Catalytic Hydroprocessing of Chlorophenols

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The disposal of halogenated organic wastes is an important and difficult environmental problem. Although incineration and some chemical degradation processes have been used in the disposal of halogenated organics, problems associated with the processes have limited their effectiveness (Hagh and Allen, 1990a). Recently, several investigators (Kalnes and James, 1989; Hagh and Allen, 1990b,c) have reported on the use of catalytic hydroprocessing for the disposal or recycling of chlorinated organics. Based on the work done to date, catalytic hydroprocessing appears to have much promise; however, only a limited number of waste streams have been examined. Most of the streams examined contained only chlorinated organics. While chlorinated organics are a significant waste stream, many organic hazardous wastes contain elements other than chlorine such as sulfur, nitrogen, and oxygen. Under typical hydroprocessing conditions, all of these heteroatoms might react, complicating the design of the hydroprocessing operation.

The goal of this work is to extend the examination of catalytic dehalogenation by considering simultaneous dehalogenation and deoxygenation. Two different types of model compound systems are used to study the reactions of oxygen and chlorine over hydrotreating catalysts. First, a single mixed feed of chlorobenzene and phenol was reacted over a $NiMo/Al_2O_3$ catalyst under typical hydrotreating conditions to determine whether deoxygenation and dechlorination occur on the same catalytic sites. Secondly, ortho-, meta and parachlorophenols were catalytically hydrotreated to study the hydrodechlorination and deoxygenation of difunctional species. Chlorinated benzenes and phenols were selected for study due to their prominence in many waste streams.

Experimental Methods

The kinetic studies were preformed in a differential microflow reactor. The details of the reactor and data analysis procedures have been described elsewhere (Hagh and Allen, 1990b) and are merely summarized here. The reactor system consisted of a 1-L stirred autoclave (Autoclave Engineers), a SSI 100 LC pump with a SSI 210 Guardian, a tubular fixed bed reactor made of 1/4 in. (6.4 mm) Hastelloy-C tubing, a Lindberg 55122 Moldatherm hinged tube furnace (rated for 1,100°C) controlled by an Omega CN911 temperature controller, a 250-μL sampling value, and two 500-mL pressure vessels (Autoclave Engineers). The stirred autoclave was typically charged with a mixture consisting of 1–2% reactants in an *n*-hexadecane solvent. The feed mixture was saturated in the autoclave with dry, oxygen-free hydrogen at a controlled temperature and pressure. The saturated mixture was then pumped at a controlled rate over a heated reactor bed. The reactor bed consisted of a catalyst section, proceeded and followed by inert alundum sections. The temperature of the catalyst section of the reactor was controlled within ±1°C as measured by an Inconel sheathed thermocouple inserted directly in the catalyst bed. The product stream was sampled using a high-pressure sampling valve.

Product analysis was carried out on a Perkin-Elmer Sigma 2000 gas chromatograph with a Perkin-Elmer LDI 100 integrator. The gas chromatograph was equipped with a 3-m-long, 0.25-mm-ID fused silica capillary column (Supelco SPB5, bonded phase) and a flame ionization detector. Helium (99.9%) was used as a carrier gas. Naphthalene (98%) was used as an internal standard. The material balance closure on the organic components was always greater than 95%.

The $NiMo/Al_2O_3$ catalyst used for the hydrodechlorination studies was a commercial hydroprocessing catalyst supplied by American Cyanamid (HDN-60). The catalyst, which contained 23.0% MoO_3, 3.0% NiO, and 3.2% P, has a N_2 BET surface area of 150 m^2/g. The catalyst was crushed to less than 250-μm grain size and was sulfided for 3 hours *in situ* with 2.0–3.0 cm^3/min of 10% H_2S in H_2 at 400°C before each run.

