

## REACTIONS OF MODEL COMPOUNDS WITH SUPERCRITICAL WATER

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### INTRODUCTION

The possible use of supercritical fluid extraction (SFE) of coal to obtain cleaner, more versatile fluid products is of significant interest. Some fluids have the opportunity to participate as reactants at process conditions, which may yield extracts of very different compositions than those obtained from other treatments and which will be dependent on the fluid used. Thermodynamic consideration of SFE leads to the prediction that the enhanced solubility (volatility) of the solute may be several orders of magnitude(1-3). Thus, this method combines many of the advantages of distillation with those of extraction. However, despite the interest in SFE, only a few studies have reported the basic chemistry that may be taking place during coal extraction at these conditions(4-8).

The current program is concerned with nitrogen removal from, and the rupture of carbon-carbon bonds between, aromatic rings in model compounds thought to be representative of structures found in fossil fuels. Because of the difficulty of removing heterocyclic nitrogen, experiments were initiated by extensively examining the reactivities of quinoline and isoquinoline, as well as brief examinations of the reactivities of other compounds(4). The selection of water as the fluid was based on its physical and chemical properties(9) and on the observation that a few studies of SFE of coal using water as the fluid have given encouraging results(10,11). Zinc chloride was chosen as a catalyst because of its reported catalytic activity for hydrocracking aromatic structures(12). This paper discusses the results of a study of the reactions of supercritical water (SW) with organic compounds that were found, or postulated, to be intermediates in the reaction of isoquinoline with SW. Since the isoquinoline reaction produced significant yields of ethyl benzene and o-xylene(4) it was assumed that benzylamine (BA) would be representative of the intermediate structure formed after the initial bond rupture in the heterocycle. It was found that benzaldehyde, benzylidenebenzylamine (BBA) and benzyl alcohol were intermediates in the BA-SW reaction(5), thus these are the primary subjects of the current study.

### EXPERIMENTAL

The experiments were carried out in a small (47 cm<sup>3</sup>) stainless steel, batch reactor, which was not equipped for the collection of gaseous products for analysis. The reactor was loaded with about 2.00 g of an organic compound. Water (10 ml) was added for the SW experiments to produce the desired pressure at reaction temperature, catalysts were added as needed, then the reactor was purged with argon and bolted

closed using a copper gasket. The reactor was placed in a fluidized sand bath furnace for the required reaction time, about 15 minutes was required to reach 375°C. Following reaction, the vessel was air cooled, opened, the reaction mixture removed and the water and organic layers separated. Portions of methylene chloride solvent were used to rinse the reactor and extract the water layer. These portions were combined with the organic layer and additional solvent added to a standard volume for quantitative determinations made gas chromatographically using peak area calibrations from known solutions. The components for these solutions were identified mass spectrometrically.

There were certain limitations on the g.c.-m.s. determinations: Some components could not be separated completely and these are reported as a total yield of mixture using an average calibration factor. Some products are reported as an isomer of a probable structure as deduced from the molecular weight and m.s. fragmentation pattern. Finally, many of the higher molecular weight minor products could be measured only with a low degree of precision by g.c. and calibration factors were estimated.

#### RESULTS AND DISCUSSION

The previous study of the isoquinoline - SW reaction(4) has indicated that following the rupture of the CN bond in the 1-2 or 2-3 position, the nitrogen portion would undergo hydrolysis and decarboxylation while the carbon end was either capped directly, or shortened and capped, by hydrogen thus producing toluene, ethylbenzene or o-xylene, the major volatile products. To help substantiate this proposed sequence of reactions, the benzylamine - SW reaction was studied(5). Since benzaldehyde, benzyl alcohol and benzyldenebenzylamine ( $C_6H_5CH_2N=CHC_6H_5$ ) were observed as intermediates in the BA - SW reaction it was necessary to determine how they contributed to the formation of the final products.

The data reported in Tables 1-4 are a small portion, but representative, of the results obtained. Ammonia was added in some experiments since it would be present in the denitrogenation of amines.

##### Benzyl Alcohol

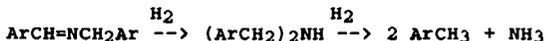
Table 1 shows that SW by itself had relatively little influence on the on the pyrolysis reaction, both giving low yields of volatile products and significant amounts of black char/tar. The added ammonia suppressed the char/tar formation, producing clear yellow solutions and significantly higher yields of volatile products. It is believed that the most important observations are: (a) that for all experiments toluene is formed in the highest yield and (b) the presence of SW does promote the formation of benzaldehyde which, as will be shown later, would lead to higher benzene yields. The second observation is consistent with other data that have shown SW capable of removing hydrogen from tetralin(4) and benzylamine (to be discussed later).

