12-1-1996

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Xiaodong Yang
Western Kentucky University

Recommended Citation

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A CHEMICAL PATHWAY TO THE FORMATION OF CHLORINATED COMPOUNDS DURING COMBUSTION

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fufillment
of the Requirements for the Degree
Master of Science

by
Xiaodong Yang
December 1996

A CHEMICAL PATHWAY TO THE FORMATION OF CHLORINATED COMPOUNDS DURING COMBUSTION

Date Recommended 09-13-96

Weiping Pan
Director of Thesis

John T. Riley

William G. Lloyd

Elmer Gray
Director of Graduate Studies

11-12-96
Date

ACKNOWLEDGEMENTS

I wish to sincerely thank Dr. Wei-Ping Pan for his supervision and patience in relation to this endeavor. I also wish to acknowledge Drs. John T. Riley and William G. Lloyd for their valuable critiques and suggestions during the course of my study. I wish to express my sincere thanks to the faculty and staff at Western Kentucky University who made learning a pleasure. I also wish to acknowledge the financial support received from the Department of Chemistry and the Huntsman Packaging Corporation without which this study would not have been possible.

Xiaodong Yang

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Directed by: Wei-Ping Pan, John T. Riley and William G. Lloyd

Department of Chemistry Western Kentucky University

Two reactions, the Deacon reaction and the chlorination of phenol, which are the postulated starting steps for the formation of chlorinated dioxins during the incineration of the refuse derived fuel, were investigated in this work. Reactions were conducted in a tube furnace, and the products were trapped and analyzed by gas chromatography/mass spectroscopy. It was shown that the Deacon reaction was favored at higher temperatures. The chlorination of phenol in vapor phase was found to begin at temperatures as low as 250°C and to be favored at higher temperatures. The ortho and para positions in the phenol ring are the favored sites for chlorine substitution.

I. INTRODUCTION

A. Challenge from Municipal Solid Waste

Approximately 185 million tons of municipal solid waste (MSW) were collected in the United States in 1991. It is projected that the amount of MSW generated by the year 2000 will be 225-250 million tons per year.[1] That result will become a massive disposal problem as municipalities face ever increasing landfill closure and higher costs in landfill disposal due to regulatory pressures and more stringent environmental controls. Even with the anticipated increases in recycling, refuse disposal is expected to remain a major national problem. One of the other alternatives is to incinerate the refuse.

There are several benefits resulting from incineration of MSW such as reduction of the need for land filling and the generation of electricity. However, incineration of MSW may have negative effects on the environment. The potential emissions of the volatile organic compounds (VOCS) from the MSW have been studied.[2,3] Exposure to these VOCS may lead to health risks. Therefore it is necessary to reduce the bad emissions, which especially include the very toxic chlorinated aromatic compounds - polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).

It has been reported that co-firing 40% MSW with 60% coal drastically reduced the toxic evolutions.[4] It is important to study the mechanism and conditions of formation of the toxins during the combustion to optimize the operating conditions and, thus, to make combustion take place in an environmentally acceptable manner.

B. PCDDs and PCDFs

The members of the PCDD and PCDF families may have between 1 and 8 chlorine atoms and, when isomers are considered, totals of 75 PCDDs and 135 PCDFs are possible.[5] The compound, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-T_4CDD) is the most toxic member of the family and is one of the most toxic synthetic chemicals known. A difference of at least three orders of magnitude in toxicity is observed between different dioxins. The most toxic dioxins are those with chlorine substituents in the 2, 3, 7 and 8 positions, with the exceptions being the two octachloro-compounds which are relatively harmless.[5] In general, the PCDFs are about one tenth as toxic as the corresponding PCDDs.

The LD_{50} values (in μg/kg body weight) of 2,3,7,8-T_4CDD vary widely with the species: guinea pig, 0.6-2; rhesus monkey, 70; and rats, 284. The LD_{50} for humans is still unknown. But it is known that it can cause severe liver damage and chloracne and it is widely believed that dioxins are carcinogenic and teratogenic to humans.[6]

C. Organic Compounds from Coal Combustion

In addition to the inorganic compounds such as CO_x , SO_x, NO_x, HCl and residues, many organic species have been reported from the combustion of coal. Of these organic compounds, the aromatic compounds most frequently reported are polynuclear aromatic hydrocarbons such as acenaphthene, anthracene, benz[a]anthracene, benzofluoranthene(s), benzo[a]pyrene, biphenyl, chrysene, dibenzofuran, dibenzothiophene, dimethylbenz[a]-anthracene, fluoranthene, fluorene, ideno[1,2,3-cd]pyrene, methylnaphthalene(s), methylpyrene(s), naphthalene, perylene, phenanthrene, phenol, and pyrene.[7-11]

In the case of chlorine existence during the combustion, chloroaromatic compounds, which are of the most concern as pollutant species, may be formed. There have been some investigations[7,12,13] that revealed the emission of the chlorinated aromatic compounds--such as polychlorobiphenyl, polychlorobenzene, and polychlorophenol, etc., during coal combustion.

As for PCDD/Fs in the emissions from the coal combustion, a review[14,15] of the old literature (1956-1979) showed no citations. However, more recent studies showed considerable variation. A British study[16] of domestic coal furnaces reports them to be a major source of PCDD/Fs. A recent Japanese report[17] indicates a utility boiler to produce traces at the part-per-trillion level, while other studies,[18-22] mostly of effluents from utility boilers, did not find detectable amounts of PCDD/Fs.

D. Organic Compounds from PVC Combustion or Pyrolysis

Polyvinyl chloride (PVC), which is flame resistant and low cost, is widely employed for conveyor belts, hose conduits, ventilation pipe, and brattice cloth. Containing nearly 50% chlorine, PVC products will be the major source of chlorine in MSW.

The thermal behavior of PVC has been studied by many researchers. Paciorek and coworkers[23] decomposed PVC containing compositions at about 400°C in oxidative conditions. The products contained C_6H_6, $C_6H_5CH_3$, $C_6H_4(CH_3)_2$, $C_6H_5CH_2Cl$, CH_3Cl, C_2H_5Cl, C_2H_3Cl, $C_6H_{13}Cl$, and possibly tolualdehyde, higher aromatics and chlorinated aromatics, as well as HCl, CO and other simple organic compounds. The production of chlorinated organic species did not appear to be necessarily dependent upon PVC content in the materials. In another study, Boettner and coworkers[24] found benzyl chloride on thermal oxidative degradation of PVC.

Pyrolysis of PVC was undertaken by E. P. Chang and others[25] from 160°C to 500°C in helium. The pyrolysis products detected by gas chromatograph (GC) and mass spectrometer (MS) included benzene, toluene, indent, methylindenes, naphthalene, methylnaphthalenes, biphenyl, methylbiphenyl, diphenylethylenes and anthracene. A recent report of PVC combustion was given by Yasuhara and Ito (Japan).[26] In their research, the main combustion products of PVC were polynuclear aromatic hydrocarbons. Only small amounts of chlorine containing compounds were formed. Formation of PCDD/Fs was confirmed. The temperature of maximum PCDD/Fs formation was 600°C. Essential profiles of PCDD and PCDF formation at various temperatures were similar. Formation amounts of PCDFs were more than those of PCDDs.

E. Formation of PCDD/Fs from MSW Incineration

Since 1977, when Olie and coworkers[27] discovered PCDD/Fs in the effluent of a municipal incinerator in The Netherlands, attention has been focused on these toxic compounds. PCDDs have since been found in fly ash from incinerators located in Canada, Japan, Switzerland, France, Norway and the U. S. A.[28-32]

Three general pathways have been proposed for explaining the production of PCDD/Fs:[33] (1) survival of trace levels in the fuel; (2) generation from precursors such as chlorinated phenols; (3) *de novo* synthesis from chemically dissimilar compounds and sources of chlorine.

In a discussion of the thermal formation of dioxin, Shaub and others[34] assumed a homogenous gas phase reaction involving a complex of free radical reaction steps. A later study[35] provided experimental evidence for the formation of small amounts of dioxins from the homogeneous gas phase pyrolysis of phenol. Other studies[36-40] favored and provided evidences for the arguments of heterogeneous reactions, as the fly ash catalyzed, heterogeneous gas-solid reactions have much more favorable kinetics than radical reactions at lower temperatures. Most of these studies suggest the chlorophenols to be the precursors of dioxins. However, some other studies[41-43] have shown that chlorobenzenes and chlorobiphenyls can also be the precursors of PCDD/Fs. Ghorishi and Altwicker[42] started with 1,2-dichlorobenzene and observed the formation of PCDD/Fs, which was then heterogeneously catalyzed within seconds in the temperature range of 390 - 430°C and in the presence of fine sand particles. The PCDD/Fs formation was not observed at substantially lower temperatures or in the presence of quartz particles. In the work of Erickson and others,[43] combustion of polychlorinated biphenyls yielded PCDFs but much lower amounts of PCDDs.

In summary, both the homogeneous gas phase reactions and the heterogeneous gas-solid reactions could be the sources of PCDD/Fs. Chlorophenols, chlorinated benzenes and biphenyls are believed to be the precursors of PCDD/Fs.

F. Purpose of This Work

One of the chemical pathways to form PCDD/Fs during MSW incineration has been proposed as follows.[44] There are four steps.

(1) PVC undergoes thermal decomposition with the release of HCl;

(2) At 300-600°C HCl is oxidized by oxygen to form molecular Cl_2, which is referred to as the Deacon reaction;[45]

$$4HCl + O_2 = 2Cl_2 + 2H_2O \quad (1)$$

(3) Molecular chlorine reacts with aromatic compounds such as phenols, to produce chlorinated aromatic compounds such as chlorophenols and polychlorophenols.

(4) Polychlorinated phenols such as 2,4,5-trichlorophenol undergo condensation reactions to produce PCDDs such as tetrachlorodibenzodioxin.

To study step 1 and step 2, Richard Lu in his work[46] showed HCl release profiles from the combustion of PVC by in a thermogravimetric analyzer (TGA) interfaced with a Fourier transform infared spectrometer (FTIR) and a mass spectrometer (MS). The appearance of phenol from the combustion of newspaper and refuse derived fuel was also determined by TGA/FTIR/MS, and the Deacon reaction was indicated by TGA/MS results.

The chlorination of phenol by Cl_2 is well known to proceed very readily under mild conditions in the liquid phase. The reaction has been conducted in aqueous solutions,[47] in polar organic media (benzene, halohydrocarbons),[48] and in nonpolar organic media (DMF, CH_2Cl_2, methanol).[49] However, no publications have specifically addressed the chlorination of phenol by Cl_2 in the vapor phase, according to a recent computer search of the Chemical Abstracts.

