STUDIES ON KINETICS AND MECHANISM OF CHLORINATION OF PHENOLS

Thesis submitted to Faculty of Science
Aligarh Muslim University Aligarh
for the award of Degree of Doctor of
Philosophy in Chemistry

MOHD. KIFAYATULLAH

M.Sc.; M.Phil. (Alig)

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Hyderabad

SYNOPSIS

Chapter I

The first chapter begins with a discussion on the orientation effects of phenols during the chlorination. This is followed by a critical review on the chlorination of phenol and cresols using various chlorinating agents, catalysts, solvents giving the present state of knowledge on chlorophenols as a 'class of organic intermediates' in a variety of industrial products. The chapter is concluded by a statement in detail of the problem chosen and the proposed work to be included in this dissertation.

Chapter II

The second chapter deals with the development of chromatographic methods suitable for the study on the kinetics and mechanism of chlorination of phenols. Three chromatographic techniques mainly TLC, GLC and HPLC have been studied in detail. A variety of solvent systems have been screened to find suitable solvent system to follow the progress of the chlorination reaction by TLC. The results obtained during these studies have been discussed in detail. Benzene : cyclohexane (9:1) and xylene have been identified as the best solvent systems to follow the progress of chlorination reaction. Separation of chlorophenols and chlorocresols on a variety of stationary phases have been taken up to standardise a GLC method which can separate all the chlorophenols and chlorocresols. Carbowax-20 M has been found to be the best stationary phase for the separation and quantitative estimations of chlorophenols. During the entire studies on chlorination of phenol GLC has been choses as a method of choice for the quantitative determination of the reaction products at every stage of reaction, the results of analysis of some typical reaction mixtures have been included here. The method has been extensively used during the kinetic studies and the results obtained are discussed in this chapter. It has been observed that except for some information available on alkyl phenols, the studies on HPLC of chlorophenols and chlorocresols have been reported for the first time. Studies to find good solvent system and stationary phase to separate and quantify the chlorinated mixture of p-cresol with TBH have also been discussed here.

Chapter III

The thid chapter contains the data on spectroscopic techniques viz., UV, IR and NMR on chlorophenols and chlorocresols. A computer-assisted ^{13}C NMR spectroscopic method for the identification and quantification of complex mixture of chlorophenols has been developed. The results obtained have been compared with those obtained by conventional method.

Chapter IV

The fourth chapter deals with the results obtained

during the studies on kinetics and mechanism of chlorination of phenol with different chlorinating agents. Kinetics of chlorination of phenol with gaseous chlorine have been studied in detail, rate constants for the entire reaction scheme have been determined. Using the data activation energies have been determined. Effect of parameters such as chlorine flowrate, solvent and temperature have been studied in detail and the results are explained in terms of activation energy. Chlorophenols being industrially important products process parameters have been standardised for the preparation of monochlorophenols viz., OCP, PCP and 2,4-DCP. An alternative route for the preparation of 2,5-DCP and 2,4,5-TCP have been proposed and process parameters have been standardised.

Chlorination of phenol with $CuCl_2$ has been studied in detail as it gives preferential formation of PCP. Kinetic parameters have been determined. Since the reaction leads to the formation of PCP exclusively, various process parameters have been standardised. A technique knowhow report has been prepared for the production of PCP.

Chlorination of p-cresol with TBH has produced very interesting results. TLC of the reaction with 1 mole of p-cresol with 1 mole of TBH has shown the formation of more than 13 compounds as against the expected two products viz., 6-chloro-p-cresol and 2,6-dichloro-p-cresol. This has led

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Possible path ways leading to the formation of compounds I, II and III has been discussed and is as also indicated below.

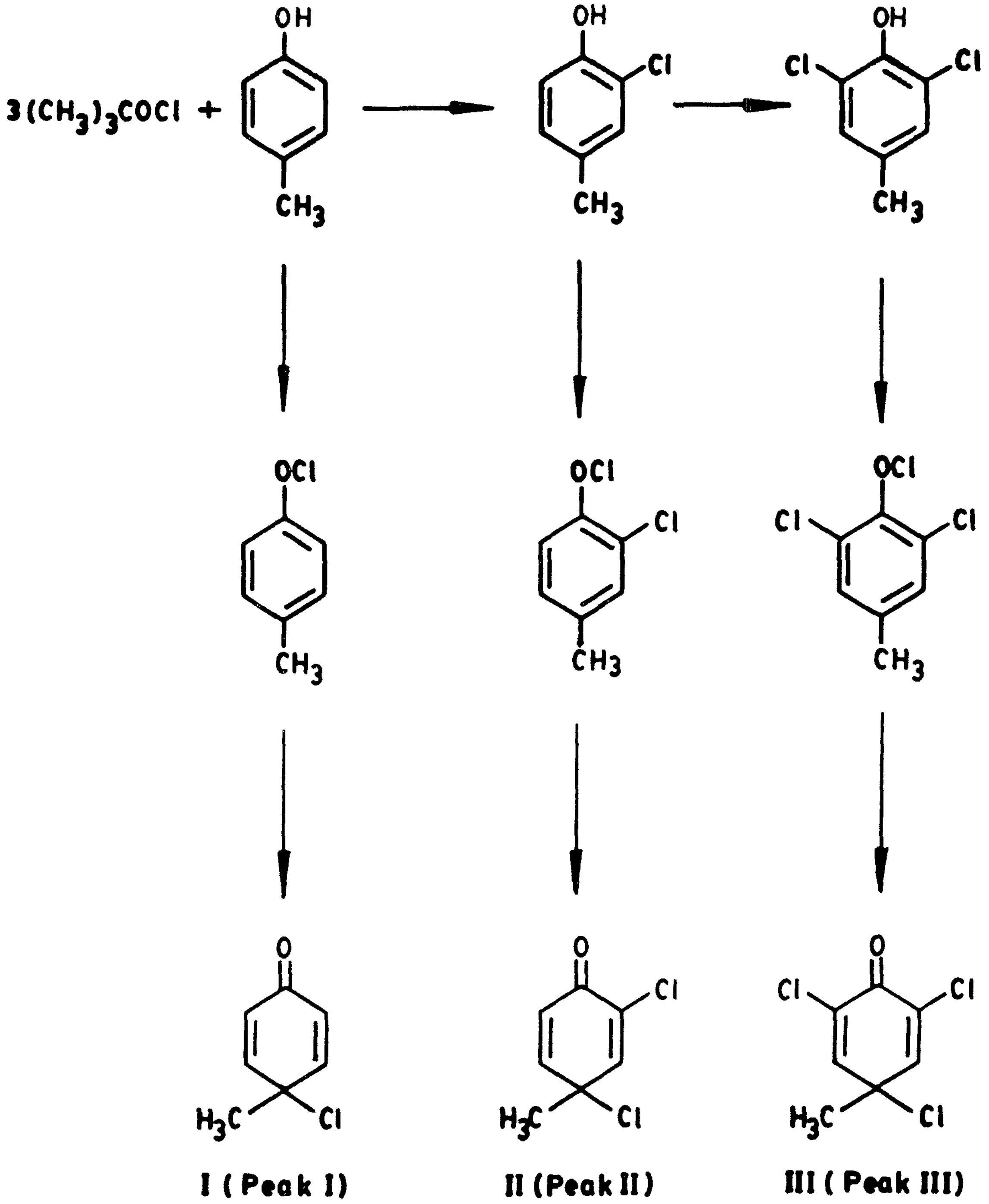
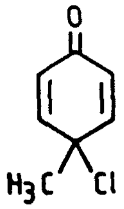


Fig. 4.5.5 Mechanism of formation of products I, II & III

to interesting results. The reaction has been repeated with two and three moles of TBH, the chromatogram of reaction product obtained with 3 moles of TBH has shown five major compounds. These compounds have been separated by preparative HPLC and their spectral data have been recorded.

The IR spectra of these compounds has exhibited IR absorption at 1710 cm^{-1} (C=O) and 1680 cm^{-1} (C=C) confirmed the presence of conjugated enone systems. The ^{1}H NMR has shown the presence of four vinylic protons which has confirmed that the enone is a dienone specially 2,5-dienone. Taking the analogy from the literature the mass spectra of these compounds have shown the parent ion at 142, 178 and 210 indicated the presence of 1,2 and 3 chlorine atoms respectively. The structures of these compounds established are



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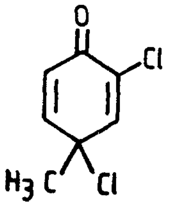

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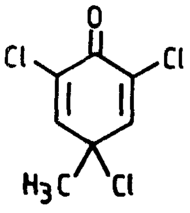

III

STUDIES ON KINETICS AND MECHANISM OF CHLORINATION OF PHENOLS

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Dated 31/3/93

CERTIFICATE

I certify that Mr. Mohd. Kifayatullah M.Sc., M.Phil., a bonafide student of Ph.D degree of Aligarh Muslim University, Aligarh has carried out research work under my direct supervision. It is certified that the investigations, findings and inferences reported by him in the form of thesis entitled "Studies on Kinetics and Mechanism of Chlorination of Phenols" for the award of Ph.D degree in Chemistry are the original contributions to the Chemical Sciences. It is also certified that he has not submitted this work in part of full to this University or any other University for the award of Ph.D degree.

(Prof. M.A.Beg)
Research Guide

DECLARATION

The research work included in this thesis entitled, **"Studies on Kinetics and Mechanism of Chlorination of Phenols"** has been carried out by me in the Indian Institute of Chemical Technology, Hyderabad under the supervision of Dr. Sajid Husain. This work is original and has not been submitted in part or full for any degree or diploma to this or any other University.

Mohd. Kifayatullah

Date : 23/8/93

Mohd. Kifayatullah

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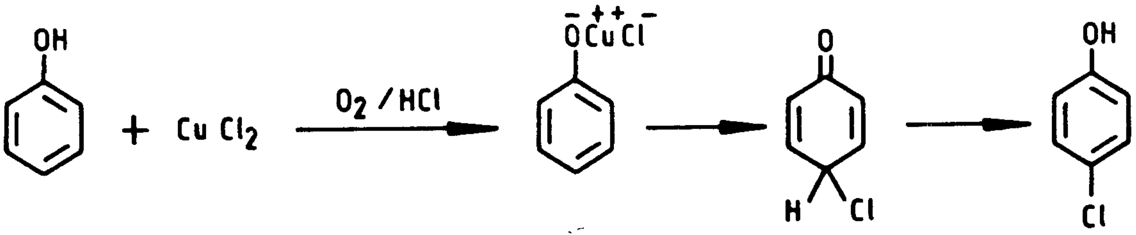
CONTENTS

Introduction

Chlorination of phenol, cresols and xylenols is known for a long time. Direct substitutive chlorination of phenol and cresols with electrophilic reagents like molecular chlorine, sulphuryl chloride etc, generally, introduces chlorine at positions where electron density is increased due to hydroxyl substituent i.e ortho and para positions. Thus ortho chloro, 2,4-dichloro and 2,4,6-trichlorophenol etc have been prepared by direct chlorination methods. Extent of chlorination and the yields of the compounds are generally dependent on the nature of chlorinating agent, experimental conditions, solvents, temperature etc. The reaction of molecular chlorine with phenol with or without solvent gives mono and dichloro derivatives. Further, chlorination leads to 2,4,6-trichlorophenol. Imamura[1] worked out the conditions for stepwise chlorination of phenol with chlorine gas employing $AlCl_3$ $FeCl_3$, Fe, $SbCl_3$ and Sb as catalysts for the preparation of mono-, di-, tri-, tetra- and penta-chlorophenols.

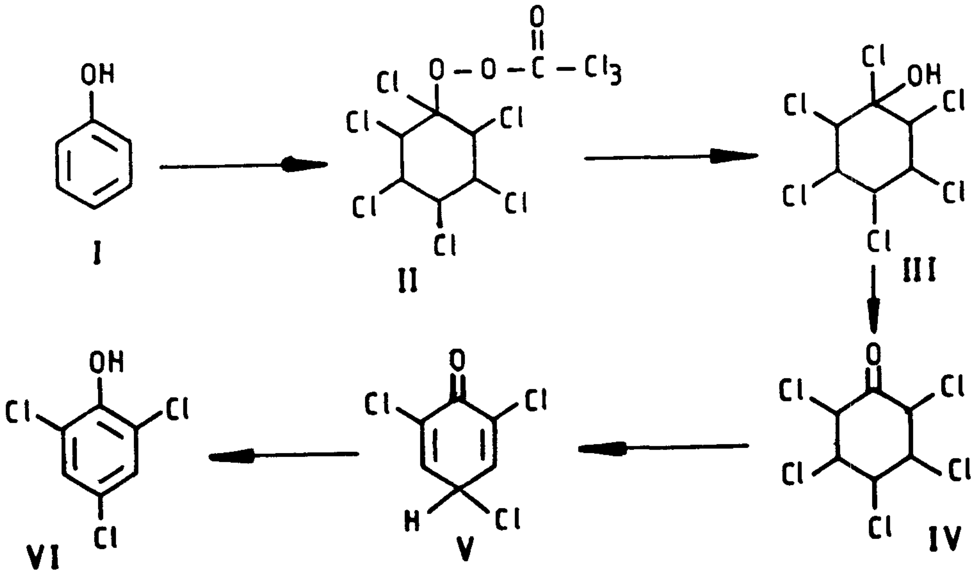
LAURENT[1a] discovered a group of chlorophenols when he chlorinated coal tar in 1836. Research on chlorinated phenoxy compounds during world war II led to the discovery of the selective herbicidal action of 2,4-Dichlorophenoxyacetic acid for control of broad leaf weeds in grass and related crops. Chlorophenols are industrially important because of their broad spectrum antimicrobial properties and their extensive use as fungicides, herbicides,insecticides, ovicides and algicides. In addition they are also used in pharmaceuticals, preservatives and dyes.

Norman [2] investigated the chlorination of molten phenol with gaseous chlorine and found 39.5% o-chlorophenol and 60.5% p-chlorophenol in the reaction mixture. Bing[3] and Zee[4] have endorsed Norman's results. Gaseous chlorination of phenol in carbon tetra chloride yields 75% of o-chlorophenol. An ionic mechanism has been proposed for the increased yield of o-chloroisomer. Extensive work has been carried out by Zubarev and coworkers[5] on the chlorination of phenol for manufacturing individual chlorophenols. p-Chlorophenol is obtained either by chlorination of phenol with sulphuryl chloride using stoichiometric quantities of the latter or by chlorination of phenol with cupric chloride in the presence of oxygen and HCl gas using hydrochloric acid as diluent. The mechanism which has been considered to be operative in this reaction and is responsible for the increased yield of p-chlorisomer has been given below schematically:



Chlorination of phenol with tert-butyl hypochlorite in hydroxylic solvents has been reported[6], to yield o-chlorophenol as a major component. Chlorination of phenol with aqueous solution of chlorine has also been studied. In this,the positive charged species (cl^{+}) is the electrophilic chlorinating agent.[7]

Rosen et al[8] carried out a study on additive chlorination of phenol. Normally phenol undergoes substitutive chlorination only, due to the presence of strong electron releasing group like hydroxyl group. These authors have modified the normal procedure by protecting the phenolic hydroxyl group as illustrated below and explained the additive chlorination to give 1,2,3,4,5,6-hexachloro cyclohexyl trichloroacetate (II). The structure (III) was established as it gave 2,4,6-trichlorophenol (VI) on subsequent acid hydrolysis.



Simonov and coworkers[9] have studied the chlorination of phenol to get 2,4-dichlorophenol in nitromehtane and it was found to be (95-97%). They also found that repeated use of nitromehane without its additional purification does not reduce the content of 2,4-dichlorophenol in the mixture of chloroproducts. In another communication they have studied[10] the effect of the solvent and molar concentration of the starting solutions on the chemical composition of the chlorophenol. They observed that the composition of the reaction mixture is highly sensitive to the nature of the solvents and the initial concentration of the phenols used.

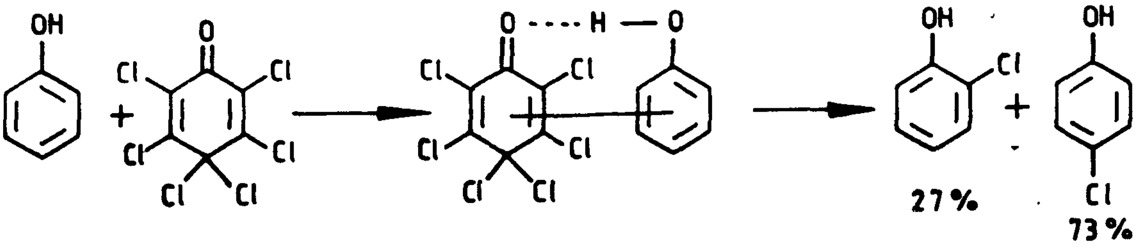
Zobarev et al[11] have thoroughly studied the role played by the solvents towards selective chlorination of phenols.They concluded that solvents do substantially affect the orientation of the chloroisomers in the chlorination of phenol

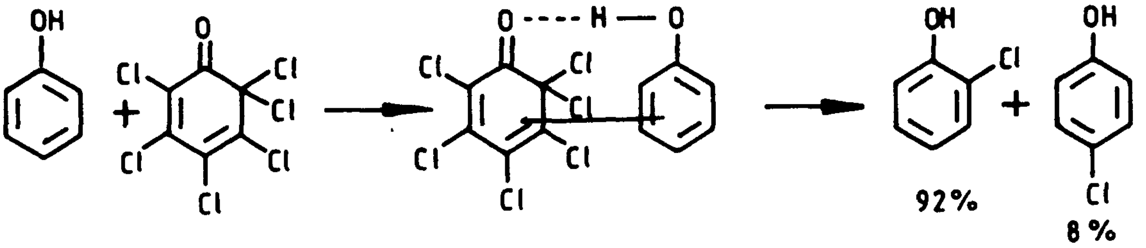
Pearson and Buchler[12] have presented a review article on "unusual electrophilic substitution in synthesis". The review states that solvent effects and temperature have a slight influence on the ortho para ratio. Recently watson[13] carried out the comparitive study on the chlorination of phenol with chlorine and t-butyl hypochlorite in different solvents at different temperatures. From the results obtained they concluded that t-butyl hypochlorite is not a selective o-chlorinating agent in either ethanol or carbon tetrachloride. Solvents can be used to change the isomer distribution from p-chlorophenol to o-chlorophenol.

Recently Milnes[14] has reviewed the current progress in the preparation of chlorophenols, by direct chlorination of phenols or by hydrolysis of polychlorobenzenes and their separations. A Russian[15] patent covers the improvement of yields of monochloroalkyl phenols by using solution of chlorine in an inert solvent as chlorinating agent at -20°C 30°C[15] . Zubarev[16] described the preparation of individual chlorphenols by direct chlorination, the extent of chlorination has been monitored by density measurements. They have reported that mono chloro isomers (viz,o-chloro- & p-chloro-) have been the first to be formed followed by the dichloro isomers (viz, 2,4-di, 2,6-dichloro phenols). Exhaustive chlorination of phenol has yeileded 2,4,6-trichlorophenol. When o-chlorophenol has been reacted with gaseous chlorine dissolved in 10 fold excess of corbon tetra chloride it resulted in 2,6-dichlorophenol.

Japanese workers[17] have studied the chlorination of phenol in a semi-batch bubble column and found that the results can be easily interpreted on a simple reactor model. A Czech patent covers the chlorination of phenol at 20-150°C to produce o-chlorophenol. After rectification the residue is further chlorinated to the 2,4- and 2,4,6-trichloro derivatives[18].

Furuya[19] and Nukiyama have investigated the chlorination of phenol with molecular chlorine and t-butyl hypochlorite and they noticed that o/p ratio increases with the decreasing phenol concentration, with the increase in temperature and polarity of the solvent. They further demonstrated that the o/p ratio is influenced when acetic anhydride is used as solvent. Based on this observation a possible mechanism has been suggested. Popova et al[20] have studied the chlorination of phenol using a variety of alcohols (C_1-C_{10}) and claimed that the structure of alcohol molecules has a definite influence on the chemical composition of the chlorinated mass. They have also found that the ratio of 2,4-DCP/2,6-DCP in normal (C_1-C_4) alcohols varies directly with the bond energies between the phenol and solvent and reverse relationships have been found in the systems of higher alcohols (C_6-C_{10}). In another comuunication they have studied the effect of different solvents on the chlorination of phenol and explained in terms of PhOH-Cl-solvent and PhOH-Cl-complexes[21] Ingles war et al[22] have studied the antibacteriological activity of the chlorinated products formed by the chlorination of thirteen phenols and observed that increase in the number of chlorine atoms in the ring increases the bgacteriological activity of chlorophenols. Chlorination of phenol with chloramine-T,gives rise to mono, di- and 2,4,6-trichlorophenol but tetra and pento-chlorophenols and their oxidation products have not been detected. Phenols have been found to be regio-selective by using 2,3,4,4,5,6-hexachloro-3,5- and 2,3,4,5,6-6-hexachloro-2,4-cyclohexadiene-1-one as chlorinating agents[23] as shown below.





Chlorination of phenol has been studied in two series of polymers. The presence of these materials influences both, the over all conversion of phenol to chlorinated products and alsothe distribution of products of chlorophenols[24].

Substituted phenols when chlorinated give rise to cis and trans pentachloro and tetrachloro cyclohexanones and their structures were confirmed by x-ray crystallographic studies[25]. Phenol was selectively chlorinated with chlorine in a perchlorinated hydrocorbon in the presence of 10-50ppm of HNRR' where R = C_3-C_{10} sec. alkyl, group R'= H,C_3-C_{10} sec. alkyl to give exclusively o-cholorphenol[26]. Orthochlorination of phenol by t-alkyl hypochlorite in methanolic and aqueous solution is markedly enhanced by the inclusion of a tertiary alcohol in a detergent chain, β to the ionic head groups[27]. Suckling claimed that chlorination of phenol was inhibited by the presence of tentacle molecule which forms complexes with small aromatic compounds in solution by protective binding.

CHLORINATION OF CRESSOLS

Reactions between molecular chlorine and cresolsgives 6-chloro, 4-chloro and 4,6-dichloro derivatives in the presence or absence of solvents. Studies on chlorination of o-cresol in organic solvents have been carried out by Campbell and Shields[28]. It has been explained that the bound solvent molecules will have a shielding effect on the ortho-position, when the para position is not blocked, however enhances the yield of the p-chloroiosmer. Chlorination of o-cresol with sulphuryl chloride in the presence of Al, Fe, Sn, Ti and Zn halides have been reported by Robert and Roberts , in a patent literature[27]. It has been reproted that when o-cresol is chlorinated with SO_2 Cl_2 in the presence of aqueous solvents, the quantity of water changes the ratio of o- and p-chloro-isomers in the final chlorinated mixture. More 6-chloroisomers are formed with increased quantity of water, Work on chlorination of o-cresol in acidic-aqueous solutions has been carried out by Eliasek and Jungwrit[29]. They suggested that at PH 2-3 chloroquinones are formed whereas at PH 7.5 photodisproportionation of chloroquinonoes takes place, yielding corresponding hydrochloroquinones which in turn polymerises to humin-like substances. Preparation of monochloro-m-cresol and its conversion to methoxy toluene has been described by stnitzyn and Glibin[30]. Teramoto and coworkers[31] have presented the chlorination of p-cresol with gaeous chlorine using reactors composed of a bubble column and stirred with various types of gas distributors. The results were explained in terms of large liquid phase mass transfer coefficients.

BASF has patented a highly selective process of chlorination of o-cresol using iron pentacarbonyl catalyst where in the reaction of o-cresol with 10% excess of SO_2 Cl_2 is carried out in the presence of iron pentacarbonyl in a three stage cascade reactor[32]. Watson[13] has reported a comprehensive discussion on the yields of 6-chloro-o-cresol with molecular chlorine and tert-butylhypochlorite reagents.

Sasaki et al[33] have prepared, 2,6-dichloro-p-cresol by chlorinating p-cresol in the presence of H_2O and heating the mixture with aqueous Na_2 SO_3. In this reaction cyclohexadienone by-products have been solubilized with Na_2 CO_3 and decomposed with H_2SO_4 to regenerate the cresol and 2-chloro-p-cresol which have been rechlorinated.

Statement of Problem - studies on Kinetics and mechanism of Chlorination of Phenols:

From the preceeding review it would be apparent that chlorophenols exhibit outstanding germicidal, insecticidal properties and have demonstrated their utility as flea repellents, fungicides, wood preservatives, plant growth regulators, antiseptic, disinfectant and also employed as selective solvent in refining mineral oils. It is also apparent that extensive studies on chlorination of phenols have so for not been conducted. Hence, a systematic study on the kinetics and mechanism of chlorination of phenols has been taken up in order to have a clear picture of over all reaction between chlorine and phenols and to generate the kinetic and thermodynamic data, which can be used in standardizing the process parameters.

In the present studies kinetics of chlorination of phenols (viz., phenol, and p-cresol) have been carried out with,

(a) gaseous chlorine

(b) cupric chloride

(c) tert-butyl hypochlorite.

Chromatographic studies on chlorophenols have been taken up with a view to standardise suitable analytical methods for the identification and quantification of products of chlorination. An imporoved method has been standrdized using Gas-liquid chromatography (GLC) for the analysis of chlorinated mixture of phenols. Since hardly any data are available on the high-pressure liquid chromatography (HPLC) of chlorophenols, chlorocresols and xylenols, a systematic investigation of the separation of these compounds by HPLC has also been initiated. This has led to the development of a new method for quantitative estimation of chlorophenols and chlorocresols. This technique has been extensively used for the separation and identification of unusual products obtained during the chlorination of p-creol with tert-butyl hypochlorite. For this class of compounds quantitative HPLC has been applied for the first time.

Apart from the TLC, GLC, and HPLC methods, other spectroscopic methods such as UV, IR, NMR and Mass spectroscopic techniques have also been used. Hyphenated techniques such as HPLC-Mass called as offline mass spectroscopy has been used to identify the products of chlorinated mixture of p-cresol with tert-butyl hypochlorite. From the data we could characterise these compounds as chlorocyclohexadienone type of compounds and these are discussed in detail. NMR spectroscopy has also been used extensively during the characterisation of these compounds. Edited 13 C NMR spectroscopic technique has been developed based on their chemical shifts to identify and quantify the chlorophenols and chlorocresols. So for this technique has been applied for the first time to this class of compounds. Uv-Vis, IR has been applied wherever necessary. Kinetic studies have been carried out to generate the kinetic data for the entire reaction scheme which comes under series cum parallel reaction. Among the chlorophenols, p-chlorophenol and 2,4-dichloro-phenol being highly important products, the process parameters for their industrial productions have been standardised. Effect of solvent on isomers distribution during the chlorination of phenol has been studied with a view to minimize the formation of 2,6-dichlorophenol, an unwanted impurity which decreases the activity of 2,4-dichlorophenol (2,4-DCP) mainly used in the production of 2,4-D. 2,4-DCP having more than 98% purity has been obtained by using polar solvent such as nitromethane and process parameters has been standardised. Detailed kinetic studies have been carried out to explain the preferential formation of 2,4-DCP in terms of phenol-solvent complex formation and also in terms of changes in activation energy. An alternative method has been developed for the production of 2,4,5-trichlorophenol, as the normal routes for its production gave benzoparadioxin which is a highly toxic compound. The process parameters for both 2,5-DCP and 2,4,5-TCP have been standardised.

Studies on oxychlorination of phenol to get exclusively p-chlorophenol has been carried out using cupric chloride as chlorinating agent which is known as parachlorinating agent. Detailed kinetic data has been generated and various parameters needed for the commercial production of p-chlorophenol have been standardised. Chlorination of p-cresol with tert-butyl hypoclorite has given unusual chlorosubstitued products which have been isolated characterised with the help of UV, IR, NMR and Mass spectral data. The details of these studies have been discussed in the thesis at appropriate places.

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CHAPTER II

Analysis of Kinetic Data - Standardisation of Analytical Methods

The accuracy of the kinetic data is of paramount importance in a kinetic study which in turn depends on the selection of suitable analytical methods for the determination of concentrations of various constituents of reaction mixture, rate constants of the reactants and products and their thermodynamic parameters. The choice of an appropriate method in turn depends upon the phase, nature of the reactants, intermediates and products.

Though it has been used and it is possible to use physical properties such as refractive index , density, viscosity, freezing point, specific rotation, boiling point, solubility and miscibility as the basis for analysing the organic samples. These are usually limited to two or three component systems. Moreover, analysis based on physical measurements is often emperical and requires rather extensive preliminary calibrations. Combination of physical and chemical methods is often more convenient as compared to chemical method alone. Besides the methods mentioned above which are primarily physical in nature and have found extensive aplications in organic analysis are nuclear magenetic resonance spectroscopy (NMR), electrom paramagnetic resonance spectfoscopy (EPR), mass spectrometry, x-raydiffraction analysis, spectrophotometers (UV , IR) chromatography, polarography etc.

It is seen in the literature that chemical analyses have been frequently used as an analytical tool during the kinetic study of chlorination of phenols and substituted phenols[1] with a variety of chlorinating agents. Spectrophotometry[2], chromatography[3,4] and polarography[4] have also foud use as analytical tools during the kinetic study of chlorination of phenols.

1. **Titration methods:** In the past titration methods such as acid-base and bromination have been widely applied. However, none of them are specific, these days they find limited application. They are well documented[5].

Chromatographic techniques are the most powerful tools among the separation sciences which are frequently used for qualitative analyses and for quantitative estimations. They are widely utilized to know the reaction rates, different energy contents and mechanisms involved. Chromatographic techniques are considered as an excellent tools to follow the progress of a chemical reaction.

In the present studies chromatographic techniques have been extensively used both for qualitative identification and quantitative estimation.

Techniques of Chromatography: Thin-layer, Chromatography (TLC) gas-liquid chromatography (GLC) and high performance liquid chromatography (HPLC) havebeen studied with a view to develop suitable methods of separation and identification of various products of chlorophenols. The results obtained by these techniques are described and discussed in this chapter. Some of these results have also been included at appropriate places in the thesis.

2.1 Thin-layer chromatography (TLC) of chlorophenols

TLC of phenols and chlorophenols has been studied extensively by many workers[6]. However, reports on chlorophenols and chlorocresols are limited. Brake and Graham[7] studied the separation of chlorophenols using the following solvent systems. (i) Cyclohexane-acetic (93:7%) (ii) Aqueous acetic acid (10%). Their results are summarised in Table 2.1.1.

Sajid Husain studied the TLC of chlorinated cresols[8,9] using (A) xylene saturated with formamide (B) Pet ether (80-100) saturated with formic acid (C) Benzene: acetic acid: water (2:2:1) v/v and the results obtained are summerised in table 2.1.2.

In the present study the above metnioned solvent systems have been found unsatisfactory for the separation of chlorophenols specially for the chlorinated mixture of p-cresol with tert-butylhypochlorite (TBH). A variety of solvent systems listed below have been used for TLC of chlorophenols, and chlorinatued mixture of p-cresol

E. Benzene : Acetic acid (5:1 v/v)

F. Benzene : Cyclohexane (9:1 v/v)

G. Chloroform : Methanol (1:1 v/v)

H. Benzene : Ethylacetate (9:1 v/v)

I. Xylene : Pure

Rf values calculated for all the chlorophenols and chloro cresol are given in table 2.1.3 and 2.1.4.

From these data it is apparent that reasonably good separation has been obtained for all the chlorophenols and chlorocresols in benzene-cyclohexane and xylene. However, 2,4-dichlorophenol, 2,6-dic-hlorophenol and 2,5-dichlorophenol exhibited close Rf values in E, F, G and H except in I. In general Rf values of mono substituted chlorophenols are higher than their parent phenol. But the Rf values of disubstituted phenols are slightly lower than the mono substituted phenols. The reduction in Rf values suggested some increase in the binding of the molecule with the substrate. It may be due to the increase in the strength of phenolic hydrogen bond as a result of inductive effect of halogen bond. Further Rf value of o-chlorophenol is higher than those of m-chloro- and p-chlorophenols. This is due to the internal hydrogen bonding present in o-chlorophenol. Likewise the higher Rf value of 2,6-dichlorophenol as compared to other dichlorophenols is due to the presence of ortho-chlorines, the chlorine atoms in 2- and 6- postions compete for phenolic hydrogen so the internal hydrogen bonding is not realised by one of the halogen atom. As a result the internal hydrogen bonding is weakened rather than strengthened by the presence of second ortho halogen atom.

The machansim of chromatographic separation of phenols is a two stage process[7].

1. Dissociation phenol in the solvent which will be favoured by the formation of internal hydrogen bonding with the hydrogen of the phenolic group:

2. Adsorption of phenol on the substrate by means of hydrogen bonds formed between the electronegative group of phenol and hydrogen atom of the hydroxyl group.

The factors which are responsible for the adsorption by solids are

A. Non-polar vander wall's forces

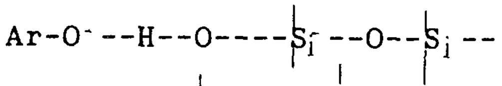
B. Formation of H-bonds

C. Covalent bond formation

D. Ion-exchange

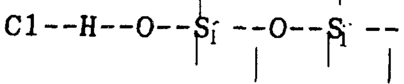
Of these, hydrogen bond formation is the most important. The following types of hydrogen bonds are possible.

(i)



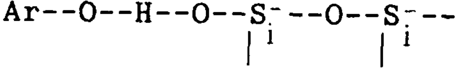
$\mathrm{Ar{-}O^{-}{-}{-}H{-}{-}O{-}{-}{-}{-}Si{-}{-}O{-}{-}Si{-}{-}}$

(ii)



$\mathrm{Cl{-}{-}H{-}{-}O{-}{-}Si{-}{-}O{-}{-}Si{-}{-}}$

(iii)



$\mathrm{Ar{-}{-}O{-}{-}H{-}{-}O{-}{-}Si{-}{-}O{-}{-}Si{-}{-}}$

However formation of covalent bond has been shown to be unlikely. In the light of these possibilities the increase in Rf values of chlorophenols may be due to.:

(1) Internal hydrogen bonding of the phenolic group in the second phase, decay the possibility of external hydrogen bonding which will decrease the adsorption.

(2) The electronic or steric effects altering the strength of the internal hydrogen bonding.

(3) Bulk effects of the groups causing some of the non-polar points of the molecule to be held away from the polar surface which decreases the adsorption.

(4) The bonding of the molecule to the polar layer by halogen group not involved in the hydrogen bonding with the phenolic group. Thus the primary mechanism in the separation of chlorophenols and chlorocresols is the hydrogen bonding between the oxygen atom of phenolic group and hydrogen atom on the surface of hydroxylated silica. Here the surface probably acts as proton donor to the halogen group resulting in the formation of hydrogen bond.

In the present studies TLC has been extensively used to follow the progress of the reaction. Conditions to get optimum results by TLC technique have been established prior to its actual application to the reaction muxtures. As already stated that many solvent systems have been tried to have proper separation. It has been found that reported solvent systems (A,B,C) are only effective to certain chloro-isomers.

However, when chlorinated product of P-cresol with TBH has been subjected to TLC analysis it has shown close spots. Therefore, it has necessitated the development of improved solvent systems. The results so obtained are recorded in table 2.1.5 From the table it is clear that excepting benzene and ethyl alcohol systems almost all the solvent systems gave good separation of the components of reaction mixture. However, when these systems have been employed for the HPLC analysis using semi-preparative column, separation has been not found to be satisfactory. Hence detailed study on solvent screening has been carried out and toluene has been found to be the best solvent. The studies on TLC have revealed that TLC can be very well used to study the progress of the reaction but yield qualitative information regarding the distribution of chloro-isomers present in a reaction mixture.

For quantitative information from TLC, one has to have either TLC-FID or TLC- densitometer detector types of system. This type of facility is not available with us.