The dechlorination and deoxygenation reaction rates were measured at temperatures ranging from 225°C to 300°C. Hydrogen concentrations at reaction conditions ranged from 4.60×10^{-2} to 4.78×10^{-2} mol/L and reactant feed concentrations ranged from 4.69×10^{-2} to 12.83×10^{-2} mol/L. The amount of catalyst used in all runs was 0.04 g. Conversions and product concentrations were measured at three flow rates in the range 1.6 to 2.0 cm^3/min. Rates were determined by plotting conversion vs. the inverse flow rate. The deviation from linearity in this plot is the combined experimental uncertainty and deviation from differential reactor behavior, and was used to calculate 95% confidence limits for the reaction rates.

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Table 1. Chlorinated Benzene and Phenol Hydrogenolysis Rates

Reactant	Conc. mol/L	Rates of Formation (mol/g cat·min)			
		Benzene	Chlorobenzene	Phenol	Chlorophenol
at 275°C					
Orthochlorophenol	2.75×10^{-2}	$3.6\pm0.4\times10^{-6}$	$8.1\pm0.4\times10^{-8}$	$9.2\pm0.2\times10^{-5}$	$-1.0\pm0.1\times10^{-4}$
Metachlorophenol	1.93×10^{-2}	$5.5\pm0.5\times10^{-7}$	$5.1\pm0.2\times10^{-7}$	$1.8\pm0.3\times10^{-4}$	$-1.8\pm0.3\times10^{-4}$
Parachlorophenol	3.97×10^{-2}	$6.6\pm0.4\times10^{-7}$	$1.5\pm0.1\times10^{-6}$	$5.4\pm0.4\times10^{-4}$	$-5.4\pm0.1\times10^{-4}$
Chlorobenzene	2.13×10^{-2}	$1.3\pm0.1\times10^{-4}$	$-1.3\pm0.1\times10^{-4}$		
Phenol	7.20×10^{-2}	$1.5\pm0.1\times10^{-5}$		$-1.5\pm0.1\times10^{-5}$	
at 250°C					
Orthochlorophenol	2.75×10^{-2}	—	$6.2\pm0.1\times10^{-7}$	$3.7\pm0.1\times10^{-5}$	$-3.9\pm0.2\times10^{-5}$
Metachlorophenol	1.93×10^{-2}	—	$5.1\pm0.2\times10^{-7}$	$4.8\pm0.5\times10^{-5}$	$-4.8\pm0.5\times10^{-5}$
Parachlorophenol	3.97×10^{-2}	—	—	$2.4\pm0.2\times10^{-4}$	$-2.6\pm0.9\times10^{-5}$
Chlorobenzene	2.13×10^{-2}	$4.1\pm0.1\times10^{-5}$	$-4.1\pm0.1\times10^{-5}$		
Phenol	7.20×10^{-2}	$4.4\pm0.1\times10^{-6}$		$-4.4\pm0.1\times10^{-6}$	
at 225°C					
Orthochlorophenol	2.75×10^{-2}	—	—	$1.8\pm0.1\times10^{-5}$	$-1.8\pm0.2\times10^{-5}$
Metachlorophenol	1.93×10^{-2}	—	—	$1.4\pm0.1\times10^{-5}$	$-1.4\pm0.1\times10^{-5}$
Parachlorophenol	3.97×10^{-2}	—	$1.1\pm0.1\times10^{-6}$	$7.6\pm0.9\times10^{-5}$	$-7.8\pm0.1\times10^{-5}$
Chlorobenzene	2.13×10^{-2}	$9.9\pm0.2\times10^{-6}$	$-9.9\pm0.2\times10^{-6}$		
Phenol	7.20×10^{-2}	$9.5\pm0.5\times10^{-7}$		$-9.5\pm0.5\times10^{-7}$	

Table 2. Chlorobenzene Hydrogenolysis Rates at 275°C with and without Phenol

Chlorobenzene Concentration mol/L	Phenol Concentration mol/L	Benzene Formation Rate mol/g cat·min	Chlorobenzene Formation Rate mol/g cat·min
2.13×10^{-2}	0	$1.3\pm0.1\times10^{-4}$	$-1.3\pm0.1\times10^{-4}$
6.84×10^{-2}	5.5×10^{-2}	$8.3\pm0.4\times10^{-5}$	$-8.3\pm0.4\times10^{-5}$