This work was focused on steps 2 and 3 outlined above. A further study was undertaken on the Deacon reaction. The chlorination of phenol by Cl_2 in the vapor phase was also studied. Investigations of the conditions for the Deacon reaction and the chlorination of phenol were undertaken using a tube reactor, cold traps and a GC/MS technique.

II. EXPERIMENTAL

A. Chemicals and Gases

The chemicals used in this study were phenol (reagent, MCB), 4-chlorophenol (99+%, Aldrich), 2-chlorophenol (99+%, Aldrich), 2,4-dichlorophenol (99%, Aldrich), 2,4,6-trichlorophenol (99+% Aldrich), dibenzofuran (99+%, Aldrich), and dichloromethane (HPLC grade, EM Scientific), cyclohexene (99%, Aldrich), and *trans*-1,2-dichlorocyclohexane (99%, Aldrich). Gases used were 0.5% Cl_2 in N_2 (Air Products & Chemicals, Inc., Allentown, PA), 10% HCl in N_2 (Specialty Gases, Louisville, KY), and compressed breathing air (Kentucky Airgas, Inc.).

B. Analysis Technique and Setup

The cold trap-GC/MS method was employed in this study. The schema of the cold-trap part of this technique is shown in Figure 1. Reactions were conducted in a quartz tube reactor (length 30 inches, internal diameter 1 inch). The reactor was mounted horizontally in an electrically heated Lindberg Sola Basic furnace. Temperatures were measured by chromel-alumel thermocouples inserted in the lower part of the oven and displayed on a digital thermometer. The flow of air and/or other gas(es) was regulated by needle valves on the top of the gas tanks and metered by calibrated teflon flowmeters. The gases were mixed in a mixing chamber filled with glass beads before being introduced into the reactor. The products and the unreacted starting compounds were

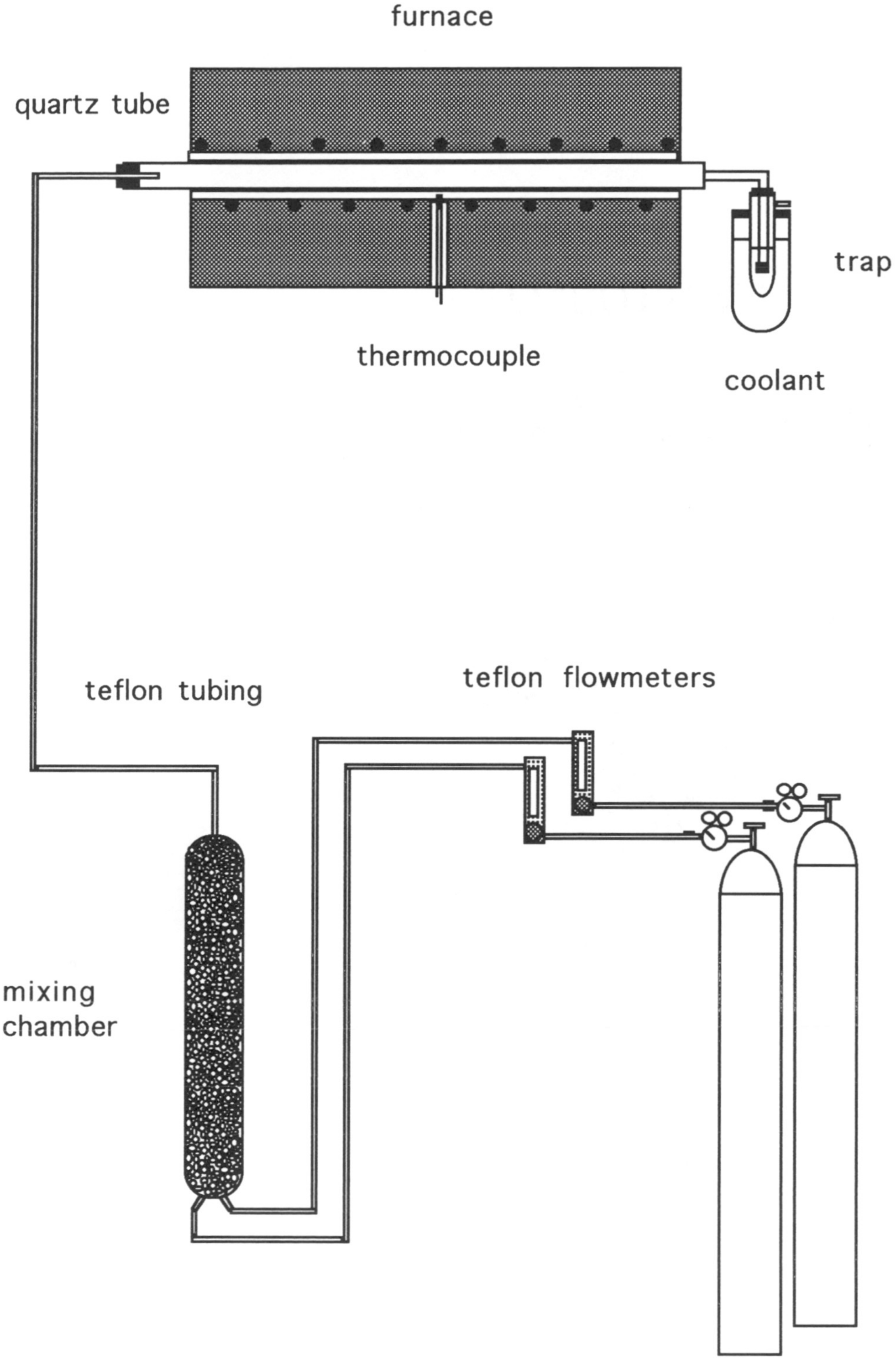

Figure 1. Schematic drawing of the setup of the tube reactor and cold trap system.

either trapped by 50 mL of CH_2Cl_2 or cooled down by liquid N_2 and condensed at the exit part of the tube and carefully washed using 100 mL of CH_2Cl_2. The trapped material or the washing was concentrated to 1 mL in a Kuderna-Danish evaporative concentrator, and then 1 μL of the concentrated sample was injected into a Shimadzu GC-17A gas chromatograph (GC) interfaced with a Shimadzu QP-5000 mass spectrometer (MS) for qualitative analysis. The GC separates the compounds first and then the MS analysis provides the structure information for each separated compound. The GC/MS system had an NIST/EPA/NIH 62,000 compound database for MS analysis library. The GC parameters set for this study are listed in Table 1.

C. Experimental Schedule

1. The Deacon Reaction

A mixture of 10% HCl in N_2 and air in the ratio of 1:2 by volume was introduced at a flow of 60 mL/min into the quartz tube placed in the preheated furnace. No catalyst was present in the reactor. The testing temperatures were 25°C, 400°C, 600°C and 800°C. The exit gas was cooled and trapped by 50 mL of phenol-methylene chloride solution, which was prepared by dissolving 50 mg of phenol in 50 mL of methylene chloride. In case any molecular chlorine was produced, it would be trapped readily by phenol in the solution to give chlorophenols. Therefore the Deacon reaction can be tested semiquantitatively by monitoring the production of chlorophenols. The reaction was run for 3 hours. Then the solutions were concentrated to one mL and injected into the GC/MS for analysis.

Table 1. Parameters Set for GC/MS Analysis

Injector			
Temp. (°C):	250.0		
Oven			
Initial Temp. (°C):	100.0		
Temp. Program:	Rate (°C/min)	Temp. (°C)	Time (min)
	5.0	150.0	5.0
	5.0	200.0	5.0
	5.0	250.0	5.0
	6.0	310.0	5.0
Flow Controller			
Carr. Gas Press. (kPa):	106.5		
Carr. Gas Press Time (min):	5.0		
Pressure Program:	Rate (kPa/min)	Press (kPa)	Time (min)
	1.6	122.5	5.0
	1.3	135.5	5.0
	1.2	147.5	5.0
	1.2	159.5	5.0
Total Flow (mL/min):	71.0		
Split Ratio:	32.0		
Interface			
Temp. (°C):	290.0		

2. Chlorination of Phenol

A 100.0 mg sample of phenol (boiling point of 182°C) in a glazed ceramic boat was put into the tube, 0.5% Cl_2 in N_2 was allowed to flow at a rate of 60 mL/min, and the tube was quickly mounted in the furnace already preheated to a specific testing temperature. Phenol was evaporated immediately and reacted with molecular chlorine to produce chlorophenols. To avoid any of the liquid phase chlorination of phenol, no solvent trap was used. The products from this vapor-phase reaction and the unreacted phenol were cooled down and condensed in the exit part of the tube by applying liquid N_2. The flow of chlorine was maintained for 15 minutes. The condensed products in the exit part of the tube were carefully washed with 100 mL of methylene chloride into a Kuderna-Danish evaporative concentrator. The washing was then concentrated to 1 mL and analyzed by GC/MS. The testing temperatures for the chlorination of phenol were 250°C, 400°C, 600°C and 800°C.

III. RESULTS AND DISCUSSION

A. The Deacon Reaction

Figure 2 represents the chromatograms of the concentrated phenol-CH_2Cl_2 solution after absorbing the molecular chlorine from the oxidation of HCl at different temperatures. The mass assignments, according to the NIST library matching accomplished with the automatic database-searching software, indicate these unknown compounds are possibly cyclohexene, phenol, 2-chlorophenol, *trans*-1,2-dichlorocyclohexane, 2,4-dichlorophenol, and 4-chlorophenol, which are represented by peak 1 through peak 6, respectively.

To identify these compounds, a number of pure compounds used as standards were run in the same GC/MS program with that for the unknowns. Figures 3 through 8 list the mass spectra of both the unknowns and the corresponding pure compounds. The comparison of the relative intensities of some major lines in each spectrum is shown in Tables 2 through 7. It can be seen that the unknowns, except those that are in such small amounts that the mass hits are very low, are in good match with the corresponding pure compounds in terms of mass spectra. In addition, the retention times of the unknowns in the gas chromatograph also match well with the corresponding pure compounds (Table 8). As a result, peak 1 through peak 6 are identified as cyclohexene, phenol, 2-chlorophenol, *trans*-1,2-dichlorocyclohexane, 2,4-dichlorophenol and 4-chlorophenol.

