	3.0	0	3.5

^a More than one trial was performed for each particular reaction condition. These are representative results.

^b This may be diphenylmethane and/or phenyltoluene isomers.

^c Includes bibenzyl, fluorene, benzophenone and other substances with molecular weights of 180, 182, 184 (diphenylcarbinol) and 196. Yields are calculated with estimated calibration factors.

^d Consists of substances with molecular weights higher than 200. A calibration factor of 5.200 is used for the yield calculations.

Table 8

Reaction of Benzaldehyde With SW and Additives

	Run									
	BAD-11	BAD-12	BAD-13	BAD-14	BAD-15	BAD-16 ^a	BAD-17 ^a	BAD-18	BAD-19	BAD-20
Temperature (° C)	400	400	400	400	450	400	450	400	450	450
Time (hour)	1	3	6	9	3	3	9	1	1	1
H ₂ O pressure (psi)	3870	3870	3870	3870	5200	3870	3870	3870	5200	5200
Added NH ₃ (M)	2	2	2	2	2	2	2	6	6	6
Added DHA (g)	0	0	0	0	0	2.0	2.0	0	0	0
Added Al (g)	0	0	0	0	0	0	0	0	0	0.42
% Reaction	72.7	87.0	93.4	95.3	99.4	89.4	99.1	94.1	97.5	98.9
Volatile products (% yield)										
Benzene	31.7	40.3	44.1	44.0	46.7	16.4	18.1	27.5	44.8	39.7
Toluene	10.6	17.9	21.1	19.6	12.2	38.8	38.3	11.7	16.0	14.8
Benzonitrile	0	1.0	0.7	0	0.1	-	-	2.2	0.9	0.6
Benzyl alcohol	2.1	3.4	2.5	0	0	-	-	3.4	1.8	0.6
Benzamide	1.2	1.5	0.7	0	0	-	-	2.5	0.9	0.4
Biphenyl	4.8	9.7	12.4	11.9	13.2	-	-	5.2	12.1	8.1
M.W. 168 isomers ^b	2.0	4.7	6.4	5.6	3.8	-	-	3.4	4.8	3.9
Mixture (total) ^c	5.7	6.8	5.5	4.0	1.8	-	-	4.9	3.6	3.1
Benzylidenebenzylamine	2.0	6.9	4.0	2.7	1.0	-	-	6.1	2.7	2.1
High M.W. products (total) ^d	13.6	7.3	5.2	6.5	4.3	-	-	13.0	2.7	4.7

^a Only % reacted and yields of benzene and toluene are calculated because DHA also reacts and decomposes.

^b This may be diphenylmethane and/or phenyltoluene isomers.

^c Consists of bibenzyl, fluorene, benzophenone and other substances with molecular weights of 181, 182 and 195.

^d Consists of substances with molecular weights above 200.

yields of toluene, and the higher the NH_3 concentration, the greater the enhancement.

In addition to NH_3 , the hydrogen donor, DHA, was added to study the effect of a hydrogen enriched environment. The results changed dramatically, toluene becomes the major product instead of benzene, indicating that the reduction sequence predominates over the oxidation/decarboxylation processes, which produces benzene. Aluminum was also added to try to generate a similar hydrogen environment. Unfortunately, the aluminum looked unchanged after reaction and the expected result was not observed at the conditions of 450°C , 6M NH_3 and 1 hour reaction, although it was found to dissolve alone in the SW. The temperature effect was studied briefly at different reaction conditions. Higher temperatures tend to give higher rates as expected but the product distribution is unchanged.

It appears, according to the data in Tables 7 and 8, that in SW, benzaldehyde could either be oxidized to form benzoic acid and subsequently decarboxylated to give benzene and products formed from phenyl radicals or be reduced to form benzyl alcohol and hence toluene and products formed from benzyl radicals, similar to a Cannizzaro disproportion reaction. Water is considered to provide a source of oxygen and hydrogen for the oxidation and reduction processes. Without the presence of DHA, the oxidation/decarboxylation sequence is predominant. However, DHA provides hydrogen which results in the reduction/formation of benzyl radicals sequence predominating. NH_3 seems to show a similar effect as does DHA but to a lesser extent. The reaction pathway for this reaction is not understood as yet.

Benzoic Acid-SW Reaction

Benzoic acid reactions generate clear solutions and simple products even for the pyrolysis. The data in Table 9 show that benzene is the only major product and the other products obtained are less than 1% of the total in the SW reaction. Therefore,

Table 9
Reaction of Benzoic Acid With SW

	Run			
	BAC-1 ^a	BAC-2	BAC-3	BAC-4
Temperature (° C)	400	400	400	400
Time (hour)	3	4	4	5
H ₂ O pressure (psi)	0	3870	3870	3870
Added NH ₃ (M)	0	0	2	2
% Reaction	95.4	57.8	100	100
Volatile products (% yield)				
Benzene	79.9	78.9	91.8	86.9
Phenol	1.4	0.3	0.1	0.1
Biphenyl	3.1	0.4	0.2	0.2
High M.W. products (total)	0.3	0	0	0

^a This is a pyrolysis.

decarboxylation appears to be almost the only reaction pathway of benzoic acid. In addition, SW tends to decrease the reaction rate compared to pyrolysis but NH_3 catalyzes the SW reaction significantly. The latter observation explains why the benzaldehyde-SW- NH_3 , benzylamine-SW and BBA-SW reactions, which all include NH_3 in the system, do not show benzoic acid as an intermediate for the formation of benzene while a portion of benzoic acid is observed in the benzaldehyde-SW reaction.

Benzyl Alcohol-SW Reaction

Benzyl alcohol was also found to act as an important intermediate in the benzylamine-SW reaction; thus, it was of interest to discover its reactivity at SW conditions. Unfortunately, the results of benzyl alcohol-SW reaction were not reproducible; therefore, the information revealed was limited. The earlier reactions of benzyl alcohol in SW gave yellow clear solutions with low reaction rates (28% reaction at 400^o C and 3 hours) and a different product distribution from that found later. The later studies gave similar results as did the pyrolysis; both gave low yields of volatile products, significant amounts of black tar/char and high reaction rates (100% reaction at 400^o C and 3 hours). Numerous modifications were tried but the reason is still not understood. Table 10 lists the most current and representative results. For the pyrolysis and SW reactions, benzyl radical products, toluene and bibenzyl, are the major substances observed. However, the presence of H_2O promotes the oxidation of benzyl alcohol and the formation of benzaldehyde.

Again, the effect of NH_3 was studied for the same reason as that for benzaldehyde. In spite of the inconsistency of benzyl alcohol-SW reactions, the of NH_3 , both 2M and 6M, gave consistent results, in which the tar/char formations are suppressed and the resulting solutions were clear. The data in Table 10 show that

Table 10
Reaction of Benzyl Alcohol With SW

	Run ^a			
	BAL-1 ^b	BAL-2	BAL-3	BAL-4
Temperature (° C)	400	400	400	400
Time (hour)	3	3	3	3
H ₂ O pressure (psi)	0	3870	3870	3870
Added NH ₃ (M)	0	0	2	6
% Reaction	100	100	98.2	98.7
Volatile products (% yield)				
Benzene	2.7	2.6	19.4	21.6
Toluene	22.1	19.7	41.7	43.8
Ethylbenzene	0.3	0.1	0	0
Benzaldehyde	0.7	6.0	9.5	4.6
Benzamide	0	0	0	0.3
Biphenyl	0.1	0.1	2.3	2.8
M.W. 168 isomers ^c	2.4	2.6	4.4	5.3
M.W. 182 isomers ^d	7.8	11.2	2.4	1.8
Mixture (total)	1.6 ^e	1.7 ^e	2.1 ^f	2.2 ^f
Benzylidenebenzylamine	0	0	1.2	2.5
High M.W. products (total) ^g	8.4	12.2	1.4	3.4

^a More than one trial was made for each particular run. These are the representative results. Run BAL-1 and BAL-2 gave black tarry solutions, BAL-3 and BAL-4 produced clear, yellow solutions.

