DECOMPOSITION OF PHENOXOCOPPER(II) COMPLEXES

by

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This thesis is dedicated to my parents for encouraging me to continue my education and to my wife, Marcia, for her patience and assistance during my latter year of research and write-up.

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Ph.D. Chemistry

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DECOMPOSITION OF PHENOXOCOPPER(II) COMPLEXES

ABSTRACT

The mechanism of decomposition of phenoxocopper(II) to polyphenylene ether is investigated, utilizing bis(2,4,6-trichlorophenoxo)bis(pyridine)copper(II). Ultraviolet-visible spectrophotometry and electron spin resonance spectroscopy provided the major tools for the mechanistic proposals. These were supported by analysis of the reaction products under varied reaction conditions (ie., temperature, concentration and solvent), and through the addition of free radical initiators, carbon tetrahalides or trichlorophenol.

The reaction was found to proceed through the formation of phenoxy radicals, which served to induce further decomposition of phenoxocopper(II). A mechanism of autoacceleration is proposed. The addition of free radical initiators and carbon tetrahalides was found to enhance the decomposition.

Oxygen or hydroperoxides were found to generate μ_4-oxocopper(II) complexes as side reaction products. Suitable adjustment of the reaction conditions permitted the formation of these complexes as the sole copper-containing product, providing a unique method of synthesis of μ_4-oxocopper(II) complexes from other phenoxo-neutral ligand-copper(II) complexes.

Decomposition of 4-bromo-2,6-dichlorophenoxocopper(II) results in a nearly-linear polymer of very high molecular weight.

Ph.D. Chimie

J.C. Carr

LA DÉCOMPOSITION DE COMPLEXES PHÉNOXYDES DE CUIVRE(II)

RÉSUMÉ

Le mécanisme impliqué dans la décomposition de phénoxydes de cuivre(II) en polyphénylène éther a été étudié à partir du bis(trichloro-2,4,6-phénoxo)bis(pyridine)cuivre(II). La spectrographie ultraviolette et visible ainsi que de résonance de spin électronique ont permis l'élaboration du mécanisme proposé. Ces résultats ont été confirmés par l'analyse des produits de réaction sous différentes conditions de réaction (i.e. température, concentration et solvant), et par l'addition d'initiateurs de radicaux libres, de tétrahalogénures de carbone ou de trichlorophénol.

On y montre que la réaction se propage par la formation de radicaux phénoxy, ceux-ci menant à la décomposition du phénoxyde de cuivre(II) un mécanisme d'auto-accélération est proposé. L'addition d'initiateurs de radicaux libres et de tétrahalogénures de carbone favorisent la décomposition.

Les complexes μ_4-oxo-cuivre(II) ont été formés comme sous-produits de la réaction en présence d'oxygène ou de péroxyde d'hydrogène. Un contrôle adéquat des conditions de réaction permit la formation de ces complexes comme seuls produits contenant du cuivre. C'est une méthode unique de synthèse des complexes μ_4-oxo-cuivre(II) à partir d'autres complexes de cuivre(II) à ligand neutre phénoxyde.

La décomposition du bromo-4-dichlorophénoxo-2,6-cuivre(II) résulte de la quasi-linéarité du polymère de très haut poids moléculaire.

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I. INTRODUCTION

III. RESULTS

IV. DISCUSSION

CLARIFICATION OF TERMINOLOGY

1. Chemical formulae:

   Py = pyridine

   TCP = 2,4,6-trichl[illegible]phenoxo

   TBP = 2,4,6-tribromophenoxo

   TIP = 2,4,6-triiodophenoxo

   Cl_2BrP = 4-bromo-2,6-dichlorophenoxo

   DMSO = dimethylsulphoxide

   DMF = dimethylformamide

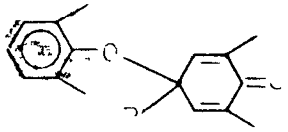
   TPPO = triphenylphosphine oxide

2. In cases where the phenol is substituted in the 2,4,6- positions by identical groups, an abreviated nomenclature will be used, e.g. 2,4,6-trichlorophenol will be referred to as trichlorophenol.

3. The phenoxo-pyridine-copper(II) complexes are abreviated as phenoxocopper(II) throughout this thesis. This is not to be confused with copper(II) trichlorophenolate, $Cu(TCP)_2$, which was used only in the preparation of various phenoxo-ligand-copper(II) complexes. In cases where neutral ligands other than pyridine are involved in the complexes, these ligands will be included in the nomenclature.

4. The terms phenoxy, phenoxyl and aroxyl radicals have been used interchangeably in the literature. Chemical Abstracts prefers phenoxy, so this term will be used in this thesis.

5. The terms quinone ketal and quinol ether are sometimes confused in the literature. Compound 1 is a quinone ketal if R = OR^1, otherwise it is a quinol ether.



1

6. The terms redistribution and equilibration are synonymous for the coupling mechanisms.

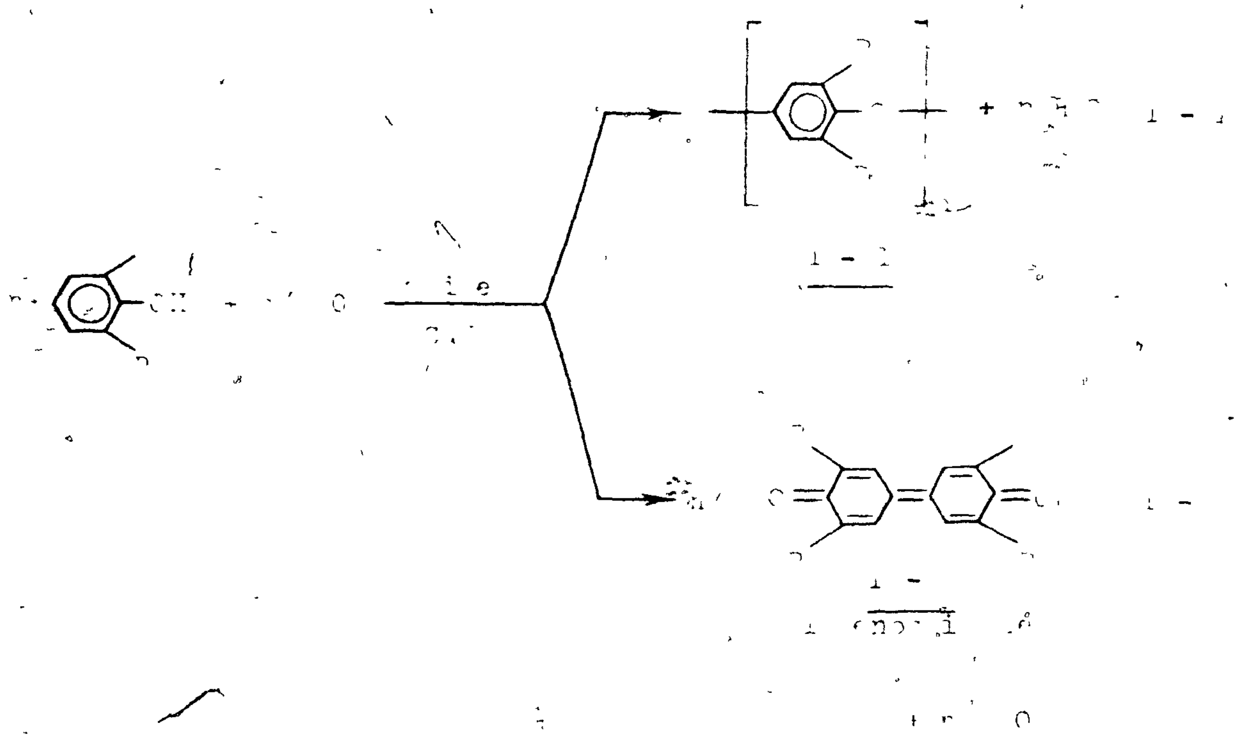
7. Poly(2,6-disubstituted-1,4-phenylene ether) will be referred to as polyphenylene ether. The name "polyphenylene oxide" is also widely used in the literature.

8. Electron spin resonance spectroscopy and nuclear magnetic resonance spectroscopy will sometimes be abbreviated ESR and NMR spectroscopy, respectively.

I - INTRODUCTION

I - 1 Origin of the Problem

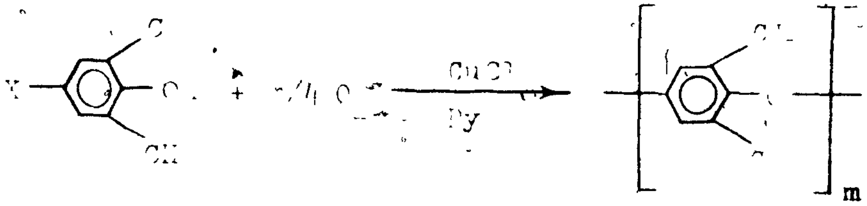
In 1959, Hay and coworkers discovered a method of oxidative coupling of phenols to yield high molecular weight poly-1,4-phenylene ethers(1). The reaction was carried out at room temperature by passing oxygen through a solution of the phenol in an organic solvent containing an amine and a copper(I) salt as catalyst.

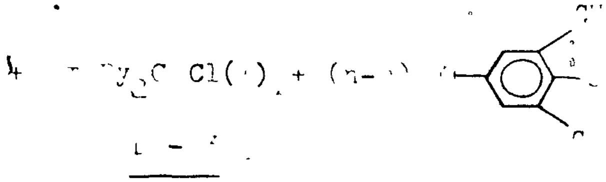


The active oxidizing agent in the oxidative coupling reaction was shown to be an amine-copper(II) complex. The role of the oxygen was to oxidize the copper(I) ions to copper(II). The reaction gave only simple products with the 2,6-disubstituted phenols, but a large number of the latter were shown to undergo reaction, equations I - 1 and 2.

When the substituents were small, such as methyl, the carbon-oxygen coupled product, <u>I - 1</u>, was mainly obtained. On the other hand, with bulky groups, such as <u>tert</u>-butyl, only carbon-carbon coupled products, <u>I - 2</u>, were obtained in substantial amounts.

2,6-disubstituted phenols with halogen substitution at the 4-position have also been oxidatively coupled by copper(I) compounds, but in a non-catalytic manner. 4-Halogenated-2,6-dimethylphenols, subjected to the oxidative coupling reaction, absorbed an amount of oxygen equivalent to the amount of copper(I) salt present and then the reaction stopped(2). This was due to the halogen released from the 4-position reacting with the copper(I) ions, producing a copper(II) halide, <u>I - 3</u>, which is incapable of oxidizing the phenol, equation I - 3.





Staffin and Price(3) prepared high molecular weight poly (2,6-dimethyl-1,4-phenylene ether) from 4-bromo-2,6-dimethylphenolate ion with a number of oxidizing agents such as lead dioxide and potassium ferricyanide.

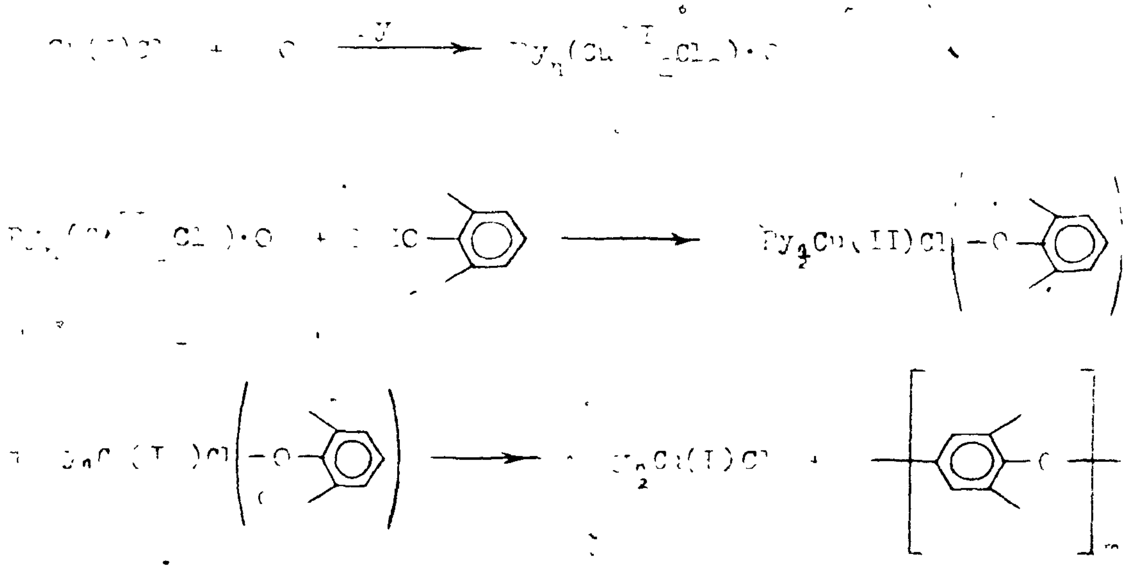
The reactions described above were extraordinary because of their apparent extreme simplicity. Furthermore, they represented the first synthesis of high molecular weight polyphenylene ethers. Previous studies on the oxidation of phenols, which are summarized in four excellent reviews(4-7), have yielded as products simple aromatic ethers, oligomers, or a variety of complex products.

When unsubstituted phenol was treated with oxygen in pyridine solution, in the presence of copper(I) chloride, a reaction occurred. However, instead of polymer forming, an intractable, tarry residue resulted(8). This is not surprising since the unsubstituted 2- and 6- positions are expected to manifest a reactivity towards coupling comparable to that of the 4-position, and extensive branching can occur. Coupling may be slightly preferred in the 4- position(9). Either carbon-carbon coupling, or carbon-oxygen coupling can occur at the 2,6- and 4- positions. The reaction will only proceed cleanly to give poly-1,4-phenylene ethers when the 2,6- positions contain relatively stable substituents such as alkyl groups. Substituents in the 2,6-positions which are readily displaced, for example halogens, lead to some branching. Polymer from the oxidation of 2-chloro-6-methylphenol showed a loss of 15% chlorine (8). It should be noted, however, that linear unsubstituted poly(phenylene ether) has been successfully prepared under certain reaction conditions(10-12).

The mechanical, chemical, and electrical properties of polyphenylene ethers (13) have provided the incentive for intensive research in this field in the past twelve years. Recent studies have shown that apart from the compounds of copper, iron, and lead first used as oxidants for the oxidative coupling reaction, it is also possible to obtain reasonable results with compounds of cobalt(14,15), manganese(16), nickel(17, 18), alumina(19), metal oxides(20), persulphates (21), tri-tert-butylphenoxy radicals(22), and organic peroxides(23). Most of these reactions, however, are unsuitable for kinetic studies since they involve either heterogeneous oxidants, or diffusion processes through the interface of aqueous alkali-aromatic solvents. Side reactions can result with tri-tert-butylphenoxy radicals or organic peroxides. The copper(I)-phenol oxidation system provides a homogeneous reaction. It therefore represents the best system for the kinetic and mechanistic study of the oxidative coupling of phenols to polyphenylene ethers.

Recently interest in the oxidation 2,6-diphenylphenol to poly(2,6-diphenyl-1,4-phenylene ether) has accelerated(24,25). It was found that problems of degradation experienced for poly(2,6-dimethyl-1,4-phenylene ether) were not as common in this polymer.

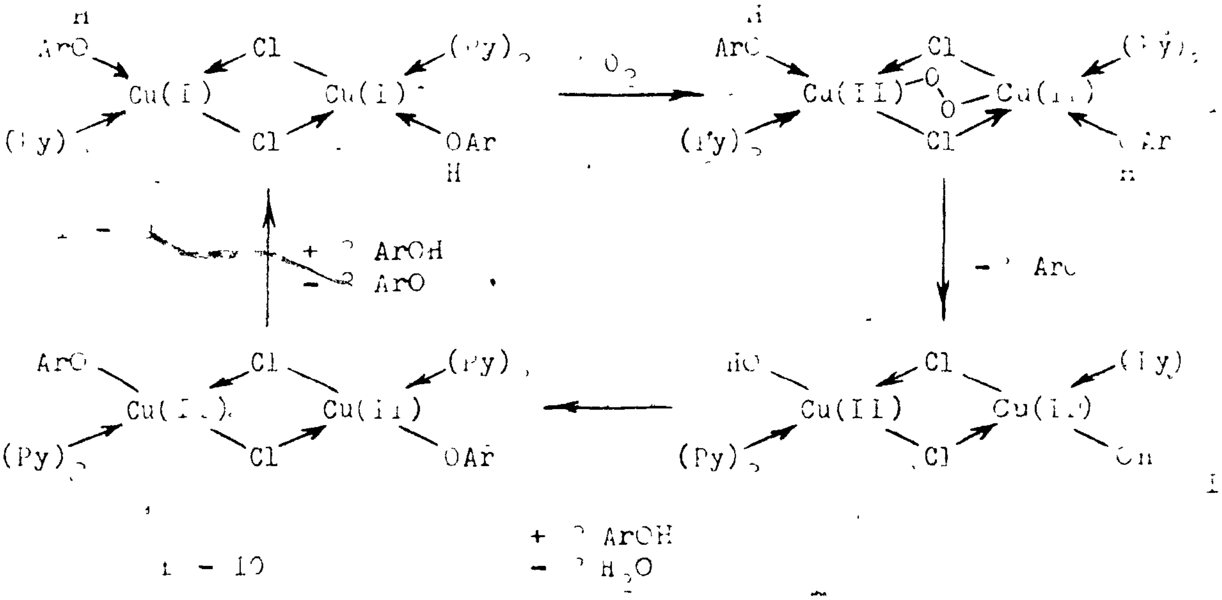
The oxidative coupling of phenols with copper(I) chloride as catalyst is very complicated as evidenced in several review articles(26-30). Despite the vast amount of literature now available, the overall mechanism is still not completely understood. This applies particularly to the role of the oxidant. It was shown(31) that the sole function of the oxygen in the catalytic reaction is to oxidize copper(I) to copper(II). Copper(I) salts would not catalyze the coupling of phenols in the absence of oxygen. Neither would autoxidation of copper(I) proceed in the absence of amine. The structure of the catalyst is not known. The exact role of the catalyst in the oxidation of phenols is not definite, although it is almost certain to involve a phenoxo-amine-copper(II) intermediate(2,31) and an overall mechanism has been proposed, equations I - 4 to 7.



[illegible]

$$[illegible]_{\frac{n}{2}}Cu(I)Cl + O_2 \longrightarrow Py_n(Cu^{II}{}_2Cl\ \ )\cdot O \qquad I - 7$$

More recently, Price and Nakaoka(32) have conducted further studies as to the role of oxygen in the oxidative coupling of 2,6-dimethylphenol using copper(I) chloride as catalyst. They have proposed a similar but more detailed mechanism, as shown in equations I - 8 to 11.

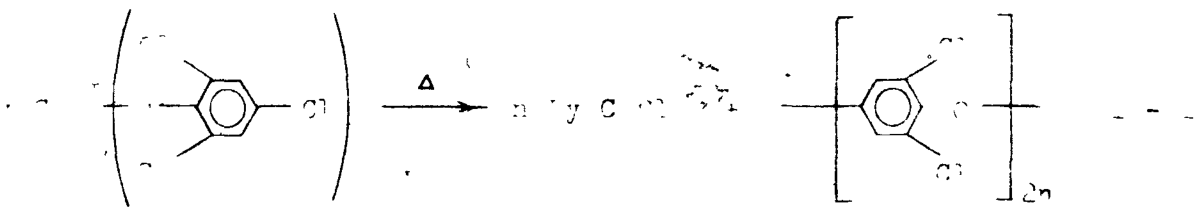


I - 10

I -

There are a number of other reaction features which are not fully understood. The reaction depends on the molar concentration of amine relative to the copper concentration(33). Using pyridine as the amine, it was found that polymerization proceeds most effectively at a molar concentration ratio of 10 to 1. The reaction is also dependent on the bulkiness of the amine.

This thesis will deal with the homogeneous thermal decomposition of bis(2,4,6-trihalophenoxo)bis(pyridine)copper(II), I - 4, to polymer, equation I - 12.



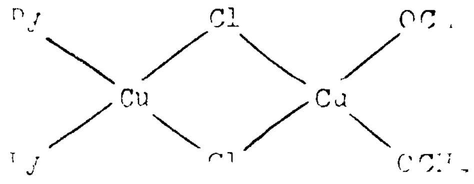
I - 4

This reaction, which was first described by Blanchard, et al(2), was chosen because it was felt that the stable phenoxocopper(II)-complex closely resembled the proposed phenoxocopper(II) intermediates in the catalytic polymerization. The overall mechanism of oxidative coupling of phenols can be described in two stages. The first stage deals with the oxidation of copper(I) to copper(II) and the formation of a phenoxocopper(II) intermediate. The second half involves the decomposition of this intermediate complex with the subsequent formation of polymer. Commencing with a stable phenoxocopper(II) complex would eliminate investigation of the first stage, and permit complete emphasis on the mechanism of carbon-oxygen coupling. This thesis will show that this stage, as well as the first stage, is very complicated.

I - 2 Reaction Mechanism

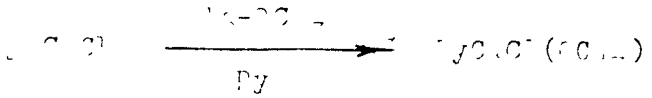
A. Role of the Copper(II) Complexes

It has been shown that only a limited number of copper(II) complexes will oxidatively couple phenols effectively(31). The most active reagents were products of the autoxidation of various copper(I) salts. Detailed studies on the autoxidation of these copper(I) complexes in the absence of phenol led to information regarding the catalyst structure. One product, which analysed as $PyCuCl(OCH_3)$, was found to be at least as active as copper(I) chloride in the oxidation of 2,6-dimethylphenol when used in equivalent amounts based on copper content. The structure I - 5 was postulated for this compound.



I - 5

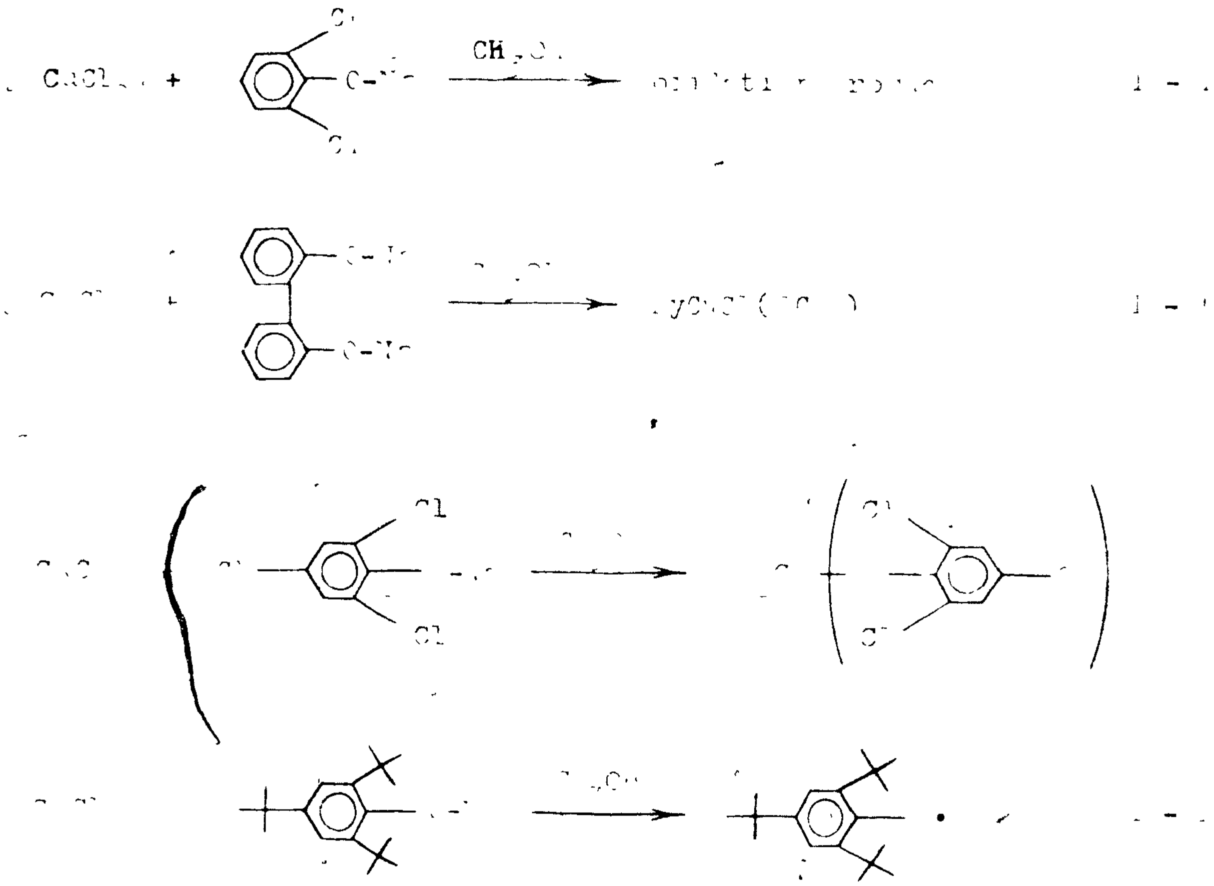
This complex was prepared from copper(I) chloride, or Py_2CuCl_2 by either reaction I - 13 or 14.



I -

A small number of copper(II) complexes containing hydroxyl groups was also found to be active oxidizing agents.

Attempts to prepare phenoxo-pyridine-copper(II) complexes by a reaction analogous to I - 14 led to a variety of results, some of which are depicted in reactions I - 15 to 18.



This sequence of reactions offers a great deal of information regarding the overall mechanism, and provides strong support for the hypothesis that phenoxocopper(II) complexes and phenoxy radicals are involved.

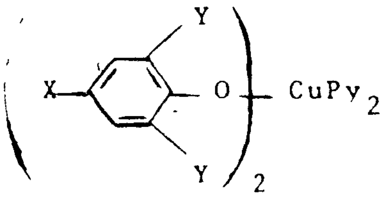
Blanchard, *et al*(2), have prepared and characterized a number of stable phenoxocopper(II) complexes from polyhalogenated phenols, Table 1. The only stable complex possessing an alkyl group was 4-<u>tert</u>-butyl-2,6-dibromophenol. Even this could not be recrystallized since it decomposed so readily. This was not surprising since previous work(8) had shown that substituents which diminish the reducing power of the phenol, ie., electro-negative groups, tend to reduce the polymerization rate. For example, 2,6-dimethylphenol polymerizes readily at room temperature, but temperatures in the neighbourhood of 60° C were required to oxidize 2,6-dichlorophenol. The products of the thermal decomposition of the aforementioned stable copper(II) complexes were characterized, Table 2 and 3, but little was offered in the way of mechanisms.

Harrod also reported the preparation and decomposition of several phenoxocopper(II) complexes(34) using 2,4,6-trichlorophenol and a variety of neutral ligands, Table 4.

A number of phenoxosilver(I) complexes **was** also prepared and decomposed, Table 5. This allowed comparison with the phenoxocopper(II) compounds and with the previous work by Hunter, <u>et al</u>(9). The low molecular weights of the polymers were attributed to the fact that the silver compounds were insoluble.

TABLE 1

Phenoxo-Pyridine-Copper(II) Complexes (2)



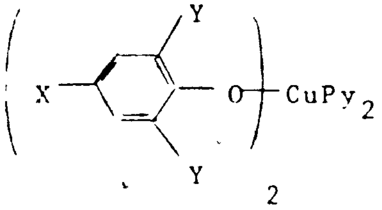
Parent phenol		Result[a]	Colour[b]	Decomp. temp. °C
X	Y			
Cl	CH_3	Low polymer	---	---
Br	CH_3	Low polymer	---	---
Cl	Cl	Stable	Deep brown	125-127
H	Cl	Stable	Deep brown	237-240
Br	Cl	Stable	Red-brown	143-145
Cl	Br	Stable	Red-brown	---
Br	Br	Stable	Red-brown	130-132
tert-Bu	Br	Stable	Red	123-125
Br	Br[c]	Stable	Deep brown	108-110
Cl	Cl[d]	Stable	Deep brown	192-195
tert-Bu	CH_3	Mixture[e]	Brown	---
CH_3	CH_3	Mixture[e]	Tan	---

a By stable is meant, the compound is capable of isolation and characterization.
b After recrystallization.
c 2,4,6-Tribromo-3-methoxyphenol.
d Pentachlorophenol.
e Mixture of complex plus decomposition products.

(2) H.S. Blanchard, H.L. Finkbeiner and G.A. Russell, J. Polym. Sci., *58*, 480 (1962).

TABLE 2

Thermal Decomposition of Phenoxo-Pyridine-Copper(II) Complexes (2)



Parent phenol		Time,	Yield, %		$[\eta]$,	
X	Y	hr.[a]	$Py_2CuX(Y)$	polymer	dl./g.[b]	M.W.[c]
Cl	Cl	2.	92	88	0.06	9,600
Br	Br	0.20	--	Unstable	--	---
H	Cl	12.[d]	0	0	--	---
Br	Br[e]	0.75	83	90	0.02	2,300
Br	Cl	0.25	84[f]	90	0.07	11,000
Cl	Br	3.	97	--	0.01	---
Cl	Cl[g]	16.	0	0	--	---
Cl	Cl[g]	2.[h]	--	87	0.02	---

[a] Time at reflux in toluene.
[b] Intrinsic viscosity, $CHCl_3$, 25°C.
[c] Ebulliometric, C_6H_6.
[d] Refluxing benzene.
[e] 2,4,6-Tribromo-3-methoxyphenol.
[f] 60% Py_2CuBr_2.
[g] Pentachlorophenol.
[h] Refluxing diphenyl ether.

(2) H.S. Blanchard, H.L. Finkbeiner and G.A. Russell, J. Polym. Sci., 58, 481 (1962).

TABLE 3

Thermal Decomposition of Bis(2,4,6-trichlorophenoxo)-bis(pyridine)Copper(II) Complex in Various Solvents. (2)

Solvent	Time, hr.[a]	Yield, %		$[\eta]$, dl./g.[b]
		Py_2CuCl_2	polymer	
C_6H_6	1.25	100	100	0.05
Py[c]	2.	0	0	--
C_6H_6/Py[c,d]	5.25	15	-	--
C_6H_6/Py[c,e]	4.	0	0	--
Isooctane[c]	4.	0	0	--
Acetone[c]	96.	0	0	--
$C_6H_5NO_2$	2.	96	92	0.05
$CHCl_3$	1.	-	-	0.025
$C_6H_5CH_3$	2.	92	88	0.06
CH_3OH[c]	2.	0	0	--
Cyclohexene[c]	3.	0	0	--
C_2Cl_4	2.	-	-	0.05

a Time at reflux.
b Intrinsic viscosity, $CHCl_3$, 25°C.
c Recovered starting material.
d 4% pyridine.
e 20% pyridine.

(2) H.S. Blanchard, H.L. Finkbeiner and G.A. Russell, J. Polym. Sci., 58, 482 (1962).

TABLE 4

Thermal Stability of Trichlorophenoxocopper(II) Complexes(34)

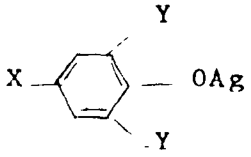
Neutral ligand	Thermal behavior
Biquinolyl	Too unstable to be isolated
Triphenylphosphine	Too unstable to be isolated
2,6-Dimethylpyridine	Stable enough to be isolated as solid. Lifetime in benzene ~ hours at room temperature*
Ammonia ethylamine	Rapid decomp. at ~ 90°C in solid. Lifetime in benzene ~ days at room temperature*
Pyridine	Sharp decomp. at 125-127°C in solid. Lifetime in benzene ~ months at room temperature*, ~ 12 hrs. at 80°C.
None	Sharp decomp. at 143-145°C in solid.
2,2'-Dipyridyl	m.p., 175-177°C; decomp. ~ 195°C
Tetraethylethylenediamine	m.p., 167-168°C.
Tetramethylethylenediamine	m.p., 182-184°C. Lifetime in benzene ~ years
o-Phenanthroline	m.p., 220°C; decomp. ~ 220°C.

* Observations made on numerous solutions.

(34) J.F. Harrod, Can. J. Chem., 47, 641 (1969).

TABLE 5

Decomposition of Phenoxosilver(I) Complexes (2)



Parent phenol X	Parent phenol Y	Method of decomposition[a]	Yield %	Softening point °C	$[\eta]$ dl./g.[b]	M.W.[c]
Br	CH_3	A	65	220	0.09	--
Br	CH_3	B	48	-	0.06	1600
Br	CH_3	C	41	210	--	--
Cl	CH_3	A	30	200	--	2100
Cl	CH_3	B	20	185	0.10	1600
Br	Br	B	72	260	0.04	7500
Br	Br	C	44	300	--	--
Br	Br[e]	B	65	180	0.04	5500
Cl	Cl	B	60	200	0.05	8000
Cl	H[f]	A	-	140	--	1500
Cl	H[f]	B	45	140	--	1500
Br	H[f]	A	40	150	--	2100
Br	H[f]	B	-	150	--	1800
Br	Cl[g]	-h	40	195	0.015	1200

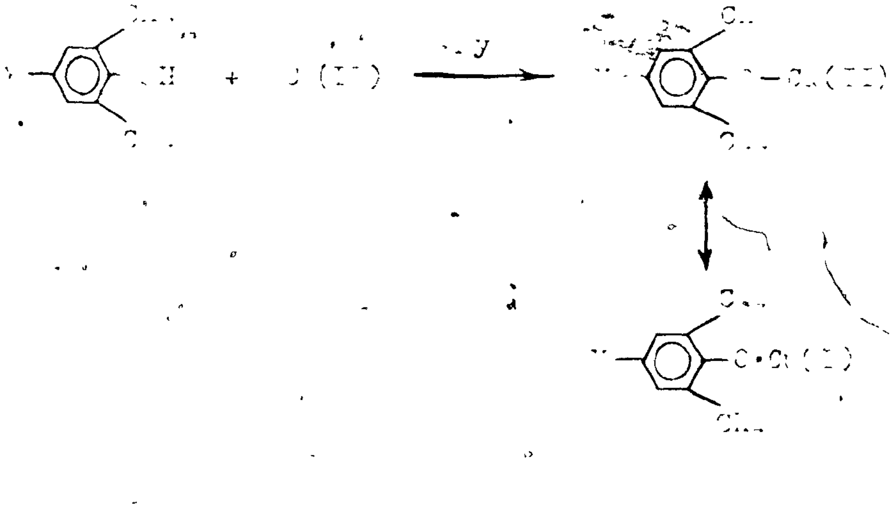
[a] A= ethyl iodide, heat; B= C_6H_6, heat; C= $Py/C_6H_5CH_3$, heat.
[b] Intrinsic viscosity, $CHCl_3$, 25°C.
[c] Ebulliometric C_6H_6 or $CHCl_3$.
[e] 2,4,6-Tribromo-3-methoxyphenol.
[f] Polymers contained 20-30% residual halogen.
[g] Pentachlorophenol.
[h] Decomposed in refluxing xylene.

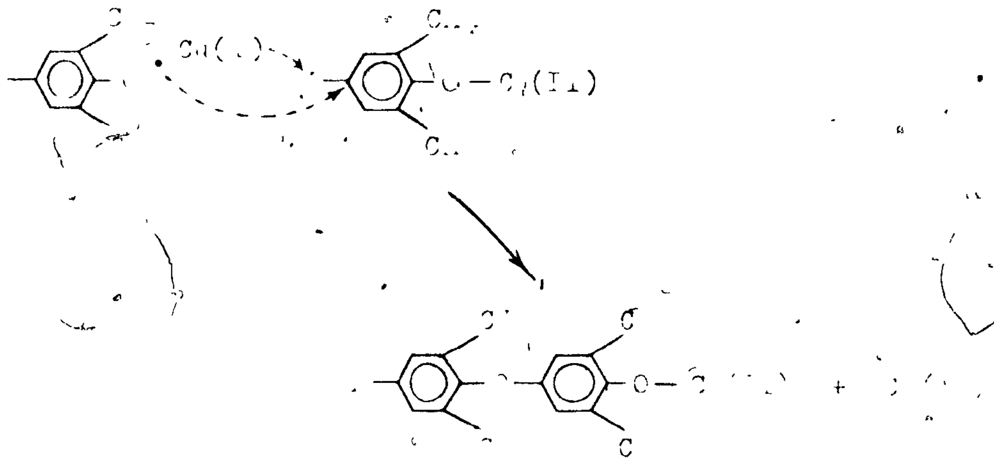
(2) H.S. Blanchard, H.L. Finkbeiner and G.A. Russell, J.Polym. Sci., 58, 483 (1962).

Decomposition was carried out under heterogeneous conditions.

B. Decomposition of Phenoxocopper(II) Complexes to Polyphenylene Ethers

Preliminary work on the oxidation of 4-halo-2,6-dimethylphenol was interpreted in terms of the formation of complexed phenoxy radicals(2), with copper-assisted transfer of halogen atom, equation I - 19 to 21. More recent work, including that described in this thesis, indicates that there is no association between the phenoxy radicals and copper(I).





The existence of phenoxy radicals is well known(35,36). If phenoxy radicals are indeed formed, then under comparable conditions, the resulting radicals should be detected by electron spin resonance spectroscopy provided they are concentrated and stable enough. This was found to be true for tri-*tert*-butylphenol(31), equation I - 18.

Cook has reported(37) that the tri-*tert*-butylphenoxy radical assumes a very deep-blue colour. As early as 1917, Hunter noted the formation of blue to blue-green colours(9) during extensive research on the decomposition of phenoxosilver(I) complexes. Staffin and Price(3) observed the formation of a green colour which faded on warming when 4-bromo-2,6-

dimethylphenol was treated with a catalytic quantity of iodine at $-70^{o}C$. Cook and Gilmour reported that when tribromophenoxosilver(I) in benzene was treated with a crystal of iodine, the benzene assumed an intense blue colour(38). This colour faded on standing for an hour. These three reactions all resulted in the formation of polymer. On repetition of these reactions, Blanchard, *et al*(2), were not able to detect any electron spin resonance signal. This would imply that either the colours were not due to phenoxy radicals or that their concentration was somehow too low to be detected. It is improbable that any colour could be detected in the decomposition of phenoxocopper(II) complexes since the latter are already intensely coloured.

Harrod reported the existence of a ligand-to-metal charge transfer band(34) in the near ultra-violet. Such a low energy photochemical charge transfer excitation is in accord with the hypothesis of a facile homolysis of the Cu-O bond.

Kopylov and Pravednikov failed to positively detect phenoxy radicals by electron spin resonance spectroscopy on decomposing a solution of 4-bromo-2-methylphenoxocopper(II) prepared from freshly autoxidized copper(II) and 4-bromo-2-methylphenol in an inert atmosphere(39). This is not surprising in view of results presented later in this thesis.