2.1.1.

Rf vllues of chlorinated phenols temperature 25+5°

Time of run 2 hrs system I = Cyclohexane - acetic acid

(93 : 7 v/v)

System (ii) Aqeuous acetic acid 10%

S. No	Compound	System (i) Rf	System (ii) Rf
	Phenol	0.160	0.620
	2-chlorophenol	0.525	0.360
	3-chlorophenol	0.195	0.330
	4-chlorophenol	0.185	0.340
5	2,3-dichlorophenol	0.455	0.180
6	2,4-dichlorophenol	0.455	0.175
	2,5-dichlorophenol	0.440	0.170
	2,6-dichlorophenol	0.630	0.260
9	3,4-dichlorophenol	0.170	0.130
	3,5-dichlorophenol	0.170	0.115
	2,4,5-trichlorophenol	0.380	0.060
	2,4,6-tirchlorophenol	0.590	0.090
	2,3,4,6-tetrachloro	0.520	0.025
	2,3,4,5,6-penchloro	0.475	0.000

Table 2.1.2 Rf values of chlorocresols in solvent A, B, and C

temperature - 25 ± 3 °C

S.No.	Compound	Solvent-A Rf	Solvent-B Rf	Solvent-C Rf
1	2-methyl phenol	0.32	0.11	0.67
2	3-methyl phenol	0.26	0.09	0.63
3	6-chloro-2-methyl phenol	0.72	0.58	0.89
4	4-chloro-2-methyl phenol	0.31	0.06	0.65
5	6-chloro-2-methyl phenol	0.47	0.55	0.89
6	4-chloro-3-methyl phenol	0.25	0.12	0.63
7	2,6-dichloro-2-methyl phenol	0.74	0.39	0.89
8	4,6-dichloro-3- methyl phenol	0.40	0.55	0.89
9	2,4,6-trichloro-3-methyl phenol	0.66	0.56	0.89

Table 2.1.3 Rf values of chiorinated phenols in solvents E, F, G, H, and I temperature 25 ± 3 ^{o}C

S.no.	Phenol	Solvent				
		E	F	G	H	I
1	Phenol	0.84	0.41	0.38	0.95	0.76
2	2-chlorophenol	0.86	0.67	0.55	0.92	0.81
3	3-chlorophenol	0.85	6.58	0.55	0.92	0.78
4	4-chlorophenol	0.84	0.50	0.50	0.91	0.78
5	2,4-dichlorophenol	0.88	0.63	0.57	0.92	0.83
6	2,5-dichlorophenol	0.89	0.63	0.59	0.92	0.81
7	2,6-dichlorophenol	0.90	0.74	0.60	0.92	0.87
8	3,4-dichlorophenol	0.88	0.51	0.62	0.79	0.73
9	2,4,5-trichlorophenol	0.95	0.71	0.64	0.93	0.87
10	2,4,6-trichlorophenol	0.85	0.74	0.66	0.93	0.87
11	2,5,6-trichlorophenol	0.90	0.77	0.61	0.85	0.91
12	2,4,5,6-trichlorophenol	0.88	0.98	0.63	0.88	0.84

Table 2.1.4 Rf values of chiorinated cresols in solvents E, F, G, H and I Temparature 25 ± 3 °C.

S.No.	Phenol	E	F	G	H	I
1	o-cresol	0.92	0.72	0.57	0.93	0.83
2	m-cresol	0.90	0.62	0.50	0.94	0.82
3	p-cresol	0.88	0.54	0.54	0.93	0.76
4	6-chloro-o-cresol	0.93	0.87	0.69	0.90	0.92
5	4-chloro-o-cresol	0.90	0.70	0.57	0.86	0.85
6	6-chloro-m-cresol	0.92	0.77	0.70	0.82	0.89
7	4-chloro-m-cresol	0.83	0.63	0.52	0.85	0.75
8	6-chloro-p-cresol	0.88	0.88	0.71	0.89	0.85
9	2,4-dichloro-m-cresol	0.90	0.77	0.71	0.88	0.91
10	2,6-dichloro p-cresol	0.90	0.77	o.75	0.82	0.87

Table 2.1.5 Rf values of the components reaction product of P-cresol with TBH in various solvent systems. Temparature 25 ± 3^{o}C.

S.No.	Compound	Dichloro-methane	Light petroleum + Acetone 90 : 10	L.P.+Me oH +cyclohexane 85:10:5	L.P.+MeoH 75 : 25	L.P.+Acetone +CH_3 COOH 85:10:5	Benzene-ethyl alcohol 95 : 5
1	Spot I	0.90	0.84	0.93	0.92	0.89	0.97
2	Spot II	0.84	0.78	0.84	0.85	0.78	0.96
3	Spot III	0.66	0.46	0.59	0.78	0.52	0.89
4	Spot IV	0.51	0.37	0.53	0.56	0.37	0.82
5	Spot V	0.33	0.27	0.32	0.33	0.19	0.77

2.2 Gas-liquid chromatography (GLC)

Though TLC separation of chlorophenols and chlorocresols using silica gel as an adsorbent has been found satisfactory but the information generated is qualitative. GLC has been selected keeping in view, of its high resolution, speed of analysis and extreme sensitivity, moreover it provides quantitative estimation of the reaction product.

According to literature, good resolution is obtained using high efficiency capillary columns and selective stationary phases. But the use of capillary column leads to a time consuming analysis[10]. A much better separation of chlorophenols is generally obtained when its derivatives are subjected to GLC rather than with free phenols. But the derivatisation technique has some limitations. Moreover those stationary phases which are effective for this kind of work are found to be unstable.

Scanty information is available in literature[11] on the GLC separation of chlorophenols and chlorocresols. Work on separation of chlorophenols using support bonded polyester columns has been reported and their results have been recorded in Table 2.2.1. One finds from it that phenol and mono-chloro derivatives have not been attempted at all in this work. Further separation of chloro-cresols by GLC technique has also not been thoroughly studied.

Following stationary phases have been tested for the separation of chloro-isomers.

A. Silicone elestomer - 30 (S.E. - 30)

B. Diethyl glycol succinate (DEGS)

C. Carbo wax - 20 M (CW - 20 M)

D. Carbo wax - 5 M (CW - 5M)

The operating conditions for the above mentioned stationary phases are given in Table 2.2.2. The relative retention times of chlorophenols (relative to phenol) and chlorocresols (relative to o-cresol) are given in Tables 2.2.3 and 2.2.4. The chromatograms obtained on carbowax-20 M are given in Figs. 2.2.1 and 2.2.2.

From Table 2.2.4 it is clear that all the chlorophenols have been separated excepting 2,4-dichlorphenol and 2,5-dichlorophenol. Separation of chlorocresols is also found to be good on C.W-20 M column.

From the above studies C.W-20 M is found to be the best column for the separation of chlorophenols and chloro cresols. From the results the following salient observations are recorded.

(a) p-chlorophenol has higher retention time than, o-chloro, 2,4'-dichloro, 2,5-dichlor, 2,4,5-trichloro and 2,4,6-trichloro phenols.

(b) Separation of pairs such as 2,4-dichloro, 2,5-dichloro, and meta-, p-cresols have not been achieved most probably they have same vapour pressure.

(c) Those compounds which have more ortho-substituted chlorine atoms in the benzene nucleus despite their higher boiling points emerged out earlier than those compounds having lower boiling points but having chlorine atoms in para and meta positions. The earlier elution of these compounds can be explained in terms of ortho effect.

(d) Ortho-chlorine substituted compounds gave sharp peaks where as broad peaks are obtained for those compounds having chlorine atoms in the meta and para positions.

(e) Similar behaviour was observed in the case of chlorocresols.

Carbowax-20 M finds extensive use in the present investigation because it has separated almost all the chlorinated phenol excepting 2,4-DCP, and 2,5-DCP. The method has been standardised by analysing several set of trainee mixtures to have the accuracy of the procedure and the results are recorded in Table 2.2.5. The developed method has been employed to monitor the progress of chlorination reactions and also for the quantitative estimation of each constituents of the reaction mixture of the samples, withdrawn at various intervals of time.

Tables 2.2.6, 2.2.7 and 2.2.8 records the results obtained by monitoring the progress of reactions of chlorination of phenol and cresol. Complete picture of the chlorinated mixture at each stage of chlorination can be had by GLC analysis as is evident from these tables. Based on this data one can predict the reaction scheme and can generate the kinetic and thermodynamic data for the entire reaction scheme. In conclusion GLC is found to be one and the best method for monitoring the progress of chlorination of phenols as well as for their quantitative estimation.

2.3 High Pressure Liquid Chromatography (HPLC)

In late 1960's a complimentary technique popularly known as high pressure liquid chromatography HPLC has been introduced. It is specially useful in case of those compounds which are thermally labile materials but soluble in some solvents. Further it is noticed that where GLC fails, it is successful.

HPLC is merely an extension of classical column technique, consisting of much smaller particles of narrow size distribution. Higher flow rates of mobile phases are achieved under high pressure. Further it has a variety of detectors which exploit the different physical properties of the samples.

HPLC is the latest innovation in chromatographic series which is used for the separation and identification of unknown compounds. There are very few reports in the literature on the use of HPLC with study of phenols and chlorophenols. L. Arose[12] et al have analysed the chlorophenols and other substituted phenols, present in the environments as pollutants using cerium (IV) sulphate detector. Sajid Husain [13] et al have developed a method for the separation of isomeric alkyl phenols by HPLC using cyclohexane and methylene dichloride in different proportions. They also studied effect of temperature on the retention times of isomeric alkyl phenols. The results are summarised in Tables 2.3.1, 2.3.2 and 2.3.3.

A method has been developed for the separation of chlorophenols and chlorocresols as there has been no systematic data available in literature on their separation and is extensively applied in the present investigation.

Experimental

P-cresol used in the entire study was obtained from Fluka and fractionally distilled. Spectral grade toluene which did not give any impurity in the 250-400 nm range was used. Other chemicals used were also of good quality.

High Performance Liquid Chromatograph

A Waters Assoc. (Milford, Mass, U.S.A.) Model ALC/GPC/244 high-performance liquid chromatograph equipped with Model 6000 A solvent delivery system, Model U6K septumless injector and Model 440 dual channel absorbance detector at 313 nm was used. The pumps are capable of operation at pressures upto 400 bar. A prepacked column of µ Porasil of 10 µm (30 cm x 4 mm I.D.) obtained from Waters Assoc. was used. Solutions (0.05) of chlorinated mixture of paracresol were prepared in toluene and 2 µl samples were injected. A several synthetic mixtures have been prepared and analysed on variety of columns using different solvent systems. Reasonably good separation have been obtained on u-porasil column using chloroform : cyclohexane (7:3 v/v) as a mobile phase. Figs. 2.3.1 and 2.3.2 gives the typical chromatograms of chlorophenols and chlorocresols. While carrying out the chlorination of p-cresol with TBH, the TLC analysis of the reaction product has shown the presence of more than five compounds, the separation of these compounds either by TLC or by column chromatography was found to be unsatisfactory. That is why HPLC technique has been tried. HPLC conditions reported in literature for the separation of isomeric chlorophenols could not be effectively employed in the present investigation. This prompted us to undertake the standardization of HPLC method for the separation of chlorophenol isomers. Four different HPLC columns viz., bondapck C_{18}, µ-bondapck, porasil and µ-porasil using suitable mobile phases have been tried. Best separation has been obtained on µ-porasil column using benzene-cyclohexane (9:1 v/v). Fig. 2.3.3 gives the typical chromatogram of the reaction product along with 2-chloro-p-cresol and 2,6-dichloro-p-cresol.

However, the best conditions of HPLC (300 x 4 mm I.D. column of µ-porasil pressure 750 psi, eluent benzenecyclohexane (9:1 v/v) when employed in semi preparative work failed in isolation of components of the reaction mixture, change of mobile phase i.e. to toluene has improved the HPLC separation. Individual compounds from the chlorination mixture of phenol could be isolated by using analytical column (μ-porasil) and have been subjected to structural elucidation. Fig. 2.3.4 gives the chromatogram of the typical reaction product. The product distribution in different reaction mixture is determined and recorded in Table 2.3.4.

TABLE : 2.2.1.

Peak Shape and Retention Data on Conventional and Support Bonded Polyester Columns

Chlorinated Phenols	5 DEGS			SB-DEGS			DSB-DEGS			SB-BDS		
	Peak Shape	Min	RRT	Peak Shape	Min	RRT	Peak Shape	Min	RRT	Peak Shape	Min	RRT
2,3-Dichloro	1	5.25	0.40	1	3.62	0.37	1	3.39	0.40	2	1.02	0.31
2,4-Dichloro	1	5.58	0.38	1	3.46	0.36	1	3.19	0.37	2	0.98	0.30
2,5-Dichloro	1	5.31	0.38	1	3.54	0.36	1	3.19	0.37	2	1.02	0.31
2,6-Dichloro	1	4.80	0.34	1	3.07	0.32	1	2.95	0.35	2	0.98	0.30
3,4-Dichloro	4	41.81	3.00	3	32.13	3.30	2	25.83	3.02	3	8.19	2.48
3,5-Dichloro	4	31.26	2.24	3	24.02	2.47	2	19.29	2.26	3	6.69	2.02
2,3,4-Trichloro	4	14.53	1.04	3	10.16	1.04	2	8.94	1.05	3	3.15	0.95
2,3,5-Trichloro	3	11.10	0.80	3	7.48	0.77	2	6.81	0.80	3	2.83	0.86
2,3,6-Trichloro	3	11.26	0.81	3	7.76	0.80	2	6.85	0.80	3	4.25	1.29
2,4,5-Trichloro	4	13.94	1.00	3	9.72	1.00	2	8.54	1.00	3	3.31	1.00
2,4,6-Trichloro	3	8.86	0.64	2	5.91	0.61	2	5.47	0.64	2	2.83	0.86
3,4,5-Trichloro	6	32.76	2.35	6	25.67	2.64	2	20.47	2.40	5	24.62	7.26
2,3,5,6-Tetrachloro	3	20.87	1.50	3	16.46	1.69	2	13.15	1.54	3	27.76	8.39
2,3,4,6-Tetrachloro	3	22.91	1.64	3	17.17	1.77	2	14.84	1.74	3	17.56	5.31
2,3,4,5-Tetrachloro	3	33.31	2.39	3	26.30	2.70	1	21.18	2.48	3	11.10	3.36
Pentachloro	4	52.68	3.78	NP	-	-	2	35.20	4.12	NP	-	-

Peak shape isdefined by numbers : 1 = sharp peak with little or no tailing; 2 = sharp but tailing; 3 = broad but symmetrical with little or no tailing; 4 = moderate tailing; 5 = severe tailing; 6 = peak poorly distinguished; N.P. = no prak. RRT = relative retention time (2,4,5-Trichlorophenol) = 1 column conditions and parameters were; DEGS, 1.8 m x 4 mm i.d., 180^{o} oven, flow 60 ml/min flow rate support bonded DEGS, oven 155, double support bonded DEGS, oven 170, both columns 1.8 m x 4 mm i.d., 60 ml/min flow rate. Butane 1,4-diol succinate (BDS), 0.6m x 4 mm i.d., oven 190 ^{o}C, 60 ml/min folw rate

Table : 2.2.2.

GLC Analysis Conditions for separation of chlorophenols and chlorocresols

	Stationary phases			
	SE-30 (A)	DEGS (B)	Carbowax-20M (C)	Carbowx -5M (D)
Support and content of stationary liquid phase	5 % (W/W) on chromsorb "P" 45-60 mesh	15 % (W/W) on chromsorb "W" 45-60 mesh	25% on chromsorb-w 45-60 mesh	5% (W/W) chromosorb-"P" 45-60 mesh
Column length ft,	8	8	8	8
Carrier gas	Hydrogen	Hydrogen	Hydrogen	Hydrogen
Flow rate litters/hr	7.2	3.6	7.2	3.6
Column temperature	200 ± 2	200 ± 2	200 ± 2	200 ± 2
Bridge current	150	150	150	150

TABLE : 2.2.3

Relative retention times of chlorophenols by GLC (Stationary liquid Phases : (A) SE -30 (B) DEGS; (C) Carbowax - 20 M: (D) Carbowax - 5M

Peak No. see fig 2.2.1	Compound	Boiling Point C°	Relative retention times (relative to o-cresol) Phase A	Phase B	Phase C	Phase D
1	O-chlorophenol	175	1.00	0.84	0.60	0.69
2	Phenol	180	1.00	1.00	1.00	1.0
3	2,5-dichloro phenol	219	2.50	2.12	1.43	1.70
4	2,4-dichloro phenol	210	1.87	2.08	1.65	1.70
5	2,5-dichloro phenol	211	1.87	2.08	1.65	-
6	2,4,6-trichloro phenol	246	2.67	3.73	2.82	3.20
7	p-chlorophenol	219	3.12	3.45	3.73	3.80
8	2,4,5-trichloro phenol	244	3.00	-	5.04	-
9	2,3,4,5-tetra-chlorophenol	-	5.00	-	7.17	-
10	3,5-dichloro phenol	233	4.00	-	10.69	-

TABLE : 2.2.4.

Relative retention times of chlorocresols by GLC

Peak No. see fig 2.2.2	Compound	Boiling Point	Relative retention times (relative to o-cresol)			
			Phase A	Phase B	Phase C	Phase D
1	6-chloro-o-cresol	188	0.62	0.87	0.63	0.62
2	o-cresol	191	1.00	1.00	1.00	1.00
3	m-cresol	202	2.00	1.56	1.18	1.40
4	p-cresol	202	2.00	1.56	1.18	-
5	6-chloro-m-cresol	197	2.16	-	1.50	1.0
6	2,4-dichloro-m-cresol	235	3.0	-	2.40	2.2
7	4-chloro-o-cresol	220	3.00	3.45	3.90	3.40
8	4-chloro-m-cresol	235	3.00	-	4.06	4.20

TABLE : 2.2.5.

GLC analysis of sythetic mixtures of chlorophnols

S. No.	Compound	Mixture I			Mixture II			Mixture III			Mixture IV		
		Taken	Found	Error	Taken	Found	Errpr	Taken	Found	Error	Taken	Found	Error
1.	Phenol	60	62.5	+2.5	40	43.79	+3.79	40	41.09	+1.09	20	23.2	+3.2
2.	O-chloro phenol	10	9.61	-0.39	15	17.29	+2.29	15	15.51	0.51	20	21.94	+1.94
3.	P-chloro phenol	10	7.06	-2.94	15	12.45	-2.55	15	17.57	+2.57	20	19.8	-0.2
4.	2,4-Dichloro phenol	10	6.65	-3.35	10	10.91	+0.91	15	12.54	-2.46	15	13.02	-1.98
5.	2,6-Dichloro phenol	5	4.61	-0.39	10	9.52	-0.48	5	5.46	+0.46	10	10.38	+0.38
6.	2,4,6-Tri-chloro phenol	5	5.41	+0.41	10	10.37	+0.37	10	10.21	+2.1	15	12.57	-2.43

TABLE : 2.2.6.

Analysis of chlorinated mixture of phenol with gaseous chlorine at differnt time intervals

S. No.	Compound	Time (min)									
		30	60	120	180	200	300	360	420	480	520
1.	Phenol	82.30	70.68	59.29	46.48	21.94	3.85	Nil	Nil	Nil	Nil
2.	O-chloro-Phenol	7.40	11.58	14.03	17.44	25.55	32.2	25.92	16.86	14.84	5.63
3.	P-chloro Phenol	8.30	14.48	23.31	27.87	45.39	50.72	43.98	26.68	16.23	4.93
4.	2,6,-dichloro Phenol	-	-	-	-	-	0.93	2.08	4.67	5.16	6.76
5.	2,4-dichloro Phenol	2.00	2.89	3.50	8.23	7.10	12.78	28.0	53.10	63.75	82.66
6.	2,4,6-trichloro Phenol	-	-	-	-	-	-	-	-	-	-

TABLE : 2.2.7.

Analysis of chlorinated mixture of oxychlorination of o-cresol to get 4-chloro-o-cresol

Compound %	Time (hrs)							
	7th	9th	11th	12th	13th	14th	15th	15.
O-cresol	49.53	39.38	29.30	25.19	18.35	12.18	4.69	1.
6-chloro-o-cresol	Nil	-	-	-	-	-	-	
4-chloro-o-cresol	50.46	60.69	70.69	74.80	81.64	87.81	94.95	98
4,6-dichloro-o-cresol	Nil	-	-	-	-	-	-	

TABLE : 2.2.8.

Analysis of the products of oxychlorination of phenol

Compound %	Time (hrs)							
	60	120	180	240	300	360	420	4
Phenol	93.83	89.34	83.36	80.17	75.46	71.19	68.74	63.
O-chloro phenol	-	-	-	-	-	-	-	1
P-chloro phenol	6.18	10.65	16.8	19.82	24.53	28.70	31.25	3
2,4-Dichloro phenol	-	-	-	-	-	-	-	
2,4,6-Trichloro phenol	-	-	-	-	-	-	-	

Table 2..3.1

RETENTION TIMES OF ISOMERIC ALKYLPHENOLS BY HPLC USING SILLICA GEL COLUMNS OF PARTICLE SIZE 30 AND 5 μm

(A) 300 x 3 mm I.D, column of LiChrosorb SI 60 (30 μm): Pressure,2500 Psi: eluent,cyclohexane-methylene dichloride (1:1): folw-rate, 1.4 ml/min; temperature, 25° (B) 250 x 2.1 mm I.D, column of zorbax sil (5 μm); pressure, 3300 psi; eluent, cyclohexane-methylene dichloride (1:1); flow-rate, 0.8 ml/min; teperature, 25 °. (C) column as B; pressure, 3800 Psi; eluent, cyclohexane-methylene dichloride (2:1); flow-rate 0.8 ml/min; temperature, 25°. (D) As C, except flow-rate, 0.95 ml/min; temperature, 40 °.

Compound	Retention time (min)			
	A	B	C	D
2,6-Dimethylphenol	2.2	2.4	3.6	2.8
2-Ethylphenol	3.6	3.6	5.9	4.2
2-Methylphenol	3.8	4.5	7.4	5.3
2,5-Dimethylphenol	3.8	4.5	7.4	5.3
2,3-Dimethylphenol	4.0	4.5	7.4	5.3
2,4-Dimethylphenol	4.2	4.8	8.2	6.0
3-Ethylphenol	6.4	6.8	12.0	8.7
Phenol 6.4	6.4	6.8	12.0	8.7
4-Ethylphenol	7.0	7.6	13.4	9.6
3-Methylphenol	7.0	7.6	13.4	9.6
4-Methylphenol	7.0	7.6	14.0	10.2
3,5-Dimethylphenol	7.0	7.6	14.0	10.2
3,4-Dimethylphenol	-	-	14.8	11.0

TABLE 2.3.2.

RETENTION TIMES OF ISOMERIC ALKYLPHENOLS BY HPLC AT DIFFERENT TEMPERATURES

(E) 250 x 2.1 mm I.D, column of Zorbas Sil (5 µm); pressure 2200 Psi; eluent, cyclohexane-methylene dichloride (3:1); flow-rate, 0.56 ml/min; temperature 46^{o}, (F) As E, except pressure, 2000 Psi; flow-rate, 0.54 ml/min; temperature 53^{o}. (G) As E, except pressure, 2000 Psi; flow-rate, 0.61 ml/min; temperature, 63^{o}.

Compound	Retention time (min)		
	E	F	G
2,6-Dimethylphenol	5.7	5.0	3.6
2-Ethylphenol	9.2	8.0	5.2
2-Methylphenol	11.7	10.0	6.6
2,5-Dimethylphenol	11.7	10.0	6.6
2,3-Dimethylphenol	12.2	10.5	6.8
2,4-Dimethylphenol	13.3	11.5	7.3
3-Ethylphenol	18.9	15.8	10.0
Phenol	19.6	16.5	10.6
4-Ethylphenol	20.8	17.3	10.9
3-Methylphenol	20.8	17.3	10.9
4-Methylphenol	21.8	18.4	10.9
3,5-Dimethylphenol	21.8	18.4	10.9
3,4-Dimethylphenol	24.3	19.8	12.6

TABLE 2.3.3.

RETENTION TIMES OF ISOMERIC ALKYLPHENOLS BY HPLC USING DIFFERENT PROPORTIONS OF THE COMPOENTS OF THE SOLVENT SYSTEM

(H) 250 x2.1 mm I.D. column of Zorbas Sil (5 μm); pressure 2200 Psi; eluent, cyclohexanemethylene dichloride (4:1); flow-rate, 0.53 ml/min; temperature, 42°. (I) column as H; pressure, 2000 Psi; eluent, cyclohexane-methylene dichloride (4.1); flow-rate, 0.5 ml/min temperature, 50°. (J) Column as H; pressure, 2100 Psi; eluent, cyclohexane-methylene dichloride (6.1); flow-rate 0.5 ml/min; temperature, 48°. (K) Column as H; pressure, 2500 Psi; eluent, cyclohexane-methylene dichloride (7.5:1); flow-rate 0.6 ml/min; temperature, 48°.

Compound	Retention time (min)			
	H	I	J	K
2,6-Dimethylphenol	6.4	6.4	8.6	8.8
2-Ethylphenol	10.8	10.2	13.9	14.3
2-Methylphenol	14.2	12.8	17.8	18.2
2,5-Dimethylphenol	14.2	12.8	18.1	19.0
2,3-Dimethylphenol	14.9	13.3	18.9	20.7
2,4-Dimethylphenol	16.0	15.8	20.3	21.4
3-Ethylphenol	23.5	20.8	28.2	30.4
Phenol	24.2	21.3	32.0	33.8
4-Ethylphenol	25.7	22.8	33.5	35.1
3-Methylphenol	25.7	22.8	33.5	35.1
4-Methylphenol	27.1	23.8	34.2	37.0
3,5-Dimethylphenol	27.1	23.8	34.2	37.0
3,4-Dimethylphenol	30.0	26.4	37.6	40.6

Table :2.3.4 Percentage composition of various components of reaction mixture of p-cresol with TBH

Compound number	Percentage composition
I	35%
II	22%
III	7%
IV	6%
V	14%

For compound numbers please refer to Fig.2.3.4.

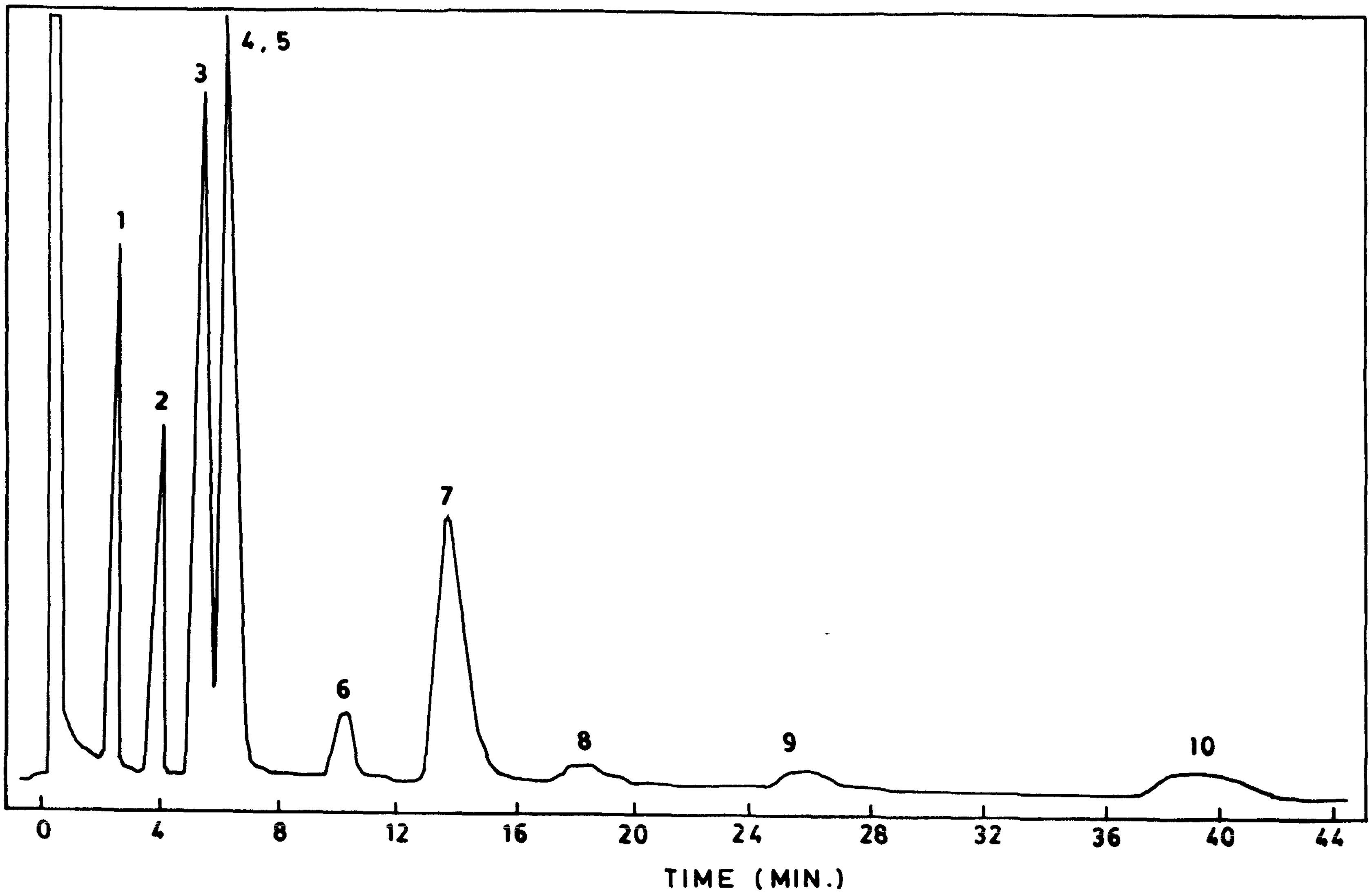


Fig. 2.2.1 Separation of isomeric chlorophenols by G L C for conditions **see table** 2.2.2 and for identification of peaks see table 2.2.3

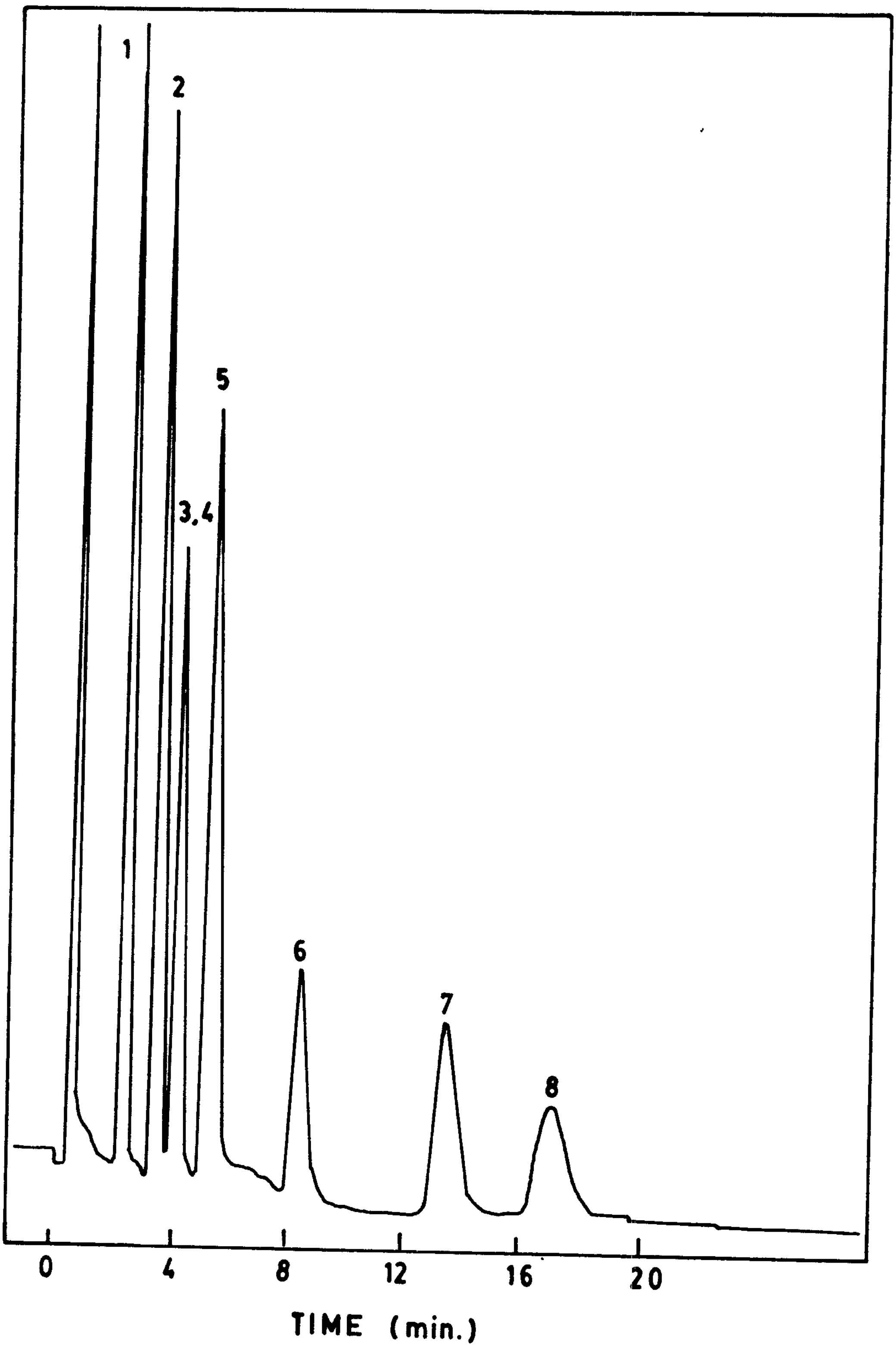


Fig. 2.2.2 Separation of isomeric chlorocresols by GLC for conditions see table 2.2.2. and for identification of peaks see table 2.2.4.

