Kinetic Study on Thermal Decomposition of Chlorobenzene Diluted in H₂

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Thermal reaction studies of dilute mixtures (0.37%) of chlorobenzene in hydrogen have been performed in tubular flow reactors at various surface to volume ratios and 1 atm total pressure. Residence times range from 0.02 to 2.5 s with temperatures between 1050 and 1275 K. HCl, benzene, and C (solids) are observed as the major products; minor products include methane, cyclopentadiene, toluene, naphthalene, and biphenyls. Chlorobenzene pyrolysis in helium yields significantly less conversion but more C (solids) for similar residence times. A detailed chemical mechanism is developed to describe this reaction system. Our modeling calculations incorporate Energized Complex QRRK analysis for accurate inclusion of temperature and pressure effects in radical addition reactions. This is a straightforward method to estimate rate constants and branching ratios as a function of both T and P. The detailed mechanism, based upon fundamental thermodynamic and kinetic principles, describes the overall reaction remarkably well. We also propose a plausible kinetic scheme describing formation of minor products. The experimental observations can be explained in terms of energized adduct formation, followed by unimolecular dissociation to low-energy exit channels. Phenyl and Cl radicals produced by the initial unimolecular decay of chlorobenzene react with H₂ to form benzene and HCl + H, respectively. Hydrogen atom addition to chlorobenzene via ipso attack, with subsequent loss of Cl from the energized complex, is required to explain the faster reaction in H₂ than He. QRRK rate constant analysis is presented for the following reaction systems, temperature range 300-1900 K, 10^{-3} to 1.0 atm, nitrogen and hydrogen bath + H.

Introduction

The chemistry and high-temperature reactions of chlorinated organic species are currently receiving significant attention due to the consistent observation of known or suspected toxic/carcinogenic chlorocarbons or chloro-oxy carbon species in effluent from waste and resource recovery incinerators.^{1,2}

Chuang and Bozzelli³ indicate that thermal reactions of chlorinated hydrocarbons in a hydrogen atmosphere may lead to complete conversion of alkyl chlorocarbon species to HCl and the hydrocarbon products acetylene and ethylene. Louw et al.⁴ in separate studies have further indicated that thermal reactions of chlorinated biphenyls with hydrogen may lead to detoxification of these species, producing nonchlorinated aromatics and HCl. Louw and his co-workers⁵⁻⁸ have performed thermal studies on a number of chloroaromatic reactions in the presence of hydrogen, postulating mechanistic pathways and some rate constants. One plausible low activation energy reaction path is the addition of a radical species, e.g. H atoms, to the aromatic ring (adduct formation) with subsequent rapid reaction of the adduct to new products, which serve to propagate a chain reaction e.g.

H + chlorobenzene ↔ [chlorocyclohexadienyl]* →

benzene + Cl

These reaction paths may be considered displacements, but do not occur on a single bond system where the outer shell of the

central atom is expanded. Instead they follow a scheme suggested by Benson and Shaw⁹ in a review of hydrogen atom reactions with propylene, benzene, toluene, and xylene where the data showed rapid reactions that could be explained within a factor of 10 by one rate constant. This rate constant, furthermore, remains nearly constant over order of magnitude variations in pressure and temperature. Benson and Shaw explained this observation in part by indicating that reactions such as

 $H + toluene \rightarrow CH_3 + benzene$

 $H + propylene \rightarrow CH_3 + ethylene$

were rapid and pointed out that the reactions could not be explained by abstraction reactions due to the high rate constants observed at lower temperatures. They further indicated, however, that stabilization should occur for any adducts that might be formed. An alternate explanation, which we advocate, when a low-energy exit channel such as displacement of methyl by H on an unsaturated hydrocarbon is present, is that unimolecular dissociation of the energized adduct is rapid and often occurs prior to any stabilization. The H atoms in the reviewed data⁹ were initially generated from unimolecular decomposition of the resonantly stabilized parent and the subsequent displacement reaction is exothermic. The ipso attack of H on the toluene carbon bonding the methyl group forms a C-H bond, which is stronger than this C_b-CH_3 bond and allows facile cleavage of the C-C single bond. Louw⁵ extended this reaction concept to the carbon chlorine bond system.

Tsang¹⁰ has recently reported a rate constant on the displacement reaction of H with chlorobenzene from shock tube studies between 1000 and 1100 K of $2.2 \times 10^{13} \exp(-9000)$ (cal/mol)/RT). He further indicates that displacement is the only significant pathway at temperatures included in his study.

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Figure 1. Experimental tubular flow reactor apparatus.



Figure 2. Reactor temperature profile: \Box , 1068 K; \diamond , 1149 K; \diamond , 1223 K; ∇ , 1273 K. Constant temperature zone (center 173/4 in.) + 5 °C.

Frenklach et al.¹¹ monitored soot formation from chlorobenzene reactions in shock tubes and showed that soot was produced at lower temperatures than occurred with benzene in pyrolysis type reactions strongly suggesting that the Cl on benzene accelerated the reaction to soot. Rao and Skinner,¹² on the other hand, studied reactions of chlorobenzene and benzene at low concentrations in shock tubes (1600–1900 K) by following atomic hydrogen concentration profiles and observed little difference in overall reaction for the two aromatic species. They concluded that little difference existed in the reaction rates of the two species.

One added complexity in reaction studies of Cl aromatics and a possible reason for chlorobenzene's acceleration of carbon (soot) formation is the role of Cl, a product in our reaction system. Here the rapid chain carrying or catalytic transfer process can take place

$$Cl + H_2 \rightarrow HCl + H$$

$H + ClBz \rightarrow Cl + Bz$

$H_2 + ClBz = HCl + Bz$ overall reaction

where abstraction by Cl has lower energies of activation than abstraction by carbon-containing radicals.

Earlier studies by Cullis and Manton¹³ on pyrolysis of chlorobenzene between 1043 and 1123 K indicated that aromatic ring rupture did not occur significantly in experiments below 1073 K where principal products were chlorobiphenyls, H_2 , and HCl. Loss of aromatic ring structure and production of vinyl chloride was, however, reported as the major pathway between 1103 and 1123 K while major products of chlorobiphenyls and HCl were again observed above 1123 K. Low concentrations of methane were also observed along with solid carbon or soot formation. Cullis and Manton also added hydrogen to the reaction system and observed significant acceleration of the reaction.





Figure 3. Experimental pseudo-first-order kinetics for C_6H_5Cl loss in hydrogen: \diamond , 1132 K; \bullet , 1177 K; \Box , 1198 K; \diamond , 1248 K; \circ , 1273 K.



Figure 4. Variation of observed first-order rate constant with reactor surface to volume ratio (S/V): \Box , 1148 K; +, 1177 K; \triangle , 1223 K; ×, 1248 K; ∇ , 1283 K.

We have elected to study and model the reactions of dilute mixtures of chlorobenzene in hydrogen and helium, at temperatures up to 1275 K in an attempt to understand and characterize the detailed reaction chemistry in these more straightforward three-element (hydrogen/carbon/chlorine) systems. We then plan to incorporate oxygen and to study combustion reactions of chloro aromatics.

Our modeling calculations incorporate the Energized Complex Quantum RRK analysis of Dean¹⁴ for accurate inclusion of temperature and pressure effects on radical addition reactions at our temperatures. Dean demonstrated the importance of chemical activation in high-temperature pyrolysis and oxidation systems and further studies^{15,16} have shown that this approach provides a reliable and straightforward method to estimate rate constants and branching ratios as a function of both T and P.

Our results indicate that complex formation and subsequent reaction to low-energy exit channels is necessary to explain the observed chlorobenzene decay kinetics. The rate constant we determine is in close agreement with the data reported by Tsang¹⁰ for the displacement reaction in this temperature regime. We also propose a plausible kinetic scheme to formation of the minor products, methane and cyclopentadiene, which are clearly observed in our study as well as those of Louw,⁵⁻⁸, and we follow some of the paths proposed by Louw.⁶⁸ We observe benzene and HCl as primary products along with carbon solids (soot) at longer reaction times.

Experimental Section

Reaction of chlorobenzene with hydrogen was carried out using the apparatus described in Figure 1. Reactions were studied at

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Figure 5. $C_6H_5Cl + H_2 \rightarrow$ products. C_6H_5Cl and product distribution vs reaction time for reaction at 1223 K: D, C₆H₅Cl; O, C₆H₆; Δ , carbon solids.



Figure 6. $C_6H_5Cl + H_2 \rightarrow$ products. C_6H_5Cl and product distribution vs temperature for 1-s reaction time: \Box , C₆H₅Cl; \diamond , C₆H₆; O, HCl; \triangle , carbon solids.



Figure 7. Effect of bath gas upon C₆H₅Cl decomposition at 1223 K and 1273 K. Comparison of hydrogen and helium as bath gases: \Box , H₂, +, He (1223 K data to right, 1273 K data to left).

1 atm total pressure with temperatures ranging from 1073 to 1283 K. Separate experiments were performed with quartz tubular reactors of 4, 10.5, and 16 mm i.d., residence time of 0.02-2.5 s, and flow conditions determined as in ref 17. Varying reactor surface to volume ratio (S/V) allows one to decouple apparent wall and bulk phase decomposition rates using a method based upon the work of Kaufman.¹⁸



Energy (Kcal/Mole)

Figure 8. Potential energy diagram for $H + C_6H_5Cl$ addition (ipso position). See Table I for rate parameters.

