

Production of Chloro and Dichlorobiphenyls, Terphenyls, and Triphenylenes
from Pyrolysis of Chloro and Dichloro-benzenes

Edward R. Ritter and Joseph W. Bozzelli,
Dept of Chemical Engineering and Chemistry, New Jersey Institute of Technology

ABSTRACT Pyrolysis reactions for chloro and m-dichloro benzene in hydrogen were studied between 1000 - 1300 K, with reagent loss and stable gas phase products monitored using on-line GC. Major products include solid carbon (soot - up to 50% of the carbon mass), benzene and HCl. GC/MS analyses on extracts from soot showed chlorinated PAH/poly-phenyl ring systems (C_{12} to C_{24}) which we explain by addition reactions as opposed to ring fragmentation paths. Rate constants obtained via Chemical Activation QRRK analyses on the various channels are developed for addition reactions which describe plausible pathways to these species.

EXPERIMENTAL: Reactions of chlorobenzene and m-dichlorobenzene in hydrogen were studied in separate experiments within a tubular flow reactor. experiments were carried out at 1 atmosphere total pressure over the temperature range 1073 - 1283 K. Residence times ranged from 0.02 - 2.5 seconds with flow conditions determined as in (1).

Reactor tubes were housed within a three zone (1.25 cm id) electrically heated tube furnace. Tight temperature control resulted in temperature profiles isothermal to within ± 5 K over 85-90% of the furnace length throughout the temperature range studied. Initial concentration of chlorinated aromatic was maintained at 0.4 mole percent with the balance hydrogen.

Reactants and stable products were quantified using on-line gas chromatography, Varian 3700, 25m x 0.32mm i.d. fused silica capillary column, methyl silicone stationary phase, automated cryofocussing (concentrator), flame ionization detection (FID), and integration with an SP 4270 integrator/plotter. Initial chloroaromatic FID peak area was obtained using a reactor bypass and was verified for each flow rate.

Products were identified by GC/Mass Spectrometry on batch samples of reactor gas collected into evacuated 25 ml stainless steel sample cylinders for later analysis.

Extracts were obtained from solid carbon deposits for GC/MS analyses.

Approximately 1 gram of particulate carbon was obtained from the reactor exit, mixed with 10 ml methylene chloride and placed in an ultrasonic bath for 5 minutes. The extract was then passed through a 0.5 μ m filter to remove particles. 2 μ l of extract was injected onto a 12m x 0.25mm i.d. capillary column. Mass spectra was obtained for several compounds in the molecular weight range 154-300 as shown in Figure 1. These compounds include biphenyl, chlorobiphenyl and dichlorobiphenyl in addition to chlorinated terphenyls and triphenylenes. We now examine addition pathways to formation of these products.

RESULTS: Bimolecular activated complex/QRRK analysis of Dean (2) was used to account for temperature and pressure effects on apparent rate constants. Addition reactions presented here and elsewhere(3,4,5) focus on likely pathways to species observed in soot extracts.

The initial reaction occurring when chlorobenzene is pyrolyzed is dissociation to phenyl radical + Cl, while m-dichlorobenzene dissociates to form m-chlorophenyl radical (m-C₆H₄Cl') + Cl. Both phenyl and m-C₆H₄Cl' additions to either chlorobenzene or m-dichlorobenzene will yield biphenyl, chlorobiphenyl, and dichlorobiphenyl products, passing through a substituted cyclohexadienyl intermediate. These systems have been discussed elsewhere (3,4,5).

Terphenyls result from subsequent additions to biphenyl species. Addition of m-C₆H₄Cl' to 3,3'-dichlorobiphenyl at a position of chlorine substitution (ipso attack) will result in rapid reaction to a dichlorinated meta-terphenyl by chlorine atom displacement. The energetics of this system favor loss of Cl (the low energy exit channel). Activated complex/QRRK calculations suggest that nearly 100% of collisions which form the energized complex, dissociate by loss of Cl.

Addition of m-C₆H₄Cl' at a position ortho to the phenyl/phenyl bond 3-chlorobiphenyl can produce a dichloroterphenyl by displacement of H atom. The carbon/carbon bond which is formed is stronger by about 5 kcal/mol than the carbon/hydrogen bond in the complex. As a result, some of this complex will dissociate by loss of H atom. The primary route of dissociation, however, is back to reactants as a result of the unfavorable entropy change for this reaction. Calculations show that greater than 47.5% of collisions forming the complex dissociate back to reactants, 52% are stabilized, and only 0.5% dissociate by loss of H atom to form dichlorinated o-terphenyl at 1000 K and 1 atm.