##### Benzyldenebenzylamine (BBA)

In this and the following sections, Ar will be used for the phenyl group ( $C_6H_5$ ). The formation of BBA in the BA - SW reaction was most probably from the standard imine preparation



since benzaldehyde was also found in this reaction. The data in Table 2 show that BBA - SW reaction produces benzene and toluene in comparable yields. However, since some benzaldehyde is also produced the above reaction must be somewhat reversible. It appears that benzene and other products formed from phenyl radicals have benzaldehyde as their precursor, the evidence for which will be given later. An important point to note is that the addition of a hydrogen donor, dihydroanthracene (DHA), promotes the formation of toluene at the expense of benzene and other species which form from benzaldehyde. The following reaction sequence is a possible explanation:



Thus, it appears that rupture of the single CN bond leads to toluene while the C=N segment can be hydrolysed by the reverse of the imine formation reaction.

#### Benzoic Acid

It has been assumed that benzene is formed from the decarboxylation of benzoic acid although it had not been observed as an intermediate in the reactions studied earlier. The data in Table 3 show that benzoic acid does react about as expected. However, while SW appears to slow the reaction compared to pyrolysis, ammonia acts as a catalyst to produce an almost quantitative yield of benzene.

#### Benzaldehyde

Again it would appear that SW has relatively little effect on the pyrolysis of benzaldehyde. The data in Table 4 show that the extents of reaction and product distributions are very similar (except the benzyl alcohol yields are increased somewhat with SW) for the reactions with and without water. However, with the addition of ammonia the reaction rates are increased as well as the toluene yields. The most important observation is that the major product is benzene indicating an oxidation/decarboxylation sequence is predominant. Clearly the presence of a source of hydrogen (DHA) promotes the benzyl alcohol sequence to form toluene at the expense of benzene. To a lesser degree ammonia has a similar effect but the mechanism by which this occurs would be very speculative.

The conclusion that can be drawn is that benzene and other products formed from phenyl radicals are produced through the oxidation of benzaldehyde. However, in that process since hydrogen is produced it is possible to reduce some unreacted benzaldehyde to the alcohol from which toluene and products formed from benzyl radicals are obtained, with some reversibility in the oxidation/reduction part of the sequence.

Another possibility is that the Cannizzaro disproportionation is taking place which is base catalyzed. However, this would be expected to lead to equal yields of benzoic acid and benzyl alcohol or their respective subsequent products. Since the products resulting from benzoic acid are predominant it appears that SW may alter the mechanism to favor this product, possible through hydrogen removal from a benzaldehyde-water adduct.

### Mechanism Considerations

The formation of biphenyl and 168 isomers (methyl biphenyls) as well as benzene demonstrate that phenyl radicals exist as intermediates. The formation of bibenzyl and other 182 isomers (benzyl toluenes) and the 168 isomers as well as toluene demonstrate the presence of benzyl radicals. The previous results with bibenzyl and SW(5) show conclusively that once benzyl radicals form, they abstract hydrogen or combine with other radicals resulting in very little (if any) oxidation/decarboxylation to benzene. These results from bibenzyl in addition to those obtained from BA, BBA and BBA plus DHA lead to the following conclusions: (a) The CN bond in the reactant is necessary for the hydrolysis/oxidation sequence to be initiated. (b) If a CN single bond exists in an aromatic side chain it may rupture to form a radical that is capped by hydrogen producing an alkylated aromatic, or hydrogen can be removed to form a CN multiple bond. (c) Once formed, the CN multiple bond can undergo the oxidation/decarboxylation process. (d) These reactions are somewhat reversible. (e) Ammonia catalyzes the hydrolysis/oxidation and decarboxylation processes. (f) Finally, it must be concluded that SW can facilitate the removal or transfer of hydrogen from many reactants and intermediates as evidenced by the results of tetralin in SW(4), benzaldehyde sequence of reactions from the BA-SW reaction(5), benzamide and from benzaldehyde-SW with added ammonia (Table 4) and for many of the hydrolytic/oxidation sequences leading to the observed products to be possible.