TABLE I: $C_6H_5Cl + H = [ClCHD^*]^{\#} = C_6H_6 + Cl$ (See Figure 8 for Potential Energy Diagram)^a

+			
k	A	Ea	source
1	1.5E+13	7.5	b
-1	3.6E+12	31.0	b
2	1.16E+13	8.9	с
			source
$\langle v \rangle = 1$	064/cm	· · · · · · · · · · · · · · · · · · ·	d
LJ para	meters		е
$\sigma = 5.6$	9Å e	k = 526.9 cal	

^a Units: A_1 , cm³/(mol s); A_{-1} and A_2 , s⁻¹; E_a , kcal/mol. ^b This work, reverse reaction (k-1) from thermodynamics. Based upon (ΔS) for $Cl + C_6H_6 = [Cl - CHD^{\circ}]$ with $A_{-2} = 2.0E+13 \text{ cm}^3/(\text{mol s})$. ^dGeometric mean frequency estimated as follows: $\langle v \rangle_{CI-CHD} = \langle v \rangle_{C_6H_5CI} + \langle v \rangle_{C_6H_7} - \langle v \rangle_{C_6H_6}$. ^eLennard Jones parameters for radical complexes are estimated by averaging two structurally similar molecules with mixing rules of Prausnitz (Molecular Thermodynamics of Fluid Phase Equilibria, Prentice-Hall: Englewood Cliffs, NJ, 1969). For example: $(\epsilon/K)_{\text{CHD}} = ((\epsilon/K)_{\text{benzene}}(\epsilon/K)_{\text{CHD}})^{1/2}$ and $\sigma_{\text{CHD}} =$ $(\sigma_{\text{benzene}} + \sigma_{\text{CHD}})/2$. Molecular L-J parameters are estimated by using the correlation of Tee, Gotoh, and Stewart (Ind. Eng. Chem. Fundam. 1966, 5, 363). Required critical property data tabulated in Reid, Prausnitz, and Sherwood (Properties of Gases and Liquids, 3rd ed.) or from Lydersen's group method for critical property estimation (also in Reid, Prausnitz, and Sherwood).

Chlorobenzene was reagent grade supplied by Aldrich Co. Hydrogen and helium gases were commercial grade supplied by Airdyne, Inc., and were filtered of O_2 , H_2O , and hydrocarbon impurities before entering the reactor system.

Reactor tubes were housed within a three-zone electric tube furnace. Temperture profiles were obtained by using a type K thermocouple probe moved axially within the 0.5 m length reactor. Thermocouple error caused by furnace wall radiation was minimized by providing a shield for sensor junctions; measurements were made with He (1-2 L/min) flowing through the reactor. Tight temperature control resulted in temperature profiles isothermal to within ± 5 K over 85-90% of the furnace length throughout the temperature range studied. Steep temperature gradients of 500 K in 5 cm occurred at the inlet and outlet of the reactor (see Figure 2). Uncertainty in absolute temperature measurements is estimated to be $\pm 1\%$ ($\pm 8-12$ K) but relative

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Figure 9. Potential energy diagram for $H + C_6H_6$ addition as evaluated in the QRRK-energized complex code. See Table II for rate parameters.



Figure 10. Isomerization sequence proposed for methylcyclopentadienyl radical formation and potential energy diagram.

temperatures are believed to be known to within ± 5 K. Hydrogen (or helium) was bubbled through 273 K liquid chlorobenzene at rates ranging from 50 to 4000 mL/min (STP). Sufficient contact time was allowed to ensure saturation of the gas (initial C₆H₅Cl mole fraction of 0.0037). The flow of the saturated vapor/gas mixture was manipulated to control the average residence time within the reactor by adjusting H₂/He flow.

Reactants and stable products were quantified by using on-line gas chromatography: Varian 3700, 25 m \times 0.32 mm i.d. fused silica capillary column, methyl silicone stationary phase, automated cryofocusing (concentrator), flame ionization detection, and integration by an SP 4270 integrator/plotter. Initial C₆H₅Cl peak area was obtained by using a reactor bypass (473 K) and was verified for each flow rate. All transfer lines were heated to 473 K to prevent condensation and suppress adsorption.

Quantitative analysis of HCl was performed for 1-s residence time. Reactor effluent was diverted through a bubbler train containing 0.01 M NaOH before being exhausted to a fume hood. The HCl produced was then calculated based upon titration of bubbler solution with 0.01 M HCl to its phenolphthalein end point.

Products were identified by GC/mass spectrometry (Kratos MS25, 50 m \times 0.22 mm i.d. methyl silicone stationary phase column) on batch samples of reactor gas drawn from the reactor exit into evacuated 25-mL stainless steel sample cylinders for later analysis.

Results

The reaction of chlorobenzene with hydrogen in excess was observed to follow pseudo-first-order kinetics throughout the temperature range studied (1025-1283 K). Figure 3 illustrates the first-order behavior obtained for several temperatures studied in a 10.5-mm reactor. Major products were benzene, HCl, and solid carbon.

Decomposition was most rapid within the 4 mm i.d. and slowest within the 16 mm i.d. reactor. This trend is expected since observed chlorobenzene loss may be the result of two parallel reaction paths, both contributing under our conditions. Clearly the relative importance of the wall reaction is greater when the surface to volume (S/V) ratio or relative extent of the wall surface is greater. The importance of wall reactions was found to drop as S/V was



Figure 11. $H + C_6H_6 \rightarrow$ products. Apparent rate constants as a function of pressure for addition at 1200 K: \Box , $[CHD^*]^0$; \triangle , $[MECPD^*]^0$; \diamond , linear C_6H_7 ; O, $[CHD^*]^* \rightarrow H + C_6H_6$. See Table III for QRRK results.

TABLE II: $C_6H_6 + H = [CHD^*]^{\#} = Products$ (See Figures 9 and 10 for Potential Energy Diagrams)^{*a*}

k	A	Ea	source	
1	4.0E+13	4.3	ь	
-1	1.53E+13	26.0	Ь	
2	2.0E+13	48.9	С	
3	5.0E+12	38.1	d	
-3	8.0E+11	40.0	d	
			source	
 $\langle v \rangle = 1$ LJ para	224/cm meters:		e f	
$\sigma = 5.40$) Å	e/k = 464.3 cal	2	

^a Units: A_1 , cm³/(mol s); A_{-1} and A_2 , s⁻¹; A_3 , s⁻¹; E_a , kcal/mol. ^b Tsang, W. J. Phys. Chem. **1986**, 90, 1152. ^c $E_a = \Delta H_f$: A factor for β scission taken as that for C=CCC*C=C = C=C* + C=CC=C. Dean, A. M. J. Phys. Chem. **1985**, 89, 4600. ^d $E_3 = \Delta H_f + 7.7$ kcal/mol. A_3 is estimated from the reverse reaction: bicyclo-C₆H₇ β scission to cyclohexadienyl radical (as in Figure 9). $A_{-3} = 10^{12.75}$ estimated from β scission for primary and secondary butyl radicals (Dean, A. M. J. Phys. Chem. **1985**, 89, 4600). E_3 is taken as the energy difference between [CHD*]⁰ and methylene cyclopentadienyl radical plus E_a for 1,2-hydrogen shift to methylcyclopentadienyl radical (see Figure 9). *Tsang, W. J. Phys. Chem. **1986**, 90, 1152. ^fSee note e in Table I.

reduced, with 16- and 10.5-mm reactors giving approximately the same results, but 4-mm reactors consistently showed higher conversion. Figure 4 demonstrates the effect of reactor diameter upon observed first-order rate constants for chlorobenzene loss at several temperatures. Data plotted here have been smoothed by fitting first-order rate data to an Arrhenius expression. Wall effects are characterized by the slope of these lines with the intercept estimating the bulk reaction rate. It is apparent that wall effects become very important at temperatures above about 1200 K for 4 mm i.d. reactors. These results are in agreement with the trends observed in previous studies at this laboratory.^{3,17}

Decoupling wall and bulk reaction rate constants can be achieved by using a linear relationship which assumes ideal plug flow behavior and is based upon the work of Kaufman,¹⁸ where observed experimental rate constants increase linearly as S/V is increased. Results of decoupling with the plug flow model are global rate constants for reaction in the homogeneous phase (k_b) and the heterogeneous wall reaction (k_w) . The Arrhenius expressions for k_b and k_w are as follows:

$$\ln (k_b \{L/s\}) = (23.15 \pm 0.96) - (54 \pm 2.26) \{kcal/mol\}/RT(K)$$

n
$$(k_w \{\text{cm/s}\}) =$$

(25.7 ± 0.78) - (62 ± 1.9) {kcal/mol}/RT(K)

with error bars determined from the scatter in the plot of k_{exp} vs S/V (2/R).

TABLE III: Apparent Reaction Rate Constants Predicted Using Bimolecular QRRK Analysis^d

bath gas	P, Torr	reaction	A factor, cm/(mol s)	n	$E_a,$ kcal/mol	range
Н,	7.6	$H + C_6 H_6 = [Me-CYPD^*]^0$	1.65E+55	-12.21	41.0	с
-	760.0		2.39E+27	-3.92	29.2	
	7.6	$H + C_6 H_6 = [CHD^*]^0$	2.79E+49	-11.55	13.59	
	760.0		4.87E+56	-12.73	26.8	
	7.6	$H + C_6 H_6 = lin - C_6 H_7$	7.96E+16	-0.88	28.8	a
	760.0		1.67E+21	-2.01	34.1	
N_{2}	7.6	$H + C_6 H_6 = [Me-CYPD^{\bullet}]^0$	1.05E+60	-13.66	43.2	с
2	760.0		5.22E+28	-4.35	28.8	b
	7.6	$H + C_6 H_6 = [CHD^{\bullet}]^0$	4.17E+46	-10.87	10.87	С
	760.0	0013	8.18E+57	-13.19	26.3	ь
	7.6	$H + C_6 H_6 = lin - C_6 H_7$	5.04E+16	-0.82	28.7	а
	760.0		9.47E+19	-1.68	32.5	

^a Valid from 300 to 1900 K. ^b Valid from 600 to 1900 K. ^c Valid from 900 to 1900 K. ^d $k = AT^n e^{-E_n/RT}$ (mol cm³ s).