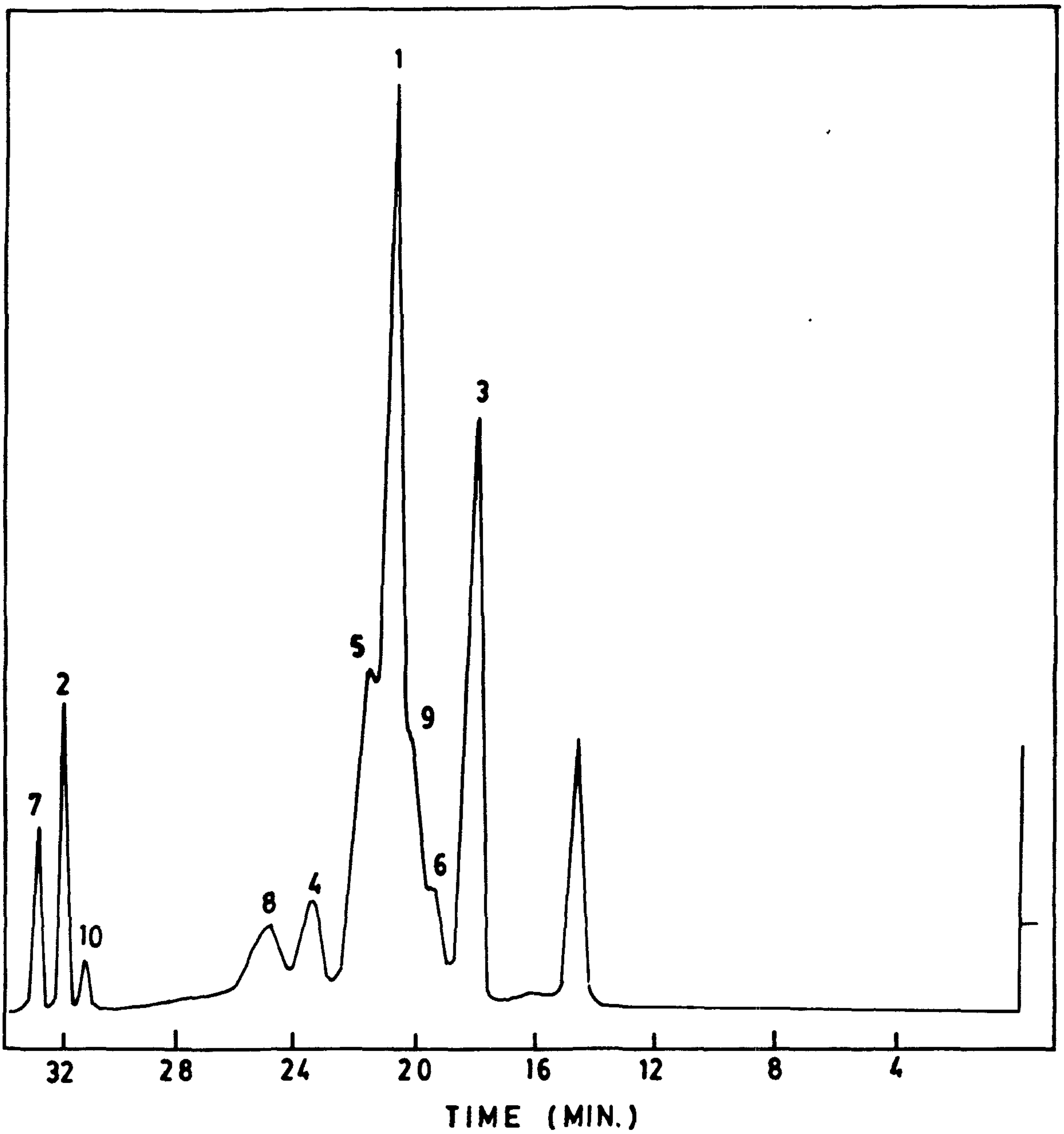


Fig. 2.3.1. Separation of chlorophenols by HPLC, for identification of peaks see table 2.2.3. 300 x 4mm i.d. column of μ-porasil, pressure - 250 psi, eluent, chloroform-cyclohaxane (7:3), flow rate, 0.3 ml/min.

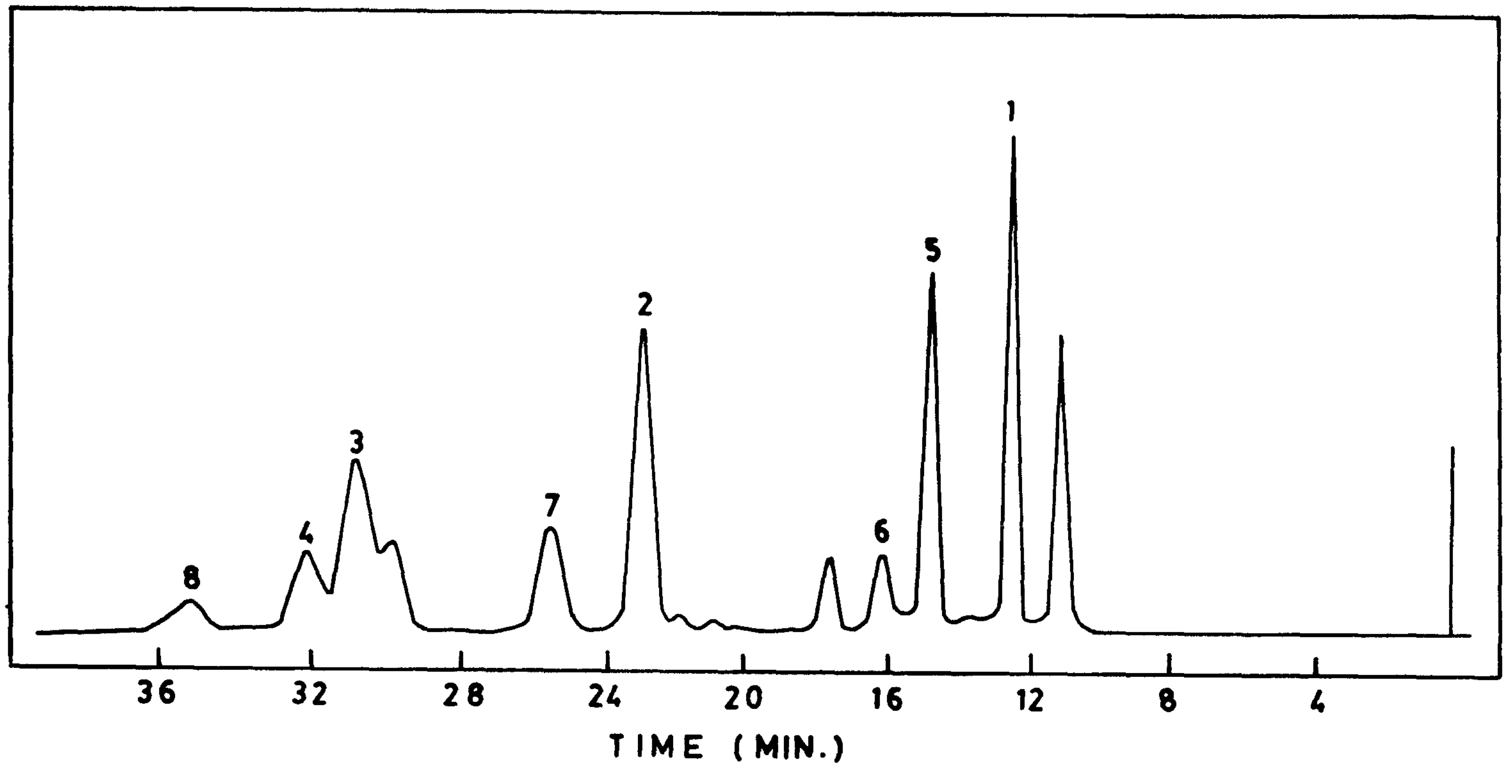


Fig.2.3.2 Separation isomeric chlorocresols by HPLC for identification of peaks see table 2.2.4 . Conditions : 300 x 4mm ID colmn of μ-porasil, pressure: 285 psi ; eluent : chloroform cyclohexane 7:3 ; flow rate :·4ml /min.

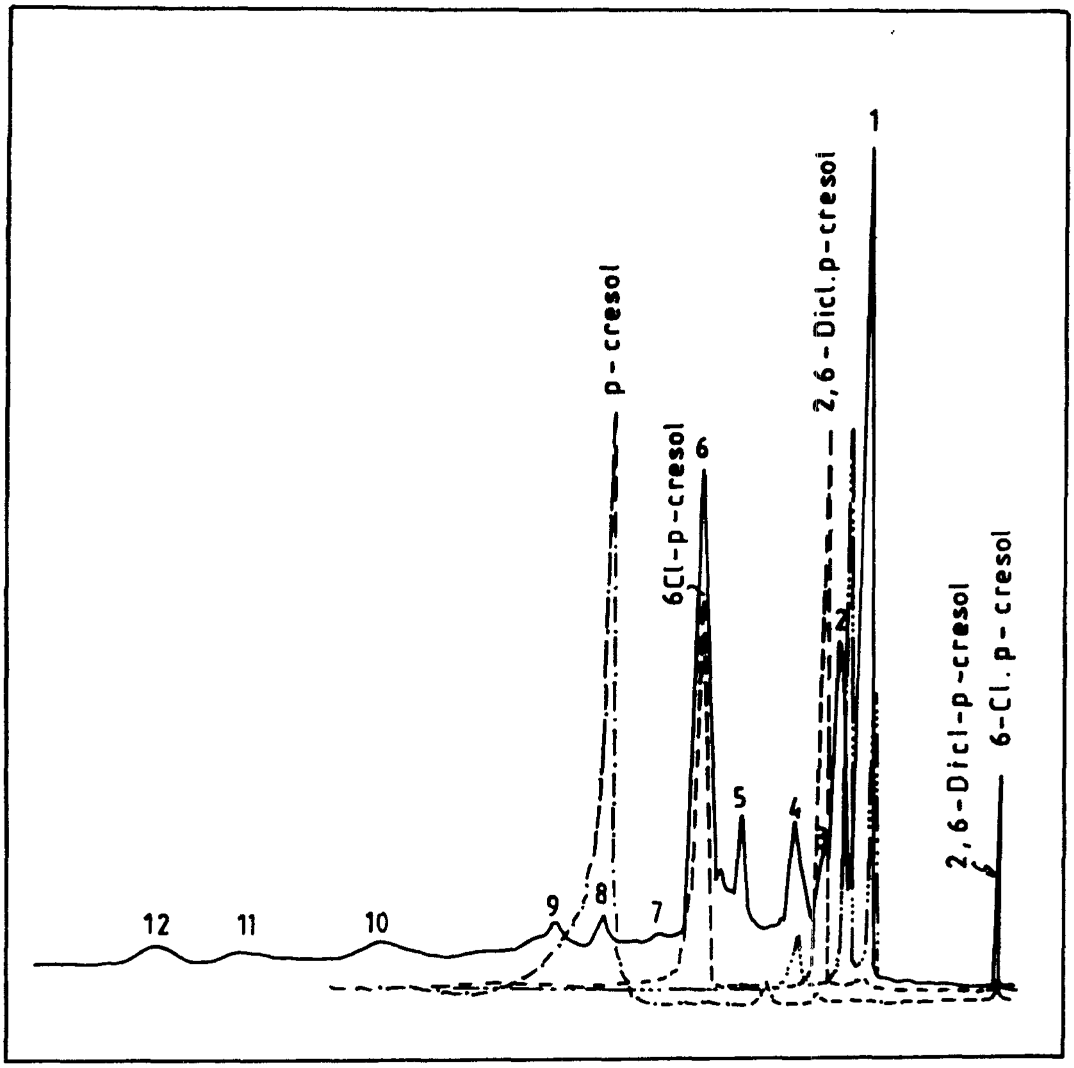


Fig. 2.3.3 Separation of chlorinated product of p-cresol with 3 moles of TBH along with 6-chloro-p-cresol and 2,6-dichloro-p-cresol.

(Column: 30cm x 4 mm i.d. μ-porasil ; pressure : 750 psi eluent toluene ; flow rate : 1.5 ml/min.)

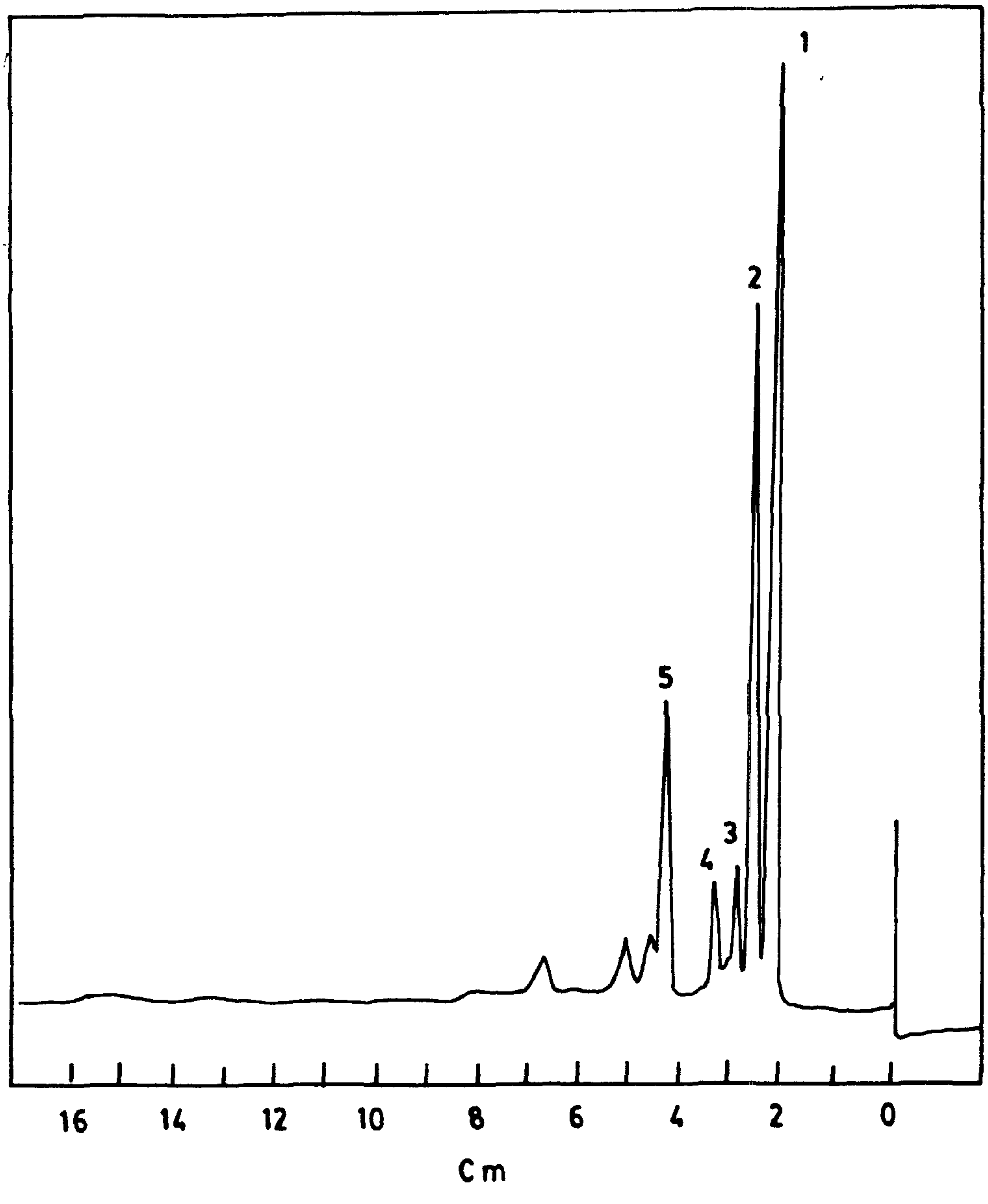


Fig. 2.3.4 Separation of chlorinated products of p-cresol by HPLC (colum.: 30cm x 4mm i.d. μ-porasil; pressure 750 psi; eluent : toluene; flow rate : 1.5ml/min.)

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3. Spectroscopy

Though it is belived that chromatographic techniques are more sophisticated among the available techniques for the separation of complex mixtures, they cannot provide detailed information about the structure of the molecules, the most powerful tool in the hands of chemist is the spectroscopy. Modern methods of spectroscopy inclueds, ultravilet and visible spectroscopy, (UV-VS) In frared (IR) and nuclear magnetic resonance spectroscopy, (NMR) mass spectrometry. The choice of a particular spectroscopic method for a specific problem mostly depends upon other factors such as structures and properties of the species. Thus, the detailed structural information on certain types of molecules may be obtained from microwave spectroscopy (ESR). Electronic spectroscopy does not give much information on the structural details of the molecules, but only throws light on their group character. Infrared spectroscopy is the most useful tool for structural investigations because of the ideal wavelength region it covers in the electronmagnetic spectrum. The infra-red spectrum has both group character as well as structural character. The nucleaar magnetic resonance gives the information about the number of protons and its electronic environment. Mass spectrometry also provides much information concerning structural details.

Spectroscopic techniques such as UV,IR, NMR and Mass spectrometry can be very well used for qualitative identification, quantitative estimation and characterisation of organic compounds. However, in the present studies these spectroscopic techniques have been used both for characterisation of new compounds, and their quantitative estimations.

3.1 Ultra-violet spectroscopy: (UV)

UV spectra of chlorophenols and chlorocresols have been reported in literature[1]. These compounds generally exhibit absorption bands between 270 nm 310 nm. The absorption maxima of a number of chloropehnols have been listed in Table 3.1.1.From the Table 3.1.1,it is clear that (i) in the case of chlorophenols the absorption maxima shifts to a longer wave length with the increase in the number of chlorine atoms in the benzene ring and (ii) Higher values of λ-maxima are observed in the case of p-substituted chlorophenols which can be attributed to the electron withdrawing effect of the chloro-substituent because of its stability through reasonance.

In our studies on chlorination of phenol with special reference to chlorination of p-cresol with t-butyl hypochlorite, formation of chlorocyclohexadienone type of compounds has been observed. These compounds have been isolated from the reaction mixture and subjected to spectral analysis, Table 3.1.2 gives the absorption maxima of these compounds.

Table : 3.1.2 UV - Absorption bands of the Compounds isolated from the reaction mixture

Compound	λ (max) nm
I	270
II	280
III	268
IV	280
V	290

The λ-maxima of these compounds fall between 260 nm and 290 nm which by comparison supports the para quinsnoid type structures. (Delails are discussed elsewhere.)

3.2 Infrared spectroscopy (IR)

Infra-red radiation promotes transitions in a molecule between rotational and vibrational energy levels of ground electronic energy state. Bond vibration modes are divisible into two distinct types, stretching and bending (deformation) vibrations. IR strectching frequency data for several different types of vibrations is well documented in literature.[2]. Although chemists are mostly concerned with the use of IR spectroscopic data for identification of organic compounds, but many other applications have also been stemed out.

1. Identification of substances

2. Determination of molecular structure
3. Determination of purity, quantitative analyis and product control
4. Reaction kinetic studies
5. Fundamental studies of molecules

Since GLC has been identified as the technique of choice for the separation and quantitative estimation of different components in the chlorinated mixture. In the present studies IR has been used for the identification of structure of new molecules obtained during the chlorination of phenols.

IR spectra of a number of chlorophenols and chlorocresols have previously been recorded and are avilable in literature[3]. The procedures for the IR analysis of chlorophenols are nearly identical. Therefore general method has been described[4]. Charactarlstic bands of different components are recorded in Table 3.2.1. It is obsevered that all the compounds show one or more intense bonds in the region of 690-1350 cm^{-1} and one can select a charactaristic band for the identification of a perticuler compound.

During the chlorination of phenol with TBH, formation of new compounds has been noticed when the reaction mixture has been subjected to HPLC analyis These compounds have been isolated and subjected to spectral studies. The spectra shows one intense band of the carbonyl group and also absence of (OH) band. This data has helped us in concluding that cyclohexadienone type of compounds are formed.

Table : 3.2.1 Recommended wave length for the infrared determination of Chlorophenols

S.No.	Compound	Wave length (μm)	Wave Number cm^{-1}
1.	o-chlorophenol	13.40 10.75	747 928
2.	p-chlorophenol	12.95 9.90	823 1010
3.	2,4-Dichlorophenol	13.80 7.50	723 1330
4.	2,5-Dichlorophenol	11.05	905
5.	2,6-Dichlorophenol	13.10	764
6.	2,4,5-Trichlorophenol	9.50	1072
7.	2,4,6-Trichlorophenol	13.65	733
8.	2,3,6-Trichlorophenol	10.90	917
9.	2,3,4,6-Tetrachlorophenol	13.30	750
10.	Penta-chlorophenol	13.00	768

3.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectroscopy is rapidly becoming the most valuable technique for fundemental analytical studies of various systems. The unique ability to resolve, assign and separate signals due to nuclei in different chemical environments make NMR specially powerful for a variety of analytical studies including chemical kinetics.

Principle NMR spectroscopy:

The nuclei of many isotopes possess an angular momentum, called spin whose magnitude is described by the spin quantum number I. This quantity which is the characteristic of the nucleus may have values: I = 0, 1/2, 1, 3/2 etc. Nuclei having I = 0 value appears to be non-spinning and they have no magnetic properties (^{12}C, ^{16}O). Nuclei having I = 1/2 appears to be spinning with spherical change distribution and those with I value other than zero and 1/2 appears to be spinning with an elliptical charge distribution either prolate or obtate. A spinning charged body generates a magnetic field and thereby gives rise to a magnetic monoment (μ). The magnetic moment (μ) has definite direction in space and therefore a vector quantity. The spinning nucleus with its magnetic moment (μ) also has an interesting property known as precession. Precession is the property of the nucleus when placed in the magnetic field and can be defined as an oscillation about a fixed direction in space analogous to the motion of a spinning top.

According to quantum mechanics a nucleus can assume only (2I + 1) energy states. In the absence of an external magnetic field the (2I +1) energy states of a nucles are identical (degeneate) and therefore are equally populated at thermal equilibrium. In the presence of applied magnetic field (HO) these (2I+1) states will assume different energy levels. This separation of energy levels in a magnetic field is called Zeeman splitting. Nuclei with I = 1/2 can assume only two orientation under the influence of Ho field, aligned with the filed (lower energy state) or opposed (higher energy state) to the magnetic field. The rate of precession of the spinning nuclei is proportional to the strength of the applied magnetic field Ho.

To perturb the nuclear transition between these two states, a secondary magnetic field H1, that has a magnetic component oscillating in the same direction as the nuclei are precessing is applied. The frequency of oscillation of the secondary field is fixed and is greater than the rate of precesion of the nuclei.

$W_o = r H_o$

Where r = magneto gyric ratio

The strength of applied field Ho is then increased which in turn increases the rate of precision of the nuclei when the rate of precession of nuclei and the frequency of secondary field are the same: the nuclei in the lower energy state absorbs energy and undergoes unclear transition to the upper energy state. The fundamental equation of NMR spectroscopy is given by:

$$V = \frac{\mu HO}{hI}$$ Where h is plank's conduct

There are two allowed transition (a) α -----> β which corresponds to absorption and (b) β -----> α which corresponds to induced emission. Any absorption signal in NMR experiment is due to the Boltzman excess:

$$\frac{N\beta}{N\alpha} = e^{-hv/KT}$$

Botlzman distribution for 1H at 1.4T is only 0.001 percent i.e.the population excess in the two spin states is only 1 in 10,000. That is why NMR is considered to be the least sensitive one, among the spectroscopic techniques.

NMR spectroscopy offers several important advantages as a tool for chemical analysis because of its non-destructive nature. But it has not gained popularity as a method of choice because of its inherent low sensitivity compared to many other spectroscopic techniques. Today NMR spectroscopy has been recognised as one of the most powerful tool for chemical analyses because of the dramatic increase in its sensitively in both NMR techniques and instrumentation. Some of the methods that are beeing used for improving the sensitivity are given as under.

(1) Lowering the sample temperature
(2) Increasing the magnetic field strength
(3) Accumulation of spectra
(4) Pulse Fourier transform techniques
(5) Double resonance methods
(6) Polarization transfer methods

Appplication of NMR spectroscopy for quantitative measurements.

(a) 1 H NMR spectroscopy

One of the most useful aspects of 1H NMR spectra is that the strength of a signal depends only on the number of nuclei involved which resonate at that particular frequency. This leads to many important application whether it is continuous wave (C.W.) or FT-spectra, although it is necessary to take precautions to get very accurate measurements.

A Mixture of organic compounds can be assayed by NMR spectroscopy if distinguishable signals from each component can be integrated separately. In addition to the mixture a measured quantity of internal standard converts the integration from relative to absolute assay. For example, the mass m_A of component A in a mixture can be determined if an amount of m_B of a known substance B is added to a weighed sample of mixture and signals assiged to A and B are integrated. The mass of a Ain the sample is given by:

$$m_A = m_B \quad \frac{N_B}{N_A} \times \frac{A_A}{A_B} \times \frac{M_A}{M_B}$$

N = Number protons responsible for the signal

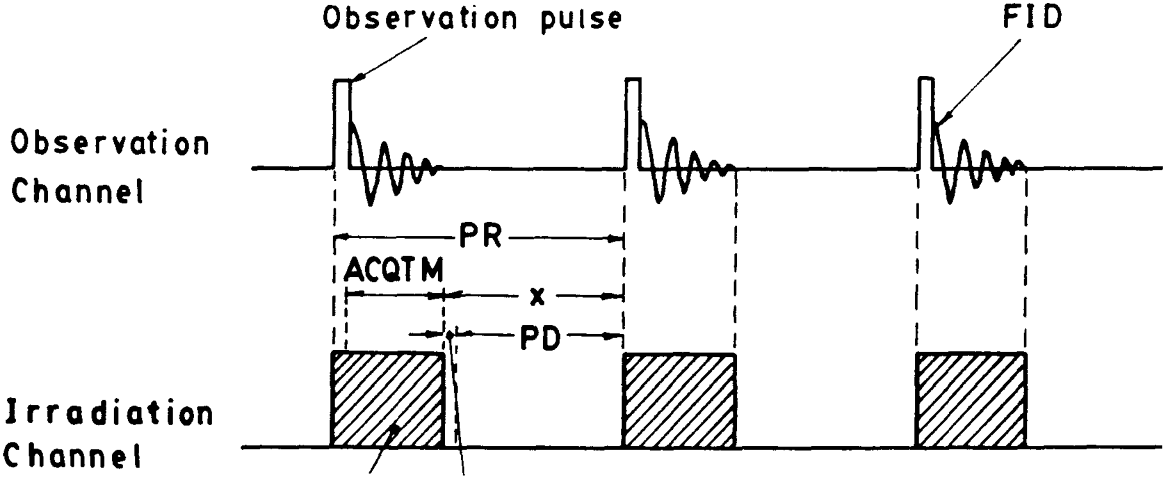
A = Integral height of the signal

M_A, M_B = Molecular weights of A and B respectively

In the present studies 1H NMR has been used for the charactarisation of new molecules isolated during the chlorination of p-cresol with TBH.

Quantitative ^{13}C NMR spectroscopy

The use of proton irradiation while observing the ^{13}C NMR spectrum has an advantage in enhancing the signal to noise ratio of the spectrum due to NOE. But the signal intensity enhancement due to NOE differs according to the environmental condition under which carbon is placed and hence use of normal ^{13}C NMR spectrum for quantitative analysis is very much restricted. Generally three methods have been employed for obtaining the quantitative results by ^{13}C NMR spectroscopy. They are based on use of long pulse delay times ($3 \sim 5\ T_1$), gated-decoupling and addition of paramagnetic relaxation reagent such Cr $(acac)_3$ and $Fe(acac)_3$. The use of relaxation reagents in obtaining the quantitative spectrum has its own limitations. The best procedure for suppressing the NOE more effectively is by using $Cr(acac)_3$ and a gated decoupling technique simultaneously. In the present studies this method has been adopted. The flow chart depicts the time relation between the observed pulse and the irradiation pulse obtained by gated decoupling mode.



Flow chart of gated-decoupled ^{13}C NMR pulse technique

Experimental

A. JNM Model FX-90 QFT-NMR spectrometer (JEOL) with a C/H dual probe containing a quadrature detection system has been used.

Reagents

All chlorophenols are (Fluka grade), W. Germany deuterated solvents (minimum isotropic purely 99.8%).

Procedure

Quantitative ^{13}C NMR spectra have been obtained by investigated decoupling pulse technique using minimum recycle time of 25 sec. between the scans. The spectrometer has been operated at a resonance frequency of 22.5. MHz with 16 K data points maintaining the probe temperature at 25°C. The spectral width is 5 KHz and pulse width 28 μ sec which is a 90° pulse for the spectrometer chemical shifts were measure for 10 mm o.d. entry with respect to TMS (internal reference).

Development of a computer-assisted program using carbon-^{13}nuclear magnetic resonance (^{13}C NMR) chemical shifts and signal intensities for identification and quantitative estimation of phenols and their chloroisomers.

Analysis of complex organic mixtures generally involves, the separation, identification and quantification. This is invariably accomplished by hyphenated techniques such as GC-Mass, GC-IR and HPLC-NMR. But these techniques suffer from a number of short comings. There have been several attempts to develop computer assisted procedures to analyse the complex organic mixtures and also to elucidate their structures based on ^{13}C NMR chemical shift data and signal intensity data. A variety of computer assisted programs for interpretation and prediction of ^{13}C NMR spectra has been reported[9,10].

Recently LAUDE and WILKINS[11] have proposed an algorithm for the separation, identification and quantification of organic mixtures using ^{13}C-NMR spectral data. Sajid Husain et al[12,13] have developed a software package based on this algorithm and incorporated several modifications to its logic in order to improve the accuracy.

In the present studies a computer program has been developed to analyse the complex organic mixtures with special reference to phenols and their chloroderivatives available either in reaction mixtures or in the environment as polluents. Application of this approach to the analysis of ^{13}C NMR data appears to be possible given sufficiently high quality spectral data as input. The capabilities of the program are

(1) Implementation of powerful algorithm for optimization of data content.

(2) Routine high accuracy spectral features including quantitative separation of over lapped signals.

(3) Versatile input routines, multiformation hard copy.

(4) Extensive usage of popling and automation control.

Methods

Our approach to use ^{13}C NMR data ian computer assisted analysis involves obtaining a set of chemical shifts of candidate structures to build and maintain a data base (CNMR:DISR). The second step involves providing input data in terms of chemical shifts and signal intensities of an unknown mixture (CNMR = INPT) to identify the components of the mixture by comparing the chemical shifts with all the chemical shifts available in the data base. If a match is found name the compound identified and store it. The procedure is repeated until all the chemical shifts are assigned to the component shifts constituting the given mixture. The third step is the use of signal intensity data to calculate the mole percent composition of the reaction mixture. Last step is to print the names of the compounds identified and their chemical composition (CNMR = OUTP). The output data descriptions have been given and the flow diagram in Fig. 3.3.1. The source list of Fortran program is given separately (I).

The method has been evaluated by determining the contents of a three component mixture of dichlorophenols viz., 2,4-DCP, 3,5-DCP and 3,4-DCP (Fi.g 3.3.2). The quantitative results obtained by computer assisted analysis are presented in Table 3.3.4. It is seen from the table the results are in agreement within the limits of experimental error.

The program developed is more general and it can handle varying type of compounds. The developed program has been applied to analyse a three component mixture of chlorolydrins and to the components of a typical reaction mixture. The results obtained are presented in Tables 3.3.5 and 3.3.6 respectively. The results obtained have been found to be in good agreement.

In conclusion the proposed method is a simple, specific, rapid and general method for the identification and quantitative estimation of organic mixture in general and phenols and chlorphenols in particular.

