

SOLVENT EFFECTS DURING THE REACTION OF COAL MODEL COMPOUNDS

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INTRODUCTION

The chemical reactions that accompany the extraction of volatiles (1) from hydrocarbon resources with supercritical solvents are frequently obscured by the complexities of the reaction system. In contrast, the comparative simplicity of model compound structures and product spectra permit resolution of reaction fundamentals (2) and subsequent inference of the factors that control the reactions of real reacting systems. Herein we use model compounds to probe the kinetics of pyrolysis and solvolysis reactions that likely occur during the extraction of volatiles from coals and lignins.

Previous studies of the reactions of guaiacol (orthomethoxyphenol) (3) and benzyl phenyl amine (4) in supercritical water elucidated parallel hydrolysis and pyrolysis pathways, the selectivity to the latter increasing linearly with water density. Reactant decomposition kinetics were interestingly nonlinear in water density, which was consistent with at least two possible mechanistic interpretations. The first possibility was that of unusual "cage" or solvent effects attributable to operation in dense fluids. The second possibility was a straightforward reaction scheme with pressure-dependent rate constants. Herein we present our analysis of these two mechanistic possibilities for reaction in water and reaction in methanol.

EXPERIMENTAL

Table I summarizes the experimental conditions of reactants' concentration, solvent loading, and holding time; all reactions were at 386°C. Measured amounts of the commercially available (Aldrich) substrate benzyl phenyl amine (BPA), the solvent (water or methanol) and the inert internal standard biphenyl were loaded into room temperature "tubing bombs" that have been described elsewhere (4). Sealed reactors were immersed into a fluidized sand bath held constant at the desired reaction temperature, which was attained by the reactors in about 2 min; this heat-up period was small compared to ultimate reaction times (up to 60 min) and was, in any case, identical for all runs. Products were identified by GC-MS and quantitated by GC as described elsewhere (4,6).

RESULTS

Table II summarizes the major products observed from BPA reaction neat, in tetralin, in water, and in methanol; BPA disappearance kinetics are shown in Figure 1. Neat pyrolysis of BPA led to toluene, aniline, and benzalaniline as major products and minor products including 1,2-diphenylethane, diphenylmethane, and 2-benzylaniline. Thermolysis in tetralin yielded qualitatively similar results, with the selectivity to toluene and aniline increased and selectivity to benzalaniline decreased relative to neat pyrolysis. BPA reaction in water was to benzyl alcohol and benzaldehyde as well as the neat pyrolysis products. BPA reaction in methanol produced a product spectrum similar to that found from reaction in water, with the addition of N-methylaniline as a major product.

The effect of water density on BPA conversion and product selectivity, for a constant reaction time of 10 minutes, is shown in Figure 2. BPA conversion passed through a minimum at a reduced water density of 0.2, whereas the selectivity to each individual product was essentially linear in solvent loading. The yield of aniline was relatively unaffected by solvent density but toluene and benzalaniline yields decreased and total yield of oxygenated products (benzaldehyde plus benzyl alcohol) increased with increases in solvent loading.

The reaction of BPA in methanol, at a constant reaction time of 60 minutes, was qualitatively

similar, as illustrated in Figure 3. Here the minimum conversion occurs at a reduced methanol density of 0.6 and the selectivity to each particular product was once again apparently linear in solvent loading. The yield of toluene was relatively unaffected by changes in the methanol density, whereas the yields of aniline and bensalaniline decreased and that of N-methylaniline and total oxygenated products increased as the solvent loading increased.

The foregoing results are consistent with the reaction pathways shown in Figure 4. The neat pyrolysis pathway, illustrated in Figure 4a, requires two molar equivalents of BPA for the formation of one mole each of toluene, aniline, and bensalaniline. The network for thermolysis in tetralin is a combination of the neat pyrolysis pathway (Figure 4a) and a pathway wherein tetralin and BPA react to one mole each of toluene, aniline, and 0.5 molar equivalents of naphthalene. Figure 4b depicts a direct solvolysis pathway for the "active" solvents water and methanol. Here the BPA can either (i) react by the neat pyrolysis pathway with the addition of another BPA, to give one mole each of toluene, aniline, and bensalaniline or (ii) can proceed through the solvation pathway to give oxygenated products and aniline (or N-methylaniline for reaction in methanol). The yield of oxygenated products would be expected to increase while the toluene yield would decrease as the solvent loading is increased; the yield of N-methylaniline would be expected to increase with increases in solvent loading during reaction in methanol.