Figure 12. (a) Potential energy diagram for $CH_3 + C_6H_6$ addition to form $C_6H_5CH_3 + H$. See Table IV for rate parameters. (b) Potential energy diagram for $CH_3 + C_6H_5Cl$ addition to form $C_6H_5 CH_3 + Cl$. See Table VI for rate parameters.

Figure 5 presents the normalized concentration of major products (HCl not included) as a function of average residence time, 1.6 cm i.d. reactor at 1223 K. The benzene yield rises consistently with time. It reaches an apparent steady-state value near 65% of the initial C_6H_5Cl after approximately 0.4 s. At this point, the C_6H_5Cl concentration has fallen to 10% of its initial value. The toluene concentration (not shown) rises from zero to an apparent steady-state value of 0.5%, the initial C_6H_5Cl concentration.

Nearly 30% the C_6H_5Cl initially present is lost to solid carbon (soot) formation. Solid carbon was estimated by difference after taking into account the relative response factors for the stable products which were measured by the GC (FID) and was obvious upon examination of the reactor tube and gas sampling filter. The propensity of chlorobenzene to form soot is well documented.¹¹ The C-Cl bond dissociation energy (97 kcal/mol, 298 K) is lower than that of C-H (113.5 kcal/mol),²³ leading to more rapid phenyl

TABLE IV: $C_6H_6 + CH_3 = [Me-CHD^*]^{\#} = C_6H_5CH_3 + H$ (See Figure 12a for Potential Energy Diagram)^a

	k	A	Ea	source	
	1	2.9E+12	11.1	Ь	
	-1	2.1E+14	22.8	b	
	2	2.7E+13	26.1	С	
				source	
$\langle v \rangle = 1200/\text{cm}$				d	
	LJ parameters			е	
	$\sigma = 5.74$	4 Å	e/k = 494 cal		

^aUnits: A_1 , cm³/(mol s); A_{-1} and E_a , kcal/mol. ^bTsang, W. J. *Phys. Chem.* **1986**, 90, 4159. Reverse reaction (k - 1) from thermodynamics. ^cBased upon (ΔS) for C₆H₅CH₃ + H = [Me-CHD[•]] with $A_{-2} = 1.2E+13$ (from footnote b). ^dGeometric mean frequency estimated as follows: $\langle v \rangle_{Me-CHD^*} = \langle v \rangle_{C_6H_5CH_3} + \langle v \rangle_{C_6H_7} - \langle v \rangle_{C_6H_6}$. ^eSee footnote e in Table I.

radical formation from C_6H_5Cl than C_6H_6 . In our system, C(s) was found in two distinct forms. Graphite-like deposits covered reactor walls in the high-temperature region, and particulate carbon (entrained by gas flow) was deposited in postreactor zones and sampling line filters. No carbon deposits were observed at the boundary of the flow tube high-temperature (reaction) and low-temperature (quenching) zones. This suggests that either particulate growth is occurring during quenching (radical loss and particle agglomeration) or particle settling occurs due to reduced flow velocities outside the reactor.

Minor products ($\leq 0.5\%$) observed in samples of the reactor gas include cyclopentadiene, toluene, dichlorobenzene, ethylene, methane, naphthalene, biphenyl, and chlorobiphenyl. Observations of products are in good agreement with previous studies.⁵⁻⁸

The distributions of major products formed at 1 s average residence time are presented as functions of temperature in Figure 6 for the 16-mm reactor. Benzene yield increases to approximately 65% the C₆H₅Cl initially present at 1223 K. Nearly 35% of C_6H_5Cl is converted to carbon. HCl yield per mole of C_6H_5Cl initially present is also shown. HCl yield rises steadily as temperature is increased. The maximum yield is about 82% and occurs at 1103 K. We do not feel that this incomplete Cl mass balance is a result of systematic error in the HCl measurement. The titration and its calibration are accurate to better than 1.0%. The reactor effluent was bubbled through a two-stage sampling train with standard NaOH solution in each stage, until an end point was reached in the first stage. The two solutions were then combined and back titrated with standard HCl to phenolphthalein end point. Complete mass balance for Cl is obtained for almost all lower temperature pyrolysis and oxidation studies on nonaromatic chlorohydrocarbons completed and ongoing in this lab.

We have looked for chlorine in the light $(C_1 \text{ and } C_2)$ hydrocarbons (FID GC, Carbosphere-G 2 mm × 2 m packed column, with excellent separation of al C_1 to C_3 hydrocarbons) and found none. It is possible that some chlorine exists in the carbon and adsorbed products at the reactor exit. Chlorine mass balance

TABLE V: Apparent Reaction Rate Constants Predicted Using Bimolecular QRRK Analysis

ł	oath gas	P, Torr	reaction	A factor, $cm^3/(mol s)$	n	$E_{a},$ kcal/mol	range
	H ₂	7.6	$CH_3 + C_6H_6 = [Me-CHd^*]^0$	6.64E+29	-6.93	-4.8	С
	4	760.0		1.49E+57	-13.84	28.3	b
		7.6	$CH_{1} + C_{6}H_{6} = C_{6}H_{3}CH_{1} + H$	6.22E+15	-1.20	17.1	а
		760.0	5 0 0 0 0 0	3.41E+26	-4.15	26.4	Ь
	N_2	7.6	$CH_3 + C_6H_6 = [ME-CHD^*]^0$	1.59E+27	-6.29	2.8	С
1.2	760.0	5 6 6 6	5.30E+48	-11.60	21.2	С	
		7.6	$CH_3 + C_6H_6 = C_6H_5CH_3 + H$	4.56E+14	-0.88	16.3	а
		760.0		8.65E+23	-3.44	24.1	b

"Valid from 300 to 1900 K. "Valid from 600 to 1900 K. "Valid from 900 to 1900 K.

TABLE VI: $C_6H_5Cl + CH_3 = [Me-Cl-CHD^*]^\# = C_6H_5CH_3 + Cl$ (See Figure 12b for Potential Energy Diagram)^{*a*}

k	A	Ε.	source
1	1 A5E±12	<u> </u>	h
-1	8.54E+12	26.5	b
2	5.6E+13	11.1	с
	······································	sc	ource
	$\langle v \rangle = 1070/\text{cm}$		d
	LJ parameters		е
	$\sigma = 5.99 \text{ Å}$		
	e/k = 548 cal		

^{*a*}Units: A_1 , cm³/(mol s); A_{-1} and A_2 , s⁻¹; E_a , kcal/mol. ^{*b*}A factor taken as ¹/₂ that for CH₃ + C₆H₆ (Table IIIa). Reverse reaction (k - 1) from thermodynamics. ^{*c*}Based upon (Δ S) for C₆H₅CH₃ + Cl = [Me-Cl-CHD⁻] with $A_{-2} = 1.0E+12(b)$. ^{*d*}Geometric mean frequency estimated as follows: $\langle v \rangle_{Me-Cl-CHD} = \langle v \rangle_{Me-CHD} + \langle v \rangle_{C_6H_5}Cl - \langle v \rangle_{C_6H_6}$ ^{*c*}See footnote e in Table I.

continues to be a problem and we are trying to develop methods to accurately quantitate Cl in milligram quantities of these solids. We cannot exclude these solids as a possible source of the Cl loss at this time.

Mass spectral analyses of solids (soot) from the reactor exit show only trace levels of high molecular weight chlorinated compounds (chloro- and dichlorobiphenyl) are present. It is felt that these accumulated in the carbon black by adsorption after a period of time. In addition, other compounds in the molecular weight range 228-380 were present. These are believed to be several PAH and chlorinated PAH (such as triphenylene and chlorotriphenylene) which result from phenyl polymerization reactions and are not more highly chlorinated PCB's.

A limited number of experiments were performed to examine C_6H_5Cl decomposition in a helium atmosphere under conditions similar to the hydrodechlorination studies. A comparison of these results is made in Figure 7, although we did not collect sufficient data to perform a rigorous kinetic analysis on pyrolysis in He. As shown in Figure 7, the presence of molecular hydrogen was found to greatly accelerate C_6H_5Cl decomposition. This was accompanied by accelerated formation of benzene, while in contrast, polyphenyl and soot formation was significantly reduced, although polymerization is not eliminated. If present, hydrogen plays a key role in C_6H_5Cl decomposition.

Kinetic Modeling Results and Discussion

Energized Complex/QRRK Theory as presented by Dean¹⁴ was used for modeling of reactions where a chemically activated adduct is formed. Calculations are based upon a geometric mean frequency $\langle v \rangle$. The algorithm presented by Dean was somewhat modified, however. Gamma function evaluations have replaced factorials for evaluation of the energy-dependent terms. Barriers (E_a/hv) are not rounded to the nearest integer before summations with respect to energy, so these summations are not forced to stop at integer values of energy (E_i/hv) . This is believed to give better estimates, especially at low temperatures where small changes in barrier height can have a large effect.