Huysmans and Waters(40,41) have reported that by passing a solution of a phenol in benzene through a thin layer of a solid oxidant (silver oxide or lead dioxide) placed in an electron spin resonance cell, it was possible to record the spectra of many unstable primary radicals, including 2,6-dimethylphenoxy radical. When the flow was stopped, strong electron spin resonance spectra of secondary radicals developed. These secondary radicals were shown to be due to coupling at the 4- position. It was found that on heating, this secondary radical spectrum increased in intensity, only to return to the original level on cooling. The reversible behaviour can be understood by assuming an equilibrium between the radicals and quinone ketal intermediates which will be described later.

Very recently, Tsuruya, et al, detected by electron spin resonance spectroscopy the formation of phenoxy radicals during the solid-state thermal decomposition of trichlorophenoxo-hexamethyl-phosphoramide-copper(II) complex to polymer(42). This result confirmed the participation of phenoxy radicals in this type of coupling reaction.

C. Polymer Formation

i) Introductory Remarks

Polymerizations are generally classified as polyadditions or polycondensations. Polyaddition implies that a growing molecular chain reacts only with monomer units. This could proceed through two possible mechanisms. The first method, known as chain-growth polymerization, involves the polymer molecule growing extremely rapidly. High polymer is formed at the very start of the reaction. If termination is occurring, the concentration of polymer molecules growing at any instant will be very low. The intermediate reaction mixture, therefore, consists mainly of inactive high polymer and unreacted monomer.

The second method of polyaddition involves polymer chain growth by a series of discrete reaction steps. The intermediate stage of polymerization consists of polymer chains capable of further growth by reaction with monomer. The number-average molecular weight of the polymer thus increases proportionately with monomer conversion. In general, the intermediates in step-growth polymerizations are relatively stable.

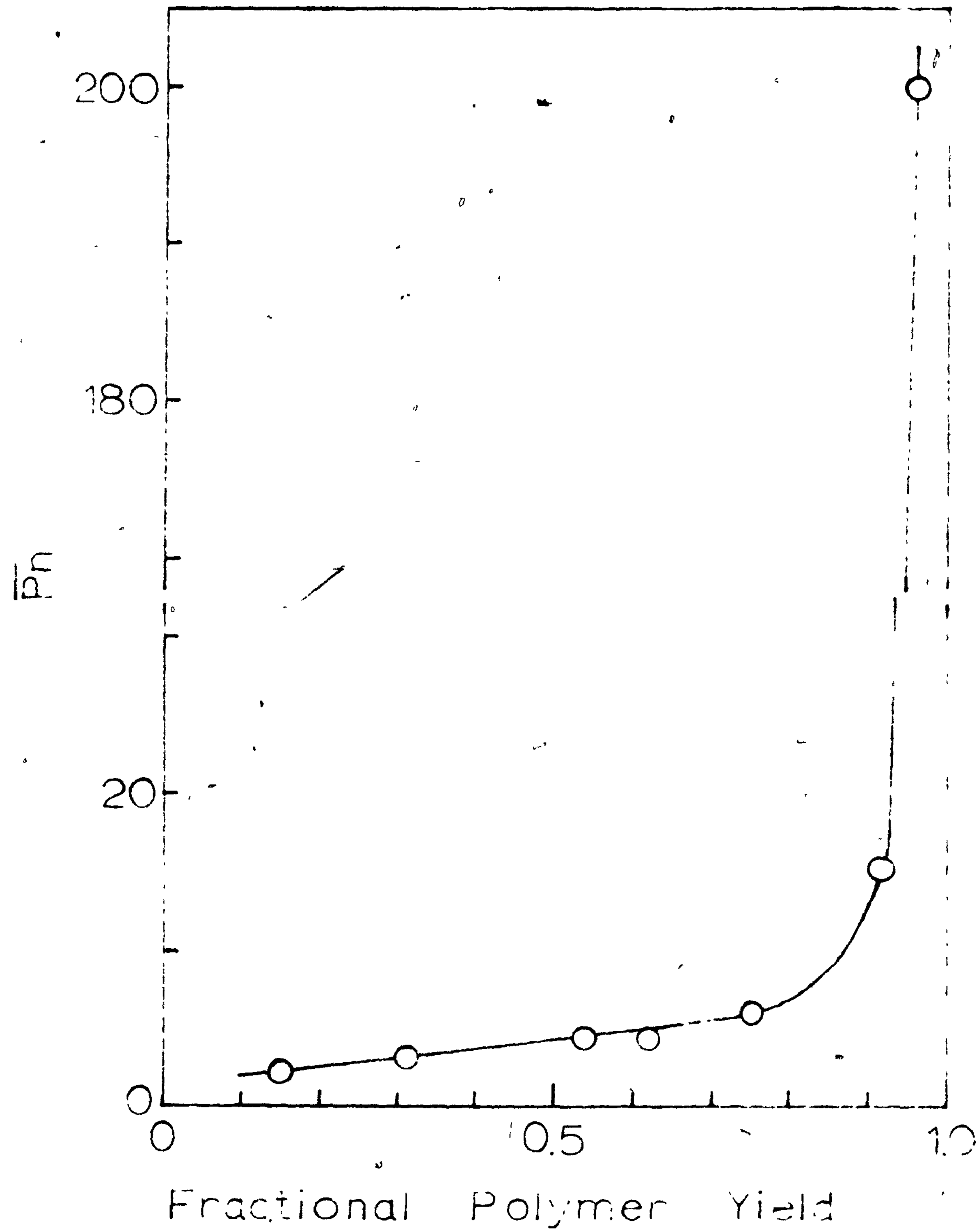
Polycondensation also implies a step-wise reaction. However, polymer growth occurs through reaction with other polymer chains as well as with monomer. Long reaction times are essential to obtain polymers of high number-average molecular weights.

During the catalytic oxidative coupling of phenols, the degree of polymerization remains quite low throughout most of the reaction, but rises sharply towards the end(43), Figure 1. Identical polymers were obtained from dimers, trimers and other oligomers which were used as "monomers". This type of behaviour can be explained only if polymer molecules are reacting with each other as well as with the monomer(43,44).

Figure I - 1

Dependence of Degree of Polymerization on Fractional Polymer Yield*

* reproduced from Ref. (43).


200
180
20
0
$\overline{P}_n$
0
0.5
1.0
Fractional Polymer Yield

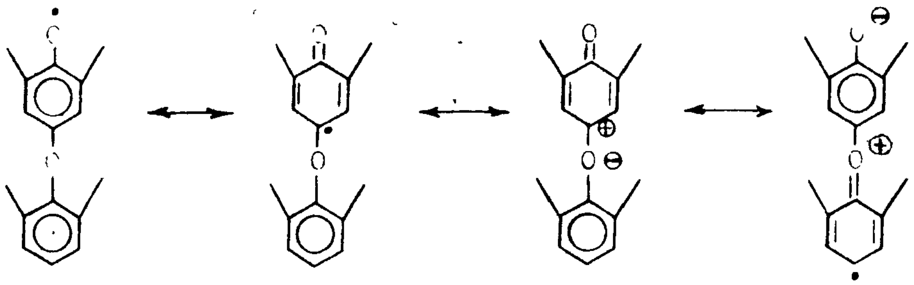
The coupling of polymer chains must also be reversible in order to account for the extremely low degree of polymerization throughout most of the course of reaction. Removal of water by addition of magnesium sulphate in equation I - 1 greatly enhanced the rate of polymerization(33). Redistribution of phenolic dimers with a number of other phenols(45,46), and the depolymerization of poly-2,6-dimethyl-1,4-phenylene ether with 2,6-dimethylphenol lend further support to the reversibility of the reactions.

ii) Suggested Mechanisms

In order to explain the above results, three mechanisms were proposed(47,48).

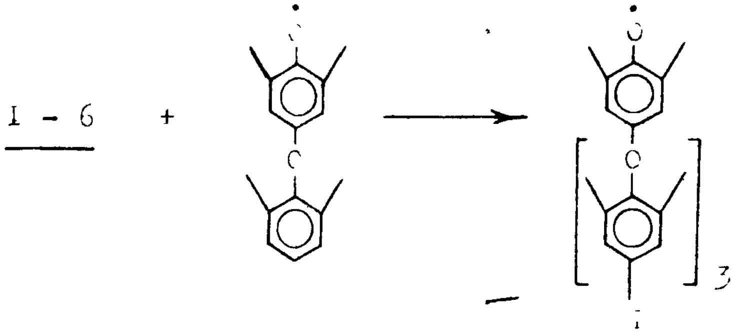
a) End-linking of Polymer Radicals

In this mechanism, which is generally referred to as the "uncoupled electron" mechanism, polymeric phenoxy radicals couple directly; with the oxygen atom of one, attacking the 4- position at the end of the chain of the other. This implies the ability of an electron to transfer from head-to-tail in a polymer chain, equation I - 22 to 23.



I - 6

I - [illegible]



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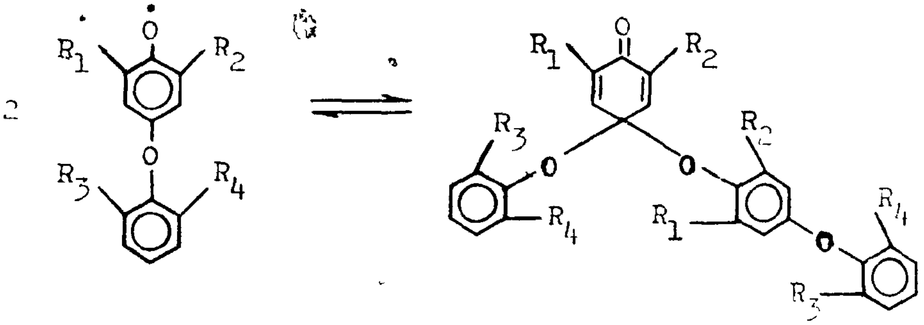
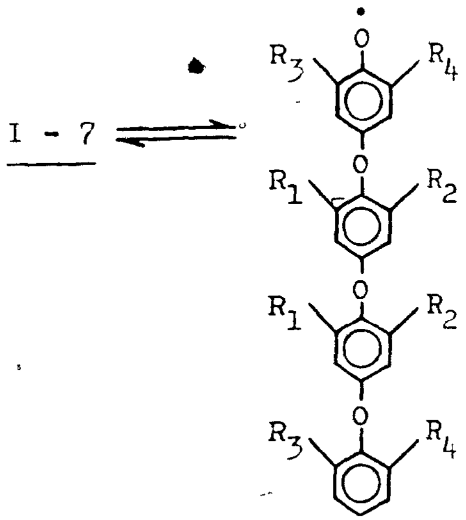
b) Quinone Ketal Rearrangement

This mechanism postulates the formation of quinone ketals by the combination of two phenoxy radicals, followed by rearrangement, equations I - 24 and 25.



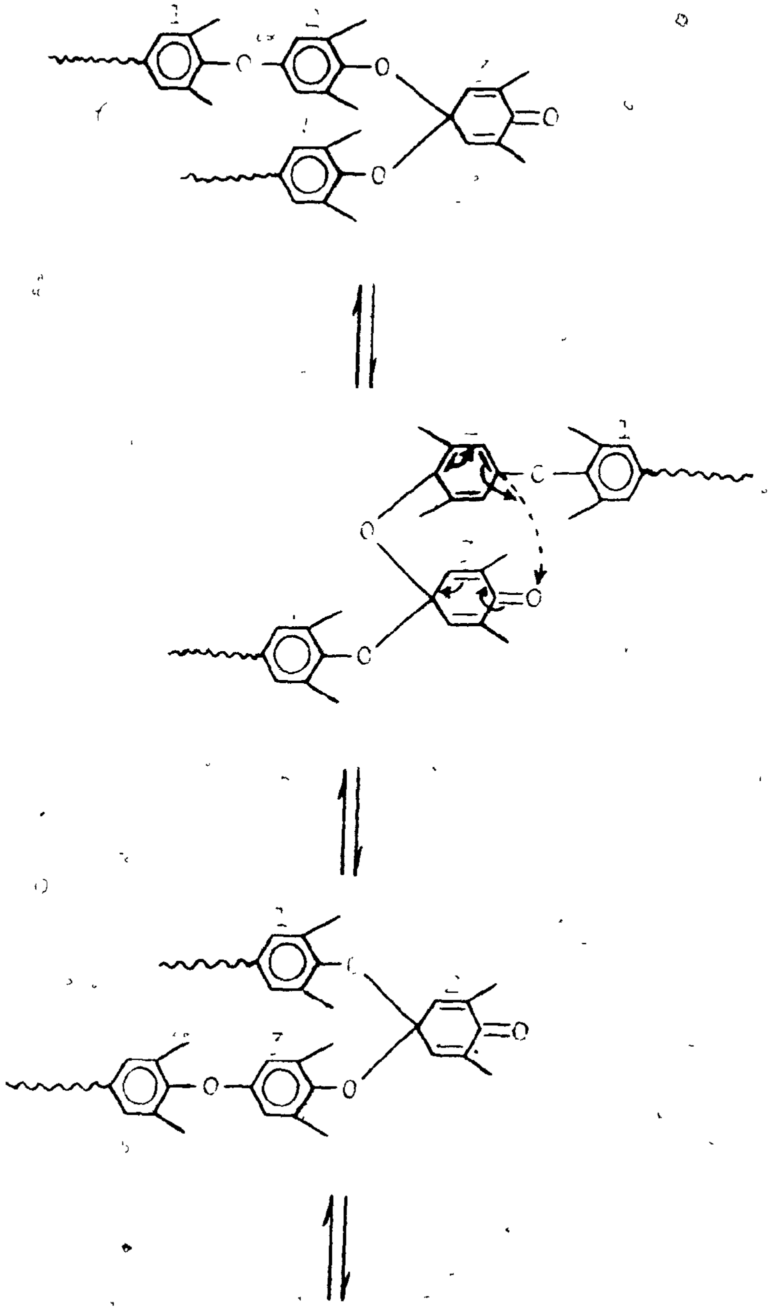
I - 7

I - 24



I - 25

Rearrangement presumably takes place by a series of electron displacements involving concerted homolytic breaking of the ketal C-O bond and formation of a new C-O bond as shown in equations I - 26 to 29.



I - 26

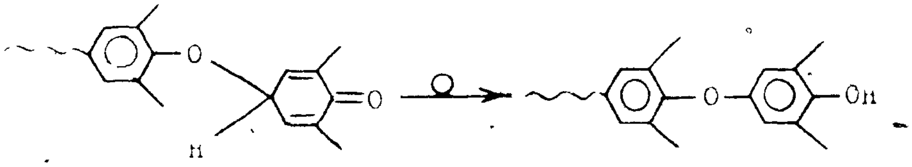
I - 27

I - 28

etc.

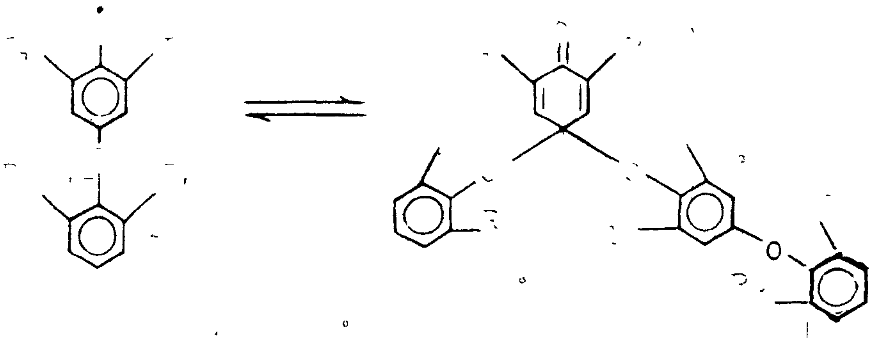
I - 29

Rearrangement usually occurs along the entire length of the molecular chain. When by successive rearrangements of this type one of the terminal rings becomes the dienone ring, enolization yields the coupled phenol, equation I - 30.

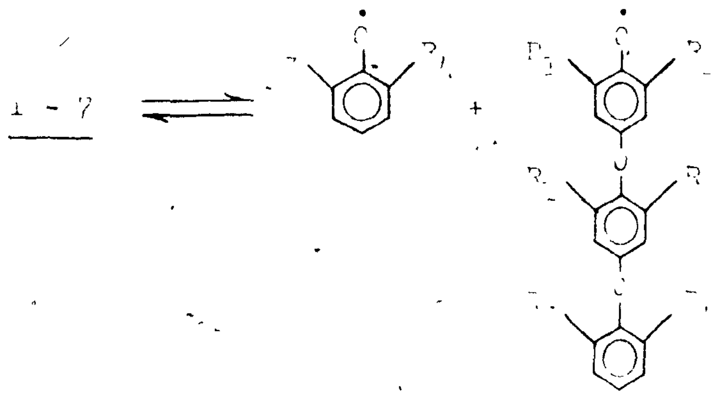


c) Quinone Ketal Equilibration

This mechanism involves the formation of a quinone ketal which then dissociates immediately to either regenerate the radicals from which it was formed, or to produce two new phenoxy radicals, one containing one more and the other one less aryloxy unit than the original, equations I - 31 and 32.



I - 7



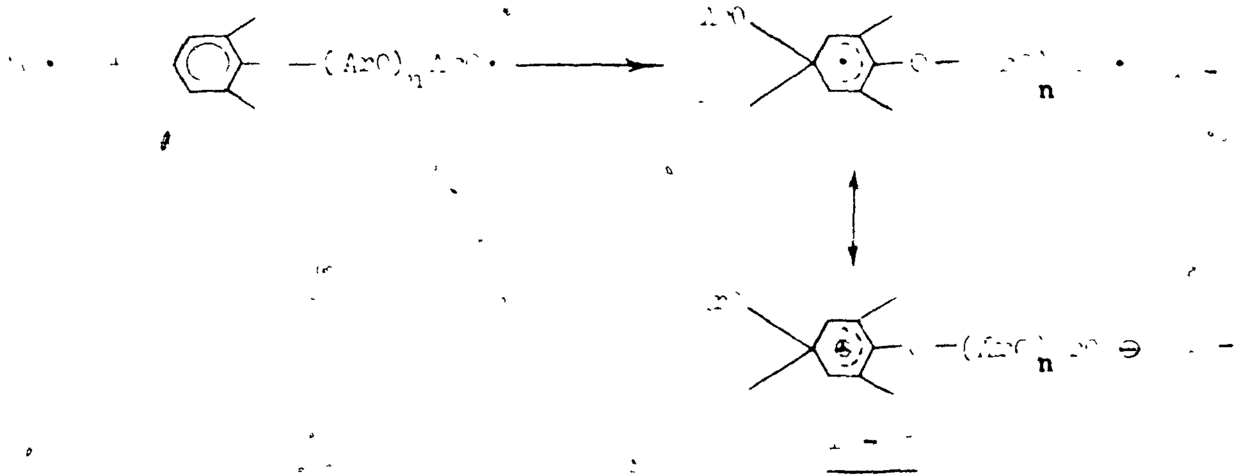
I -

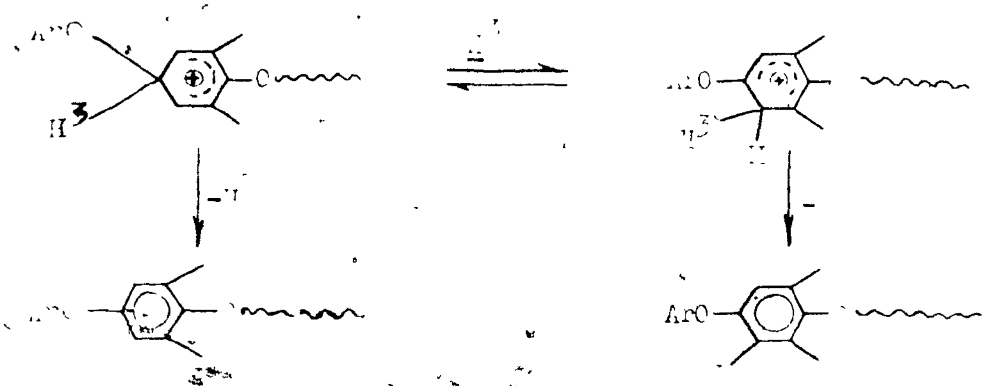
The coupling of polymer radicals to polymeric phenols is the result of rapid redistribution of polymeric phenols to produce monomer, which couples with another phenolic species.

iii) Discussion of the Proposed Mechanisms

The mechanism of coupling is best determined by examination of the reaction products at various stages of reaction. The oxidation of a mixture of phenols has resulted in copolymers of random structure (49), although block copolymers have been obtained under special conditions(50). Numerous techniques were employed to determine the mechanism of coupling of phenols. However, much of the evidence rested on the identification of the initial products from the oxidation of "dimers", either with themselves or redistributed with other phenols. These dimers often contained mixed substitution patterns to facilitate product structural identification.

Butte and Price(51) found that in the oxidative polymerization of 4-H^3-2,6-dimethylphenol or 3-H^3-2,6-dimethylphenol, 23% of the label in the former was retained while 16% of the label in the latter was lost. To account for this, an extension of the "uncoupled electron" mechanism was proposed, equations I - 33 to 37. The phenonium ion, <u>I - 8</u>, could lose the 4- proton directly or undergo simple migration. This migration allows better resonance stability at the 2,6- positions.





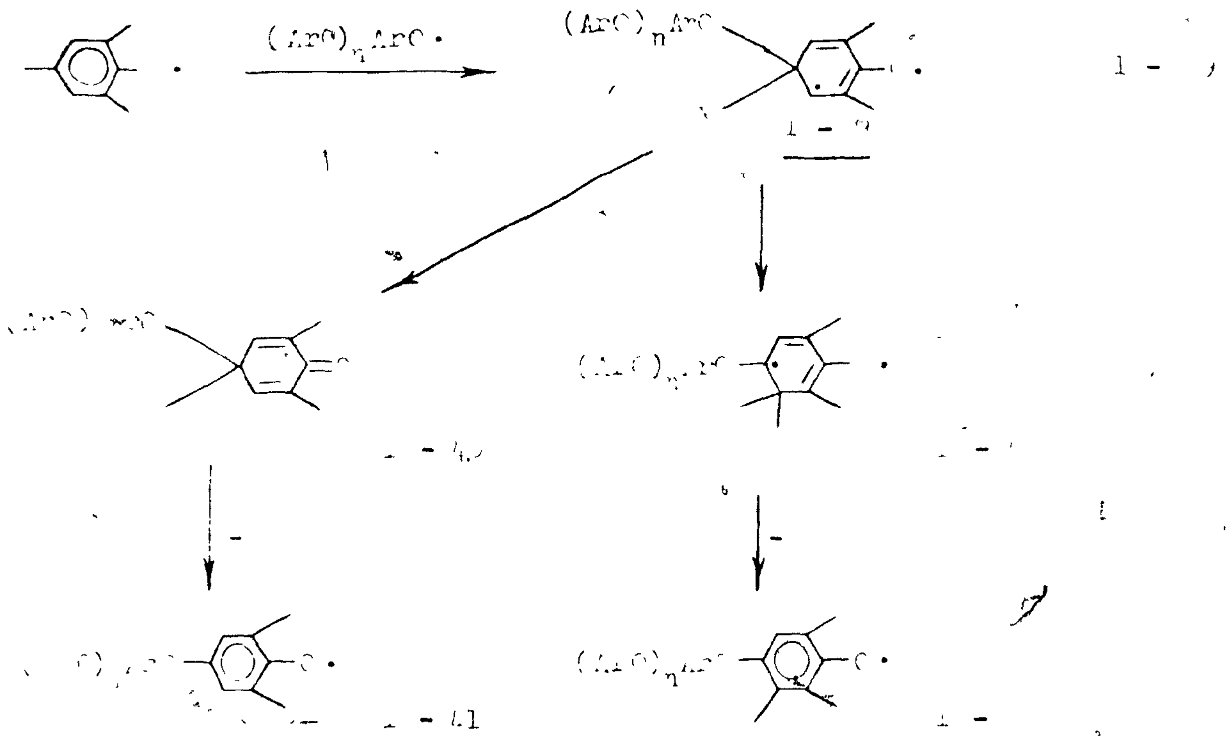
I -

I - 36 [illegible]

I - 37

[illegible]

McNelis suggested an alternate scheme to explain proton migration(52). Here, the "tail" of the monomer interacts with the "head" of the macromolecule; the opposite of that proposed by Butte and Price. Since the work by McNelis was performed in an acidic medium and involved the effect of hydrogen ions, Kopylov and Pravednikov(53) modified this mechanism for a basic solution, equation I - 38 to 43.



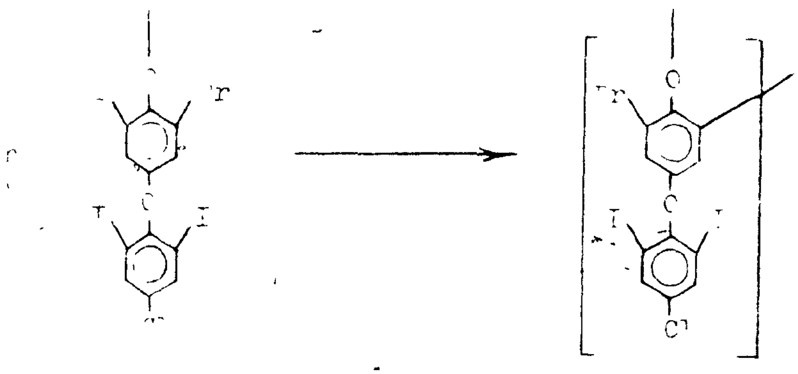
It was suggested that the reaction proceeds mainly by route I - 40 when X is a halogen. On the other hand, where X is hydrogen, tritium or methyl, the process could involve both routes I - 40 and I - 42, giving an isotopic product.

There is considerable evidence against the "uncoupled electron" mechanism.

1) The reaction is carried out in an organic amine or in an inorganic base as medium, where the existence

of a phenonium cation is improbable.

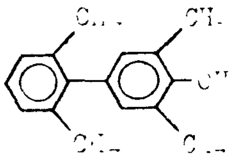
2) Kopylov and Pravednikov(53) have shown that the proposed transfer of a resonance electron through the whole polymer chain is impossible without rupture of the chain. It was suggested that electron transfer could not proceed past the second aryl ether oxygen. This can be more dramatically emphasized(54) in the products of oxidation of 4-(4'-chloro-2',6'-diiodophenyl)-2,6-dibromophenoxosilver(I), I - 10, equation I - 44.



- 10

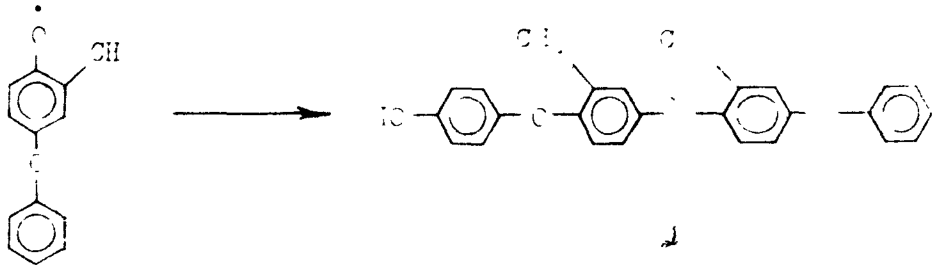
If the electron transfer were permitted into the second unit, coupling would be expected by displacement of the more reactive iodine, contrary to the experimental result. Bolon prepared the stable 2,6-di-tert-butyl-4-phenylphenoxy radical and found no detectable spin transmission through even a single diaryl ether linkage(55).

3) 4-(2',6'-dimethylphenyl)-2,6-dimethylphenol, I - 11, should be reactive by the uncoupled electron mechanism. It was found to be incapable of oxidative coupling (32).



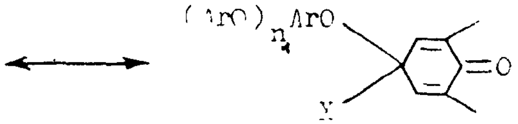
I - 11

4) Analysis of the products of oxidation of various phenol dimers have shown the existence of products which cannot be explained by this mechanism(45). A typical example is shown in equation I - 45.



From equation I - 39, it can be seen that the mechanism proposed by Kopylov and Pravednikov(53) is essentially an extension of the quinone ketal mechanisms. Quinol ethers, I - 12, are formed by the attack of polymeric radicals on monomeric radicals rather than with other oligomers, equation I - 46.

I - 9



I - 19

I - 40

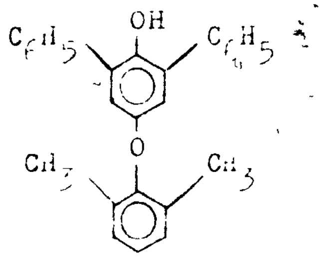
Cooper, *et al*(48), have separated monomer, trimer, tetramer and unreacted dimer at early reaction times from the oxidative coupling of 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol. This result can only be accounted for in the quinone ketal equilibration mechanism. The other two mechanisms do not justify the formation of products with an odd number of rings. This finding, however, does not rule out the possibility of the subsistence of the other two mechanisms, nor does it prove the existence of quinone ketals.

The dimers from several 2,6-disubstitutedphenols have been redistributed with tri-*tert*-butylphenoxy radicals(46). Analysis of the various reaction products lends additional support to the idea that equilibration is an important process that occurs during the polymerization of 2,6-disubstitued phenols. The formation of quinone ketals is demanded by the nature of these products.

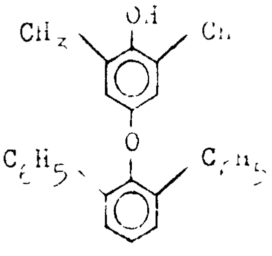
White investigated the redistribution of polymer with different phenols(23). The resulting mixed dimers can only be explained by the quinone ketal equilibration mechanism.

"Mixed" dimers can be labelled AB, where A and B represent the top and terminal rings, respectively. Structural determination of the products from the oxidation of these dimers offers evidence for the mechanism of coupling. The end-linking mechanism would predict a perfectly alternating product, ABAB... The quinone ketal rearrangement mechanism would predict many different sequences of rings in an oligomeric product, but none with more than two similar rings in succession. The sequences ABA, AAB, BBA, etc. were possible, but not BBB or AAA. The phenolic ring of every product must be a B ring. The quinone ketal equilibration mechanism would predict products having any sequence of rings, with either ring of the dimer appearing as the phenolic ring of the polymer. Intensive research by Mijs, and coworkers(45), showed that the coupling of phenoxy radicals, using several mixed dimers, proceeds through the formation of quinone ketals. It was also noted that rearrangement can be competitive with equilibration. The higher the temperature and the bulkier the substituents, the more preferable the equilibration mechanism. This was further supported by White(56).

The dimers examined previously (23,45,46,56-58) contained either the same substitution pattern in both rings, so that the rings could not be distinguished in the product, or had an open 2,6- position in one or both rings, preventing the formation of linear high molecular weight polymers. Cooper and Bennett(59) have reported the oxidative polymerization of two "mixed dimers", I - 13 and I - 14, in which both rings correspond to phenols capable of being oxidized to linear high polymers. This permitted the mechanism of coupling to be inferred from the structure of a polymeric product. Analysis of the polymer by nuclear magnetic resonance gave results which could only result from equilibration. Even under conditions preferring rearrangement(45,46), the equilibration process determined the polymer structure.



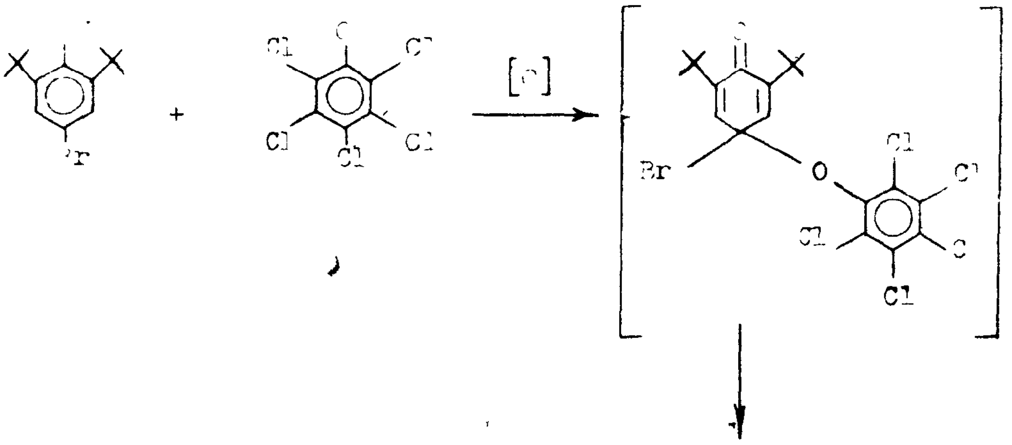
I - 13



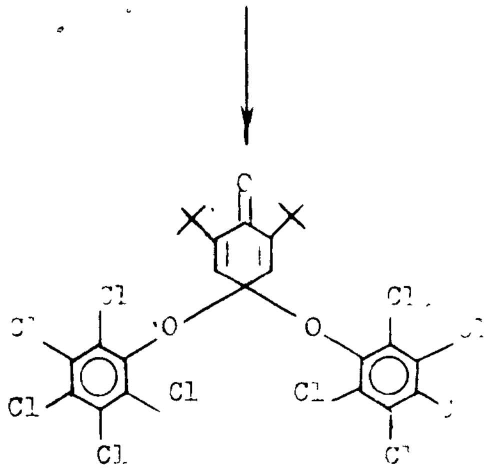
I - 14

Equilibration and rearrangement involve the same quinone ketal intermediate and are complementary reactions. The number of individual rearrangement steps required for producing a polymer molecule solely by coupling and rearrangement of polymeric radicals is extremely large. There is a high probability that dissociation and equilibration will occur at some stage of the process. Equilibration may therefore proceed by transfer of more than one unit from one molecule to another. The polymer coupling reaction likely involves both equilibration and rearrangement, with their relative importance determined by reaction conditions.

Becker(60) showed that the oxidation of 2,6-di-*tert*-butyl-4-bromophenol in the presence of pentachlorophenol gave a quinone ketal, I - 15. This could then dissociate at room temperature, equations I - 47 to 49.

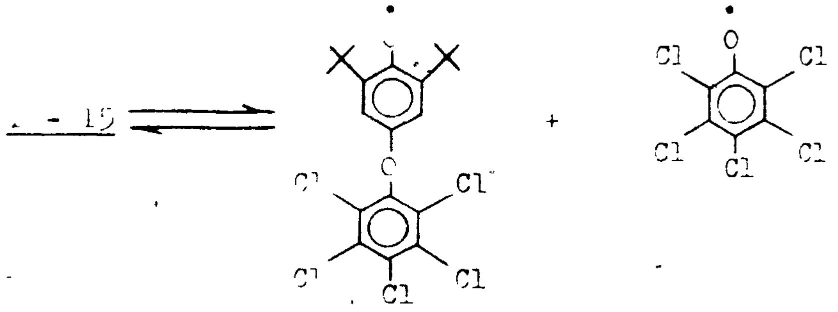


I - 15



I - [illegible]

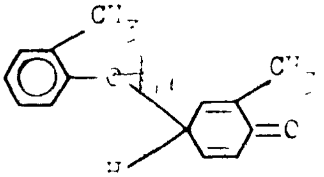
I - 15



[illegible] - [illegible]

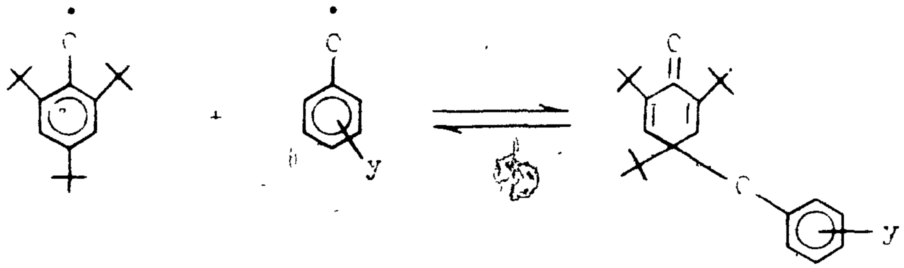
iv) Evidence of Quinol Ethers

It is well established that the carbon-oxygen dimerization of numerous phenols results in the formation of quinol ethers(35). It is also known that this process is reversible. Dimroth, et al have isolated a quinol ether(61) in the oxidation of 2,4,6-triphenylphenol. Similarly, Kopylov and Pravednikov(39) obtained a reaction product which analyzed as quinol ether, I - 16, during the oxidation of 2-methylphenol.



I - 16

Mahoney and DaRooge (62,63) performed kinetic and thermochemical studies of the reaction of tri-tert-butylphenoxy radical with a number of unhindered phenols, equation I - 50. Quinol ethers, I - 17, were isolated as reaction product. The rate of decomposition of these quinol ethers back to phenoxy radicals was calculated.



I - 50

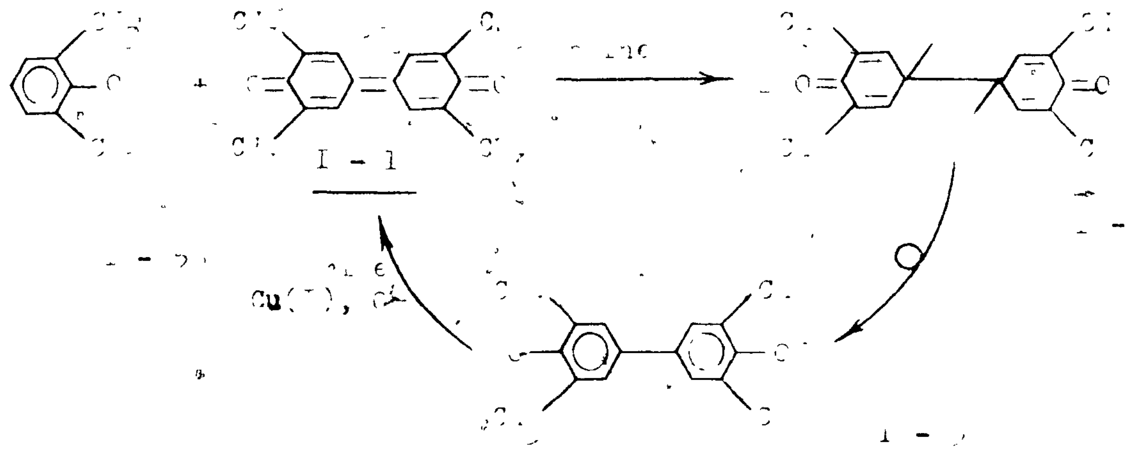
I - 17

[illegible]
[illegible] of [illegible]tituents
[illegible].