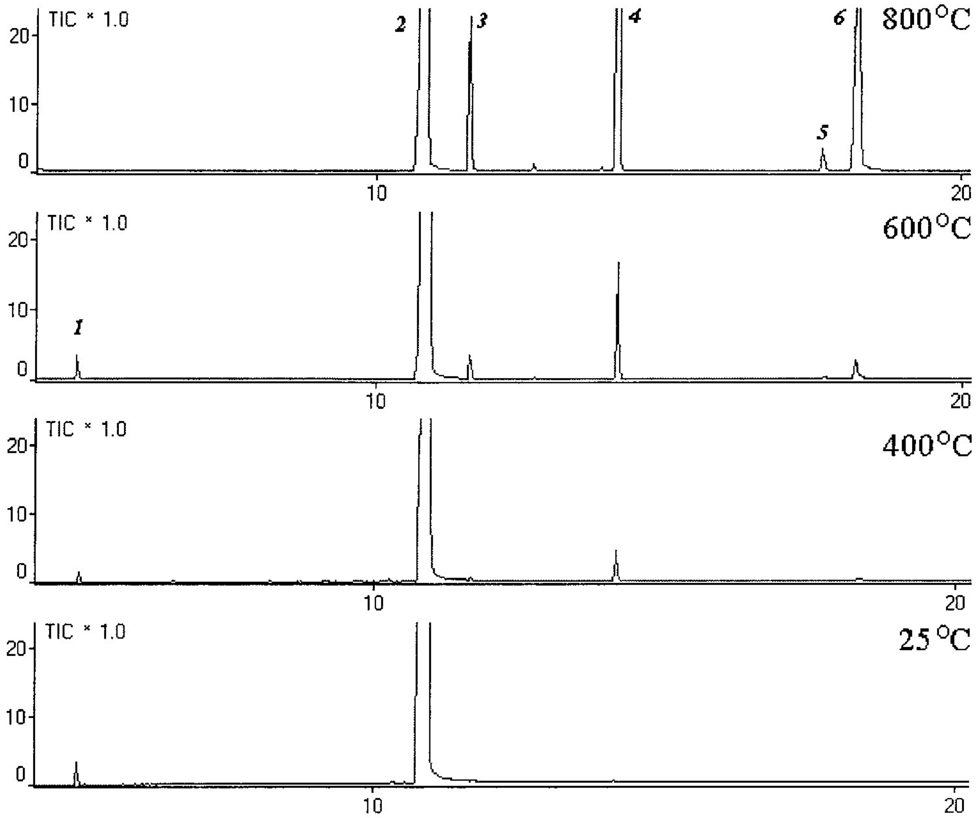

Figure 2. Chromatograms of the products from the reaction of HCl heated in air at different temperatures and trapped in a phenol-CH_2Cl_2 solution, concentrated, and analyzed by GC/MS.

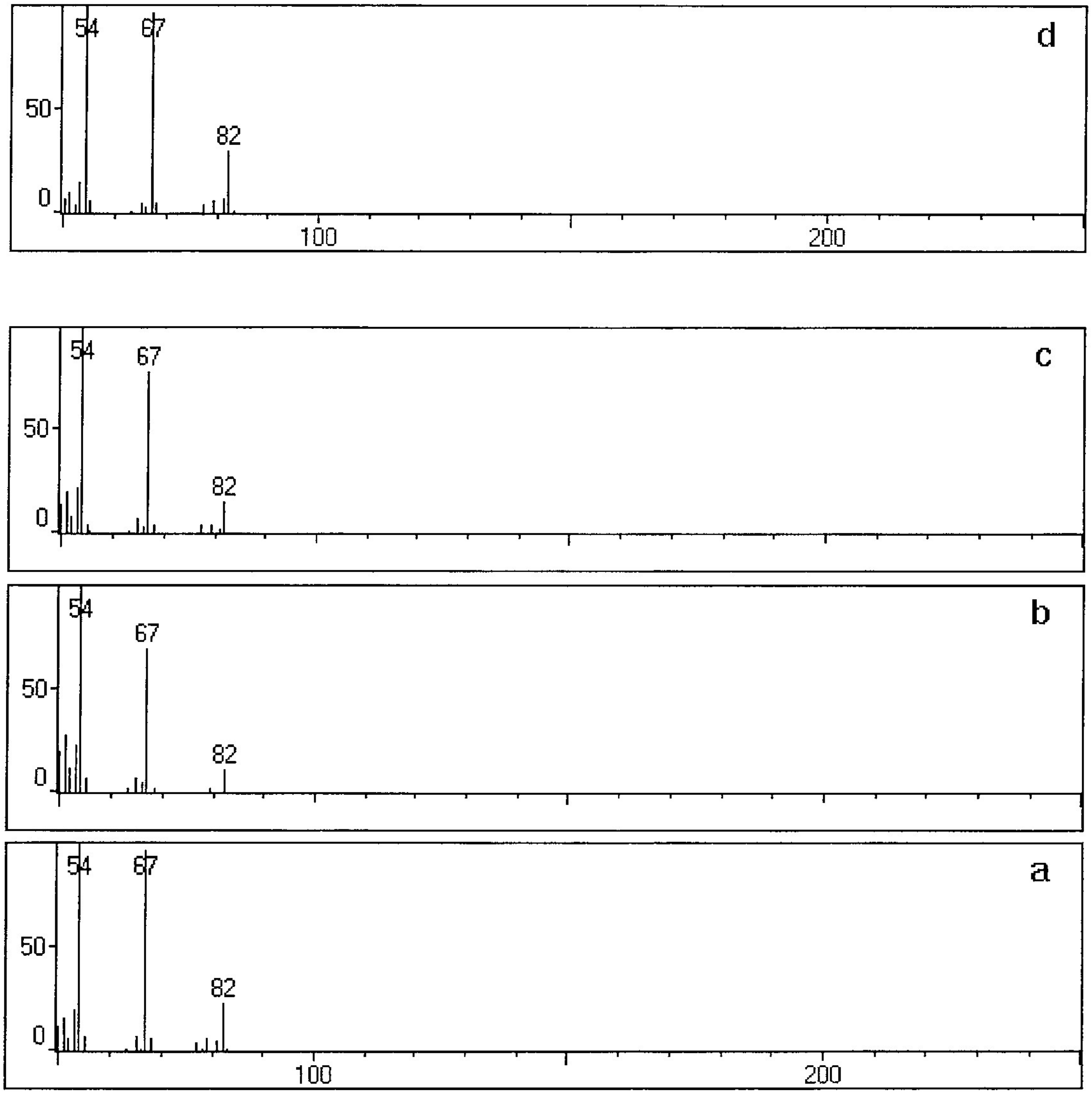

Figure 3. A comparison of the spectra of unknowns represented by peak 1, as labeled in Figure 2, with those of pure cyclohexene. a. 600°C; b. 400°C; c. 25°C; d. pure cyclohexene.

Table 2. Comparison of the Spectral Line Intensities of Unknowns Represented by Peak 1 with Those of the Cyclohexene Standard

Mass/Charge Ratio	Intensity of Unknown Spectra			Intensity of Standard
	25°C	400°C	600°C	
82	15.77	11.15	23.40	30.70
81	2.79		5.56	7.28
79	4.37	2.91	6.47	6.49
67	78.52	69.92	96.99	97.46
65	7.72	7.34	7.22	5.20
55	4.31	8.24	7.43	6.80
54	100.00	100.00	100.00	100.00
53	22.12	23.41	20.53	14.97
51	20.20	28.69	16.83	9.99
50	14.62	20.60	12.87	7.05

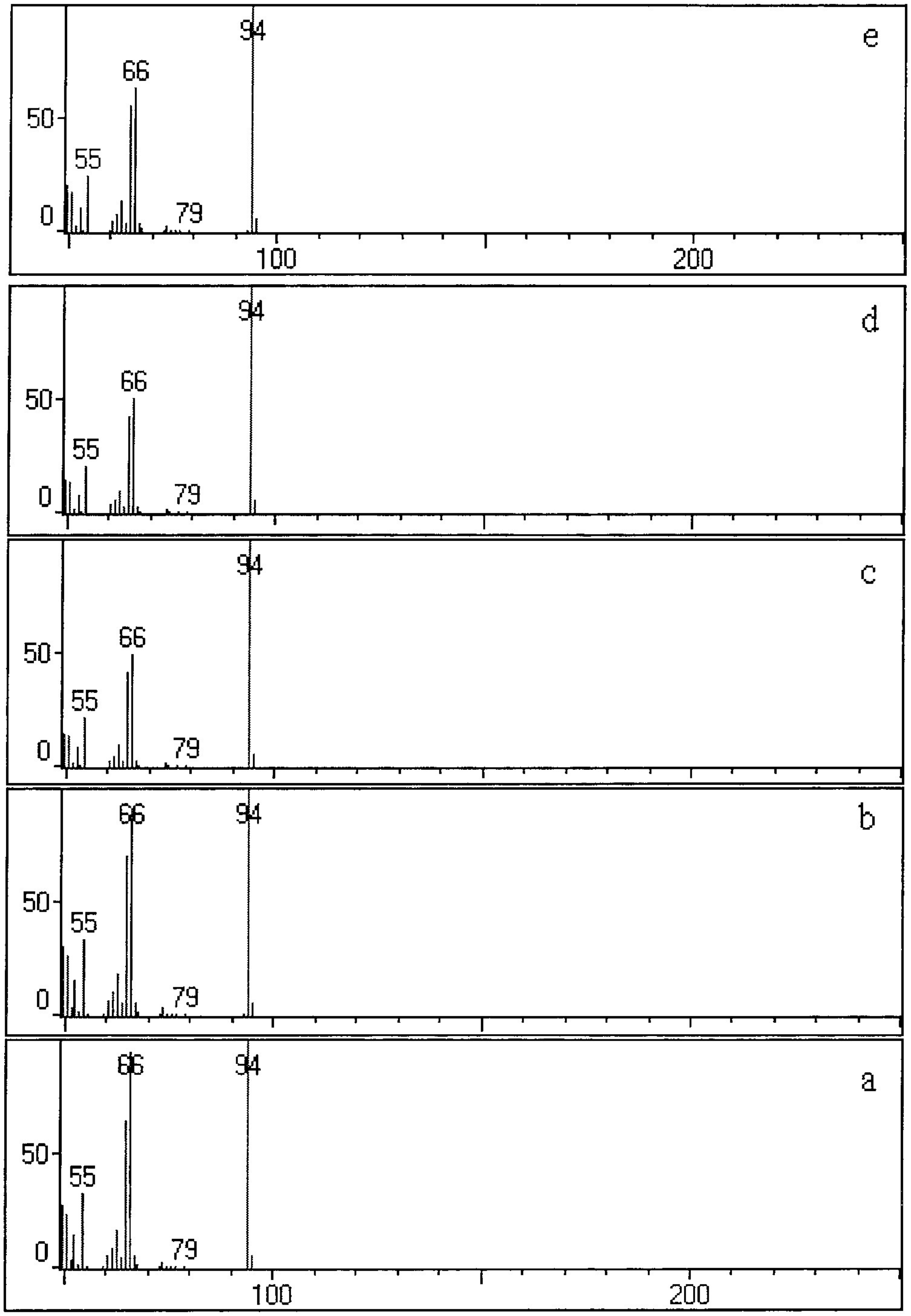

Figure 4. A comparison of the spectra of unknowns represented by peak 2, as labeled in Figure 2, with those of pure phenol. a. 800°C; b. 600°C; c. 400°C; d. 25°C; e. pure phenol.