Results and Discussion

Table 1 lists the rates of dechlorination and deoxygenation for orthochlorophenol, metachlorophenol, parachlorophenol, chlorobenzene, and phenol. Table 2 lists the reaction rates observed for a mixed feed of chlorobenzene and phenol. In the tables, each row reports the product distributions from an experiment performed with the model compound named in the row. Negative rates denote the disappearance of reactants, while positive rates denote formation of products.

To determine rate constants from these data, we must assume a functional form for the rate expression. In a previous work (Hagh and Allen, 1990b), it was shown that for concentration ranges similar to those used in this work, the dechlorination rate of chlorobenzene can be assumed to be pseudo-first order in the concentration of chlorobenzene. The rate dependence on chlorine and hydrogen concentration can be very complex in other concentration regimes; however, in the concentration regimes used in this work, it should be reasonable to assume a pseudo-first order rate dependence. Competition for catalytic sites will be ignored since the concentrations of intermediates is relatively low. The pseudo-first-order rate constants at 275°C are reported in Figure 1.

Dechlorination rates for the chlorophenols are approximately two orders of magnitude greater than deoxygenation rates. The differences in dechlorination and deoxygenation rates can be rationalized based on the differences in bond dissociation energies. The reported bond dissociation energies of aromatic carbon to chlorine and aromatic carbon to oxygen are 406 kJ/mol and 469 kJ/mol, respectively (Sanderson, 1976).

The location of the oxygen functionality in chlorophenol influences the dechlorination rate substantially. In the case of orthochlorophenol, the dechlorination rate was reduced to roughly half that of chlorobenzene dechlorination rate at 275°C. For metachlorophenol and parachlorophenol, the presence of a hydroxyl group at the meta- and the paraposition led to approximately twofold and threefold increase in dechlorination reactivity, respectively, to that of chlorobenzene dechlorination activity. The dechlorination activities of chloro-

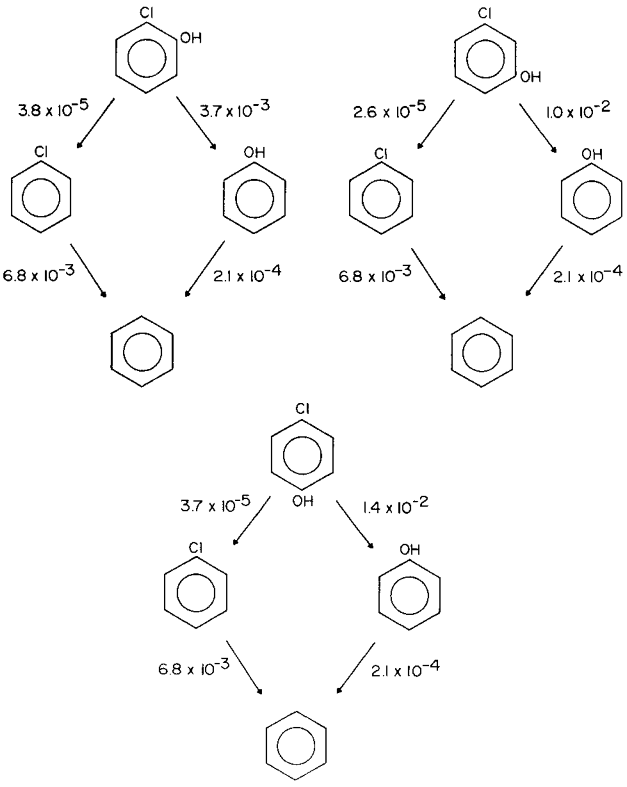

Figure 1. Hydroprocessing pathways and pseudo-first-order rate constants for chlorophenols.

Rate constants L/(g cat·min) at 275°C are reported.