^b This is a pyrolysis.

^c This may be diphenylmethane or its isomers.

^d This may be bibenzyl or its isomers.

^e Includes yields of substances with molecular weights of 178 and 196 (possibly phenanthrene and phenylbenzyl ketone).

^f Includes yields of substances with molecular weights of 166, 182 and 180 (fluorene, benzophenone and possibly stilbene).

^g Consists of substances with molecular weight above 200.

NH₃ helps to promote the formation of volatile products while keeping the high reactivities.

Although not many conclusions can be drawn from the studies so far, two points about the benzyl alcohol reactions can be made: (1) toluene appears to be the major volatile product in all the experiments, meaning that the rupture of C-O bond is predominant; and (2) H₂O helps to remove hydrogen from benzyl alcohol, giving a higher benzaldehyde yield. This dehydrogenation is also found in the benzylamine-SW reaction.

Bibenzyl-SW Reaction

Bibenzyl was found to be about as reactive in SW as it was in pyrolysis, indicating that the -CH₂-CH₂- group between aromatic rings is labile and unaffected by SW. The data, including pyrolysis and reaction with additives, are summarized in Tables 11 and 12. The most abundant product is toluene with yields of 37-46% at 400° C in the absence of DHA and other additives, indicating that the formation of benzyl radicals is the most favorable pathway. Stilbene and small amounts of dihydrophenanthrene (DHP), which could not be separated quantitatively by our GC, are the next major products for which the yield decreases at higher extents of reaction. The multiringed products are also formed in a significant quantities; their molecular weights range from 178 (phenanthrene) and 192 (methyl phenanthrene) to 280 in most experiments and 306 (quaterphenyl) in the 410° C pyrolysis.

The data in Table 11 show that SW appears to have very little effect on bibenzyl reactivity. ZnCl₂, which acts as a Bronsted acid catalyst (19), and NH₃, which is found to catalyze benzaldehyde-SW and benzoic acid-SW reactions, have no apparent effect on the bibenzyl reactivity. However, the addition of the hydrogen transfer agent, DHA, significantly reduces the reactivity, with or without SW,

Table 11
Reaction of Bibenzyl With SW

	Run					
	BB-1 ^a	BB-2 ^a	BB-0 ^b	BB-4	BB-5	BB-6
Temperature (° C)	400	410	400	400	400	450
Time (hour)	3	6	3	4	6	3
H ₂ O pressure (psi)	0	0	3870	3870	3870	5200
% Reaction	28.5	87.9	30	30.8	35.3	93.2
Volatile products (% yield)						
Benzene	1.5	1.0	-	2.4	1.0	2.8
Toluene	44.3	46.2	45	40.8	37.3	49.4
Ethylbenzene	0.8	1.8	-	0.6	0.8	1.3
Xylene isomers	0.3	0.1	-	0	0.4	0.1
Diphenylmethane	7.1	10.5	-	3.0	4.5	6.6
M.W. 182 isomers ^c	5.3	1.8	-	2.3	2.5	1.5
Mixture	0	0	30	0	0	0
Stilbene & DHP ^d	40.5	10.6	-	37.6	41.8	16.1
Phenanthrene	2.9	3.9	-	6.2	4.1	8.1
High M.W. products (total) ^e	15.1	12.4	-	6.4	7.0	4.6

^a These are pyrolyses.

^b This is adopted from literature (2) for comparison. The product "mixture" is not identified.

^c It may be 1, 1-dephenylethane and/or benzyl toluene isomers.

^d Contains mostly stilbene and a small amount of dihydrophenanthrene.

^e Contains substances with molecular weights above 190.

Table 12

Reaction of Bibenzyl With SW and Additives

	Run					
	BB-3 ^a	BB-7 ^a	BB-8 ^a	BB-9 ^a	BB-10	BB-11
Temperature (° C)	400	400	400	400	400	400
Time (hour)	6	4	6	6	6	6
H ₂ O pressure (psi)	0	3870	3870	3870	3870	3870
Added DHA (g)	2.0	2.0	2.0	1.0	0	0
Added ZnCl ₂ (g)	0	0	0	0	0.41	0
Added NH ₃ (M)	0	0	0	0	0	6
% Reaction	19.5	14.1	16.0	19.3	31.3	28.5
Volatile products (% yield)						
Benzene	0	3.1	0	0	1.6	3.2
Toluene	91.4	67.9	75.0	60.6	42.4	40.4
Ethylbenzene	-	-	-	-	0.8	0.7
Xylene isomers	-	-	-	-	0	0.2
Diphenylmethane	-	-	-	-	3.0	2.5
M.W. 182 isomers ^b	-	-	-	-	2.6	3.0
Stilbene & DHP ^c	-	-	-	-	34.1	35.4
Phenanthrene	-	-	-	-	5.1	6.1
High M.W. products (total) ^d	-	-	-	-	6.7	9.2

^a Only % reacted and yields of toluene and benzene are calculated because DHA also reacts and decomposes. Run BB-3 is a pyrolysis.

^b It may be 1, 1-dephenylethane and/or benzyl toluene isomers.

^c Consists of mostly stilbene and a small amount of dihydrophenanthrene.

^d Consists of compounds with molecular weights above 200.

and promotes the formation of toluene. This observation indicates that the formation of benzyl radical and hence toluene are by a radical chain mechanism and that this chain is shortened by the rapid combination of benzyl radicals and hydrogen.

A very important point to note is the difference in the products formed from bibenzyl-SW and benzylamine-SW reactions. Both reactions do form benzyl radicals in the initial steps as indicated by the formation of toluene. However, there is no evidence to indicate that the oxidation sequence occurs with bibenzyl because of the absence of benzaldehyde and benzyl alcohol and the ignorable quantity of benzene. Therefore, it can be concluded that the C-N bond is essential for the oxidation/decarboxylation sequence to occur which removes the benzylic carbon, possibly through the formation of an unsaturated C-N bond.

Kinetic Study of the Benzaldehyde-SW Reaction

For the kinetic calculations of the benzaldehyde-SW reaction, the assumption of a second-order reaction with inhibition by the product is made. This assumption is based on the observations that for all of the three temperatures (380, 400 and 425° C), the rate constants obtained using the first-order assumption tend to decrease as reaction time increases, and the second-order rate constants stabilize with only a minor decreasing trend as reaction time increases. Because the calculated second-order rate constants were consistent in the initial reaction periods but decreased at longer reaction times, a second-order reaction with inhibition by the formation of product is suggested. Subsequently the data proved this assumption to be reasonable. Therefore,

$$-dC / dt = kC^2 / [1 + b (C_0 - C)] \quad (5)$$

where C_0 is the initial concentration of benzaldehyde in molarity, C is the concentration at time t , t is the reaction time in hours, k is the rate constant and b

represents an inhibition constant. Equation (5) shows that the reaction rate will drop faster than regular second-order reaction because the term of $Co - C$ in the denominator. After rearrangement of equation (5) and integration, the following equation is obtained:

$$(1 + b Co) / C + b \ln C = kt + \text{constant} \quad (6)$$

At $t=0$, $C= Co$. Thus,

$$\text{constant} = (1 + b Co) / Co + b \ln Co \quad (7)$$

Substitution of equation (7) into (6) and rearrangement gives:

$$(1 + b Co) / C - (1 + b Co) / Co + b \ln (C / Co) = kt \quad (8)$$

By plugging in the appropriate values of C and Co and the assumed value of b , a plot of the value from the left side of equation (8) versus the reaction time can be made. The least squares linear regression was used to calculate the slopes and intercepts for different values of b . The best linear relationship, having the highest critical coefficient (R^2) and about a zero intercept, determines the best value of b . It is calculated that $b = 1.0$ fits the experimental data best with corresponding R^2 of 0.956, 0.843 and 0.929 for 380° C, 400° C and 425° C respectively. Tables 13, 14 and 15 show all the kinetic data with an estimated value of $b = 1.0$. The rate constants from the slopes using $b = 1.0$ are 0.263, 0.646 and 2.204 ($M^{-1}hr^{-1}$) for 380, 400 and 425° C respectively.