Table 3. Comparison of the Spectral Line Intensities of Unknowns Represented by Peak 2 with Those of the Phenol Standard

Mass/Charge Ratio	Intensity of Unknown Spectra				Intensity of Standard
	25°C	400°C	600°C	800°C	
95	6.64	6.62	6.62	6.63	6.57
94	100.00	100.00	100.00	100.00	100.00
66	94.15	92.04	51.29	51.07	63.47
65	64.97	71.31	43.22	43.42	56.09
63	16.92	19.14	10.88	10.90	14.36
55	33.46	34.24	22.19	21.00	24.75
53	14.87	16.32	9.15	8.84	11.31
51	24.50	26.95	14.38	14.22	17.70
50	27.77	30.90	15.94	15.72	20.87

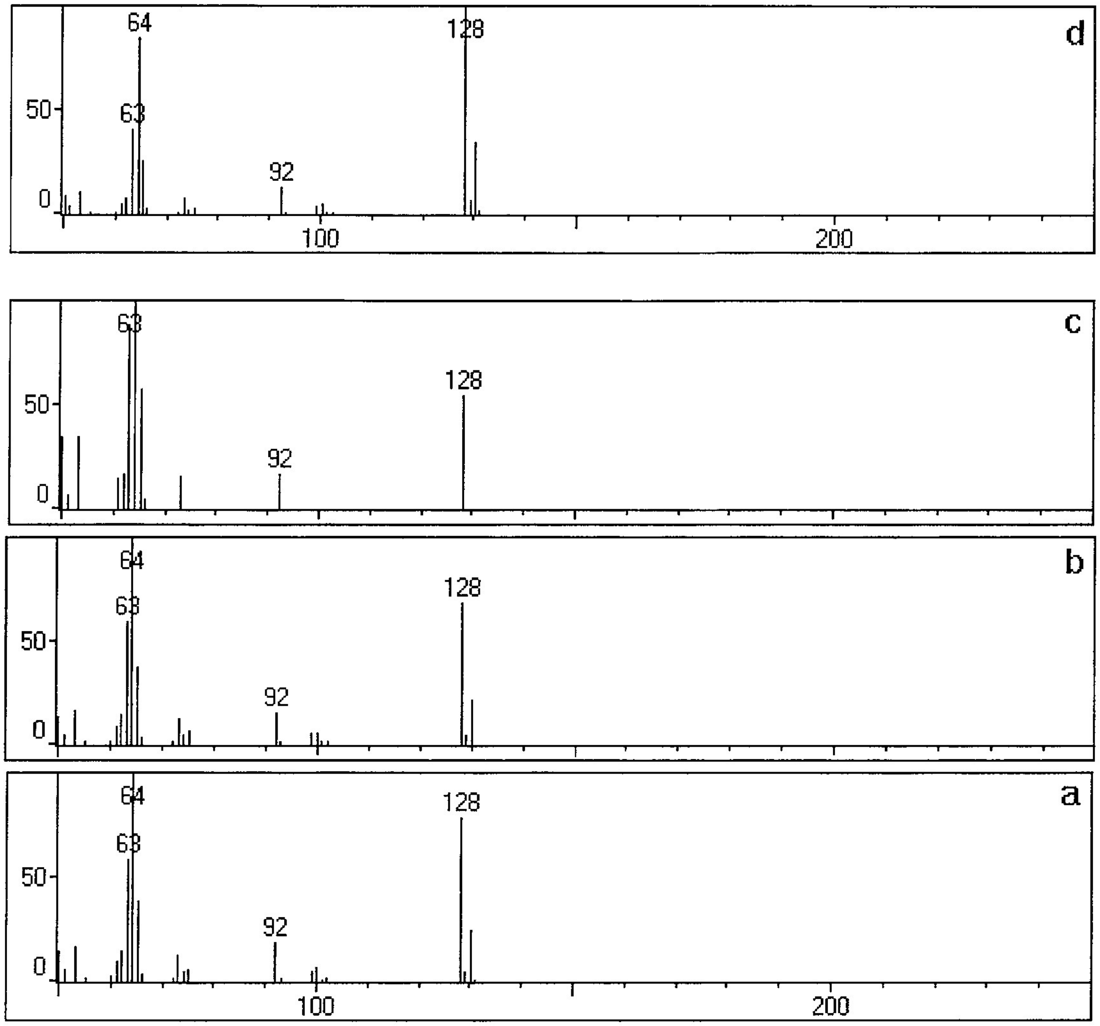

Figure 5. A comparison of the spectra of unknowns represented by peak 3, as labeled in Figure 2, with those of pure 2-chlorophenol. a. 800°C; b. 600°C; c. 400°C; d. pure 2-chlorophenol.

Table 4. Comparison of the Spectral Line Intensities of Unknowns Represented by Peak 3 with Those of the 2-Chlorophenol Standard

Mass/Charge Ratio	Intensity of Unknown Spectra			Intensity of Standard
	400°C	600°C	800°C	
130		25.27	25.29	24.71
128	46.46	71.76	79.73	77.85
92	14.87	16.50	19.36	21.86
73	15.22	13.15	13.21	10.61
65	67.26	37.09	39.15	37.40
64	100.00	100.00	100.00	100.00
63	74.06	59.33	59.03	54.10
62	16.62	15.59	15.21	13.03
53	26.82	17.20	16.90	16.14
50	24.38	14.14	15.15	13.35

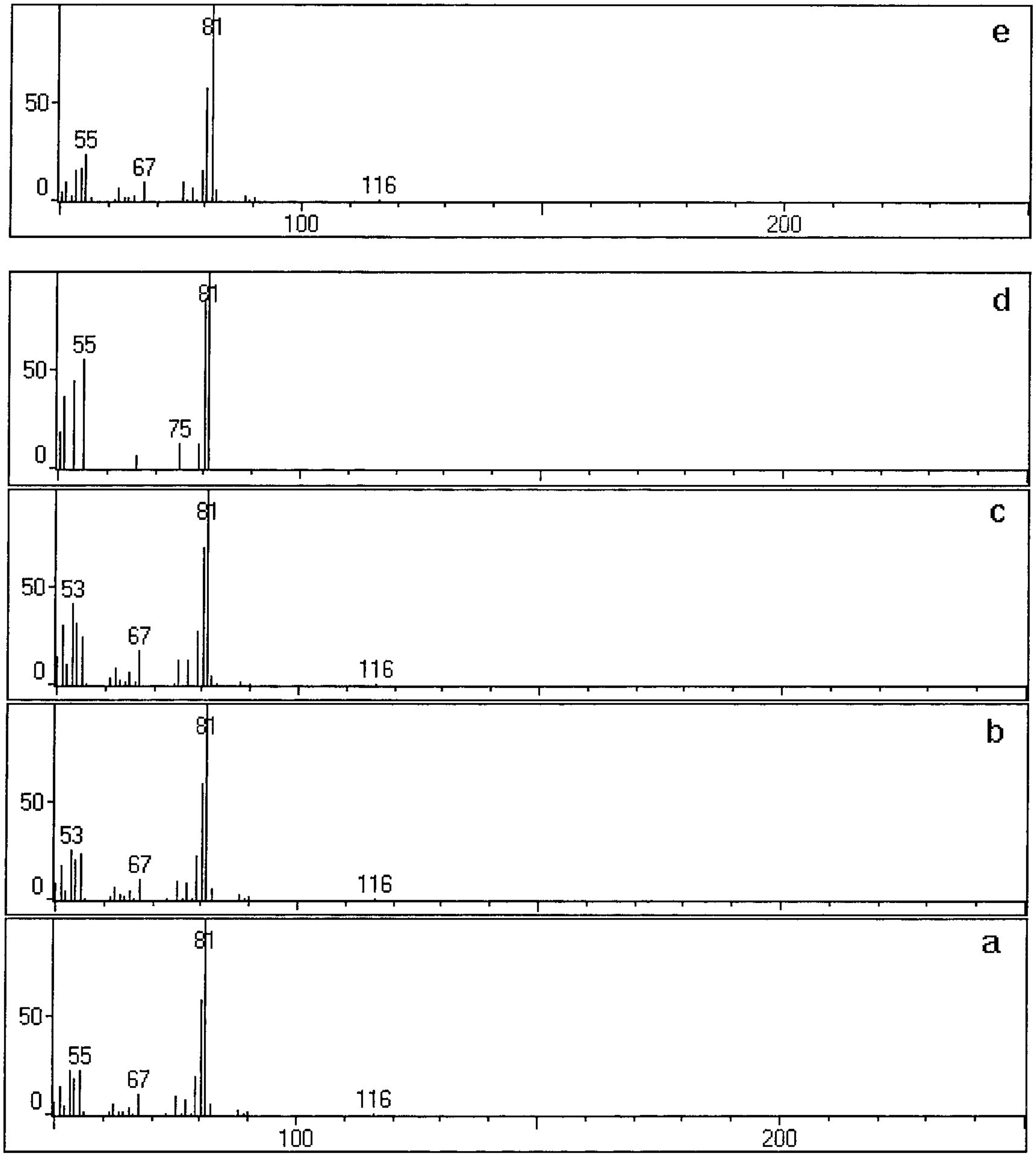

Figure 6. A comparison of the spectra of unknowns represented by peak 4, as labeled in Figure 2, with those of pure *trans*-1,2-dichlorocyclohexane. a. 800°C; b. 600°C; c. 400°C; d. 25°C; e. pure *trans*-1,2-dichlorocyclohexane.