Table : 3.1.1. UV - Data of chlorophenols

Compound	λ max nm			ε, mol^{-1} cm^{-1}		
	Nondissociated from	Dissociated form I	Dissociated form II	Nondissociated form	Dissociated form I	Dissociated form II
Phenol	269	233	286	1180	8660	2390
2-chlorophenol	273	236	293	1680	7770	3660
3-chlorophenol	273	240	292	1634	8240	2920
4-chlorophenol	279	244	298	1440	10460	2410
2,3-dichlorophenol	276	240	298	1850	4140	4160
2,4-dichlorophenol	284	246	305	2110	8760	3570
2,5-dichlorophenol	279	242	299	2450	7270	4640
2.6-dichlorophenol	276	238	299	1940	6390	4960
3.4-dichlorophenol	282	243	302	1830	10600	3020
3,5-dichlorophenol	276	2444	297	1620	7680	3370
2,3,4-trichlorophenol	289	246	309	2000	9940	3800
2,3,5-trichlorophenol	280	-	308	1960	-	4090
2,3,6-trichlorophenol	284	-	304	2070	-	5580
2,4,5-trichlorophenol	288	244	310	2769	9510	4660
2,4,6-trichlorophenol	286	245	311	2230	8710	4920
3,4,5-trichlorophenol	292	246	307	1930	10610	3190
2,3,4,6-tetrachlorophenol	296	247	315	2300	8880	5210
2,3,5,6-tetrachlorophenol	284	-	308	2120	-	5380
pentachlorophenol	310	249	319	2130	10220	5280

```
C     ========================================================================
C     PROGRAM CNMR . Source Program
C     ------------------------------------------------------------------------
C
C     THIS PROGRAM CALCULATES % MOLE FRACTION COIMPOSITION OF MIXTURES OF
C     ORGANIC COMPOUNDS FROM MEASURED CHEMICAL SHIFTS & INTENSITIES IN 13C NMR
C     QUANTITATIVE SPECTRUM , USING DATA BANK OF CHEMICAL SHIFTS OF PURE
C     COMPONENTS
C
C     ------------------------------------------------------------------------
C
      DIMENSION IS(210),AN(210,30),VD(210,8),L1(25),L2(25),L3(25),L4(25)
      DIMENSION VC(25),VA(25),VR(25),VS(25),VB(25),FW(25),FR(25)
      DIMENSION AAN(25,30),AM(70),JV(25),VVC(25,8),VVS(25,8),VVB(25,8)
      DATA LR,LP,LD,M,MJ,MI,MC/4,5,3,33,8,8,25/
C
C     ------------------------------------------------------------------------
C     DATA BANK OF CHEMICAL SHIFTS OF PURE COMPONENTS ARE IN FILE .. CNMR:DISK
C     INPUT DATA ARE STORED IN FILE ................................ CNMR:INPT
C     RESULTS ARE PRINTED IN FILE .................................. CNMR:OUTP
C
      OPEN(LD,FILE='CNMR:DISK')
      OPEN(LR,FILE='CNMR:INPT')
      OPEN(LP,FILE='CNMR:OUTP')
C
C     ------------------------------------------------------------------------
C
C     M IS NUMBER OF COMPOUNDS  & MJ IS MAX NUMBER OF CHEMICAL SHIFTS FOR
C     EACH COMPOUND IN DATA BANK
C
C     READ CHEMICAL SHIFTS OF PURE COMPOUNDS FROM DATA BANK
C
C     ------------------------------------------------------------------------
C     WRITE(LP,122)M,MJ
      DO 600 I=1,M
      READ (LD,123)IS(I),(AN(I,K),K=1,30),(VD(I,J),J=1,MJ)
C     ........................................................................
C     WRITE(LP,124)IS(I),(AN(I,K),K=1,30),(VD(I,J),J=1,MJ)
  600 CONTINUE
  500 WRITE(LP,1000)
C     ........................................................................
C     READ INPUT DATA : CHEM SHIFT & INTENSITY
C     ........................................................................
      READ(LR,125,ERR=98,END=99)N,IN,AM
C     ........................................................................
      WRITE(LP,126)AM,IN
      S=0.
      WRITE(LP,127)
      DO 225 I=1,N
      READ(LR,23)VR(I),VA(I)
C     ........................................................................
      WRITE(LP,24)VR(I),VA(I)
      S=S+VA(I)
  225 CONTINUE
C     ........................................................................
C     CALCULATE SUM OF INTENSITIES
C     ........................................................................
      WRITE(LP,66)
      WRITE(LP,224)N,S
C     ........................................................................
      WRITE(LP,66)
C     ........................................................................
C     MATCH CHEM SHIFTS
C     ........................................................................
C     SELECT TOLERANCE
```

```
      DO 50 IT=1,IN,2
      ER=FLOAT(IT)/100.0
C     ..................................................................
C     SELECT VD(I,K)
      IL=0
      DO 60 I=1,M
      L=0
      SS=0
      DO 60 K=1,MI
      IF(ABS(VD(I,K))-0.01)161,161,162
 161  L=L+1
      VC(L)=0.0
      VB(L)=0.0
      VS(L)=0.0
      GO TO 173
 162  DO 70 J=1,N
      IF(ABS(VD(I,K)-VR(J))-ER)71,71,70
C     ..................................................................
C     STORE INDEX CHEMICAL SHIFTS & INTENSITIES OF IDENTIFIED COMPONENT
 71   L=L+1
      VC(L)=VD(I,K)
      VB(L)=VR(J)
      VS(L)=VA(J)
      SS=SS+VS(L)
 70   CONTINUE
 173  IF(L-MI)60,72,72
 72   CONTINUE
C     ..................................................................
C     CALCULATE MOLE FRACTION
      SSS=SS/S
      IL=IL+1
      JV(IL)=IS(I)
      DO 75 II=1,30
 75   AAN(IL,II)=AN(I,II)
      DO 375 KK=1,MI
      VVC(IL,KK)=VC(KK)
      VVB(IL,KK)=VB(KK)
 375  VVS(IL,KK)=VS(KK)
      FR(IL)=SSS
      FW(IL)=SS
 60   CONTINUE
C     ..................................................................
C     CHECK IF SUM OF MOLE FRACTIONS IS EQUAL TO 1
      SA=0
      DO 150 LL=1,IL
      SA=SA+FR(LL)
 150  CONTINUE
      IF(SA-1.0)151,152,152
C     ..................................................................
 151  WRITE(LP,153)ER
      GO TO 155
C     ..................................................................
 152  WRITE(LP,65)IL,ER
C     ..................................................................
      WRITE(LP,154)
C     DO 350 II=1,IL
C     ..................................................................
C     WRITE(LP,62)JV(II),(AAN(II,IK),IK=1,30),(VVC(II,KK),VVS(II,KK),
C    1KK =1,MI)
C     WRITE(LP,62)JV(II),(AAN(II,IK),IK=1,30),(VVC(II,KK),VVS(II,KK),
C    1VVB(II,KK),KK =1,MI),FW(II),FR(II)
C350  CONTINUE
C     ..................................................................
C     INTESITY CALCULATIONS
C     ..................................................................
```

```
      WRITE(LP,66)
      IL1=IL-1
      JA=0
      DO 371 K=1,IL1
      DO 371 LQ=1,MI
      IF(ABS(VVS(K,LQ)).LE.0.01)GO TO 371
      K1=K+1
      DO 372 KK=K1,IL
      DO 372 JJ=1,MI
      IF(ABS(VVS(KK,JJ)).LE.0.01)GO TO 370
      IF(ABS(VVS(K,LQ)-VVS(KK,JJ)).GT.0.1)GO TO 370
      JA=JA+1
C     ..................................................................
C     WRITE(LP,385)JA,K,LQ,JV(K),VVC(K,LQ),VVS(K,LQ),VVB(K,LQ)
C    1,KK,JJ,JV(KK),VVC(KK,JJ),VVS(KK,JJ),VVB(KK,JJ)
      L1(JA)=K
      L2(JA)=LQ
      L3(JA)=KK
      L4(JA)=JJ
  370 CONTINUE
  372 CONTINUE
  371 CONTINUE
C     ..................................................................
C     APPLY INTENSITY CORRECTIONS
C     ..................................................................
      DO 400 K=1,JA
      K1=L1(K)
      K2=L2(K)
      K3=L3(K)
      K4=L4(K)
C     ..................................................................
C     WRITE(LP,585)K1,K2,K3,K4
      DO 44 LL=1,MI
      IF(ABS(VVS(K3,LL)).LE.0.01)GO TO 44
      VVM=VVS(K3,LL)
      DO 45 LM=1,MI
      IF(ABS(VVS(K3,LM)).LE.0.01)GO TO 45
      IF(VVM.LE.VVS(K3,LM))GO TO 45
      VVM=VVS(K3,LM)
   45 CONTINUE
   44 CONTINUE
C     ..................................................................
C     WRITE(LP,23)VVM
      DO 441 LL=1,MI
      IF(ABS(VVS(K1,LL)).LE.0.01)GO TO 441
      VVM1=VVS(K3,LL)
      DO 451 LM=1,MI
      IF(ABS(VVS(K1,LM)).LE.0.01)GO TO 451
      IF(VVM1.LE.VVS(K1,LM))GO TO 451
      VVM1=VVS(K1,LM)
  451 CONTINUE
  441 CONTINUE
C     ..................................................................
C     WRITE(LP,23)VVM1
      IF(VVM-VVM1)432,431,431
  431 VVS(K1,K2)=VVS(K3,K4)-VVM
      VVS(K3,K4)=VVM
      GO TO 400
  432 VVS(K3,K4)=VVS(K1,K2)-VVM1
      VVS(K1,K2)=VVM1
  400 CONTINUE
C     ..................................................................
C     PRINT RESULT
C     ..................................................................
      DO 450 K=1,IL
```

```
      FW(K)=0
      DO 270 J=1,MI
  270 FW(K)=FW(K)+VVS(K,J)
C     ...........................................................................
C     WRITE(LP,62)JV(K),(AAN(K,II),II=1,30),(VVC(K,KK),VVS(K,KK),
C    1KK =1,MI),FW(K)
C     WRITE(LP,62)JV(K),(AAN(K,II),II=1,30),(VVC(K,KK),VVS(K,KK),
C    1VVB(K,KK),KK =1,MI),FW(K)
 450  CONTINUE
C     ...........................................................................
      WRITE(LP,66)
      DO 300 K=1,IL
      FR(K)=FW(K)/S
      DO 290 KK=1,MI
 290  VVS(K,KK)=VVS(K,KK)/S
C     ...........................................................................
      WRITE(LP,62)K,(AAN(K,II),II=1,30),FR(K)
C     WRITE(LP,62)JV(K),(AAN(K,II),II=1,30),(VVC(K,KK),VVS(K,KK),
C    1VVB(K,KK),KK=1,MI),FR(K)
 300  CONTINUE
C     ...........................................................................
      WRITE(LP,67)
      GO TO 500
C     ..........................................................................
 155  WRITE(LP,66)
 50   CONTINUE
C     ..........................................................................
      GO TO 500
C     ..........................................................................
1000  FORMAT(20X, ' .......... PROGRAM CNMR .......... ')
C122  FORMAT(2X, ' MI = ',I3,' MJ = ',I3,2X,' DATA BASE ',/)
  127 FORMAT(2X,/,2X,' QUANTITATIVE 13C NMR SPECTRAL DATA FOR A MIXTURE'
     1,/,2X,' CH.SH.PPM ', ' INTENSITY  ',/)
  126 FORMAT(2X,/,2X,' TITLE = ',2X,70A1,2X,/,
     1 2X,' MAX ALLOWED TOL*100= ',I3,/)
 123  FORMAT(I4,30A1,8F7.2)
 124  FORMAT(2X,I4,1X,30A1,8(F10.3,1X))
  125 FORMAT(I3,I3,70A1)
 224  FORMAT(2X,'TOTAL INTENSITY OF',I3,' OBSERVED CHEM SHIFTS = ',
     1,1X,10F10.3)
  23  FORMAT(10F7.2)
  24  FORMAT(2X,10F10.3)
 66   FORMAT(2X,65('--'))
 153  FORMAT(2X,' ERROR ASSUMED IS +-',F7.3,' ,EXTRA SHIFTS FOUND ',/
     1,2X,' SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR')
 65   FORMAT(2X,I3,' COMPONENTS IN MIXTURE ARE EXPECTED  WITHIN  +-   =
     1',F7.3,/)
 154  FORMAT(2X, ' GIVEN CHEM SHIFTS  MATCHED WITH THOSE OF EXPECTED
     1COMPONENTS IN THE MIXTURE ')
  62  FORMAT( 2X,I4,1X,30A1,F8.3,/,2X,12(F8.3,1X))
 67   FORMAT(2X,65('=='),/)
 385  FORMAT(2X,I3,1X,I3,1X,I3,1X,I3,1X,F10.3,1X,F10.3,1X,F10.3,
     11X,I3,1X,I3,1X,I3,1X,F10.3,1X,F10.3,1X,F10.3)
 585  FORMAT(2X,' K1= ',I3,' K2= ',I3,' K3= ',I3,' K4= ',I3)
C     ..........................................................................
  98  WRITE(LP,97)
  97  FORMAT(2X,' DATA ERROR ')
  99  CLOSE(LD)
      CLOSE(LR)
      CLOSE(LP)
      STOP
      END
```

```
            007 10  8T-1 EXPECTED LINE MIXT-1 5 25% 8 34% 10 41%
  071.46 082.50
  070.54 172.00
  063.23 085.50
  051.20 139.50
  046.65 134.50
  045.57 254.00
  044.92 137.50
 011 14 14T-2 EXPD LN MIXT-2 5(39.5),8(20.6),9(18.2),10(11.9),11(9.8)
  072.10 136.00
  071.40 109.50
  070.50 253.00
  063.20 247.50
  061.90 187.50
  052.20 189.50
  051.20 364.00
  046.70 367.50
  045.60 357.50
  044.90 359.50
  043.90 191.50
 014050 18T-7 EXPECT INTEGRATION  MIXTR 3,5(29.37);3,4(26.50);2,4(44.13)
 156.700   11.0
 154.600   10.0
 150.300   14.0
 135.288   21.5
 132.795    8.0
 130.793    8.0
 128.480   47.0
 125.808   15.0
 124.343    8.0
 121.365   11.0
 120.442   13.0
 117.660   35.0
 115.132    9.0
 114.430   22.0
 014050 20T-5 EXPECT MIX- 3,5(29.37);3,4(26.50);2,4(44.13)
 156.980 28.370
 154.874 33.910
 150.540 39.650
 135.288 61.510
 132.795 22.290
 130.793 22.250
 128.463 83.500
 125.808 47.470
 124.343 29.710
 121.365 25.030
 120.442 45.050
 117.315 74.520
 115.132 31.1
```

```
                    .....output. PROGRAM CNMR ..........

 TITLE =   T-1 EXPECTED LINE MIXT-1 5 25% 8 34% 10 41%
 MAX ALLOWED-TOL*100=  10


 QUANTITATIVE 13C NMR SPECTRAL DATA FOR A MIXTURE
 CH.SH.PPM  INTENSITY

    71.460    82.500
    70.540   172.000
    63.230    85.500
    51.200   139.500
    46.650   134.500
    45.570   254.000
    44.920   137.500
-------------------------------------------------------------------------------
TOTAL INTENSITY OF  7 OBSERVED CHEM SHIFTS =    1005.500
-------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .010 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
 ------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .030 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
 ------------------------------------------------------------------------------
  3 COMPONENTS IN MIXTURE ARE EXPECTED  WITHIN  +-    =    .050

 GIVEN CHEM SHIFTS  MATCHED WITH THOSE OF EXPECTED COMPONENTS IN THE MIXTURE
-------------------------------------------------------------------------------
-------Table 3.3 ---------------------------------------------------------------
   1  1-CHLORO-2-HYDROXYPROPANE          .249

   2  1,3-DICHLORO-2-HYDROXYPROPANE      .342

   3  1-CHLORO-2,3-EPOXYPROPANE          .409

===============================================================================


 TITLE =   T-2 EXPD LN MIXT-2 5(39.5),8(20.6),9(18.2),10(11.9),11(9.8)
 MAX ALLOWED TOL*100=  14


 QUANTITATIVE 13C NMR SPECTRAL DATA FOR A MIXTURE
 CH.SH.PPM  INTENSITY

    72.100   136.000
    71.400   109.500
    70.500   253.000
    63.200   247.500
    61.900   187.500
    52.200   189.500
    51.200   364.000
    46.700   367.500
    45.600   357.500
    44.900   359.500
    43.900   191.500
-------------------------------------------------------------------------------
TOTAL INTENSITY OF 11 OBSERVED CHEM SHIFTS =    2763.000
-------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .010 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
-------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .030 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
-------------------------------------------------------------------------------
```

```
 ERROR ASSUMED IS +-    .050 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
-------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .070 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
-------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .090 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
-------------------------------------------------------------------------------
  5 COMPONENTS IN MIXTURE ARE EXPECTED  WITHIN  +-   =    .110

 GIVEN CHEM SHIFTS MATCHED WITH THOSE OF EXPECTED COMPONENTS IN THE MIXTURE
-------------------------------------------   ----------------------------------
                                     Table 3.3.6
-------------------------------------------   ----------------------------------
    1  1-CHLORO-2-HYDROXYPROPANE          .118

    2  1,3-DICHLORO-2-HYDROXYPROPANE      .183

    3  1,2,3-TRIHYDROXYPROPANE            .098

    4  1-CHLORO-2,3-EPOXYPROPANE          .395

    5  1,2-EPOXY-3-HYDROXYPROPANE         .206

===============================================================================


 TITLE =   T-7 EXPECT INTEGRATION  MIXTR 3,5(29.37);3,4(26.50);2,4(44.13)
 MAX ALLOWED TOL*100=  50


 QUANTITATIVE 13C NMR SPECTRAL DATA FOR A MIXTURE
 CH.SH.PPM  INTENSITY

   156.700    11.000
   154.600    10.000
   150.300    14.000
   135.288    21.500
   132.795     8.000
   130.793     8.000
   128.480    47.000
   125.808    15.000
   124.343     8.000
   121.365    11.000
   120.442    13.000
   117.660    35.000
   115.132     9.000
   114.430    22.000
-------------------------------------------------------------------------------
TOTAL INTENSITY OF 14 OBSERVED CHEM SHIFTS =     232.500
-------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .010 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
-------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .030 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
-------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .050 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
-------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .070 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
-------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .090 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
```

```
     132.795     22.290
     130.793     22.250
     128.463     83.500
     125.808     47.470
     124.343     29.710
     121.365     25.030
     120.442     45.050
     117.315     74.520
     115.132     31.170
     114.430     51.310
--------------------------------------------------------------------------------
TOTAL INTENSITY OF 14 OBSERVED CHEM SHIFTS =     595.740
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .010 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .030 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .050 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .070 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .090 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .110 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .130 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .150 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .170 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .190 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .210 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .230 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .250 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .270 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .290 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .310 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .330 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-   .350 ,EXTRA SHIFTS FOUND
```

```
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .110 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .130 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .150 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .170 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .190 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .210 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .230 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .250 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .270 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .290 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .310 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .330 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
 ERROR ASSUMED IS +-    .350 ,EXTRA SHIFTS FOUND
 SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
--------------------------------------------------------------------------------
  3 COMPONENTS IN MIXTURE ARE EXPECTED  WITHIN  +-   =     .370

 GIVEN CHEM SHIFTS MATCHED WITH THOSE OF EXPECTED COMPONENTS IN THE MIXTURE
--------------------------------------------------------------------------------
--------------------------------Table 3.3.4 -------------------------------------
   1  2,4-DICHLOROPHENOL               .422

   2  3,4-DICHLOROPHENOL               .297

   3  3,5-DICHLOROPHENOL               .282

================================================================================


 TITLE =   T-5 EXPECT MIX- 3,5(29.37);3,4(26.50);2,4(44.13)
 MAX ALLOWED TOL*100=  50


 QUANTITATIVE 13C NMR SPECTRAL DATA FOR A MIXTURE
 CH.SH.PPM  INTENSITY

   156.980    28.370
   154.874    33.910
   150.540    39.650
   135.288    61.510
```

```
SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
---------------------------------------------------------------------------
ERROR ASSUMED IS +-    .370 .EXTRA SHIFTS FOUND
SEARCH WILL BE CONTINUED  WITH NEW ASSUMED ERROR
----------------------------------------------------------------------------
 3 COMPONENTS IN MIXTURE ARE EXPECTED  WITHIN  +-   =    .390

GIVEN CHEM SHIFTS MATCHED WITH THOSE OF EXPECTED COMPONENTS IN THE MIXTURE
----------------------------------------------------------------------------
-----------------------------------Tablee 3.3.4 -----------------------------
  1  2,4-DICHLOROPHENOL                .414

  2  3,4-DICHLOROPHENOL                .307

  3  3,5-DICHLOROPHENOL                .279

============================================================================
```

Data bank of chemical shifts of chlorophenols

0002	PROPANE	015.40	015.90	000.00	000.00	000.00	000.00	000.00	000.00
0003	1-HYDROXYPROPANE	010.00	025.80	063.80	000.00	000.00	000.00	000.00	000.00
0004	2-HYDROXYPROPANE	025.10	000.00	000.00	063.40	000.00	000.00	000.00	000.00
0005	1-CHLORO-2-HYDROXYPROPANE	045.60	063.20	000.00	071.50	000.00	000.00	000.00	000.00
0006	2-CHLORO-1-HYDROXYPROPANE	020.90	073.20	000.00	058.10	000.00	000.00	000.00	000.00
0007	1,2-DICHLORO-3-HYDROXYPROPANE	000.00	053.80	000.00	069.30	000.00	000.00	000.00	000.00
0008	1,3-DICHLORO-2-HYDROXYPROPANE	000.00	045.60	000.00	070.50	000.00	000.00	000.00	000.00
0009	1,2,3-TRIHYDROXYPROPANE	000.00	063.20	000.00	072.10	000.00	000.00	000.00	000.00
0010	1-CHLORO-2,3-EPOXYPROPANE	000.00	041.90	046.70	051.20	000.00	000.00	000.00	000.00
0011	1,2-EPOXY-3-HYDROXYPROPANE	000.00	043.90	052.20	061.90	000.00	000.00	000.00	000.00
0012	3-CHLORO-1-PROPENE	000.00	117.50	048.70	133.70	000.00	000.00	000.00	000.00
0013	3-HYDROXY-1-PROPENE	000.00	114.90	063.40	137.50	000.00	000.00	000.00	000.00
0014	1-CHLORO-2,3-DIHYDROXYPROPANE	000.00	093.60	058.20	081.50	000.00	000.00	000.00	000.00
0015	2-CHLORO-1,3-DIHYDROXYPROPANE	000.00	068.50	000.00	068.10	000.00	000.00	000.00	000.00
0016	METHANOL	49.9							
0017	O-CRESOL	153.50	124.00	131.00	121.40	127.70	115.90	016.70	000.00
0018	M-CRESOL	154.90	116.10	139.30	122.20	130.30	112.70	020.90	000.00
0019	P-CRESOL	152.60	115.30	130.20	130.50			020.60	000.00
0020	O-TOLUIDINE	145.20	122.20	130.40	118.30	127.00	115.00	017.00	000.00
0021	M-TOLUIDINE	147.20	116.10	138.80	119.10	129.20	112.50	021.30	000.00
0022	PHENOL	155.50	115.40	129.80	121.00	129.80	115.40	000.00	000.00
0023	2-CHLOROPHENOL	151.80	120.30	129.20	121.50	128.50	116.50	000.00	000.00
0024	4-CHLOROPHENOL	154.10	116.80	129.70	125.90	129.70	116.80	000.00	000.00
0025	3-CHLOROPHENOL	156.30	116.10	135.10	121.30	130.60	113.90	000.00	000.00
0026	2,6-DICHLOROPHENOL	148.10	121.30	128.50	000.00	000.00	000.00	000.00	000.00
0027	2,4-DICHLOROPHENOL	150.30	120.60	128.70	125.80	000.00	117.30	000.00	000.00
0028	2,3-DICHLOROPHENOL	152.90	119.20	132.80	122.30	128.20	114.60	000.00	000.00
0029	2,5-DICHLOROPHENOL	152.00	118.50	129.70	121.80	133.90	116.80	000.00	000.00
0030	3,4-DICHLOROPHENOL	151.60	117.70	133.10	124.40	131.00	115.40	000.00	000.00
0031	3,5-DICHLOROPHENOL	156.70	114.70	135.60	121.40	000.00	000.00	000.00	000.00
0032	2,4,6-TRICHLOROPHENOL	147.10	121.80	128.20	125.50	128.20	121.80	000.00	000.00
0033	PENTACHLOROPHENOL	148.30	119.90	131.60	125.20	000.00	000.00	000.00	000.00

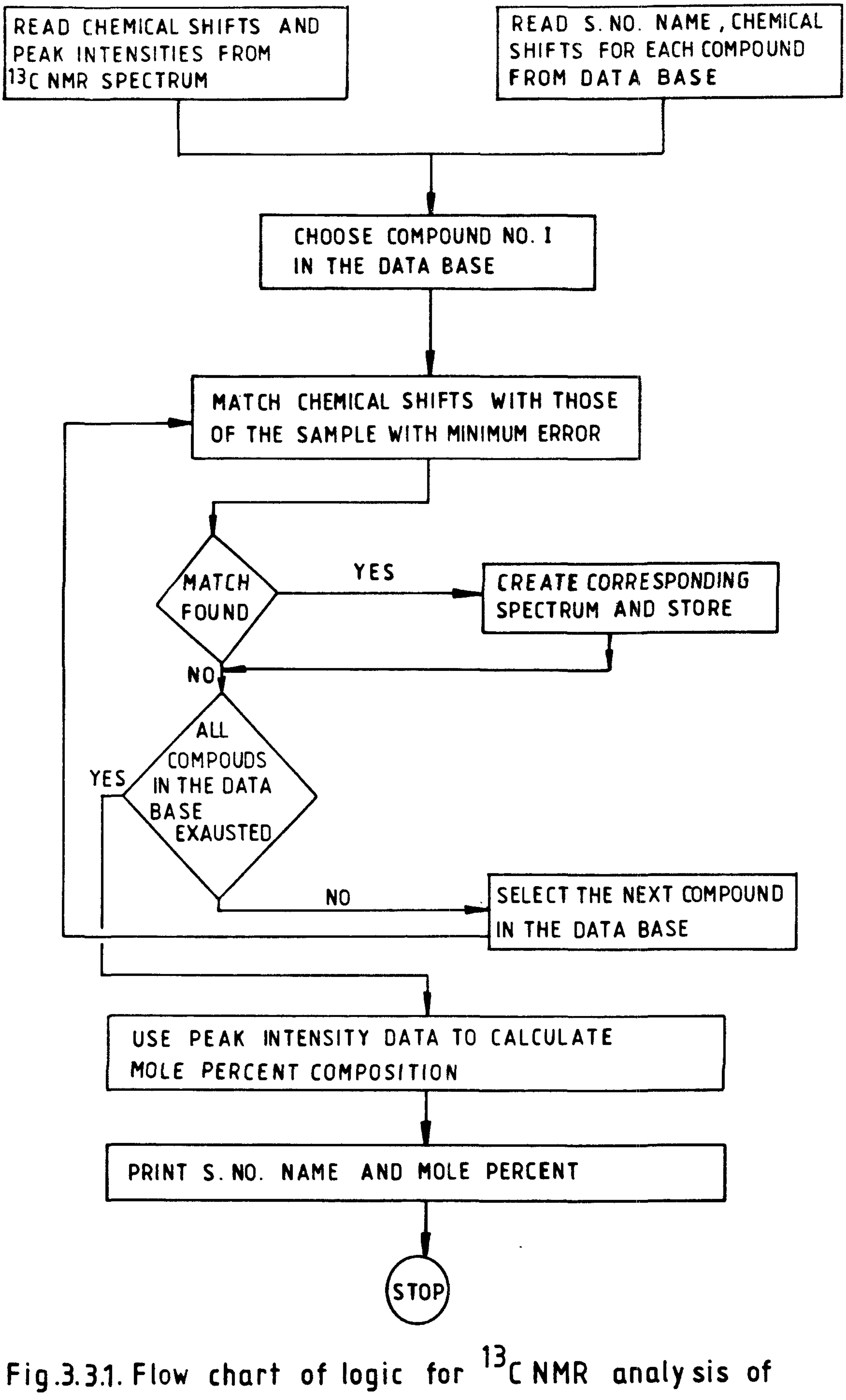


Fig.3.3.1. Flow chart of logic for ^{13}C NMR analysis of mixtures of chlorophenols.

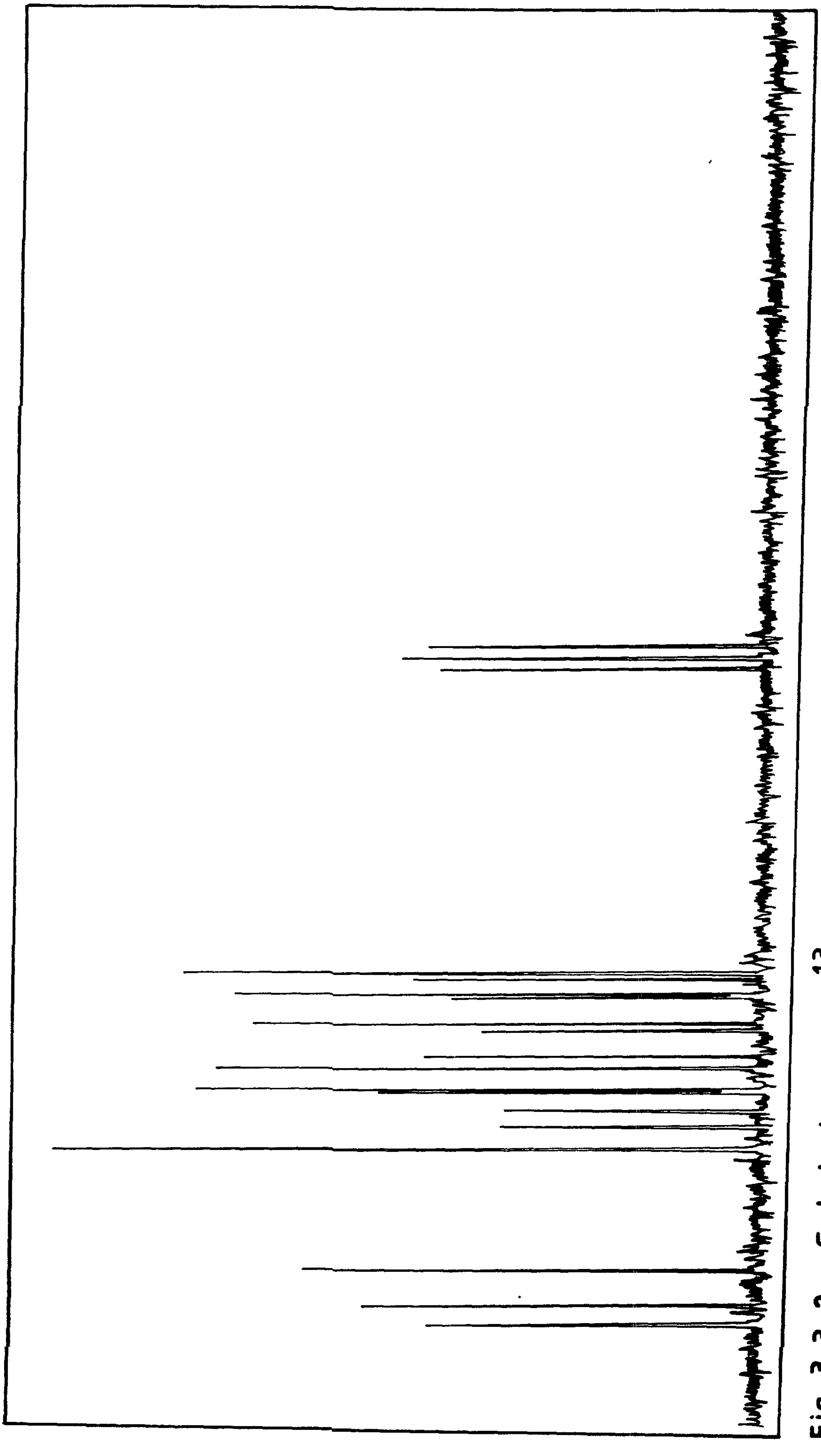


Fig. 3.3.2 Gated-decoupled ^{13}C NMR spectrum of mixtur of chlorophenols

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Chapter IV

4. Chlorination of Phenols

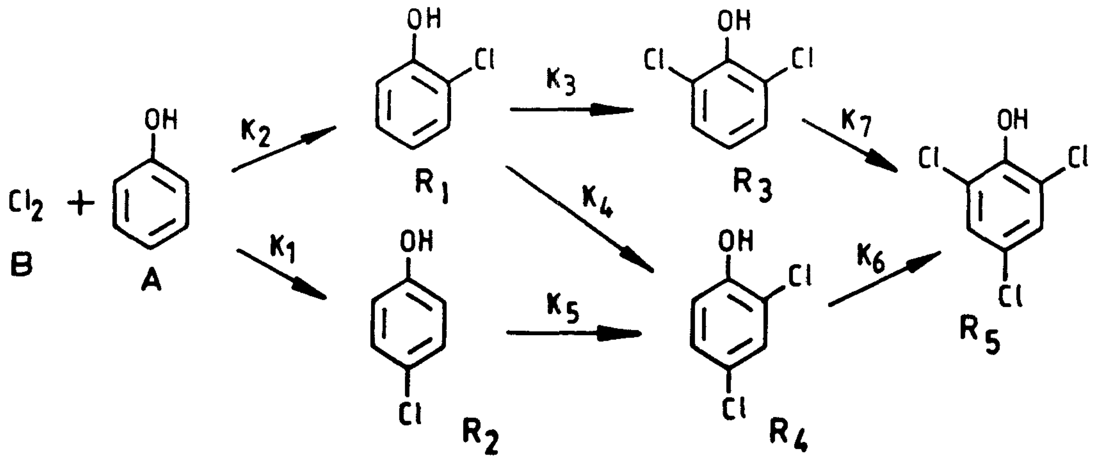
Chlorinated phenols and their derivatives belong to an important class of organic intermediates. These chemicals have wide practical applications in chemical, pesticide and pharmaceutical industries. Recognising the industrial importance of the chlorinated phenols, systematic studies on the chlorination of phenols have been taken up with a view to optimize the reaction conditions to get the maximum yield of the desired products and also to generate the kinetic and thermodynamic data. Though most of the chlorophenols have industrial importance, present studies are mainly confined to the most important chlorophenols such as p-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol and p-cresol.

For the chlorination of phenols a variety of chlorinating agents are described in the literature[1]. Among them we have used in our studies mainly the following (1) gaseous chlorine, (2) tert-butyl hypochlorite and (3) cupric chloride.

4.1 Chlorination of phenol with gaseous chlorine

Phenol (A) under molten condition is reacted with gaseous chlorine at 65 ± 2°C and the progress of the reaction has been studied by TLC. A sample of the reaction product has been with drawn after half an hour, TLC analysis is performed which has shown the presence of o-chlorophenol

(R_1) and p-chlorophenol (R_2) and unreacted (A). Subsequent analysis of the samples withdrawn at regular intervals has indicated the increase in the percentage of monochlorophenols. When mono chlorination is attained to its maximum, further chlorination leads to the simultaneous formation of 2,4-dichlorophenol (R_4) and 2,6-dichlorophenol (R_3). The continuation of further chlorination appears to enhanced the formation of dichlorophenol and reduce the amounts of monochlorophenols. Finally, 2,4,6-trichlorophenol (R_3) has been found to be the ultimate product. This has taken about 3-5 hours depending upon the rate of chlorination. A close examination of the results of analysis of reaction products reveals that monochlorination proceeds immediately, further chlorination leads to the formation of dichlorophenols which is converted to R_5 . Based on the just mentioned observation the progress of the chlorination of phenol has been represented as given below :



KINETIC STUDIES

Though there are few reports on the kinetics of chlorination of phenols employing various chlorinating agents, detail studies on kinetics and mechanism of chlorination of phenols have not been reported.

Fred, Lee et al[2] have studied the kinetics of chlorination phenol to establish the optimum condition in order to minimize the chlorophenolic taste and odour. Kat Sumi et al[3] have reported kinetics of chlorination of phenol in bubble column reactor and various reaction condition have been explained. Zubarev[4] et al have studied the kinetics of chlorination of phenol in cascade type reactor and established the conditions for preparation of 2,4-DCP. On the basis of inferences drawn from the literature, experiments have been carried out to generate the kinetic data and reaction mechanism for chlorination of phenols with gaseous chlorine.

Experimental Investigations

Materials used : Phenol (BDH grade) is used as such. Solvents acetic acid, carbon tetrachloride (Pfizer Duchem reagent) benzene, nitromethane (BDH) reagent are used. All other chemicals used are of good quality.

Experimental set up : The details of the experimental set up shown in Fig. 4.1.1. The main feature of the experimental apparatus is a round bottommed glass reaction vessel (250 ml). The contents of which have been thermostated and have been stirred with a glass stirrer. Known quantity of chlorine gas has been introduced into the vessel via a glass inlet tube into the liquid phase and out going gases have been discharged through a reflux condenser.

Kinetic measurements

A total of 94 grams (1 mole) of phenol and the required quantity of solvent have been added to the reaction vessel. The reaction vessel has been flushed with nitrogen to remove air, stirring and heating have then been started. When the reaction vessel temperature has attained 10°C or below, the chlorine gas has been introduced into the reaction vessel by adjusting the flowrate of chlorine to the pre-determined value with the help of a calibrated flow meter. The temperatures have been maintained to pre-determined value permitting a fluctuation in the temperature within about ± 1°C. Six to ten samples of the reaction mixtures have been pipetted out at determined time intervals and have been quenched in 5 ml of 5% sodium bicarbonate solution to remove the free chlorine gas. The samples have then been extracted with ether and analysed by GLC. The different components of phenol and its chloro derivatives have been quantitatively estimated using GLC technique as has already been described in Chapter II.

The changes in concentration of phenol and its chloro-derivatives during the chlorination of phenol with gaseous chlorine at temperatures $65 \pm 1^{\circ}C$ obtained by GLC are shown in

Table 4.1.1. A graph is given between concentration (moles/lit) and time for the entire reaction (Scheme I) in Fig. 4.1.2. It is seen from it that when the concentration of A is decreased in the reaction mixture then the concentrations of the components R_1 and R_2 are found to be increasing. It is further observed that R_3 and R_4 starts forming before a maximum concentration of R_1 and R_2 is formed. Finally R_5 is obtained on total chlorination. Therefore, the experimental data indicates that the chlorination of phenol with gaseous chlorine is a series cum parallel reaction represented by Scheme I.

From the reaction scheme I reactants and products are represented by A, B, R_1, R_2, R_3, R_4 and R_5 where

A = phenol
B = chlorine
R_1 = o-chlorophenol
R_2 = p-chlorophenol
R_3 = 2,6-dichlorophenol
R_4 = 2,4-Dichlorophenol and
R_5 = 2,4,6-trichlorophenol

Let the rate constant for the various consecutive reactions be represented as follows :

$$A + B \xrightarrow{K_1} R_2 + S \qquad (1)$$

$$A + B \xrightarrow{K_2} R_1 + S \qquad (2)$$

$$R_1 + B \xrightarrow{K_3} R_3 + S \qquad (3)$$

$$R_1 + B \xrightarrow{K_4} R_4 + S \qquad (4)$$

$$R_2 + B \xrightarrow{K_5} R_4 + S \qquad (5)$$

$$R_3 + B \xrightarrow{K_7} R_5 + S \qquad (6)$$

$$R_4 + B \xrightarrow{K_6} R_5 + S \qquad (7)$$

The assumptions in the calculation are (a) each chlorination step (1) to (7) is second order, that is first order with respect to both chlorine and phenolic compounds from A to R_4. (b) Initial concentration of phenol (C_{Ao}) and chlorine (C_{Bo}) is unity.

For this experiments have been conducted at temperatures 65°, 85°, 120° and 140°C. The samples with drawn at regular intervals of time have been analysed by GLC. The data obtained has been tested for first order reaction. Fig. 4.1.3 represents the concentration vs time graphs obtained at different temperatures. The straight line graphs confirms that the reaction in first order with respect to phenol. To evaluate the experimental data interms of rate constants and activation energies differential rate equations have been derived.

Differential Rate Equations

(1) Rate of disappearance of A is determined by the reactions (1) and (2).

$$-\frac{dC_A}{dt} = K_1 C_A C_B + K_2 C_A C_B$$

$$\frac{dC_A}{dt} = -(K_1 + K_2)\, C_A\, C_B \tag{8}$$

(2) Rate of formation of R_1

From reactions (1) and (3) we have

$$\frac{dC_{R_1}}{dt} = (K_2 C_A - K_3 C_{R_1} - K_4 C_{R_1})\, C_B \tag{9}$$

Dividing equation (9) by equation (8), we have

$$\frac{dC_{R_1}}{dC_A} = \left(\frac{K_4 + K_3}{K_1 + K_2}\right) \frac{C_{R_1}}{C_A} - \frac{K_2}{K_1 + K_2}$$

Let $\alpha = \left(\frac{K_2}{K_1 + K_2}\right)$ and $\beta = \left(\frac{K_4 + K_3}{K_1 + K_2}\right)$

Substituting α and β the equation takes the form

$$\frac{dC_{R_1}}{dC_A} = \beta \left(\frac{C_{R_1}}{C_A}\right) - \alpha \ , \tag{10}$$

The solution for the equation (10) given by

$$C_{R_1} C_A^{-\beta} = -\alpha \int_{C_{A_0}}^{C_A} C_A^{-\beta}\, dC_A$$

The following boundary conditions are used in getting the above equation.