If the Arrhenius law applies to the benzaldehyde-SW reaction, then:

$$k = A e^{-(Ea / RT)} \quad (9)$$

Taking logarithms on both sides of equation (9) gives:

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

where k is the rate constant, A is the frequency factor, Ea is the activation energy, R is the ideal gas constant and T is the reaction temperature. A plot of $\ln k$ versus $1/T$ gives a straight line with a critical coefficient (R^2) of 0.999 by a linear regression.

Table 13

Kinetic Data of the Benzaldehyde-SW Reaction at 380° C

Time(hr)	% Reaction	Co(M)	C(M)
2	18	0.418	0.342
3	23	0.418	0.320
4	29	0.418	0.298
6	28	0.418	0.299
6	33	0.418	0.279
8	40	0.418	0.253
10	49	0.418	0.215
12	54	0.418	0.192
16	56	0.418	0.185
16	63	0.418	0.156
2	29	0.836	0.596
2	21	0.836	0.659
3	37	0.836	0.526
3	30	0.836	0.588
4	36	0.836	0.539
5	40	0.836	0.498
7	50	0.836	0.421
10	60	0.836	0.338
14	69	0.836	0.256
$k^a(\text{M}^{-1}\text{hr}^{-1})$	0.263		

^a The k represents the rate constant of a 2nd-order reaction inhibited by the product and is calculated based on the equation $(1 + b \text{ Co}) / \text{C} - (1 + b \text{ Co}) / \text{Co} + b \ln (\text{C} / \text{Co}) = kt$ by assuming $b = 1.0$.

Table 14

Kinetic Data of the Benzaldehyde-SW Reaction at 400° C

Time(hr)	% Reaction	Co(M)	C(M)
2.2	27	0.213	0.155
3	37	0.213	0.145
3	33	0.213	0.126
3	40	0.213	0.135
4	39	0.213	0.131
4	42	0.213	0.123
5	47	0.213	0.114
6	55	0.213	0.097
7	48	0.213	0.112
7	55	0.213	0.096
8	52	0.213	0.103
8	55	0.213	0.096
1	25	0.418	0.313
1	24	0.418	0.319
2	33	0.418	0.281
2	33	0.418	0.280
3	43	0.418	0.247
3	41	0.418	0.239
4	50	0.418	0.208
4	47	0.418	0.222
4	51	0.418	0.203
5	54	0.418	0.191
5	55	0.418	0.188
6	56	0.418	0.186
6	58	0.418	0.176
7	59	0.418	0.171
7	61	0.418	0.174
7	58	0.418	0.161
8	62	0.418	0.160
8	64	0.418	0.149
1	29	0.836	0.591
2	46	0.836	0.449
2	40	0.836	0.503

Table 14--Continued

Time(hr)	% Reaction	Co(M)	C(M)
3	59	0.836	0.343
3	48	0.836	0.276
3	67	0.836	0.431
4	67	0.836	0.278
4	59	0.836	0.343
5	67	0.836	0.277
6	70	0.836	0.247
<hr/>			
$k^a(\text{M}^{-1}\text{hr}^{-1})$	0.646		

^a The k represents the rate constant of a 2nd-order reaction inhibited by the product and is calculated based on the equation $(1 + b \text{ Co}) / C - (1 + b \text{ Co}) / \text{Co} + b \ln (C / \text{Co}) = kt$ by assuming $b = 1.0$.

Table 15

Kinetic Data of the Benzaldehyde-SW Reaction at 425° C

Time(hr)	% Reaction	Co(M)	C(M)
2	37	0.108	0.068
4	47	0.108	0.057
6	62	0.108	0.041
8	65	0.108	0.038
2	48	0.219	0.114
3	53	0.219	0.103
4	63	0.219	0.081
5	65	0.219	0.076
6	71	0.219	0.064
1	37	0.418	0.264
2	58	0.418	0.174
2	70	0.418	0.127
3	63	0.418	0.154
3	72	0.418	0.117
4	72	0.418	0.116
<hr/>			
$k^a(\text{M}^{-1}\text{hr}^{-1})$	2.204		

^a The k represents the rate constant of a 2nd-order reaction inhibited by the product and is calculated based on the equation $(1 + b \text{ Co}) / \text{C} - (1 + b \text{ Co}) / \text{Co} + b \ln (\text{C} / \text{Co}) = kt$ by assuming $b = 1.0$.

The slope and intercept are determined to be -21196 ± 559 and 31.11 ± 0.83 .

Therefore, the activation energy and frequency factor of the benzaldehyde-SW reaction are calculated to be $-\text{slope} \times R$ and $\exp(\text{intercept})$ respectively:

$$E_a = -(-21196 \times 8.3144) = 176230 \pm 4650 \text{ (J / mole)} = 176.2 \pm 4.6 \text{ (kJ / mole)}$$

$$A = e^{31.11} = (3.2 \pm 2.7) \times 10^{13} \text{ (M}^{-1}\text{hr}^{-1}\text{)}$$

$$= (9.0 \pm 7.5) \times 10^9 \text{ (M}^{-1}\text{sec}^{-1}\text{)}$$

CHAPTER IV

CONCLUSIONS

Two general types of products were present in all the SW reactions studied. One includes benzene, biphenyl, diphenylmethane, etc., which are formed through the intermediate of phenyl radicals, while the other type of product has benzyl radicals as an intermediate, which include toluene, bibenzyl, etc. Several conclusions about the reactivities of the six compounds studied and the mechanistic considerations leading to the formation of phenyl and benzyl radicals are summarized as follows:

1. SW showed greatest influence on benzylamine. In addition to the direct rupture of the C-N bond and hence the generation of toluene, SW provided a pathway to produce benzene through the intermediates, benzaldehyde, benzyl alcohol and benzoic acid (Figure 4). Besides, SW helps to reduce the formation of the multiringed products found in the pyrolysis, giving higher yields of lower molecular weight products.

2. The oxidation sequence to produce benzene requires the presence of an unsaturated C-N bond as evidenced by the BBA-SW and benzonitrile-SW reactions (14). Thus, in the benzylamine-SW reaction, hydrogen must be removed to form a multiple C-N bond and undergo hydrolysis/oxidation/decarboxylation process as shown in Figure 4.

3. The fact that NH_3 promotes the reactivities of the benzaldehyde-SW and benzoic acid-SW reactions demonstrates the catalytic effect of NH_3 on the oxidation/decarboxylation process which leads to the formation of benzene.

