

REACTIONS OF SOME ORGANIC CHLORINE AND SULFUR COMPOUNDS IN SUPERCRITICAL WATER

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Keywords: supercritical water, organic chloride and sulfur removal, reactor corrosion

INTRODUCTION

Because of the possible use of supercritical water (SW) for fuels processing and coal extraction to obtain cleaner, less polluting products, and its potential use as a medium for the efficient oxidation and destruction of environmentally hazardous materials there has been an increase in the number of reports on the basic chemistry that may be taking place in the presence of SW [1-24]. The results that are being reported are primarily concerned with the reactions of organic model compounds thought to contain functional groups representative of hazardous materials, and/or coal structures. Because of the difficulty of removing heterocyclic nitrogen, our previous experiments were initiated by extensively examining the reactivities of quinoline and isoquinoline, as well as brief examinations of the reactivities of other compounds [1]. The selection of water as the fluid was based on its physical and chemical properties [25]. Zinc chloride was chosen as a catalyst in the previous studies because of its reported catalytic activity for hydrocracking aromatic structures [26]. The current study examines the reactions of SW with 1-chloro-3-phenylpropane (CPP), 2-chlorotoluene (CT), and 4-chlorophenol (4CP). A problem that we observed in our results with SW - chlorocarbon reactions which had not been adequately addressed in previous studies [11, 13] was the fate of HCl assumed to be formed. In our studies HCl was not found but significant amounts of soluble metal salts were observed. This led to the conclusions that significant corrosion of the reactor walls takes place which may also occur in the entrance lines of flow systems if reaction is initiated there, and the chemistry of the chloride - SW reaction may be affected by this wall reaction. These conclusions are consistent with the observations of previous investigators [10, 24]. In addition, the HCl formed may erode oxide supported metal catalysts. Thus, experiments were conducted with Vycor ampoule inserts, the results of which are compared to those obtained from the metal reactors.

In addition, a few experiments were conducted to determine the influence of SW on the destruction of benzyl sulfide and thianaphthene.

EXPERIMENTAL

The experiments were carried out in small, cylindrical, Inconel 600, batch reactors, (10.2 cm long x 1.9 cm dia.), which were not equipped for the collection of gaseous products for analysis. The reactor was loaded with about 0.3 to 0.6g of an organic compound. The liquid reactants were introduced using about 0.5 ml. from a 1.0 ml. syringe; however since 4CP is a solid and the necks of the Vycor ampoules were too narrow for efficient solid loading, a solution of 54 wt% in toluene was used. The ampoules were constructed of standard 15mm. Vycor tubing, closed at one end and drawn to a thin capillary at the other for easy sealing once they were loaded. Their internal volumes were about 9ml. which were determined by filling with water and weighing; their external volumes were about 13ml. which were determined by water displacement. After the reactants were introduced the deionized, conductivity water was added for the SW experiments to produce the desired density or pressure at reaction temperature (the 0.255 M NiCl₂ and 0.050M FeCl₂ solutions or CaO were added as needed), then the reactor was bolted closed using a copper gasket as a seal. The reactant concentrations ranged between 1.5 and 7 mole %. For the ampoule experiments the water was added in amounts such that the internal and external densities were equal. The reactor was placed in a fluidized sand bath furnace for the required reaction time, about 5-10 minutes were required for a thermocouple embedded in the flange of the reactor to reach a temperature of 375°C. It was reasonable to assume that for those experiments with inserts the temperature rise of the reaction mixture would be more gradual due to slow heat transfer across the Vycor barrier. However, it was not possible to measure the temperatures of these mixtures. Thus, several insert experiments were run for longer reaction times than those without inserts at the same temperature setting to insure that the observed lower extents of reaction when inserts were used were not due to shorter times at the reaction temperature.