At t = 0	At t = t
$C_A = C_{A_o}$	$C_A = C_A$
$C_{R_1} = 0$	$C_{R_1} = C_{R_1}$

$$C_{R_1} C_A^{-\beta} = \frac{-\alpha}{1-\beta} \left[C_A^{1-\beta}\right]_{C_{A_o}}^{C_A}$$

$$= \frac{-\alpha}{1-\beta} \left[C_A^{1-\beta} - C_{A_o}^{1-\beta}\right]$$

$$C_{R_1} C_A^{-\beta} = \frac{-\alpha}{1-\beta} \left[(C_A)^{1-\beta} - 1\right]$$

$$C_{R_1} = \frac{-\alpha}{1-\beta} \left[C_A - C_A^{\beta}\right]$$

$$= \frac{\alpha}{1-\beta} \left[C_A^{\beta} - C_A\right]$$

$$C_{R_1} = \frac{\alpha}{1-\beta} C_A \left[C_A^{\beta-1} - 1\right] \tag{11}$$

(3) Rate of formation of R_2 :

From equations (2) and (4) we have

$$\frac{dC_{R_2}}{dt} = K_1 C_A C_B - K_5 C_{R_2} C_B \tag{12}$$

Dividing (12) by (8)

$$\frac{dC_{R_2}}{dC} = \frac{K_5 \; C_{R_2}}{K_1 + K_2 C} - \frac{K_1}{K_1 + K_2}$$

$$= \delta \frac{C_{R_2}}{C_A} - \gamma \tag{13}$$

Where $\delta = \left(\frac{K_5}{K_1 + K_2} \right)$ & $\gamma = \frac{K_1}{K_1 + K_2}$

This is similar to the equation (10) so that the solution can be directly written as

$$C_{R_2} = \frac{\gamma C_A}{1 - \delta} \left[C_A^{\delta - 1} - 1 \right] \qquad (14)$$

(4) Rate formation of R_3

From equations (3) and (6) we have

$$\frac{dC_{R_3}}{dt} = K_3 C_{R_1} C_B - K_7 C_{R_3} C_B$$

Dividing equation (15) by equation (8)

$$\frac{dC_{R_3}}{dC_A} = \frac{K_7}{K_1 + K_2} \frac{C_{R_3}}{C_A} - \frac{K_3}{K_1 + K_2} \frac{C_{R_1}}{C_A}$$

$$= \psi \frac{C_{R_3}}{C_A} - \mu \frac{C_{R_1}}{C_A} \qquad (15)$$

Where $\psi = \frac{K_6}{K_1 + K_2}$ $\quad \mu = \frac{K_3}{K_1 + K_2}$

(5) Rate of formulation of R_4

From equations (4), (5) and (7)

$$\frac{dC_{R_4}}{dt} = K_4 C_{R_1} C_B + K_5 C_{R_2} C_B - K_6 C_{R_4} C_B$$

dividing by equation (8)

$$\frac{dC_{R_4}}{dC_A} = \frac{K_6}{K_1 + K_2} \frac{C_{R_4}}{C_A} - \frac{K_4}{K_1 + K_2} \frac{C_{R_1}}{C_A} - \frac{K_5}{K_1 + K_2} \frac{C_{R_2}}{C_A}$$

$$= \lambda \frac{C_{R_4}}{C_A} - \eta \frac{C_{R_1}}{C_A} - \delta \frac{C_{R_2}}{C_A} \qquad (16)$$

Since the equations (15) and (16) are similar equations (10) and (12), the solution of these equations can be derived by proceeding similar lines.

(6) Rate of formulation of R_5

$$C_A + C_{R_1} + C_{R_2} + C_{R_3} + C_{R_4} + C_{R_5} = 1$$

$$C_{R_5} = 1 - (C_A + C_{R_1} + C_{R_2} + C_{R_3} + C_{R_4}) \tag{17}$$

Determination of relative rate constants - conditions for maximum yield

In a consecutive parallel reaction. The concentration of substrate generally falls gradually in a simple exponential manner. In the present studies, also the concentration of phenol falls off in a simple exponential manner and those of C_{R1}. C_{R2}, C_{R3}, C_{R4}, and C_{R5}, have been initially zero. As the reaction proceeds the concentration of isomers increases gradually but does not accumulate definitely, as they react further to give the corresponding isomers. For example, the concentration of C initially increases, reaches its maximum and then falls to zero. Therefore, at any particular concentration C_B $dC_{R1}/dt = 0$. Using this condition relative rate constants have been determined.

$$\frac{dC_{R2}}{dC_{R1}} = \frac{K_1}{K_2} \tag{18}$$

$$\frac{C_{R1}\,(\text{max})}{C_A\,[B]} = \frac{K_2}{K_3} \tag{19}$$

$$\frac{C_{R2}\,(\text{max})}{C_A} = \frac{K_1}{K_5} \tag{20}$$

Considering the industrial importance of 2,4-dichloro phenols, a systematic and detailed study to optimise various parameters for their preparations using gaseous chlorine as a chlorinating agent has been taken up.

(i) Effect of chlorine flow rate on the rate of chlorination

Rate of chlorination has been the first parameter selected to study for optimization studies in preparation of chlorophenols. Experiments have been conducted by varying the molar flow rate of chlorine and keeping tne phenol content constant. The progress of the reaction was followed by withdrawing samples at regular intervals of time and analysisng them by GLC. The reaction was stopped with R_4 attained maximum and phenol and monochlorophenols have been almost consumed. The results obtained are presented in Table 4.1.2 and the rate constant in Table 4.1.3.

Another set of experiment has been carried out where chlorine flow rate has been kept constant but the contents of phenol have been changed. The reactants have been subjected to same type of analysis as just mentioned. The data so obtained is listed in Table 4.1.4 and the rate constants are given in Table 4.1.5.

It could be concluded from the data that the rate of chlorination depends on both i.e. flow rate of chlorine as well as on the molar concentration of phenol. However, distribution of isomer has been found almost independent of molar concentration of phenol and flow rate of chlorine.

(ii) Effect of solvent

With a view to determine the effect of solvent on the isomer distribution during the chlorination of phenol with gaseous chlorine, experiments have been conducted in both polar and non-polar solvents.

Dry chlorine has been passed through at a rate between 10 to 25 litre/hour maintaining temperature (15-65°C) at atmospheric pressure. Phenol (1 gram mole) dissolved in a solvent (1 to 3 gram mole). The course of the chlorination has been followed by withdrawing samples periodically and subjecting them to GLC analysis. Chlorination has been stopped when the product contained maximum percentage of dichlorophenols. Using this procedure experiments have been conducted in polar solvents (viz., Acetic acid; acetic acid-water; nitromethane) and also in non-polar solvents (viz., benzene, CCl_4). The results obtained are presented in Table 4.1.6. From these results it is seen that maximum yield of 2,4-DCP is achieved in polar solvents, whereas 2,6-DCP is found in increased quantities in non-polar solvents was found to be comparatively more than in polar solvents. It is evident from the data that ortho-chloro isomers are preferentially formed when non-polar solvents are used. Further, the increase in temperature increases the ratio of chloro isomers in the reaction mixtures. However, polar lvents and lower temperatures favour the p-chlorination.

The expected results are not obtained when one considers the solvent polarity index as a criterion for rtho/para distribution in the chlorination of phenol. etter explanation can be had if one examines the effect of hese solvents from the point of view of hydrogen bonding. When phenol is taken in a polar solvent, there is a shielding effect on the ortho-position by virture of ydrogen bonding with the -OH group of phenol thereby leaving the para position free for attack and thus ncreasing the yield of 4-chloro isomers and their higher derivatives.

The shielding effect of solvent molecules on the ortho position of phenol depends upon the stability of hydrogen bond formed. The results obtained in the present investigations are in accordance of the reported literature[5]. Further, the polar solvents that solvate the hydroxyl group such as nitrobenzene, nitromethane which form stable 6-membered hydrogen bonded complexes with phenol give the highest yield of p-chloro isomers, whereas non-polar solvents such as CCl_4 and benzene which do not solvate the hydroxyl group and actually weaken the hydrogen bonding between the molecules gives the highest yield of ortho-isomer. To explain these facts in terms of their activation energies, experiments have been conducted in nitromethane, acetic acid, acetic acid-water (50% v/v). Benzene and CCl_4

at different temperatures (15-85^{o}C). Rate constants (K_1 to K_7) have been calculated for all the isomeric chlorophenols obtained during the chlorination phenol to get 2,4,6-trichlorophenol and the results are shown in Table 4.1.7. From the Arrhenius plots the activation energies have been determined and summarised in Table 4.1.8. The activation energies obtained for the chloro-isomers are low as expected for the aromatic hydrocarbons possessing substituent with unshared pair of electron. The low activation energies of chlorophenols in the polar solvents can be explained in terms of formation of hydrogen bonding complexes which are thermally unstable and are the reaction intermediates. The relatively low activation energy for para substitution in polar solvents when compared to ortho chloro substituted isomers responsible for predominantly the formation of para-isomer in the reaction mixture. This is also in accordance with the fact that the attacking chlorine molecule selects the nuclear position which allows the attainment of lowest possible energy level in the transition state because molecular chlorinations are more selective to stearic and electronic effects.

(iii) Effect of temperature

Experiments have been conducted at different temperatures (140^{o}, 120^{o}C, 85^{o}C and 65^{o}C) and the rate constants (K_1 to K_7) have been calculated for the entire reaction (Scheme I) and the results obtained are given in

Table 4.1.9. Making use of these values Arrhenious plots have been drawn and activation energies have been calculated and are also shown in Table 4.1.9. From Table 4.1.9 it is evident that activation energies are low as expected as for the chlorination of aromatic compounds with substituents possessing unshared pair of electrons. The low activation energies obtained for the formation of para and 2,4-DCP isomers as compared to ortho and 2,6-DCP isomers substantiates the ratios of para/ortho and 2,4-DCP, 2,6-DCP obtained during the chlorination of phenol.

4.2 Process Development Work

As has already been stated that most of the chlorphenols viz., o-chlorophenol (OCP), p-chlorophenol (PCP), 2,4-Dichlorophenols (2,4-DCP), 2,5-dichlorophenol (2,5-DCP) and 2,4,5-trichlorophenols (2,4,5-TCP) are important intermediates in the manufacture of pharmaceuticals, drugs, pesticides, dyes and fire resistant resins. Since these compounds are industrially important an attempt has been made to standardise the reaction condition to develop processes for their production. The present studies are mainly concerned with the development of processes for (1) OCP, (2) PCP, (3) 2,4-DCP, (4) 2,5-DCP and 2,4,5-TCP which should be economically viable.

4.2.1 Process for the production of OCP and DCP

Chlorophenols are generally obtained by the chlorination of phenols. Since three sites (2-, 4-, & 6-, where the electron densities are increased are available in the phenol molecules for the substitution of electrophibi species thereby giving a complex mixture of mono, di and trichlorophenols. Hence controlled chlorination of phenol choosing appropriate conditions are employed to have the desire chloro isomer.

A process for the production of PCP & OCP has been developed by carrying out partial gaseous chlorination of phenol selecting a low molecular weight fatty acid (viz., acetic acid) maintaining the reaction temperature in the range of 35-85^{o}C. The reaction is stopped at that stage when maximum mono chloro isomers have been formed in the reaction mixture without going to dichloro-isomer stage. The GLC analysis of a typical reaction mixture gives 27 percent of OCP; 40 percent of PCP and remaining unreacted phenol. When this mixture has been subjected for fractionation using a glass helics packed column having 32 theoretical plates, it could separate all the components of the reaction mixture i.e. acetic acid; phenol; OCP & PCP in the purest form. The acetic acid and phenol are recycled. The details of this work has already been covered in a patent.

One can take PCP as a raw material and do the controlled chlorination employing the above mentioned reaction conditions. It yields exclusively 2,4-DCP.

4.2.2 Process for the production of 2,4-DCP

Direct chlorination of phenol to get 2,4-DCP involves partial chlorination of phenol and subjecting the chlorinated mixture for fractionation to separate OCP to avoid the formation of 2,6-DCP. Since this process is a two stage, one its industrial feasibility is questionable, therefore, an alternative process has been developed. The main task in this process is to minimize the formation of 2,6-DCP and this has been achieved making one of the reaction sites inaccessible to chlorine to react by forming complex with the solvent which causes the required steric hindrance. To select the suitable reaction medium and to standardise the reaction conditions, experiments has been conducted in both polar and non-polar solvents at different temperatures and by passing CO_2 gas.

Studies on the effect of CO_2

Phenol (1 gr. mole) and acetic acid (2 g moles) have been taken and chlorine gas (35-40 l/hr) and carbon dioxide (12-15 l/hr) have been passed with stirring. It has been presumed that by passing CO_2 one can make one of the reaction sites i.e. (ortho to hydroxy) inaccessible to chlorine by forming a complex between phenol and CO_2 which causes steric hindrance to one of the ortho substitution.

Experiments have been conducted by varying the flow rates of both chlorine and CO_2 and it has been found that 15/lit/hr flowrate of CO_2 gives rise to maximum yield of

2,4-DCP. However, comprehensive examination of data obtained with and without CO_2 led to the conclusion that by passing CO_2 there is no significant change in isomer distribution. From the results of solvent studies (Table 4.1.7) it has been found that polar solvents such as nitrobenzene and nitromethane gives 2,4-DCP conversion of 98%.

Systematic work on chlorination of phenol has been taken up by using the nitromethane (CH_3NO_2) as solvent for the preparation of 2,4-DCP. Experiments have been conducted to study the effect of phenol to solvent molar ratio on the maximum yield of 2,4-DCP. The results of most representation experiments conducted by taking different ratios (1:05, 1:1, 1:1.5, 1:2) and the results are recorded in Table 4.2.2.1. Observing the results of the table it is clear that molar ratio 1:2 produces the maximum yield of 2,4-DCP (98%). These experiments have been repeated at different temperatures (35-50°C) to optimize the reaction conditions and results obtained are presented in Table 4.2.2.2. It is concluded from the results that there is no significant influence of temperature on the yield of 2,4-DCP. However, it has been noted that experiments conducted in the range of 35-50°C gives maximum yield of 2,4-DCP.

Details of this work are covered in a patent and also a know-how packet has been prepared for the production of 2,4-DCP with a view to transfer the technology to industry.

It has already been pointed out that the use of polar solvents in chlorination of phenol has dramatic effect on the increased yield of para-chloro-isomer which in turn on further chlorination yields 2,4-DCP in increased yields. Nitromethane has been found (Table 4.1.6) as the best solvent in this regard.

Table : 4.1.1

GLC analysis of the reaction products

Compound	Time (minutes)											
	10	20	30	45	60	90	120	150	180	210	240	270
Phenol	93.52	82.35	72.75	57.44	50.28	21.08	3.78	-	-	-	-	-
O-chlorophenol	2.04	9.19	9.27	14.49	14.28	27.18	31.12	22.65	15.05	-	-	-
P-chlorophenol	4.42	8.30	17.79	27.91	35.28	43.31	48.05	32.21	7.10	-	-	-
2,6-Dichlorophenol	-	-	-	-	-	-	-	2.68	2.97	6.36	7.98	4.25
2,4-Dichlorophenol	-	-	-	-	-	8.48	17.05	42.44	74.88	88.50	61.97	13.25
2,4,6-Trichlorophenol	-	-	-	-	-	-	-	-	-	5.09	30.04	82.50

Table 4.1.2

Effect of flow rate of chlorine on isomer distribution

Reaction time (min)	Concentration of phenol mole	Chlorine flowrate lit/hr	Chemical composition			
			Phenol	OCP	PCP	2,4-DCP
60	1	33.0	13.55	33.79	48.37	4.26
80	1	26.5	21.85	24.42	47.88	5.52
100	1	22.5	11.99	32.19	49.49	6.37
120	1	18.0	3.28	31.31	48.25	17.55
240	1	13.0	4.0	36.25	49.77	9.66

Table : 4.1.3

Values of rate constants (K_1 to K_7) at different Chlorine flow rates :

Temperature 65 ^{o}C

Molar Conc. of phenol	Flow rate of chlorine Lit/hrs	K_1	K_2	K_3	K_4	K_5	K_6	k_7
1.0	13.5	1	0.544	0.0672	0.0356	0.005	0.0029	0.0023
1.0	18.5	1	0.504	0.0672	0.0395	0.0138	0.0031	0.0025
1.0	22.5	1	0.553	0.1092	0.0603	0.0171	0.0041	0.0030
1.0	26.5	1	0.634	0.1850	0.1330	0.0510	0.0044	0.0042

Table 4.1.4

Effect of molar ratio of phenol to chlorine on isomer distribution

Reaction time (min)	Concentration of phenol mole	Chlorine flowrate lit/hr	Chemical composition			
			Phenol	OCP	PCP	2,4-DCP
60	0.5	26.5	5.57	33.67	51.94	9.80
150	1.5	26.5	6.58	26.85	54.34	12.34
180	2.0	26.5	4.50	33.33	53.72	8.88
240	2.5	26.5	13.34	24.43	56.41	5.80
290	3.0	26.5	9.30	32.26	59.93	5.40

Table : 4.1.5

Values of rate constants (K_1 to K_7) at different molar ratios of phenol :

Temperature 65 °C

Molar Conc. of phenol	Flow rate of chlorine Lit/hrs	K_1	K_2	K_3	K_4	K_5	K_6	k_7
0.5	26.5	1	0.568	0.1220	0.0719	0.2216	0.01370	0.00550
1.5	26.5	1	0.552	0.0822	0.0248	0.1044	0.01040	0.00313
2.0	26.5	1	0.553	0.0182	0.0130	0.0302	0.00870	0.00171
2.5	26.5	1	0.469	0.0143	0.0097	0.0134	0.00464	0.00118

Table 4.1.6

Chlorination of phenol with gaseous chlorine (solvent studies)

Reaction time : 3.5 hrs

S.No.	Solvent	Temp °C	Chemical composition, %		
			2,4-DCP	2,6-DCP	2,4,6-DCP
1.	Acetic acid	20	90.83	5.02	4.15
		45	89.26	6.53	4.20
		65	88.21	7.57	4.22
		85	87.5	10.05	4.44
2.	Acetic acid	20	90.4	6.45	3.42
	H_2O(50% v/v)	45	88.19	7.67	4.14
		65	87.90	7.98	4.17
		85	81.68	9.53	8.74
3.	CH_3NO_2	45	97.74	0.78	1.48
		65	97.13	2.86	-
		85	96.42	3.56	-
4.	Benzene	15	81.46	18.48	-
		25	80.53	19.46	-
		50	80.09	17.67	2.23
		65	75.24	18.32	6.40
5.	CCl_4	20	85.44	14.56	-
		40	84.57	13.33	2.10
		50	84.84	10.85	4.28
		65	78.41	10.74	10.87

Table : 4.1.7

Values of rate constants (K_1 to K_7) in various solvents at different temperatures

Temperature	K_1	K_2	K_3	K_4	K_5	K_6	k_7
Acetic acid							
85	1	0.653	0.191	0.0765	0.0098	0.0096	0.0084
65	1	0.626	0.164	0.0644	0.0090	0.0088	0.0065
45	1	0.602	0.119	0.0520	0.0075	0.0083	0.0060
20	1	0.500	0.110	0.0481	0.0067	0.0075	0.0055
Acetic acid water (50% v/v)							
85	1	0.1820	0.3483	0.1147	0.0503	0.00131	0.0252
65	1	0.1562	0.3060	0.0541	0.0301	0.00123	0.0228
45	1	0.1428	0.1489	0.0453	0.0309	0.00100	0.0243
20	1	0.1195	0.1047	6.0421	0.0259	0.00054	0.0236
Nitromethane ($_3NO_2$)							
85	1	0.450	0.0428	0.0866	0.0064	0.00480	0.00441
65	1	0.382	0.0256	0.0228	0.0052	0.00245	0.00097
45	1	0.289	0.0187	0.0156	0.0024	0.00063	0.00060
20	1	0.235	0.0045	0.0124	0.0019	0.00056	0.00045
Carbontetrachloride (CCl_4)							
65	1	0.926	0.2774	0.0454	0.0425	0.0202	0.0098
50	1	0.981	0.2000	0.0403	0.0224	0.0147	0.0031
40	1	0.984	0.0727	0.0381	0.0167	0.0064	0.0026
20	1	1.079	0.0443	0.0221	0.0075	0.0027	0.0024
Benzene							
65	1	1.121	0.1212	0.0538	0.0242	0.0045	0.00380
50	1	0.881	0.0882	0.0410	0.0068	0.0034	0.00097
25	1	0.602	0.0620	0.0289	0.0055	0.0032	0.00081
15	1	0.526	0.0588	0.0185	0.0041	0.0004	0.00064

Table : 4.1.8

Activation energies of chlorophenols in different solvents (Kcals/mole)

Solvent	Phenol -OCP	Phenol -PCP	OCP- 2,4-DCP	PCP- 2,4-DCP	OCP- 2,6-DCP	2,6-DCP 2,4,6-TCP	2,4-DCP 2,4,6-TCP
Acetic acid	1.823	1.209	1.769	0.960	2.284	1.843	1.720
Acetic acid -H_2O (50% v/v)	1.821	1.455	1.794	1.425	1.825	2.487	2.560
Nitromethnaee	3.462	1.03	2.923	0.325	5.309	8.23	1.888
CCl_4	0.845	0.920	2.006	1.313	2.043	4.250	3.002
Benzene	0.745	0.925	2.034	0.958	2.550	2.654	2.544

Table : 4.1.9

Effect of temperature-Rate constants and activation energies

Rate Constants	Temperture C°				
	140°C	120°C	85°C	65°C	E*(activation energy K cal/mole
K_1	1	1	1	1	3.05
K_2	0.714	0.564	0.550	0.544	13.15
K_3	0.0461	0.040	0.031	0.027	10.11
K_4	0.0713	0.055	0.045	0.035	3.87
K_5	0.0081	0.007	0.006	0.005	2.86
K_6	0.00072	0.00052	0.00038	0.0029	3.05
K_7	0.00051	0.00031	0.00029	0.00023	6.72

Table 4.2.2.1

Solvent-phenol molar ratio studies phenol 1 mole, temperature = 40^oC

Chlorination time = 4 hrs

Compound	Phenol - Nitromethane ratio			
	0.5 moles	1 mole	1.5 moles	2 moles
OCP	5.27	0.36	-	-
PhOH	-	-	-	-
2,6-DCP	4.37	6.17	2.86	1.77
2,4-DCP	75.30	92.36	92.34	98.20
2,4,6-TCP	-	1.00	4.78	Traces
PCP	15.04	-	-	-

Table 4.2.2.2

Chlorination phenol in CH_3NO_2

Reaction time = 3.5 hrs at different temperatures

Chlorophenol	Temperature °C		
	30	40	50
OCP	-	-	5.78
PhOH	-	-	-
2,6-DCP	2.45	1.77	4.30
2,4-DCP	97.5	98.22	72.69
2,4,6-TCP	-	-	-
PCP	-	-	17.28

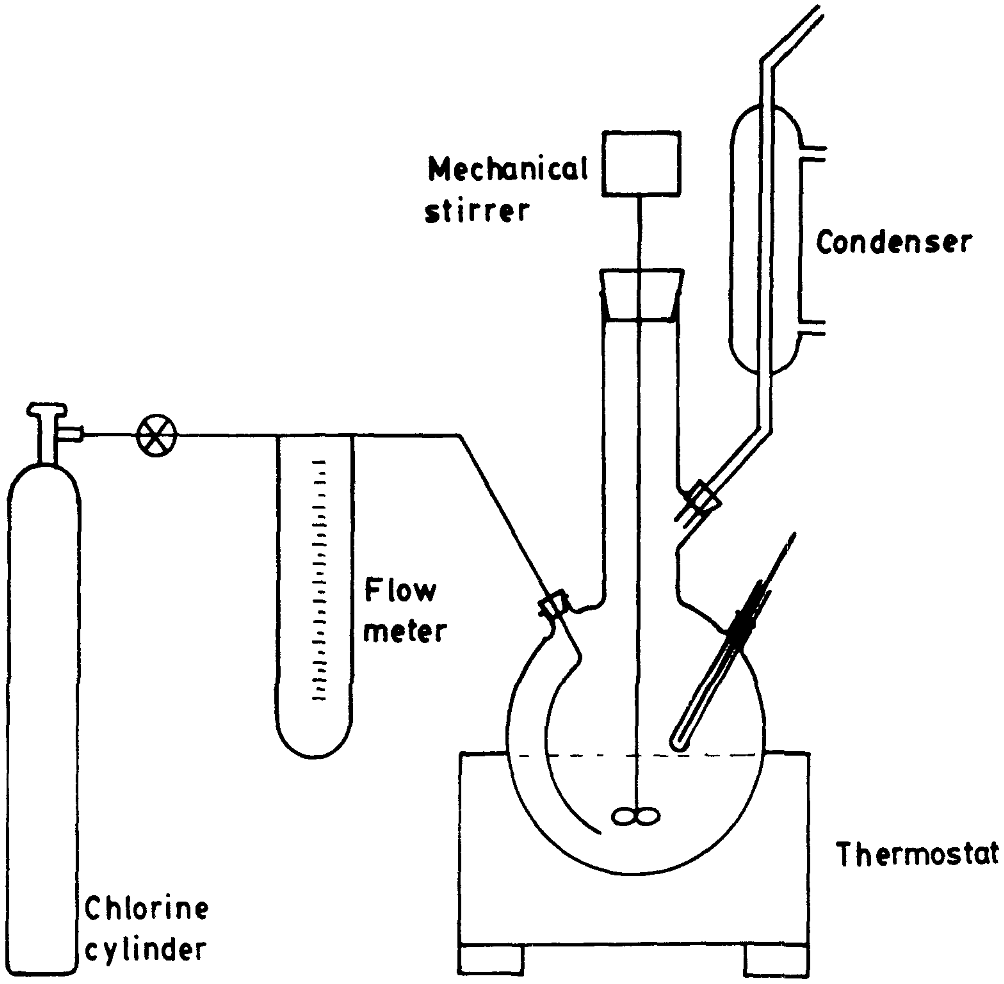


Fig. 4.1.1 Experimental setup used for the chlorination of phenol with chlorine.

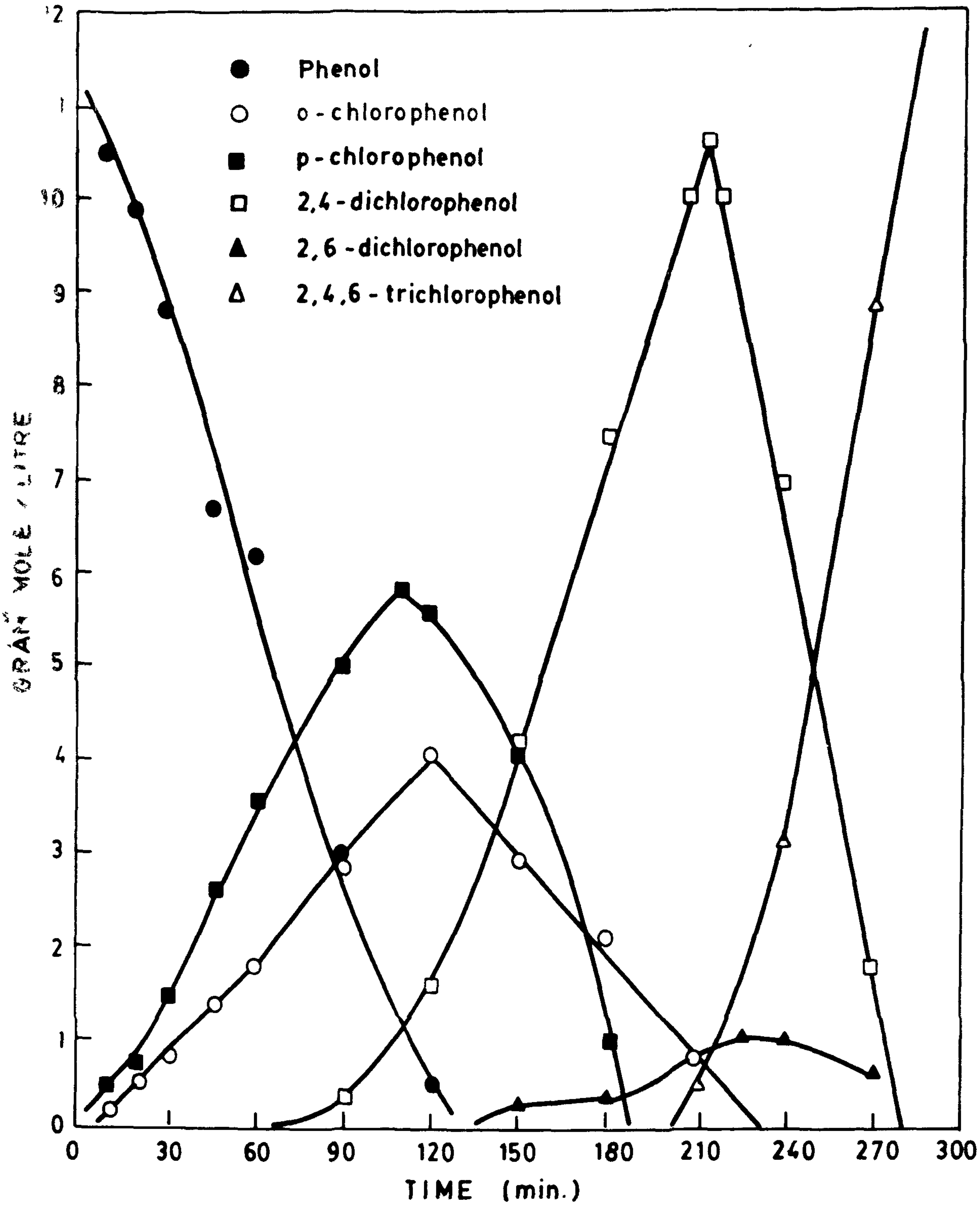


Fig. 4.1.2 Concentration vs time graph of reaction scheme - I

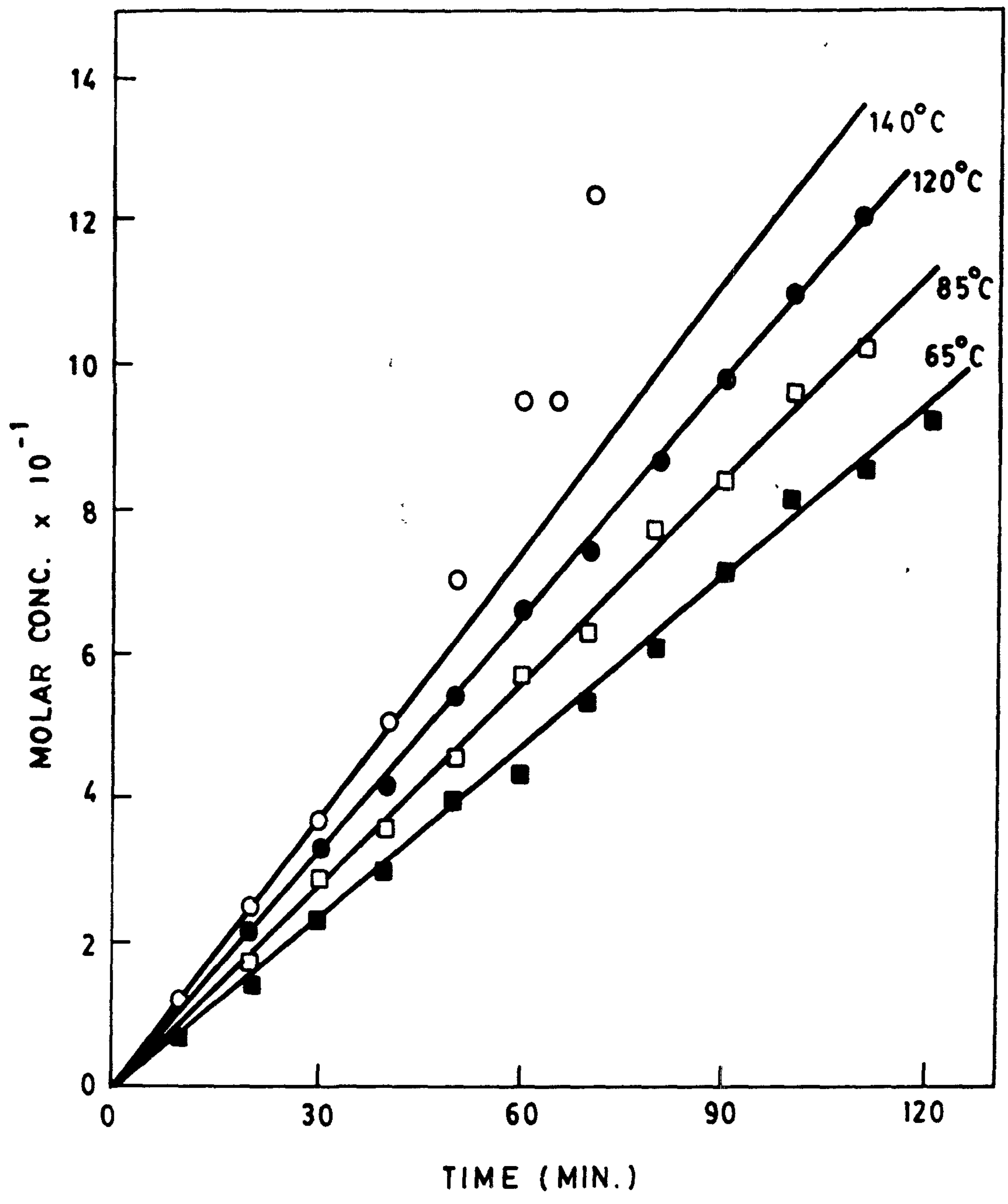


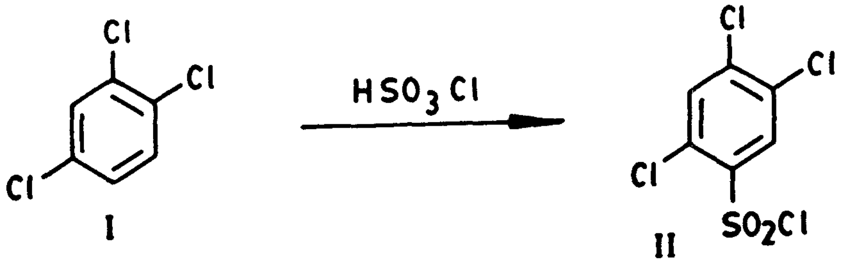
Fig. 4.1.3 Graph indicating of the reaction has been first order with respect to phenol

4.3 Process for the preparation of 2,4,5-trichlorophenol

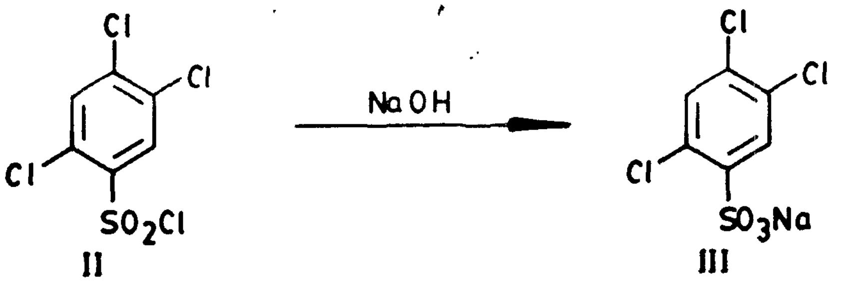
2,4,5-trichlorophenol (2,4,5-TCP) is mainly used in the manufacture of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) which is a well known non-selective weedicide. The conventional industrial route for the preparation of 2,4,5-TCP is the hydrolysis of 1,2,4,5-Tetrachlorobenzene. However, this route has been rejected on the ground that there is a possibility of accidental formation of 2,3,7,8-tetrachlorobenzoparadiaxin which is two million times toxic than 2,4,5-TCP. Hence, an alternative route has been proposed for the preparation of 2,4,5-Trichloropheno.l. The scheme for the production of 2,4,5-TCP by the proposed method involves the preparation of 2,5-Di-chlorophenol which in turn is converted to 2,4,5-TCP by controlled gaseous chlorination. (Scheme II).