4. For BBA-SW reaction, that a comparable yield of benzene and toluene is

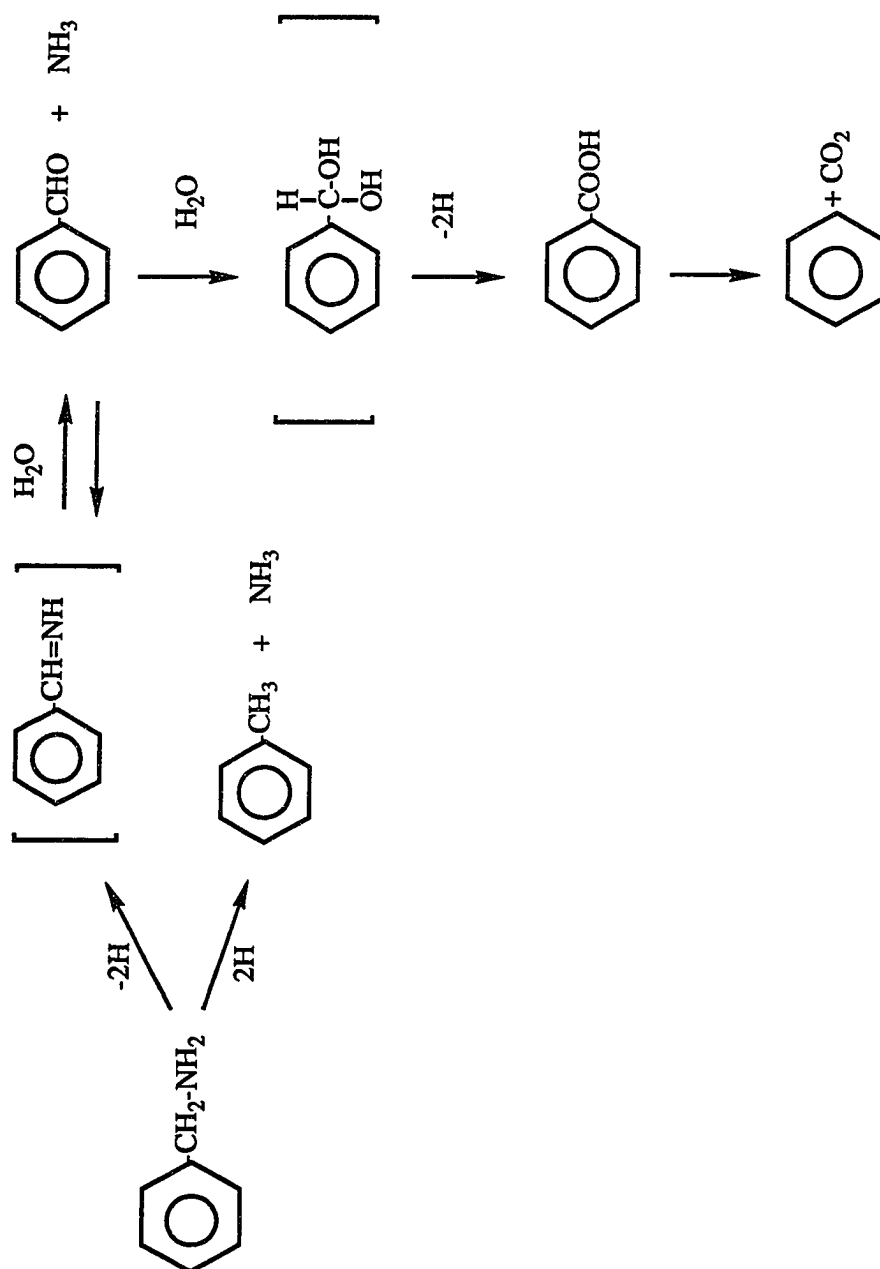


Figure 4. Benzylamine-SW Reaction Scheme.

observed and that the addition of DHA promotes the formation of toluene at the expense of benzene suggest a decomposition pathway where the rupture of the single C-N bond leads to the formation of toluene and the C=N segment is responsible for the formation of benzene. The suggested reaction scheme is drawn in Figure 5.

5. Benzaldehyde undergoes the oxidation/decarboxylation sequence in SW, primarily producing benzoic acid and benzene. Water may provide a source of oxygen for the oxidation while the hydrogen from the water may reduce benzaldehyde to form benzyl alcohol similar to a Cannizzaro reaction. The second-order kinetics are consistent with a Cannizzaro reaction if a rapid equilibrium is established to form a benzaldehyde/water complex which then reacts with a second benzaldehyde (Figure 6). That the addition of DHA promotes toluene formation at the expense of benzene shows the predominance of the reduction sequence over the oxidation process.

6. Benzyl alcohol forms toluene as the most abundant product at all conditions, possibly through the breaking of the C-O bond. NH_3 tends to catalyze the oxidation reaction preferentially and produce higher yields of benzaldehyde and benzene.

7. Bibenzyl is not influenced by SW and appears to form the benzyl radical as an intermediate at all reaction conditions. DHA tends to terminate the radical chain, as evidenced by the significantly increased toluene yield and decrease in extents of reaction.

8. The small yield of benzene in the bibenzyl-SW reaction indicates that the benzyl radical is inert to oxidation from water, and that the C-N bond is required for hydrolytic oxidation to occur.

9. The studies by Klein et al. indicated that the dibenzyl ether-SW reaction produced benzyl alcohol and benzaldehyde which did not proceed to benzene but oligomers instead (20), and that the benzylphenylamine-SW reaction produced benzyl

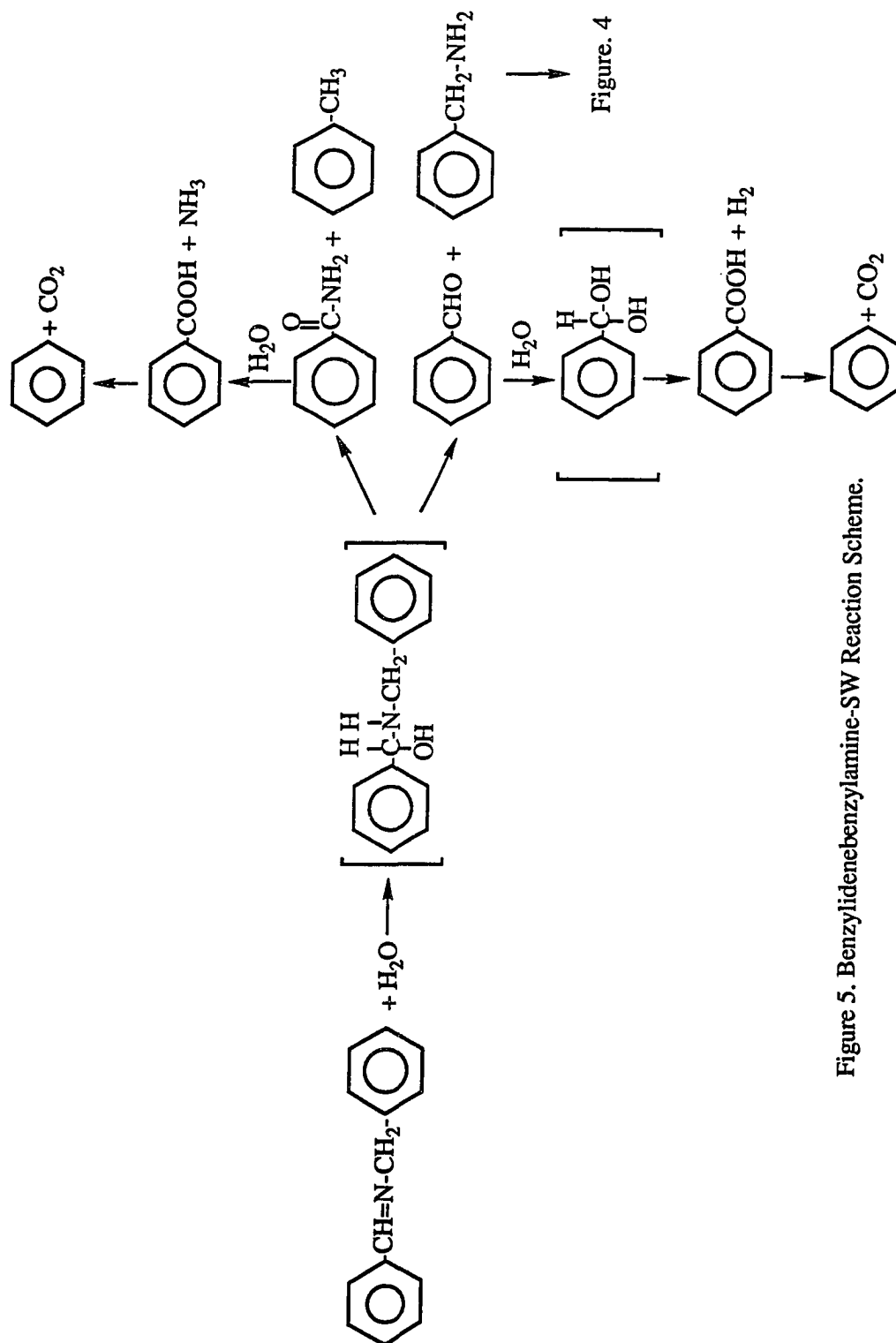


Figure 5. Benzylidenedibenzylamine-SW Reaction Scheme.