The minima in BPA conversion observed for reaction of BPA in water and methanol were explained by allowing the rate constants of Figure 4b to be dependent on pressure. For each solvent loading (and thus pressure) studied the pseudo-first order rate constants for the pathways of Figure 4b are shown in Table 3. These were calculated using a sequential simplex search where the objective function was the square of the deviations between predicted and experimental values. The pressure generated by water was estimated from PVT data (7) and the methanol pressure was estimated using a Peng-Robinson equation of state.

DISCUSSION

BPA reaction in water or methanol yielded solvation products in addition to those observed from pyrolysis neat. BPA conversion passed through a minimum at a reduced solvent density of 0.6 and 0.2 for reaction in methanol and water respectively; product selectivity was essentially linear in solvent density. These results are consistent with reaction networks comprising parallel pyrolysis and solvolysis pathways with pressure-dependent rate constants; the selectivity to the latter pathway increased with increasing solvent loading. Results qualitatively similar to those observed in Figures 2 and 3 have been noted previously for reactions in solution with reaction networks containing pressure-dependent rate constants (8).

The effects of pressure on the rates of chemical reactions in solution have been summarized (5,8). These effects can be interpreted in terms of transition state theory, which shows that

$$\frac{\partial \ln k}{\partial P} = \frac{\Delta V_{\ddagger}}{RT} \quad (1)$$

where ΔV_{\ddagger} is the volume of activation, i.e. the difference between the partial molar volumes of the reactants and the activated state. ΔV_{\ddagger} is strictly a function of pressure which is often approximated by the expression

$$\ln k = a + bP + cP^2 \quad (2)$$

Generally, volumes of activation are of the order of $\pm 25 \text{ cm}^3$ and thus rate constants for reactions in solution do not begin to show a significant pressure dependence below approximately 1000 atm (5). Also, the volume of activation is often broken into two separate values, $\Delta_1 V_{\ddagger}$ and $\Delta_2 V_{\ddagger}$, where the

former represents a structural contribution and the latter represents a change in the volume of the solvent shell.

It is important to note that, although the operating pressures in the present study were of the order of 10 - 1000 atm., the minimum in reactant conversion, from which we have inferred a likely kinetic effect of pressure, occurred at pressures of only 100 atm. Thus the apparent global volume of activation associated with the present interpretation of the non-linear kinetics of Figures 2 and 3 would be an order of magnitude larger than that observed for liquid systems. These apparent volumes of activation may consist of at least three components; first, $\Delta_1 V^\ddagger$ associated with structural changes, second, $\Delta_2 V^\ddagger$ associated with changes in the solvent shell, and third, a contribution due to the compressibility of the fluid. The supercritical fluid is highly compressible in the critical region and lack of an unequivocal equation of state for the reaction mixture has hindered unambiguous analysis of the compressibility term. Further analysis is being undertaken to ascertain the quantitative contributions of each of these factors to the overall global volume of activation.

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Table 1
Experimental conditions for reaction of BPA

Solvent	BPA concentration (mol/lit)	solvent loading (ml)	holding time (min)
Neat	.54	-	5 - 50
Tetrafin	.59	.225	5 - 60
Water	.59	0.1 - .25	5 - 50
Methanol	.59	0.02 - .35	5 - 60

Table 2
Major products of BPA thermolysis

Solvent	Products
Neat	Toluene, Aniline, Benzalaniline
Tetrafin	Toluene, Aniline
Water	Toluene, Aniline, Benzyl alcohol, Benzalaniline
Methanol	Toluene, Aniline, N-Methylaniline, Benzaldehyde, Benzalaniline

Table 3
Pseudo-first order rate constants

Reaction in water at 386°C			
Reduced density	Estimated pressure [psi]	k_1 [min^{-1}]	k_2 ($\times 10^3$) [lit/(mol)(min)]
0.0	0.0	.193	-
0.1	1280	.0276	8.98
0.3	2720	.0272	3.95
0.5	3350	.0301	4.12
0.8	3660	.0255	2.85
1.2	3880	.0240	1.95
Reaction in methanol at 300°C			
Reduced density	Estimated pressure [psi]	k_1 ($\times 10^3$) [min^{-1}]	k_2 ($\times 10^3$) [lit/(mol)(min)]
0.0	0.0	22.1	-
0.1	526.1	15.8	3.31
0.3	1294.9	7.86	2.62
0.5	1819.8	4.32	2.06
0.8	2413.9	1.98	1.59
1.2	3391.2	0.613	1.44