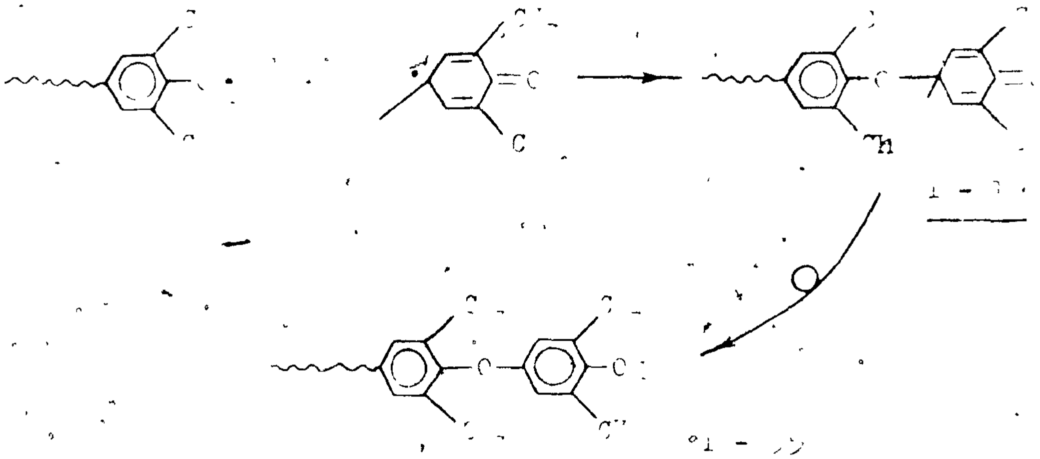
The forward and backward rate constants in this reversible reaction indicated a rapid equilibrium in the case of trichlorophenol, with the redistribution step relatively slow compared to the dimerization step.

D. Termination of Polymer Growth

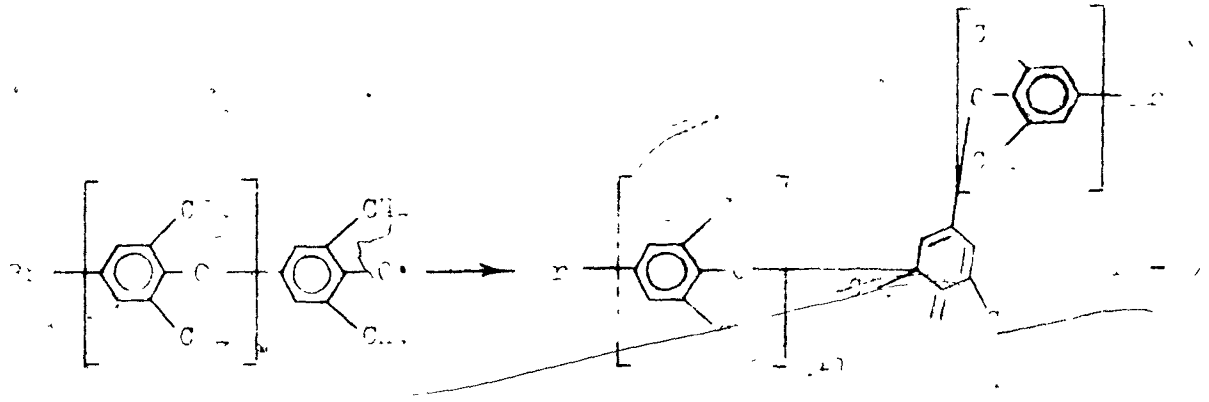
The process of termination in the oxidative coupling of phenols is not understood. It is obvious that it must somehow involve the destruction of phenoxy radicals. One mechanism of termination would involve the destruction of the monomer radicals through carbon-carbon coupling. Factors which favour carbon-carbon coupling over carbon-oxygen coupling include increased bulkiness of the substituent on the phenol(I), higher temperatures, increased steric hindrance in the amine, or amine-to-copper ratios(33). This competition between the two types of coupling at varying ligand ratios was explained (31-33) by means of two distinctly different, catalytically active pyridine-copper(II) complexes. These two complexes were thought to differ in the coordination number with respect to the amine ligand. The complex with the lower coordination number leads to carbon-carbon coupling, and vice versa. This notion was later discredited by the observation that tetramethyldiphenoquinone, I - 18, reacted very rapidly with 2,6-dimethylphenol to regenerate more diphenoquinone(64,65) under the conditions of oxidative coupling. Repetition of this process eventually removes all monomer phenoxy radicals by carbon-carbon coupling, equations I - 51 to 53.



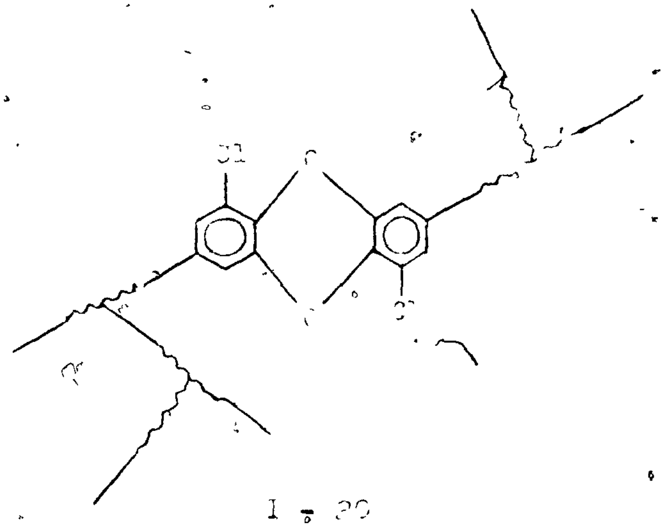
Termination also takes place by the removal of the polymeric phenoxy radicals. Endres and **Kwiatek** reported the existence of one hydroxyl group per molecular chain(43) in the polymerization of 2,6-dimethylphenol. This was based on the hydroxyl absorption at 3580 cm^{-1} by infrared spectroscopy, and on molecular weight data. These hydroxyl groups presumably result from extraction of hydrogen from the reaction medium. The "head" of the polymeric phenoxy radicals could react with the "tail" of monomer phenoxy radicals, producing a quinol ether, I - 19. These quinol ethers could then enolize giving an hydroxyl group (57,58,66), equations I - 54 and 55. The number-average molecular weight of the polymer depends on the equilibrium conditions of the coupling reactions.



Price and Chu(67) discovered that the oxidative coupling of 4-bromo-2,6-dimethylphenol with freshly autoxidized pyridine-copper(II) salts in the absence of oxygen, resulted in polymer containing much less than one hydroxyl group per polymer chain. They postulated termination involving radical coupling through the 2,6- position, equation I - 56.



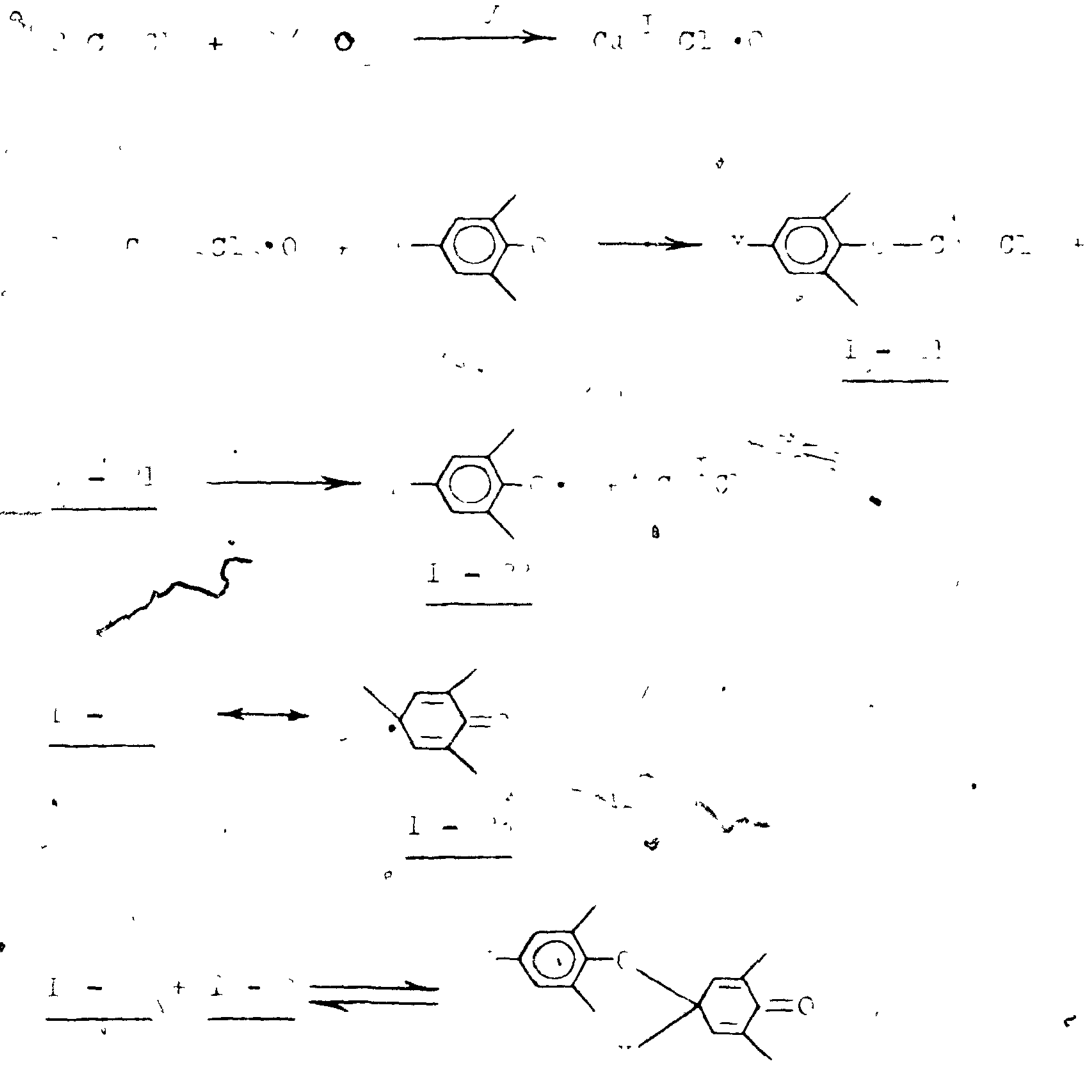
The polymers prepared from polyhalogenated phenols are not only branched, but seem to have very little residual hydroxyl. Golden(68) suggested that the formation of 2,6-dichloro-1,4-phenylene ether is terminated by dioxin formation, I - 20.



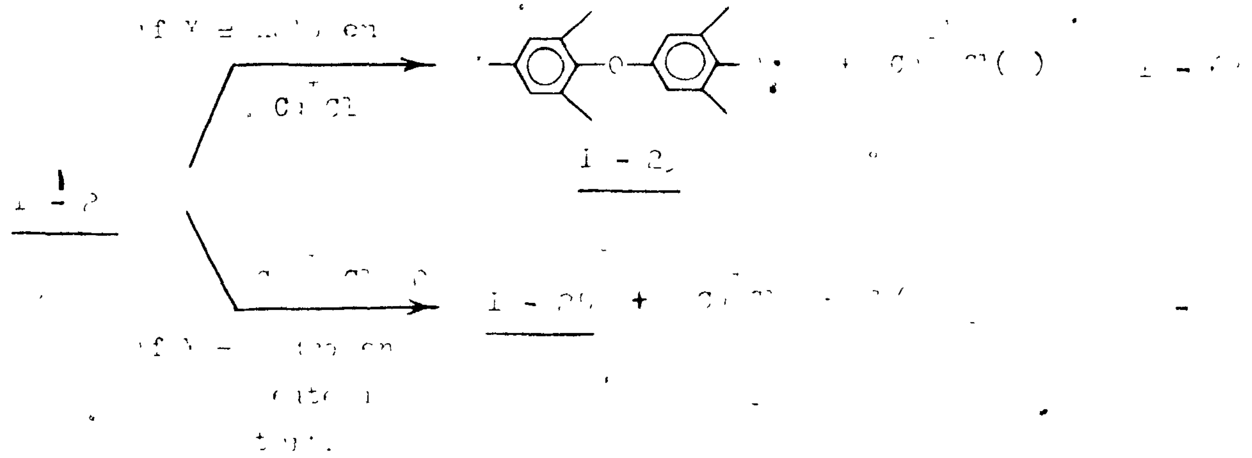
I - 20

E. Present State-of-the-Art of the Oxidative Coupling Mechanism

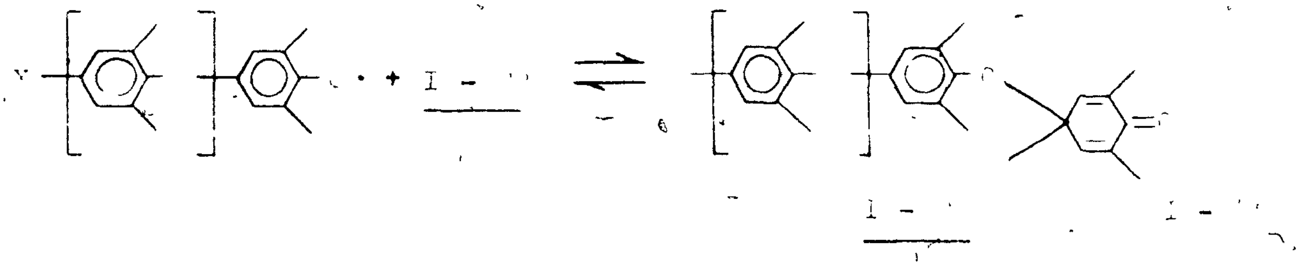
Compilation of the literature on the mechanism of copper catalyzed oxidative coupling of 2,6-disubstituted phenols has led to the conclusions shown in equations I - 57 to 70. The first stage of the reaction involves autoxidation of copper(I) to copper(II). The phenol reacts with copper(II) giving a phenoxocopper(II) complex, equation I - 58. Subsequent decomposition of this complex produces a phenoxy radical and a copper(I) intermediate, equation I - 59. Polymerization results from the carbon-oxygen coupling of the phenoxy radicals, equations I - 59 to 67. Cooper, et al(48), have shown the existence of the quinone equilibration mechanism, equation I - 67. The proton migration reported by Butte and Price (51) can only be explained by coupling of the "head" of the polymeric radical to the "tail" of the monomer radical, equation I - 64. Finally, Mijs and coworkers(45), proved that quinone ketal rearrangement could also occur, equation I - 66. The results of the studies on the degree of polymerization at various reaction times(43) can best be explained by quinone ketal equilibration. This mechanism would therefore be predominant for the oxidative coupling of 2,6-dimethylphenol under normal reaction conditions. Equation I - 62 clearly indicates that the oxidation of 4-halophenols does not proceed catalytically. Phenols unsubstituted in the 4- position do not destroy the catalyst and permit re-autoxidation of the copper(I) produced. Equations I - 68 to 70 represent the termination steps.



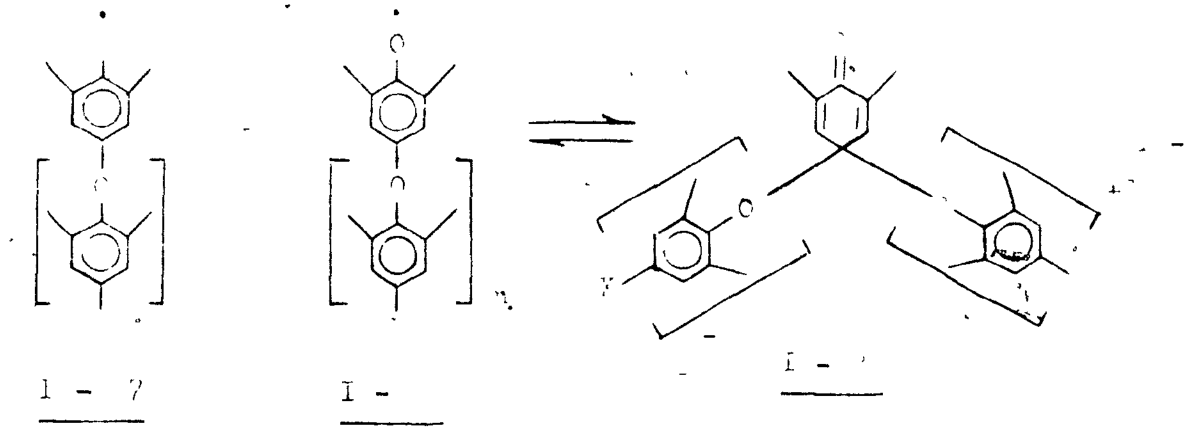
I - 74



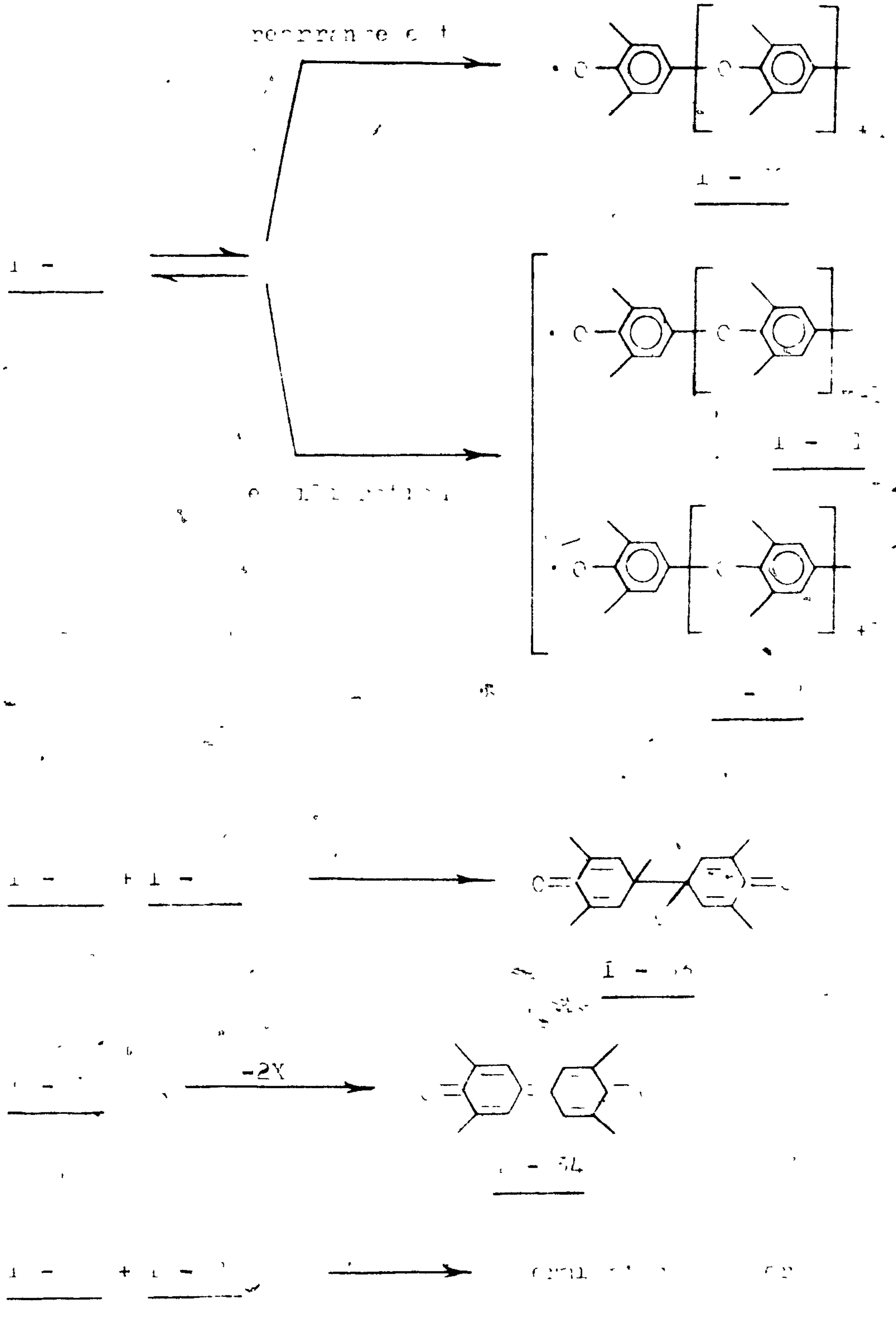
I - 2



Y
I -



Y
I - 7
I -



I - 6

F. Review of Polyhalophenylene Ethers

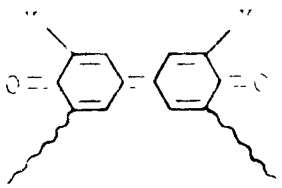
Hunter and coworkers(9,54,69-72), reported extensive investigations of polymers prepared from silver salts of various polyhalophenols. It was established that the polymers were branched, but that 4-halogen was more reactive than 2,6-halogen. It was also found that the order of reactivity of halogens was I>Br>Cl.

Similar polymers prepared by Blanchard <u>et al</u>(2), were shown to be highly branched, as evidenced by their low intrinsic viscosity compared to linear poly(2,6-dimethylphenylene ether) of approximately the same molecular weight. Extensive branching has also been demonstrated by nuclear magnetic resonance(42).

Poly-2,6-dibromophenylene ether was also found to be highly branched(2). Dewar(73) and Price(3) have both shown that bromine is very readily displaced by a phenoxy radical.

The polymers prepared from polyhalogenated phenols(2) generally featured very low number-average molecular weights (Table 2). Data presented in this thesis will show that this is due to the reactions having been quenched before maximum coupling had been achieved.

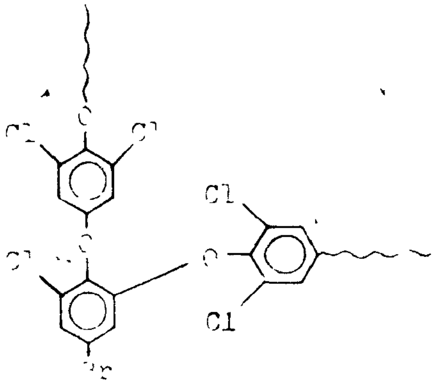
Hunter found that polymerization of triiodophenol yielded red or white products(72) depending on the reaction conditions. Similar findings of green and white polymers were obtained(2) from 2,4,6-tribromo-3-methoxy-phenol. Elemental analysis and infrared spectoscopy indicated identical structures in the latter cases. The colours were attributed to quinone portions(27) from coupling at the 2,6- position, I - 35.



I - 35

This thesis will report the existence of trapped "free" phenoxy radicals in the polymer which could account for the colour of the polymers in the above work.

Stamatoff has reported the formation of linear poly(2,6-dichlorophenylene ether) from 4-bromo-2,6-dichlorophenol(74). This polymer, I - 36, contains only a very small amount of bromine. Unfortunately, no additional information such as molecular weight was provided. Repetition of this work, reported in this thesis, shows evidence that a small degree of branching may also be present. The molecular weight of the polymer is also felt to be relatively low compared to values reported in this thesis.



I - 36

The polyhalophenols have the potential for outstanding mechanical, chemical, electrical and thermal properties, provided that they can be prepared linearly at high molecular weight. They can also be modified by the addition of stabilizers, autoxidants, fillers, pigments and similar additives known in the art. Polyhalophenols have been found to be extremely fire resistant(75). Copolymers of 2,6-dialkylphenols and polyhalophenols, containing only small amounts of the dihalophenylene ether units, offer the advantage of fireproofing with no sacrifice in other physical properties.

Knowledge of the mechanism of halogen displacement of polyhalophenols could aid tremendously in the preparation of a number of other linear poly-(2,6-dihalophenylene ethers). It could perhaps also explain why attempts at polymerization of compounds, such as 2,6-dichlorophenol and 4-chlorophenol, have been unsuccessful.

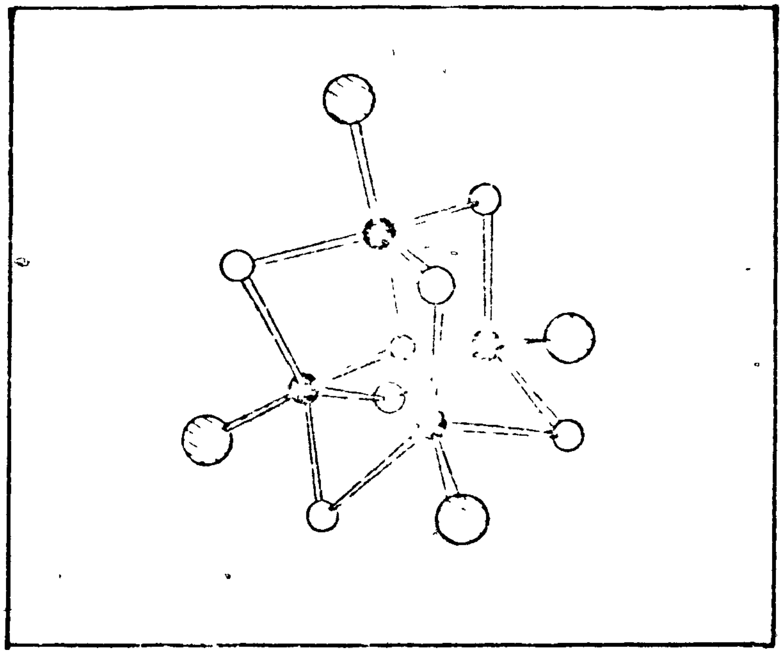
I - 3 The History of μ_4-oxo-hexa-μ-halotetra-copper(II) Complexes

This thesis reports the formation of μ_4-oxo-hexa-μ-halotetra-copper(II) complexes, $L_4Cu_4X_6{\cdot}O$, I - 37, as side products in the thermal decomposition of bis(trihalophenoxo)bis(amine)copper(II) where L = neutral ligand and X = Cl or Br. The appearance of this compound offered a great deal of insight into some unforeseen complexities in the overall mechanism of oxidative coupling of phenols.

During the course of the present study, a large number of copper(II) complexes (76-84) containing the structural unit $Cu_4X_6{\cdot}O$, Table 6, have been reported by other workers. In these complexes, a central

I - 37

◍	L
○	X
●	Cu
⊙	O

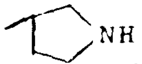


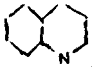
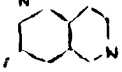
1 - 41

⊙	O
●	Mg
○	Br
◍	$O(C_2H_5)_2$

TABLE 6

Various μ_4-oxocopper(II) complexes, $L_4Cu_4X_6 \cdot O$, prepared

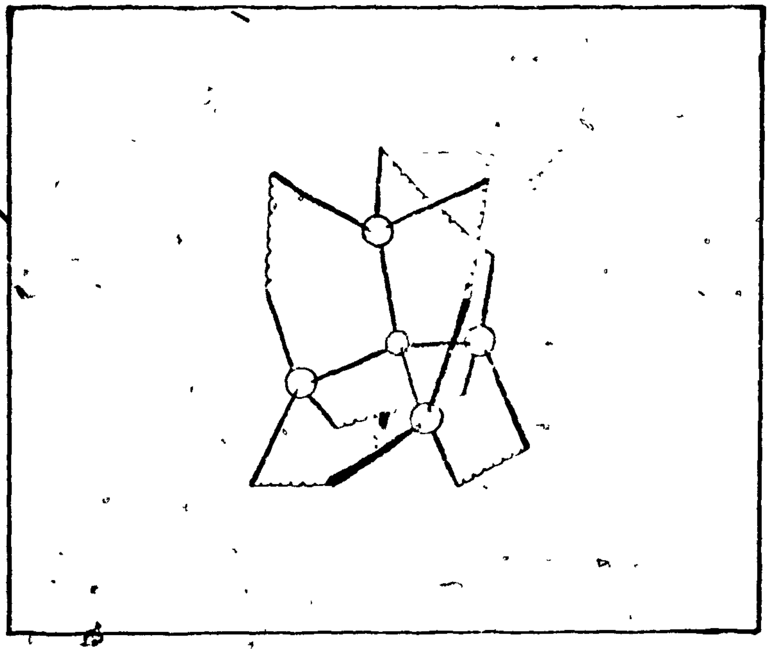
L	X	Ref.
Pyridine, C_5H_5N	Cl	76
Methanol, CH_3OH	"	82
Methanol, excess CH_3OH	"	"
N-cyano-pyrrolidine, N ≡ C 	"	"
N-cyano-piperidine, N ≡ C 	"	"
Dicyclohexylcyanamide, $(C_6H_{11})_2N-C\equiv N$	"	"
Diisopropylcarbodiimide, $(CH_3)_2CH-N=C=N-CH(CH_3)_2$	"	"
Acetonitrile, $CH_3-C\equiv N$	"	"
Benzylcyanide, $(C_6H_5)-CH_2-C\equiv N$	"	"
Dimethylformamide, $(CH_3)_2N-CHO$	"	"
α-picoline, $2-CH_3-C_5H_5N$	"	77
β-picoline, $3-CH_3-C_5H_5N$	"	82
γ-picoline, $4-CH_3-C_5H_5N$	"	"
Pyridine-N-oxide, $C_5H_5N=O$	"	"
Dimethylnitrosoamine, $(CH_3)_2N-N=O$	"	"
Dimethylsulphoxide, $(CH_3)_2S=O$	"	"
Triphenylphosphine, $(C_6H_5)_3P$	"	"
Triphenylphosphine oxide, $(C_6H_5)_3P=O$	"	78,79
Chloride $[N(CH_3)_4]^+$, Cl	"	81
Chloride K^+	"	82
Chloride NH_4^+		

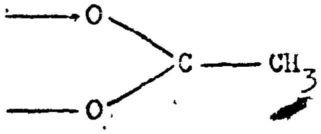
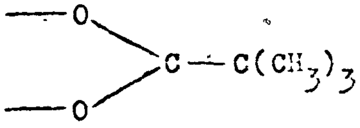
L	X	Ref.
Bromide $[N(CH_3)_4]^+$, Br	Cl	82
Quinoline, 	"	83
Isoquinoline, 	"	"
Diisopropylcarbodiimide	Br	82
N-cyano-pyrrolidine	"	"
N-cyano-piperidine	"	"
Pyridine	"	84
α-picoline	"	82
β-picoline	"	"
γ-picoline	"	"
Triphenylphosphine	"	"
Quinoline	"	83
Isoquinoline	"	"
Amine, NH_3	"	77

oxygen atom is coordinated tetrahedrally to four copper atoms, bridged in pairs by six halogen atoms. Somewhat similar arrangements have been found for $Be_4(CH_3COO)_6 \cdot O$ (85), I - 38, $Zn_4(CH_3COO)_6 \cdot O$(86), I - 39, and $Co_4[OCO.\ C(CH_3)_3]_6 \cdot O$(87), I - 40, where the metal atoms are regarded as four-coordinate. In contrast, the copper complexes, by virtue of an additional ligand, are five-coordinate and assume a distorted trigonal bipyramidal arrangement, I - 37. Magnetic measurements indicate that there is no direct bonding between the copper atoms(76). A similar structure has been reported for $[(C_2H_5)_2O]_4Mg_4Br_6 \cdot O$ (88), I - 41.

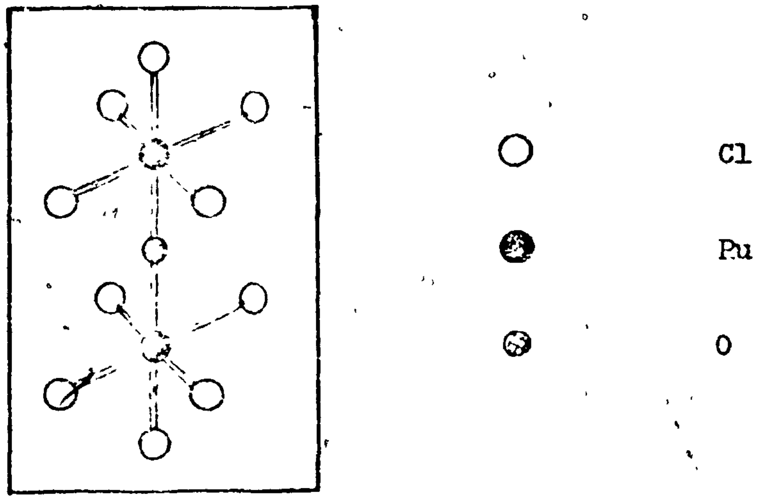
The μ_4-oxocopper(II) complexes can be considered as one of a series in which metal atoms are bridged by oxygen. Such a series would consist of linear, e.g. $[(RuCl_5)_2 \cdot O]^{4-}$ (89), I - 42, triangular, e.g. $[Cr_3(CH_3COO)_6 \cdot O \cdot 3H_2O]^+$ (90), I - 43, and the copper complexes representing the tetrahedral form.

Initially these polynuclear copper complexes were obtained accidentally as side products during the synthesis of other compounds(76-78). As interest in these complexes increased, they were found to be prepared quite easily by refluxing CuX_2, CuO and the

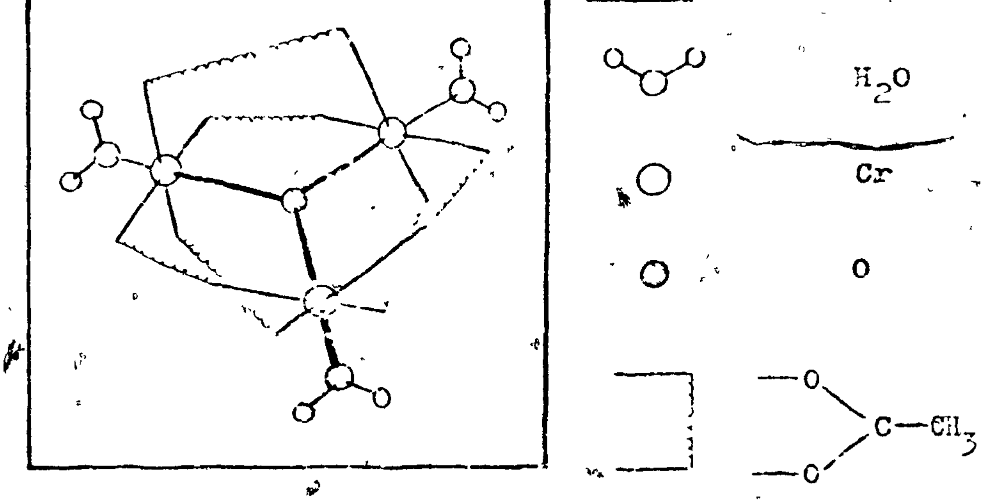


	I - 38	I - 39	I - 40
○	Be	Zn	Co
◦	O	O	O
⊐			

I - 42



I - 43



desired ligand in an appropriate solvent; such as, dichloromethane. Crystals of the complex were isolated after a few days(82,83).

μ_4-oxo-hexa-μ-chlorotetrakis-(pyridine copper(II)) was apparently obtained by Finkbeiner, et al(31), while studying the role of copper in the oxidative coupling of 2,6-dimethylphenol. However, other than elemental analysis, no further characterization was performed since there was little interest in the autoxidation product at the time.

II - EXPERIMENTAL

II - 1 Mechanistic Studies

A. Chemicals

2.4.6-trichlorophenol (Eastman Chemical Co.), 4-bromo-2,6-dichlorophenol (Aldrich Chemical Co.), copper(II) sulphate (Fisher Scientific Co.) and pyridine (Fisher Scientific Co.) were used as obtained from the suppliers. All other chemicals, including solvents, for the preparation and isolation of the stable phenoxocopper(II) complexes were of reagent grade quality, and used without further purification.

For the thermal decomposition of these complexes, all solvents were of reagent grade quality, but dried by overnight reflux and distillation in the presence of calcium dihydride.

Spectroscopic grade solvents were used in the characterization of polymers and complexes.

B. Synthesis of Phenoxocopper(II) Complexes

i) Preparation from Aqueous Solutions

The phenoxo-amine-copper(II) complexes, where the amine ligand is pyridine and tetramethylethylenediamine and the phenol is 2,4,6-tribromophenol, 2,4,6-trichlorophenol, 2,4,6-triiodophenol and 4-bromo-2,6-dichlorophenol, were prepared in aqueous solutions of reagents as described by Harrod(34). The general procedure was to add the required amount of neutral ligand to a solution of copper(II) sulphate, $CuSO_4 \cdot 5H_2O$, (0.02 mole) in distilled water (50 ml.). This solution was stirred for about one-hour. A suspension of the phenol (0.04 mole) and sodium hydroxide (0.04 mole) in distilled water (50 ml) was then added to the copper solution with vigorous stirring. The resulting dark-brown slurry was filtered, washed with water, and vacuum dried overnight on a medium frit. Recrystallization was performed by dissolution in a minimum of benzene, filtration, addition of excess hexane, and refrigeration overnight. A second recrystallization was performed to ensure complete removal of unreacted phenol. ~~Well-~~formed, dark crystals resulted in near quantitative yield. The general structure was confirmed by infrared analysis.

ii) Preparation from Bis(pyridine)bis-(2,4,6-trichlorophenoxo)copper(II)

The high solubility of the above complex in benzene permitted the simple preparation of other complexes by displacement of the pyridine in solution. Conplexes containing ammonia and ethylamine were prepared in a manner described by Harrod(34). These latter complexes were quite insoluble in benzene and could be precipitated by careful addition of the appropriate ligand to a benzene solution of the pyridine complex at room temperature. The ammonia complex was prepared by bubbling gaseous anhydrous ammonia into the benzene solution. Ethylamine was added as solution in benzene. Addition of these ligands had to be regulated in order to prevent displacement of the phenoxo ligand from the coordination sphere by excess amine. The identities of the products were confirmed by infrared spectroscopy.

iii) Preparation of Copper(II) Trichlorophenolate

Copper(II) trichlorophenolate was prepared by the dissolution of sodium hydroxide (0.04 moles) in distilled water (150 ml), addition of 2,4,6-trichlorophenol (0.04 moles), and stirring for about one hour. A solution of copper(II) sulphate, $CuSO_4 \cdot 5H_2O$, (0.02 moles) was then added with stirring. The resulting dark, purple-brown precipitate was washed with methanol to remove any excess phenol. A near quantitative yield of product was obtained.

iv) Preparation of Phenoxocopper(II) Complexes from Copper(II) Trichlorophenolate

Complexes containing dimethylformamide or dimethylsulphoxide as neutral ligand were prepared by dissolution of copper(II) trichlorophenolate (0.02 moles) in an excess (100 ml.) of either ligand and stirring for one hour. The light brown solutions were then added to distilled water (250 ml.) with stirring. The resulting crystals were washed with distilled water and dried.

In the case of dimethylformamide, a dark brown precipitate was obtained which was recrystallized by dissolution in benzene and addition of hexane. The resulting product had the empirical formula $[(CH_3)_2N \cdot CHO] \cdot Cu \cdot [C_6H_2Cl_3O]_2$ and was presumably a formamide bridged dimer analogous to the hexamethylphosphoramide-bridged dimer described by Tsuruya, <u>et al</u>(42).