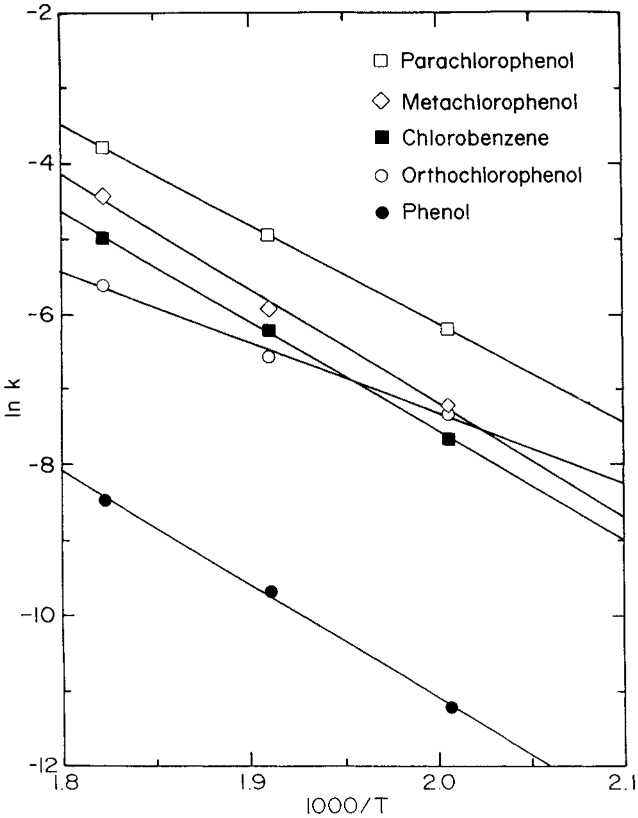

Figure 2. Temperature dependence of hydroprocessing rate constants.

k is the pseudo-first-order rate constant in units of L/(g cat · min).

phenols are therefore para > meta > ortho, with the hydroxyl group activating the dechlorination in the para- and metaposition and deactivating dechlorination in the orthoposition.

The increased dechlorination rate of parachlorophenol and metachlorophenol relative to the dechlorination of chlorobenzene is probably due to the electron-donating effect of the hydroxyl functionality. Parachlorophenol is more reactive than metachlorophenol, since the hydroxyl functionality is an ortho- and para-activating group. While the increased activity of the para- and metachlorophenol is due to an electronic effect, a steric effect is probably responsible for the reduced activity of orthochlorophenol relative to that of chlorobenzene. The low reactivity of the orthoposition has been observed in other studies. Odebunmi and Ollis (1983) have observed that in the hydrodeoxygenation of cresols, the orthocresols were less reactive than meta- and paracresols, although the methyl group found in cresols is an ortho- and para-activating functionality. Rollmann (1977) and Gates et al. (1979) have observed that the hydrogenolysis reactions of orthosubstituted aromatics were less reactive than meta- or parapositions. Odebunmi and Ollis (1983), Rollmann (1977), and Gates et al. (1979) have all postulated that the low reactivity of orthoposition is due to steric hindrance at this position.

Figure 2 shows the temperature dependence of the hydrodechlorination rates of orthochlorophenol, metachlorophenol, parachlorophenol and chlorobenzene and the hydrodeoxygenation rate of phenol over the range 225°C to 275°C. The apparent activation energies for orthochlorophenol, metachlorophenol, parachlorophenol, and chlorobenzene hydrodechlorination are approximately 80 kJ/mol, 109 kJ/mol, 126 kJ/mol, and 126 kJ/mol, respectively, while the apparent activation energy for hydrodeoxygenation of phenol is 126 kJ/mol. Odebunmi and Ollis (1983) have reported the activation energies of 96 kJ/mol, 113 kJ/mol, and 155 kJ/mol for the hydrodeoxygenation of ortho-, meta-, and paracresols, respectively. Thus, these results are in reasonable agreement with previous investigations.

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