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**Table 1** Benzyl Alcohol - SW Reaction\*

Water Pressure (psi)	0	3870	3870	3870
Added NH <sub>3</sub> (Molar)	0	0	2M	6M
Volatile Products <sup>b</sup> (%Yield)				
Benzene	2.8	2.6	19	21
Toluene	24	20	42	44
Benzaldehyde	0	6.0	9.5	5.5
Biphenyl	0.1	0	2.3	2.6
168 Isomers	3	3	4	5
182 Isomers	8	11	2	2
DHF/Stilbene	0	0	1.6	1.4
Benzylidenebenzylamine	-	-	1.2	1.6
Above 190	8	-	1	3

a. All experiments were at 400C for 3 hrs, all extents of reaction were about 100% and the two experiments without ammonia gave black tarry products, the others gave clear yellow solutions.

b. The numbers represent molecular weights of mixtures, DHF is dihydrophenanthrene.

**Table 2** Benzylidenebenzylamine - SW Reaction\*

Time (h)	1	3	6	9	3	3
Additive	0	0	0	0	6M NH <sub>3</sub>	2g DHA
Volatile Products <sup>b</sup> (%Yield)						
Benzene	22	29	35	34	28	11
Toluene	24	26	28	29	29	54
Benzaldehyde	22	11.0	3.4	2.0	3.1	0
Benzyl alcohol	2.8	2.4	0.2	0.1	0.4	0
Benzamide	0.6	0.4	0	0	0.5	0
Biphenyl	4.1	6.4	7.3	7.2	4.2	0.4
168 Isomers	4	6	7	7	5	-
Fluorene	0.1	0.4	0.6	0.8	0.4	-
Bibenzyl	2.7	2.6	2.0	1.9	3.4	-
Benzophenone	1.3	1.9	1.0	0.8	1.2	-
182-196 Mixture	4	4	2	2	2	-
Above 200	6	6	8	8	15	-

a. All experiments were at 400C and about 3870 psi water pressure. The extents of reaction were all above 95%. All solutions were clear.

b. The numbers represent molecular weights of product mixtures.

**Table 3** Benzoic Acid - SW Reaction\*

Time (h)	3	4	4
Water Pressure (psi)	0	3870	3870
Added NH <sub>3</sub>	0	0	2 M
% Reaction	95	58	100
Volatile Products(%Yield)			
Benzene	80	79	92
Phenol	1.5	0.4	0.1
Biphenyl	3.1	0.4	0.2

\* All experiments were at 400C<sub>446</sub>

**Table 4 Benzaldehyde - SW Reaction<sup>a</sup>**

	1 <sup>b</sup>	6 <sup>b</sup>	1	3	6	1	3	6	1	3	6	3	9	1
Time (h)	0	0	0	0	0	2M	2M	2M	2M	2M	2M	2M	2M	6M
NHs (M)	0	0	0	0	0	0	0	0	0	0	0	0	2	0
DHA (g)	0	0	0	0	0	0	0	0	0	0	0	0	2	0
% Reaction	29	76	25	53	71	73	85	93	89	99	99	89	99	94
Volatile Products <sup>c</sup> (% Yield)														
Benzene	70	54	36	49	50	32	41	44	16	18	28	16	18	28
Toluene	6.7	7.3	5.9	8.3	6.4	11	17	21	39	38	12	21	39	12
Benzyl Alcohol	1.7	0	6.8	1.2	0.9	2.1	2.8	2.5	-	-	3.4	2.8	2.5	3.4
Benzoic Acid	10	6.9	14	7.5	4.7	0	0	0	-	-	0	0	0	0
Benzamide	-	-	-	-	-	1.2	1.0	0.7	-	-	2.6	1.0	0.7	2.6
Biphenyl	11	14	3.4	6.1	8.3	4.8	9.2	12	-	-	3.4	9.2	12	3.4
168 Isomers	6	9	2	3	4	2	4	6	-	-	3	4	6	3
166,180-196 Mixture	19	8	10	8	5	6	7	5	-	-	5	7	5	5
Benzylidenebenzylamine-	-	-	-	-	-	2.0	4.3	4.0	-	-	6.1	4.3	4.0	6.1
Above 200	1	3	<1	2	4	20	7	5	-	-	13	7	5	13

a. All experiments were at 400C.

b. These experiments were pyrolyses, the others had about 3870 psi water pressure.

c. The numbers represent molecular weights.