<u>Anal</u>. calcd. for $C_{15}H_{11}N_1Cl_6O_3Cu$: C, 33.99%, H, 2.07%, N, 2.64%.
found: C, 34.40%; H, 2.11%, N, 2.53%.

In the case of dimethylsulphoxide, deep-purple crystals were obtained which decomposed readily in solution precluding purification of the product. Infrared spectroscopy indicated the presence of both trichlorophenoxo and dimethylsulphoxide in the complex.

C. Synthesis of Phenoxo Complexes Using Metals Other Than Copper

i) Preparation of Trichlorophenoxo-nickel(II)

$NiSO_4 \cdot 6H_2O$ (0.02 moles) was added to MeOH (100 ml.) which resulted in a green suspension. To this was poured a solution of NaOH (0.04 moles) and 2,4,6-trichlorophenol (0.04 moles) in MeOH (100 ml.) and then pyridine (0.08 moles). This milky-green suspension was stirred for 2 hours, and then the Na_2SO_4 (white powder) formed was removed by filtration. The green solution was evaporated down somewhat by heating and then cooled in the refrigerator. Dark green crystals resulted which were then recrystallized with hot benzene, and stored in a vacuum desicator. Elemental analysis indicates the structure $Py_2Ni(TCP)_2$.

Anal. Calcd. for $C_{22}H_{14}Cl_6N_2O_2 \cdot Ni$: C, 43.32%, H, 2.32%, Cl, 34.87%, N, 4.60%.

Found. C, 43.54%, H, 2.48%, Cl, 35.28%, N, 4.90%.

ii) Preparation of Trichlorophenoxo-pyridine-cobalt(II)

$CoSO_4$ (0.02 moles) was added to MeOH (100 ml.) with constant stirring. To this pink suspension was poured a solution of NaOH (0.04 moles) and 2,4,6-trichlorophenol (0.04 moles) in MeOH (100 ml.), and then immediately afterwards pyridine (0.08 moles). This resulted in a bluish-pink suspension which was then stirred for 2 hours. The Na_2SO_4 present was filtered off, the solvent evaporated down somewhat by heating, and the solution was then allowed to cool in the refrigerator. Purple, needle-shaped crystals precipitated down. These were recrystallized in hot benzene, and stored in a vacuum descicator. Elemental analysis indicated a 50/50 mixture of $Py_2Co(TCP)_2$ and $Py_4Co(TCP)_2$.

Anal. Calcd. for $C_{22}H_{14}Cl_6N_2O_2\cdot Co$: C, 43.31%, H, 2.32%; Cl, 34.86%, N, 4.59%.

Calcd. for $C_{32}H_{24}Cl_6N_4O_2\cdot Co$. C, 50.01%, H, 3.16%, Cl, 27.68%; N, 7.30%.

Found: C, 46.43%; H, 2.78%, Cl, 31.71%, N, 6.17%.

It is not uncommon for cobalt complexes to exist as equilibrium mixtures of tetra and hexa-coordinated complexes (91).

D. Thermal Decomposition of the Phenoxo-amine-copper(II) Complexes

1) General Remarks

The principal experimental techniques employed to investigate the thermal decomposition of phenoxocopper(II) complexes were gravimetric analysis and spectrophotometric analysis. Decompositions were carried out homogeneously in an organic solvent (i.e., benzene, toluene, or cumene). The phenoxocopper(II) complex most frequently studied was bis(trichlorophenoxo)bis(pyridine)-copper(II). Other complexes were utilized mainly to compare results obtained with trichlorophenoxocopper(II).

ii) Gravimetric Analysis

The course of the polymerization reaction was studied by dissolving the phenoxocopper(II) complex in an appropriate organic solvent, heating in a loosely corked erlenmeyer flask, and determining the yield and properties of the decomposition products at various reaction times. The method of separation of these decomposition products was similar to that described by Blanchard, et al(2). The reaction was quenched by rapid cooling in liquid nitrogen. The precipitated dihalogenobisaminecopper(II) complex was removed by filtration, washed with the solvent used in the decomposition and dried. Polymer was precipitated from the filtrate with methanol. It was then isolated by filtration, washed with methanol containing a slight amount of hydrochloric acid, and dried overnight at 100°C.

The extent of decomposition of the phenoxocopper(II) complex could be determined by the yield of copper(II) precipitate or polymer. In all cases, the yield of copper reaction product determined the extent of reaction. Polymer was difficult to recover completely because of the method of precipitation and because of some loss during filtration.

A series of thermal decompositions of bis(trichlorophenoxo)bis(pyridine)copper(II) was carried out under vacuum. Evacuation of the phenoxocopper (II) complex was performed in a reaction vessel on a standard vacuum line. Solvent, which had been previously outgassed, was then vacuum distilled into the reaction flask. The vessel was sealed and immersed in a constant temperature bath.

iii) Spectrophotometric Analysis

a) Visible Spectroscopy

Spectrophotometric studies were performed with a Perkin-Elmer 124 ultraviolet-visible spectrophotometer equipped with a temperature control unit. Bis(trichlorophenoxo)bis(pyridine)copper(II) shows a maximum absorption in the visible region at 22,500 cm^{-1} (34). Disappearance of this absorption as the reaction progresses provides a convenient method for following the decomposition of the phenoxocopper(II) complex. Solutions of the complex (1.35 x 10^{-3} M) in benzene, or toluene, as solvent were placed in TSL-Far UV cells fitted with polyethylene caps to prevent solvent evaporation. A small amount of air was left in the vessel to allow for solvent expansion on heating. The insoluble dichlorobispyridinecopper(II) formed as a reaction product quickly settled to the bottom of the cell and did not interfere with the photometric measurements on the remaining solution.

b) Electron Spin Resonance Spectroscopy

Thermal decomposition of bis(trichlorophenoxo)bis(pyridine)copper(II) was followed using a Varian E-3 ESR spectrometer. Operating conditions were: microwave frequency, 9.17 Gc, microwave power, 300 mW, field set, 3230 G, scan range, - 0.5 x 10^3 G, modulation amplitude, 1 x 1 G; modulation frequency, 100 Kcs, receiver gain, 8 x 10^2 (initially), time constant, 1.0 sec., and scan time, 4 min. (30 min. for phenoxy radical signal). Temperatures were regulated with a nitrogen gas flow.

Solutions of the sample (8.14×10^{-2} M) in benzene, or toluene, were placed in quartz tubes under atmospheric conditions and lightly capped to prevent solvent evaporation.

II - 2 Characterization of Polymers and Complexes

A) Molecular Weight Data

1) Vapour Pressure Osmometry

The number-average molecular weight of polymer, if less than 20,000, was measured by vapour pressure osmometry employing a Hewlett-Packard 301A instrument. The apparatus was operated at 25°C. Benzene was used as solvent. The calibration constant was determined with polystyrene ($\bar{M}_n$ = 10,300) supplied by Pressure Chemical Company.

The instrument was checked for accuracy with trial runs of polymers of known molecular weights. Accuracy was within 1% for molecular weights less than 1000. However, as the polymer number-average molecular weight increased, errors as large as 10-15% were possible in the upper regions.

ii) Membrane Osmometry

Number-average molecular weights greater than 20,000 were determined on a Hewlett-Packard 502 High Speed membrane osmometer. The apparatus utilized 0-6 membranes (Schleicher and Schuell) and was operated at 30°C with toluene as solvent.

A polystyrene standard ($\bar{M}_n$ = 50,000), supplied by Pressure Chemical Company, showed an accuracy within 2%. It was found that the polymers prepared from polyhalogenated phenols, presumably because of their branching, had a tendency to diffuse through the membrane. This resulted in apparent values of molecular weight higher than reality. For number-average molecular weights in the range 20,000-25,000 this diffusion was quite rapid. The problem decreased as the molecular weight increased, and did not exist for values greater than 40,000.

B) Nuclear Magnetic Resonance Spectroscopy of Polymers

The protons on the aromatic rings of the polymers were analysed with a Varian T60 spectrometer at 35°C and 60 Mhz. Solvent used was carbon disulphide. Due to the relatively low number of hydrogen atoms in the polymer, very concentrated solutions (350 g/l) were required. Concentrations varied somewhat from run-to-run due to the viscosity of the solution, the hydrostatic properties of the polymer, and the rapid evaporation rate of the solvent.

C) Infrared Spectroscopy

Spectra in the range 4000-625 cm^{-1} were measured using a Perkin-Elmer 257 spectrophotometer. Samples were dispersed in potassium bromide pellets. On occasion, polymers were dissolved in carbon disulphide.

Absorptions in the range 625-470 cm^{-1} utilized a Perkin-Elmer 521 spectrophotometer. Samples were dispersed in a nujol mull on potassium bromide plates.

Far-infrared spectra were measured in a nujol mull on polyethylene plates with a Perkin-Elmer FIS-3 spectrophotometer.

The spectra of a number of phenoxocopper(II) complexes and their resulting decomposition products are shown in a separate section of this thesis.

D) Vapour Phase Chromatography-Mass Spectrometry

An LKB-9000 Gas Chromatogram Mass Spectrometer was used to analyse the reaction products from the decomposition of bis(trichlorophenoxo)bis(pyridine)-copper(II) in the presence of carbon tetrahalides as additives. This instrument permitted the study of reaction product mixtures in solution without previous separation. As each successive compound was isolated by chromatography, a mass spectrum of that species was recorded. The technique required only a very small quantity of product. Samples were the methanol/benzene solutions obtained after preliminary removal of the dihalogenocopper(II) complex and polymer as described above.

Instrument conditions were as follows: injector, 200°C; column, 6' x ½" glass containing 3% OV-1 on Chromosorb W, High Performance; 290°C; helium flow rate, 30 ml/min.; and ionizing energy, 70 eV at 60×10^{-6} A..

II - 3 Synthesis of μ_4-oxo Copper(II) Complexes

A) μ_4-oxo-hexa-μ-chloro-tetrakis[pyridine copper(II)]

Bis(trichlorophenoxo)bis(pyridine)copper(II) (5 g) was dissolved in cumene (100 ml) and heated in air at 72°C for 24 hours. The resulting precipitate was filtered and extracted with dichloromethane to give gold needle-shaped crystals of $(C_5H_5N)_4Cu_4Cl_6{\cdot}O$ (1.6 g, 97% yield).

Anal. Calcd. for $C_{20}H_{20}N_4Cl_6Cu_4{\cdot}O$: C, 30.03%, H, 2.50%, N, 7.01%, Cl, 26.65%; Cu, 31.78%; O, 2.00%.
Found: C, 30.48%; H, 2.50%; N, 7.04%; Cl, 27.06%; Cu, 32.29%; O, 0.35%. Molecular weight in dichloromethane 797 by vapour pressure osmometry. Melted with decomposition at 251°C.

B) μ_4-oxo-hexa-μ-bromo-tetrakis[pyridine copper(II)]

Bis(tribromophenoxo)bis(pyridine)copper(II) (5 g) was dissolved in cumene (100 ml) and heated in air at 50°C for 24 hours. The resulting dark green precipitate was extracted with tethrahydrofuran and recrystallized by evaporation, giving dark brown crystals of $(C_5H_5N)_4Cu_4Br_6{\cdot}O$ (0.6 g, 40% yield).

Anal. Calcd. for $C_{20}H_{20}N_4Br_6Cu_4 \cdot O$: C, 22.51%; H, 1.88%; Br, 23.80%; Cu, 45.30%.

Found: C, 23.70%; H, 2.01%; Br, 23.71%; Cu, 45.30%.

Melted with decomposition at 217°C.

C) μ_4-oxo-hexa-μ-chloro-tetrakis[ethylamine copper(II)]

Bis(trichlorophenoxo)bis(ethylamine)copper(II) (2 g) was dissolved in toluene (75 ml) containing carbon tetrachloride (5 ml) and heated at 72°C for 4 hours. The resulting olive green precipitate (0.7 g), upon extraction with dichloromethane and recrystallization with hexanes, gave a lime-green complex (0.5 g, 82% yield).

Anal. Calcd. for $C_8H_{28}N_4Cl_6Cu_4 \cdot O$: C, 14.48%; H, 4.22%, N, 8.45%; Cl, 32.31%.

Found: C, 15.51%; H, 4.77%; N, 8.91%, Cl, 31.44%.

Melted with decomposition at 162°C. The poor analysis for this compound is probably due to the fact that it decomposes slowly in air.

D) μ_4-oxo-hexa-μ-chloro-tetrakis[triphenylphosphine oxide copper(II)]

The phenoxocopper(II) complex containing triphenylphosphine oxide as neutral ligand could not be isolated in the solid state. However, it appeared to be readily obtained in solution by the addition of copper(II) trichlorophenolate (0.01 moles) to triphenylphosphine oxide (0.01 moles) in cumene (125 ml). This resulted in a brown solution which was filtered to remove any unreacted materials. This solution was then reacted in air at 72°C for 24 hours. Extraction of the precipitate with dichloromethane and recrystallization gave orange crystals of the μ_4-oxocopper(II) complex.

Anal. Calcd. for $C_{72}H_{60}P_4Cl_6Cu_4O_5$: C, 54.17%; H, 3.76%; Cu, 15.92%.

Found: C, 53.53%; H, 3.79%, Cu, 15.72%.

Melted with decomposition at 239°C.

E) μ_4-oxo-hexa-μ-chloro-tetrakis[dimethylformamide copper(II)]

Trichlorophenoxo-dimethylformamide-copper(II) (2 g) was dissolved in cumene (100 ml) and heated in air at 50°C for 24 hours. The resulting yellow-brown precipitate was extracted with dichloromethane. Evaporation gave a yellow crystalline product.

F) μ_4-oxo-hexa-μ-chloro-tetrakis[dimethylsulphoxide copper(II)]

Trichlorophenoxo-dimethylsulphoxide-copper(II) (2 g) was dissolved in cumene (100 ml) and heated in air at 50°C for 24 hours resulting in a yellow-brown precipitate containing a mixture of copper complexes. Isolation by extraction with dichloromethane led to further decomposition. However, an infrared spectrum of the unextracted yellow-brown precipitate gave an absorption at 583 cm^{-1}, suggesting the presence of $[(CH_3)_2SO]_4Cu_4Cl_6O$ (82).

III - RESULTS

III - 1 INTRODUCTORY REMARKS

There are two principal techniques which permit examination of the overall mechanism of polyphenylene ether formation by the decomposition of phenoxocopper(II). The first involves the common spectrometric methods (i.e., ultraviolet-visible spectroscopy and electron spin resonance spectroscopy). The second method entails investigation of the various reaction products and intermediates. These latter compounds can be related back to the mechanistic course by their very existence. The reaction products from the decomposition of phenoxocopper(II) were dihalocopper(II) complexes and polymer.

Bis(trichlorophenoxo)bis(pyridine)copper(II) gave dark brown solutions. As the decomposition reactions proceeded, the solutions faded to a "straw" colour. The dichlorobis(pyridine)copper(II) complex precipitated out as blue-green crystals. Polymer, and any other reaction products, appeared to remain in solution. Similar results were obtained for the other phenoxocopper(II) complexes studied. In the so-called "gravimetric" methods of mechanistic study, the stage of reaction was determined by the formation of precipitate, or by the lack of any further change in solution colour. Solutions were generally permitted to remain in the temperature bath for periods of time much longer than perhaps necessary, in order to ensure complete reaction.

There were many reaction variables which influenced the decomposition of phenoxocopper(II) complexes. These included temperature, concentration, solvent, and naturally, the particular phenoxocopper(II) complex used. These factors were studied individually in some detail.

The number-average molecular weight of the polymers provided a direct proof of certain features of the overall mechanism of the reaction. Apart from a study of molecular weight, a limited amount of polymer characterization with regards to structure was carried out.

The decomposition of phenoxocopper(II) complexes led, in certain cases, to the formation of μ_4-oxocopper(II) complexes as reaction product. An understanding of how these compounds resulted offered a great deal of information with regard to the overall mechanism of decomposition. A general, unique synthesis of these μ_4-oxocopper(II) complexes is also included in this thesis.

III - 2 MECHANISTIC ASPECTS

A) Decomposition of Bis(trichlorophenoxo)bis(pyridine)copper(II) Under Constant Reaction Conditions.

i) Gravimetric Analysis

a) Reaction Under Vacuum

Initially, it was felt that the decomposition of bis(trichlorophenoxo)bis(pyridine)copper(II) would best be followed under vacuum. This would permit investigation of the reaction under the most pure conditions. Samples were prepared individually by dissolving the phenoxocopper(II) complex in reagent benzene (2g/30ml), degassing the solution under conditions of "sticky" vacuum on a standard vacuum line, and sealing the reaction vessel. The extent of reaction was measured by the yield of copper(II) complex precipitated as reaction product. A theoretical yield of 0.95 grams Py_2CuCl_2 was expected for complete decomposition. Results for a series of runs are shown in Table III - 1.

It was obvious from this table

TABLE III - 1

Decomposition of $Py_2Cu(TCP)_2$ in Benzene*

Reaction time	Temperature(°C)	Yield Cu(II) complex (g)
10 min	101.5	0.77
20 min	"	0.73
40 min	"	0.79
1 hr	"	0.88
1 hr	"	0.74
3 hr	"	0.87
5 hr	"	0.87
24 hr	"	0.89
48 hr	"	0.90
1 hr	84.5	0.04
1 hr	"	0.79
1 hr	"	0.85
1.5 hr	"	no reaction
1.5 hr	"	0.76
2 hr	"	0.53
2 hr	"	0.81
2 hr	"	0.88
5 hr	"	0.87

* 2.0g reactant in benzene (30ml)

that there was considerable deviation of the observed yields from that predicted. The yield of copper(II)dihalide precipitate was expected to increase with reaction time. It should also have been identical for duplicate reaction times. Neither of these features was observed.

It should be noted that the reactions were quenched with liquid nitrogen immediately on removal from the constant temperature bath. The reaction products were also separated as quickly as the experimental procedures would permit. This was to prevent possible further decomposition after cooling. The phenoxocopper(II) complexes were stable up to several months in solution at room temperature(2). However, it was possible that once the reaction was initiated, it would then proceed rapidly, even on cooling to room temperature. Evidence supporting this proposal is shown in Table III - 2. Three phenoxocopper(II) solutions were reacted under identical conditions for two hours. They were then set aside at room temperature for different times before work-up.

TABLE III - 2

Decomposition of $Py_2Cu(TCP)_2$ in Benzene (2g/30 ml) at 84.5°C. Reaction Time = 2 hrs.

Time before work-up	Yield Cu(II) complex (g)
2 hrs.	0.26
24 hrs.	0.56
7 days	0.76

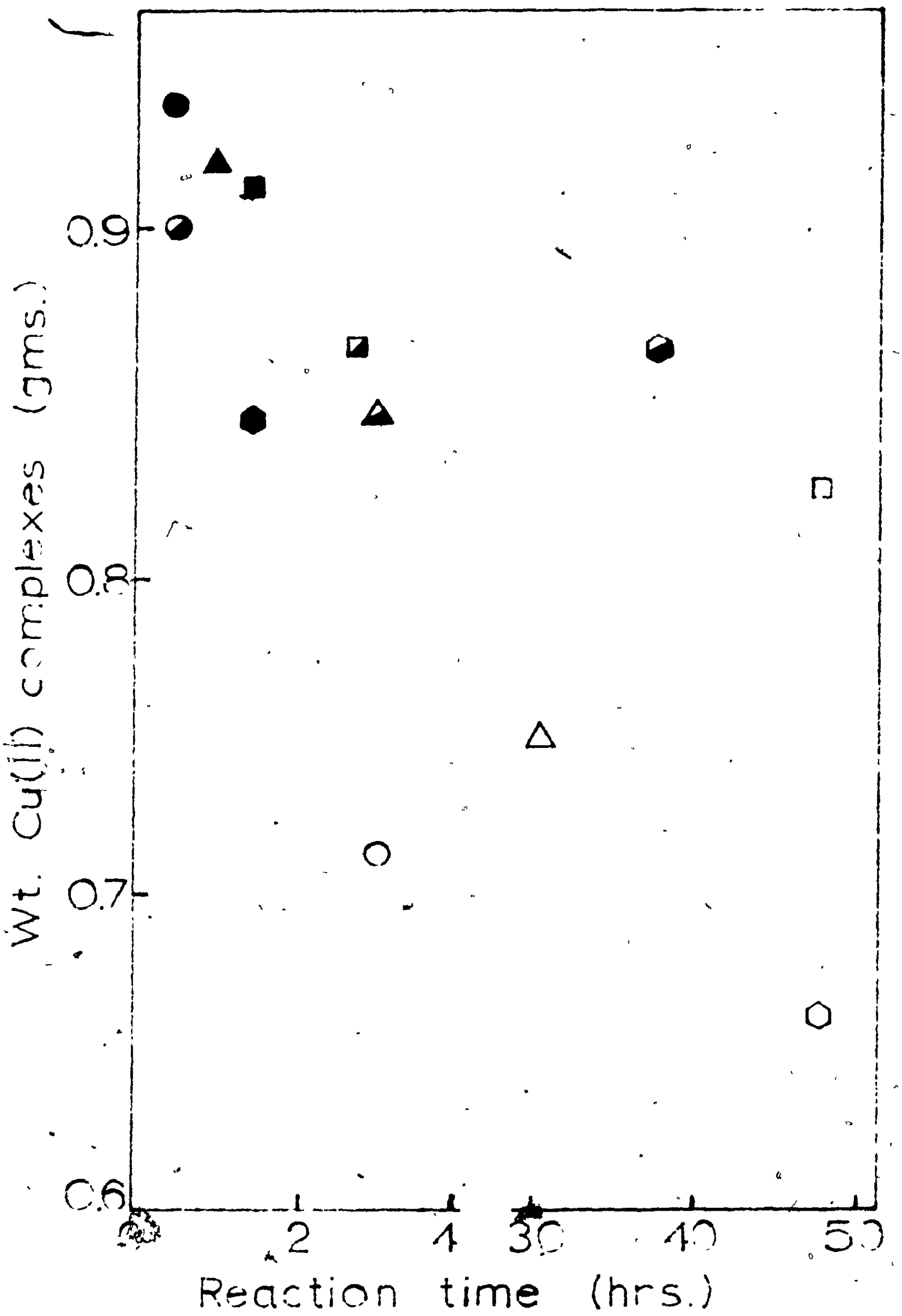
A modified technique was employed in an attempt to remedy the inconsistent results from run-to-run. Each run consisted of several samples prepared simultaneously. The phenoxocopper(II) complex and benzene were degassed separately. The solvent was then vacuum distilled into the reaction vessel containing the phenoxocopper(II) complex. The results of several runs are shown in Figure III - 1. Reactions were quenched as soon as there was evidence of the dihalocopper(II) reaction product. It was necessary to stop the reaction at an intermediate stage in order to determine if the decompositions were proceeding simultaneously. Unfortunately it was impossible

FIGURE III - 1

Yield of Copper(II) Reaction Products at Various Reaction Times for a Series of Decompositions of $Py_2Cu(TCP)_2$ in Benzene at 84.5°C Under Vacuum.

LEGEND

	Vessel		
Run	1	2	3
I	○	◕	●
II	△	◭	▲
III	⊡	◪	■
IV	⬡	⬣	⬢


Wt. Cu(II) complexes (gms.)
0.9
0.8
0.7
0.6
0
2
4
30
40
50
Reaction time (hrs.)

to predict an exact equivalent stage of decomposition from vessel-to-vessel due to the intense colour of the remaining phenoxocopper(II) complex in solution, which tended to obscure any precipitate.

The decomposition rate followed the order vessel 3>vessel 2>vessel 1. The vessels had received solvent in the reverse order to this. Reagent benzene had been used, and in each run, only the amount of benzene required for three vessels (90 mls) had been degassed. It was possible that any impurities, such as water, could have been vacuum distilled with the solvent. If so, it would be found in more concentrated levels with each successive reaction vessel. This occurance could account for the inconsistent results of each run.

As a final precaution, spectroscopic benzene was utilized, with further purification by reflux and distillation over calcium dihvride. Results for a series of runs are shown in Table III - 3.

TABLE III - 3

Decomposition of $Py_2Cu^{II}(TCP)_2$ at 84.5°C in Benzene

	Run I		Run II	
	reaction time	wt.complex	reaction time	wt.complex
vessel #1	1½ hr.	0.94	3½ hr.	0.78
vessel #2	1½ hr.	0.95	3½ hr.	0.79
vessel #3	1½ hr.	0.95	3½ hr.	0.78
vessel #4	1½ hr.	0.96	3½ hr.	0.67

Although the reactions now seemed to be progressing simultaneously for each run, there was a variation from run-to-run. This suggested two possibilities:

1. the decomposition rate varied from run-to-run. This seemed improbable since the temperatures were identical.
2. the reactions experienced an induction period which varied from run-to-run. This induction period would be highly sensitive to any slight change in reaction conditions. This seemed the more likely of the two proposals.

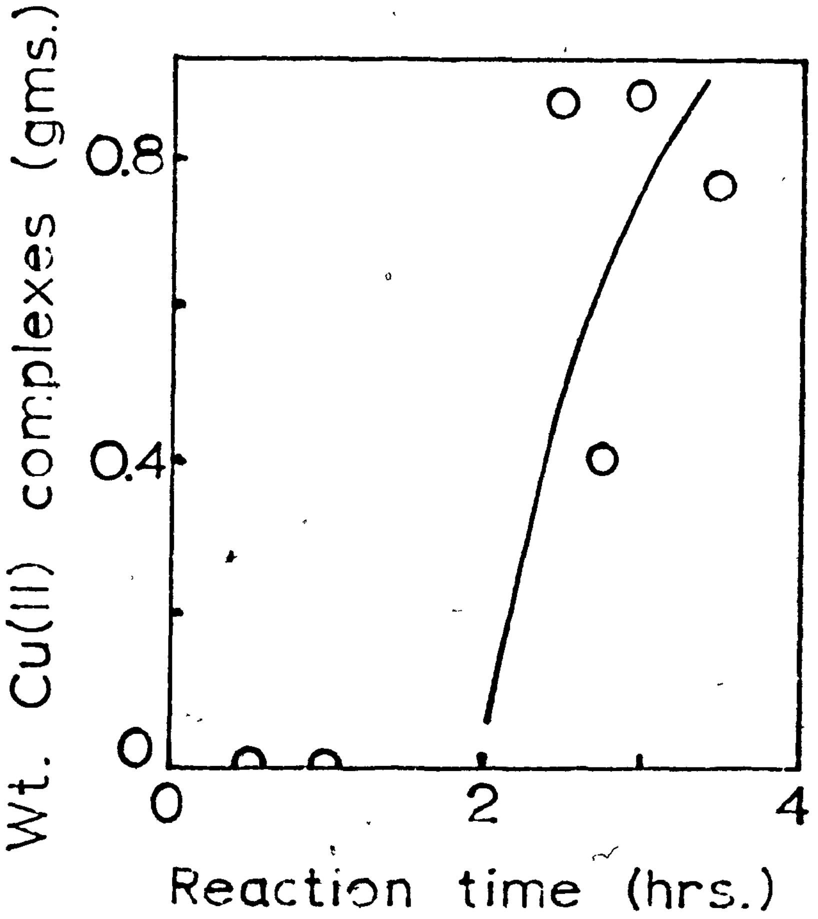
To investigate the existence of this induction period, six samples were reacted simultaneously, and removed at various reaction times. The results are shown in Figure III - 2. Although the yields were still somewhat scattered, there was strong evidence of an induction period.

An additional run of four vessels was prepared under the highest purity obtainable on the vacuum line. The entire line was heated (under vacuum) with a Bunsen flame in order to remove any absorbed water. The phenoxocopper(II) complex was recrystallized four times, and degassed overnight. The benzene, which had been purified by reflux and distillation over calcium dihydride, was degassed five times. It was then vacuum distilled into the reaction vessels. In all samples, no decomposition occurred at 84.5°C over a reaction time of seven days.

At this point, it was decided that further investigation of the decomposition of bis(trichlorophenoxo)bis(pyridine)copper(II), under conditions of vacuum, was not worthwhile. Vessel construction and sample preparation consumed too much time. Added to this, it was not possible to obtain complete consistency of results. Consequently, all subsequent reaearch was conducted under atmospheric conditions.

FIGURE III - 2

Yield of Copper(II) Reaction Products with Time in the Decomposition of $Py_2Cu(TCP)_2$ in Benzene at 84.5°C Under Vacuum.


Wt. Cu(II) complexes (gms.)
0.8
0.4
0
0
2
4
Reaction time (hrs.)

b) Under Atmospheric Conditions

The decomposition of bis(trichlorophenoxo)bis(pyridine)copper(II) was again examined for an induction period. A series of solutions (40gms/l), using toluene as solvent, was reacted at 84.5°C and removed at various reaction times. The extent of reaction was measured by the yield of copper(II) precipitate, and in some cases, by the number-average molecular weight of polymer. The results are shown in Figures III - 3 and III - 4.

An analogous run was performed in benzene. In this case, the trichlorophenoxo-pyridine-copper(II) complex was decomposed in benzene (50gms/l) at 71°C. The results are shown in Figures III - 5 and III - 6.

ii) Spectrophotometric Analysis

a) Ultraviolet-visible Spectroscopy

The visible spectrum of bis(trichlorophenoxo)bis(pyridine)copper(II) is shown in Figure III - 7. A maximum absorption occurred at 22,500 cm^{-1}, as previously reported by Harrod(34). This absorption obeyed Beer's Law (Figure III - 8), and had an extinction coefficient of 1160

FIGURE III - 3

Yield of Copper(II) Reaction Products vs Time in the Decomposition of $Py_2Cu(TCP)_2$ in Toluene (2gm/150 ml) at 84.5°C.

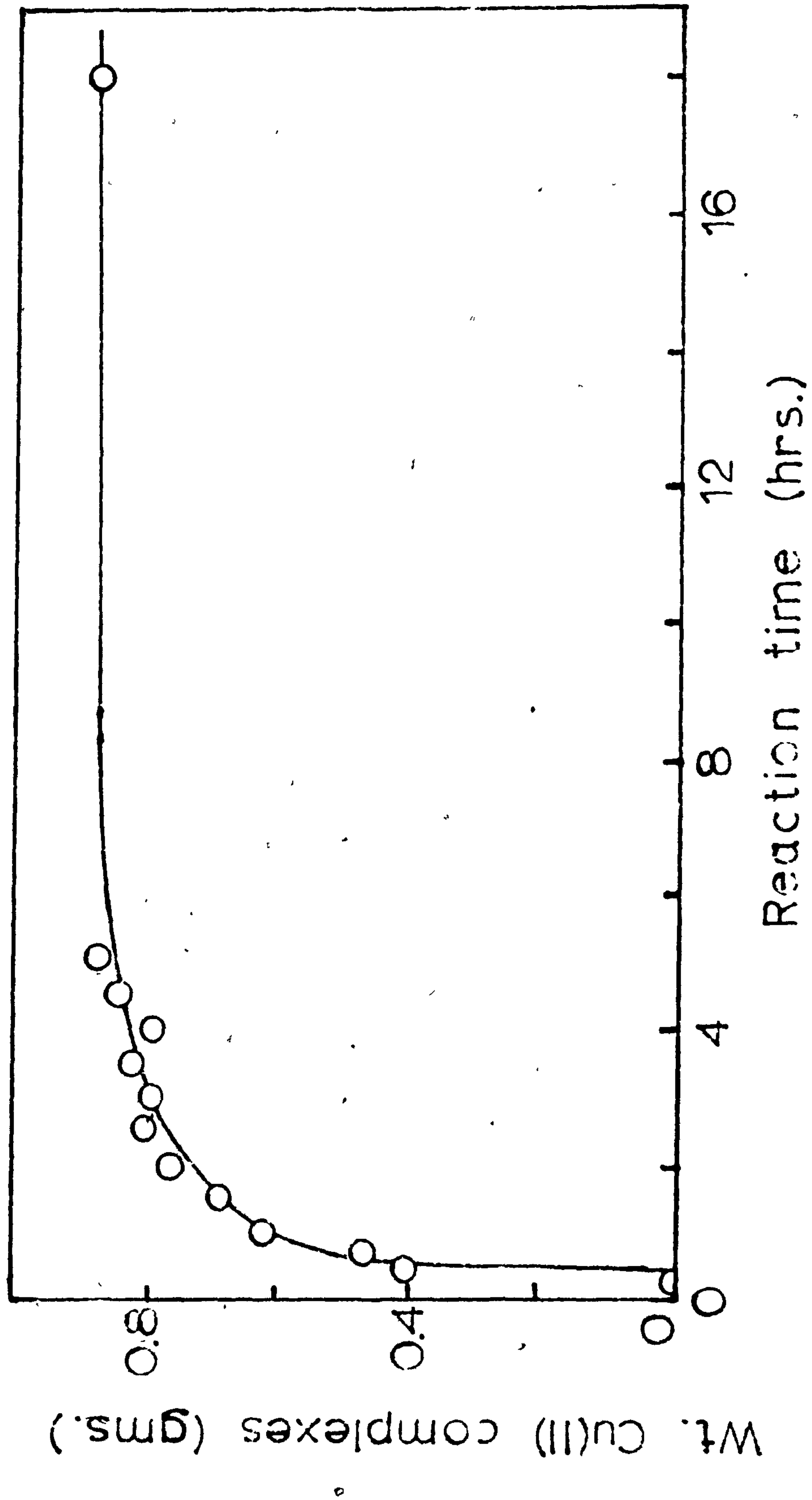

Wt. Cu(II) complexes (gms.)
0
0.4
0.8
Reaction time (hrs.)
0
4
8
12
16

FIGURE III - 4

$\bar{M}_n$ of Polymer vs Time in the Decomposition of $Py_2Cu(TCP)_2$ in Toluene (2gm/50 ml) at 84.5°C.

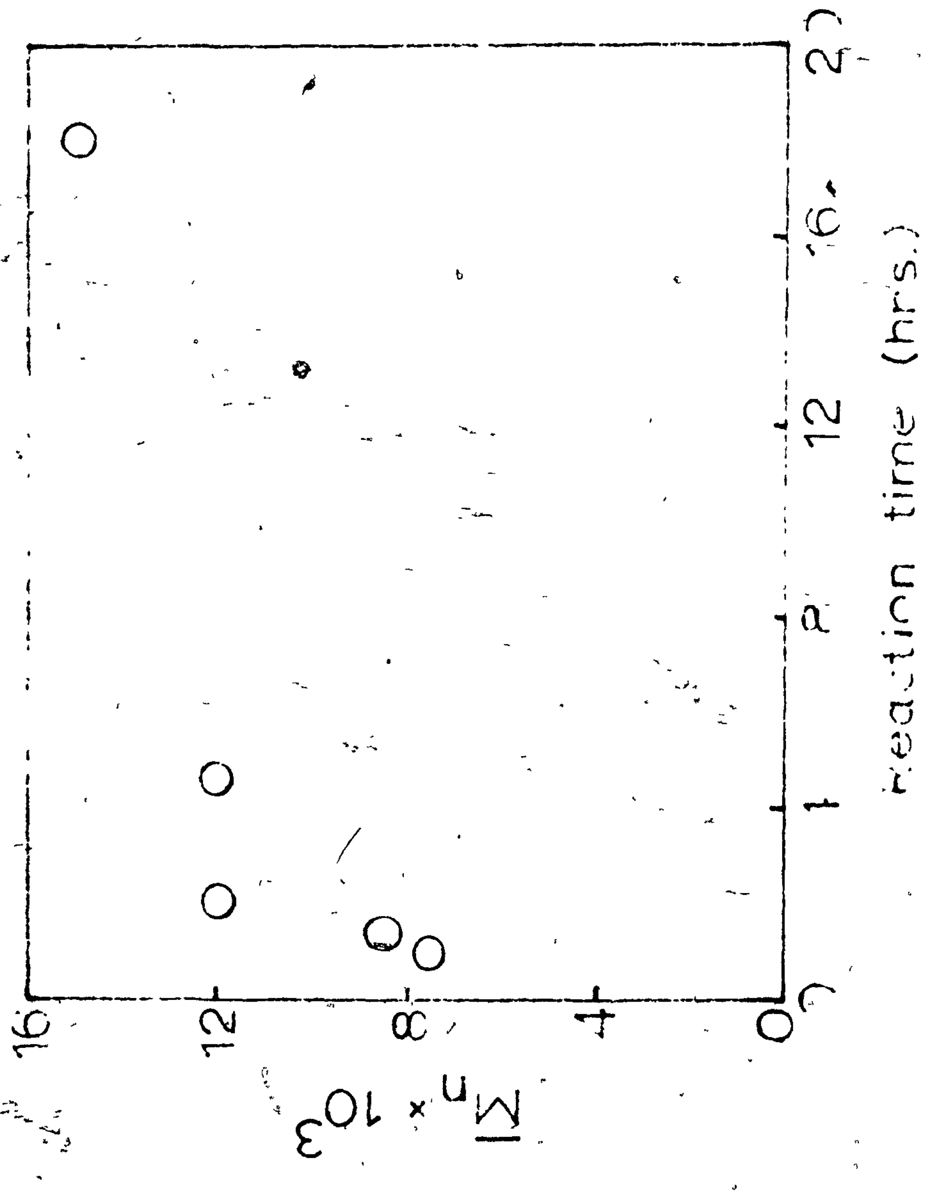

$\overline{M}_n \times 10^3$
16
12
8
4
0
0
4
8
12
16
20
Reaction time (hrs.)

FIGURE III - 5

Yield of Cu(II) Reaction Products in the Decomposition of $Py_2Cu(TCP)_2$ (50 g/l) in Benzene at 71°C for various Reaction Times. Theoretical Maximum Yield = 2.35 gm.