Step I Sulfonation of 1,2,4-trichlorobenzene to 1,2,4-trichlorobenzene-5-sulfonyl chlorides

1,2,4-trichlorobenzene (0.75 to 1.5 gram moles) has been reacted with chlorosulfonic acid (1-gram moles) at 80^{o} -100^{o}C to yield 1,2,4-trichlorobenzene-5-sulfonyl chloride mp 61.5 ^{o}C.

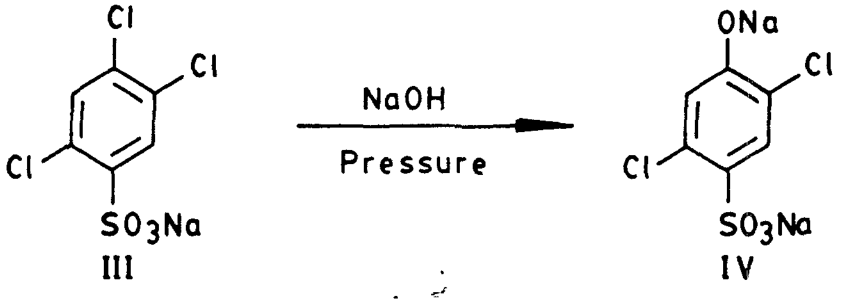


Step II : Preparation of sodium salt of 1,2,4-Trichlorobenzene-5-sulfonic acid



1,2,4-Trichlorobenzene-5-sulfonyyl chloride (3 moles) has been mixed with aqueous sodium hydroxide (3 moles) by slow addition of alkali in 1-1.5 hours and the contents are allowed to react for 3 hrs maintaning temperature at 95 - 98°C to get sodium salt of 1,2,4-Trichlorbenzene-5-sulfonic acid in almost qualitative yields. The temperature has been maintained by water bath. The product has been dried at 110°C for about 3 hours.

Step III : Hydrolysis of sodium salt of 1,2,4-Trichlorobenzene-5-sulfonic acid



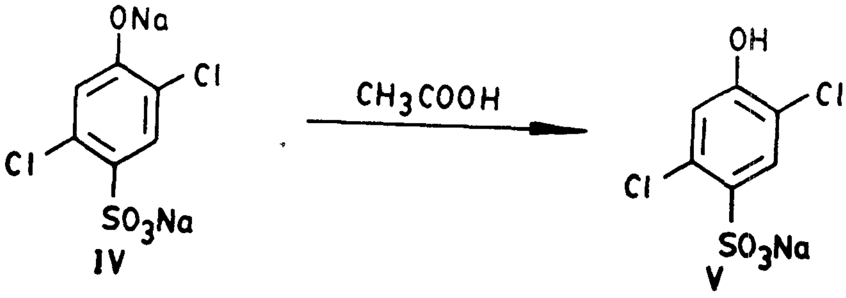
Sodium salt of 1,2,4-trichlorobenzene-5-sulfonic acid (1 mole) has been dissolved in 1.6 - 1.7 moles of NaOH taken in 550 ml of water and hydrolysis at 195.200 °C and 15 kg/cm^2 pressure to get sodium salt of 2,5-dichloro-phenol -4-sulfonic acid to optimize the conditions of hydrolysis the following parameters viz., Effect of pressure, temperature, NaOH and water content have been studied.

Effect of Pressure and temperature:

Experiments have been conducted varying both temperature (155-225°C) and pressure (6 kg/cm^2-22.5kg/cm^2) and the results obtained are given in table 4.3.1 It is seen from the table that a maximum yield of 2,5-DCP has been obtained at pressure 15 kg/cm^2 and temperature 195°C.

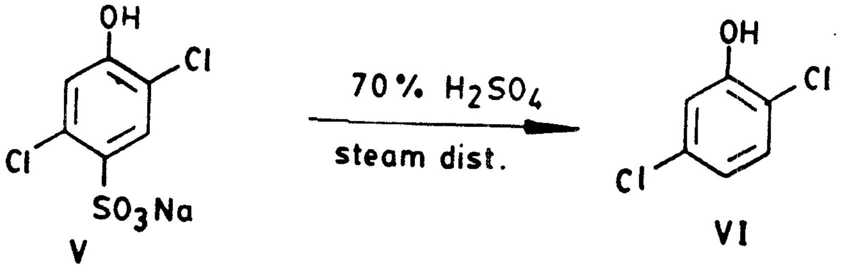
Effect of NaOH and water: Experiments have also been on conducted changing the sodium hydroxide content and water content maintaining optimum pressure (15 kg/cm^2) temperature (195°C) and the results obtained are given in tables 4.3.2 and 4.3.3. From these studies it is evident that use of 65 grams of sodium hydroxide has given the maximum yield of 2,5-DCP and water content has almost no effect on the hydrolysis product.

Step IV : Acdidification of sodium salt of 2,5-dichlorophenol-4-sulfonic acid



After completing the hydrolysis reaction (step III) the compound has been acidified with 80-90 ml of glecial acetic acid to get 2,5-dichlorophenol-4-sulfonic acid.

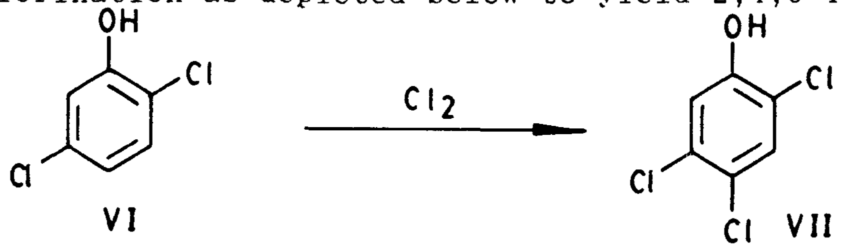
Step V : Desulfonation and recovery of 2,5-DCP by steam distillation



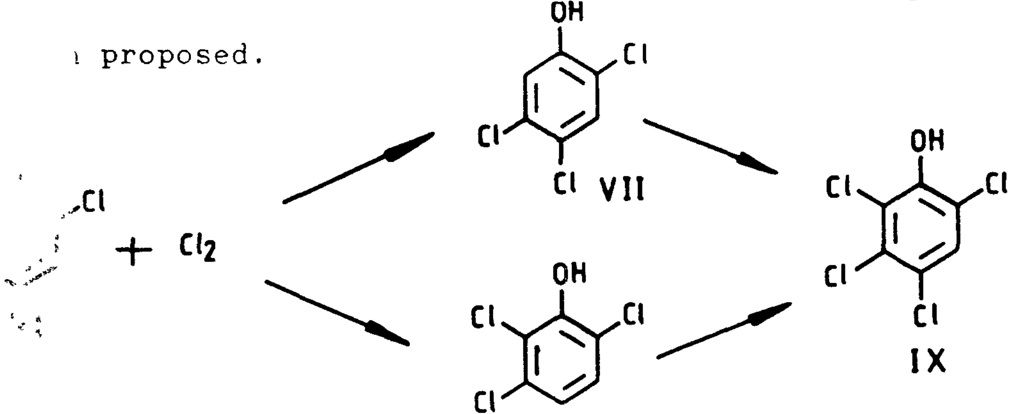
Removal of sulfonic group has been done by heating the 2,5-dichlorophenol-4-sulfonic acid with 1000 ml of sulfuric acid 70% for two hours and the product has been steam distilled to get 2,5-DCP mp 54°C (yield 88% purity 99%). The product obtained has been subjected to GLC to check its purity. It has been found that the purity of the product is comparable with authentic sample. The details of these results have been filed in a patent.

Synthesis of 2,4,5-trichlorophenol (2,4,5-TCP)

The 2,5-DCP so obtained is subjected to the controlled gaseous chlorination as depicted below to yield 2,4,5-TCP.



2,5-dichlorophenol (one grame mole) was dissolved in 1 to 3 gram moles of acetic acid and chlorine was introduced into the solution at 5 lit/hr flowrate at temperature 40-45°C and at atmospheric presure. The progress of their reaction was followed by drawing the samples periodically and subjecting them to GLC analysis. The GLC analysis showed ultaneous formation of two products whichwere fied as 2,5,6-trichlorophenol and 2,4,5- orophenol. Analysis of the samples with drawn at intervals has indicated that there is progressive e in the formation of these products with respect to orination time. Exhaustive chlorination leads to the conversion of these two products to 2,4,5,6- lorophenol. Formation of pentachlorophenol has not tected. Based on these results the following scheme proposed.



ation was stopped when the reaction mixture contained aximum percent of 2,4,5-trichlorophentol. At this stage a quantity of 2,5,6-trichlorophenol was also present. analysis of the reaction products is given in table

2,5,6-trichlorophenol is an undesired product whose mation should be minimized to improve the purity of ,5-TCP. In order to optimize the conditions of nation a series of experiments have been carried out n polar solvents (CH_3 COOH), CH_3 NO_2 and nitrobenzene) n a non-polar solvent (CCl_4) at different tures. The results of the representative experiments ven in Table 4.3.5.It can be seen from Table that the m yield of 2,4,5-TCP (ca., 90%) can be achieved in polar solvents such as nitromethane and nitrobenzene in the temparature range of 15-45°C. The product obtained was subjected to fractional distillation, 100% pure 2,4,5-TCP has been obtained. The process developed has been patented.

Table : 4.3.1

Effect of pressure and temparature on the conversion of 2,5-DCP

S. No.	Wt. of sod. salt	NaOH gr	Water ml	Pressure Kg/cm^{-2}	Temp ^oC	Yield %
1.	200	65	550	6	155	70
2.	200	65	550	12	185	77
3.	200	65	550	15	195	87
4.	200	65	550	15	195	88.7
5.	200	65	550	20	210	43.5
6.	200	65	550	22.5	225	42

Table : 4.3.2.

Effect of NAOH on the conversion of 2,5-Dichlorophenol

Sl. No.	$Cl_3\ C_6H_2\ SO_3Na$ gms	NaOH gms	$H_2\ O$ ml	Pressure kg/cm^2	Temperature ^oC	Yield %
1	200	60	550	15	195-200^{o}C	52
2	200	65	550	15	195-200^{o}C	88.7
3	200	70	550	15	195-200^{o}C	87

Table 4.3.3.

Effect of water content on the conversion of 2,5-Dichlorophenol

Sl. No.	Cl_3 C_6H_2 SO_3Na gms	NaOH gms	H_2 O ml	Time in hrs	Temperature °C	Pressure kg/cm^2	Yield %
1	200	65	550	3hrs	195.200	15	86.05
2	200	65	550	4hrs	195.200	15	88.79
3	200	65	600	4hrs	195.200	15	86.35
4	200	65	650	3hrs	195.200	15	86.35
5	200	65	650	4hrs	195.200	15	89.61

TABLE :4.3.4

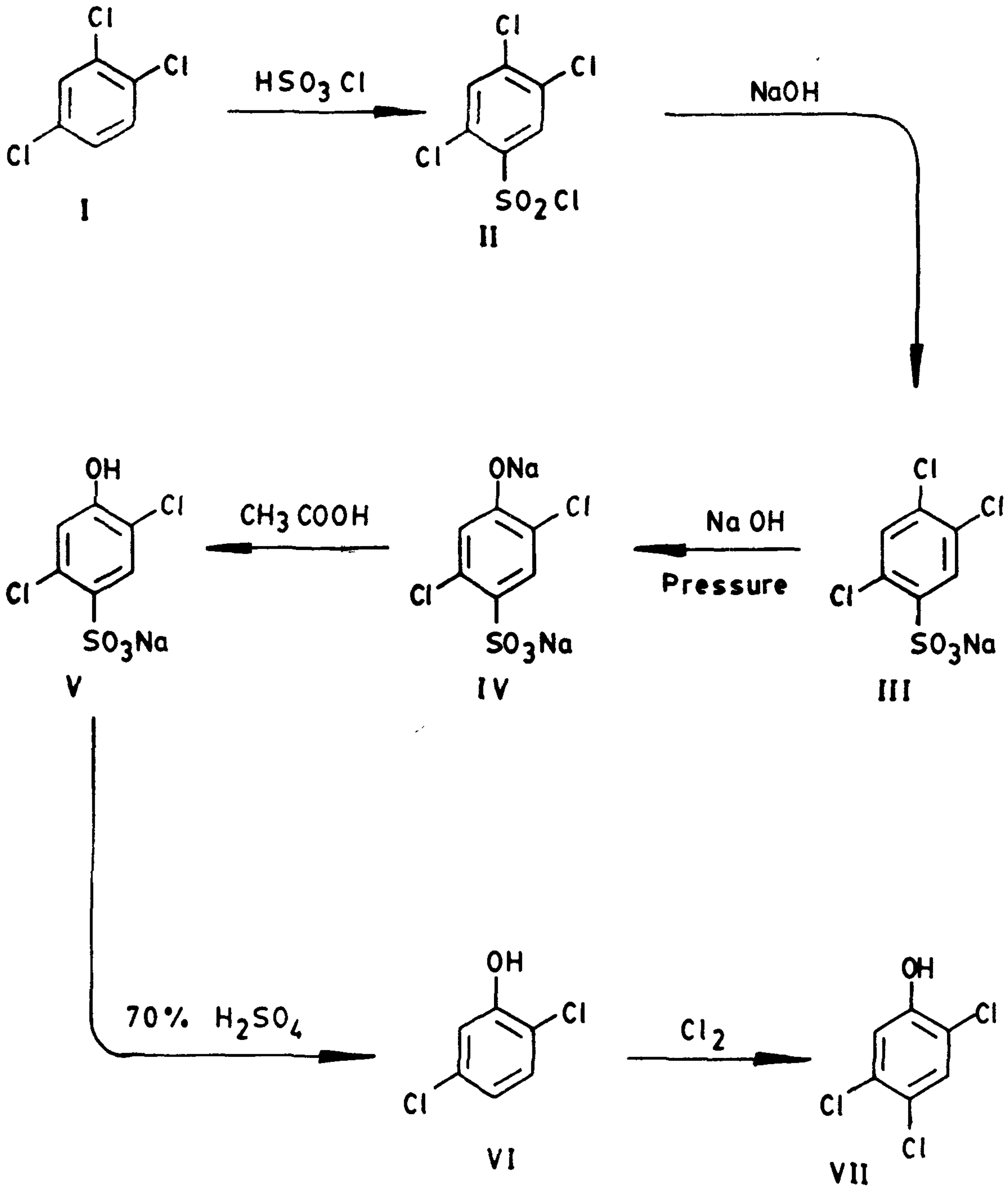
GLC Analysis of reaction mixture of chlorinated productsof 2,5-Dichlorophenol to get 2,4,5-Trichlorophenol

Compound	Time (hrs)							
	30	40	55	70	80	90	100	115
2,5-DCP	82.7	71.3	52.9	30.8	10.2	2.4	-	-
2,4,5-TCP	17.3	28.7	47.1	62.3	81.7	88.8	79.0	60.
2,5,6-TCP	-	-	-	7.9	8.1	8.8	12.5	17.
2,4,5,6-tetrachloro phenol	-	-	-	-	-	-	8.5	21.

Table : 4.3.5

Solvent studies on the conversion of 2,5,4-Trichlorophenol

Solvent	Temp °C	Percent conversion of Chlorophenols		
		2,5,6-TCP	2,4,5-TCP	2,4,5,6-Tetra
CCl_4	15	58.93	31.69	9.37
	25	51.68	48.32	-
	35	48.04	51.87	-
CH_3 COOH	15	12.0	87.8	-
	25	12.1	87.9	-
	35	10.8	88.8	-
CH_3 NO_2	15	8.8	91.2	-
	35	9.27	89.74	-
	45	10.9	88.6	-
C_6 H_5 NO_2	15	8.45	91.55	-
	25	8.10	91.90	-
	35	11.21	88.51	-
	45	12.12	87.88	-


I
HSO_3Cl
II
NaOH
III
Na OH
Pressure
IV
CH_3COOH
V
70% H_2SO_4
VI
Cl_2
VII

SCHEME-II

4.4 Chlorination of phenol using cuprichloride as a chloral agent

There are many chlorinating agents reported in the literature. Among them sulphuryl chloride (SO_2Cl_2) and cupric chloride ($CuCl_2$) are known as p-chlorinating agents. Application in large scale manufacture of chloro products is not feasible on account of the high cost of sulphuryl chloride. On the other hand $CuCl_2$ is used, along with air or oxygen for the chlorination and the process is known as oxychlorination. Chlorination of phenol via oxychlorination route using $CuCl_2$, air and hydrochloric acid has been found to yield a large quantities of PCP.

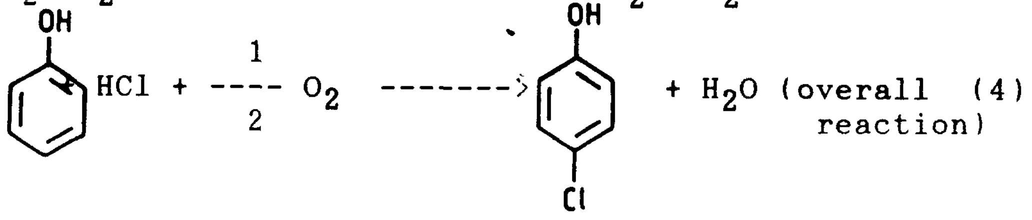
The reaction of phenol with cupric chloride results in mixture of chlorophenols in which para/ortho ratio varies from 6:1 to 12:1 indicating a marked presence for the para substituted product.

In this method oxygen and hydrogen chloride are employed for regeneration of the cupric chloride. The overall process is represented as follows :

$$\text{RH (phenol)} + 2CuCl_2 \text{------>} 2CuCl + RCl + HCl \qquad (1)$$

$$2CuCl + \frac{1}{2} O_2 \text{------>} Cu_2\,OCl_2 \qquad (2)$$

$$Cu_2OCl_2 + 2\,HCl \text{------>} 2CuCl_2 + H_2O \qquad (3)$$



(4)

It could be seen from equation (2) and (3) that oxygen and hydrogen chloride are used for the regeneration of cupric chloride.

Kinetics of oxychlorination of phenol

Several studies on the oxychlorination of phenol have been reported in literature, but very little is known about the kinetics and mechanism of the reaction.

Crocker et al[6] carried out extensive study on the chlorination of phenols with cupric chloride and studied the effect of solvent, effect of added metal salts and also the effect of hydrochloric acid concentration on the para/ortho ratio of the product. In the present investigation, experiments have been designed to arrive at a kinetic model and to establish a reaction mechanism for the chlorination of phenol with cupric chloride.

Materials used

Phenol = (BDH grade) reagent

Cupric chloride = (BDH grade) reagent

Hydrogen chloride gas generated by addition of hydrochloric acid to concentrated H_2SO_4.

Oxygen gas compressed oxygen gas of 99.7 purity from cylinders.

Experimental set up

Details of experimental set up are shown in Fig. 4.4.1. The reaction vessel is a round bottomed four necked flask of one litre (1). The glass reactor has been fitted with a stirrer (2) and has been driven by means of an induction motor connected to an auto transfer thermostate regulator to regulate its speed. Oxygen and HCl gas have been introduced into the reactor through two separate glass bubblers (3,4) whose exit have been immersed into the content of vessel for facilitating continuous bubbling of these gases. A condenser (5) has been attached to the mercury seal for the condensation of the reactants which are likely to escape along with unreacted gases. The glass reactor has been heated electrically by an isomantle controlled by the regulator.

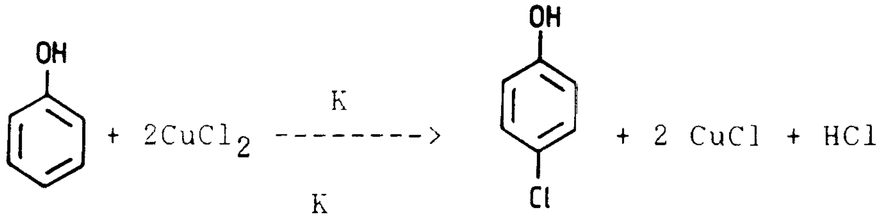
Analytical methods

The samples collected during the chlorination phenol with cupric chloride have been analysed on carbowax-30M column (details of the method are described elsewhere in thesis). Table 4.4.1 gives results of GLC analysis of the reaction mixtures and Fig. 4.4.2 gives the chromatogram.

Order of the reaction

To explain the kinetics of non-elementary reactions it is assumed that a sequence of elementary reactions are actually occuring but one finds it diffult to estimate the concentration of intermediate formed if they are present only in very minute quantities at a given time. In the present investigation consideration has been given to the initial concentration of the reactants and of the final products which appears to be a single reaction. The elementary reactions have not been considered in compiling the rate equation.

There are only two reactants viz., phenol (A) and cupric chloride (B) the latter is used as the chlorinating agent and the reaction is assumed to be first order with respect to A and B if considered as elementary reactions and to be secondary order if overall reaction is considered. The reaction can be represented by the following equation :



$$A + 2B \xrightarrow{K} \text{product} \qquad (5)$$

Rate of disappearance of A

$$-r_A = -\frac{dC_A}{dt} = K\,C_A\,C_B \text{ (pseudo-order reaction)}$$

$$C_Ao\,\frac{dX_A}{dt} = K\,C_{Ao}\,(1 - X_A)\,(C_{Bo} - C_{Ao}\,2\,X_A)$$

$$C_Ao\,\frac{dX_A}{dt} = K\,C_{Ao}^2\,(1 - X_A)\,(M - 2X_A)$$

where $M = \frac{C_{Bo}}{C_{Ao}} = 1$

$$C_{A^o} \frac{dX_A}{dt} = KC_{Ao}{}^2 (1 = X_A) (1 - 2X_A)$$

$$\frac{d\ X_A}{dt} = K_{CAo} (1 - X_A) (1 - 2X_A) \qquad (6)$$

upon integration equation (6) reduces to $\ln \frac{1-X_A}{1-2X_A} = C_{Ao}\ kt$

Thus a plot of $\ln \frac{1-X_A}{1-2X_A}$ vs t shuold be a straightline which is the test for the order reaction.

Experiments have been conducted at 70°C, 80°C, 90°C and 100°C and the results obtained are given in Table 4.4.2. Using the data, plots have been drawn between $\ln (\frac{1-X_A}{1-2X_A})$ vs t. The plots have been found to be curved rather than straight lines which is contradictory to the assumption one. For knowing the exact order of the reaction it has been assumed to be of the form 2A ----> P, when P denotes the product and 2A comprises of A + B. the mathematical treatment of the equation is given as below.

$$-r_A = \frac{-dC_A}{dt} = KC^2{}_A$$

$$+C_{Ao} \frac{dX_A}{dt} = K\ C_{Ao}{}^2\ (1 - X_A)^2)$$

$$\frac{dX_A}{dt} = K\ C_{Ao}\ (1 - X_A)^2$$

$$\frac{dX}{(1-X_A)^2} = K\, C_{A}o\, dt$$

upon integration

$$\frac{1}{1 - X_A} = K\, C_{A}o \quad t + C$$

$$\frac{1}{1 - X_A} = K\, C_{A}o \quad t + 1$$

or $$\frac{X_A}{1 - X_A} = K\, C_{A}o\ t$$

Using the data recorded in Table 4.4.3 plots have been drawn between $X_A/1-X_A$ vs t, which have provided straight line (Fig. 4.4.3). From the slope of these plots rate constant is determined (Table 4.4.4).

With a view to optimise the condition of chlorination for getting the maximum yield of PCP the following experimental parameters have been studied.

Activation energy

The K values determined at different temperature 70°C, 80°C, 90°C and 100°C) are presented in Table 4.4.4. Fig. 4.4.4 gives the Arrhenius plot i.e. ln k vs 1/T having slope (E/R). From the plot the activation energy has been calculated using the slopes of the plots (Fig. 4.4.5) and is found to be 2.88 K Cal/g mole. The low value of activation energy indicates that the reaction is predominantly a temperature sensitive one.

ratio of phenol to cupric chloride

xperiments have been conducted using 1 mole, 1.5 moles moles of cupric chloride anhydrous for each mole of l. It is found that with the increase in cupric ide content in the reaction mixture the content of 2,4- also increased, thereby reducing the PCP content in lorinated mixture. The amount of PCP in the reaction e is also found to decrease when cupric chloride is han one mole for every mole of phenol. Therefore, um ratio of phenol to cupric chloride has been fixed as

of oxygen on the rate of chlorination

xperiments have been conducted by varying the ratio of keeping the other conditions constant to study the of oxygen on these rates. The results of the most sentative experiments are shown in Table 4.4.5. It has been found that with the increased rates of oxygen the oxy-ination reaction has been found to be proceeding at a er rate resulting in a maximum yield of 53% of PCP. Higher rates of oxygen resulted in the formation of olymerised product.

ct of hydrogen chloride gas rate on the conversion of

Experiments have been conducted by increasing HCl gas from 3.8 N litres to 12.5 N litres maintaining the other parameters constant and the results obtained are recorded in Table 4.4.6. It can be seen from the results that the maximum yield of PCP is obtained at 6.0 N litres of hydrogen chloride gas.

Effect of temperature on the conversion of PCP

Experiments have been carried out by varying the temperatures from 50°-150°C. The maximum conversion of PCP was obtained at 85°C. The results of most representative experiments are tabulated in Table 4.4.7. From the table it can be seen that the yield of PCP is found to decrease with increase of temperature.

Effect of pre-heated oxygen on the conversions

The solubility of oxygen in water is a function of temperature i.e. the solubility of oxygen increases with the increase of temperature. Experiments have been conducted by passing oxygen at different pre-heated temperatures and the results are recorded in Table 4.4.8. It is obvious from 4.4.8 that the maximum conversion of 49% of PCP is achieved when pre-heated oxygen (44.54) is passed for four hours into the reaction mixture. It is evident from the Table 4.4.8 that conversion to PCP is Ca., 22% when no pre-heated oxygen is used.

Effect of stirrer speed

The influence of stirrer speed on the conversion of phenol to PCP has been studied considering the fact that the reactants are in homogeneous phase and are depending upon the mass transfer.

Experiments have been conducted at varying speeds of the stirrer from 1000 rpm to 3000 rpm with an internal of 500 rpm. The results obtained are recorded in Table 4.4.9. It is noticed that increase of stirrer speed increased the percent conversion of phenol to PCP from 29% to 50%.

Effect of normality of hydrochloric acid

The effect of normality of hydrochloric acid on the conversion of phenol to PCP has also been studied. The results of the experiments studied at 3N and 5N of hydrochloric acid have been recorded in Table 4.4.10. It can be seen from table that better conversion has been achieved with 5N hydrochloric acid.

Effect of temperature on reaction time

Experiments have been conducted at different temperatures maintaining the other conditions constant, to study the effect of temperature on the conversion of phenol to PCP as a function of time. The results of experiments conducted in the range of 70°-100°C are shown in Fig. 4.4.3. From the graph it is clear that the percent conversion of phenol to PCP is directly proportional to the temperature.

After establishing the opimum conditions experiments have been conducted using a molar ratio of phenol to cupric chloride 1:1, hydrogen chloride gas rate of 18.1 M litres/hr and oxygen rate of 105.8 N litres/hrs at 80° with 5 N hydrochloric acid the yield of PCP at the end of four hours has been found to be 53%. Based on the data generated fruther work was carried out on a bench scale maintaining exactly same conditions using the column reactor.

Table 4.4.1

GLC Analysis of the Reaction Mixture

Conditions of chlorination : Time of Chlorination = 8 hrs

Molar ratio of phenol to $CuCl_2$ = 1:1,

Reaction temperature $80^\circ C$, HCl 5N = 900 ml

S.No.	Air rate NL/hr	HCl g rate NL/hr	G.L.C. Analysis			Remarks
			Phenol	p.c.p.	o.c.p.	
1.	17.0	6.1	92.20	7.18	0.16	
2.	34.2	6.1	91.26	7.35	0.38	
3.	102.4	6.1	86.21	12.76	1.02	
4.	153.6	6.1	75.09	23.71	1.19	
5.	198.6	6.1	74.61	24.20	1.17	
6.	119.0	18.1	80.90	19.10	Nil	
7.	198.0	18.1	73.89	26.11	Nil	
8.	238.1	18.1	75.38	24.62	Nil	
9.	277.4	18.1	76.42	23.58	Nil	
10.	317.5	18.1	76.27	23.73	Nil	

Table 4.4.2

Concentration of P.C.P. (moles) with respect to time

Time hrs	70^{o} Temperature				80^{o} Temperature				90^{o} C Temperature				100^{o} C Temperature			
	% P.C.P.	$1-X_A$	$1-2X_A$	$\frac{1-X_A}{1-2X_A}$	% P.C.P.	$1-X_A$	$1-2X_A$	$\frac{1-X_A}{1-2X_A}$	% P.C.P.	$1-X_A$	$1-2X_A$	$\frac{1-X_A}{1-2X_A}$	% P.C.P.	$1-X_A$	$1-2X_A$	$\frac{1-X_A}{1-2X_A}$
1.	0.5	0.9934	0.9868	1.0068	4	0.9970	0.9941	1.0056	6	0.9562	0.9124	1.048	4	0.9717	0.9415	1.03
2.	2.3	0.9368	0.9737	1.0134	8	0.9932	0.9865	1.0088	10	0.9197	0.8394	1.095	5	0.9488	0.8976	1.05
3.	3.6	0.9799	0.9598	1.0209	12.5	0.9876	0.9767	1.0111	16	0.8832	0.7664	1.152	12.5	0.9086	0.8172	1.11
4.	4.0	0.9723	0.9446	1.0293	16.5	0.9793	0.9593	1.0200	19	0.8504	0.7008	1.213	22.0	0.8611	0.722	1.19
5.	4.30	0.9635	0.9270	1.0393	18	0.9711	0.9421	1.0307	24	0.8232	0.6461	1.274	25.0	0.7733	0.6345	1.28
6.	6.0	0.9533	0.9066	1.0515	23	0.9615	0.9230	1.0417	28	0.7956	0.5912	1.348	26.5	0.7734	0.5468	1.41
7.	8.0	0.9416	0.8832	1.0672	25	0.940	0.800	1.1750	31	0.7750	0.5512	1.407	35.0	0.7369	0.4738	1.55
8.	10.5	0.9160	0.8320	1.1009	26	0.935	0.770	1.2143	33	0.7610	0.5270	1.457	40	0.7150	0.4300	1.66

Table 4.4.3

Data on chemical kinetics for the preparation of para-chlorophenol

Time	70° Temperature				80° Temperature				90° C Temperature				100° C Temperature			
hrs	% P.C.P.	$1 - X_A$	$1-2X_A$	$\frac{1-X_A}{1-X_A} \times 10^{-2}$	% P.C.P.	$1-X_A$	$1-2X_A$	$\frac{1-X_A}{1-X_A} \times 10^{-2}$	% P.C.P.	$1-X_A$	$1-2X_A$	$\frac{1-X_A}{1-X_A} \times 10^{-2}$	% P.C.P.	$1-X_A$	$1-2X_A$	$\frac{1-X_A}{1-X_A} \times 10^{-2}$
1.	0.9	0.0067	0.9934	0.65	4.5	0.351	0.9649	3.64	6.0	0.438	0.9562	4.6	5.0	0.3665	0.9634	3.8
2.	1.8	0.1315	0.9868	1.33	9.2	0.0672	0.9328	7.20	11.0	0.803	0.9197	8.73	12.4	0.9064	0.0936	9.96
3.	2.75	0.0201	0.9799	2.05	13.2	0.0965	0.9053	10.7	16.0	0.1168	0.8832	13.21	18.05	0.1319	0.8680	15.18
4.	3.8	0.0277	0.9723	2.8	16.6	0.1213	0.8786	13.8	20.5	0.1496	0.8504	17.59	23.4	0.1710	0.8289	20.6
5.	5.0	0.365	0.9635	3.8	19.8	0.1447	0.8553	16.92	24.25	0.1770	0.8232	21.5	25.75	0.1882	0.8118	23.18
6.	6.4	0.0467	0.9533	4.9	22.6	0.1652	0.8348	19.79	28.0	0.2044	0.7956	25.69	31.0	0.2266	0.7734	29.29
7.	8.0	0.0584	0.9416	6.2	25.2	0.1842	0.8158	22.58	30.75	0.2244	0.7756	28.92	36.0	0.2631	0.7368	35.11
8.	11.5	0.840	0.9160	9.15	27.2	0.1988	0.8012	24.81	32.75	0.2390	0.7610	31.40	39.0	0.2851	0.7149	39.87

X_A = moles of p.c.p formed/moles of phenol fed

Table 4.4.4

K values determined at different temperatures

S.No.	Temperature	$1/T \times 10^{-3}$	$K \times 10^{-2}$
1.	70^{o}	2.91	0.459
2.	80^{o}	2.83	1.528
3.	90^{o}	2.75	1.929
4.	100^{o}	2.68	2.237

Table 4.4.5

Effect of oxygen on the rate of chlorination

Conditions of chlorination :

Time of chlorination = 4 hrs

Molar ratio of phenol to $CuCl_2$ = 1:1

Reaction temperature = 85°C

HCl rate = 6.1 NL/hrs

HCl (5 N) = 900 ml

S.No.	Oxygen flowrate L/hr	GLC analysis		
		% Phenol	% PCP	% OCP
1.	8	72.76	25.65	1.56
2.	17.50	57.02	40.12	2.86
3.	30	43.74	52.82	3.44
4.	40	43.66	52.88	3.46

Table 4.4.6

Effect of hydrogen chloride gas on the rate of chlorination

Conditions of chlorination :

Time of chlorination = 4 hrs

Molar ratio phenol to $CuCl_2$ = 1:1

Reaction temperature = 85°C

Oxygen rate = 25.6 NL/hr

HCl (5 N) = 900 ml

S.No.	HCl (g) rate L/hr	GLC analysis		
		% Phenol	% PCP	% OCP
1.	3.8	49.0	48.2	2.8
2.	6.1	38.0	59.0	3.0
3.	9.1	52.5	46.8	0.7
4.	12.5	77.0	22.0	1.0

Table 4.4.7

Effect of reaction temperature

Conditions of chlorination :

Time of chlorination = 4 hrs

Molar ratio of phenol to $CuCl_2$ = 1:1

Reaction temperature = 85°C

Oxygen rate = 25.6 L/hr

HCl (g) rate = 18.1 L/hr

HCL (5N) = 900 ml

S.No.	Reaction temperature °C	GLC analysis		
		% Phenol	% PCP	% OCP
1.	50	88.04	11.96	Nil
2.	70	74.77	23.86	1.37
3.	75	68.50	30.38	1.12
4.	85	49.58	47.63	2.79
5.	95	55.75	44.43	1.82
6.	100	67.72	30.46	1.82
7.	105	68.93	28.39	2.65

Table 4.4.8

Effect of pre-heat temperature of oxygen on the rate of chlorination

Conditions of chlorination :

Time of chlorination : 4 hrs

Molar ratio of phenol to cubic chloride = 1:1

Reaction temperature = 85°C

Oxygen flow rate = 25.6 NL/hr

HCl (g) rate = 18.1 NL/hr

HCl (5 N) = 900 ml

S.No.	External temperature of coil °C	Tempeature of gas °C	GLC analysis		
			Phenol	PCP	OCP
1.	60	40	63.12	35.02	1.86
2.	80	44.5	47.39	49.64	2.97
3.	90	49.0	55.76	42.12	2.12
4.	96	52	55.25	42.5	2.60
5.	120	58	61.55	37.00	1.95
6.	160	62	61.01	37.16	1.83

Table 4.4.9

Effect of stirrer speed

Conditions of chlorination :

Time of chlorination = 4 hrs

Molar ratio of phenol to $CuCl_2$ = 1:1

Reaction temperature = 85^oC

Oxygen rate = 25.6 NL/hr

HCl (gas) rate = 18.1 NL/hr

HCl (5N) = 900 ml

S.No.	Stirrer speed rpm	GLC Analysis			
		Phenol	PCP	OCP	2,4-DCP
1.	1000	70.82	27.68	1.58	Nil
2.	1500	68.71	28.77	2.52	Nil
3.	2000	59.20	38.62	2.18	Nil
4.	2500	53.70	44.98	1.82	Nil
5.	3000	45.81	50.18	3.57	0.49

Table 4.4.10

Effect of normality of hydrochloric acid

Conditions of chlorination :

Time of chlorination = 4 hrs

Molar ratio of phenol to $CuCl_2$ = 1:1

Reaction temperature = $85^{o}C$

Oxygen rate = 25.6 NL/hr

HCl (gas) rate = 18.1 NL/hr

Hydrochloric acid = 900 ml

S.No.	Normality of HCl	GLC analysis		
		% Phenol	% PCP	% OCP
1.	3M	56.3	41.0	2.70
2.	5M	47.4	50.0	2.60

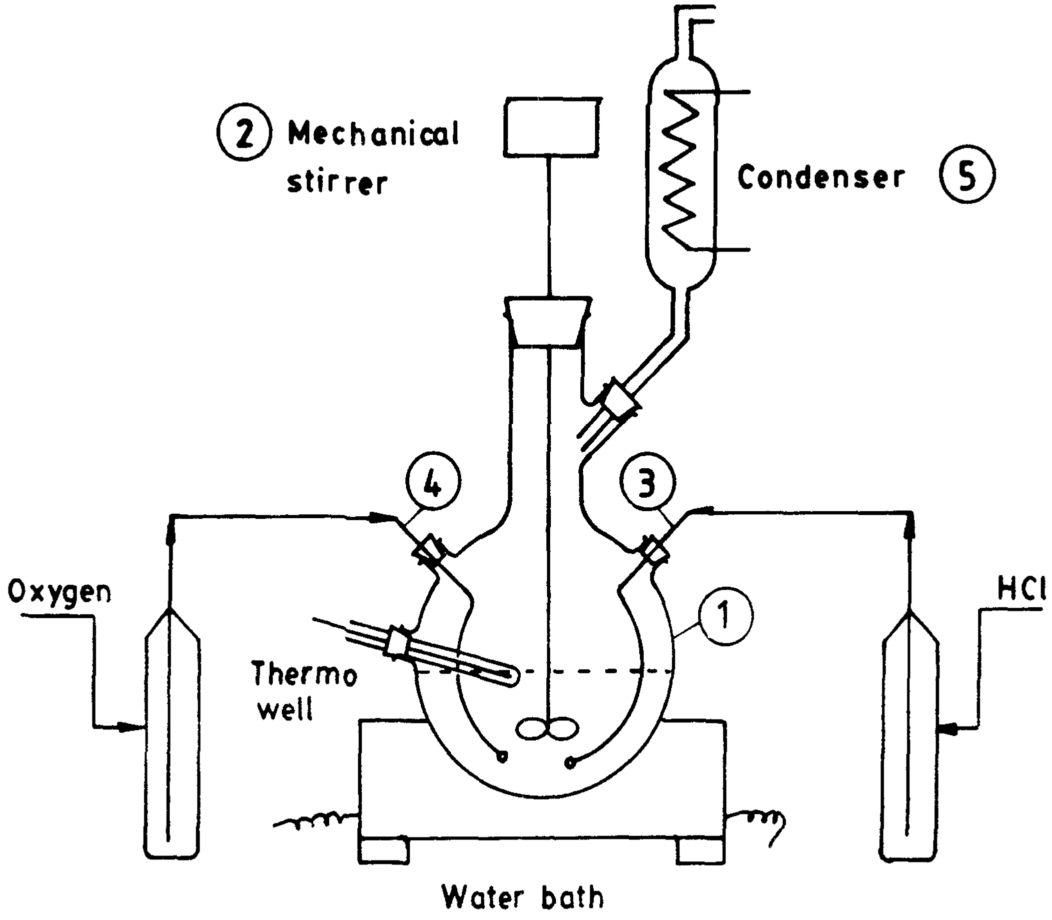


Fig. 4.4.1 Batch type chlorinator used for preparation of P C P.