The mechanistic considerations in this paper make use of chemical activation principles for reactions involving atom or radical addition to an unsaturated bond and for atom + radical or radical + radical combination reactions. Consider the addition of two species, A and B, to form a chemically activated complex AB[#], which has energy equal to the sum of the thermal energies of A and B plus the bond energy from adduct formation. This chemically activated adduct AB[#] can now undergo the following reactions: (i) reaction to new products; (ii) stabilizing collisions to form AB⁰; (iii) back reaction to initial reagents A + B.

$$A + B \xrightarrow[k_{-1}]{k_{1}} AB^{\#} \xrightarrow{k_{2}} C + D$$
$$\downarrow k_{\text{stab}}$$
$$AB^{\circ}$$

The Quantum RRK chemical activation treatment provides apparent reaction rate constants k_{rxn} to products C + D and k_{stab} to AB⁰. The unimolecular reaction of AB⁰ to C + D is incorporated into the mechanism separately with consideration for falloff.¹⁴ (The channel AB⁰ \rightarrow A + B is included as the reverse of k_{stab}).

This approach can be compared to a more conventional thermal equilibrium analysis of the above system, which would consider the reaction as

$$A + B \stackrel{k_1}{\leftrightarrow} AB \stackrel{k_2}{\longrightarrow} C + D$$

For conditions of steady state

$$(AB)_{ss} = k_1[A][B]/(k_{-1} + k_2)$$

$$\frac{d([C] + [D])}{dt} = \frac{k_2 k_1 [A] [B]}{(k_{-1} + k_2)} = k_2 K_{eq} [A] [B]$$

in the limit that $k_{-1} \gg k_2$ and where K_{eq} is the equilibrium constant $K_{eq} = [AB]/([A][B])$

We will show that there can be substantial differences in the computed rate formation of C + D, depending upon whether one uses a thermal or chemical activation approach. The two approaches only become equivalent at the high-pressure limit, where all of the AB[#] is stabilized prior to reaction. An important finding is that the pressure required for this complete stabilization varies dramatically with temperature.¹⁴ As a result, we find that chemical activation is important in this chlorobenzene/hydrogen system at temperatures 1100–1300 K and pressures of 1 atm. Furthermore, the chemical activation approach becomes significantly more important as the temperature is increased.

We feel that the concept of energized complex formation and consideration of its stabilization, forward and reverse reaction channels, is a more accurate way to both view and treat the reaction process. We include microreversibility for all reactions in our mechanism so equilibrium can be established for any reaction should the necessary conditions exist.

The initial reaction occurring is chlorobenzene dissociation to phenyl radical + Cl. These initial products will both react rapidly with H_2 (if present) to generate benzene and HCl in addition to reactive H atoms. Hydrogen atom addition to the Cl carbon in chlorobenzene (ipso position) forms an energized complex and results in rapid dissociation of the adduct to benzene plus Cl, the low-energy exit channel (see Figure 8). This addition reaction is believed to be a major pathway for the hydrodechlorination of chlorobenzene to form benzene and HCl under our conditions (H_2

TABLE VII: Apparent Reaction Rate Constants Predicted Using Bimolecular QRRK Analysis

bath gas	P, Torr	reaction	A factor, $cm^3/(mol s)$	n	$E_{a},$ kcal/mol	range
H ₂	7.6	$CH_3 + C_6H_5Cl = [ME-Cl-CHD^{\bullet}]^0$	5.91E+25	-5.78	13.5	a
-	760.0		1.98E+28	-5.93	13.9	
	7.6	$CH_3 + C_6H_5Cl = C_6H_5CH_3 + Cl$	5.15E+13	-0.49	11.6	
	760.0		1.96E+14	-0.65	12.0	
N_2	7.6	$CH_3 + C_6H_5Cl = [Me-Cl-CHD^{\bullet}]^0$	2.31E+25	-5.76	13.5	
-	760.0		4.17E+27	-5.83	13.7	
	7.6	$CH_{3} + C_{6}H_{5}Cl = C_{6}H_{5}CH_{3} + Cl$	5.11E+13	-0.49	11.6	
	760.0		9.80E+13	-0.53	11.8	

"Valid from 300 to 1900 K.



Figure 13. Potential energy diagram for $C_6H_5^* + C_6H_5Cl$ addition to form biphenyl + Cl. See Table VIII for rate parameters.



Figure 14. Potential energy diagram for $C_6H_5^* + C_6H_5Cl$ addition to form chlorobiphenyl + H. See Table X for rate parameters.

in excess). Virtually every energized complex formed by this addition decomposes to $C_6H_6 + Cl$, because the exit barrier is so small. This is an example where the rate constant has virtually no pressure dependence, even though the process is not an elementary reaction. Parameters used in these calculations appear in Table I. The apparent rate constant for reaction to benzene + Cl is, therefore, just the rate constant for formation of the adduct, or $1.5 \times 10^{13} \exp(-7500 \text{ (cal/mol)}/RT)$.

Atomic H will add to benzene to form cyclohexadienyl radicals (CHD[•])* as shown in Figures 9 and 10. Also shown are some of the subsequent reactions of this radical. The CHD[•] complex is initially "hot" since, in addition to the thermal energy, it contains energy resulting from formation of the new chemical bond. Prior to stabilization it may unimolecularly isomerize through a bicyclo intermediate to a cyclopentadiene methyl radical (CpdMe[•]), which can abstract H from H_2 , undergo a hydrogen shift to a resonantly stabilized methyl cyclopentadienyl radical (MeCpd[•]) or β scission to either fulvene + H or back to CHD radical. The energetics for these isomerizations are significantly less than ring opening reaction to linear C_6H_7 as shown in Figure 9. Calculations for ring opening to linear C_6H_7 show that the energy requirement limits this path to less than 0.01% of collisions which form cyclohexadienyl radical complex at our conditions. This channel has been omitted from our reaction mechanism since it was not

TABLE VIII: $C_6H_5CI + C_6H_5 = [Ph-Cl-CHD^*]^{\#} = C_6H_5C_6H_5 + Cl$ (See Figure 13 for Potential Energy Diagram)^{*a*}

k	A	Ea	source
1	1.0E+12	4.3	Ь
-1	1.6E+15	33.2	b
2	1.9E+14	10.0	С
			source
$\langle v \rangle = 975/cm$			d
LJ parameters			е
$\sigma = 6.66 \text{ Å}$		e/k = 694 cal	

^a Units: A_1 , cm³/(mol s); A_{-1} and A_2 , s⁻¹; E_a , kcal/mol. ^b Louw, R.; Dijks, J. H.; Mulder, P. J. Chem. Soc., Perkin Trans. 2 1973, 40, 1635. ^cA factor based upon entropy change for reverse. Cl + Ph-Ph = [Ph-Cl-CHd[•]] (ipso attack) with $A_{-2} = 1.2E+13$ and $E_{-2} = 2.0$ kcal/mol. ^d Geometric mean frequency estimated as follows: $\langle v \rangle_{Ph-Cl-CHD•} = \langle v \rangle_{Ph-Ph} + \langle v \rangle_{Cl-CHD•} - \langle v \rangle_{C_6H_6}$. ^eSee footnote *e* in Table I.

observed to play a significant role. However at temperatures near 2000 K, this channel may become more significant.

Methane probably arises from further reactions of methylcyclopentadiene and MeCpd[•] radical. Both unimolecular dissociation of MeCpd and H addition to MeCpd[•] yield methyl + cyclopentadiene radicals, with the methyl reacting with H₂ to form the CH₄. A similar scheme has been proposed by Louw et al. to account for the methane observed in their study.⁷

A QRRK analysis of the chemically activated system, using generic or literature values for high-pressure rate constants¹² and species thermodynamic properties for the reaction sequence, yields the apparent rate constants shown in Figure 11. Rate parameters used in these calculations are summarized in Table II, with results in Table III. Dissociation of the complex back to reactants (no reaction) clearly dominates and is consistent with work of Skinner.^{12,19} The isomerization channel, however, may result in MeCpd[•] for slightly more than 0.1% of collisions which create the CHD[•] complex at 1200 K and 1 atm pressure. Analysis predicts that direct production of MeCpd* will be favored at lower pressures. At higher pressures (above 760 Torr) the stabilized CHD[•] species are predominant and require additional collisions to make MeCpd[•] or revert to initial reagents. Although our calculations predict that isomerizations will occur to form stabilized MeCypd[•], the reverse reaction is also rapid due to a low-energy barrier so that only a small steady-state concentration will exist in equilibrium with the CHD radical and $C_6H_6 + H$.

We can use this reaction to compare the results of the chemical activation QRRK calculations with those where the products are calculated from thermal activation. Consider

$$H + C_6H_6 \leftrightarrow CyC_6H_7 \qquad K_{eq}$$
$$CyC_6H_7 \rightarrow linC_6H_7 \qquad k_d$$

where the $linC_6H_7$ would unimolecularly decompose to acetylene and butadienyl radical. The butadienyl radical would further decompose to acetylene plus vinyl.