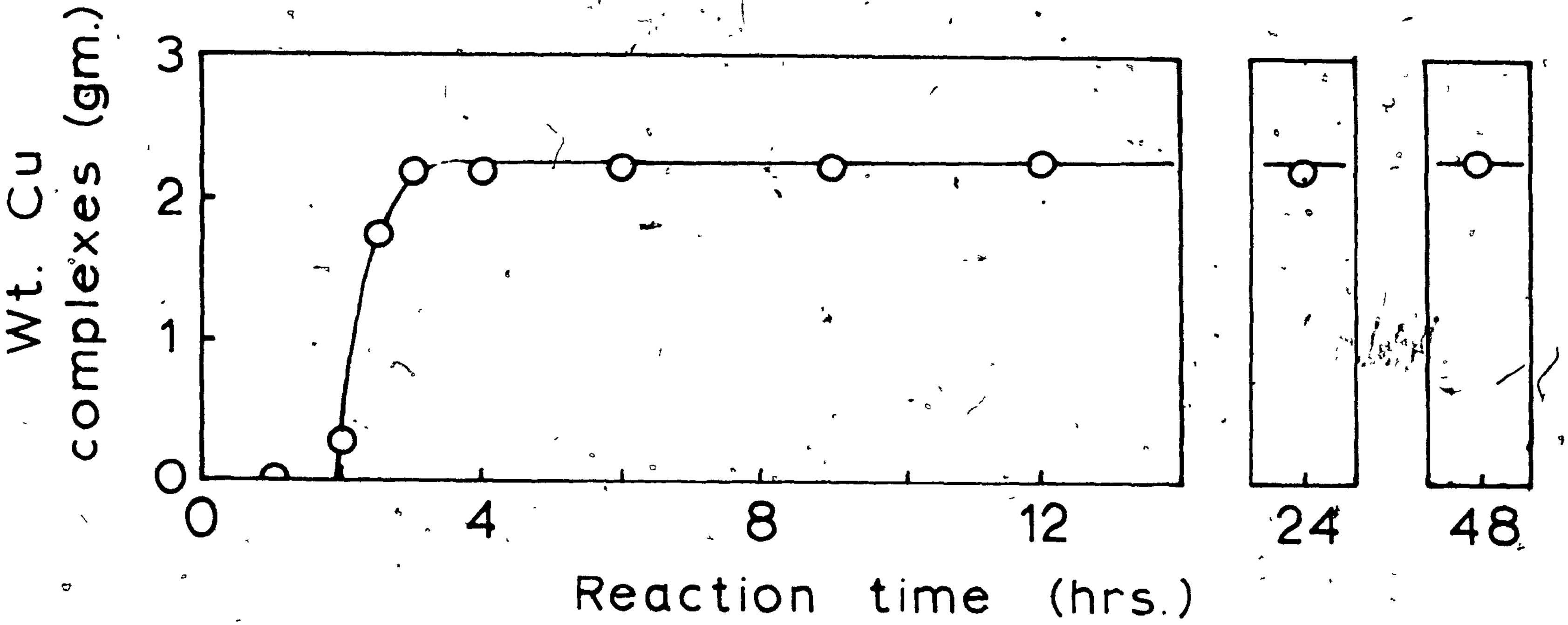

Wt. Cu complexes (gm.)
3
2
1
0
0
4
8
12
24
48
Reaction time (hrs.)

FIGURE III - 6

Polymer molecular Weight at various Reaction Times in the Decomposition of $Py_2Cu(TCP)_2$ (50 g/l) in Benzene at 71°C.

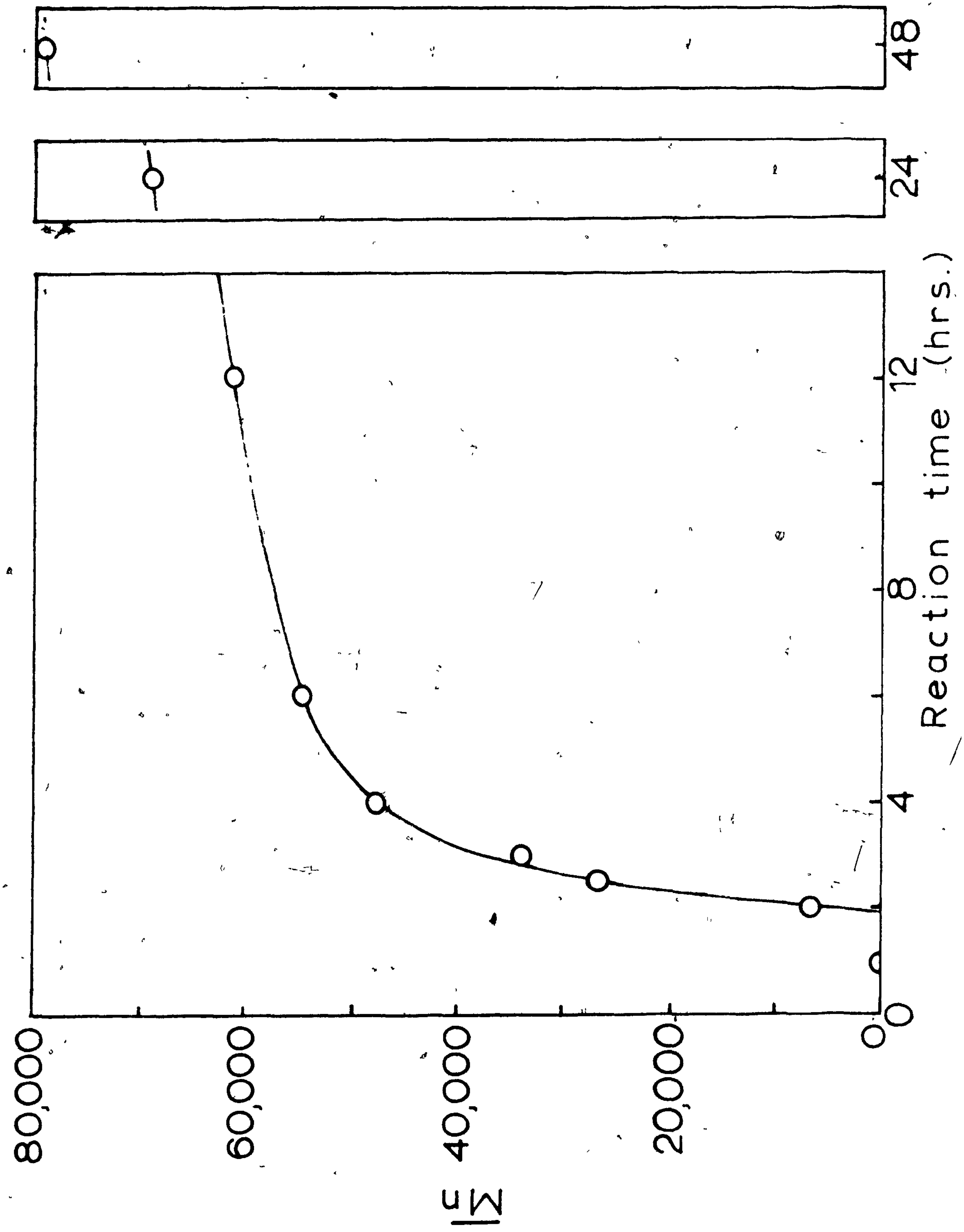

$\overline{M}_n$
80,000
60,000
40,000
20,000
0
0
4
8
12
24
48
Reaction time (hrs.)

FIGURE III - 7

Visible Spectrum of $Pv_2Cu(TCP)_2$ in Benzene ($1.35x10^{-3}$mole/l)

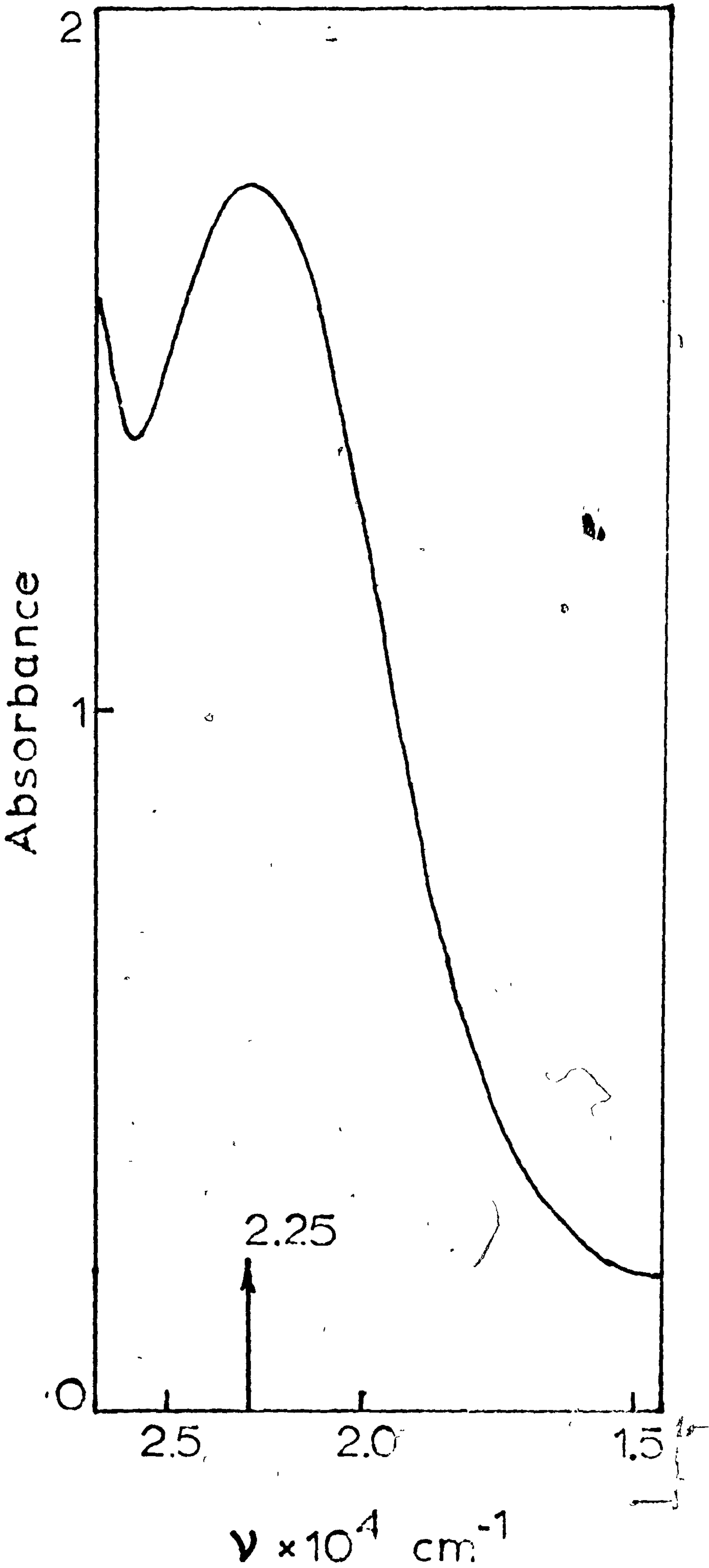
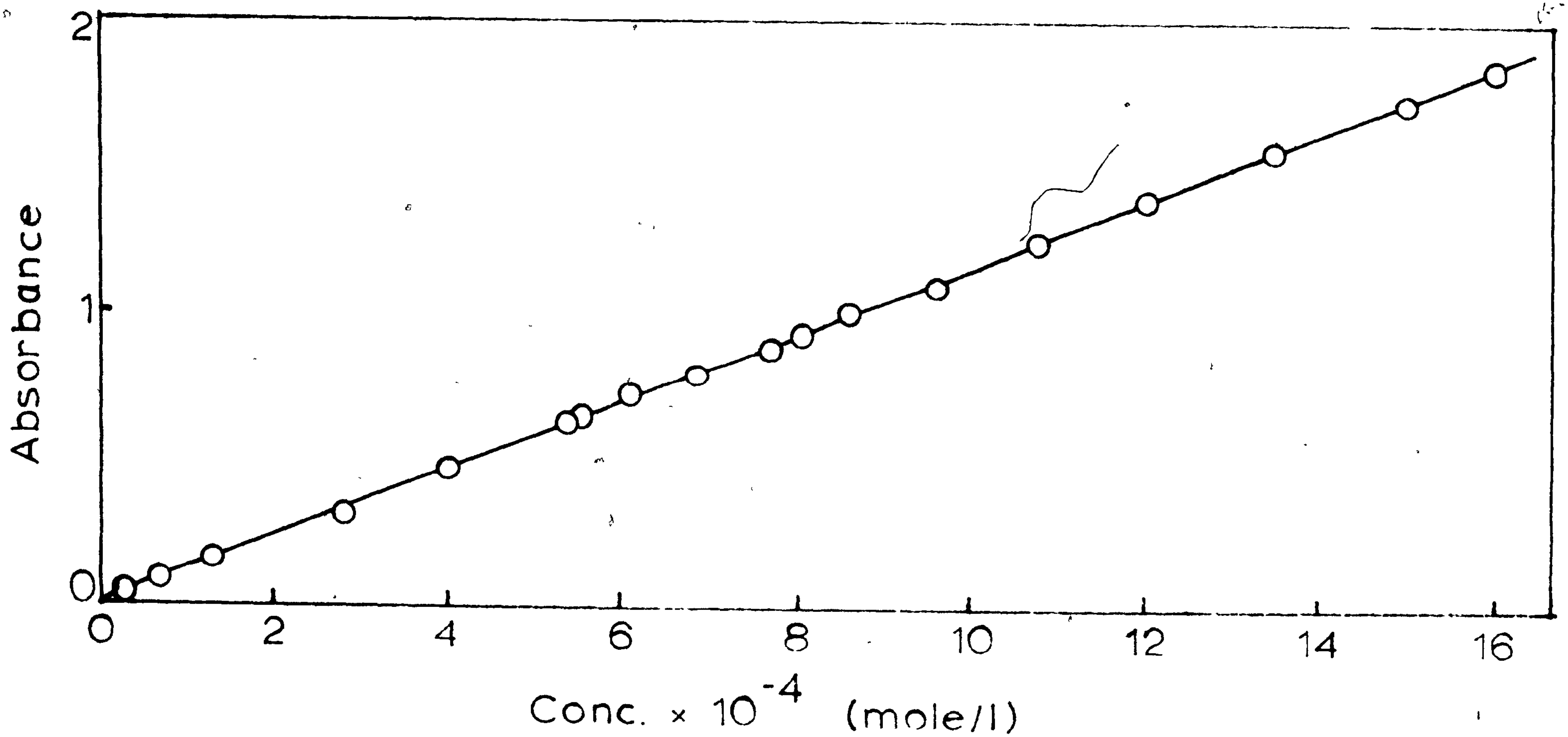

2
1
0
Absorbance
2.25
2.5
2.0
1.5
ν × 10⁴ cm⁻¹

FIGURE III - 8

Absorbance at 22,500 cm^{-1} vs Concentration of $Py_2Cu(TCP)_2$ in Benzene showing Beer's Law.


Absorbance
2
1
0
0
2
4
6
8
10
12
14
16
Conc. × 10^{-4} (mole/l)

(compared to ϵ = 1100 reported by Harrod(34)). Examination of the disappearance of this absorption, as the reaction proceeded, was expected to provide kinetic and mechanistic information.

An absorbance/time plot for decomposition of bis(trichlorophenoxo)bis(pyridine)copper(II) in benzene is shown in Figure III - 9. The existence of an induction period, strongly suggested by the aforementioned gravimetric study, is clearly evident from this curve. An unforeseen feature of this result is the marked hump appearing in the absorbance curve well after the onset of reaction.

Two other features of the curve in Figure III - 9 which are of major importance, and to be discussed in detail below are a) the marked auto-acceleration after onset of reaction and b) the residual absorbance at the end of the reaction. The latter was somewhat surprising since, at this time, none of the reaction products was believed to absorb significantly at 22,500 cm^{-1}.

Visible spectra, taken at various times during the decomposition of phenoxocopper(II) at 70°C are shown in Figure III - 10. The ultraviolet spectra of the phenoxocopper(II) complex, the remaining straw-coloured

FIGURE III - 9

Decomposition of $Py_2Cu(TCP)_2$ in Benzene at 75°C following Absorbance at 22,500 cm^{-1}.

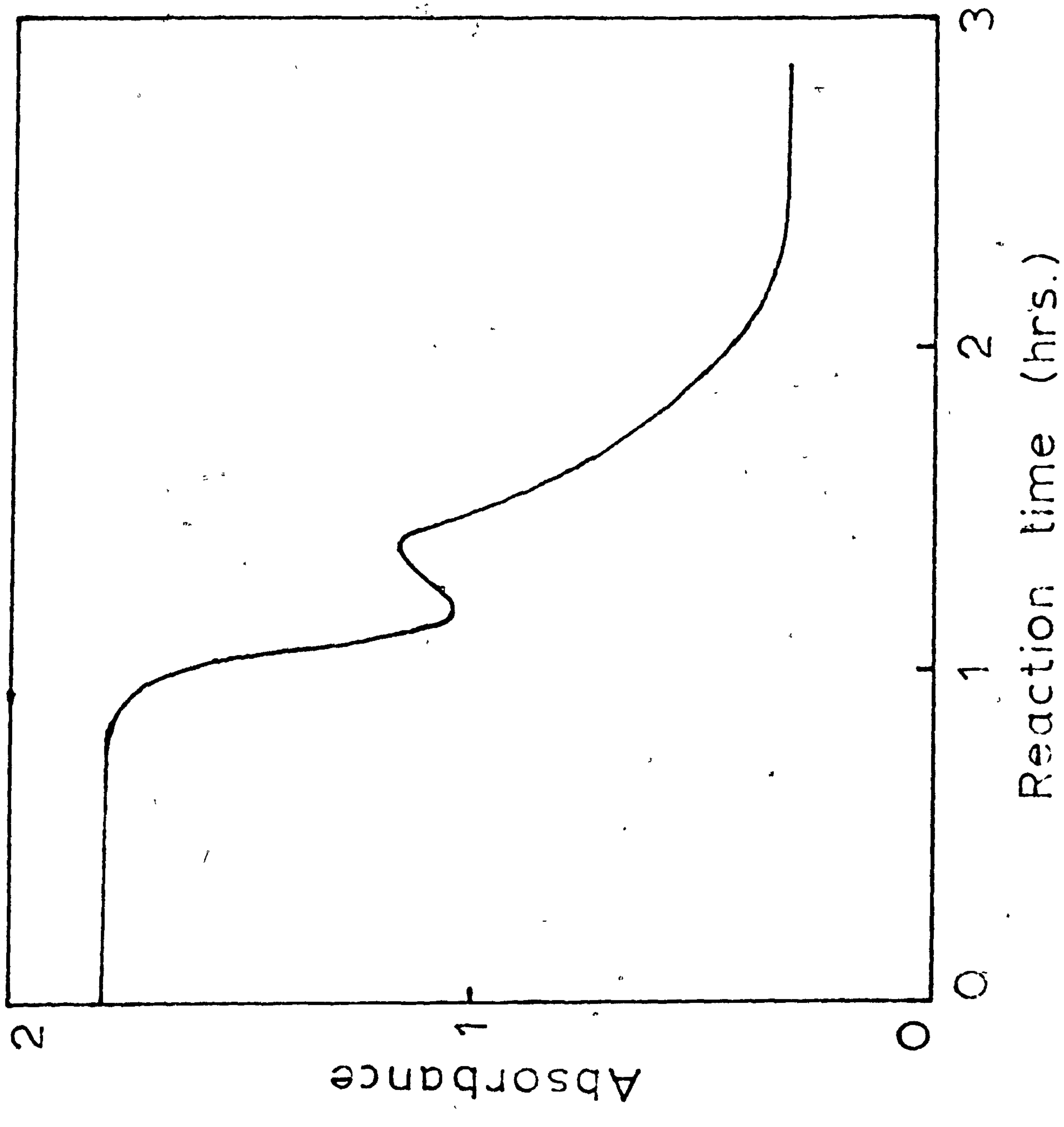

Absorbance
0
1
2
Reaction time (hrs.)
0
1
2
3

FIGURE III - 10

Decomposition of $Pv_2Cu(TCP)_2$ in Benzene at 70°C

a) 0 min

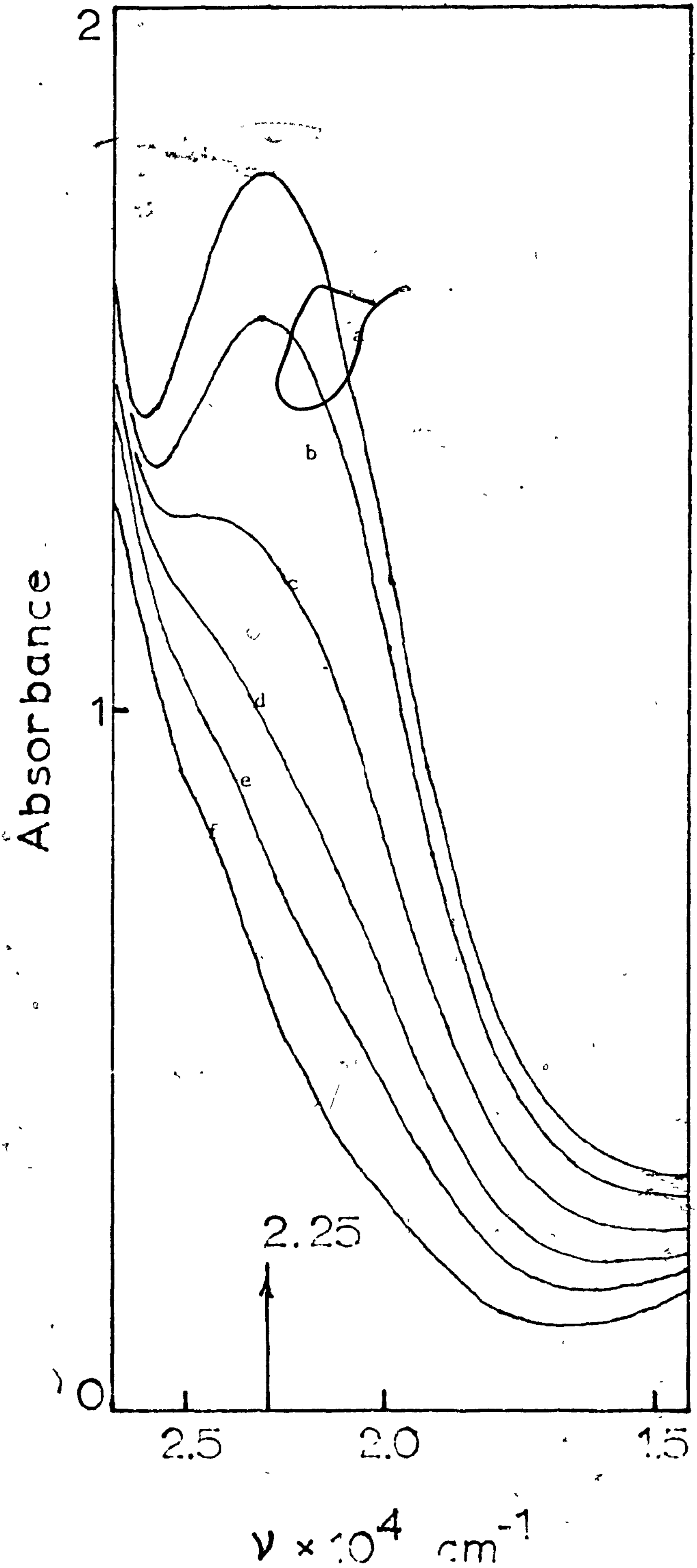
b) 90 min

c) 130 min

d) 150 min

e) 180 min

f) 270 min


Absorbance
2
1
0
a
b
c
d
e
f
2.25
2.5
2.0
1.5
$\nu \times 10^4$ cm^{-1}

solution and polymer are shown in Figure III - 11.

b) Electron Spin Resonance Spectroscopy

As reported earlier in Chapter I, the oxidation of phenols to polyphenylene ethers is believed to proceed through the formation of phenoxy radicals. For this reason, the decomposition of bis(trichlorophenoxo)bis-(pyridine)copper(II) was examined by electron spin resonance spectroscopy. The phenoxocopper(II) complex, in toluene (50 gms/l), was reacted at 100°C. The change in copper(II) signal with decomposition is shown in Figure III - 12. The phenoxocopper(II) complex had decomposed completely in less than one hour. At this stage, a slight irregularity was detected on the high-field tail of the copper(II) signal. The sensitivity of the detector was increased, revealing a well defined singlet. An example of this radical signal is shown in Figure III - 13.

A value of $g = 2.007$ was calculated for this signal from equation III - 1.

FIGURE III - 11

Ultraviolet Spectra of: a) $Py_2Cu(TCP)_2$

b) poly(2,6-dichlorophenylene ether)

c) straw-coloured soln. after decomposition of $Py_2Cu(TCP)_2$.

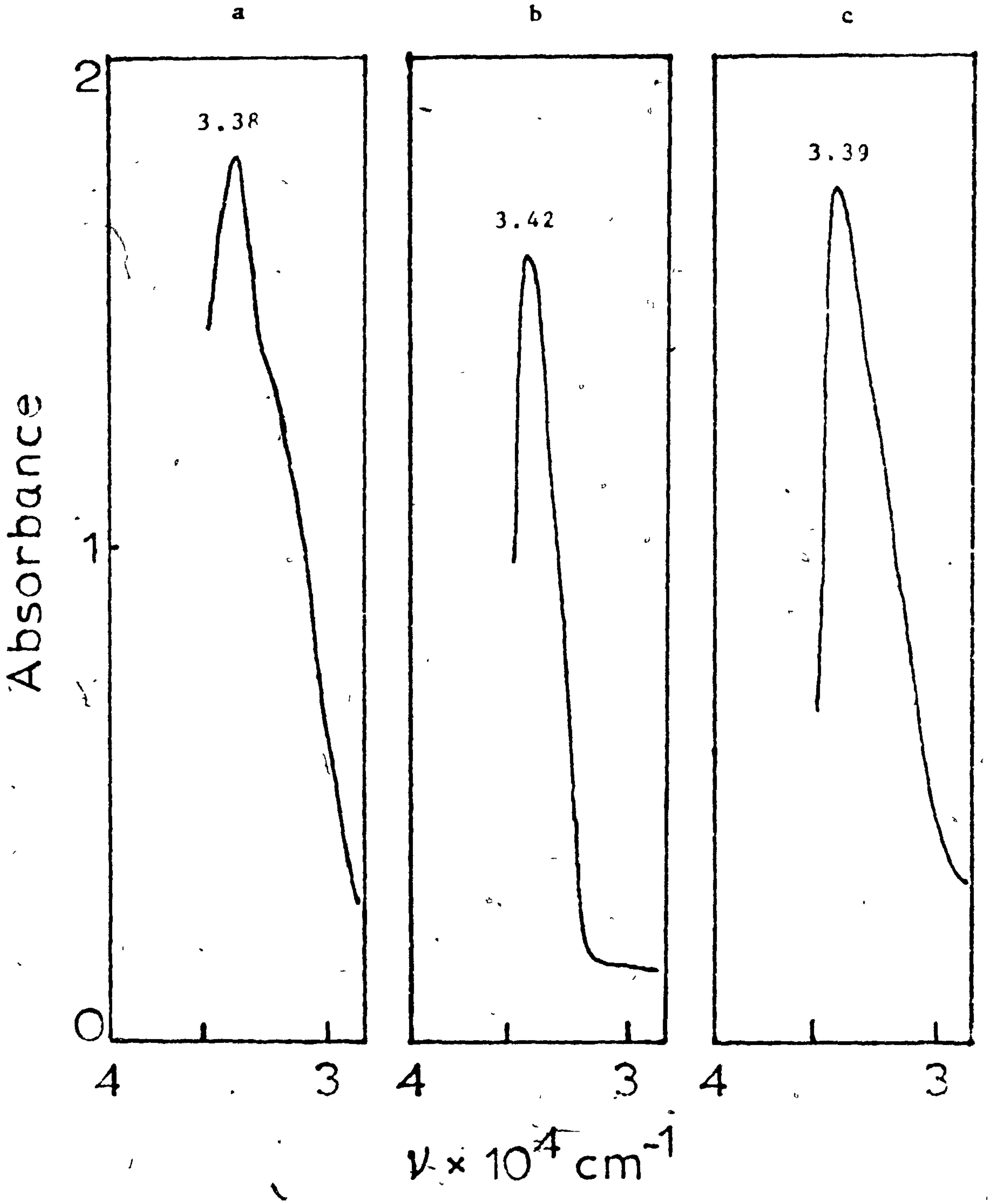

a
b
c
3.38
3.42
3.39
Absorbance
2
1
0
4
3
4
3
4
3
ν × 10⁴ cm⁻¹

FIGURE III - 12

Change in Copper(II) Complex Signal by Electron Spin Resonance Spectroscopy During the Decomposition of $Py_2Cu(TCP)_2$ in Toluene at 100°C.
The marked area at g = 2.007 (lowest curve) is shown at gain x 100 in Figure III - 13.

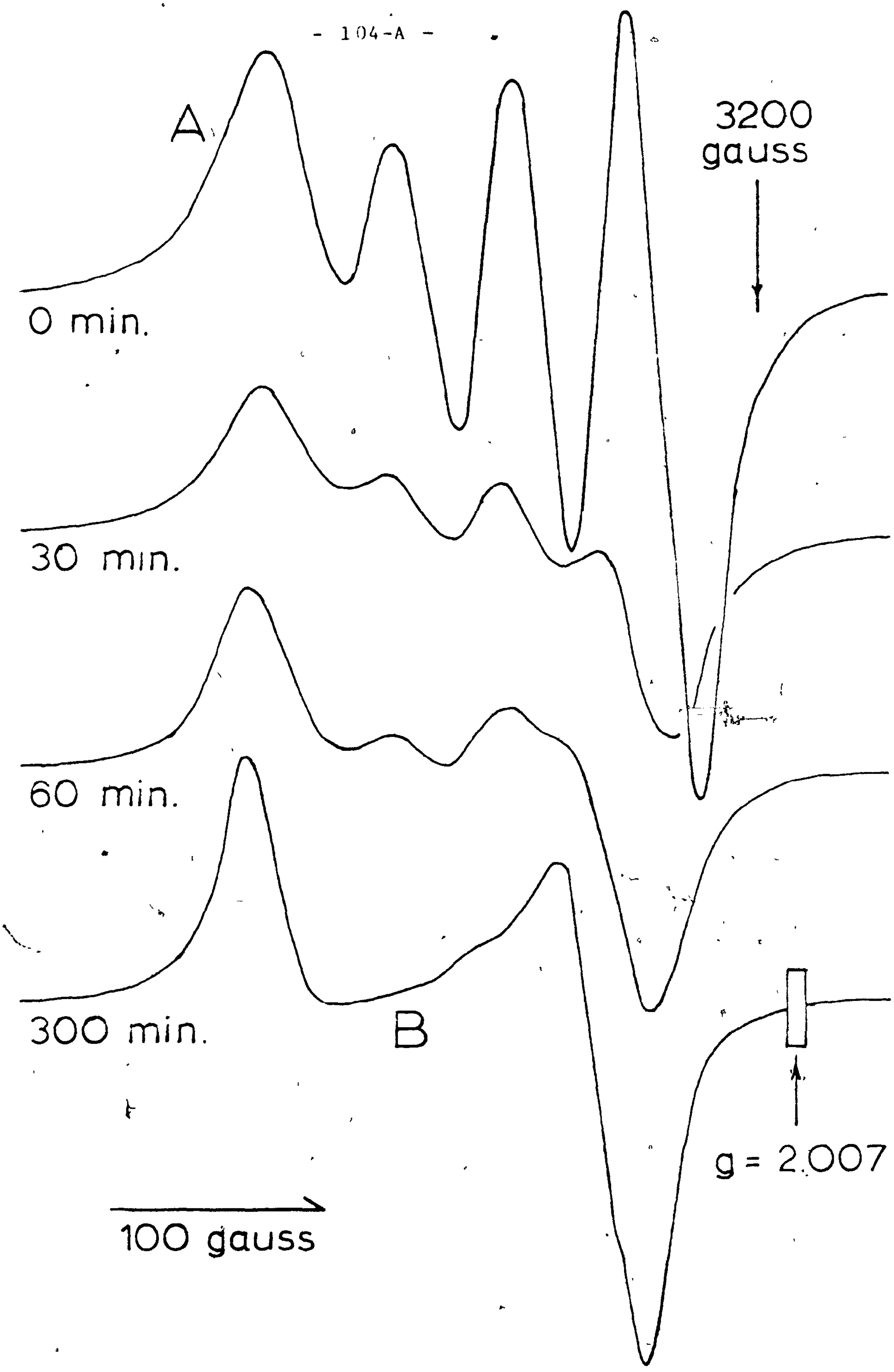
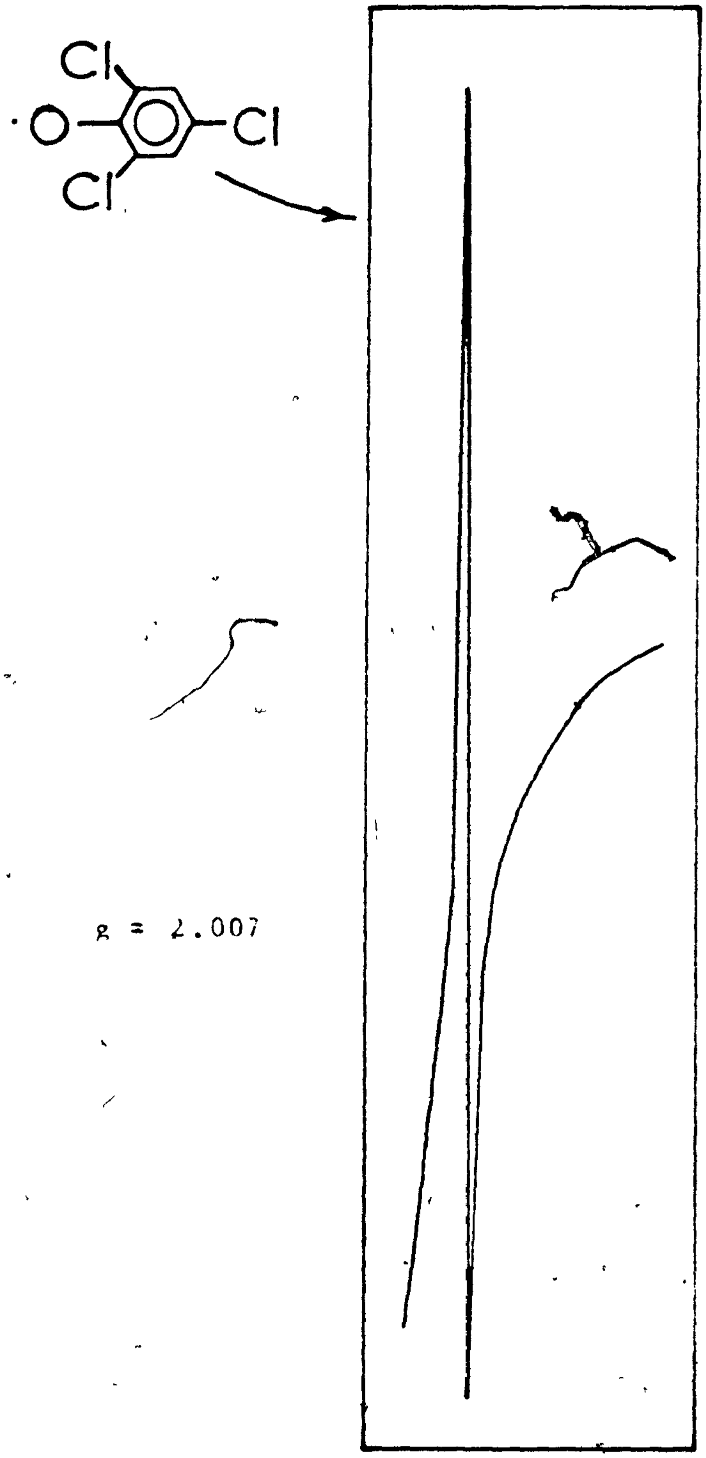

A
3200
gauss
0 min.
30 min.
60 min.
300 min.
B
g = 2.007
100 gauss

FIGURE III - 13

2,4,6- Trichlorophenoxy Radical Signal by Electron Spin Resonance Spectroscopy. The location of this singlet is indicated in the lower curve in Figure III - 12.



g = 2.007

$$g = \frac{h\nu . 2\pi}{\beta H} \qquad \text{III - 1}$$

where $h = 1.05 \times 10^{-27}$ erg. sec.

$\beta = 0.927 \times 10^{-20}$ erg./gauss

$\nu = 9.17 \times 10^{9}$ Hertz

$H = 3250$ gauss

This is in agreement with values of $g = 2.0056$ and 2.007 reported by Tsuruya, et al, (42) and Borg and Elmore (95), respectively for a trichlorophenoxy radical. This is similar to a value of $g = 2.006$ for 2,6-dimethylphenoxy radical (41) or a value of $g = 2.0065$ reported during the thermal oxidation and photo-oxidation of poly(2,6-dimethyl-1,4-phenylene ether) (96). The value for a completely free electron is $g = 2.0023$ (97). The instrument was checked for accuracy with "strong pitch", a standard provided by the Varian Corporation. A value of $g = 2.0027$ was obtained, compared to the theoretical value of $g = 2.0028$.

The trichlorophenoxy radical signal increased in intensity over the time examined. This is shown in Table III - 4. Following these measurements, the sample was allowed to stand in a constant temperature bath at 100°C for five days. After this time, no phenoxy radical signal could be detected.