FIGURE 1
Summary of BPA yield for all solvents

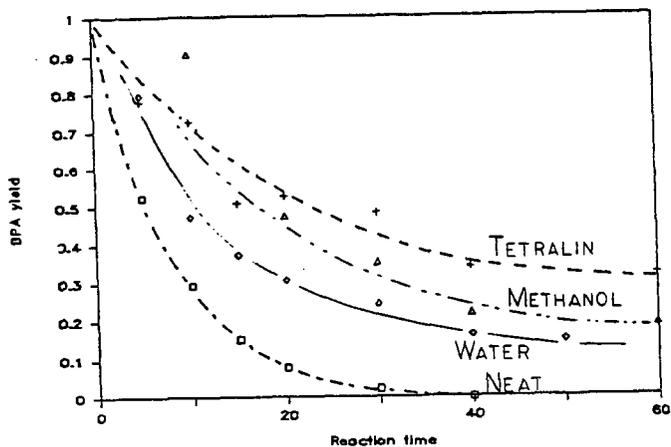


FIGURE 2
BPA conversion and product selectivity

BPA reaction in water, $t = 10$ min

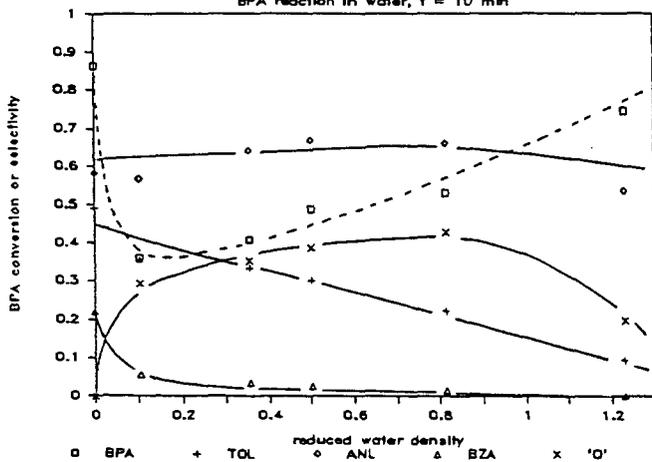


FIGURE 3
BPA conversion and product selectivity

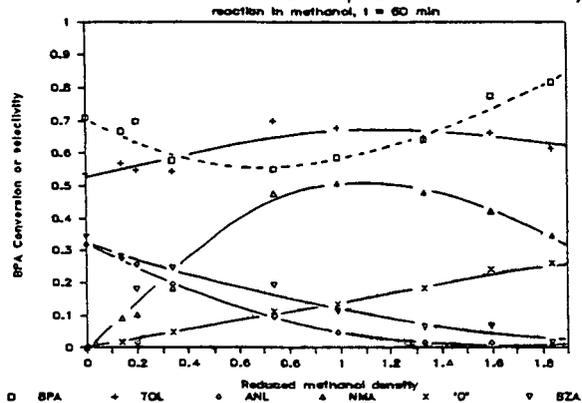


Figure 4
Proposed reaction pathways

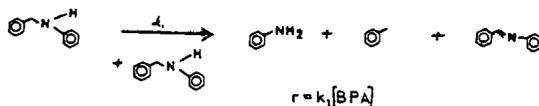


Figure 4a: Neat pyrolysis

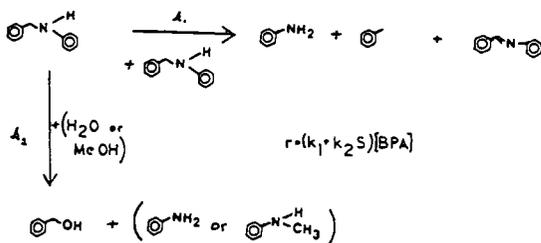


Figure 4b: Reaction in supercritical solvent