Following the reaction, the vessel was air cooled, opened, the reaction mixture or

ampoule removed, the ampoule broken open when applicable, and the water and organic layers separated. Portions of solvent, methylene chloride, were used to rinse the reactor or ampoule and extract the water layer; however some solids could not be removed from the walls of the ampoules. These portions were combined with the organic layer and additional solvent plus a known amount of an internal standard were added to a fixed volume for quantitative determinations made gas chromatographically using peak area calibrations from known solutions. The GC system consisted of a Varian model 3700 which used a 50cm x 1/8" column packed with 5% OV-101 (liquid methyl silicone) on chromosorb G-HP (100/120) and an HP 3396 A integrator. The peak areas were normalized using a ratio of compound area to area of standard/mole. The product yields and extents of reaction were determined from calibration factors (normalized area/mole compound) obtained from known solutions. Because of the pressure buildup in the ampoules when there was significant reaction some solids and gases were lost when they were opened, liquid losses appeared negligible. The components of these solutions were identified using a Hewlett Packard Model 5890 GC with a 1.2m x 0.2mm x 0.33 μ m capillary column packed with HP-1 (crosslinked methyl silicone gum), and an HP Model 5970 Mass Selective Detector. There were certain limitations on the GC-MS determinations: some products are reported as an isomer of a probable structure as deduced from the molecular weight and MS fragmentation pattern. In addition, many of the higher molecular weight minor products could be measured only with a low degree of precision by GC and calibration factors were estimated.

RESULTS AND DISCUSSION

The volatile product yields are presented as moles formed/mole of reactant consumed. The terms char and tar refer to insoluble solids and non volatile liquids respectively and are reported as mass formed/mass reactant consumed. Many experiments did not produce significant amounts of char or tar.

1-Chloro-3-phenylpropane. CPP was used to represent alkyl chlorides; Table I presents the data for its reactions. The CPP was completely consumed at all conditions and the products and their yields were very similar from the SW reactions in metal and Vycor. However, some small differences were observed, the most significant of which was that the yields of the 118 molecular wt species (isomers of dihydroindene, methylstyrene, etc.) were below detection limits from the reaction in Vycor but were easily measured from the reaction in metal. The odor of HCl was not detected in the evolved gases from any of the SW- chloride experiments without inserts, but was readily noted on breaking open the ampoules. In addition, the water layer color from experiments without inserts indicated significant concentrations of metal ions. The metal ion concentrations in the water layer were determined by Inductively-Coupled Plasma (ICP) analysis, and show an amount about equivalent to the CPP loading. Thus, the reactant, or any HCl formed, reacted with the metal walls to form metal chlorides which dissolved in the water layer on cooling. An ICP analysis of the water layer from a 1-chlorohexane - SW reaction discussed previously, [16], also showed metal ion amounts equivalent to the reactant loading. The addition of CaO did reduce the HCl attack on the metal walls but did not eliminate it. ICP analysis showed only trace amounts of metal ions in the water layers from reactions when chlorine was absent.

2-Chlorotoluene. The most interesting results were obtained with CT. Table II shows that SW had a very significant effect on the rate of consumption of CT, increasing extents of reaction at 450°C from only about 10% up to 80 to 100% at the same reaction times; similar increases were observed at 500°C. Thus, the presence of SW does facilitate the removal of aromatic chlorine at a lower temperature (450°C) where less char and tar are formed and produces good yields of toluene. At 500°C more C-C bond rupture took place increasing char/tar and benzene yields at the expense of toluene. However, the results of the experiments with Vycor inserts show that these increases in extents of reaction in the SW experiments are promoted, both directly and indirectly, by the metal walls, Table III. The extents of reaction with added NiCl₂ and FeCl₂ clearly show that these have a catalytic effect on CT consumption; however, these extents are still less than those obtained directly in the metal reactor, at 450°C and shorter times, indicating that both metal salts and metal walls are catalysts. The 0.255 and 0.050 molar concentrations for the NiCl₂ and FeCl₂ respectively were chosen since they were about the values calculated from the ICP analysis of the water layer from the CPP experiment. This catalytic effect appears to be considerably reduced in the absence of SW, however it is still present in the dry reactor, as indicated by extents of reaction at 500°C without water and at 495°C with SW in Vycor. For example, if first order kinetics are assumed and that the extents of reaction with inserts represent the uncatalyzed reaction, a very rough calculation of the activation energy leads to a predicted value for the uncatalyzed extent of reaction at 500°C and 60 min of about 17%, well below that observed in the dry metal reactor.