TABLE III - 4

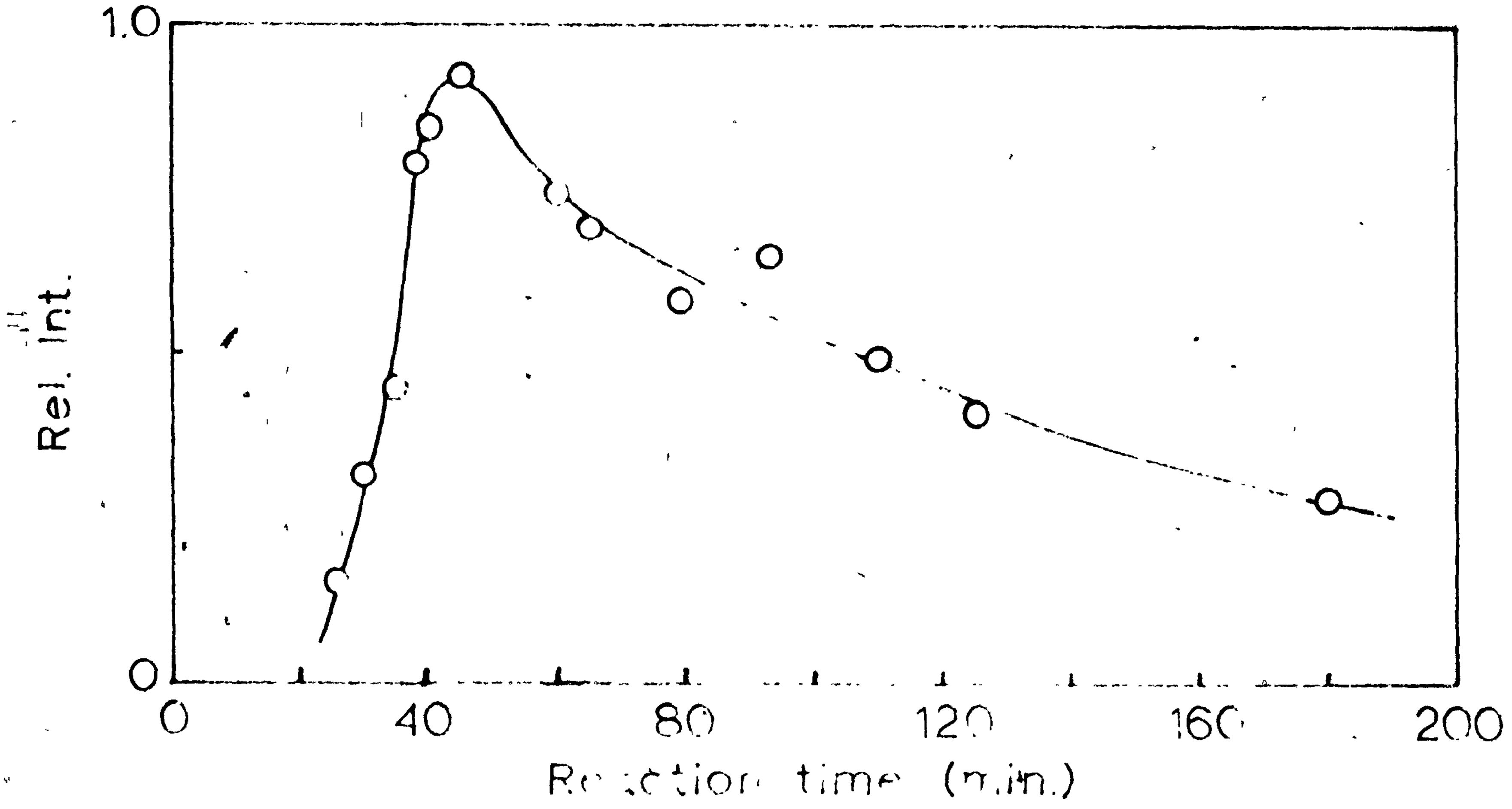
Variation of Intensity of Phenoxy Radical with Time in the Decomposition of $Py_2Cu(TCP)_2$ in Toluene at 100°C

Time (min.)	Intensity (Arbitrary Units)
70	0.05
90	0.09
110	0.16
150	0.22
180	0.37
220	0.44
250	0.61
280	0.73
300	0.80
335	0.94

A similar run was performed at 71°C using benzene as solvent, in the presence of a small amount of carbon tetrachloride (carbon tetrahalides were found to greatly enhance the decomposition, and will be discussed in Section III-2D). This permitted complete investigation over a much shorter period of time. The results, shown in Figure III - 14, demonstrate a rapid build-up of the phenoxy radical signal, followed by a slow decay.

FIGURE III - 14

2,4,6- Trichlorophenoxy Radical Signal at Various Reaction Times in the Decomposition of $Py_2Cu(TCP)_2$ in Benzene at 71°C in the Presence of CCl_4.


Rel. Int.
1.0
0
0
40
80
120
160
200
Reaction time (min.)

B) Decomposition of Bis(trichlorophenoxo)bis(pyridine)copper(II) Under Varied Reaction Conditions.

i) Various Temperatures

The decomposition of bis(trichlorophenoxo)bis(pyridine)copper(II) was followed photometrically at 22,500 cm^{-1} in benzene or toluene (50 gms/l) at various temperatures. Some results are shown in Figure III - 15. As expected, the rate of decomposition increased with temperature. There was also a dramatic change in the induction period.

The number-average molecular weights of the polymers resulting from the decomposition of phenoxocopper(II) at various temperatures are shown in Table III - 5. In all cases, the solutions were given sufficient time to permit complete reaction.

FIGURE III - 15

Decomposition of $Py_2Cu(TCP)_2$ (1.35×10^{-3} moles/l) in Benzene or Toluene at Various Temperatures. Decompositions followed at 22,500 cm^{-1}.

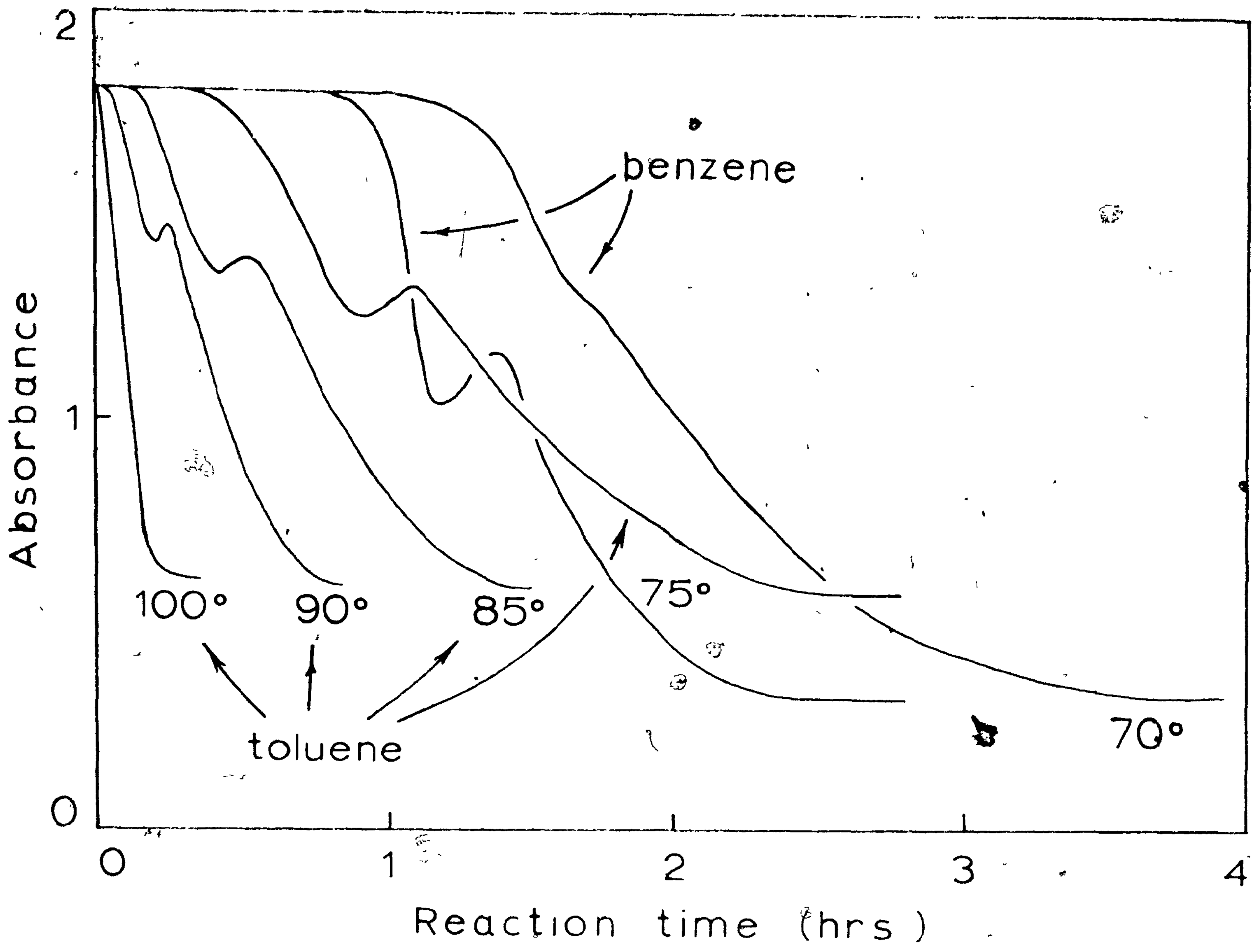

2
1
0
Absorbance
benzene
100°
90°
85°
75°
70°
toluene
0
1
2
3
4
Reaction time (hrs)

TABLE III - 5

$\bar{M}_n$ of Polymers from Decomposition of $Py_2Cu(TCP)_2$ at Various Temperatures

Conc. (gms/1)	Solvent	Temp. (°C)	$\bar{M}n$
40	toluene	20	24,000
40	"	60	16,700
40	"	90	16,600
50	benzene	20	80,000
50	"	71	80,000

ii) Various Concentrations

Bis(trichlorophenoxo)bis(pyridine)copper(II) was decomposed at 71°C for 48 hours at a number of concentrations in benzene. The polymers were isolated and analysed for molecular weight. A plot of concentration versus polymer number-average molecular weight is shown in Figure III - 16. A plot of the square root of these concentrations in moles/l versus molecular weight is shown in Figure III - 17.

The polymer molecular weights from run-to-run for the same concentration were identical assuming constant reaction conditions. This is summarized in Table III - 6.

FIGURE III - 16

Polymer Molecular Weight at Various Concentrations of $Py_2Cu(TCP)_2$ in Benzene at 71°C. Reaction Time = 48 hrs.

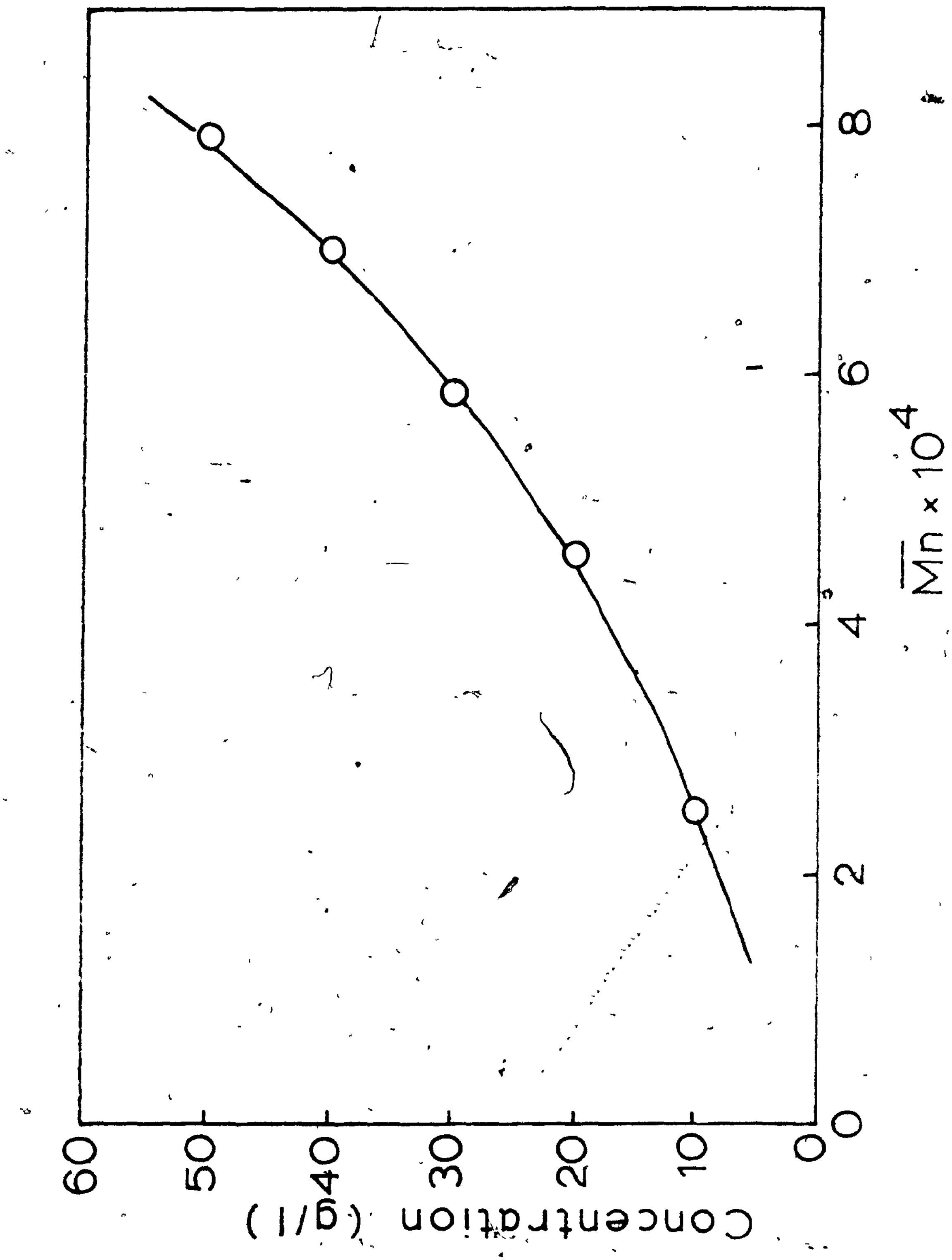

Concentration (g/l)
0
10
20
30
40
50
60
$\overline{Mn} \times 10^4$
0
2
4
6
8

FIGURE III - 17

Polymer Molecular Weight at Various Concentrations of $Py_2Cu(TCP)_2$ in Benzene at 71°C. Reaction Time = 48 hrs.

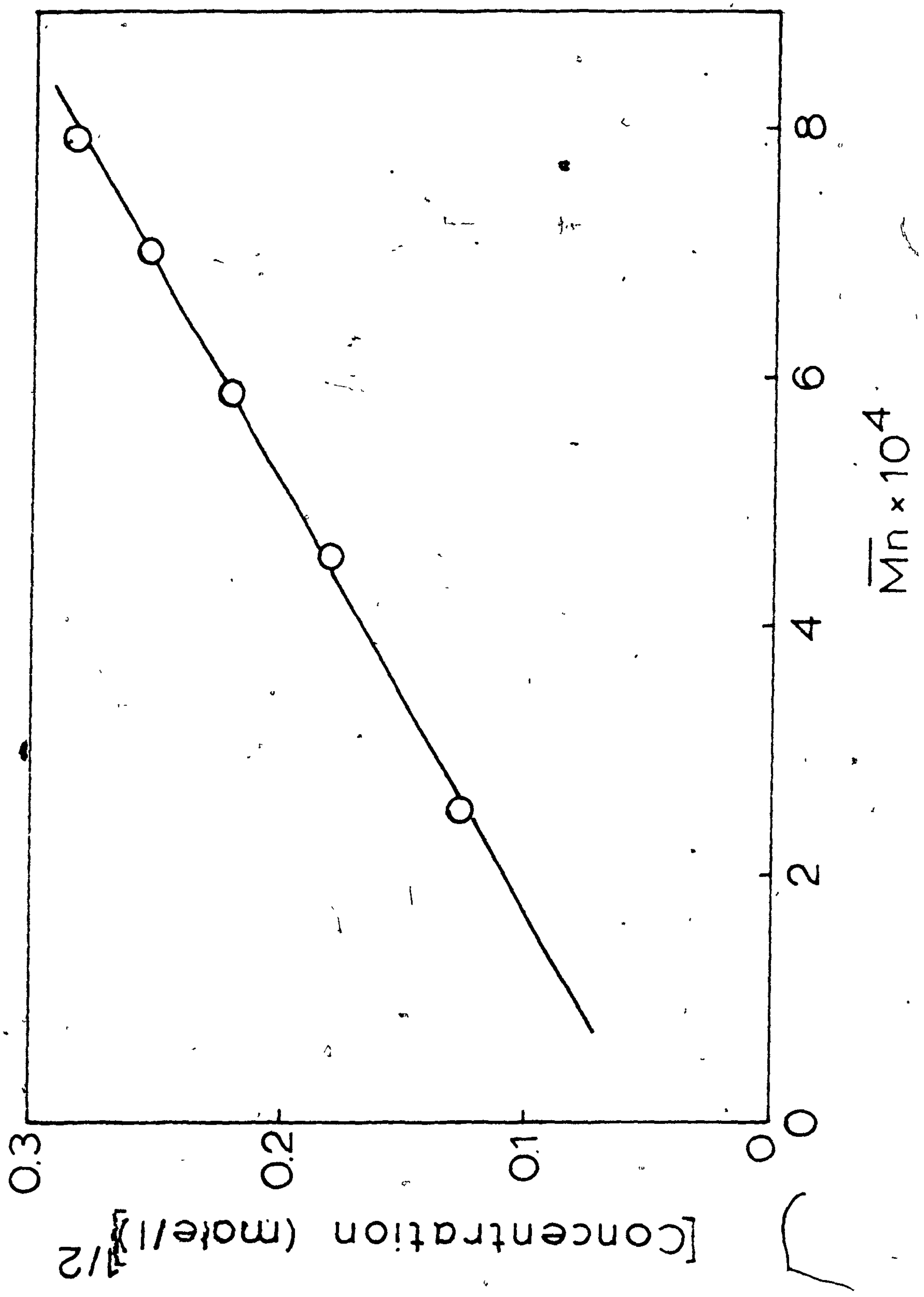

0.3
0.2
0.1
0
[Concentration (mole/l)]$^{1/2}$
0
2
4
6
8
$\overline{Mn} \times 10^4$

TABLE III - 6

$\bar{M}_n$ of Polymers from Decomposition of $Py_2Cu(TCP)_2$ in Benzene (40 gms/l)

Temp. (°C)	Conc. (gms/l)	$\bar{M}_n$
71	1 gm/25ml	44,500
71	2 gm/50ml	46,000
71	3 gm/75ml	46,000
71	4 gm/100ml	45,600

iii) Various Solvents

The decomposition of bis(trichlorophenoxo)bis(pyridine)copper(II) in benzene, toluene or cumene at 75°C was examined photometrically at 22,500 cm^{-1}. The results are shown in Figure III - 18.

It was found that the solvent utilized had an adverse effect on the reaction products produced. The effect on polymer is shown in Table III - 7. The effect on the copper(II) complexes will be discussed in Section III - 4.

FIGURE III - 18

Decomposition of $Py_2Cu(TCP)_2$ (1.35×10^{-3} moles/l) in Various Solvents at 71°C at 22,500 cm^{-1}.

○ ○ ○ benzene

△ △ △ toluene

□ □ □ cumene

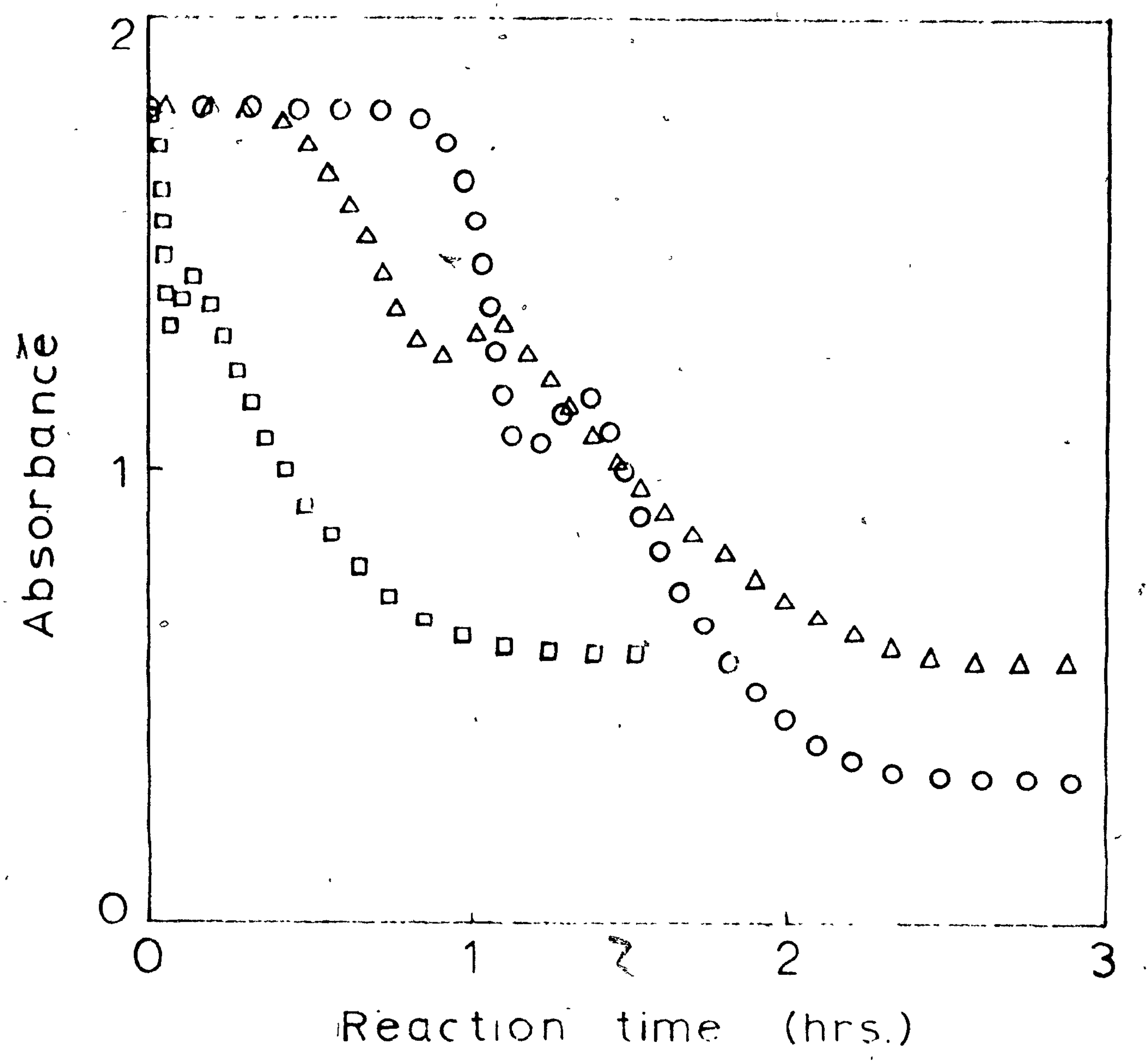

2
1
0
Absorbance
0
1
2
3
Reaction time (hrs.)

TABLE III - 7

$\bar{M}_n$ of Polymers from Decomposition of $Py_2Cu(TCP)_2$ for 48 hours in Various Solvents

Conc. (gms/l)	Solvent	$\bar{M}_n$
50	benzene	79,000
50	toluene	39,000
50	cumene	13,000

C) Decomposition of Other Phenoxo-metal Complexes

i) Phenoxo Complexes Containing Metals Other Than Copper.

a) Trichlorophenoxo-pyridine-nickel(II)

The infrared spectrum of this green complex is shown in Chapter VII, and contains evidence of both trichlorophenoxo and pyridine ligands. The ultra-violet-visible spectrum is demonstrated in Figure III - 19.

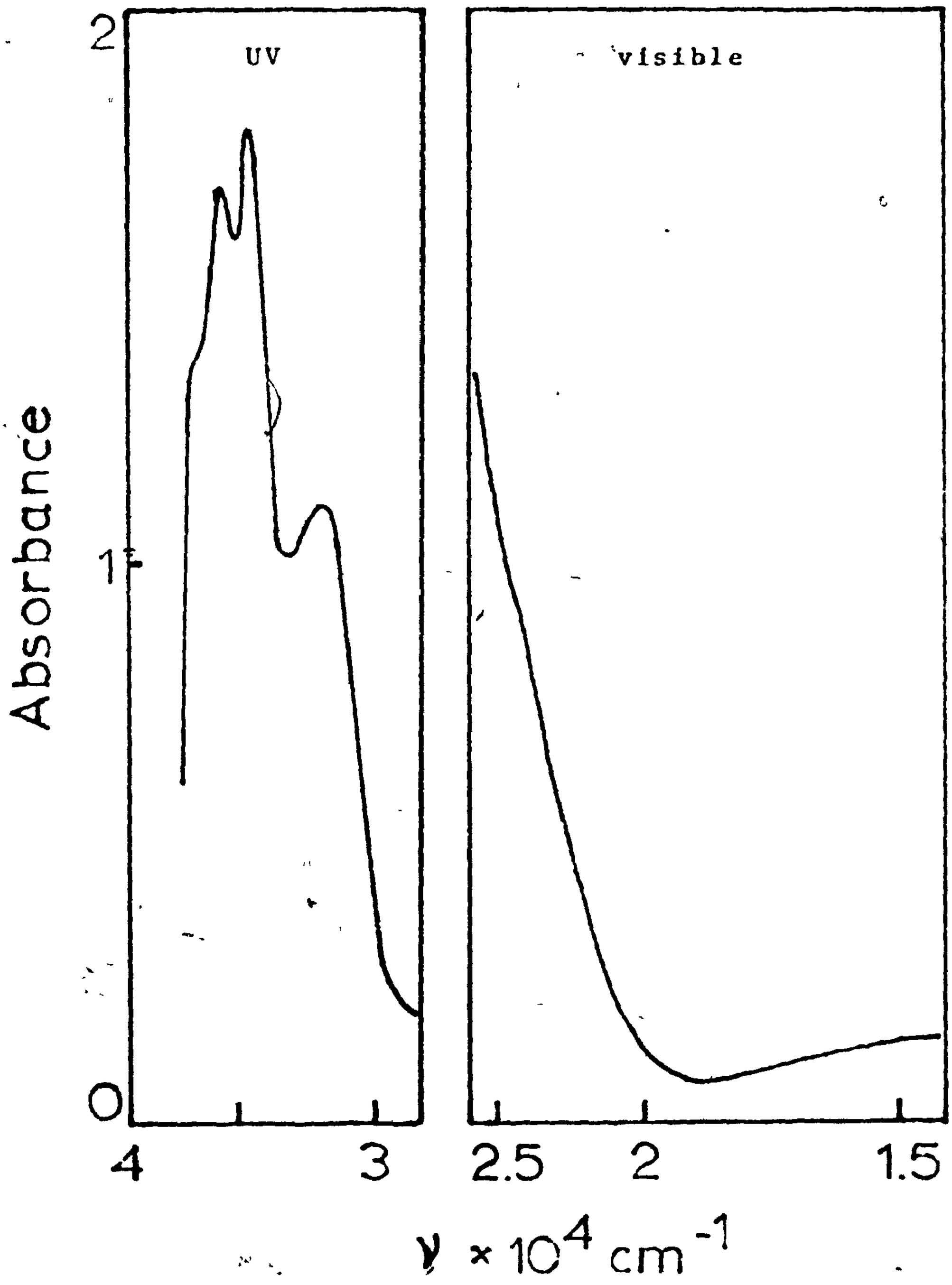
The complex was found to be relatively stable in air. In organic solvents, such as benzene, the complex showed no sign of decomposition, even at 70°C for a reaction time of 24 hours.

FIGURE III - 19

Ultraviolet-Visible Spectrum of $Py_2Ni(TCP)_2$ in Benzene

Conc. = 4 x 10^{-3} M in visible region

= 4 x 10^{-4} M in ultraviolet region


UV
visible
Absorbance
2
1
0
4
3
2.5
2
1.5
ν × 10^4 cm^{-1}

No further experiments were performed with this complex.

b) Trichlorophenoxo-pyridine-cobalt(II)

The infrared spectrum of these purple crystals is shown in Chapter VII. The presence of trichlorophenoxo and pyridine ligands were clearly indicated. The ultraviolet-visible spectrum is shown in Figure III - 20.

This complex was found to be stable in both air and solution. There was no indication of decomposition in benzene at 70°C for 24 hours.

No further experiments were performed on this complex.

ii) Polyhalophenoxo-pyridine-copper(II) Complexes

a) Bis(4-bromo-2,6-dichlorophenoxo)-bis(pyridine)copper(II)

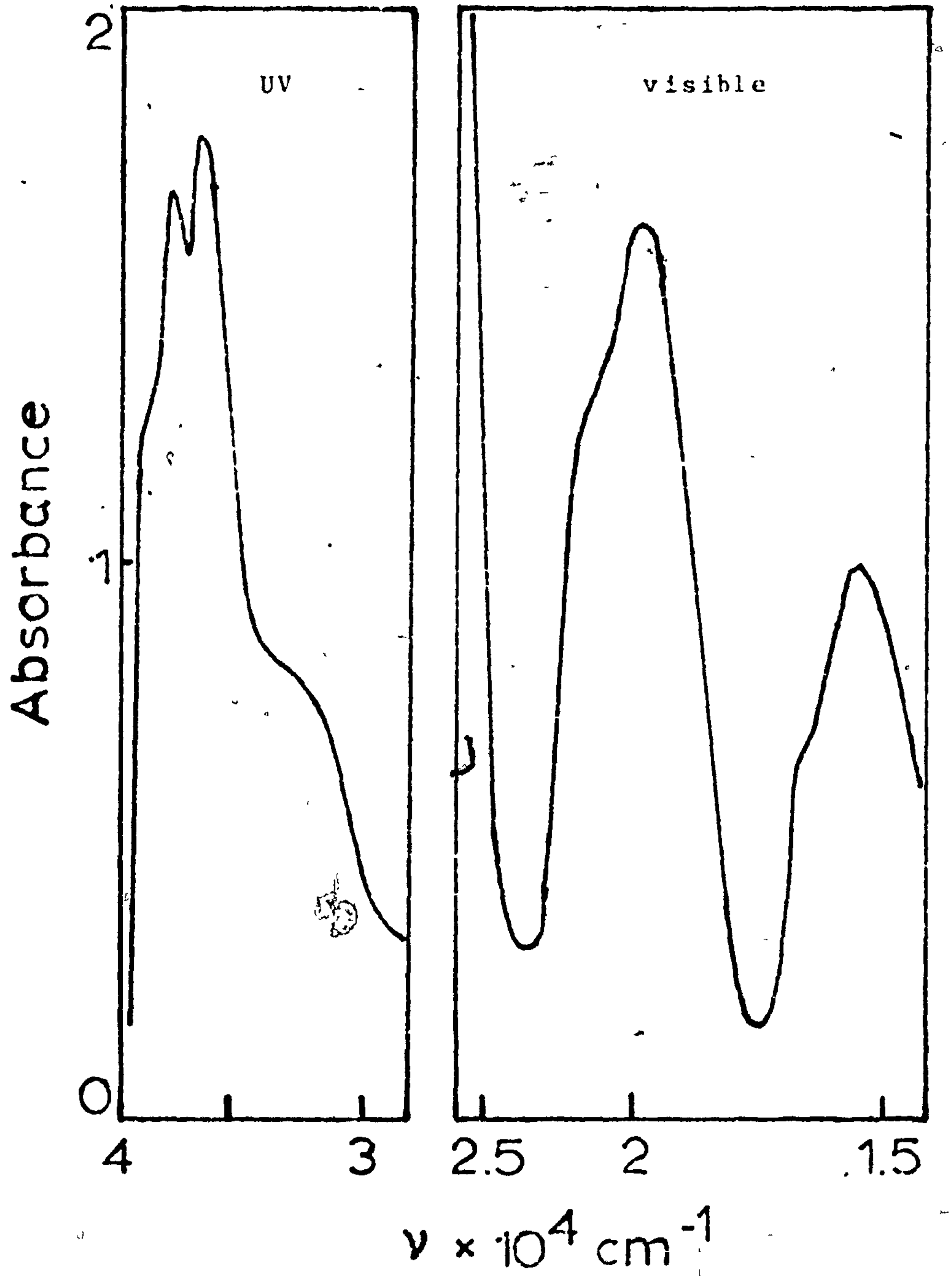
The ultraviolet-visible spectrum

FIGURE III - 20

Ultraviolet-Visible Spectrum of $PyCo(TCP)_2$ in Benzene

Conc. = 4×10^{-3} M in visible region

= 2×10^{-4} M in ultraviolet region


UV
visible
Absorbance
2
1
0
4
3
2.5
2
.1.5
ν × 10⁴ cm⁻¹

of this complex is shown in Figure III - 21. The absence of any well defined maximum absorption in the visible region prevented following the reaction by ultraviolet-visible spectrophotometry.

The phenoxocopper(II) complex, first reported by Blanchard, *et al*, (2), was decomposed in benzene or toluene (5 gms/l) at 71°C for 24 hours. It had been hoped that there would be increased reactivity at the 4- position, due to the more readily displaced bromine atom (69). Linear poly(2,6-dichloro-1,4-phenylene ether) was the ultimate goal. Stanatoff (74) had reported the succesful preparation of this polymer with exclusive 1,4- linkage using 4-bromo-2,6-dichlorophenol and benzoyl peroxide as initiator.

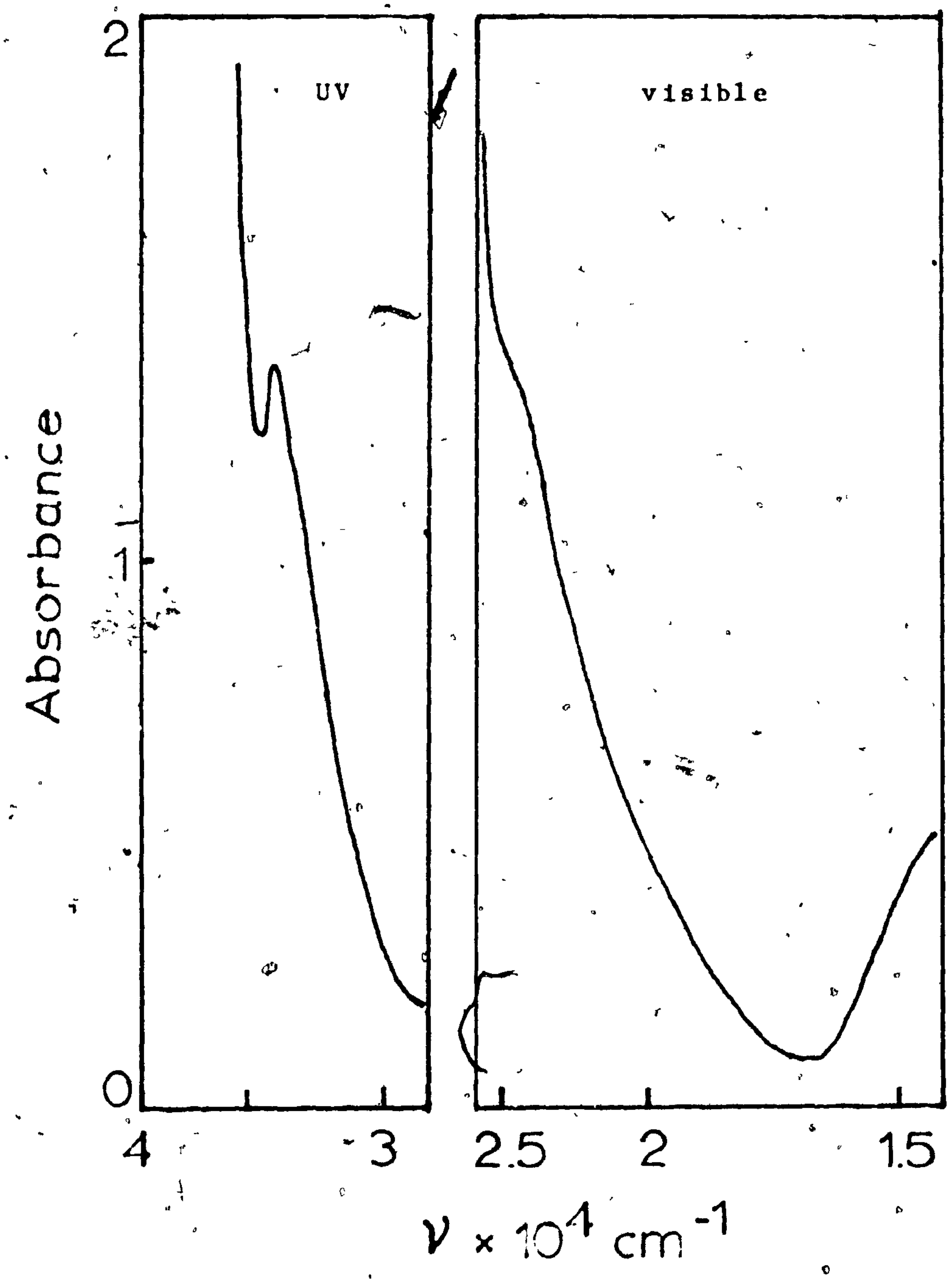
In order to have exclusively 1,4- linkage, the dihalocopper(II) reaction product from the decomposition of the phenoxocopper(II) complex would have to be entirely Py_2CuBr_2. The precipitated complex turned out to be caked with insoluble polymer. The polymer was separated with hot toluene. Analyses of both the copper(II) complex and polymer, in the case where benzene was used as solvent, are shown in Table III - 8. Similar results were obtained with toluene as solvent. The presence

FIGURE III - 21

Ultraviolet-Visible Spectrum of $Py_2Cu(Cl_2BrP)_2$ in Benzene

Conc. = 1.2×10^{-3} in visible region

= 1.5×10^{-4} in ultraviolet region


Absorbance
2
1
0
UV
visible
4
3
2.5
2
1.5
$\nu \times 10^4\ cm^{-1}$

of some Py_2CuCl_2 was also indicated by far-infrared spectroscopy.

TABLE III - 8

Elemental Analyses of Reaction Products from Decomposition of $Py_2Cu(Cl_2BrP)_2$ in Benzene at 71°C

	Theor. for Py_2CuBr_2	Anal. %	Theor. for polymer	Anal. %
C	31.5	32.51		
H	2.6	2.52		
Cl	0.	3.84	44.1	35.29
Br	42.	35.87	0.	5.38
N	7.3	7.62		
Cu	16.6	17.60		

The molecular weight of the polymer was found to be: benzene as solvent, $\bar{M}_n$ = 126,000, toluene as solvent, $\bar{M}_n$ = 130,000.

The 4-bromo-2,6-dichlorophenoxocopper(II) complex was also decomposed at room temperature for 1.5 months in benzene. It was hoped that reaction at lower temperature would result in greater selectivity towards coupling at the 4-position. The analysis for the polymer produced in this reaction was as follows:

Calcd. for linear polymer: Cl, 44.1%; Br, 0%.

Found: Cl, 39.23%; Br, 6.68%.

This analysis indicates no increase in selectivity at lower temperature.

The low temperature polymer was found to be soluble in toluene above 70°C. The resulting gummy solution of polymer in hot toluene was separated from the copper(II) precipitate by decantation instead of filtration. Several washings with hot toluene were made to ensure complete isolation. No suitable solvent was found for determination of the molecular weight of this polymer at ambient temperature. It can be assumed, however, that $\bar{M}_n$ was considerably higher than that found for other similar polymers prepared at higher temperature.

b) <u>Bis(tribromophenoxo)bis(pyridine)-copper(II)</u>

This tribromophenoxocopper(II) complex, first reported by Blanchard, et al (2), was decomposed in benzene, or toluene, (50 gms/l) at 71°C. Reaction took place very rapidly. The green copper(II) precipitate resulting from the reaction was shown to be Py_2CuBr_2 by far-infrared spectroscopy, (cf. Chapter VII). Confirmation of structure was made by comparison with results reported by Goldstein, et al (92). The visible spectrum of tribromophenoxocopper(II) and the resulting solution after decomposition is shown in Figure III - 22. A photometric study of the decomposition of tribromophenoxocopper(II) at 22,300 cm^{-1} in benzene at 75°C is shown in Figure III - 23.

The infrared spectrum of the polymer agreed with that obtained by Tsuruya, et al (96), for poly(2,6-dibromophenylene ether). The infrared spectrum is shown in Chapter VII.