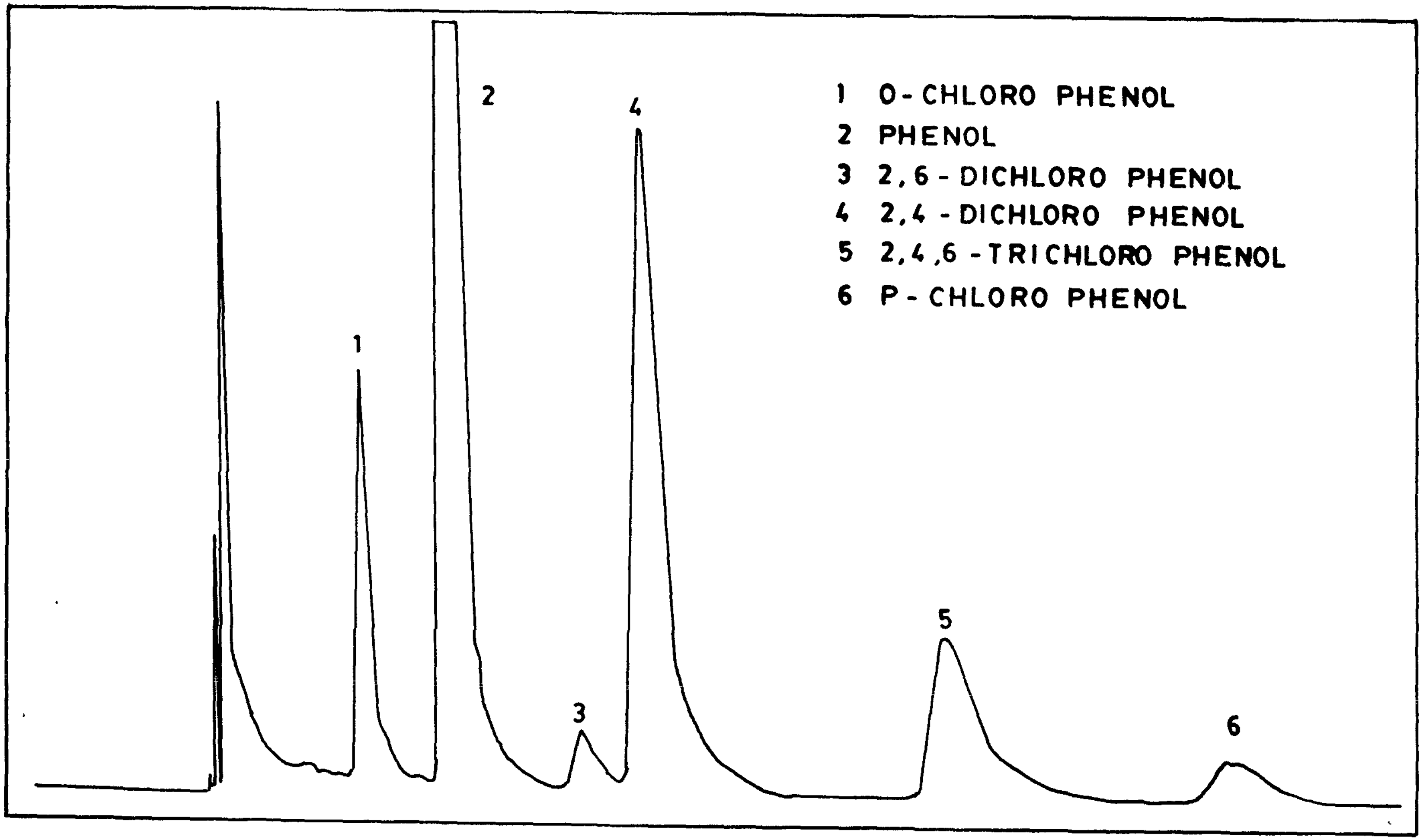


Fig. 4.4.2 GLC of the chlorinated mixture of phenol (column : carbowax - 25 %, length - 4 ft., temp. - 200 °C)

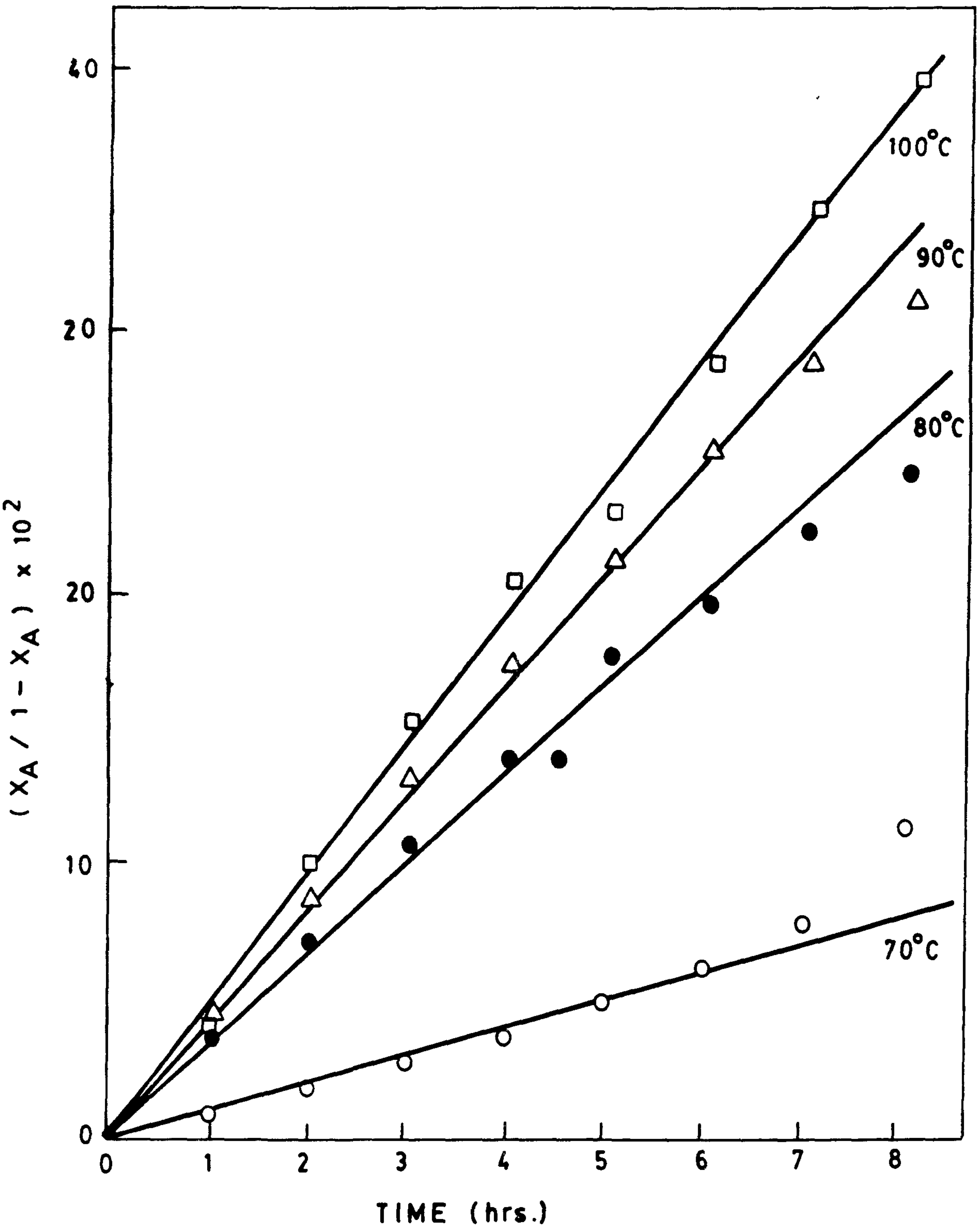


Fig. 4.4.3. Graph indicating second order plots

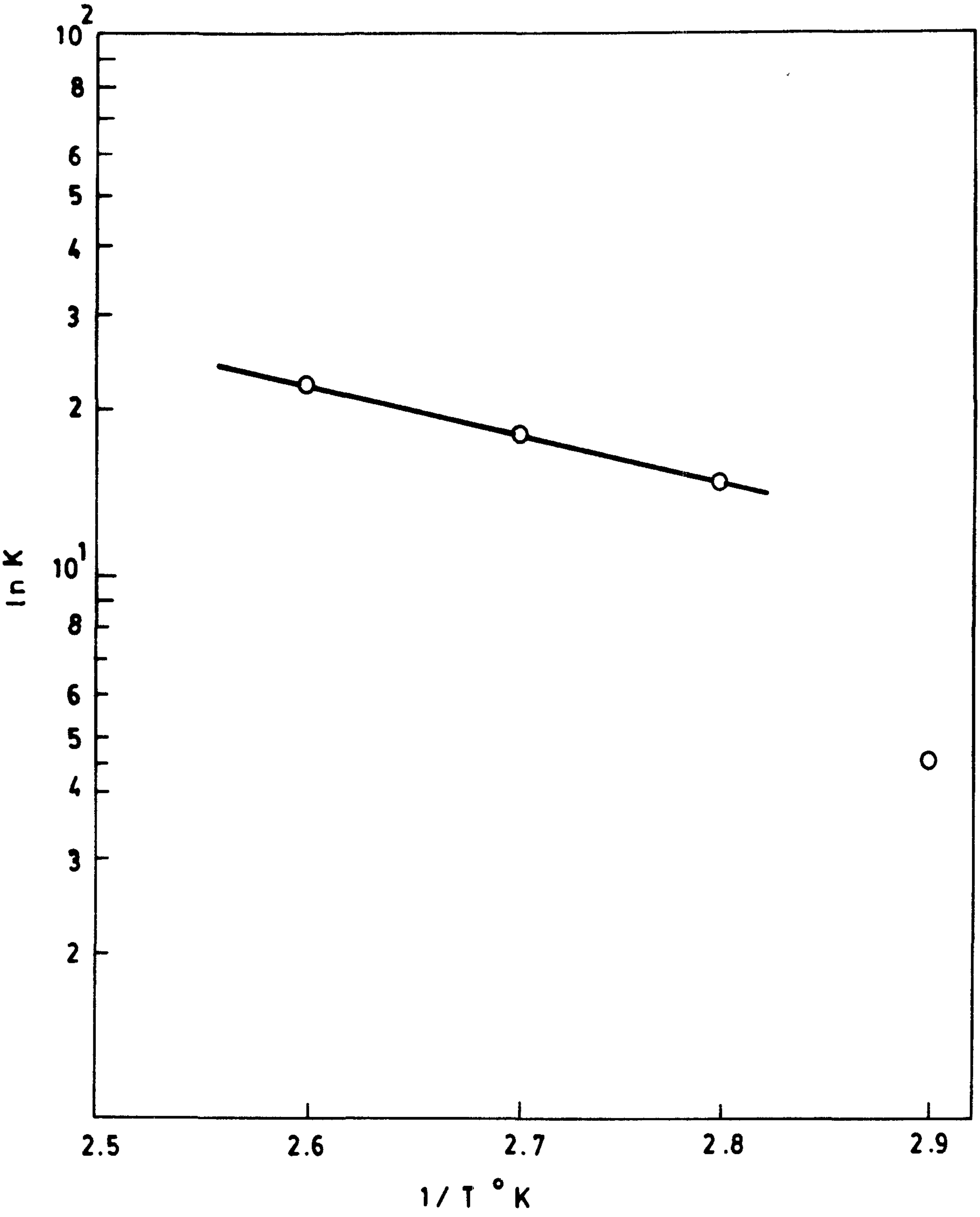


Fig. 4.4.4 Graph indicating arrhenius plot

4.5 Chlorination of p-cresol with tert-Butylhypochlorite (TBH)

The action of THB on phenol, cresols and xylenols has been extensively studied[7-9] , with one apparent exception (thymol), THB introduces the chlorine atom at ortho to the hydroxyl group of monohydric phenols even when on steric considerations, other protons might be expected to be attacked. Thus phenol gives o-chlorophenol which yield 2,6-dichlorophenol and m-cresol gives 2-chloro-m-cresol when reacted with one mole of TBH. The preference for ortho-chlorination is reminiscent of the attack phenol by peroxide this may point to a free radical mechanisem in the chlorination of phenol by, TBH. Harvey and norman[9] have recently shown that in acetic solution the attacking entity is the highly reactive chloronium ion (Cl^+) whereas under non acidic conditions it is molecular chlorine into which TBH slowly decomposes.

Further phenols and chlorophenols usually undergo phenol-dienone rearrangement when acted upon by reagents of electrophilic or radical type[10-12]. The conversion of phenol into cyclohexadienone structures has been termed as phenol-dienone rearrangement[13-14]. The formation of halo cyclohexadienones with a variety of chlorinating agents[15-18] is well documented. Studies relativing to unusual pathways in the chlorination of parasubstituted phenols become increasingly important[19] specially when such intermediates are recognised at an early stage of the reaction, as they undergo rearrangements leading to the formation of unexpected products.The formation of cyclohexadienone type of products has been confirmed by modern spectroscopic techniques (UV, IR NMR and Mass).

Considering the fact TBH is a orthochlorinating agent and also produces cyclohexadienone type of compounds systematic studies have been taken up for the chlorination of p-cresol using this reagents, in order to understand the mechanisms involved.

Experimental

Materials

P-cresol : Fluka reagent

TBH : Freshly prepared as per the proceured described in the literature and freshly distilled has been used. Other chemicals are also of good quality. The details of the experimental set up has been presented in fig (4.5.1).

Analytical methods

A HPLC method has been developed for the separation and qualification of samples collected during the chlorination of p-cresol with TBH. (Details of the method have already been discussed).

Chlorination of p-cresol with one mole of TBH

P-cresol (1 mole) in acetic acid (99%, 50 ml) has been cooled to 0-2^{o}C in a four necked flask with a constant stirring. Freshly distilled TBH (1 mole) has been added to it gradually over a period of 15 minutes. The contents have been allowed to react for four hours. After the reaction is over, the contents have been poured over ice and subsequently extracted with ether. The etherial layer is separated, washed with water and sodium carbonate and finally dried with anhydrous sodium sulphate . The reaction product so obtained has been subjected to HPLC analysis. Fig. 4.5.2 is the HPLC chromatogram. About 13 compounds have been obtained, among them four compounds have been present in larger proportions. According to the normal rules of orientation only two chloro products viz., 6-chloro-p-cresol and 2,6-dichloro-p-cresol are expected. The presence of so many compounds confirms that other than chlorination, some other simulataneous reactions are also taking place. TLC analysis confirms the presence of phenolic compounds in the reaction mixture. Further working up of the mixture has not been done.

Chlorination of para cresol with two mole of TBH.

Para cresol (1 mole) has been reacted with (2 moles) of TBH keeping other conditions constant as described above. The reaction product has been subjected to HPLC analysis fig 4.5.3. It is seen from the chromatogram that number of products have been available in the reaction mixtures. The presence of phenol in the reaction mixture has also been confirmed by the chemical method. Further work on isolation and identification has not been carried out.

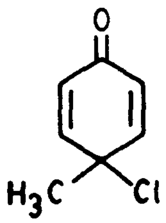
Chlorination of para cresol with three moles of TBH

P-cresol (1 mole) has been reacted with (3 moles) of THB keeping other experimental conditions constant as just described. The reaction product has shown the absence of phenolic compounds when it has been subjected to chemical test. The HPLC of the reaction product is given in Fig. 2.3.4. There are several compounds present in the reaction mixture as revealed by the HPLC profile. However, five compounds are present in larger proportions. The reaction mixture has been subjected to preparative HPLC where these compounds marked as I, II, III, IV and V in the HPLC chromatogram have been isolated. These have been subjected to spectroscopic analysis with a view to elucidate their structures.

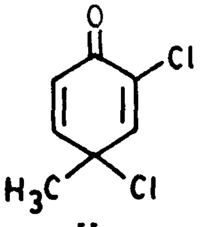
Identification of compounds (I, II, III, IV, V)

The infrared spectra of (I, II, III, IV and V) showed absorption at 1720 (c = 0). 1680 (C = C) confirms the presence of the conjugated enone system. This may occur either by replacement of phenolic group by oxidation during chlorination. The UV spectra of these compounds has shown absorption bands between 260 and 280 nm (Table 4.5.1) supporting the para quinonoid structures. The NMR spectra of these compounds has indicated that there are four vinylic protons consisting of two pairs and a methyl. It has also shown the absence of hydroxyl proton. Therefore the enone is dienone and specially 2,5-dienone.

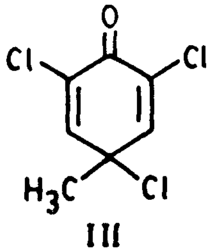
Based on the above observations and taking the analogy from literature[20] , the following structures have been assigned for compound I, II and III.



I



II



III

In aromatic electrophilic substitution, formation of carbocationic intermediates is well known[21]. The possibility of isomers for the carbocationic intermediates includes not only those including ortho meta and para alkyls by the electrophile but also that involving the position bearing a substituent ipsoto alkyl. The carbocationic intermediate formed as a result of ipsoattack involving the loss of a cation from the α-atom of the substitutent, thereby leading to the formation cyclohexadienes.

Further, evidence for the formation of compoundsI, II and III can be sought from their mass spectra. Mass spectrum of compound I has shown the fragment ions at 142 (M+), 107 (M-Cl) and 79 corresponding to loss of chlorine and Co. Mass spectrum of compound II has exhibited the parent in at M/z 178 corresponding to a dichloro compound. Further, isotopic ratio of parent ion has the intensity ratio (1:2:1) representing two cholorine atoms. The major fragments are 143 (M-Cl); 107 (M-2Cl) and 79 (M-99). The mass spectrum of compound III (Fig 4.5.4) has shoen the parent ion at M/z 210 and base peak at 175 The isotopic ratio of the parent ion has the intensity (1:3:3:1)representing three chlorine atoms.

The other important fragments are at (M-35), (M-71) and (M-99) indicating the successive loss of chlorine followed by carbon monooxide. Thus the compounds I, II and III have been confirmed as 4-chloro-4-methyl cyclohexa-2,5-diene-1-one 2,4-dichloro-4-methyl cyclohexa-2,d-diene-1-one and 2,4,6-trichloro 4-methyl chclohexa-2,5-dienon-1 one respectively. The mechanism of formation of compounds I, II and III has been shown in Fig 4.5.5. Spectral data obtained from compound I and II has been found to match with the reported data.

The formation of compound IV corresponding to Fig 4.5.6 has been found to be very interesting. When we have compared the mass spectra of compound III and IV, both the compound exhibited parent ion at m/z 210 and the isotopic ratio of the parent ion has indicated three chlorine atoms. The major peaks common to both the spectra corresponded to the fragments (M-35) (M-71) and (M-99) indicating the successive loss of chlorine followed by carbon mono oxide. However, further fragmentation pattern is different in each case indicating III and IV to be isomeric compounds. Their structures have been supported by PMR spctra. The PMR spectrum of III exhibited a singlet at δ7.48 assginable to the protons β to carbonyl group whereas that of PMR spectrum of IV displayed a chemical shift δ 7.0 assignable to protons α to carbonyl group. Further it is seen that in HPLC the ortho substituted compounds are eluted first than the meta substituted compounds. Considering above facts, compound IV has been assigned as 3,4,5-trichloro-4methyl cyclohexa-2, 5-dien-1-one. The mechanism of formation of compound, 3,4,5-trichloro-4-methyl 2,5-cyclohexa-dien-1-one (IV) can be explained by assuming stepwise chlorination and phenol dienone rearrangement. These dienones aromatise in the presence of an acid which is a typical rearrangement and is usually accompanied by a migration of substituents within the ring and is called dienone-phenol rearrangement. Phenols are known to undergo such rearrangements. The general raaction pathsay is shown in (Fig 4.5.7).

Discussion on the formation of compound V

Fig. 4.5.8 gives the mass spectrum of the compound V The mass spectrum of V shows molecular ion at m/z 318, isotopic ratio of the parent ion (1:3:3:1) indicates the presence of three chlorine atoms in the molecule. The major fragment ion at m/z 282 (M-HCL), 219 (M-$CoCl_2$) and 177 (M-C_7H_6ClO) supports the assigned structure.

2,6-Dichloro-4-methyl-4-(2-chloro-4-methyl phenoxy)-2,5-cyclohexadien-1-one for compound V.

Formation ofcompound V can be explained in terms of coupling of phenols. Phenols are known to couple via an anodically generated phenoxinium ion which gives cyclohexa-2,5-dienones through a mechanism involving phenoxinium ion shown in Fig. 4.5.9.

Formation of Phenoxinium ion occurs in neutral of slightyly basic conditions in the presence of anodic oxidants[21,22]. However, in the reaction conditions the possibility of the existence of phenoxinium ion intermediate is not possible, and more over the reaction has been carried out in acetic acid. Under this condition the feasibility of coupling of phenols via phenoxinium ion is ruled out. Hence a probable alternative path way of the coupling of phenols has been postulated. Phenols are also known for their dimerization via a mechanism involving aroxyl free radical by C-4 coupoing t give unsymmetrically coupled cyclohexa-2,5-dienones[23,24]. The mechanism of formation is shown in Fig. 4.5.10.

Table : 4.5.1 UV - data of Compounds I, III, IV, and V.

Wave lenth μm	Absorbance or OD			
	Spot I	Spot III	Spot IV	Spot V
300	0.120	0.170	0.204	0.740
290	0.443	0.358	0.399	1.082
280	0.461	0.474	0.414	0.920
270	0.343	0.891	0.378	0.770
260	0.251	1.094	0.374	0.847
250	0.098	0.110	0.131	0.250
240	0.098	0.109	0.129	-
230	0.109	0.121	1.380	0.255
220	0.119	0.130	0.145	0.257
210	0.118	0.317	0.146	0.260
200	0.113	0.130	0.144	0.264

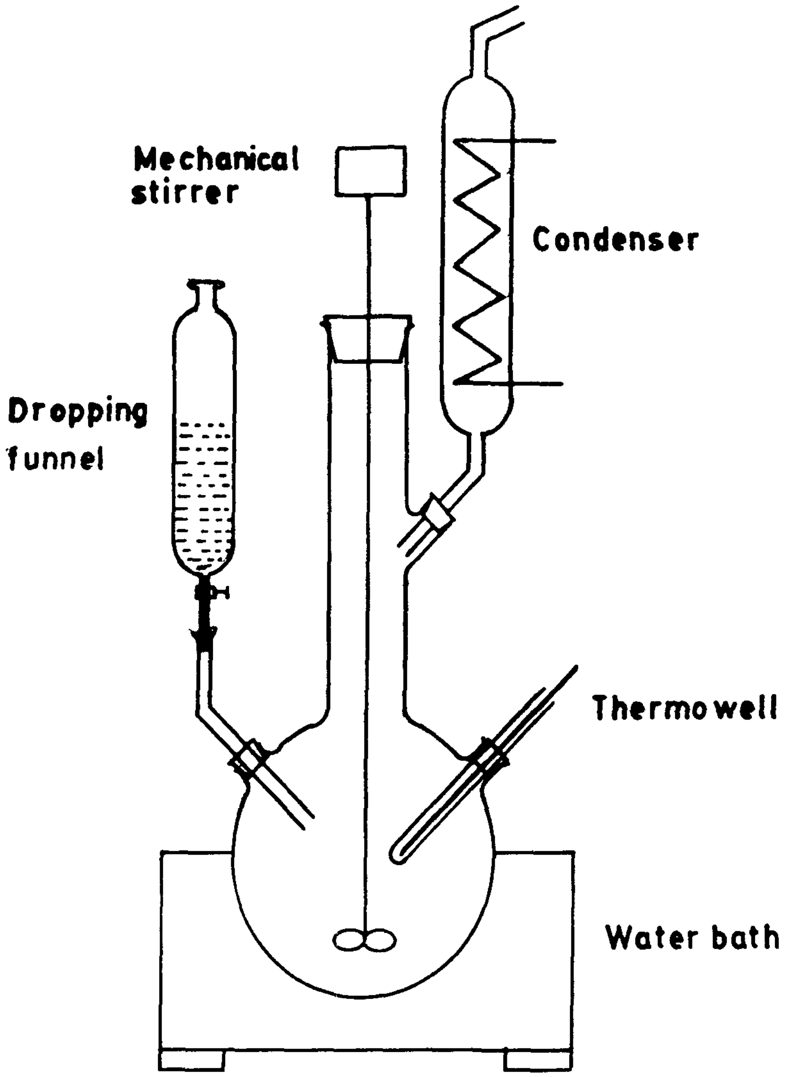


Fig. 4.5.1. Experimental setup for the chlorination of p-cresol with TBH

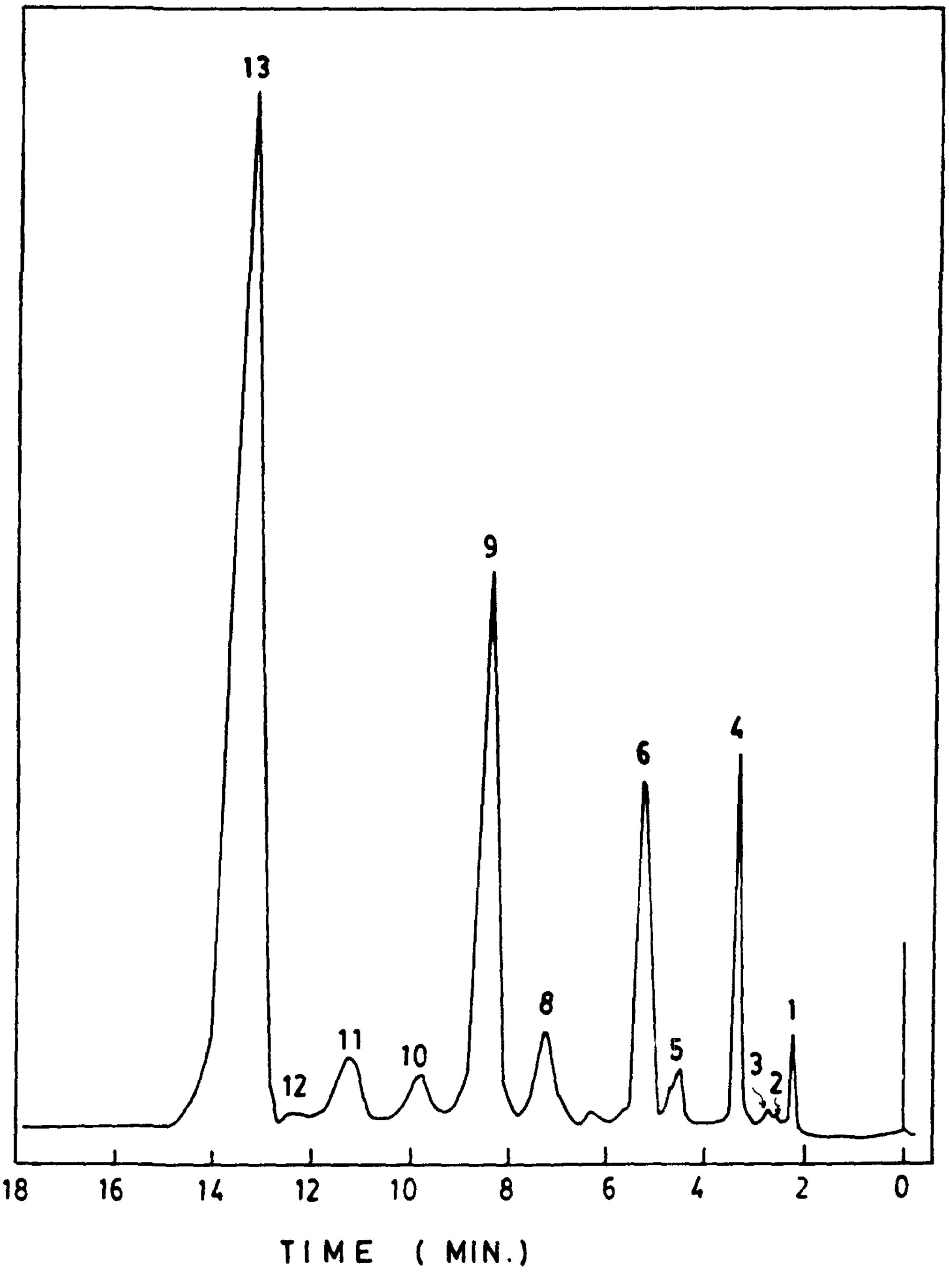


Fig. 4.5.2 HPLC Chromatogram of the reaction mixture of p-cresol with 1 mole of TBH (column : 30 cm x 4mm i.d., μ-porasil; pressure 750 psi; eluent : toluene; flow rate : 1.5ml / min.)

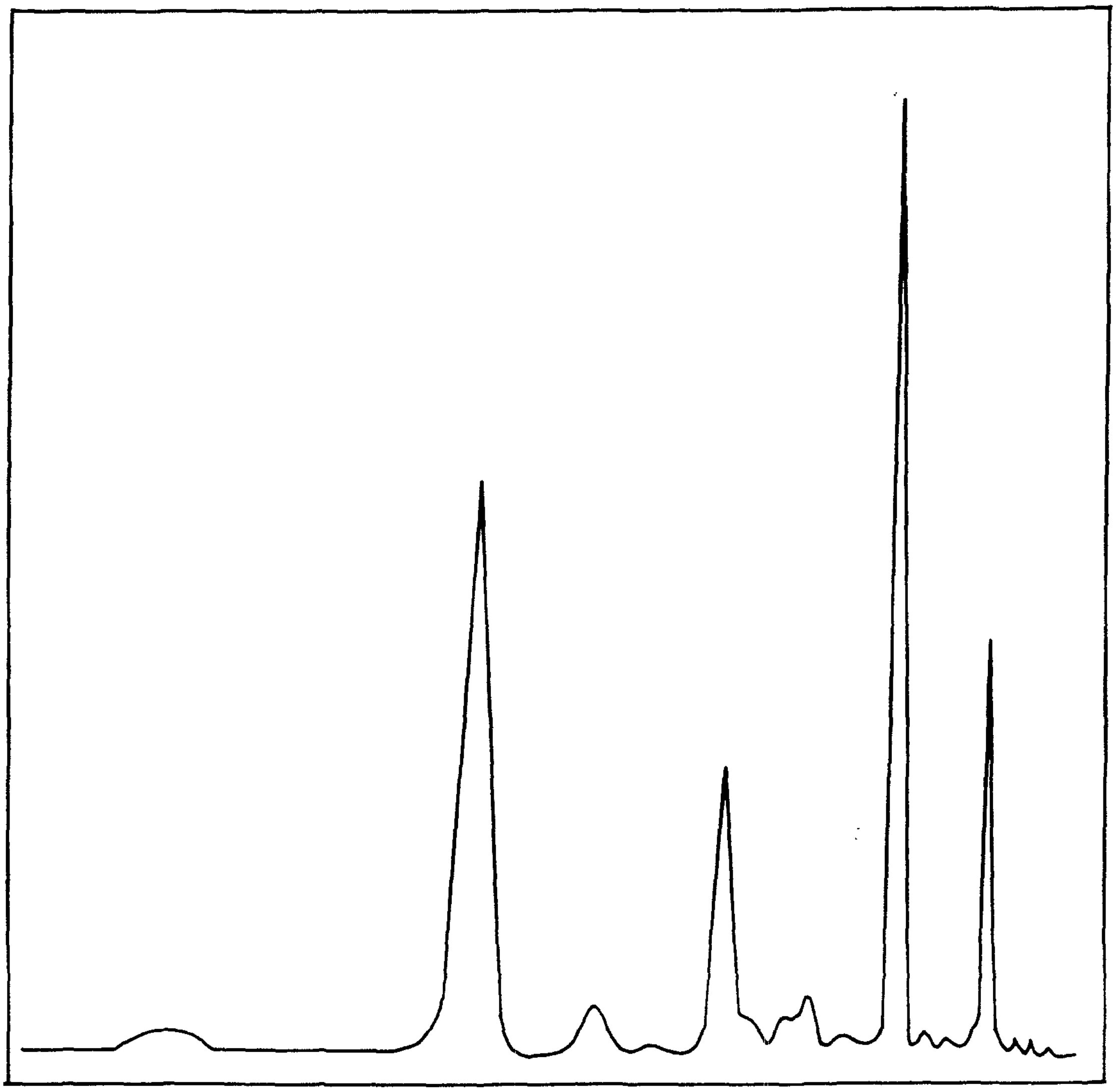


Fig. 4.5.3. HPLC Analysis of reaction mixture of p-cresol with 2 moles of TBH.
(Column : 30 cm x 4 mm i.d. μ-porasil; pressure 750 psi ; eluent : toluene ; flow rate : 1.5 ml/min.)