Table 5. Comparison of the Spectral Line Intensities of Unknowns Represented by Peak 4 with Those of the *Trans*-1,2-dichlorocyclohexane Standard

Mass/Charge Ratio	Intensity of Unknown Spectra				Intensity of Standard
	25°C	400°C	600°C	800°C	
116		1.04	1.52	1.53	1.47
82		5.90	6.84	6.97	6.81
81	100.00	100.00	100.00	100.00	100.00
80	79.84	70.05	59.83	59.12	57.49
79	15.87	28.23	23.08	20.98	16.31
75	12.29	12.99	10.79	10.48	10.64
67		18.16	11.44	11.01	10.77
55	54.69	25.33	24.21	22.48	24.33
54		31.96	21.09	19.38	17.31
53	41.39	41.91	25.85	23.09	16.42
51	37.74	31.51	17.83	15.05	10.48

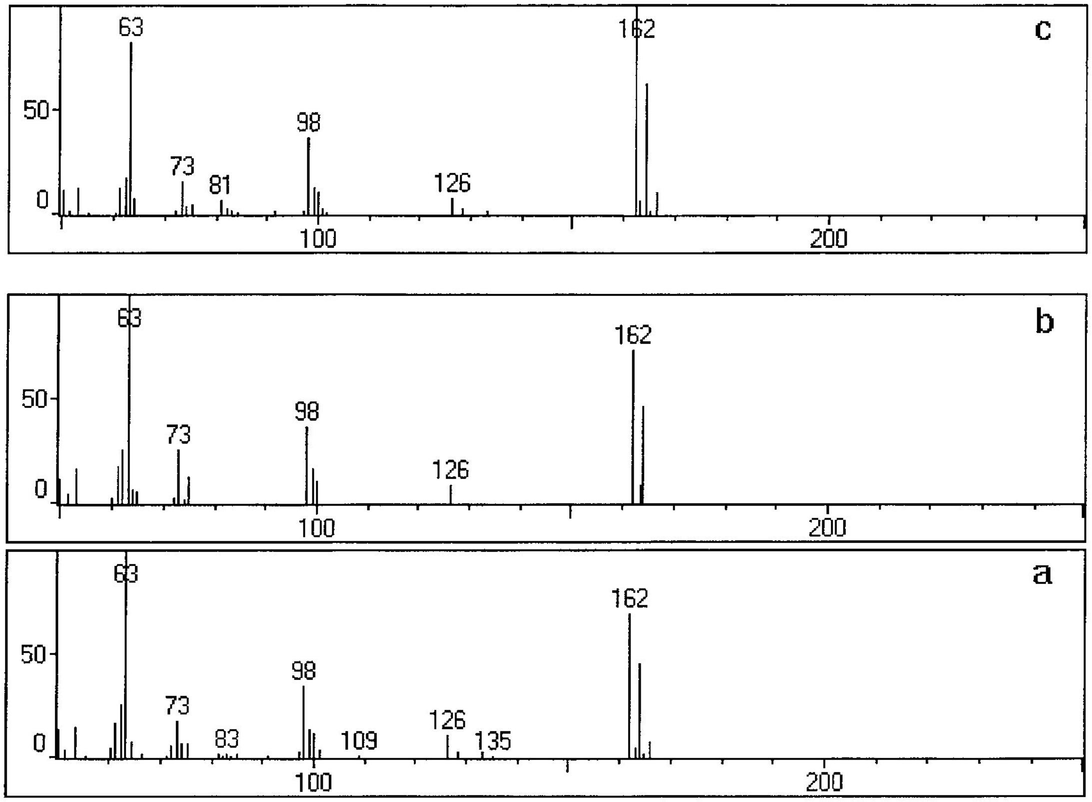

Figure 7. A comparison of the spectra of unknowns represented by peak 5, as labeled in Figure 2, with those of pure 2,4-dichlorophenol. a. 800°C; b. 600°C; c. pure 2,4-dichlorophenol.

Table 6. Comparison of the Spectral Line Intensities of Unknowns Represented by Peak 5 with Those of the 2,4-Dichlorophenol Standard

Mass/Charge Ratio	Intensity of Unknown Spectra		Intensity of Standard
	600°C	800°C	
166		8.15	8.27
164	46.28	47.87	51.04
162	72.08	71.22	76.80
126	6.13	12.03	9.62
100	7.91	12.11	11.50
99	14.89	14.28	12.67
98	32.33	35.78	34.88
73	20.96	18.43	17.49
63	100.00	100.00	100.00
62	25.81	25.04	24.68
61	15.69	17.66	16.68
53	16.63	16.53	15.95
50	13.22	13.92	15.55

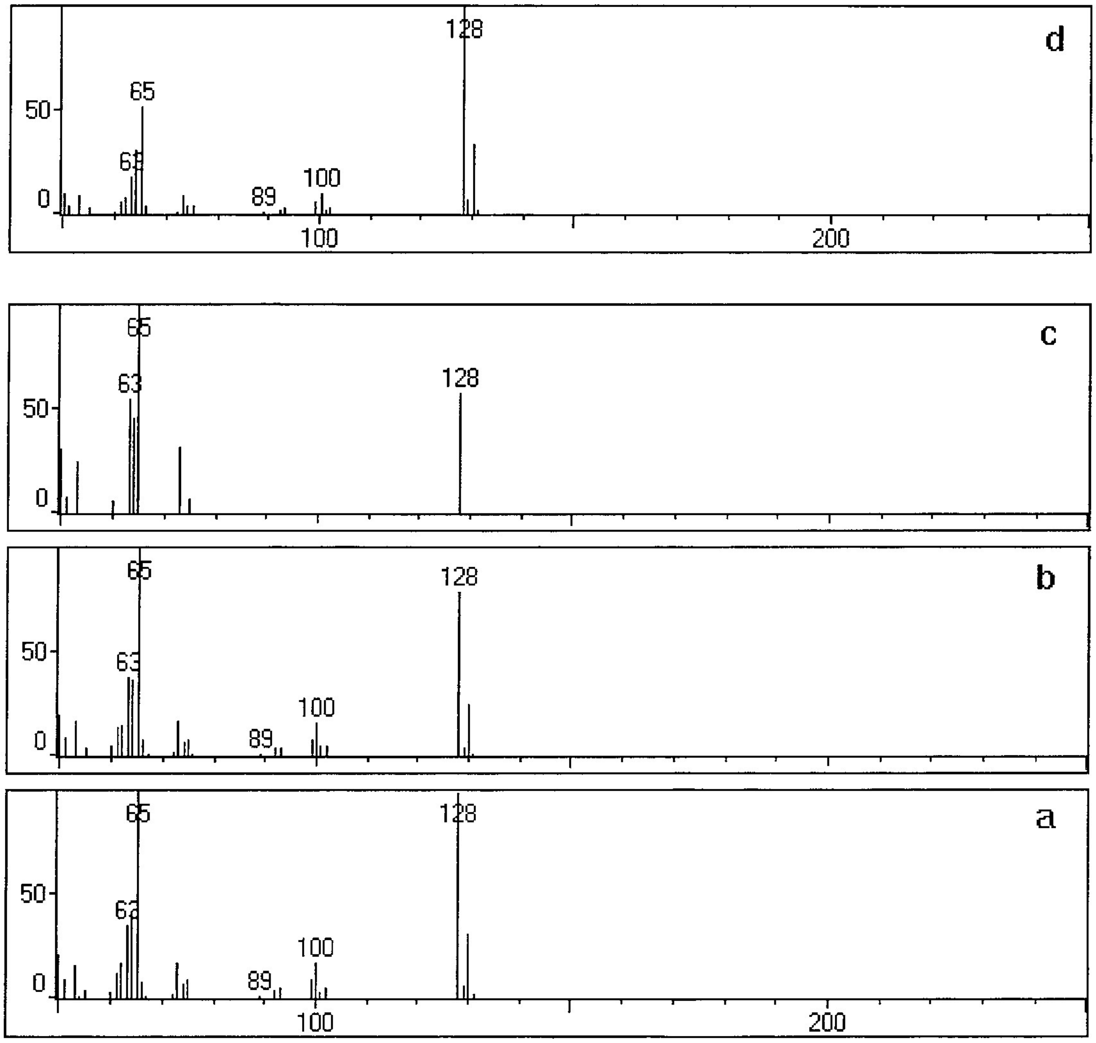

Figure 8. A comparison of the spectra of unknowns represented by peak 6, as labeled in Figure 2, with those of pure 4-chlorophenol. a. 800°C; b. 600°C; c. 400°C; d. pure 4-chlorophenol.

Table 7. Comparison of the Spectral Line Intensities of Unknowns Represented by Peak 6 with Those of the 4-Chlorophenol Standard

Mass/Charge Ratio	Intensity of Unknown Spectra			Intensity of Standard
	400°C	600°C	800°C	
130		25.77	31.26	32.55
128	57.58	79.26	100.00	100.00
100		16.39	17.57	17.23
73	32.57	17.22	17.36	16.87
65	100.00	100.00	97.76	95.67
64	46.03	37.48	40.35	39.34
63	54.81	37.99	33.58	34.84
62		15.07	15.79	16.53
53	25.66	17.26	15.71	16.55
50	31.62	19.95	20.61	20.01

Table 8. The Comparison of the Retention Times (min) of Pure Compounds and Those of Unknown Products from the Test of the Deacon Reaction

Unknown	Retention Time				Pure Compound	Retention Time
	25°C	400°C	600°C	800°C		
Peak 1	4.89	4.91	4.88		cyclohexene	4.95
Peak 2	10.90	10.87	10.85	10.86	phenol	10.90
Peak 3		11.72	11.63	11.64	2-chlorophenol	11.75
Peak 4	14.20	14.22	14.16	14.18	*trans*-1,2-dichlorocyclohexane	14.20
Peak 5			17.70	17.68	2,4-dichlorophenol	17.68
Peak 6		18.37	18.23	18.27	4-chlorophenol	18.44

Of these identified compounds, phenol is the reactant and cyclohexene is the impurity present in CH_2Cl_2, which was found by blank analysis of CH_2Cl_2 using GC/MS. The other chlorides are products from the interaction between molecular chlorine and the phenol-CH_2Cl_2 solution.

At room temperature none of the chlorophenols was detected, thus indicating that HCl did not react with phenol to produce chlorophenols. *Trans*-1,2-dichlorocyclohexane is formed from the addition reaction of cyclohexene and molecular chlorine that is possibly the product from the Deacon reaction at room temperature. At 400°C, small peaks of 2-chlorophenol and 4-chlorophenol and a larger peak of *trans*-1,2-dichlorocyclohexane were detected. When the temperature was 600°C, additional small peaks of 2,4-dichlorophenol appeared. When the reaction took place at 800°C, much larger peaks of 2-chlorophenol, 4-chlorophenol, 2,4-chlorophenol and *trans*-1,2-dichlorocyclohexane appeared. However, no cyclohexene was observed. Consequently, the higher the temperature, the more chlorides were produced, meaning more molecular chlorine had been produced since chlorination is not from HCl but from molecular chlorine that has been converted from HCl by the Deacon reaction. So the Deacon reaction is experimentally more favored at higher temperatures.