Apart from results reported in Section III - 4, for the formation of μ_4-oxocopper(II) complexes, no further investigations were carried out on this compound.

c) Bis(triiodophenoxo)bis(pyridine)copper(II)

The visible spectrum of this phenoxocopper(II) complex and the solution after decomposition is shown in Figure III - 24. These maroon-coloured crystals were found to be relatively unstable in the solid state. In solution, using benzene as solvent, the complex decomposed readily, giving a white polymer. The infrared spectrum of this polymer is shown in Chapter VII. A photometric study

FIGURE III - 22

Visible Spectrum of $Py_2Cu(TBP)_2$ and Solution After Decomposition.

a) $Py_2Cu(TBP)_2$

b) solution after decomposition.

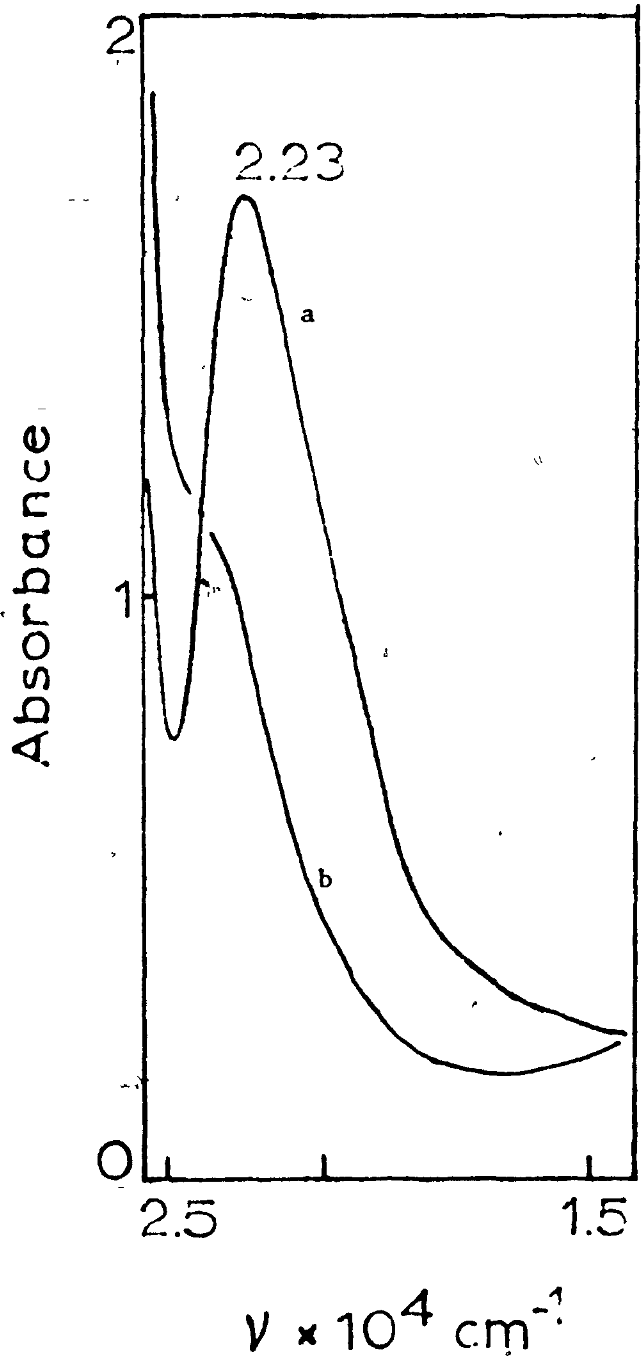

2
1
0
Absorbance
2.23
a
b
2.5
1.5
ν × 10⁴ cm⁻¹

FIGURE III - 23

Decomposition of $Py_2Cu(TBP)_2$ at 22,300 cm^{-1} in Benzene at 75°C.

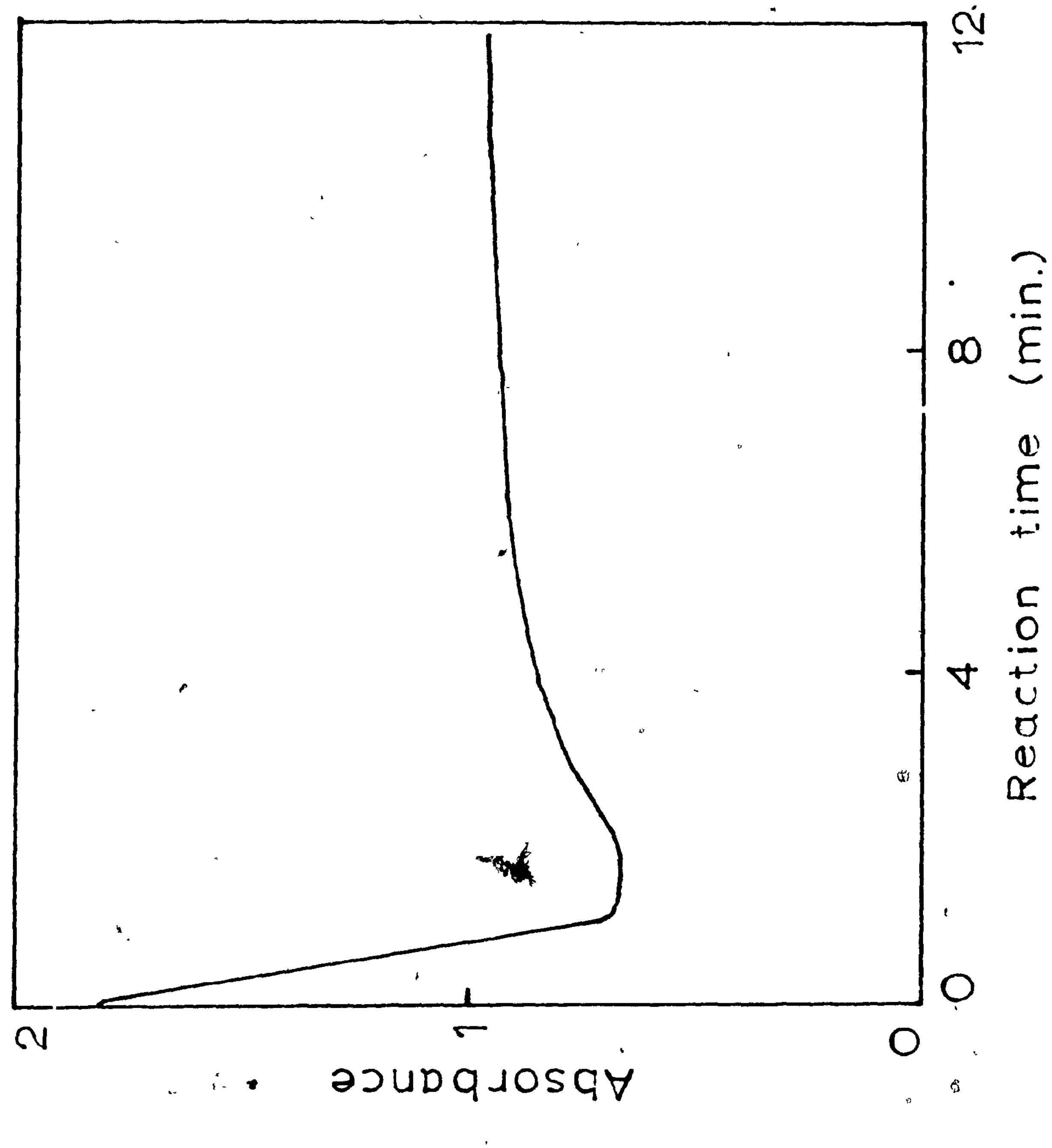
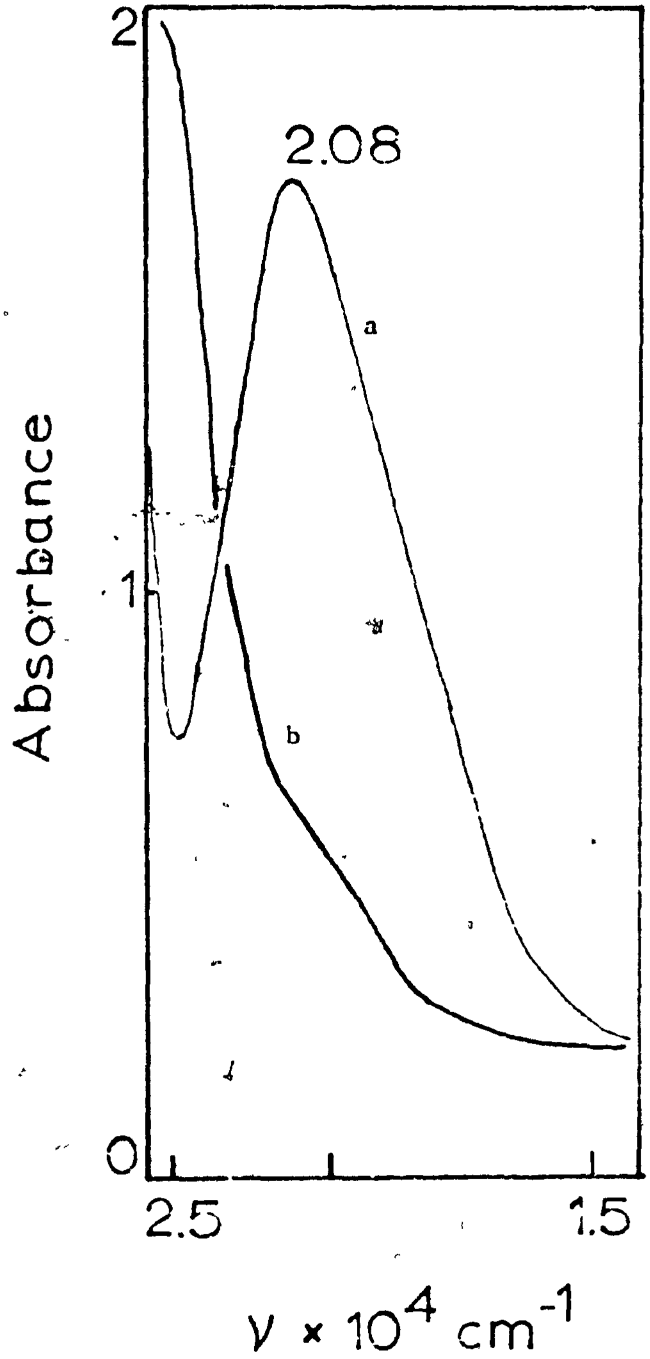

Absorbance
2
1
0
Reaction time (min.)
0
4
8
12

FIGURE III - 24

Visible Spectrum of $Py_2Cu(TIP)_2$ and Solution After Decomposition

a) $Py_2Cu(TIP)_2$

b) solution after decomposition.


2
1
0
Absorbance
2.08
a
b
2.5
1.5
$\nu \times 10^4$ cm^{-1}

of the decomposition of triiodophenoxocopper(II) at 20,800 cm^{-1} in benzene at 75°C is shown in Figure III - 25.

No further studies were conducted on this phenoxocopper(II) complex.

iii) Trichlorophenoxocopper(II) Complexes Containing Neutral Ligands Other Than Pyridine.

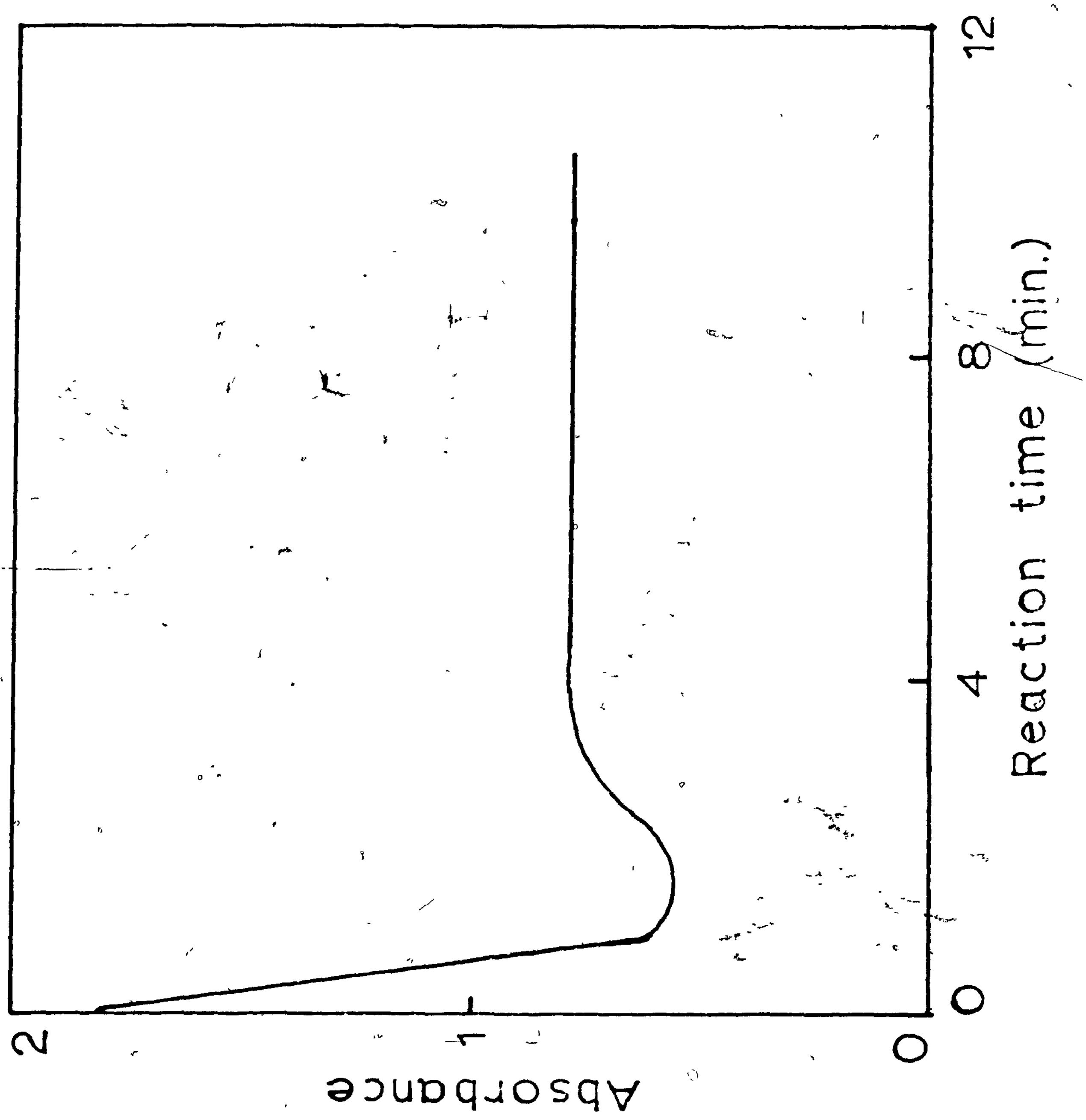
a) N,N,N',N'-Tetramethylethylenediamine as Neutral Ligand

Bis(trichlorophenoxo)(tetramethylethylenediamine)copper(II), first reported by Harrod (34), was decomposed in benzene (saturated solution) at room temperature for five months. The reaction products were a blue copper(II) complex and polymer. The polymer was identical to polymer from the decomposition of trichlorophenoxo-pyridine-copper(II) as evidenced by its infrared and nuclear magnetic resonance spectra. The number-average molecular weight was found to be 161,000.

Bis(4-bromo-2,6-dichlorophenoxo)-(tetramethylethylenediamine)copper(II) was formed as dark red-

FIGURE III - 25

Decomposition of $Py_2Cu(TIP)_2$ at 20,800 cm^{-1} in Benzene at 75°C.


Absorbance
2
1
0
Reaction time (min.)
0
4
8
12

brown crystals. These were stable in air in the solid state. The ultraviolet-visible spectrum is shown in Figure III - 26.

This complex was decomposed in benzene (25 gms/l) at room temperature for four months. The reaction products were a dark green copper(II) precipitate and a partially insoluble polymer. The latter compound gave infrared and nuclear magnetic resonance spectra identical to polymer obtained from the corresponding pyridine complex.

Although these phenoxo-tetramethylethylenediaminecopper(II) complexes exhibited clearly defined maxima at 20,500 and 20,600 cm^{-1} respectively, their decompositions were not studied photometrically.

b) Other Compounds as Neutral Ligand

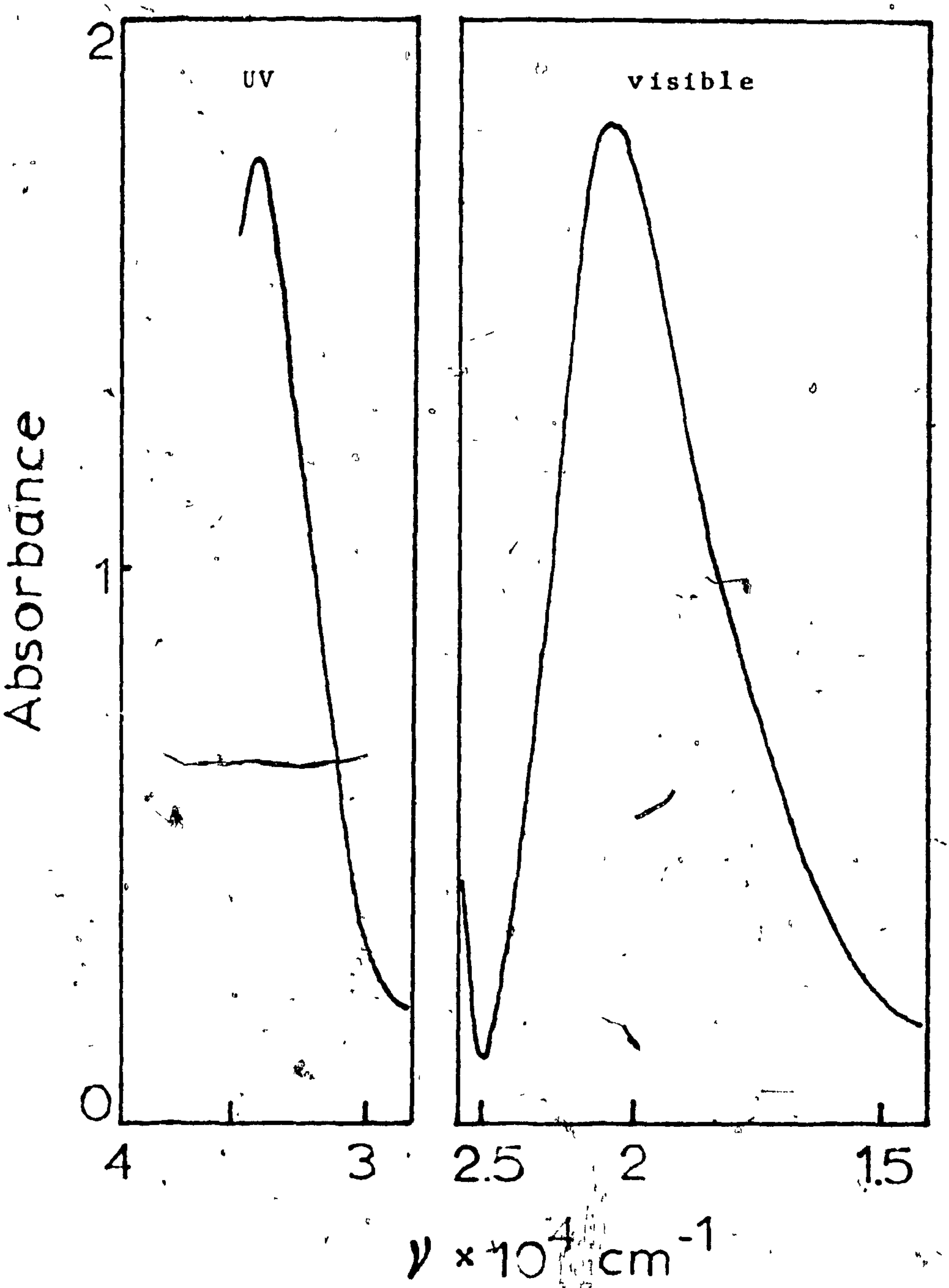
Phenoxocopper(II) complexes containing ammonia, ethylamine, dimethylformamide or dimethylsulphoxide as neutral ligand were decomposed in various solvents in an attempt to prepare the corresponding μ_4-oxocopper(II) complexes. The results are discussed in Section III - 4. No other studies were performed on these complexes.

FIGURE III - 26

Ultraviolet-Visible Spectrum of $(TMED)Cu(Cl_2BrP)_2$ in Benzene

concentration = 6×10^{-4} in visible region

= 6×10^{-5} in ultraviolet region


Absorbance
2
1
0
UV
visible
4
3
2.5
2
1.5
$\nu \times 10^4$ cm^{-1}

D) Effect of Additives on the Decomposition of Bis(trichlorophenoxo)bis(pyridine)copper(II).

i) Free Radical Initiators

The reaction rate of bis(trichlorophenoxo)bis(pyridine)copper(II) was strongly affected by the addition of free radical initiators. The decomposition was studied photometrically at 22,500 cm^{-1}. Some results are shown in Figure III - 27. A number of peroxides and hydroperoxides were examined, as well as azobispropionitrile.

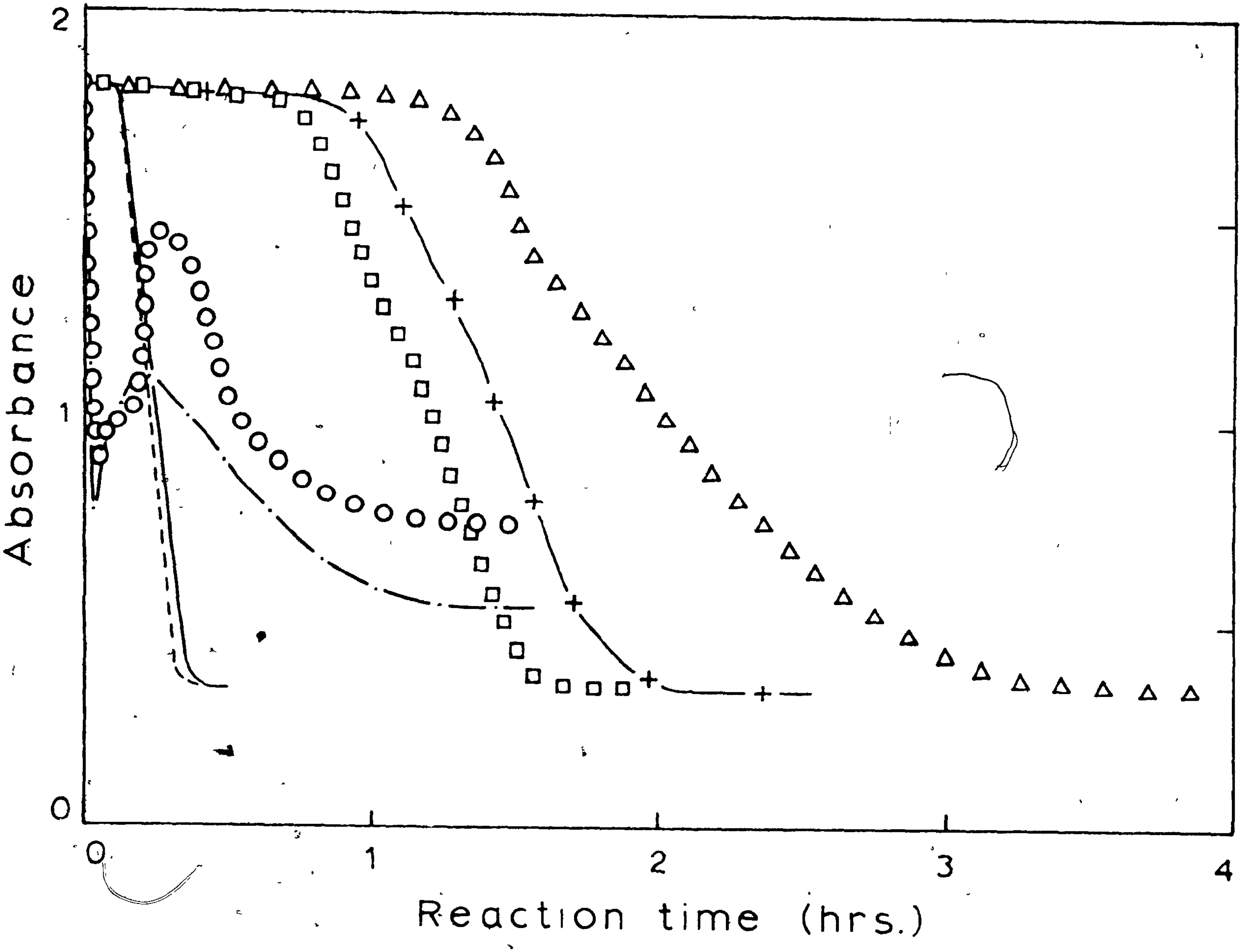
From Figure III - 27, the peroxide and azo initiators appeared to reduce the induction period and increase the reaction rate. The hydroperoxides, however, seemed to have a more complicated effect. This will be discussed further in Section III - 4.

Analysis of polymers by infrared spectroscopy showed no evidence of initiator fragments. The number-average molecular weight of polymer, from trichlorophenoxocopper(II) in the presence of a 1:1 molar ratio of cumyl hydroperoxide, reacted in benzene (50 gms/l) at $71^{\circ}C$ for 24 hours, was 44,000. In comparison, polymer obtained under identical circumstances, but in the absence of hydro-

FIGURE III - 27

Decomposition of $py_2Cu(TCP)_2$ (1.35×10^{-3} m) in Benzene at 71°C in the Presence of a 10:1 Molar Ratio of Various Free Radical Initiators (Initiator to $Py_2Cu(TCP)_2$). Reactions followed at 22,500 cm^{-1}.

△ △ △	no initiator
—+—	*tert*-butyl peroxide
□ □ □	dicumyl peroxide
———	benzoyl peroxide
—·- - -	2,2'-azobis[propionitrile]
—·—	*tert*-butyl hydroperoxide
○ ○ ○	cumene hydroperoxide


Absorbance
2
1
0
0
1
2
3
4
Reaction time (hrs.)

peroxide, had a molecular weight of 49,000.

The effect of benzoyl peroxide on the induction period in the decomposition of trichlorophenoxocopper(II) is shown in Figure III - 28.

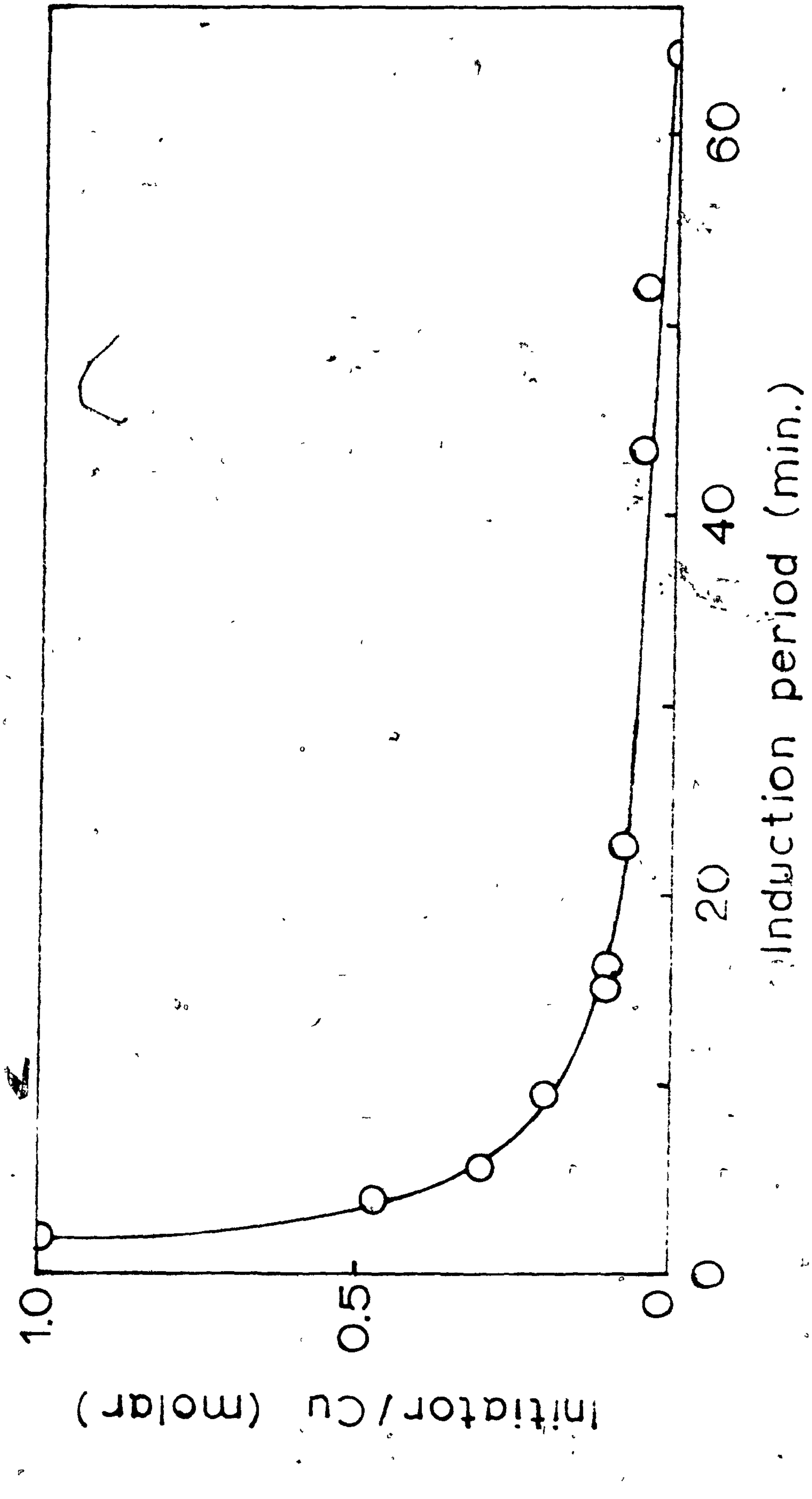
ii) Carbon Tetrahalides

The addition of carbon tetrahalides to a solution of bis(trichlorophenoxo)bis(pyridine)-copper(II) was found to greatly enhance the decomposition rate. A solution of this phenoxocopper(II) complex in benzene (50 gms/l) took three months to decompose at room temperature. On the other hand, an identical solution, containing a 10:1 molar ratio ($CCl_4/Py_2Cu(TCP)_2$) of carbon tetrachloride, reacted in less than one week. Similar results were obtained with bis(trichlorophenoxo)(tetramethylethylenediamine)copper(II), using carbon tetrabromide.

Similar findings were also obtained at elevated temperatures. The dihalocopper(II) precipitate was detected within fifteen minutes for a 10:1 molar solution ($CX_4/Py_2Cu(TCP)_2$) of the phenoxocopper(II) complex in benzene (4 gms/l) at 71°C. Without the carbon

FIGURE III - 28

Effect on the Induction Period at Various Concentrations of Benzoyl Peroxide as Initiator in the Decomposition of $Py_2Cu(TCP)_2$ (1.35×10^{-3} M) in Benzene at 71°C.


Induction period (min.)
0
20
40
60
Initiator / Cu (molar)
1.0
0.5
0

tetrahalides, approximately three hours were required to reach the equivalent stage of reaction.

The effect of carbon tetrabromide on the rate of decomposition of trichlorophenoxocopper(II) in benzene at 70°C was studied photometrically at 22,500 cm^{-1}. The results are shown in Figure III - 29.

The reaction products from the decomposition of trichlorophenoxocopper(II) in the presence of a 10:1 molar ratio of carbon tetrabromide were analysed for the presence of bromine. The results are summarized in Table III - 9.

TABLE III - 9

Analysis of Reaction Products from the Decomposition of $Py_2Cu(TCP)_2$ in the Presence of CBr_4 at 71°C

product	% Cl	% Br
Py_2CuX_2	23.75	4.00
polymer	44.1	0.

The polymer number-average molecular weight did not appear to be affected by the addi-

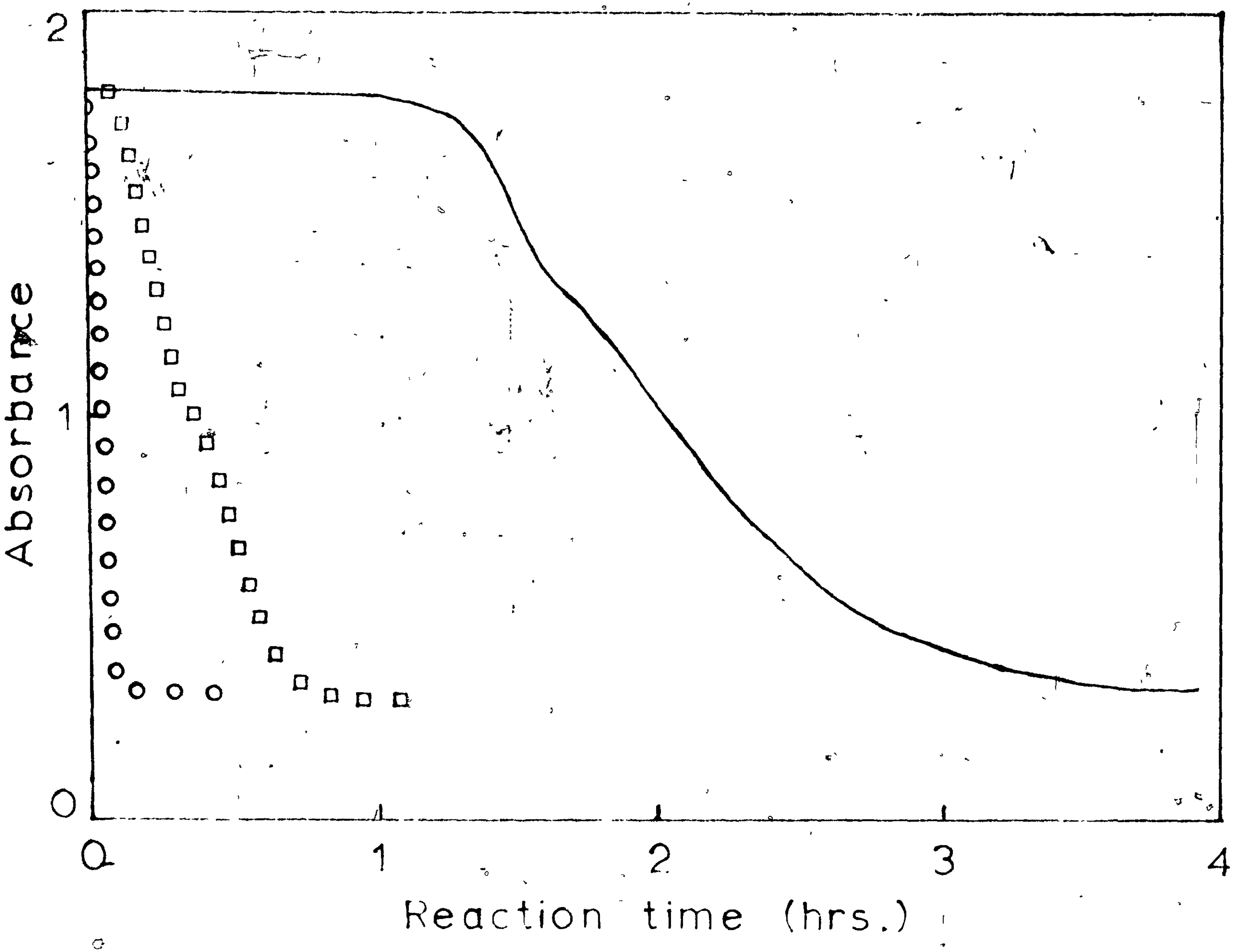
FIGURE III - 29

Effect of the Addition of CBr_4 on the Decomposition of $Py_2Cu(TCP)_2$ in Benzene at 70°C. Reactions followed at 22,500 cm^{-1}.

——— no CBr_4

□ □ □ trace of CBr_4

○ ○ ○ 10:1 Molar Ratio (CBr_4 to $Py_2Cu(TCP)_2$)


Absorbance
2
1
0
Reaction time (hrs.)
0
1
2
3
4

tion of carbon tetrahalides. This is shown in Table III - 10.

TABLE III - 10

$\bar{M}_n$ of Polymer from the Decomposition of $Py_2Cu(TCP)_2$ (50 gms/l) in Benzene at 71°C in the Presence of CX_4

Rxn. time (hrs.)	$\bar{M}_n$	CX_4
68	49,000	none
68	49,000	CCl_4
68	46,000	CBr_4

The additional reaction products, due to the presence of carbon tetrahalides, were analysed by a coupled gas chromatograph-mass spectrometer. Samples were prepared by preliminary removal of the dihalocopper(II) complex and polymer. About 75% of the benzene/methanol was then removed by distillation on a rotary evaporator.

For an initial 1:1 molar concentration ($CBr_4/Py_2Cu(TCP)_2$), dichlorobenzene was detected. This is shown in Figure III - 30. Dichlorobenzene was not evident as a reaction product from the decomposition of phenoxocopper(II) in the absence of carbon tetrahalides.

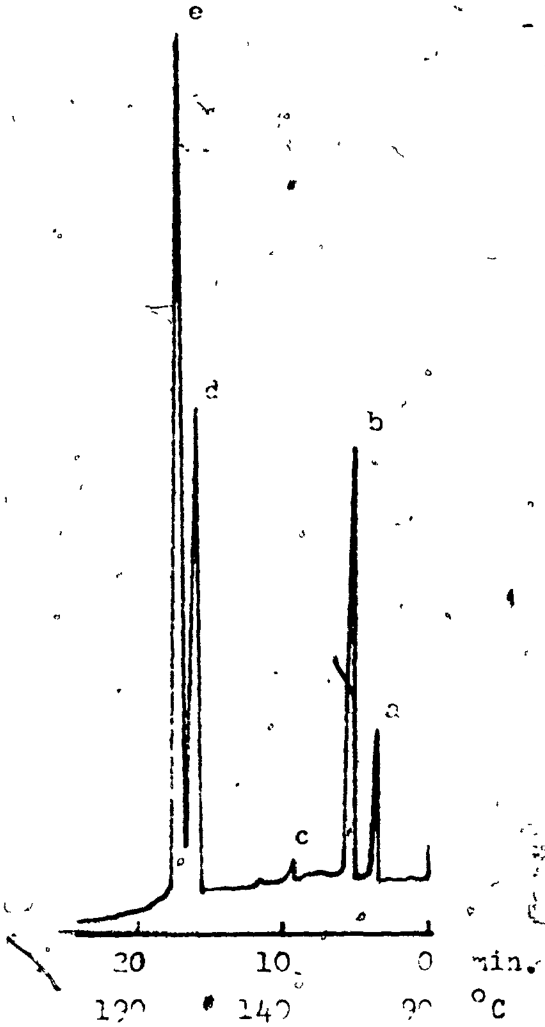
FIGURE III - 30

i) Gas-Chromatogram of Reaction Mixture in Presence of 1:1 Molar Ratio of CBr_4 (CBr_4 to $Py_2Cu(TCP)_2$).