4-Chlorophenol. A brief examination of 4 CP indicated a similar behavior to that of CT although somewhat more reactive. Again the catalytic effect of metal walls and/or salts was evident, Table IV. The extents of reaction may have been influenced by toluene used as a solvent to aid in loading the ampoules. However, if it had reacted with radicals formed from 4 CP some bibenzyl should have been formed, but none was observed. The ampoules will be modified in future experiments to allow loading of solid reactants.

Sulfur Compounds. Table V shows benzyl sulfide reacts completely at our mildest conditions with and without SW. However, the SW reaction yielded cleaner products, in the organic layer only hydrocarbon compounds were detected. Since pyrolysis formed significant amounts of thiophenes, yields of which were estimated, the complete removal of sulfur without SW would be much more difficult, as shown by the lack of reactivity of thianaphthene discussed next. The formation of these thiophenes appears to come at the expense of the benzene yield. There were several very minor products that were detected by GC-MS but could not be measured by our GC, as well as small amounts of tar were formed. Finally, there was a strong odor of H₂S from the SW reaction which was absent from the pyrolysis.

Table VI shows that SW may promote the reaction of thianaphthene somewhat and the addition of NH₃ further increases the extents of reaction. However, these reactions were still not very rapid and a more effective catalyst, ZnCl₂, was used again producing some improvement. The NH₃ was tried as a catalyst because it was previously found to promote the reaction between SW and benzaldehyde [14]. It should be noted that in some experiments small amounts of styrene and a C₃ benzene were detected, however, no odor of H₂S was evident. From these data it is clear that extreme conditions are needed for heterocyclic sulfur to be removed.

ACKNOWLEDGEMENTS

Supported by, or in-part by, the U.S. Army Research Office.

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Table I: 1-Chloro-3-phenylpropane Pyrolysis and SW Reaction Data at 400 °C *

Vycor Insert	No	Yes	Yes	Yes
Time (min)	60	60	120	50
Water Pressure (bar)	270	270	270	270
CaO added (g)	0	0	0	0
<i>Volatile Product Yields (mols/mol reactant-all 100% consumed)</i>				
Benzene	<0.01	0.026	0.017	0.021
Toluene	<0.01	0.014	0.021	<0.01
Ethyl Benzene	0.010	<0.01	<0.01	<0.01
Ethyl Toluene	0.036	0.06	0.06	0.06
Propyl Benzene	0.28	0.17	0.18	0.17
C ₉ H ₁₀ ^b	0.05	-	-	-
M.W. 196-236 ^c	0.13	0.11	0.04	0.03
Tar (g/g reacted)	0.23	0.33	0.29	0.22

^a Dashes indicate these products were not detected.

^b Estimated yield. Several isomers of 118 M.W. were present, they could be cyclopropyl benzene, dihydroindene, methyl styrene and propenyl benzene.

^c Estimated yields. These are principally isomers of diphenyl cyclohexane, with very small amounts of several compounds with molecular weights between diphenyl propane (196) and diphenyl cyclohexane (236).

Table II: 2-Chlorotoluene Pyrolysis and SW Reaction Data, without Vycor Inserts.