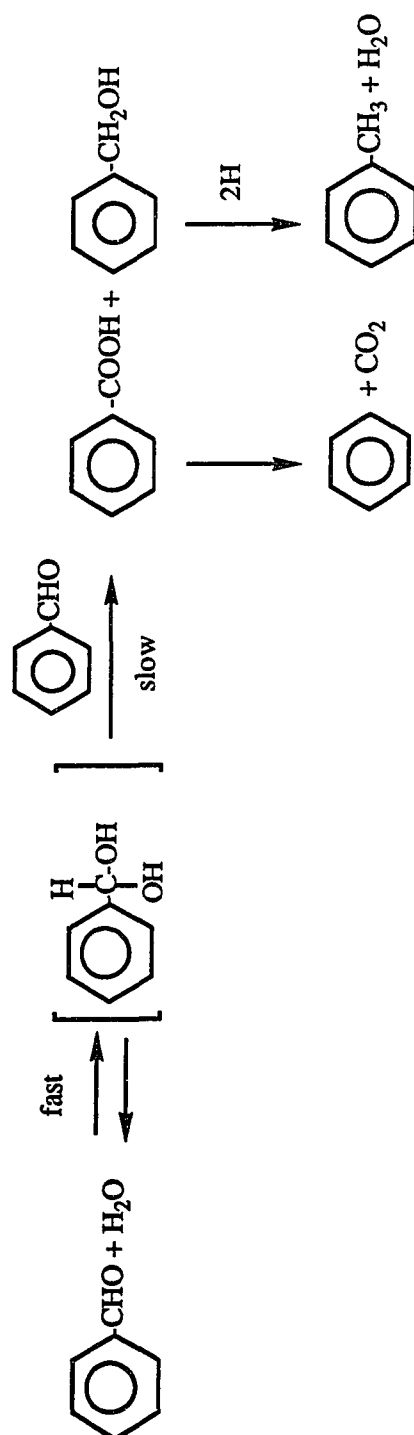


Figure 6. Benzaldehyde-SW Reaction Scheme.

alcohol but no benzene was reported (21). Although the results above are not consistent with this work, possibly due to their shorter reaction times, the conclusion can be made that SW is an important reactant under liquefaction conditions for some functional groups.

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Appendix A
Average Retention Times and Calibration Factors

Table 16

Average Retention Times and Calibration Factors

Compound	M.W.(g/mole)	R.T. ^a (min.)	C.F. ^b (AA/ μ L/mmol)
Benzene	78.11	0.43	2.586
Toluene	92.14	1.07	3.208
Ethylbenzene	106.17	2.11	3.437
Xylene ^c	106.17	2.50	3.437
Benzaldehyde ^d	106.13	3.15-3.63	3.215
Aniline	93.13	3.52	3.277
Benzonitrile	103.12	3.57	3.213
Propylbenzene ^c	120.19	3.75	3.437
Phenol	94.11	3.86	3.106
Benzylamine	107.15	4.29	3.388
Benzyl alcohol ^d	108.24	4.40-5.12	3.593
Indan	118.18	4.49	3.121
Cresol	108.14	4.84	3.549
Toluidine	107.15	4.86	3.844
Dihydroquinoline ^c	131.18	5.64	3.790
Xylidine	121.18	5.79	3.658
Xylenol	122.17	5.87	3.836
Naphthalene	128.17	6.22	3.968
Quinoline	129.15	6.90	3.673
Benzoic acid	122.12	6.97	3.964
Indole	117.15	7.22	4.107
Quinaldine	143.19	7.42	4.259
Tetrahydroquinoline	133.19	7.62	3.908
Benzamide	121.14	7.65	3.210
Biphenyl	154.24	7.98	4.294
Diphenylmethane	168.24	8.43	4.343
Dimethylquinoline	157.21	8.53	4.297
Diphenylethane ^c	182.26	8.92	4.958
Bibenzyl	182.27	9.20	4.958
Fluorene	166.22	9.71	4.727
Benzophenone	182.21	9.84	4.912
Dihydrophenanthrene	180.25	10.41	4.230

Table 16--Continued

Compound	M.W.(g/mole)	R.T. ^a (min.)	C.F. ^b (AA/ μ L/mmol)
Dihydroanthracene	180.25	10.46	4.607
Fluorenone ^c	180.21	10.57	4.230
Stilbene	180.25	10.57	4.588
Benzylphenylketone ^c	196.25	10.63	5.000
Benzylidenebenzylamine ^d	195.27	10.72-10.86	5.360
Phenanthrene	178.24	11.06	4.244
Anthracene ^c	178.24	11.27	4.244
Phenylnaphthalene	204.27	12.21	4.706
Methylcarbazole ^c	181.24	13.43	4.958
Phenylanthracene	254.33	14.63	4.346
Biquinolyl ^c	256.31	15.70	5.533
Triphenylimidazole	296.37	17.38	5.533
Tetraphenylpyrrole ^c	371.48	18.38	5.533

^a Retention Times were measured relative to the air peak. They were obtained under the standard GC operating conditions described in Chapter II.

^b Most of the calibration factors were obtained from the average of 25 mL standard solutions of different concentrations.

^c These compounds used estimated calibration factors for yield calculations; their retention times reported came from the reaction product solution directly.

^d Their retention times depended on the peak areas.

Appendix B
Program of Product Distribution Calculation

Program R_Data (input, out_data);

```

Var mon      : array [1..3] of char;
  solvent    : array [1..3] of char;
  o_react     : array [1..15] of char;
  name       : array [1..30] of char;
  title      : array [1..50] of char;
  uaa, Ahrt, hrt, rt : array [1..50] of real;
  uy, vaa, F1, F2, Fy : array [1..3] of real;
  tot, k, n, temp, hour, yr, j, dy, id: integer;
  o_Mmole, v_sol, m, cf, Trt, Trrt, Taa, Tm1, Tm2, Ty, Art, Arrt, Aaa, Am1,
  Am2, Ay: real;
  ucf, TTuaa, Tum1, Tum2, Tuy, Auaa, Aum1, Aum2, Auy, Tf1, Tf2, Af1, Af2,
  um : real;
  t1, tr, a, aa, t, rrt, i, m1, m2, d, y, rm1, rm2, Tuaa, um1, um2, ry, ud
      : array [1..3] of real;
  out_data : text;
  ans      : char;

```

begin

```

  writeln('Please input the Title for this reaction ');
  readln(title);
  writeln('Please input the original reactant ');
  readln(o_react);
  writeln('Please input the Mmole of original reactant ');
  readln(o_Mmole);
  writeln('Please input the solvent ');
  readln(solvent);
  writeln('Please input the value of solvent left ');
  readln(v_sol);
  writeln('Please input the date :');
  writeln('Year ');
  readln(yr);
  writeln('Month ');
  readln(mon);
  writeln('Day ');
  readln(dy);
  writeln('Please input the temperature ');
  readln(temp);
  writeln('How many hours does this reaction process ');
  readln(hour);
  assign(out_data,'b:\d.dat');
  rewrite(out_data);
  writeln(out_data);
  writeln(out_data);
  writeln(out_data,title);
  writeln(out_data);
  writeln(out_data,o_react,'    =' ,o_Mmole:3:3,'Mmole');
  writeln(out_data,solvent,' left = ',v_sol:2:1,'ml. ');
  writeln(out_data,'Date      : ',mon,' ',dy:2,yr:5);
  writeln(out_data,'Temperature : ',temp:3,'°C');
  writeln(out_data,'Time       : ',hour:3,' hour(s)');