For the thermal calculation we assume the equilibrium

$$H + C_6H_6 \leftrightarrow CyC_6H_7$$

or
$$k_{-1} \gg k_2$$
 from the earlier discussion

$$K_{eq} = [CyC_6H_7]/[H][C_6H_6]$$

TABLE IX: Apparent Reaction Rate Constants Predicted Using Bimolecular QRRK Analysis

H ₂ 7.6 $C_6H_5 + C_6H_5CI = [Ph-CI-CHD^{-}]^0$ 4.45E+22 -5.06 5.7	(
760.0 7.97E+24 -5.13 5.87	
7.6 $C_6H_5 + C_6H_5Cl = C_6H_5C_6H_5 + Cl$ 9.85E+11 0.0 4.29	
2.59E+12 -0.12 4.53	
N ₂ 7.6 $C_6H_5 + C_6H_5Cl = [Ph-Cl-CHD^*]^0$ 1.68E+22 -5.03 5.7	
760.0 2.17E+24 -5.06 5.79	
7.6 $C_6H_5 + C_6H_5C_1 = C_6H_5C_6H_5 + C_1$ 9.85E+11 0.0 4.29	
760.0 1.0E+12 0.0 4.32	

^a Valid from 300 to 1900 K.

TABLE X: $C_6H_5Cl + C_6H_5 = [Ph-Cl-ChD^*]^{\#} = C_6H_5C_6H_4Cl + H$ (See Figure 14 for Potential Energy Diagram)^{*a*}

k	A	Ea	source
1	2.0E+12	4.3	a
-1	2.2E+15	32.74	а
2	6.7E+13	24.5	b
			source
$\langle v \rangle =$	975/cm		d
LJ par	ameters		е
$\sigma = 6.0$	56 Å	e/k = 694 cal	

^aUnits: A_1 , cm³/(mol s); A_{-1} and A_2 , s⁻¹; E_a , kcal/mol. ^bLouw, R.; Dijks, J. H.; Mulder, P. J. Chem. Soc., Perkin Trans. 2 1973, 40, 1635. Reverse reaction (k - 1) from thermodynamics. ^cA factor based upon entropy change for reverse. H + Cl-Ph-Ph = [Cl-Ph-CHD[•]] with $A_{-2} = 1.3E+13$ and $E_{-2} = 4.0$ kcal/mol. ^dGeometric mean frequency estimated as follows: $\langle v \rangle_{Ph-Cl-CH•} = \langle v \rangle_{Ph-Ph} + \langle v \rangle_{Cl-CHD•} - \langle v \rangle_{CeH6•}$. ^eSee footnote e in Table I.

then $[CyC_6H_7] = K_{eq}[H][C_6H_6]$ and with the rate constant for production of $linC_6H_7$ from above

$$d[linC_{6}H_{7}]/dt = k_{d}K_{eq}[H][C_{6}H_{7}] = k_{therm}[H][C_{6}H_{7}]$$

with k_{therm} the thermal bimolecular rate constant.

We calculate k_d at 1200 K and 1 atm with the energetics and rate constants illustrated in Figure 9 and Table II as 4.5×10^3 , 19% of the high-pressure limit 2.4×10^4 . Other dissociation channels, forward to products and back to reactants, were also considered in the calculation of k_d . Combining this with an equilibrium constant of 2.18×10^4 yields a value for k_{therm} of 9.8 $\times 10^7$ cm³/(mol s) for production of linC₆H₇. The QRRK analysis at these same conditions yields a chemically activated rate constant of 6.4×10^8 , 6.5 times faster than the thermal calculation result. This demonstrates the importance of these reactions involving energized adducts at high temperatures, prior to their collisional stabilization, even at pressures as high as 1 atm.

Toluene may be formed by methyl addition at the ipso position in chlorobenzene followed by rapid loss of Cl from the complex (Figure 12b). Methyl addition to benzene would not be as important in this system since the C-H bond in MeCHD[•] is nearly 10 kcal/mol stronger than C_{benzene}-CH₃ (Figure 12a). Methylcyclohexadienyl radical will dissociate back to CH₃ + C₆H₆ reactants at our conditions. We estimate the reaction of methyl radical with chlorobenzene forms toluene 10 times faster than addition of methyl to benzene. The high-pressure A factors and barriers are listed in Tables IV and VI, with results tabulated in Tables V and VII. While it is clear from Figure 12 that enthalpy favors reaction of CH₃ + C₆H₅Cl to produce Cl + toluene, close analysis shows that entropy counters this effect to some extent.

The reaction of methyl radicals with benzene to form toluene plus H atoms through the $MeCyC_6H_6$ (methylcyclohexadienyl radical) intermediate provides another comparison between chemical and thermal activation

$$CH_3 + C_6H_6 \leftrightarrow MeCyC_6H_6 \rightarrow H + MeCyC_6H_5$$
 (toluene)

The equilibrium constant for methyl plus benzene to $MeCyC_6H_6$ is calculated as 2.5 at 1200 K. The rate constant for dissociation of $MeCyC_6H_6$ to toluene + H is calculated as 3.2×10^7 , 7% of the high-pressure limit 4.9×10^8 . Initial input data for the unimolecular dissociation of $MeCyC_6H_6$ are illustrated in Figure 12 and Table IV. These data yield a value of k_{therm} to H + toluene of 7.9 × 10⁷ cm³/(mol s). The chemical activation apparent rate constant from the energized complex calculation at 1200 K and 1 atm pressure is 1.04×10^9 cm³/(mol s), 13 times the result obtained assuming equilibrium with the thermally stabilized adduct.

Phenyl radical addition to either chlorobenzene or benzene will yield some biphenyl product, again going through a substituted cyclohexadienyl intermediate, shown in Figures 13 and 14. Calculations show that more than 90% of the collisions result in biphenyl + Cl for phenyl addition to the chlorobenzene ipso position at 1 atm pressure with H_2 bath gas. This appears to be a primary route to biphenyl production in this system. Phenyl addition at C-H positions in benzene or chlorobenzene results in nearly equal amounts of stabilized intermediate and the biphenyl or chlorobiphenyl + H products. While dissociation of the complex is again important, the QRRK calculations show 20% of the phenyl + benzene collisions dissociate to biphenyl + H products at 1200 K and 1 atm. A similar result was obtained for phenyl + chlorobenzene (for all positions except ipso addition). Rate parameters used in the calculations in addition to results are summarized in Tables VIII-XIII. It is noteworthy that our calculation for the reaction of phenyl radical + benzene to give biphenyl + H, 6.7 \times 10¹⁰, is in excellent agreement with results recently published by Stein²¹ (6.0 \pm 2) \times 10¹⁰ cm³/(mol s).

Lowering the heat of formation for the phenyl radical to 78.6 kcal/mol, the value recommended by McMillen and Golden,²² versus 81.4 kcal/mol determined by Tsang²³ (used throughout this study), will lower the entrance barrier relative to the exit barrier for phenyl attack on chlorobenzene (non ipso); cf. Figure 14. The effect of this change is to lower both the stabilization and the chlorobiphenyl + H product channel formation rates by 30% and 47%, respectively, at 1200 K and 1 atm. This effect is much less significant where there is a larger difference in the two exit channels for the energized complex, for example, addition of H or methyl radical to chlorobenzene, Figures 8 and 12, respectively.

We feel it important to note that improvements in accuracy of the thermodynamic properties for these molecules are critical to improvements in our thermochemical based reaction mechanisms. A listing of thermochemical data used in this study is included in Table XV.

We have developed a detailed reaction mechanism for chlorobenzene pyrolysis in hydrogen which appears in Table XIV. Elementary reaction rate parameters for abstraction reactions are based upon literature comparison, thermodynamic estimations, and transition state theory methods of Benson.²⁰ QRRK calculations, as described above, were used to estimate apparent rate parameters for addition and dissociation reactions (1 atm).

Experimental pyrolysis data are compared with model predictions in Figures 15 and 16 for chlorobenzene decomposition at 1126 and 1177 K in H₂. Predictions for chlorobenzene loss match experiment well. Prediction of benzene formation, on the other hand, is not quite as good except at low conversions (<50%) where significant soot formation has not yet occurred. Figure 17 compares predicted and experimental C₆H₅Cl decay curves as functions of residence time for several temperatures. Our model (Table XIV) is a first-principles description of the C₆H₅Cl chain decomposition, and we feel predictions shown are quite acceptable.

TABLE XI: Apparent Reaction Rate Constants Predicted Using Bimolecular QRRK Analysis

bath gas	P, Torr	reaction	A factor, $cm^3/(mol s)$	n	$E_a,$ kcal/mol	range
Н,	7.6	$C_6H_5 + C_6H_5Cl = [Ph-Cl-CHD^*]^0$	6.82E+47	-12.12	6.62	a
-	760.0	•••••	2.80E+69	-17.31	29.2	b
	7.6	$C_6H_5 + C_6H_5Cl = C_6H_5C_6H_4Cl + H$	9.52E+19	-2.51	7.08	а
	760.0		4.50E+49	-10.65	33.3	ь
N_2	7.6	$C_6H_5 + C_6H_5Cl = [Ph-Cl-CHD^{\circ}]^{\circ}$	3.34E+42	-10.76	2.36	а
-	760.0	•••••	5.42E+72	-18.39	29.94	ь
	7.6	$C_6H_5 + C_6H_5Cl = C_6H_5C_6H_4Cl + H$	3.43E+32	-6.04	15.97	
	76.0	• • • • • • • • •	4.50E+49	-10.65	31.95	

"Valid from 900 to 1900 K. "Valid from 600 to 1900 K.