According to physical chemistry data,[50] the Deacon reaction (Equation 1) is favored thermodynamically and is exothermic at 25°C ($\Delta H = -114$ kJ/mol, $\Delta G = -76$ kJ/mol). The increase of the temperature will cause the equilibrium to move toward the reactants, which will lower the conversion of HCl to Cl_2. Before the equilibrium is reached, however, the reaction is predominantly kinetically-controlled. A rise in temperature will lead to a higher yield of products.

In the case where the reaction takes place in a steady moving flow and no catalysts are present, the reaction is far from equilibrium. Consequently, a higher temperature will lead to a higher reaction rate, meaning more Cl_2 will be produced.

By comparing the *trans*-1,2-dichlorocyclohexane peak in each chromatogram in Figure 3, we notice that no chlorinated compounds--except *trans*-1,2-dichlorocyclohexane--were detected at room temperature, and that the peak intensity of *trans*-1,2-dichlorocyclohexane changed more than those for the other chlorophenols while the reaction temperature was varied. Cyclohexene (impurity) is effective in reacting with molecular chlorine in the trap and the product formed, trans-1,2-dichlorocyclohexane, is more sensitive than chlorophenols for GC detection. It is believed, therefore, cyclohexene might be a better absorbent, especially for trace amounts of molecular chlorine.

B. Chlorination of Phenol

Chlorination of phenol was conducted in the tube reactor at various temperatures. The products were analyzed by GC/MS. The chromatograms of the products from the chlorination of phenol at different temperatures are shown in Figure 9. The products represented by peak 1 though peak 5, as labeled in Figure 9, are possibly phenol, 2-chlorophenol, 2,4-dichlorophenol, 4-chlorophenol and dibenzofuran, according to the NIST library mass matching accomplished with the automatic database-searching software.

The pure compounds of phenol, 2-chlorophenol, 2,4-dichlorophenol, 4-chlorophenol and dibenzofuran, which were used as standards, were run in the same GC/MS program with that for the unknowns. Figures 10 through 14 list the mass spectra of both the unknowns and the corresponding pure compounds. The comparison of the relative intensities of some major lines in each spectrum is shown in Tables 9 through 13. It can be seen that the unknowns, except those which are in so small amounts that the mass hits are very low, are in good agreement with the corresponding pure compounds in terms of mass spectra. The retention times of the unknowns in the gas chromatograph also agree well with the corresponding pure compounds (Table 14). As a result, peak 1 through peak 5 in Figure 9 are identified as phenol, 2-chlorophenol, 2,4-dichlorophenol, 4-chlorophenol and dibenzofuran. (The spectra and the retention times here are slightly different from those in Section A due to some services to the GC/MS.)

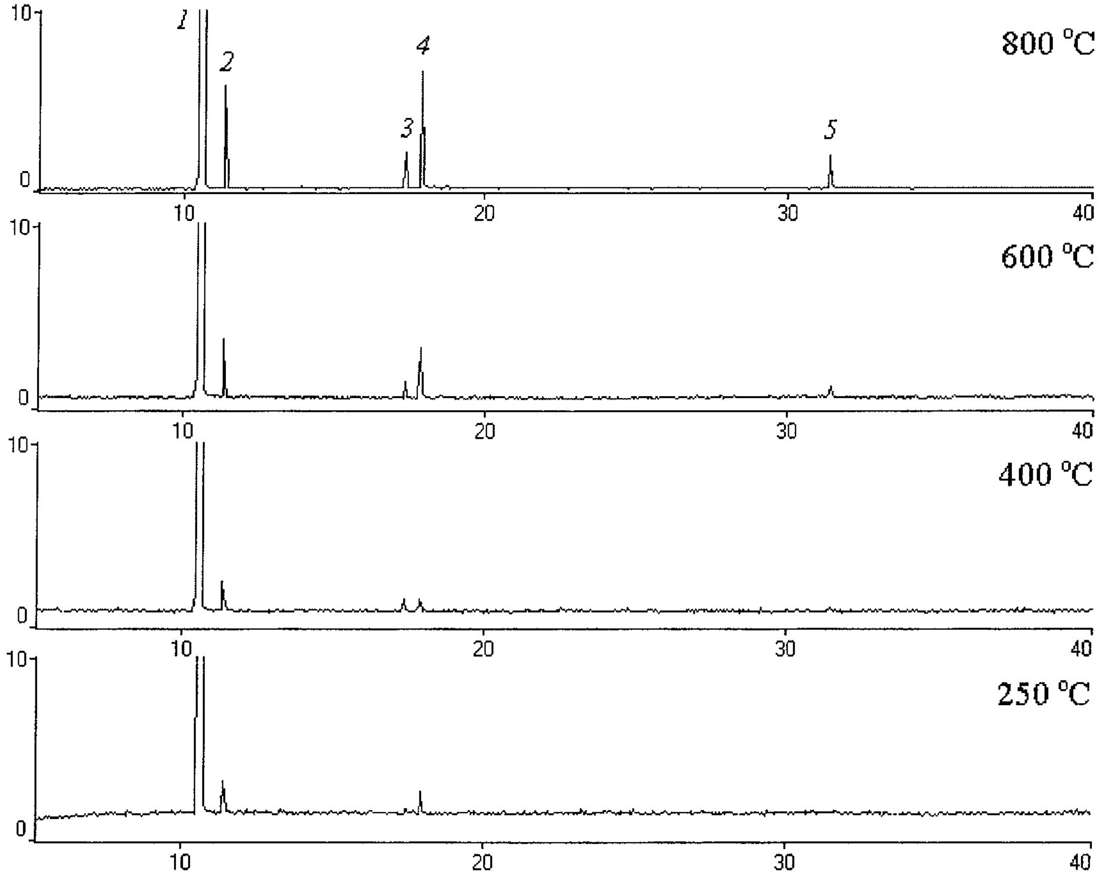

Figure 9. Chromatograms of the products from the chlorination of phenol at different temperatures and analyzed by GC/MS.

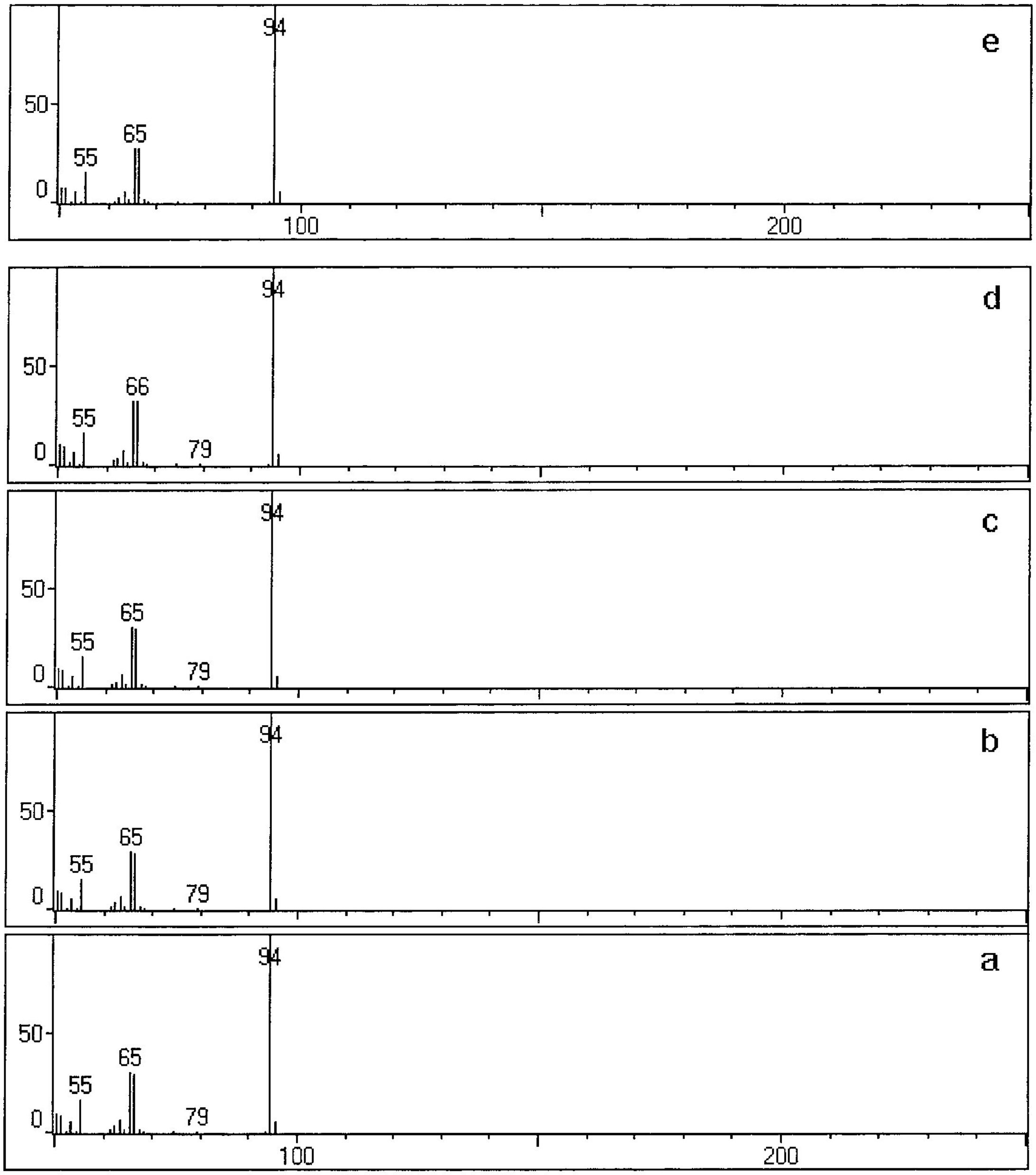

Figure 10. A comparison of the spectra of unknowns represented by peak 1, as labeled in Figure 9, with those of pure phenol. a. 800°C; b. 600°C; c. 400°C; d. 250°C; e. pure phenol.