Temperature (°C)	400	400	450	450	450	450	500	500	500	500
Time (min)	60	60	30	60	30	60	30	60	30	60
Water Pres. (bar)	0	270	0	0	364	364	0	0	454	454
% Reaction	0	0	11	10	82	99	36	87	100	100
<i>Volatile Product Yields (mols/mol reacted)^a</i>										
Benzene	-	-	0	<.01	<.01	<.01	0.02	0.04	0.18	0.15
Toluene	-	-	0.29	0.45	0.67	0.68	0.41	0.46	0.27	0.43
Char/Tar Yields (g/g reacted)	-	-	0.08	0.11	0.11	0.12	0.37	0.29	0.34	0.32

^a Very small amounts of phenol, cresol and an isomer of C₁₄H₁₃Cl were detected in some experiments.

Table IV: 4-Chlorophenol - SW Reaction at 450 °C and 310 bar Water Pressure

Vycor Insert	No	Yes	Yes
Time (min)	60	75	120
% Reaction	100	30	41
<i>Detectable Products</i>			
Phenol (mol/mol reacted)	0.65	0.15	0.31
Tar (grams/gram reacted)	-	-	0.15

Table III: 2-Chlorotoluene - SW Reaction Data with Vycor Inserts

Temperature (°C)	425	450	450	495	450	450	450
Time (min)	60	120	365	260	95	95	155
Water Pressure: (bar)	280	320	320	280	320	320	320
% Reaction	0	0	8	46	54	28	83
Catalyst ^a	0	0	0	0	NiCl ₂	FeCl ₂	NiCl ₂
<i>Volatile Product Yields (mols/mol reacted)</i>							
Benzene	-	-	-	0.014	0.015	0.032	0.030
Toluene	-	-	-	0.049	0.45	0.35	0.47
C ₁₄ H ₁₃ Cl ^b	-	-	-	0.07	0.04	-	-
Tar ^c (g/g reacted)	-	-	-	0.14	0.27	-	0.19

^a The concentrations of NiCl₂ and FeCl₂ were 0.255 and 0.050 molar respectively.

^b Estimated yields; this product appears to be 2-Chlorodiphenyl methane.

^c Chars could not be removed quantitatively from inserts, thus were not measurable.

Table V: Benzyl Sulfide Pyrolysis and SW Reactions

Temperature (°C)	400	400	400	450
Time (min)	30	30	30	60
Water Pressure (bar)	0	260	260	340
<i>Volatile Product Yields (mols/mol reactant - all 100% reacted)</i>				
Benzene	0.011	0.359	0.413	0.408
Toluene	0.816	0.849	0.811	0.832
C ₁₃ H ₁₂ Isomer	-	0.011	-	0.006
C ₁₄ H ₁₄ Isomer	-	-	-	0.011
Bibenzyl	0.154	0.031	0.041	0.052
Stilbene	0.033	0.063	0.099	0.023
Phenyl Benzothiophene	0.055	-	-	-
Tetraphenyl Thiophene	0.125	-	-	-

Table VI: Thianaphthene Pyrolysis and SW Reaction Data

Temperature (°C)	450	450	475	475	475	505	500	500	500
Time (min)	120	300	300	300	300	300	360	300	360
% Reaction	1	44	28	51	62	17	39	45	55
H ₂ O Pres. (bar)	370	283	365	365	269	0	335	335	335
NH ₃ added	0	0	2M	6M	0	0	0	6M	6M
ZnCl ₂ (g)	0	0.677	0	0	0.513	0	0	0	0
<i>Volatile Product Yields (mols/mol reacted)</i>									
Benzene	-	0.06	0.08	0.05	0.05	0.08	0.09	0.05	0.05
Toluene	-	0.18	0.20	0.21	0.12	0.02	0.20	0.19	0.22
Ethyl Benzene	-	0.18	0.19	0.38	0.23	<.01	0.09	0.20	0.26
C ₈ H ₆ C ₂ HSCH ₃	-	0.03	-	-	0.01	0.03	0.02	0	0.01
C ₈ H ₆ C ₂ H ₂ S	-	0.05	-	-	0.03	-	-	-	-