TABLE XII: $C_6H_6 + C_6H_5 = [Ph-CHD^*]^{\#} = C_6H_5C_6H_5 + H^a$

	k	A	Ea	source	
	1	2.0E+12	4.3	Ь	_
	-1	3.9E+14	29.4	b	
	2	1.1E+13	23.55	с	
				source	_
·	$\langle v \rangle = 1050/cm$ LJ parameters			d	
				е	
	$\sigma = 6.4$	5 Å	e/k = 662 cal		

^a Units: A_1 , cm³/(mol s); A_{-1} and A_2 , s⁻¹; E_a , kcal/mol. ^b Louw, R.; Dijks, J. H.; Mulder, P. J. Chem. Soc., Perkin Trans. 2 1973, 40, 1635. Reverse reaction (k - 1) from thermodynamics. ^cA factor based upon entropy change for reverse. H + Ph-Ph = [Ph-CHD[•]] with $A_{-2} = 2.0E+13$ and $E_{-2} = 4.0$ kcal/mol. ^dGeometric mean frequency estimated as follows: $\langle v \rangle_{Ph-CHC} = \langle v \rangle_{Ph-Ph} + \langle v \rangle_{CHD} - \langle v \rangle_{C_6H_6}$. See footnote e in Table I.

Rate parameters for several reactions appearing in Table XIV were varied over small intervals to give a better fit of our experimental data on both chlorobenzene and dichlorobenzene reactions in hydrogen (a discussion of pyrolysis of dichlorobenzene is beyond the scope of this paper). Optimization was performed primarily on three reactions. For example, the A factor for chlorobenzene dissociation to phenyl radical and chlorine atom was set at 3.0E+15. This yields a reasonable value for A_{-1} of 9.612, with activation energy ($E_1 = 97.5 \text{ kcal/mol}$ at 298 K). The high-pressure A factor for hydrogen atom addition to chlorobenzene's ipso position ($A_{16} = 1.5E+13$) was taken as being between 6.0E+12 and 2.2E+13 (with E_a between 4.5 and 9.0 kcal/mol); upper limit values are those of Tsang.¹⁰ Abstraction of hydrogen from H₂ by phenyl radical was assumed to have an activation energy E_a between 6.0 and 9.5 kcal/mol.²⁹ The A factor for this abstraction was estimated as 2.0E+13. These reactions along with the H atom combination $H + H + M = H_2 + M$ were found to have the greatest influence (sensitivity) on predictions by the model.

Sensitivity analysis indicates that H atom recombination is the second most important reaction affecting the concentrations of chlorobenzene and benzene in the system. Manion et al.⁸ (and references cited therein) have indicated that the recombination of hydrogen on the walls is efficient and that H recombination is probably in equilibrium. Changing this recombination rate in our mechanism clearly indicated that we did not have the H in thermal equilibrium with H₂. To achieve equilibrium in the model, we needed to increase the H atom recombination rate to greater than 5.0E19. This slowed the chlorobenzene decomposition dramatically, to a point where we could not match our data with realistic rate constants. Recombination rate constants in the range of $10^{17}-10^{18}$, which are ca. 1 order of magnitude greater than typical reported homogeneous k's, did permit fitting of our data for both chlorobenzene and dichlorobenzene experiments (rate constants consistent in both mechanisms).

The ratio of H atom concentration relative to equilibrium H concentration $[H]/[H]_{eq}$ is a function of both time and temperature throughout the reaction. At lower temperatures, slower reaction, [H] is above [H]_{eq} throughout the entire experimental time (2 s), while at higher temperatures where conversion is nearly complete in a short length of reactor [H] approaches [H]_{eq} (ratios ca. 1.3) at times longer than that required for near complete conversion. The maximum or peak H atom concentrations predicted by our kinetic model can be compared with equilibrium H atom concentrations. The peak [H] is always greater than $[H]_{eq}$. The ratio $[H]_{max}/[H]_{eq}$ ranged from 2.46 at 1225 K and 12 ms to 3.52 at 1000 K and 900 ms.

A question then arises. Can we assume equilibrium and a higher displacement rate constant k_{16} to explain our results? Using a rate constant k_{16} which is 2 times higher than our recommended value and $[H]/[H_2]$ in equilibrium predicts a chlorobenzene concentration more than 2 times higher than that observed. We do not feel it is reasonable to use a rate constant larger than this and conclude that an equilibrium H atom concentration will not explain the rapid reaction which is observed. In addition, the results for our dichlorobenzene experiments and model (manuscript in preparation), where the current model is a required subset, yield $[H]_{max}/[H]_{eq}$ which range from 6.38 at 1000 K and 0.360 s to 4.05 at 1225 K and 4 ms, which further suggests that H atom is not in equilibrium with H_2 .

The rate constant with highest sensitivity in the mechanism to chlorobenzene and benzene concentrations is the unimolecular decomposition of chlorobenzene, a chain branching reaction. We report a best fit of the data with an A factor of 1.0E15 and an $E_{\rm a}$ of 95.5 in the temperature range of the experiment. The reaction with third highest sensitivity to the above species is H atom displacement of chlorine atoms. We report a best fit to our data with a rate constant slightly faster than 2.2E13 exp(-9 (kcal/mol)/RT reported by Tsang¹⁰ with a value of 1.5E13 exp(-7.5 (kcal/mol)/RT). While we could not fit the experimental data on chlorobenzene and dichlorobenzene with the reported rate constants of Tsang, we note that these numbers are very similar in the same temperature range; we have a slightly lower A and E_a , changes which are nearly offsetting.

A fourth reaction which is important in this mechanism is the abstraction of H from H_2 by phenyl radicals. We use an A factor of 2.0E13 and an E_a of 9.0 kcal/mol. The only references to this abstraction reaction are those of Fielding and Prichard²⁴ and Duncan²⁵ who both report an E_a of 6 kcal/mol, but Stein and Fahr²⁶ indicate that there is some inconsistency in the two reported rate constants, i.e. a factor of 4 difference when referenced to the one common reagent, methane, and indicate that the E_a is probably not well-known. Lowering the E_a for this reaction speeds up the reaction slightly.

It is our objective to present a detailed mechanism that is thermochemically realistic and that models chlorobenzene decay. We do not wish to convey that the rate constants are all absolutely correct, but that each k is reasonable in the realm of current thermochemical kinetics.

At the higher conversions, where we overpredict benzene, it should be noted that solid carbon is a significant fraction of product (ca. 30%) and that the present mechanism makes no attempt to account for this carbon formation. Since we intuitively expect benzene to be instrumental in the production of carbon in this system, this overprediction is not surprising.

We have tried several qualitative tests to check this hypothesis. We have evaluated the addition of several irreversible reactions

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 (25) Duncan, F. J.; Trotman-Dickinson, A. F. J. Chem. Soc. 1962, 462.

- (26) Stein, S.; Fahr, A. J. Phys. Chem. 1988, 92, 4951.

TABLE XIII: Apparent React

 $C_6H_5 + C_6H_6 = [Ph-CHD^*]^0$

 $C_6H_5 + C_6H_6 = C_6H_5C_6H_5 + H$

Reaction Rate Constants Predicted Using Bimolecular QKKK Analysis								
P, Torr	reaction	A factor, $cm^3/(mol s)$	n	E_{a} , kcal/mol	range			
7.6	$C_6H_5 + C_6H_6 = [Ph-CHD^*]^0$	1.92E+45	-11.24	6.61	a			
760.0		3.30E+60	-15.18	26.43				
7.6	$C_6H_5 + C_6H_6 = C_6H_5C_6H_5 + H$	1.21E+20	-2.56	7.29	Ь			

-9.39

-9.89

-14.15

-5.42

-4.42

31.0

2.38

16.42

14.64

13.11

1.61E+45

1.09E+40

4.11E+56

1.91E+30

7.31E+26

760.0

^aValid from 900 to 1900 K. ^bValid from 600 to 1900 K.

760.0

760.0

7.6

7.6

IABLE XIV: Reaction N	iecnanism [.]
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bath gas H_2