Table 9. Comparison of the Spectral Line Intensities of Unknowns Represented by Peak 1 with Those of the Phenol Standard

Mass/Charge Ratio	Intensity of Unknown Spectra				Intensity of Standard
	250°C	400°C	600°C	800°C	
95	6.85	6.58	6.76	6.74	6.38
94	100.00	100.00	100.00	100.00	100.00
66	33.20	30.06	29.66	30.21	28.51
65	33.19	30.65	30.45	30.77	28.48
63	8.13	7.31	7.25	7.41	6.97
55	17.40	16.36	16.75	17.03	16.02
53	7.39	6.52	6.71	6.69	6.26
51	10.18	9.34	9.31	9.46	9.00
50	11.35	10.28	10.32	10.47	9.02

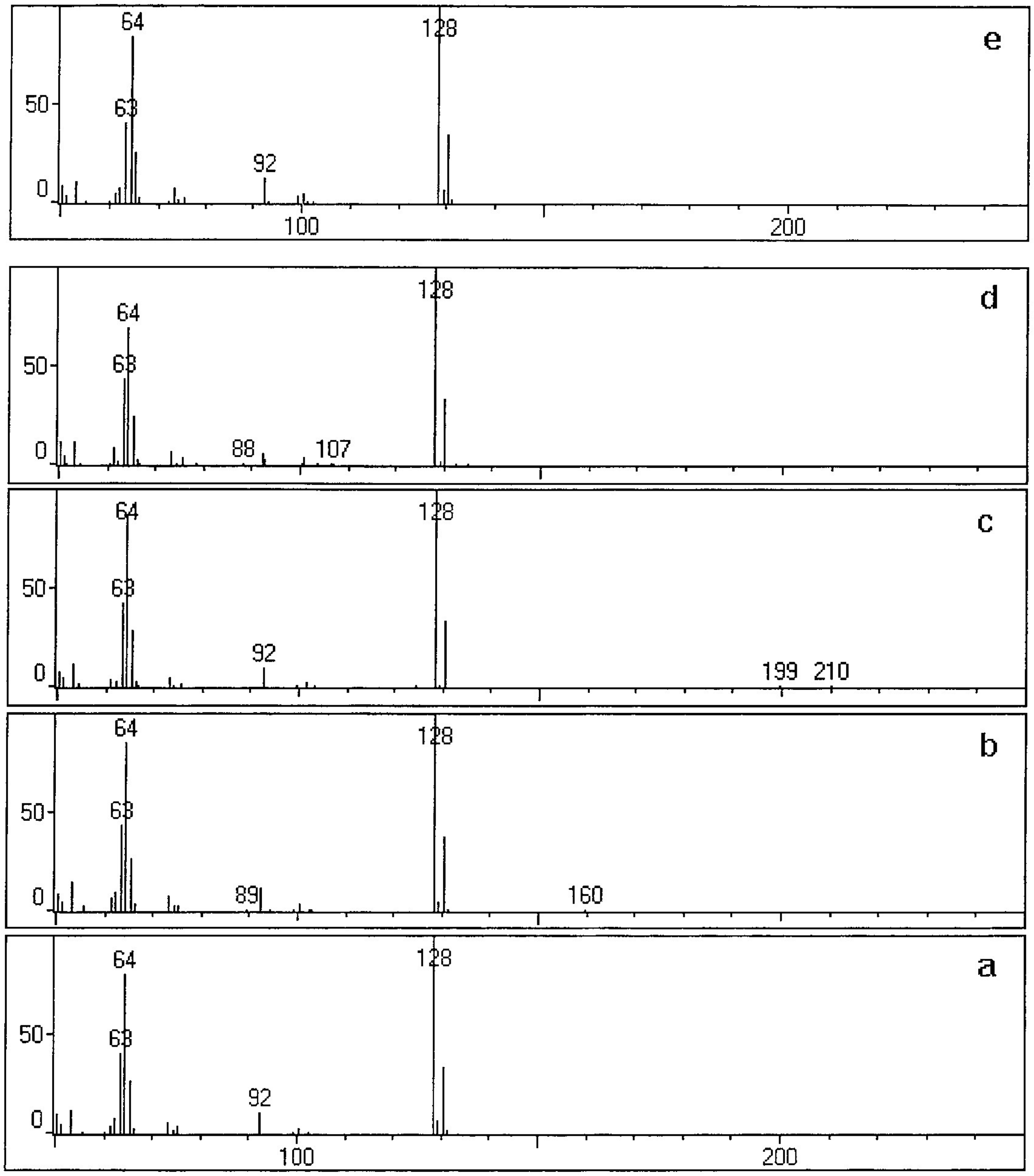

Figure 11. A comparison of the spectra of unknowns represented by peak 2, as labeled in Figure 9, with those of pure 2-chlorophenol. a. 800°C; b. 600°C; c. 400°C; d. 250°C; e. pure 2-chlorophenol.

Table 10. Comparison of the Spectral Line Intensities of Unknowns Represented by Peak 2 with Those of the 2-Chlorophenol Standard

Mass/Charge Ratio	Intensity of Unknown Spectra				Intensity of Standard
	250°C	400°C	600°C	800°C	
130	34.16	33.20	35.81	33.97	35.00
128	100.00	100.00	100.00	100.00	100.00
92	6.08	8.92	13.18	11.78	13.84
73	7.27	3.71	8.62	6.73	8.23
65	25.18	26.95	27.50	27.47	26.52
64	69.39	87.62	85.31	78.71	84.94
63	44.07	42.01	41.92	40.73	41.68
62	2.21	4.22	7.62	8.55	8.78
53	12.55	10.57	14.62	11.97	11.78
50	12.81	7.15	8.63	10.14	9.55

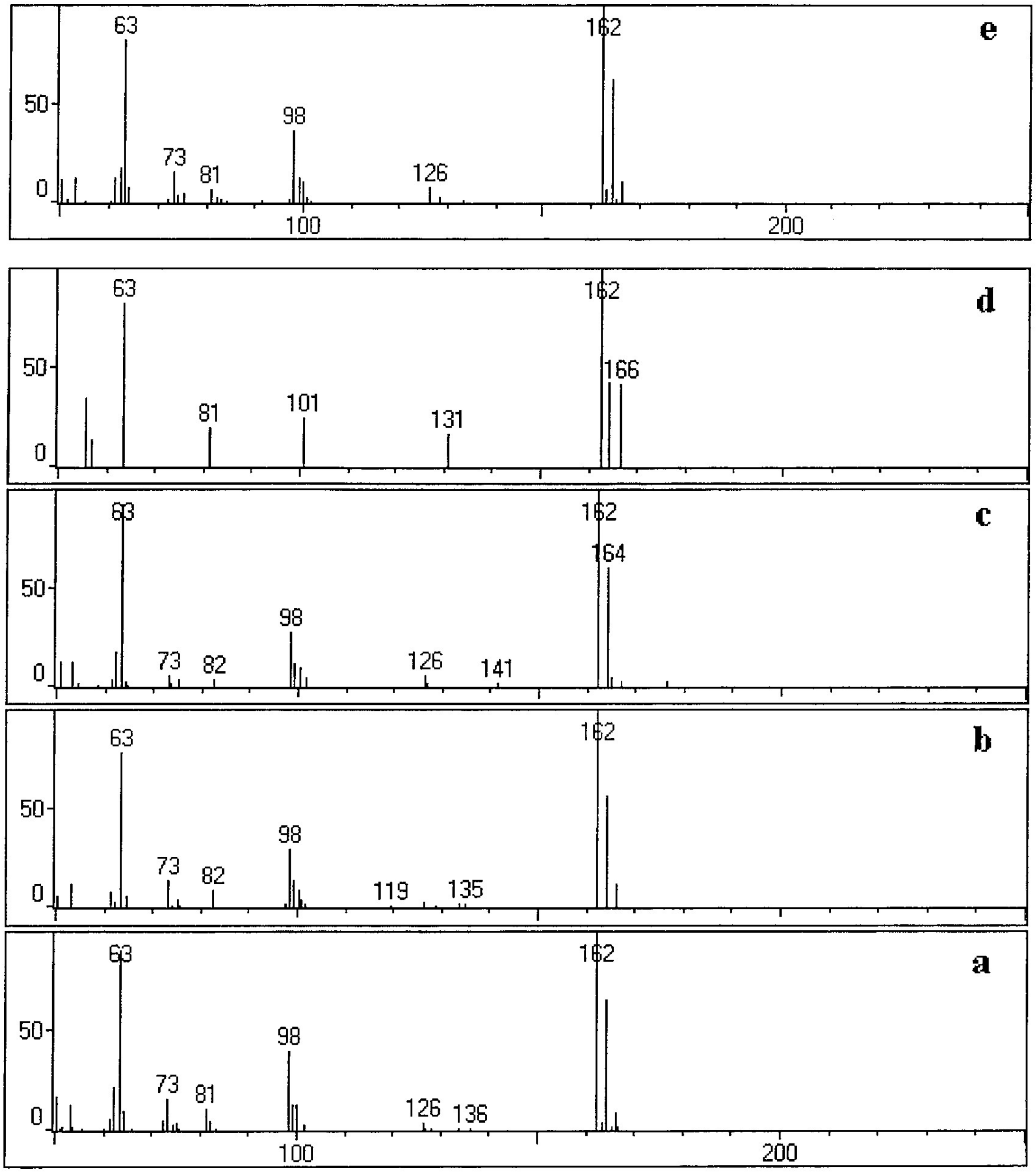

Figure 12. A comparison of the spectra of unknowns represented by peak 3, as labeled in Figure 9, with those of pure 2,4-dichlorophenol. a. 800°C; b. 600°C; c. 400°C; d. 250°C; e. pure 2,4-dichlorophenol.

Table 11. Comparison of the Spectral Line Intensities of Unknowns Represented by Peak 3 with Those of the 2,4-Dichlorophenol Standard

Mass/Charge Ratio	Intensity of Unknown Spectra				Intensity of Standard
	250°C	400°C	600°C	800°C	
166		4.09	10.56	10.54	11.07
164	44.20	61.14	60.89	65.39	62.71
162	100.00	100.00	100.00	100.00	100.00
126		6.34		5.45	8.16
100		10.38	12.31	13.78	11.07
99		12.03	12.73	13.27	12.98
98		28.32	31.60	40.80	36.83
73		6.56	15.61	15.76	16.53
63	81.22	91.82	81.13	88.54	83.04
62		18.14	7.01	21.74	18.24
61		4.25		5.75	13.60
53		13.68	11.53	14.90	13.42
50		13.38	9.56	17.18	12.42