```

```

writeln(out_data);
writeln(out_data,'R.T. R.R.T. AA/ $\mu$ l C.F. Mmoles yields(%)');
writeln(out_data,'----- ----- ----- -----');
writeln(out_data);
writeln('Please input the injection volume 1 ?');
readln(i[1]);
writeln('Please input the injection volume 2 ?');
readln(i[2]);
writeln('Please input the injection volume 3 ?');
readln(i[3]);
writeln('How many products ?');
readln(tot);
writeln('How many identified products ?');
readln(id);
writeln('Please type in reactant left name :');
readln(name);
writeln(out_data,name);
writeln('Please input the C.F. for the reactant left ?');
readln(cf);
writeln('Multiply by ?');
readln(m);
Trt:=0; Trtt:=0; Taa:=0; Tm1:=0; Tm2:=0; Ty:=0;
writeln('If Mmole of reactant left is 0 or not ? (type y or n)');
readln(ans);
if (ans='N') or (ans='n') then begin
  for k:=1 to 3 do begin
    writeln('Please input the ',k:2,' time for the reactant left ?');
    readln(t1[k]);
    writeln('Please input the ',k:2,' area for the reactant left ?');
    readln(a[k]);
    rrt[k]:=round(t1[k]/t1[k]*100);
    rrt[k]:=rrt[k]/100;
    aa[k]:=round(a[k]/i[k]*1000);
    aa[k]:=aa[k]/1000;
    rm1[k]:=round(aa[k]/cf*1000);
    rm1[k]:=rm1[k]/1000;
    if m=2 then begin
      rm2[k]:=rm1[k]*2;
      rm2[k]:=round(rm2[k]*1000);
      rm2[k]:=rm2[k]/1000;
    end;
    if m=0.5 then begin
      rm2[k]:=rm1[k]*0.5;
      rm2[k]:=round(rm2[k]*1000);
      rm2[k]:=rm2[k]/1000;
    end;
    ry[k]:=rm2[k]/o_Mmole*100;
    ry[k]:=round(ry[k]*100);
    ry[k]:=ry[k]/100;
    if rm2[k]=rm1[k] then begin
      writeln(out_data,t[k]:3:2,' ',rrt[k]:3:2,' ',aa[k]:3:3,' ',cf:3:3,
        ' ',rm1[k]:3:3,' ',ry[k]:3:2,'% (left)');
    end;
  end;
end;

```



```

end;
if m=2 then begin
    writeln(out_data,t[k]:3:2,' ',rrt[k]:3:2,' ',aa[k]:3:3,' ',cf:3:3,
    ' ',rm1[k]:3:3,'*2= ',rm2[k]:3:3,' ',ry[k]:3:2,'%');
end;
if m=0.5 then begin
    writeln(out_data,t[k]:3:2,' ',rrt[k]:3:2,' ',aa[k]:3:3,' ',cf:3:3,
    ' ',rm1[k]:3:3,'*0.5= ',rm2[k]:3:3,' ',ry[k]:3:2,'%');
end;
Trt:=Trt + t[k];
Trrt:=Trrt + rrt[k];
Taa:=Taa + aa[k];
Tm1:=Tm1 + rm1[k];
Tm2:=Tm2 + rm2[k];
Ty:=Ty + ry[k];
end;
Art:=Trt/3; Art:=round(Art*100); Art:=Art/100;
Arrt:=Trrt/3; Arrt:=round(Arrt*100); Arrt:=Arrt/100;
Aaa:=Taa/3; Aaa:=round(Aaa*1000); Aaa:=Aaa/1000;
Am1:=Tm1/3; Am1:=round(Am1*1000); Am1:=Am1/1000;
Am2:=Tm2/3; Am2:=round(Am2*1000); Am2:=Am2/1000;
Ay:=Ty/3; Ay:=round(Ay*100); Ay:=Ay/100;
if Am1=Am2 then
    writeln(out_data,Art::3:2,' ',Arrt:3:2,' ',Aaa:3:3,' ',
    Am1:3:3,' ',Ay:3:2,'% (Ave)')
else
    writeln(out_data,Art::3:2,' ',Arrt:3:2,' ',Aaa:3:3,' ',
    Am1:3:3,' ',Am2:3:3,' ',Ay:3:2,'% (Ave)');
for k:=1 to 3 do
    Fy[k]:=0;
for n:=2 to id do
    begin
        writeln('Please type in the ',n:3,' product name :');
        readln(name);
        writeln('Please input the C.F. for ',n:3,' product ?');
        readln(cf);
        writeln('Multiply by ?');
        readln(m);
        writeln(out_data);
        writeln(out_data,name);
        Trt:=0; Trrt:=0; Taa:=0; Tm1:=0; Tm2:=0; Ty:=0;
        for k:=1 to 3 do begin
            writeln('Please input the ',k:2,' time for the ',n:3,' product ?');
            readln(t[k]);
            writeln('Please input the ',k:2,' area for the ',n:3,' product ?');
            readln(a[k]);
            rrt[k]:=t[k]/t1[k]; rrt[k]:=round(rrt[k]*100); rrt[k]:=rrt[k]/100;
            aa[k]:=a[k]/i[k]; aa[k]:=round(aa[k]*1000); aa[k]:=aa[k]/1000;
            m1[k]:=aa[k]/cf[k];m1[k]:=round(m1[k]*1000);m1[k]:=m1[k]/1000;
            if m=1 then m2[k]:=m1[k];
            if m=2 then begin
                m2[k]:=m1[k]*2; m2[k]:=round(m2[k]*1000); m2[k]:=m2[k]/1000;
            end;
        end;
    end;
end;

```

```

end;
if m=0.5 then begin
  m2[k]:=m1[k]*0.5; m2[k]:=round(m2[k]*1000);
  m2[k]:=m2[k]/1000;
end;
d[k]:=o_Mmole - rm2[k];
y[k]:=m2[k]/d[k]*100; y[k]:=round(y[k]*100); y[k]:=y[k]/100;
if m2[k]=m1[k] then
  begin
    writeln(out_data,t[k]:3:2,' ',rrt[k]:3:2,' ',aa[k]:3:3,' ',
      cf:3:3,' ',m1[k]:3:3,' ',y[k]:3:2,'%');
  end;
if m=2 then
  begin
    writeln(out_data,t[k]:3:2,' ',rrt[k]:3:2,' ',aa[k]:3:3,' ',
      cf:3:3,' ',m1[k]:3:3,'*2 ',m2[k]:3:3,' ',y[k]:3:2,'%');
  end;
if m=0.5 then
  begin
    writeln(out_data,t[k]:3:2,' ',rrt[k]:3:2,' ',aa[k]:3:3,' ',
      cf:3:3,' ',m1[k]:3:3,'*0.5=',m2[k]:3:3,' ',y[k]:3:2,'%');
  end;
Trt:=Trt + t[k];
Trrt:=Trrt + rrt[k];
Taa:=Taa + aa[k];
Tm1:=Tm1 + m1[k];
Tm2:=Tm2 + m2[k];
Ty:=Ty + y[k];
Fy[k]:=Fy[k] + y[k];
end;
Art:=Trt/3; Art:=round(Art*100); Art:=Art/100;
Arrt:=Trrt/3; Arrt:=round(Arrt*100); Arrt:=Arrt/100;
Aaa:=Taa/3; Aaa:=round(Aaa*1000); Aaa:=Aaa/1000;
Am1:=Tm1/3; Am1:=round(Am1*1000); Am1:=Am1/1000;
Am2:=Tm2/3; Am2:=round(Am2*1000); Am2:=Am2/1000;
Ay:=Ty/3; Ay:=round(Ay*100); Ay:=Ay/100;
if Am1=Am2 then
  writeln(out_data,Art:3:2,' ',Arrt:3:2,' ',Aaa:3:3,' ',
    Am1:3:3,' ',Ay:3:2,'% (Ave)')
else
  writeln(out_data,Art:3:2,' ',Arrt:3:2,' ',Aaa:3:3,' ',
    Am1:3:3,' ',Am2:3:3,' ',Ay:3:2,'% (Ave)');
  writeln(out_data);
end;
for j:=1 to (tot-id) do hrt[j]:=0;
writeln(out_data);
writeln(out_data);
writeln(out_data,'High M.W. Peaks');
for k:=1 to 3 do begin
  writeln(out_data,'RT = ');
  for j:=1 to (tot-id) do begin
    writeln('Please input the ',j:1,' R.T. of High M.W. compounds for ',