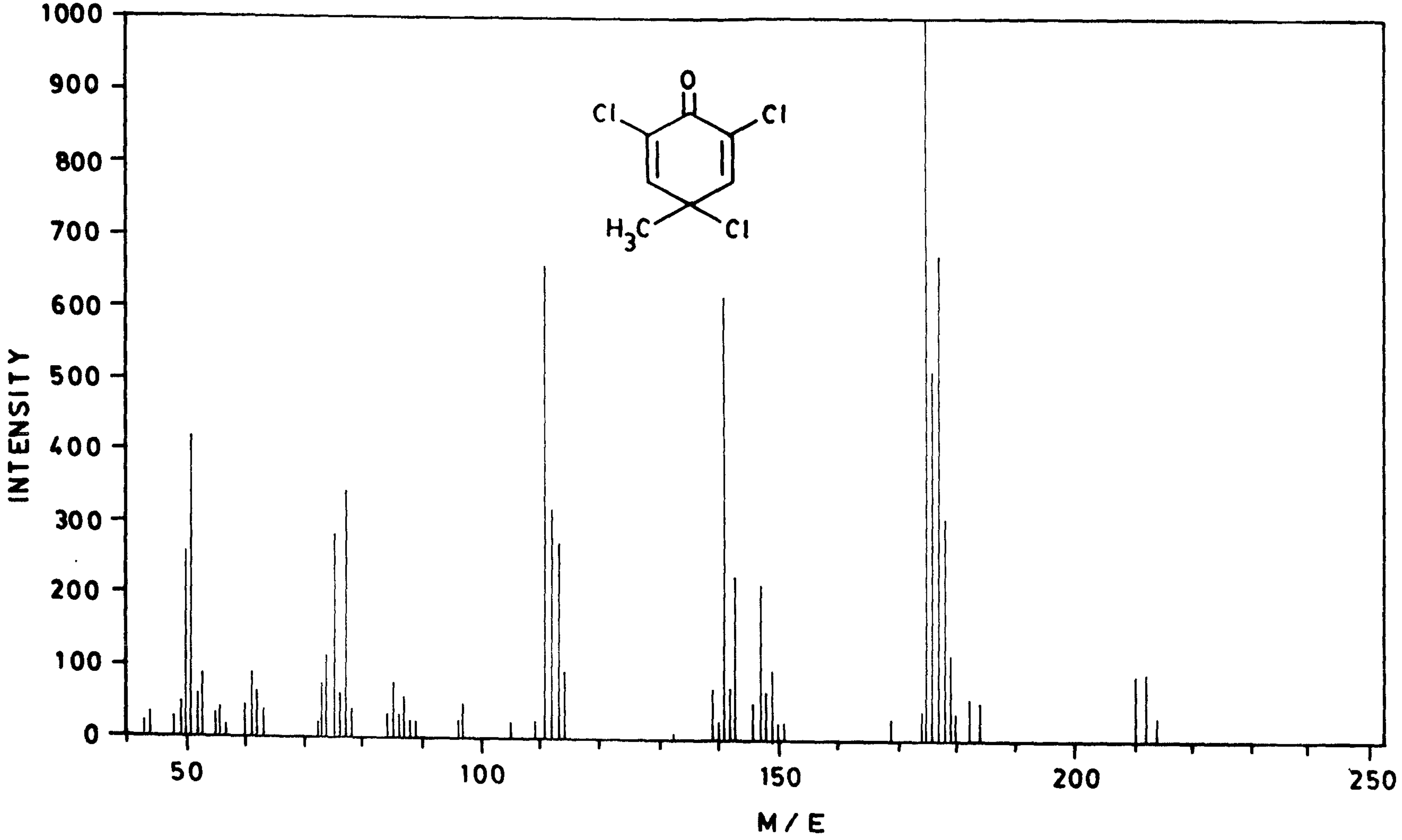
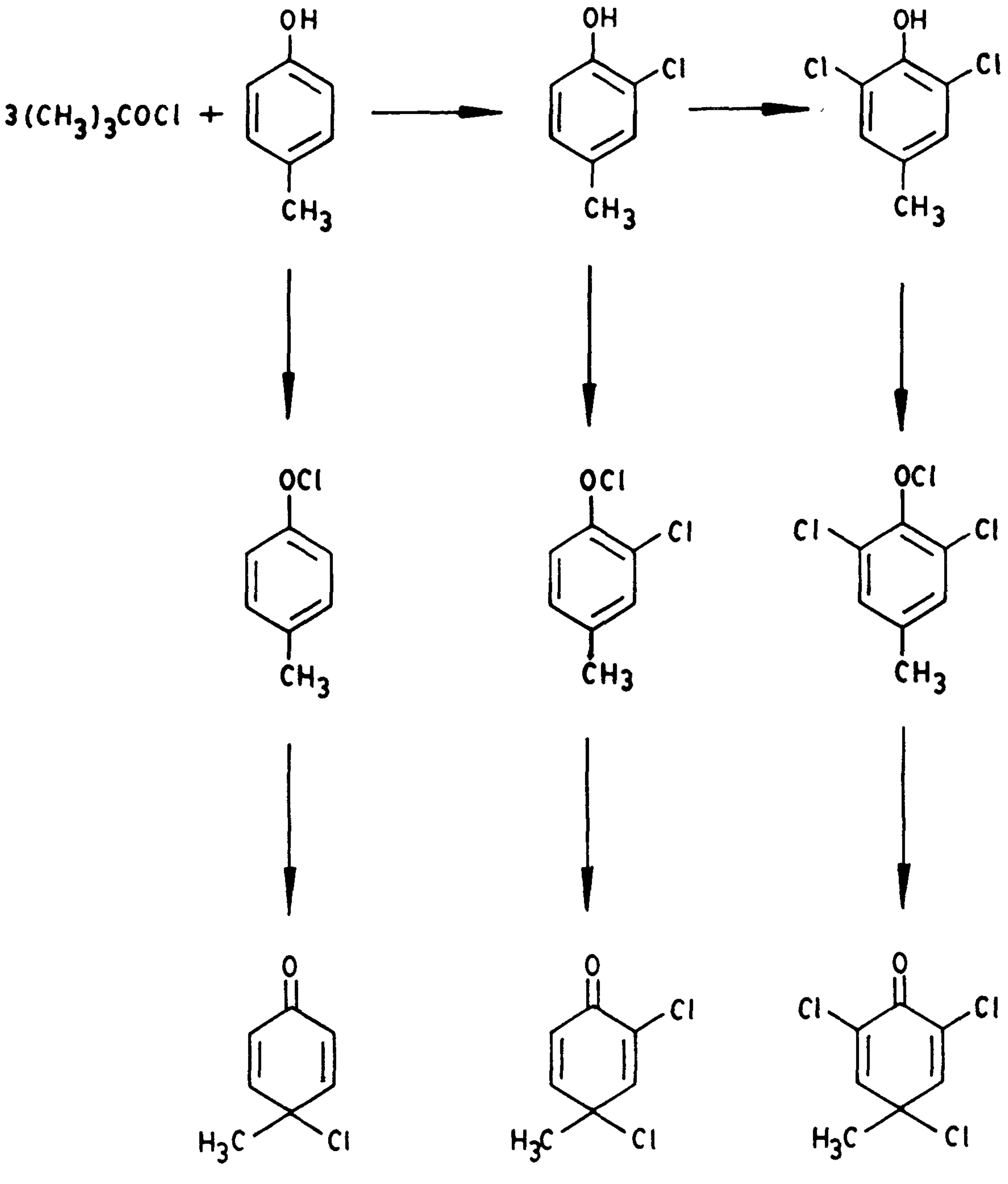


Fig.4.5.4. Mass spectrum of 2,4,6-trichloro-4-methyl-2,5-cyclohexadienone (III)



I (Peak I) II (Peak II) III (Peak III)

Fig. 4.5.5 Mechanism of formation of products I, II & III

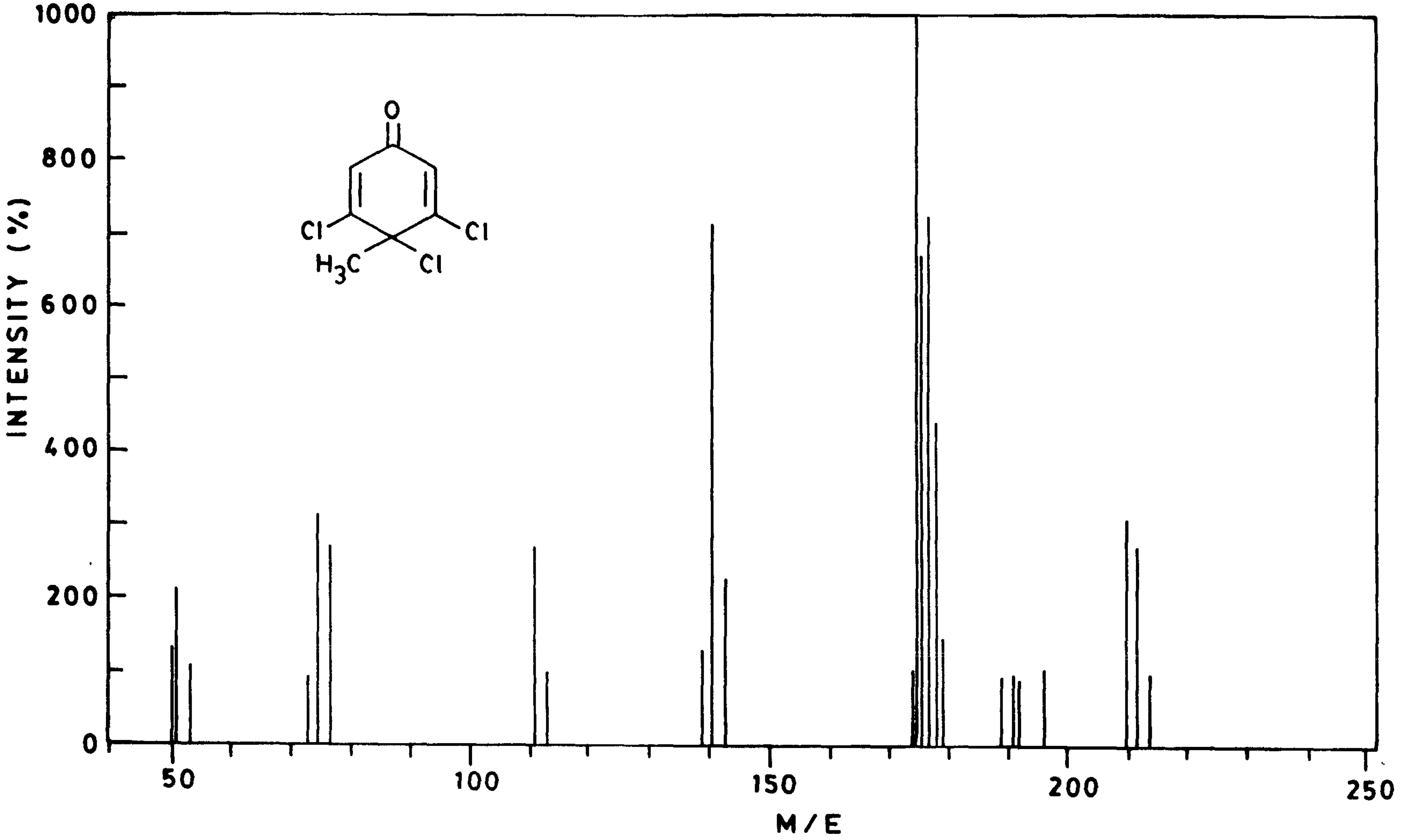


Fig. 4.5.6 Mass spectrum of 3,4,5-trichloro-4-methyl-2,5-cyclohexa dienone(IV)

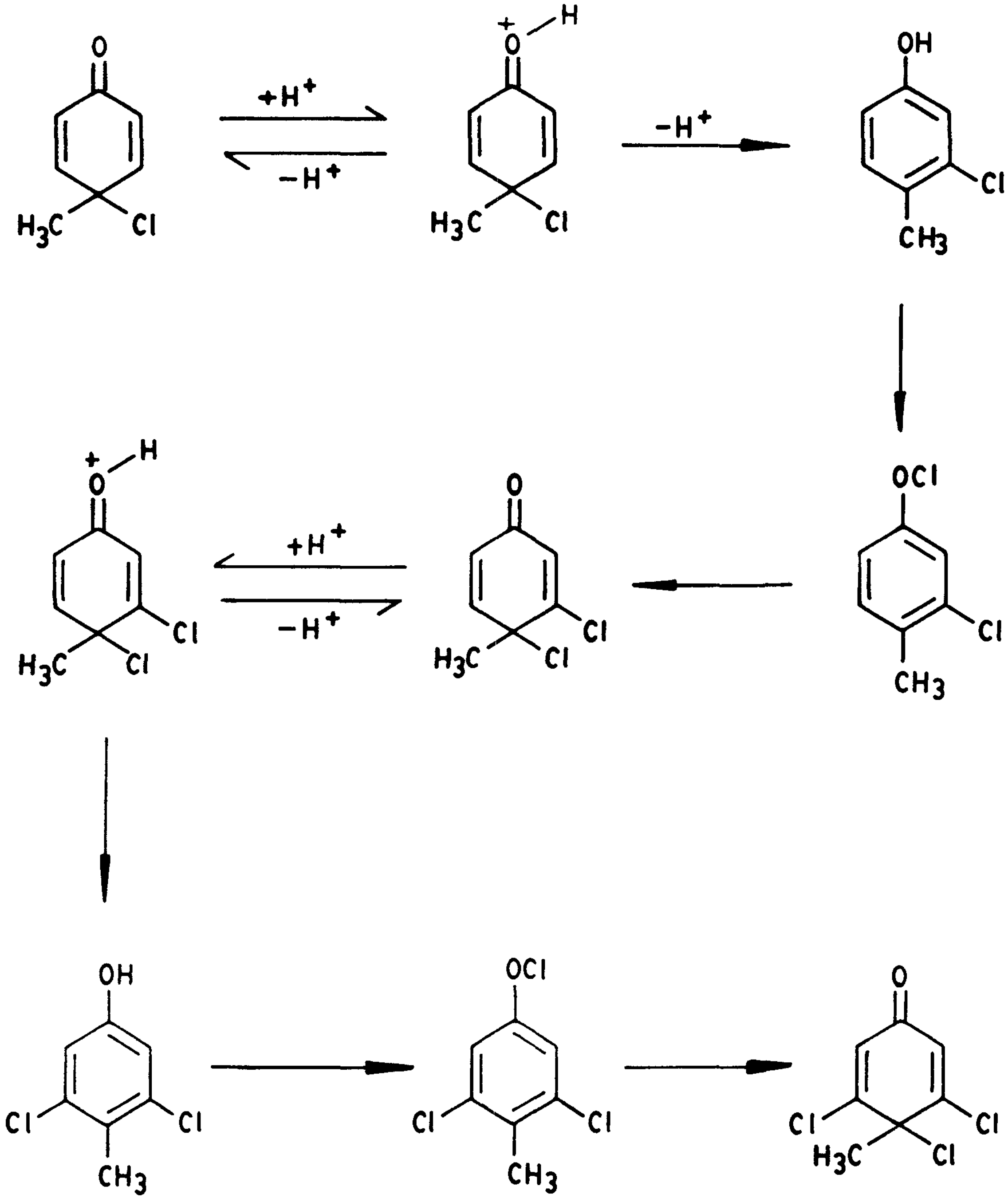


Fig. 4.5.7 Possible intermediates and pathways in the formation of IV

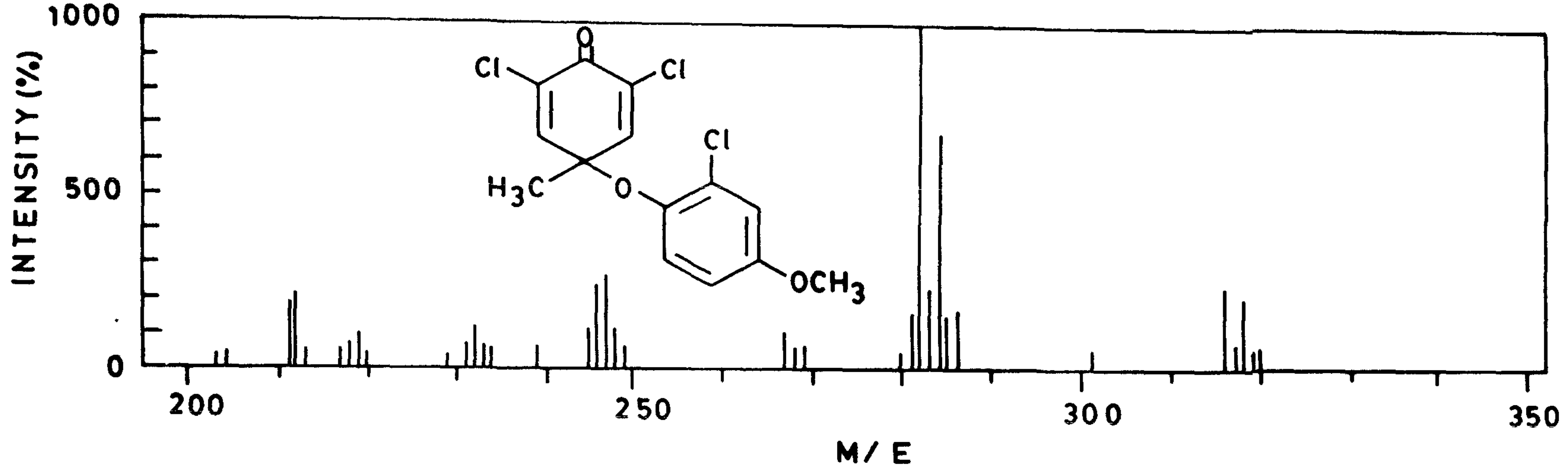


Fig. 4.5.8 Mass spectrum of 2, 6 - dichloro - 4 - methyl - 4 (2 - chloro - 4 - methyl-phenoxy) 2,5 - cyclohexa dienone (V).

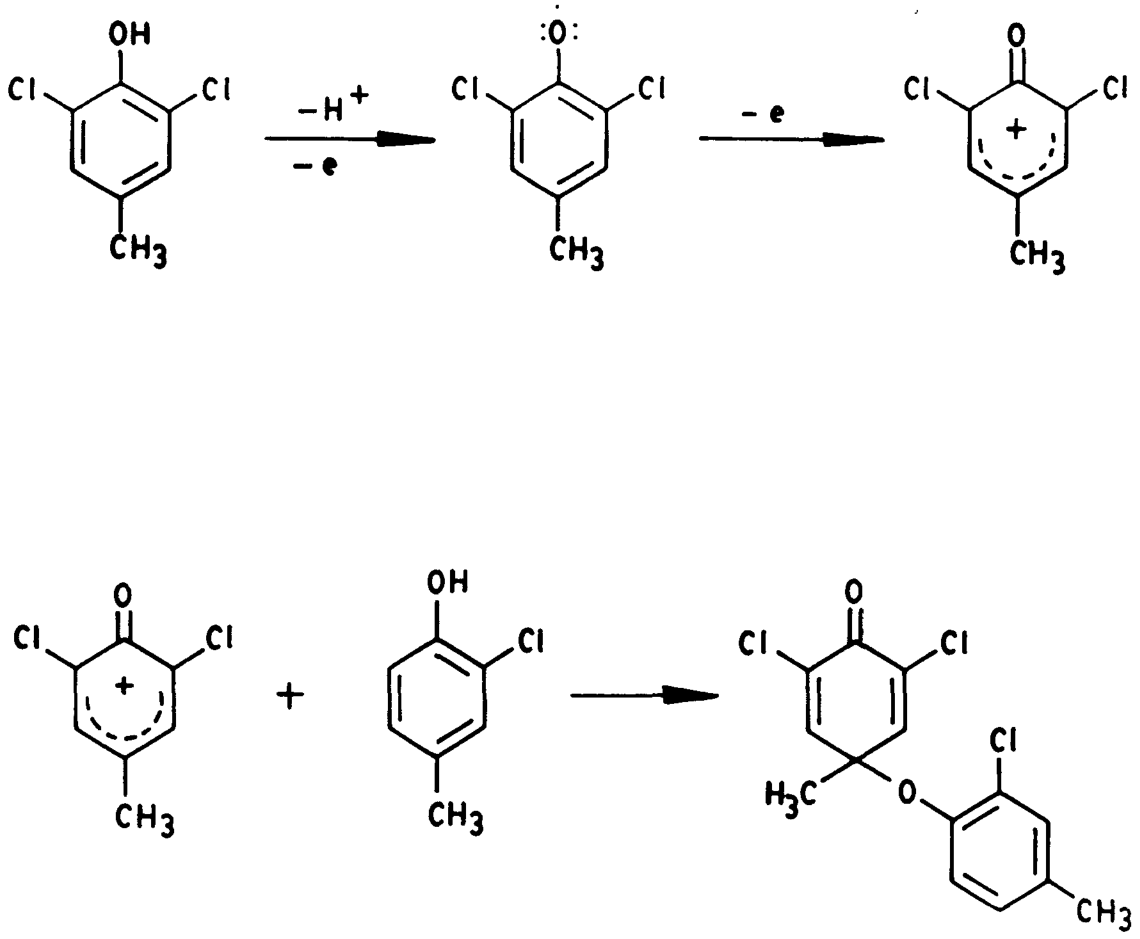


Fig. 4.5.9 Mechanism of coupling of phenols through phenoxinium ion.

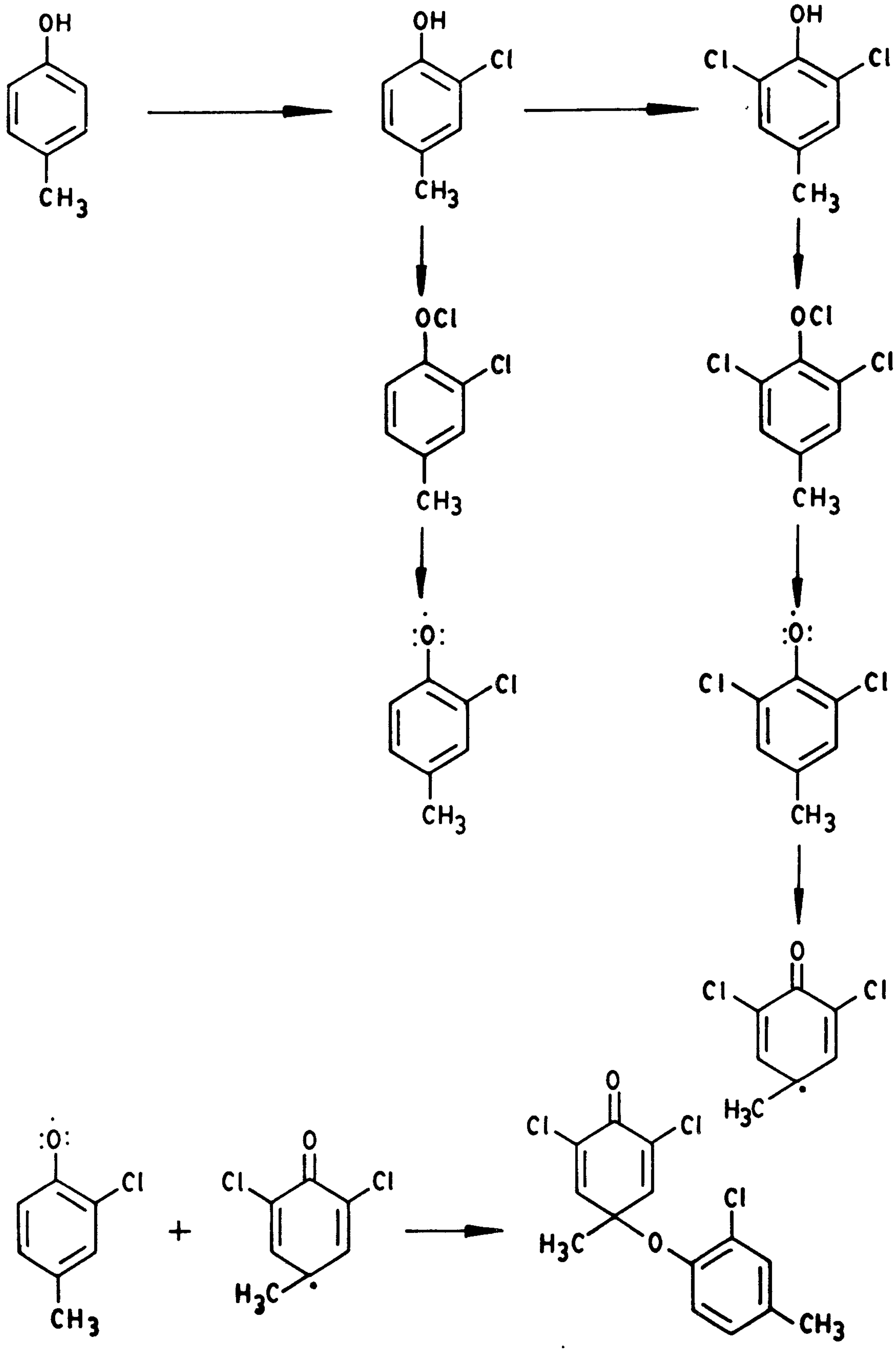


Fig. 4.5.10 Mechanism of formation of V involving coupling of phenols via aroxyl free radicals.

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SUMMARY

Chapter I

The first chapter begins with a discussion on the orientation effects of phenols during the chlorination. This is followed by a critical review on the chlorination of phenol and cresols using various chlorinating agents, catalysts, solvents giving the present state of knowledge on chlorophenols as a 'class of organic intermediates' in a variety of industrial products. The chapter is concluded by a statement in detail of the problem chosen and the proposed work to be included in this dissertation.

Chapter II

The second chapter deals with the development of chromatographic methods suitable for the study on the kinetics and mechanism of chlorination of phenols. Three chromatographic techniques mainly TLC, GLC and HPLC have been studied in detail. A variety of solvent systems have been screened to find suitable solvent system to follow the progress of the chlorination reaction by TLC. The results obtained during these studies have been discussed in detail. Benzene : cyclohexane (9:1) and xylene have been identified as the best solvent systems to follow the progress of chlorination reaction. Separation of chlorophenols and chlorocresols on a variety of stationary phases have been taken up to standardise a GLC method which can separate all the chlorophenols and chlorocresols. Carbowax-20 M has been found to be the best stationary phase for the separation and quantitative estimations of chlorophenols. During the entire studies on chlorination of phenol GLC has been choses as a method of choice for the quantitative determination of the reaction products at every stage of reaction, the results of analysis of some typical reaction mixtures have been included here. The method has been extensively used during the kinetic studies and the results obtained are discussed in this chapter. It has been observed that except for some information available on alkyl phenols, the studies on HPLC of chlorophenols and chlorocresols have been reported for the first time. Studies to find good solvent system and stationary phase to separate and quantify the chlorinated mixture of p-cresol with *TBH* have also been discussed here.

Chapter III

The thid chapter contains the data on spectroscopic techniques viz., UV, IR and NMR on chlorophenols and chlorocresols. A computer-assisted ^{13}C NMR spectroscopic method for the identification and quantification of complex mixture of chlorophenols has been developed. The results obtained have been compared with those obtained by conventional method.

Chapter IV

The fourth chapter deals with the results obtained

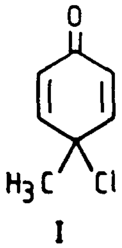
during the studies on kinetics and mechanism of chlorination of phenol with different chlorinating agents. Kinetics of chlorination of phenol with gaseous chlorine have been studied in detail, rate constants for the entire reaction scheme have been determined. Using the data activation energies have been determined. Effect of parameters such as chlorine flowrate, solvent and temperature have been studied in detail and the results are explained in terms of activation energy. Chlorophenols being industrially important products process parameters have been standardised for the preparation of monochlorophenols viz., OCP, PCP and 2,4-DCP. An alternative route for the preparation of 2,5-DCP and 2,4,5-TCP have been proposed and process parameters have been standardised.

Chlorination of phenol with $CuCl_2$ has been studied in detail as it gives preferential formation of PCP. Kinetic parameters have been determined. Since the reaction leads to the formation of PCP exclusively, various process parameters have been standardised. A technique knowhow report has been prepared for the production of PCP.

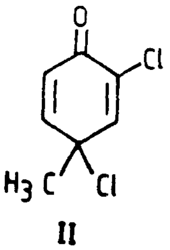
Chlorination of p-cresol with TBH has produced very interesting results. TLC of the reaction with 1 mole of p-cresol with 1 mole of TBH has shown the formation of more than 13 compounds as against the expected two products viz., 6-chloro-p-cresol and 2,6-dichloro-p-cresol. This has led

to interesting results. The reaction has been repeated with two and three moles of TBH, the chromatogram of reaction product obtained with 3 moles of TBH has shown five major compounds. These compounds have been separated by preparative HPLC and their spectral data have been recorded.

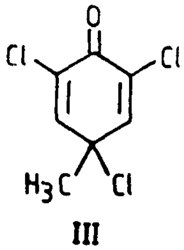
The IR spectra of these compounds has exhibited IR absorption at 1710 cm^{-1} (C=O) and 1680 cm^{-1} (C=C) confirmed the presence of conjugated enone systems. The ^1H NMR has shown the presence of four vinylic protons which has confirmed that the enone is a dienone specially 2,5-dienone. Taking the analogy from the literature the mass spectra of these compounds have shown the parent ion at 142, 178 and 210 indicated the presence of 1,2 and 3 chlorine atoms respectively. The structures of these compounds established are



I



II



III

Possible path ways leading to the formation of compounds I, II and III has been discussed and is as also indicated below.

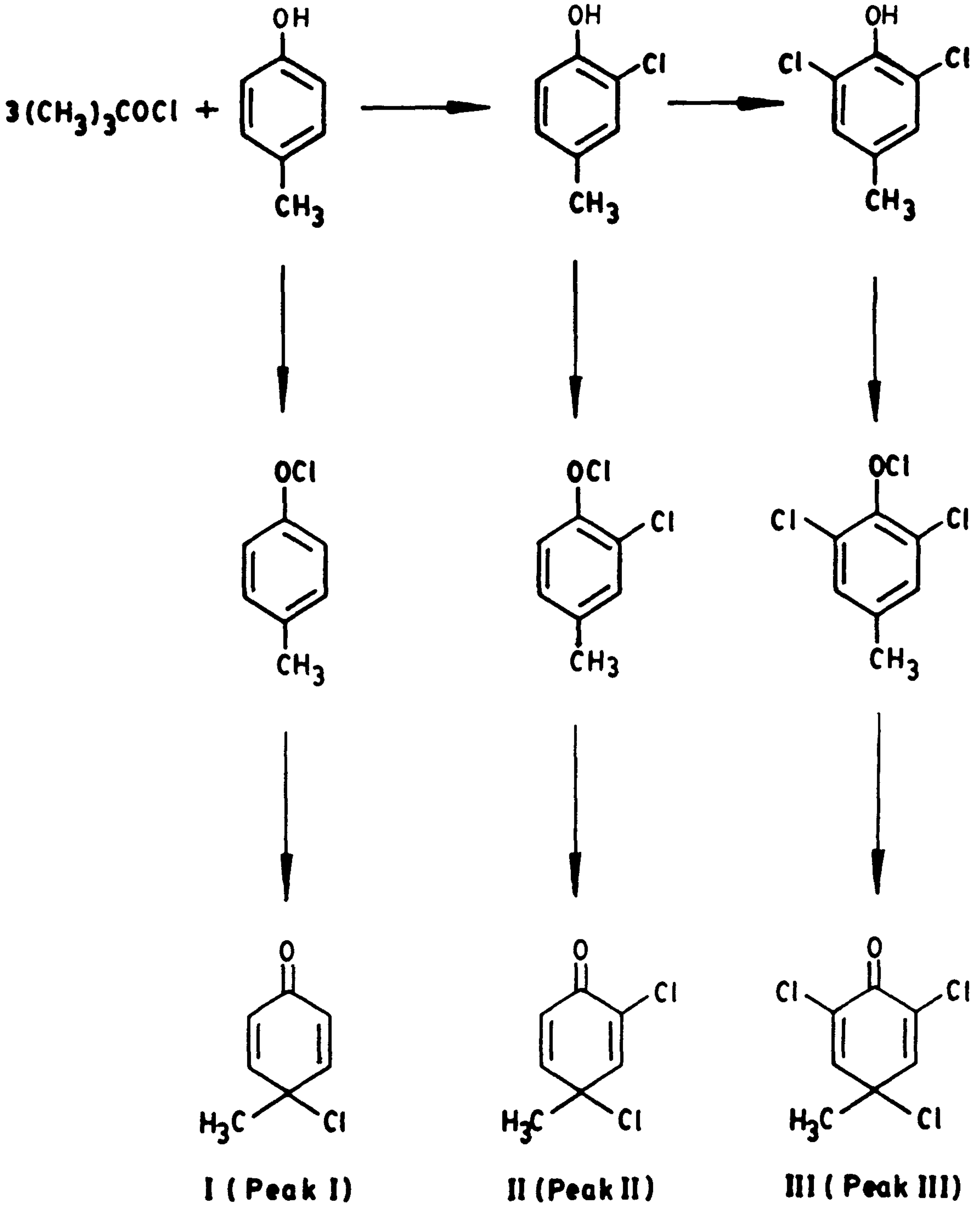
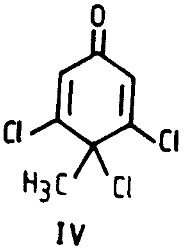


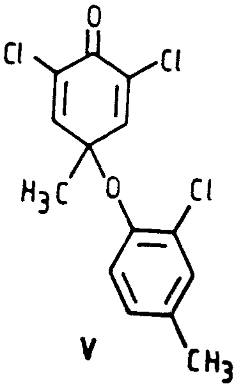
Fig. 4.5.5 Mechanism of formation of products I, II & III

The mass spectrum of compound IV has been found to be identical with that of compound III and confirmed that it has also three chlorine atoms. The formation of this compound has been explained and discussed on the basis of phenol-dienone rearrangement via Ipsi attack. The structure of it is confirmed as



IV

The mass spectrum of the compound V has exhibited the molecular ion peak at 318 and also indicated the presence of three chlorine atoms. The mass spectra fragmentation pattern has supported the assigned structure i.e.



V