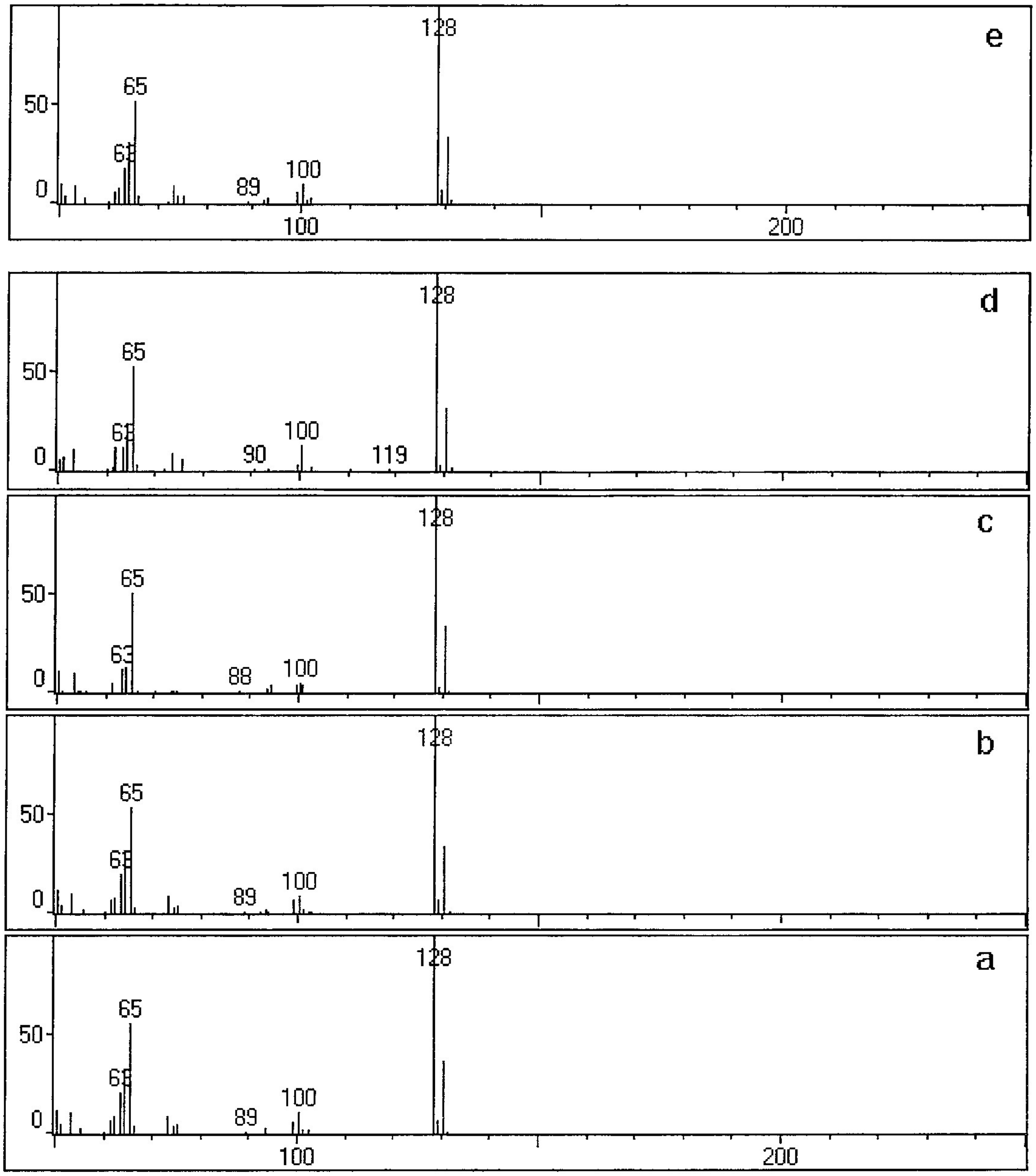

Figure 13. A comparison of the spectra of unknowns represented by peak 4, as labeled in Figure 9, with those of pure 4-chlorophenol. a. 800°C; b. 600°C; c. 400°C; d. 250°C; e. pure 4-chlorophenol.

Table 12. Comparison of the Spectral Line Intensities of Unknowns Represented by Peak 4 with Those of the 4-Chlorophenol Standard

Mass/Charge Ratio	Intensity of Unknown Spectra				Intensity of Standard
	250°C	400°C	600°C	800°C	
130	30.85	39.06	32.80	37.04	35.24
128	100.00	100.00	100.00	100.00	100.00
100	9.66	7.24	9.81	10.92	10.36
73	9.27	5.27	11.17	9.73	9.37
65	52.31	60.33	55.65	56.96	52.78
64	22.97	20.43	31.97	32.92	31.87
63	11.39	13.13	19.80	20.12	18.84
62	12.20	4.17	8.31	9.07	8.08
53	9.61	13.13	11.16	11.13	10.08
50	8.33	9.32	12.59	12.83	11.06

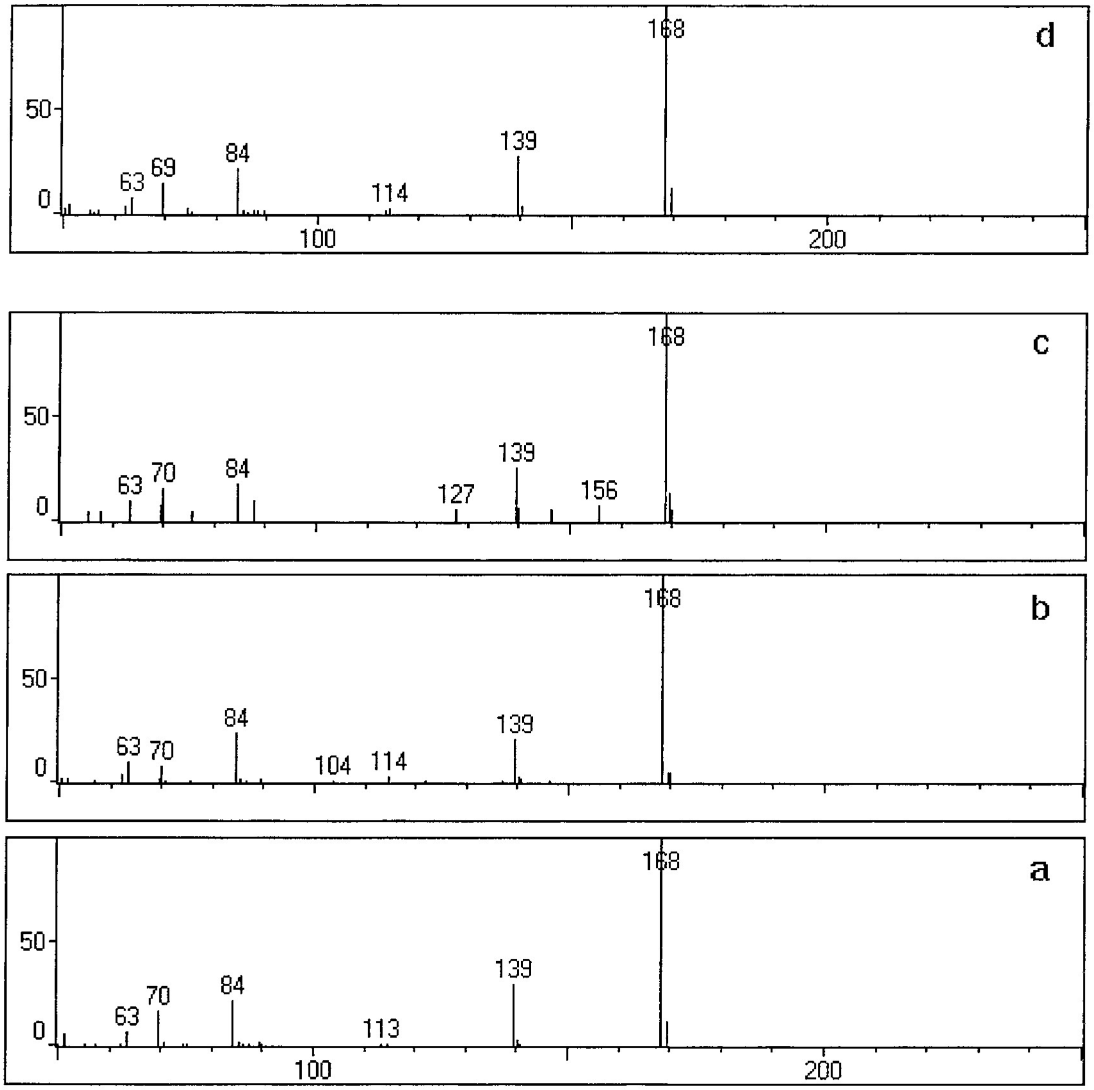

Figure 14. A comparison of the spectra of unknowns represented by peak 5, as labeled in Figure 9, with those of pure dibenzofuran. a. 800°C; b. 600°C; c. 400°C; d. pure dibenzofuran.

Table 13. Comparison of the Spectral Line Intensities of Unknowns Represented by Peak 5 with Those of the Dibenzofuran Standard

Mass/Charge Ratio	Intensity of Unknown Spectra			Intensity of Standard
	400°C	600°C	800°C	
169	14.96	6.75	12.83	13.41
168	100.00	100.00	100.00	100.00
140	7.34	4.72	3.87	4.45
139	27.62	22.22	29.87	28.62
84	18.94	21.11	22.12	22.21
70	16.59	7.35	17.78	11.89
69	8.53	5.10	8.95	15.37
63	10.71	8.71	7.64	8.00

Table 14. The Comparison of the Retention Times (min) of Pure Compounds and Those of Unknown Products from the Chlorination of Phenol

Unknown	Retention Time				Pure Compound	Retention Time
	250°C	400°C	600°C	800°C		
Peak 1	10.67	10.61	10.60	10.59	phenol	10.52
Peak 2	11.45	11.38	11.39	11.39	2-chlorophenol	11.43
Peak 3	17.45	17.38	17.38	17.38	2,4-dichlorophenol	17.39
Peak 4	17.98	17.92	17.91	17.91	4-chlorophenol	17.95
Peak 5		31.45	31.46	31.45	dibenzofuran	31.46

Therefore, the chlorination of phenol yielded 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol under the conditions conducted in this study. This result indicates that the chlorination involves only the ortho and the para position. It was found that chlorination readily begins at temperatures as low as 250°C and maybe lower. Comparing the chromatograms in Figure 9, we can see that the higher the temperature, the more heavily chlorinated phenols are produced. At higher temperatures, dibenzofuran was produced.

IV. SUMMARY AND CONCLUSION

Thus far the two steps of the proposed four-step pathway to the formation of PCDD/Fs, the Deacon reaction and the chlorination of phenol, have been successfully demonstrated:

1. The Deacon reaction was tested at different temperatures by trapping the downstream gases from heating mixtures of HCl and air in a quartz tube reactor with phenol-methylene chloride solution and then using GC/MS to analyze the chlorophenols in the concentrated trap. Within the temperature range (20°C to 800°C), more molecular chlorine was produced at higher temperatures.
2. Investigation of the chlorination of phenol in the tube reactor indicates that only the ortho and para positions of phenol are involved in chlorine substitution. More heavily chlorinated phenols are produced at higher temperatures. The chlorination of phenol by Cl_2 in the vapor phase began at temperatures as low as 250°C.

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