 N_2

				$E_{\mathbf{a}},$	
	reaction	A	n	kcal/mol	source
1	$C_6H_5Cl = CYC_6H_5 + Cl$	3.0E+15	0.0	95.5	a
2	$CYC_6H_6 = CYC_6H_5 + H$	1.67E+16	0.0	111.5	Ь
3	$CYC_6H_7 = MeCY_{24}Pd_1$	5.0E+12	0.0	38.1	С
4	$MeCY_{24}PD = CY_{13}PD_5 + CH_3$	1.0E+16	0.0	67.5	d
5	$CY_{13}PD = CY_{13}PD_5 + H$	6.0E+14	0.0	75.1	е
6	$C_6H_5C_6H_5 = CYC_6H_5 + CYC_6H_5$	5.0E+16	0.0	117.0	g
7	$PHPHCI = CYC_6H_5 + C_6H_4CI$	1.9E+16	0.0	117.0	ĥ
8	$CYC_6H_5 = LINC_6H_5$	3.16E+13	0.0	55.2	i
9	$LINC_6H_5 = C \# CC^*C^* + C_2H_2$	6.09E+14	0.0	47.6	j
10	$LINC_6H_7 = C^*CC^*C^* + C_2H_2$	5.50E+14	0.0	41.0	j
11	H + CI + M = HCI + M	1.0E+17	0.0	0.0	k
12	$Cl_2 = Cl + Cl$	7.69E+08	0.0	55.6	k
13	$H + H + M = H_2 + M$	1.0E+18	0.0	0.0	m
14	$C_6H_5CI = C_6H_4CI + H$	1.3E+16	0.0	110.5	f
15	$CYC_6H_6 + H = MeCY_{24}PD_1$	2.39E+27*	-3.92	29.2	l
16	$C_6H_5CI + H = CYC_6H_6 + CI$	1.5E+13*	0.0	7.5	l
17	$CYC_6H_6 + H = CYC_6H_7$	4.87E+56*	-12.73	26.8	I
18	$CYC_6H_6 + H = LINC_6H_7$	1.22E+22*	-1.87	31.2	l
19	$CH_3 + C_6H_5CI = C_6H_5CH_3 + CI$	1.96E+14*	-0.65	12.0	1
20	$CH_3 + CYC_6H_6 = C_6H_5CH_3 + H$	3.4E+26*	-4.15	26.4	1
21	$CH_3 + H = CH_4$	8.09E+36*	-7.19	9.2	1
22	$CYC_6H_5 + C_6H_5CI = PHPHCI + H$	4.5E+49*	-10.65	33.3	l
23	$CYC_6H_5 + C_6H_5C_1 = C_6H_5C_6H_5 + C_1$	2.6E+12*	-0.12	4.5	1
24	$CYC_6H_5 + CYC_6H_6 = C_6H_5C_6H_5 + H$	1.6E+45*	-9.39	31.0	l
25	$C_6H_4CI + C_6H_4CI = PHCIPHCI$	1.8E+13*	0.0	0.0	l
26	$C_6H_4CI + C_6H_5CI = PHPHCI + CI$	2.6E+12*	-0.13	4.43	1
27	$C_6H_4CI + C_6H_5CI = PHCIPHCI + H$	5.43E+15*	-1.39	3.85	1
28	$C_6H_4Cl + CYC_6H_6 = PHPHCl + H$	9.92E+37*	-5.48	19.97	1
29	$CYC_6H_6 + H = CYC_6H_5 + H_2$	2.0E+13	0.0	18.6	m
30	$CH_3 + H_2 = CH_4 + H$	5.0E+12	0.0	11.0	n
31	$C_6H_5CI + H = CYC_6H_5 + HCI$	1.0E+13	0.0	11.3	m
32	$H + C_6H_5CI = H_2 + C_6H_4CI$	2.0E+13	0.0	18.6	m
33	$CI + H_2 = HCI + H$	4.8E+13	0.0	5.0	р
34	$CI + C_6H_5CI = HCI + C_6H_4CI$	1.0E+13	0.0	12.5	т
50	$C_1 + C_1 C_6 H_6 = HC_1 + C_1 C_6 H_5$	1.12+13	0.0	12.5	m
30	$H + U_2 = U + HU$	/.94E+13	0.0	1.2	p
<i>ا</i> ز ۵۹	$MeCY_{24}PD_1 + H = CY_{13}PD_5 + CH_3$	8.0E+13	0.0	0.0	q
38	$C_1C_6H_7 = Me^{-C_1}V_{24}PD$	5.5E+10	0.0	23.5	r
39	$Me^{-}CY_{24}PD + H_2 = MeCY_{24}PD + H$	3.98E+12	0.0	14.0	S

^a A factor from reverse with $A_{-1} = 9E+12$: this work. ^b A factor based upon reverse with $A_{-2} = 1E+14$. H addition to secondary C₄ radicals (Allara, D. L. and Shaw, R. J. Phys. Chem. Ref. Data 1980, 9, 523). ^cSee Table II: QRRK/Energized complex analysis of H + C₆H₆. ^d A factor from reverse with $A_{-4} = 1E+13$. CH₃ addition to C₄ radicals (Allara, D. L.; Shaw, R. J. Phys. Chem. Ref. Data 1980, 9, 523). ^c A factor from reverse with $A_{-4} = 1E+13$. CH₃ addition to C₄ radicals (Allara, D. L.; Shaw, R. J. Phys. Chem. Ref. Data 1980, 9, 523). ^c A factor from reverse with $A_{-4} = 1E+13$. CH₃ addition to C₄ radicals (Allara, D. L.; Shaw, R. J. Phys. Chem. Ref. Data 1980, 9, 523). ^c A factor from reverse with $A_{-4} = 1E+13$. CH₃ addition to C₄ radicals (Allara, D. L.; Shaw, R. J. Phys. Chem. Ref. Data 1980, 9, 523). ^c A factor from reverse with $A_{-4} = 1E+13$. CH₃ addition to C₄ radicals (Allara, D. L.; Shaw, R. J. Phys. Chem. Ref. Data 1980, 9, 523). ^c A factor from reverse with $A_{-4} = 1E+13$. CH₃ addition to C₄ radicals (Allara, D. L.; Shaw, R. J. Phys. Chem. Ref. Data 1980, 9, 523). ^c A factor from reverse with $A_{-4} = 1E+13$. CH₃ addition to C₄ radicals (Allara, D. L.; Shaw, R. J. Phys. Chem. Ref. Data 1980, 9, 523). ^c A factor from reverse with $A_{-4} = 1E+13$. CH₃ addition to C₄ radicals (Allara, D. L.; Shaw, R. J. Phys. Chem. Ref. Data 1980, 9, 523). ^c A factor from reverse with $A_{-4} = 1E+13$. CH₃ addition to C₄ radicals (Allara, D. L.; Shaw, R. J. Phys. Chem. Ref. Data 1980, 9, 523). ^c A factor from reverse with $A_{-4} = 1E+13$. reverse with $A_{-5} = 1E+14$: see footnote b. ^fA factor from reverse with $A_{-14} = 7.5E+13$: see footnote b. ^gA factor from reverse with $A_{-6} = 1E+12$ (Louw, R.; Dijks, J. H.; Mulder, P. J. Chem. Soc., Perkin Trans. 2 1984, 10⁴, 271). ^hSee footnote g. ⁱTaken as linear $C_6H_7 = C_4H_7 + C_2H_2$ (Dean, A. M. J. Phys. Chem. 1985, 89, 4600). ⁱA factor and E_a from C=CC=C⁺ + C_2H_2 (see footnote i). ^kHandbook of Bimolecular and Termolecular Gas Reactions V I and II; Kerr, J. A., Moss, S. J. Eds.; CRC Press: 1981. ⁱQRRK/Energized complex analysis presented in this work (Table I-XIII) or by analogy to those in tables. "Optimized reaction: this work. " $CH_3 + H_2$ from Allara and Shaw (see footnote d). $C_3H_5 + H_2$ from Allara and Shaw (see footnote d). P Handbook of Bimolecular and Termolecular Gas Reactions Vol. I and II; Kerr, J. A., Moss, S. J., Eds.; CRC Press: 1981. *See ref b. 'Pressure dependence accounted for with QRRK analysis of Dean (see footnote j). *A factor taken as CCC* + H₂. Allara, D. L.; Shaw, R. J. Phys. Chem. Ref. Data **1980**, 9, 523. 'See Figures 15–17 for comparison of experimental data with model results. Asterisk indicates values are pressure dependent, rate expression given for 760 Torr. Temperature ranges given in Tables II-XIV. " $k = AT^n e^{-E_n/RT}$ (mol cm³) s).

to our mechanism, attempting to improve agreement between predicted and experimental C6H6 production. Irreversible reactions such as

 $C_6H_5 + C_6H_6 \rightarrow \text{soot} \quad \{k = 10^{11} \exp(-3000.0/RT)\}$ (S1)

were found to slow the predicted chlorobenzene conversion, and benzene was still overpredicted. The decrease in conversion is

expected, however, since this is a chain termination reaction and the decomposition occurs via a chain mechanism. It is not unusual in high-temperature addition reactions (complex formation) to observe C-H bond cleavage in the complex, so that one might expect an irreversible reaction of the type

 $C_6H_5 + C_6H_6 \rightarrow \text{soot} + H$ $\{k = 10^{11} \exp(-3000.0/RT)\}$ (S2)