Ortho-terphenyl radicals may be produced by abstraction of an ortho hydrogen by Cl, H, or aryl radical. Conversion of o-terphenyl radical to triphenylene and H atom is a thermodynamically favorable isomerization. Similar to the previous example, the carbon/carbon bond formed in isomerization to the complex is stronger than the carbon/hydrogen bond which must be broken for reaction to products to occur. Calculations show that stabilization and reaction to form triphenylene plus H atom are nearly equal in importance while dissociation backwards to reactants has little importance at our conditions.

Temperature dependence of apparent rate constants obtained for these and other pathways to the observed products are summarized in Table I for hydrogen bath gas at 1 atm. total pressure.

TABLE I

rate constants valid from 800-1500 K for H ₂ bath gas at 1 atm total pressure	
chlorobenzene + m-C ₆ H ₄ Cl' <----> 3-chlorobiphenyl + Cl A = 1.8E+12 * T ^{-0.08} (cc/mol sec) Ea = 4.41 kcal/mol	
chlorobenzene + m-C ₆ H ₄ Cl' <----> 3,3'-dichlorobiphenyl + H A = 6.8E+60 * T ^{-14.0} (cc/mol sec) Ea = 38.7 kcal/mol	
m-dichlorobenzene + C ₆ H ₅ ' <----> 3-chlorobiphenyl + Cl A = 4.9E+12 * T ^{-0.11} (cc/mol sec) Ea = 4.5 kcal/mol	
m-dichlorobenzene + C ₆ H ₅ ' <----> 3,5-dichlorobiphenyl + H A = 2.6E+57 * T ^{-12.7} (cc/mol sec) Ea = 42.4 kcal/mol	
m-dichlorobenzene + m-C ₆ H ₄ Cl' <----> 3,3'-dichlorobiphenyl + Cl A = 4.1E+13 * T ^{-0.4} (cc/mol sec) Ea = 4.8 kcal/mol	
3,3'-dichlorobiphenyl + m-C ₆ H ₄ Cl' <----> m-dichloroterphenyl + Cl A = 5.7E+19 * T ^{-2.26} (cc/mol sec) Ea = 8.42 kcal/mol	
3-chlorobiphenyl + m-C ₆ H ₄ Cl' <----> o-dichloroterphenyl + H A = 7.1E+30 * T ^{-5.73} (cc/mol sec) Ea = 20.69 kcal/mol	
o-terphenyl radical <----> triphenylene + H A = 2.15E+37 * T ^{-7.62} (sec ⁻¹) Ea = 18.88 kcal/mol	
o-chloroterphenyl radical <----> chlorotriphenylene + H A = 1.5E+17 * T ^{-1.7} (sec ⁻¹) Ea = 8.3 kcal/mol	
o-dichloroterphenyl radical <----> dichlorotriphenylene + H A = 1.6E+18 * T ⁻² (sec ⁻¹) Ea = 8.9 kcal/mol	

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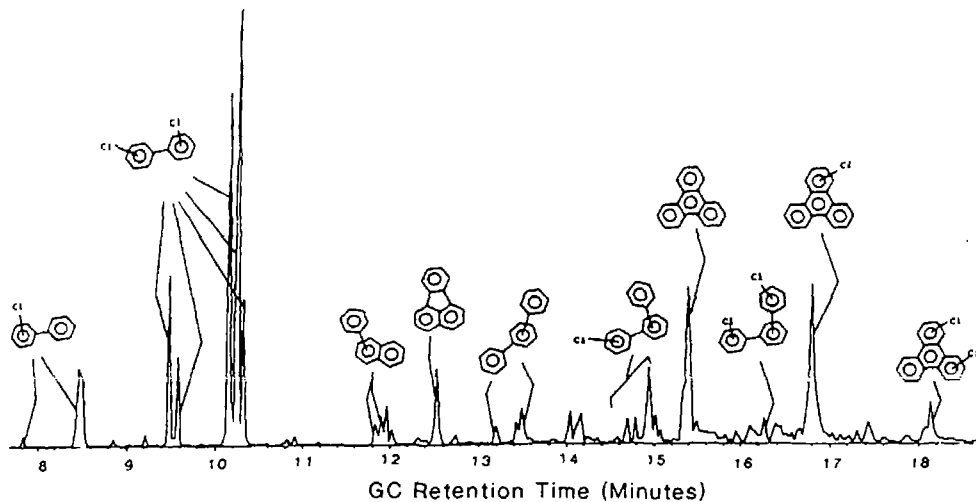


FIGURE 1 Total ion mass chromatogram for a methylene chloride extract of carbon solid deposits from reaction of $m\text{-C}_6\text{H}_4\text{Cl}_2$. Bonds drawn to the centers of aromatic rings denote substitution at an undetermined position.