```

```

k:1, ' set of data :');
readln(rt[j]);
writeln(out_data,rt[j]:2:2,' ');
hrt[j]:=hrt[j] + rt[j];
end;
writeln(out_data);
end;
writeln(out_data,'Ave ');
for j:=1 to (tot-id) do begin
  Ahrt[j]:=hrt[j]/3; Ahrt[j]:=round(Ahrt[j]*100); Ahrt[j]:=Ahrt[j]/100;
  write(out_data,Ahrt[j]:2:2,' ');
end;
writeln(out_data);
writeln(out_data);
writeln(out_data,'AA/ $\mu$ L    C.F.    Mmoles    yield(%));
writeln(out_data,'-----    -----    -----    -----');
writeln('Please input the C.F. for unidentified products ');
readln(ucf);
writeln('Multiply by ');
readln(um);
Tum1:=0; Tum2:=0; Tuy:=0; TTuaa:=0;
for k:=1 to 3 do Tuaa[k]:=0;
for k:=1 to 3 do begin
  writeln(k:2,' area for product # ',j:2,' ');
  readln(uaa[j]);
  Tuaa[k]:=Tuaa[k] + uaa[j];
end;
vaa[k]:=Tuaa[k]/i[k]; vaa[k]:=round(vaa[k]*1000); vaa[k]:=vaa[k]/1000;
um1[k]:=vaa[k]/ucf; um1[k]:=round(um1[k]*1000); um1[k]:=um1[k]/1000;
if um=1 then um2[k]:=um1[k];
if um=0.5 then begin
  um2[k]:=um1[k]*0.5; um2[k]:=round(um2[k]*1000);
  um2[k]:=um2[k]/1000;
end;
if um=2 then begin
  um2[k]:=um1[k]*2; um2[k]:=round(um2[k]*1000);
  um2[k]:=um2[k]/1000;
end;
ud[k]:=o_Mmole - rm2[k];
uy[k]:=um2[k]/ud[k]*100; uy[k]:=round(uy[k]*100); uy[k]:=uy[k]/100;
Fy[k]:=Fy[k] + uy[k];
if um=1 then
  writeln(out_data,vaa[k]:2:3,'    ',ucf:2:3,'    ',um1[k]:1:3,'    ',
    uy[k]:2:2,'%');
if um=0.5 then
  writeln(out_data,vaa[k]:2:3,'    ',ucf:2:3,'    ',um1[k]:1:3,'*0.5=',
    um2[k]:1:3,'    ',uy[k]:2:2,'%');
if um=2 then
  writeln(out_data,vaa[k]:2:3,'    ',ucf:2:3,'    ',um1[k]:1:3,'*2 =',
    um2[k]:1:3,'    ',uy[k]:2:2,'%');
TTuaa:=TTuaa + vaa[k];
Tum1:=Tum1 + um1[k];

```

```

    Tum2:=Tum2 + um2[k];
    Tuy:=Tuy + uy[k];
end;
Auaa :=TTuaa/3; Auaa:=round(Auaa*1000); Auaa:=Auaa/1000;
Aum1:=Tum1/3; Aum1:=round(Aum1*1000); Aum1:=Aum1/1000;
Aum2:=Tum2/3; Aum2:=round(Aum2*1000); Aum2:=Aum2/1000;
Auy:=Tuy/3; Auy:=round(Auy*100); Auy:=Auy/100;
if um=1 then
    writeln(out_data,Auaa:2:3,' ',Aum1:1:3,' ',Auy:2:2,'% (Ave)')
else
    writeln(out_data,Auaa:2:3,' ',Aum1:2:3,' ',Aum2:2:3,' ',Auy:2:2,
    '% (Ave)');
writeln(out_data);
writeln(out_data,'*****');
writeln(out_data);
writeln(out_data,'          Reaction          Yield');
Tf1:=0; Tf2:=0;
for k:=1 to 3 do begin
    F1[k]:=100 - ry[k]; F2[k]:=Fy[k];
    writeln(out_data,'          ',F1[k]:2:2,'% ',          ',F2[k]:2:2,'%');
    Tf1:=Tf1 + F1[k];
    Tf2:=Tf2 + F2[k];
end;
Af1:=Tf1/3; Af1:=round(Af1*100); Af1:=Af1/100;
Af2:=Tf2/3; Af2:=round(Af2*100); Af2:=Af2/100;
writeln(out_data,'          -----');
writeln(out_data,'          Ave ',Af1:2:2,'% ',          Ave ',Af2:2:2,'%')
end else begin
    for k:=1 to 3 do Fy[k]:=0;
    for n:=2 to id do begin
        writeln('Please type in the ',n:3,' product name ');
        readln(name);
        writeln('Please input the C.F. for the',n:3,' product ');
        readln(cf);
        writeln('Multiply by ');
        readln(m);
        writeln(out_data);
        writeln(out_data,name);
        Trt:=0; Trrt:=0; Taa:=0; Tm1:=0; Tm2:=0; Ty:=0;
        for k:=1 to 3 do begin
            writeln('Please input the ',k:2,' time for the ',n:3,' product ');
            readln(t[k]);
            writeln('Please input the ',k:2,' area for the ',n:3,' product ');
            readln(a[k]);
            aa[k]:=a[k]/i[k]; aa[k]:=round(aa[k]*1000); aa[k]:=aa[k]/1000;
            m1[k]:=aa[k]/cf;m1[k]:=round(m1[k]*1000);m1[k]:=m1[k]/1000;
            if m=1 then m2[k]:=m1[k];
            if m=2 then begin
                m2[k]:=m1[k]*2; m2[k]:=round(m2[k]*1000); m2[k]:=m2[k]/1000;
            end;
            if m=0.5 then begin
                m2[k]:=m1[k]*0.5; m2[k]:=round(m2[k]*1000);
            end;
        end;
    end;
end;