a

TABLE XV: Thermodynamic Properties^a

species H _F (298) S(298) 300 500 800 1000 1500 2000	formula
CH3 34.82 46.38 9.26 10.81 12.90 14.09 16.26 17.56 C	CH ₃
CH4 -17.90 44.49 8.49 11.15 14.98 17.13 20.57 22.61 C	CH₄
C ₂ H ₂ 54.19 48.00 10.60 13.03 15.29 16.30 18.34 19.57 (C,H,
MECY24PD1 48.10 75.50 23.11 36.37 49.85 55.84 64.70 68.39 (Сн,
BICYC6H7 71.86 71.52 27.62 34.98 48.20 55.52 63.32 67.20 C	$\mathbf{\tilde{H}}_{7}$
H 52.11 27.39 4.97 4.97 4.97 4.97 4.97 4.97 H	Ĩ
CYC6H5 81.37 69.20 18.79 30.52 41.70 46.37 53.18 56.21 C	CH.
CYC6H6 19.82 64.34 19.55 33.07 48.14 54.77 62.27 67.35 C	L'HZ
CYC6H7 49.86 72.01 20.79 35.11 48.74 54.33 62.34 67.34 C	ČH,
CHD14 26.16 70.80 22.63 37.47 52.04 58.27 67.47 72.45 C	С.Н.
CHD 25.40 72.49 22.67 37.73 52.30 58.45 67.56 72.55 C	С, H.
CY13PD5 54.30 62.40 17.24 29.40 39.46 43.13 49.10 53.20 C	ČH.
CY13PD 32.40 64.20 17.64 30.01 41.29 45.81 52.80 57.30 C	C.H.
MECY14PD3 48.06 75.36 23.11 36.37 49.85 55.84 64.70 68.39 C	L'H
MECY24PD 28.30 73.00 23.03 36.74 51.51 58.23 67.83 73.50 C	C ₂ H.
NAPTH 36.10 80.21 31.89 52.13 70.77 78.43 90.21 94.66 C	С.H.
C*CC*C 26.33 66.62 19.22 28.36 36.95 40.57 46.34 49.44 C	L'HA
C#CC*C* 126.27 69.60 17.50 22.98 27.91 29.93 33.27 34.91 C	LH.
ME [•] CY24PD 75.10 76.42 23.11 36.36 49.64 55.53 64.71 69.20 C	2H-
C6H5CH3 11.95 76.41 24.88 40.53 55.73 62.22 71.78 75.20 C	С-н.
H2 0.00 31.21 6.90 6.99 7.10 7.21 7.72 8.17 H	-,, 1-
CL 28.90 39.47 5.20 5.40 5.35 5.30 5.20 3.14 C	
CL2 -0.01 53.29 8.10 8.59 8.91 8.99 9.10 9.16 C	1.
C6H5CL 12.35 74.79 23.27 36.47 47.96 52.41 59.17 61.16 C	L'H.Cl
PHCLPHCL 28.72 112.76 44.07 66.94 86.58 93.99 104.92 108.68 C	J.H.Cl
C6H5C6H5 43.50 93.85 35.74 59.44 81.20 90.05 103.37 108.73 C	12
PHPHCL 35.82 105.39 39.90 63.17 83.88 92.03 104.14 108.25 C	LaHaCl
HCL -22.06 44.64 6.96 6.99 7.29 7.56 8.10 8.40 F	IČI
C6H4CL 72.45 77.78 22.92 34.33 45.16 49.86 57.75 61.39 C	CHLCI
LINC6H5 136.55 80.70 25.50 36.41 45.21 48.39 53.56 55.10 C	C ₄ H ₄
PHCYC6H4 104.47 98.02 38.20 62.11 83.59 92.10 104.90 110.93 C	C ₁ -H ₀
NAPTH 36.00 79.49 31.92 52.07 70.74 78.27 89.14 94.37 C	JoH.
BICYC6H7 68.95 76.97 21.04 35.51 48.62 54.14 63.67 67.32 C	2H-
CLCHD• 40.83 82.80 23.45 38.43 51.35 56.29 63.90 67.48 C	C ₄ H ₂ Cl
MECHD• 42.92 79.32 25.76 43.62 59.87 66.44 76.69 82.15 C	C ₇ H ₀
ICLMECHD 31.78 85.62 29.42 47.45 63.0 68.98 78.48 83.27 C	C-H.CI
PHCHD• 76.05 100.40 38.79 65.90 89.97 99.33 113.26 120.62 C	L'H'
ICLPHCHD* 64.91 106.70 42.45 69.74 93.11 101.87 115.04 121.75 C	
CLIPHCHD [•] 65.36 107.43 42.39 69.22 92.56 101.39 114.35 121.31 C	$H_{10}Cl$

^aUnits: H_f , kcal/mol; S and C_p , cal/(mol K).



Figure 15. Comparison of model predictions (solid lines) with experimental data (\blacksquare , C₆H₅Cl; +, C₆H₆) for reaction at 1126 K. Mechanism listing appears in Table XIV.

to be a viable path. Inclusion of this reaction did inhibit benzene formation somewhat without significantly decreasing the rate of chlorobenzene disappearance but was not sufficient to explain the benzene profile.

Use of equilibria²⁶ such as

3benzenes \leftrightarrow terphenyl + 3H₂

does permit accurate modeling of the observed benzene product concentration profile. We shall report on this and on a model allowing a fraction of the benzene collisions with soot particles, concentrations estimated from mass balance and size fraction



Figure 16. Comparison of model predictions (solid lines) with experimental data (\blacksquare , C_6H_5Cl ; +, C_6H_6) for reaction at 1177 K. Mechanism listing appears in Table XIV.

determined from Harris et al.,²⁷ to irreversibly stick to soot particles (as Harris did for acetylene) in a more appropriate future publication. These calculations are not, however, based on radical kinetics and do not constitute an elementary mechanism to soot. Our attempts to model soot formation from the gas-phase chemistry described here, were unsuccessful. The use of a homogeneous reaction mechanism may not adequately describe the processes which occur when a significant quantity of soot particles have been

⁽²⁷⁾ Harris, S. J.; Weiner, A.; Ashcoft, C. C. Combust. Flame 1986, 64, 65.



Figure 17. Model predictions for C_6H_5Cl decomposition at five temperatures (solid lines, model; \blacksquare , 1126 K; \diamondsuit , 1150 K; \square , 1177 K; \blacklozenge , 1200 K; \ltimes , 1223 K. Mechanism listing appears in Table XIV.

formed, since heterogeneous effects may become important.

Phenyl dissociation reactions suggested by Frenklach et al.²⁸ and Kiefer²⁹ have not helped to account for these observations. Their reactions to form soot are not fast enough at our temperatures. Our model does not predict significant phenyl dissociation to linear C_6H_5 at our conditions due to a large excess of H_2 and high energy required for dissociation. Phenyl radical is believed to be reactive toward H_2 and as a result phenyl dissociation would not be an important reaction channel.

Predictions shown in Figures 15–17 were obtained without the use of irreversible "bleed" reactions.

We have obtained mass spectral evidence on the nonvolatile species contained in the carbon residue which are believed to be triphenylene, chlorotriphenylene, and larger PAH and phenyl adducts which support this reaction pathway. In addition, no significant amounts of acetylene, vinyl acetylene, or other ring fragmentation products were observed. In chlorinated aromatic systems, polymerization may be even more favorable due to the relative ease with which chlorine may be eliminated from the PAH/phenyl adducts to promote ring condensation and growth.

Direct phenyl polymerization was suggested by Gordon et al.³⁰ and more recently by Stein³¹ as a possible mechanism for soot growth in benzene systems where conditions such as temperature and H_2 concentration make ring opening and fragmentation reactions unlikely.

Phenyl radical is believed to add to biphenyl and chlorobiphenyl producing orthoterphenyl plus hydrogen and chlorine atoms, respectively. Orthoterphenyl is relatively unstable²¹ and would either dissociate or condense to triphenylene. Ring growth may then result from successive additions of phenyl (chlorophenyl) followed by condensation to increasingly larger PAH. Such a mechanism would compete with hydrogen abstraction for phenyl radicals resulting in reduced benzene production. Inclusion of these ring addition pathways improves predictions by the mechanism slightly, similar to irreversible "bleed" reactions mentioned above.

The mechanism predicts essentially complete conversion of chlorine to HCl, while experimentally we observe only ca. 82% mas balance for the Cl at 100% loss of chlorobenzene. Trace levels of chlorobiphenyls are observed in the solids by GC/mass spectrometry analysis. Most other reaction studies in this laboratory, inclusive of chlorocarbon oxidations, show complete mass balance for chlorine, with HCl the major product at high conversions. One difference between this and other studies in our lab is that this experiment operated at 100–200 K higher temperatures. We do not know if the Cl is in the carbon solids and not extractable, if it reacts with the quartz reactor, which clearly shows vitrification with use or is lost in the heated transfer lines to the titrator. This is an important issue that needs to be resolved.

The experimental results show production of cyclopentadiene, methane, toluene, biphenyl, and chlorobiphenyl as trace products or stable intermediates present at levels less than 0.5% of the initial chlorobenzene.

Model predictions for biphenyl indicate a maxima 0.2% of the initial chlorobenzene at 0.24 s reaction time (40% parent conversion), 1177 K, with the decrease in concentrations at longer times producing benzene. This is in fair agreement with the experimental levels of 0.05% in vapor, plus GC/mass spectrometry on methylene chloride extracts of solids consistently showing significant amounts of biphenyl and chlorobiphenyl. We feel a fair fraction of the biphenyl species were lost by adsorption on particulate in the reactor exit and sample transfer line to the GC. The model predicts chlorobiphenyl levels approximately 0.02% with maxima at 0.28 s corresponding to 45% conversion of the parent chlorobenzene, and the experimental levels are 0.05% of the initial chlorobenzene.

Cyclopentadiene levels predicted by the model are ca. 0.01% of CLBZ₀, where the observed concentrations are between 0.1% and 0.5%. The model and the experiment both show cyclopentadiene levels increasing with temperature, reaction time, and/or conversion. Experimental observations on toluene show that it is present in concentrations below 0.5% with the model not predicting these levels. Methane is predicted at the 0.01% level, with experimental levels ranging between 0.04% and 0.06%.

While one can describe the reagent and major product concentration profiles with a less detailed reaction mechanism than that used here, we wanted to present a more complete reaction description by trying to model the observed high molecular weight and trace level species. We feel it is worthwhile to the include these reactions; they illustrate plausible pathways and product concentrations. The model calculations also indicate that inclusion of ring addition reactions, which terminate at formation of biphenyls and chlorobiphenyls in this mechanism, do not explain the observed benzene loss at high conversions. Work is ongoing to explain formation of the observed PAH's plus multiphenyl ring systems and especially the benzene loss. The reactions listed form a complete subset of the mechanism which accurately describes our dichlorobenzene results and our separate attempts to predict the observed PAH's (up to four fused rings) plus triphenylene and chlorotriphenylene.

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Registry No. C₆H₅Cl, 108-90-7; H₂, 1333-74-0.

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 (29) Kiefer, J. H.; Mizerka, L. J.; Patel, M. R.; and Wei, H. C. J. Phys. Chem. 1985, 89, 2013.

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⁽³¹⁾ Stein, S. E. J. Phys. Chem. 1978, 82, 566.