```

```

        m2[k]:=m2[k]/1000;
    end;
    y[k]:=m2[k]/o_Mmole*100; y[k]:=round(y[k]*100); y[k]:=y[k]/100;
    if m2[k]=m1[k] then begin
        writeln(out_data,t[k]:3:2,'      ',aa[k]:3:3,' ',
            cf:3:3,' ',m1[k]:3:3,'      ',y[k]:3:2,'%');
    end;
    if m=2 then begin
        writeln(out_data,t[k]:3:2,'      ',aa[k]:3:3,' ',
            cf:3:3,' ',m1[k]:3:3,'*2 =' ,m2[k]:3:3,'      ',y[k]:3:2,'%');
    end;
    if m=0.5 then begin
        writeln(out_data,t[k]:3:2,'      ',aa[k]:3:3,' ',
            cf:3:3,' ',m1[k]:3:3,'*0.5=' ,m2[k]:3:3,'      ',y[k]:3:2,'%');
    end;
    Trt:=Trt + t[k];
    Taa:=Taa + aa[k];
    Tm1:=Tm1 + m1[k];
    Tm2:=Tm2 + m2[k];
    Ty:=Ty + y[k];
    Fy[k]:=Fy[k] + y[k];
end;
Art:=Trt/3; Art:=round(Art*100); Art:=Art/100;
Aaa:=Taa/3; Aaa:=round(Aaa*1000); Aaa:=Aaa/1000;
Am1:=Tm1/3; Am1:=round(Am1*1000); Am1:=Am1/1000;
Am2:=Tm2/3; Am2:=round(Am2*1000); Am2:=Am2/1000;
Ay:=Ty/3; Ay:=round(Ay*100); Ay:=Ay/100;
if Am1=Am2 then
    writeln(out_data,Art:3:2,'      ',Aaa:3:3,'      ',
        Am1:3:3,'      ',Ay:3:2,'% (Ave)')
else
    writeln(out_data,Art:3:2,'      ',Aaa:3:3,'      ',
        Am1:3:3,'      ',Am2:3:3,'      ',Ay:3:2,'% (Ave)');
    writeln(out_data);
end;
for j:=1 to (tot-id) do hrt[j]:=0;
writeln(out_data);
writeln(out_data);
writeln(out_data,'High M.W. Peaks');
for k:=1 to 3 do begin
    writeln(out_data,'RT = ');
    for j:=1 to (tot-id) do begin
        writeln('Please input the ',j:1,' R.T. of High M.W. compounds for ',
            k:1,' set of data :');
        readln(rt[j]);
        writeln(out_data,rt[j]:2:2,' ');
        hrt[j]:=hrt[j] + rt[j];
    end;
    writeln(out_data);
end;
writeln(out_data,'Ave ');
for j:=1 to (tot-id) do begin

```

```

    Ahrt[j]:=hrt[j]/3; Ahrt[j]:=round(Ahrt[j]*100); Ahrt[j]:=Ahrt[j]/100;
    write(out_data,Ahrt[j]:2:2,' ');
end;
writeln(out_data);
writeln(out_data);
writeln(out_data,'AA/ $\mu$ L    C.F.    Mmoles    yield(%));
writeln(out_data,'-----    -----    -----    -----');
writeln('Please input the C.F. for unidentified products ?');
readln(ucf);
writeln('Multiply by ?');
readln(um);
Tum1:=0; Tum2:=0; Tuy:=0; TTuaa:=0;
for k:=1 to 3 do Tuaa[k]:=0;
for k:=1 to 3 do begin
    writeln('Please input the areas for unidentified products :');
    for j:=1 to (tot-id) do begin
        writeln(k:2,' area for product # ',j:2,' ');
        readln(uaa[j]);
        Tuaa[k]:=Tuaa[k] + uaa[j];
    end;
    vaa[k]:=Tuaa[k]/i[k];vaa[k]:=round(vaa[k]*1000); vaa[k]:=vaa[k]/1000;
    um1[k]:=vaa[k]/ucf;um1[k]:=round(um1[k]*1000);
    um1[k]:=um1[k]/1000;
    if um=1 then um2[k]:=um1[k];
    if um=0.5 then begin
        um2[k]:=um1[k]*0.5; um2[k]:=round(um2[k]*1000);
        um2[k]:=um2[k]/1000;
    end;
    if um=2 then begin
        um2[k]:=um1[k]*2; um2[k]:=round(um2[k]*1000);
        um2[k]:=um2[k]/1000;
    end;
    uy[k]:=um2[k]/o_Mmole*100;uy[k]:=round(uy[k]*100);
    uy[k]:=uy[k]/100;
    Fy[k]:=Fy[k] + uy[k];
    if um=1 then
        writeln(out_data,vaa[k]:2:3,'    ',ucf:2:3,'    ',um1[k]:1:3,'    ',
            uy[k]:2:2,'%');
    if um=0.5 then
        writeln(out_data,vaa[k]:2:3,'    ',ucf:2:3,'    ',um1[k]:1:3,'*0.5=',
            um2[k]:1:3,'    ',uy[k]:2:2,'%');
    if um=2 then
        writeln(out_data,vaa[k]:2:3,'    ',ucf:2:3,'    ',um1[k]:1:3,'*2 =',
            um2[k]:1:3,'    ',uy[k]:2:2,'%');
    TTuaa:=TTuaa + vaa[k];
    Tum1:=Tum1 + um1[k];
    Tum2:=Tum2 + um2[k];
    Tuy:=Tuy + uy[k];
end;
Auaa :=TTuaa/3; Auaa:=round(Auaa*1000); Auaa:=Auaa/1000;
Aum1:=TTuaa/3; Aum1:=round(Aum1*1000); Aum1:=Aum1/1000;
Aum2:=TTuaa/3; Aum2:=round(Aum2*1000); Aum2:=Aum2/1000;

```

```

Auy:=Tuy/3;    Auy:=round(Auy*100);    Auy:=Auy/100;
if um=1 then
    writeln(out_data,Auaa:2:3,'    ',Aum1:1:3,'    ',Auy:2:2,
    '% (Ave)');
else
    writeln(out_data,Auaa:2:3,'    ',Aum1:2:3,' ',Aum2:2:3,
    ' ',Auy:2:2,'% (Ave)');
writeln(out_data);
writeln(out_data,'*****');
writeln(out_data);
writeln(out_data,'          Reaction          Yield');
Tf1:=0; Tf2:=0;
for k:=1 to 3 do begin
    F1[k]:=100 - ry[k]; F2[k]:=Fy[k];
    writeln(out_data,'          ',F1[k]:2:2,'%','          ',F2[k]:2:2,'%');
    Tf1:=Tf1 + F1[k];
    Tf2:=Tf2 + F2[k];
end;
Af1:=Tf1/3; Af1:=round(Af1*100); Af1:=Af1/100;
Af2:=Tf2/3; Af2:=round(Af2*100); Af2:=Af2/100;
writeln(out_data,'          -----');
writeln(out_data,'          Ave ',Af1:2:2,'%','          Ave ',Af2:2:2,'%')
end;
close(out_data);
end;

```

Appendix C
Abbreviations and Structures of Some Organic Compounds

Table 17
Abbreviations and Structures of Some Organic Compounds

Name and / or Abbreviation	Structure	
Anthracene	$C_{14}H_{10}$	(3 fused rings)
Benzophenone	$(C_6H_5)CO(C_6H_5)$	
Benzylidenebenzylamine (BBA)	$(C_6H_5)CH=NCH_2(C_6H_5)$	
Carbazole	$(C_6H_4)NH(C_6H_4)$	(fused)
Carbinol	CH_3OH	
Cresol	$C_6H_4(CH_3)(OH)$	
Fluorene	$(C_6H_4)CH_2(C_6H_4)$	(fused)
Fluorenone	$(C_6H_4)CO(C_6H_4)$	(fused)
Imidazole	$-N=CH-NH-CH=CH-$	(ring)
Indan	$C_6H_4(-CH_2-CH_2-CH_2-)$	(fused)
Indene	$C_6H_4(-CH=CH-CH_2-)$	(fused)
Indole	$C_6H_4(-CH=CH-NH-)$	(fused)
Naphthalene	$C_{10}H_8$	(2 fused rings)
Phenanthrene	$C_{14}H_{10}$	(3 fused rings)
Pyrene	$C_{16}H_{10}$	(4 fused rings)
Pyrrole	$-NH-CH=CH-CH=CH-$	(ring)
Quinaldine (2-methylquinoline)	$C_6H_4(-N=C(CH_3)-CH=CH-)$	(fused)
Quinoline	$C_6H_4(-N=CH-CH=CH-)$	(fused)
Stilbene	$(C_6H_5)CH=CH(C_6H_5)$	(trans)
Toluidine	$C_6H_4(CH_3)(NH_2)$	
Xylene	$C_6H_4(CH_3)_2$	
Xylenol	$C_6H_3(CH_3)_2(OH)$	
Xylidine	$C_6H_3(CH_3)_2(NH_2)$	