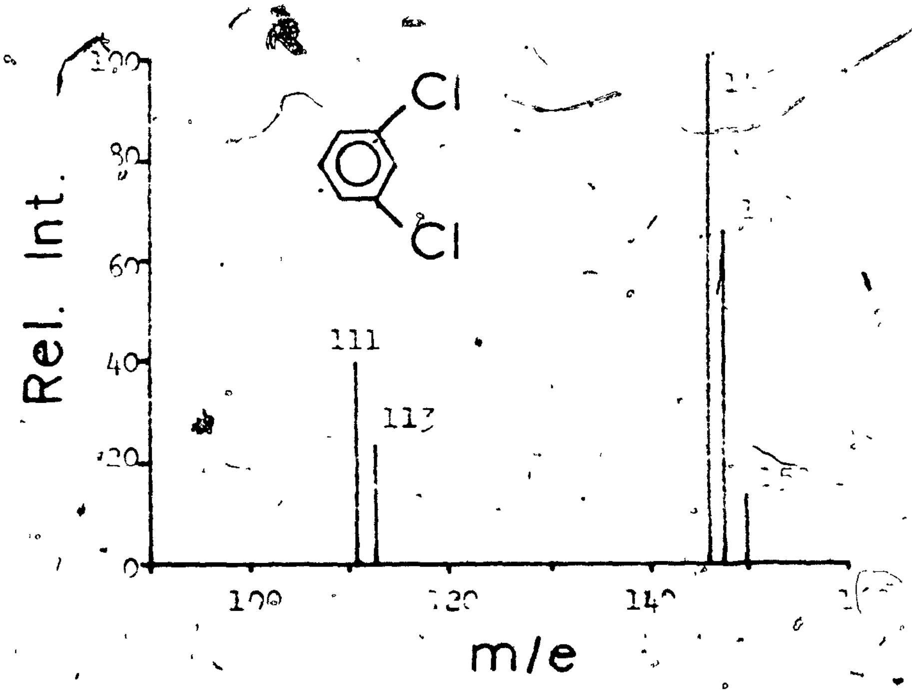
- a) methanol
- b) benzene
- c) $CHBr_3$?
- d) dichlorobenzene
- e) CBr_4

ii) Mass Spectrum of Dichlorobenzene.

i)


e
d
b
a
c
20
10
0
min.
190
140
90
°C

ii)


Rel. Int.
100
80
60
40
20
0
Cl
Cl
111
113
100
120
140
m/e

For an initial 10:1 molar concentration ($CBr_4/Py_2Cu(TCP)_2$), chlorotribromomethane, CBr_3Cl, was detected. This is shown in Figure III - 31. There was no indication of the presence of dichlorobenzene.

The mass spectrum of carbon tetrabromide is shown in Figure III - 32.

iii) Trichlorophenol

The decomposition of bis(trichlorophenoxo)bis(pyridine)copper(II) was studied in the presence of added trichlorophenol. Solutions of the phenoxocopper(II) complex in benzene (50 gms/l), containing various amounts of trichlorophenol, were reacted for 24 hours at 71°C. The polymers were isolated and washed several times with methanol to remove any trichlorophenol. The effect on the number-average-molecular weight of the polymer is shown in Figure III - 33.

The polymers were studied in solution (0.04 gms./2 ml CS_2) by infrared spectroscopy. The intensity of thehydroxyl absorption at 3530 cm^{-1} was found to increase with the concentration of trichlorophenol.

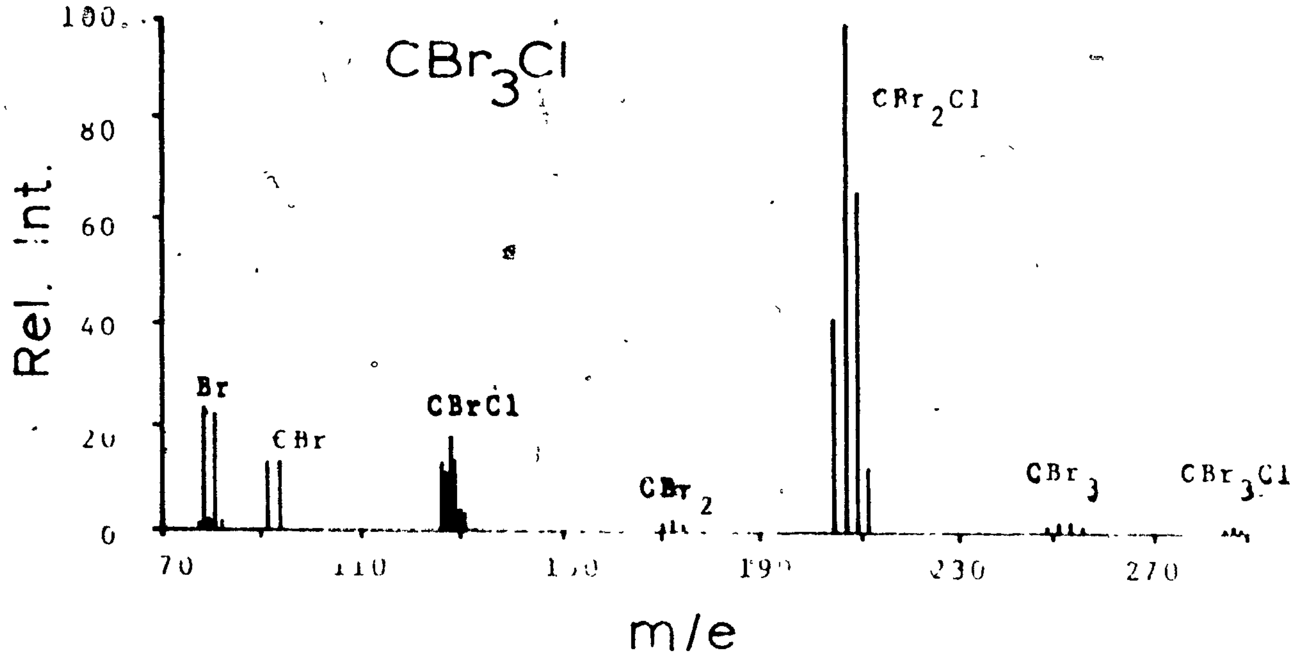
FIGURE III - 31

i) Mass Spectrum of CBr_3Cl.

ii) Gas-Chromatogram of Reaction Mixture in Presence of 10:1 Molar Ratio of CBr_4 (CBr_4 to $Py_2Cu(TCP)_2$).

- a) methanol
- b) benzene
- c) CBr_3Cl
- d) CBr_4

i)


CBr3Cl
Rel. Int.
100
80
60
40
20
0
Br
CBr
CBrCl
CBr2
CBr2Cl
CBr3
CBr3Cl
70
110
190
230
270
m/e

ii)

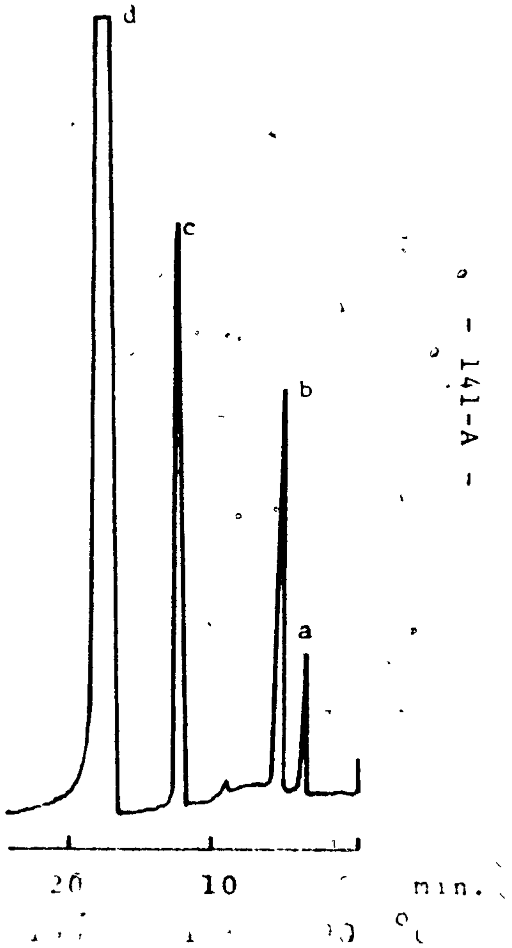

d
c
b
a
20
10
min.

FIGURE III - 32

Mass Spectrum of CBr_4

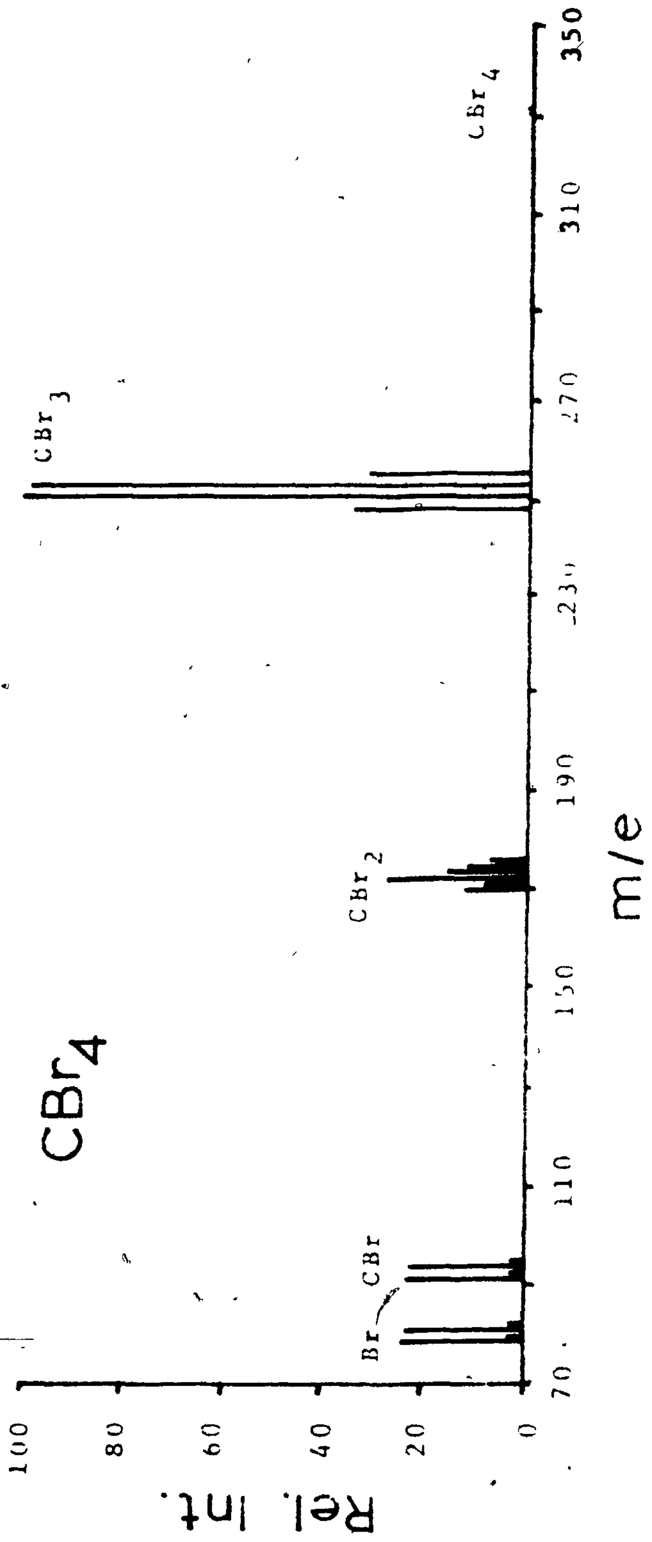
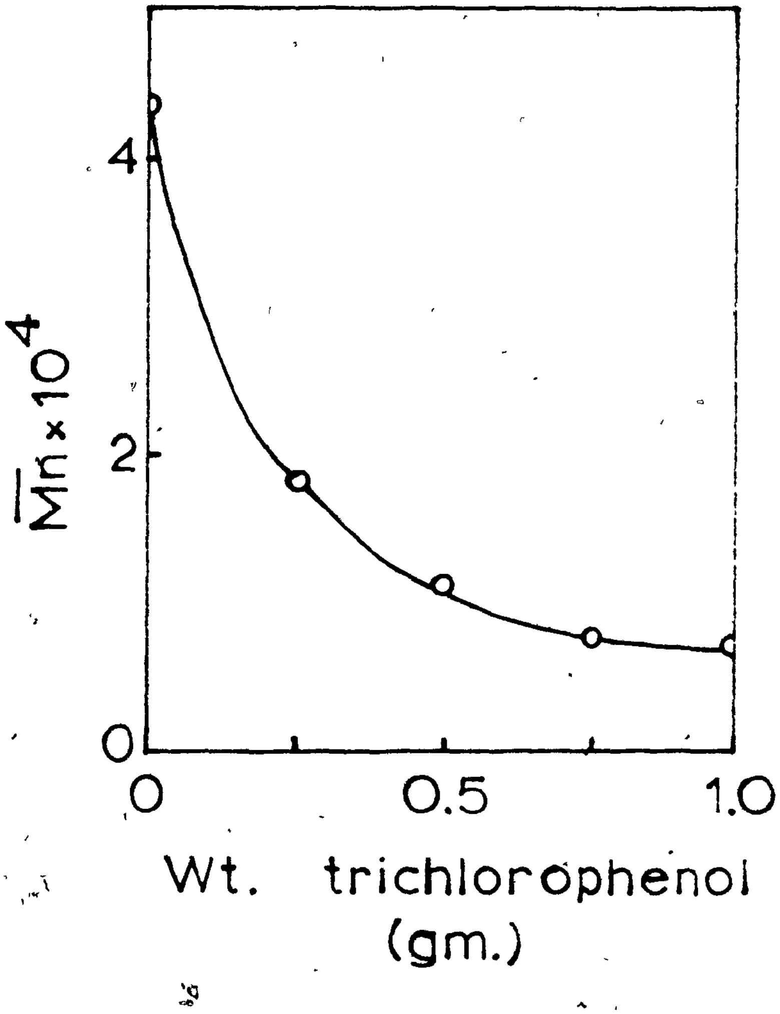

CBr$_4$
CBr$_4$
CBr$_3$
CBr$_2$
CBr
Br
Rel. Int.
0
20
40
60
80
100
m/e
70
110
150
190
230
270
310
350

FIGURE III - 33

Effect of the Addition of Trichlorophenol on Polymer Molecular Weight in the Decomposition of $Py_2Cu(TCP)_2$ in Benzene at 71°C for 24 hrs. Trichlorophenol is added to a solution of 5 gm. $Py_2Cu(TCP)_2$ in 100 ml. benzene.



$\overline{Mn} \times 10^4$
4
2
0
0
0.5
1.0
Wt. trichlorophenol (gm.)

This is shown in Figure III - 34.

iv) Other Additives

The addition of pyridine to a solution of the trichlorophenoxocopper(II) complex in benzene was found to prevent reaction. This agrees with results reported by Harrod (34) and Blanchard et al (2).

The use of styrene as solvent for bis(trichlorophenoxo)bis(pyridine)copper(II) inhibited the reaction. It had been hoped that if the decomposition of phenoxocopper(II) indeed did proceed through the formation of phenoxy radicals, the formation of polystyrene or a copolymer of styrene and phenylene ether units might occur. The reaction was performed under vacuum and in view of the highly irreproducible behaviour of the reaction in benzene under vacuum, perhaps this result should not be taken too seriously.

Trichlorophenoxocopper(II) in benzene (50 gms/l) was reacted at 71°C for seven hours, while bubbling oxygen through the solution. The number-average molecular weight of the resulting polymer was the

FIGURE III - 34

Infrared Spectra of Polymer from the Decomposition of $Py_2Cu(TCP)_2$ (50 g/1) in Benzene at 71°C for 24 hrs. in the Presence of Various Amounts of 2,4,6-trichlorophenol.

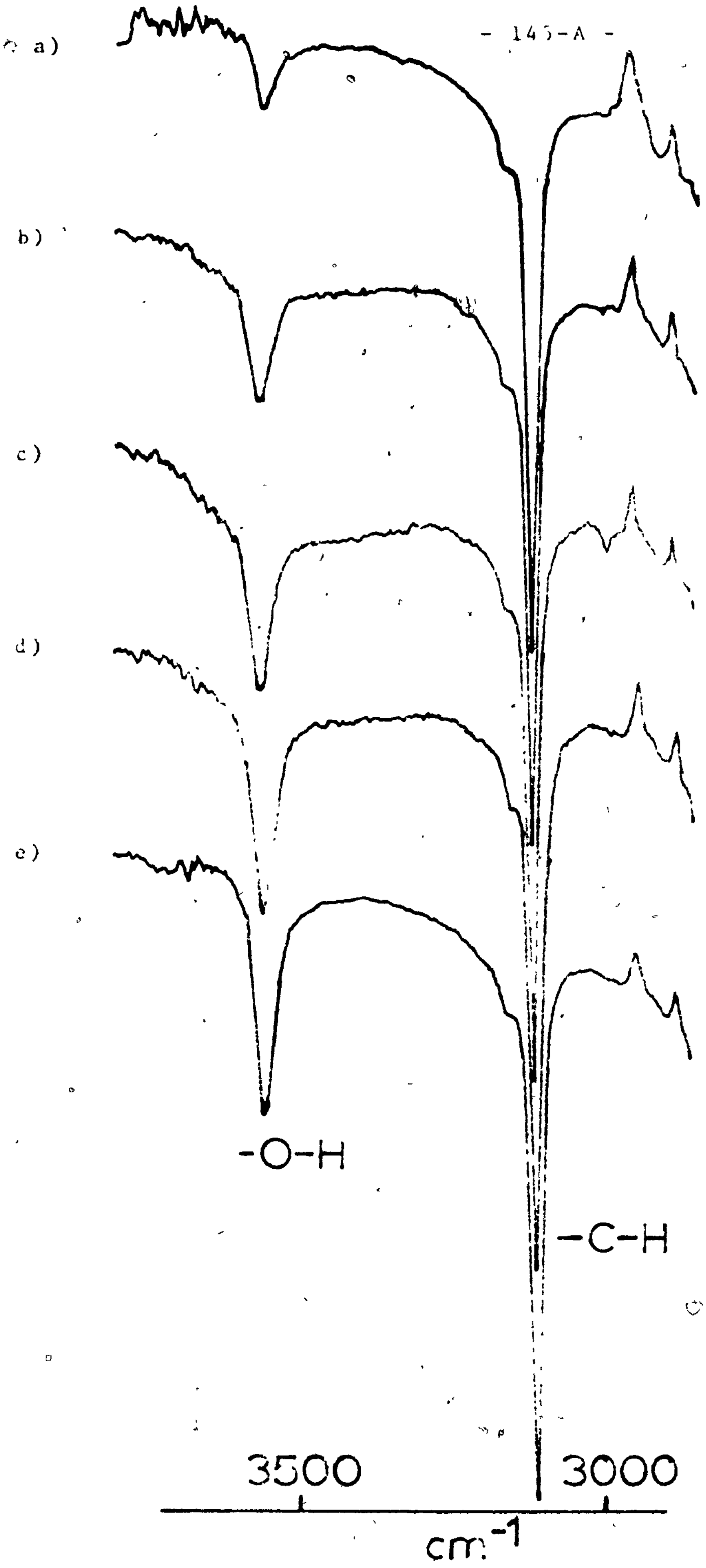
a) no trichlorophenol

b) 0.25 gm/5 gm $Py_2Cu(TCP)_2$

c) 0.50 gm/5 gm $Py_2Cu(TCP)_2$

d) 0.75 gm/5 gm $Py_2Cu(TCP)_2$

e) 1.00 gm/5 gm $Py_2Cu(TCP)_2$


a)
b)
c)
d)
e)
-O-H
-C-H
3500
3000
cm.-1

same as that obtained under normal atmospheric conditions. Oxygen had no detectable effect on the product copper complexes either.

III - 3 POLYMER CHARACTERIZATION

The nuclear magnetic resonance spectra of polymers prepared from bis(trichlorophenoxo)bis-(pyridine)copper(II) and bis(4-bromo-2,6-dichlorophenoxo)-bis(pyridine)copper(II) are shown in Figure III - 35.

The intrinsic viscosity of several polymers is shown in Table III - 11.

FIGURE III - 35

Nuclear Magnetic Resonance Spectra of Polymer

N.M.R. of Polymers

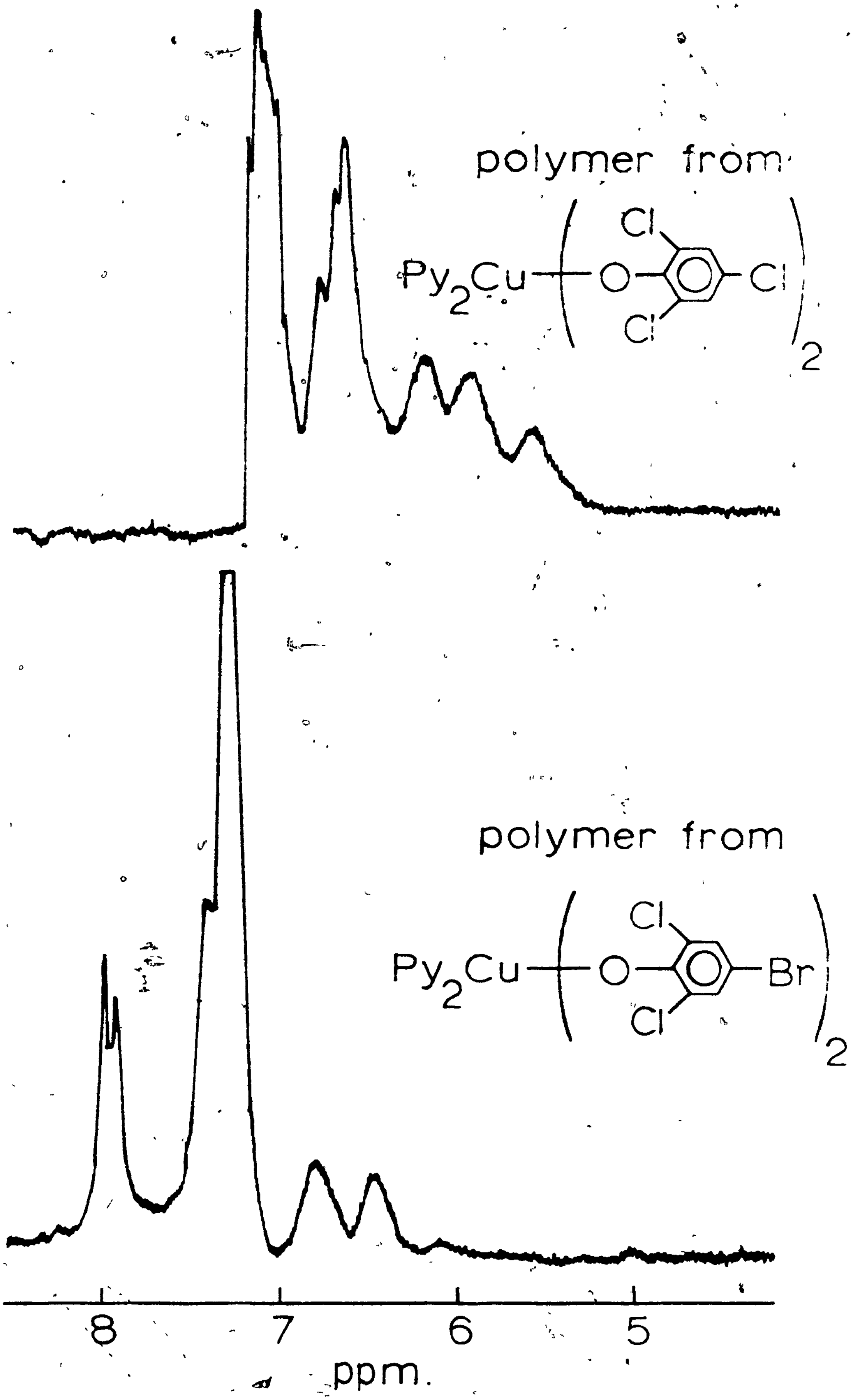


TABLE III - 11

[η] for Polymers from the Decomposition of Phenoxocopper(II) at 71°C

Phenoxo	Reaction Solvent	[η]*	$\bar{M}_n$
TCP	benzene	0.038	26,000
"	"	0.054	34,000
"	"	0.054	47,000
"	"	0.066	54,000
"	"	0.073	61,000
"	"	0.073	69,500
"	toluene	0.043	39,000
Cl_2BrP	"	0.112	130,000
"	benzene	0.112	126,000

* Data obtained in dichloromethane at 25°C.

The infrared spectra of the polymers prepared from trichlorophenoxocopper(II) were identical, regardless of solvent, temperature, concentration or reaction time. There was no change in peak positions or in relative intensity of any absorptions.

Polymer prepared from the decomposition of bis(4-bromo-2,6-dichlorophenoxo)bis(pyridine)-copper(II) in benzene at room temperature could be isolated as a thin, clear film by evaporation of the solvent. Addition of methanol to the solution resulted in a white powder. X-Ray analysis of the polymer showed no indication of crystallinity. On the other hand, no definite glass transition temperature could be obtained by differential scanning calorimetry.

Poly(2,6-dichlorophenylene ether) of $\bar{M}_n$ = 25,000 (see Figure III - 16) was found to contain trapped "free" radicals, by electron spin resonance spectroscopy.

III - 4 FORMATION OF μ_4-OXOCOPPER(II) COMPLEXES

A) Decomposition of Bis(trichlorophenoxo)bis(pyridine)copper(II).

In the course of a spectrophotometric study of the phenoxocopper(II) complex in benzene, toluene or cumene as solvent, it was noticed that the absorbance of the solutions did not go to negligibly small levels at 22,500 cm^{-1} on completion of reaction, as expected. The dichlorocopper(II) reaction product was completely insoluble. Even on removal of polymer from solution, the anomalous absorption remained. The result suggested the presence of a hitherto unidentified reaction product.

Under microscopic examination, the dichlorocopper(II) precipitate was found to be contaminated by a small amount of crystalline material which could be removed by extraction with dichloromethane or acetone. The amount of this compound in the precipitate was usually about 3% by weight. A trace amount was in solution in the reaction solvent, resulting in the aforementioned "straw" colour.

Repetition of the above procedures in toluene and in cumene as reaction solvents gave the same compound in ca. 15% and ca. 100% yields respectively. Repetition of the reaction in benzene in the presence of a five to one molar ratio (hydroperoxide/$Py_2Cu(TCP)_2$) of cumyl hydroperoxide gave a near quantitative yield of the gold coloured crystals.

These crystals analysed as $Py_4Cu_4Cl_6$ using elemental analysis and molecular weight determination. On dissolution, the resulting "straw" coloured solution had a visible spectrum identical to that of the solution at completion of reaction. This provided at least partial explanation for the finite absorption at the end of reaction.

Preliminary X-Ray data (99)

indicated a tetrahedral copper cluster with each edge occupied by a chloride atom and each apex by a pyridine. At about the same time as this work, Kilbourn and Dunitz (76) reported the synthesis and structure determination of μ_4-oxo-hexa-μ-chlorotetrakis(pyridine copper(II)). It quickly became evident that the gold crystals obtained as reaction product from phenoxocopper(II) were the same compound. The oxygen had initially been missed due to insufficient sensitivity in chemical analysis. Refinement of our own X-Ray data confirmed the identity of this complex with that of Kilbourn and Dunitz. The structure of the compound is shown in Figure III - 36.

A series of decompositions of bis(trichlorophenoxo)bis(pyridine)copper(II) in benzene in the presence of some common free radical initiators, followed spectrophotometrically, is shown in Figure III - 27. Although all of the initiators caused diminution of the normally observed induction period, the behaviour of hydroperoxides was distinctly different from that of peroxide and azo initiators. It was evident that hydroperoxides underwent a very rapid reaction with the phenoxocopper(II) complex which was qualitatively different from that occurring with other initiators. This difference was also reflected in the difference of reaction products, as shown in Table III - 12.

FIGURE III - 36

Structure of μ_4-oxo-hexa-μ-chlorotetrakis [(pyridine) copper(II)]

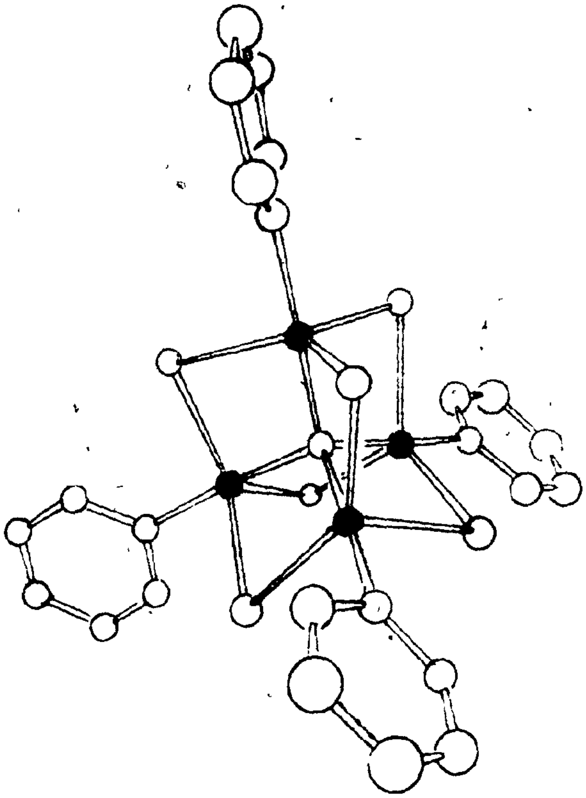


TABLE III - 12

Effect of Various Initiators on the Reaction Products in the Decomposition of Bis(trichlorophenoxo)bis(pyridine)-copper(II) in Benzene at 72°C, Molar Ratio 5:1 I/Cu

Initiator	Wt. % $_4$-oxo*
No initiator	4%
Benzoyl peroxide	3%
t-Butyl peroxide	4%
Dicumyl peroxide	3%
t-Butyl hydroperoxide	100%
Cumene hydroperoxide	100%

*Precipitated reaction product is a mixture of Py_2CuCl_2 and $Py_4Cu_4Cl_6O$

B) Synthesis of Other μ_4-oxocopper(II) Complexes

The synthesis of a number of other μ_4-oxocopper(II) complexes was attempted by first preparing the respective phenoxocopper(II) complex, and then decomposing in the same manner as for the formation of μ_4-oxo-hexa-μ-chloro-tetrakis(pyridine copper(II)).

i) μ_4-oxo-hexa-μ-bromo-tetrakis(pyridine-copper(II))

Decomposition of bis(2,4,6-tribromophenoxy)bis(pyridine)copper(II), in benzene or toluene produced a green crystalline precipitate which was shown to be Py_2CuBr_2, by infrared and far-infrared spectroscopy, in quantitative yield. Further extraction with benzene and dichloromethane showed no additional complexes.

Decomposition of the phenoxocopper(II) complex in cumene gave a dark green precipitate which was found to be a mixture of approximately 60% Py_2CuBr_2 and a dark brown complex which on extraction with tetrahydrofuran and recrystallization by evaporation was shown to be $Py_4Cu_4Br_6 \cdot O$, by infrared spectroscopy and elemental analysis. Repetition of the decomposition in benzene, in the presence of a one to one molar ratio of cumyl hydroperoxide gave only a small trace of the μ_4-oxocopper(II) complex.

ii) μ_4-oxo-hexa-μ-chloro-tetrakis(ethylamine copper(II))

Thermal decomposition of the corresponding phenoxocopper(II) complex in benzene, toluene or cumene, or in benzene in the presence of a hydroperoxide yielded only intractable products, possibly due to autoxidation of the ethylamine ligand. However, catalysed decomposition in the presence of traces of carbon tetrachloride yielded a precipitate which contained 75% of a lime green dichloromethane soluble complex and an intractable gold coloured residue. Spectra and elemental analyses of the former complex were in accord with those expected for the complex $(C_2H_5NH_2)_4Cu_4Cl_6{\cdot}O$.

iii) μ_4-oxo-hexa-μ-chloro-tetrakis(triphenyl-phosphine oxide copper(II))

It was impossible, under the conditions attempted, to prepare and characterize stable bis(trichlorophenoxo)bis(triphenylphosphine oxide)copper(II), because of the extreme ease with which this complex lost neutral ligand. However, a mixture of uncomplexed copper(II) trichlorophenolate and triphe[illegible]phosphine oxide (both individually completely insoluble in cumene) in cumene gave a dark brown solution which on thermal decomposition precipitated a large amount of orange-yellow powder, admixed with a small quantity of green material. Extraction of this mixture with dichloromethane, followed by evaporation, produced a large yield of beautiful, well-formed orange crystals. All physical measurements agreed with the formulation of this complex as $((C_6H_5)_3PO)_4Cu_4Cl_6 \cdot O$, previously synthesized by Bertrand and Kelley (78) by a different method.

iv) Other Attempted Syntheses

Attempts were made to synthesize μ_4-oxocopper(II) complexes with dimethylformamide, dimethylsulphoxide or hexamethylphosphoramide as ligand. Although strong evidence for the formation of the desired products in the former two cases was obtained, the extreme facility with which these ligands dissociated, frustrated complete isolation and characterization.

Bis(trichlorophenoxo)diamminecopper(II) was decomposed under all of the various conditions described above. In all cases the complexes produced were intractable and could not be satisfactorily characterized.

C) Spectra of μ_4-oxocopper(II) Complexes

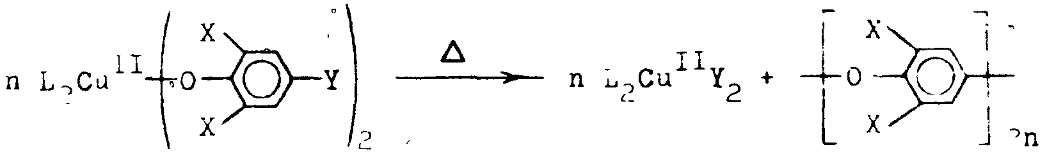
The principal infrared and far-infrared absorptions, respectively of the dihalocopper(II) and μ_4-oxocopper(II) complexes are shown in Chapter VII. Tom Dieck and Brehm (82) have reported that a band at 588-515 cm^{-1} assigned to an asymmetric group vibration of the Cu_4O tetrahedron is a facile method of identifying the μ_4-oxocopper(II) complexes. These reported values in this region, along with values in other regions by other authors (78,79) provided substantial support for identification of the μ_4-oxocopper(II) complexes reported in this thesis.

IV - DISCUSSION

IV - 1 Preliminary Discussion

As reported in Section I, the catalytic oxidative coupling of phenols to polyphenylene ethers, using copper(II) salts as oxidants, is believed to proceed through the formation of phenoxocopper(II) intermediates. The reaction is complicated since it not only proceeds very rapidly at room temperature, but the initial intermediate compounds are extremely unstable. The ability to isolate stable phenoxocopper(II) complexes would not only prove their existence, but also, facilitate an investigation of the overall reaction. Emphasis could be placed entirely on the later stages of oxidative coupling; ignoring all steps leading to the formation of phenoxocopper(II). Blanchard, et al(2), and Harrod(34) reported the preparation and decomposition of several stable polyhalophenoxocopper(II) complexes. Analysis of the decomposition products resulted in equation IV - 1. This thesis deals with the overall mechanism of decomposition, utilizing several phenoxocopper(II) complexes.

These complexes, IV - 1, are thought to be related to the unstable phenoxocopper(II) intermediates in the oxidative coupling of 2,6-dialkylphenols reported initially by Hay, et al(1). The reactions in equation IV - 1


IV - 1 IV - 2 IV - 3

IV - 1

L = C_5H_5N	X = Cl	Y = Cl	a†
C_5H_5N	Cl	Br	b*
C_5H_5N	Br	Br	c*
C_5H_5N	I	I	d
$(CH_3)_2NCH_2CH_2N(CH_3)_2$	Cl	Cl	e‡
$(CH_3)_2NCH_2CH_2N(CH_3)_2$	Cl	Br	f
$C_2H_5NH_2$	Cl	Cl	g‡
NH_3	Cl	Cl	h‡
$(C_6H_5)_3PO$	Cl	Cl	i
$(CH_3)_2NCHO$	Cl	Cl	j
$(CH_3)_2SO$	Cl	Cl	k

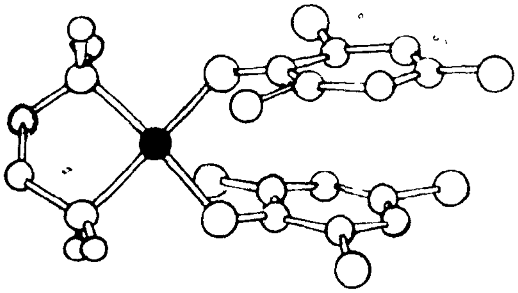
* reported by Reference (2)

† reported by References (2) and (34)

‡ reported by Reference (34)

may be carried out in solution or in the solid state(2,34). Most of the research reported in this thesis was conducted with compound IV - 1a. All decompositions were performed in solution, using benzene, toluene or cumene as solvent.

Trichlorophenoxocopper(II) complexes, IV - 1a, exhibit no dipole moment(34), suggesting the phenoxo ligands to be trans to each other. On the other hand, the tetramethylethylenediamine complexes, IV - 1e and f, must have the phenoxo ligands cis to each other due to the bidentate neutral ligand. This has been confirmed by X-Ray analysis(100), and is shown below.



IV - 1e and f

These latter complexes assume a slightly distorted square planar configuration.

Chemical analysis, molecular weight data and infrared spectra indicate that the majority of the stable phenoxocopper(II) complexes are four-coordinated and monomeric(2,34). Of the phenoxocopper(II) complexes studied and reported in this thesis, only the dimethylformamide complex, IV - 1j, is thought to be dimeric, from elemental analysis. In the present study, structural confirmation could not be obtained with the triphenylphosphine oxide and dimethylsulphoxide complexes, IV - 1i and k, respectively, because of their instability. However, it would not seem unreasonable to suggest that all trichlorophenoxocopper(II) complexes studied in this work, possessing neutral ligands bonded through oxygen, are dimeric. They would assume a structure similar to the hexamethylphosphoramide bridged dimer reported by Tsuruya, et al(42).

IV - 2 Discussion of Mechanism

A. Earlier Proposals

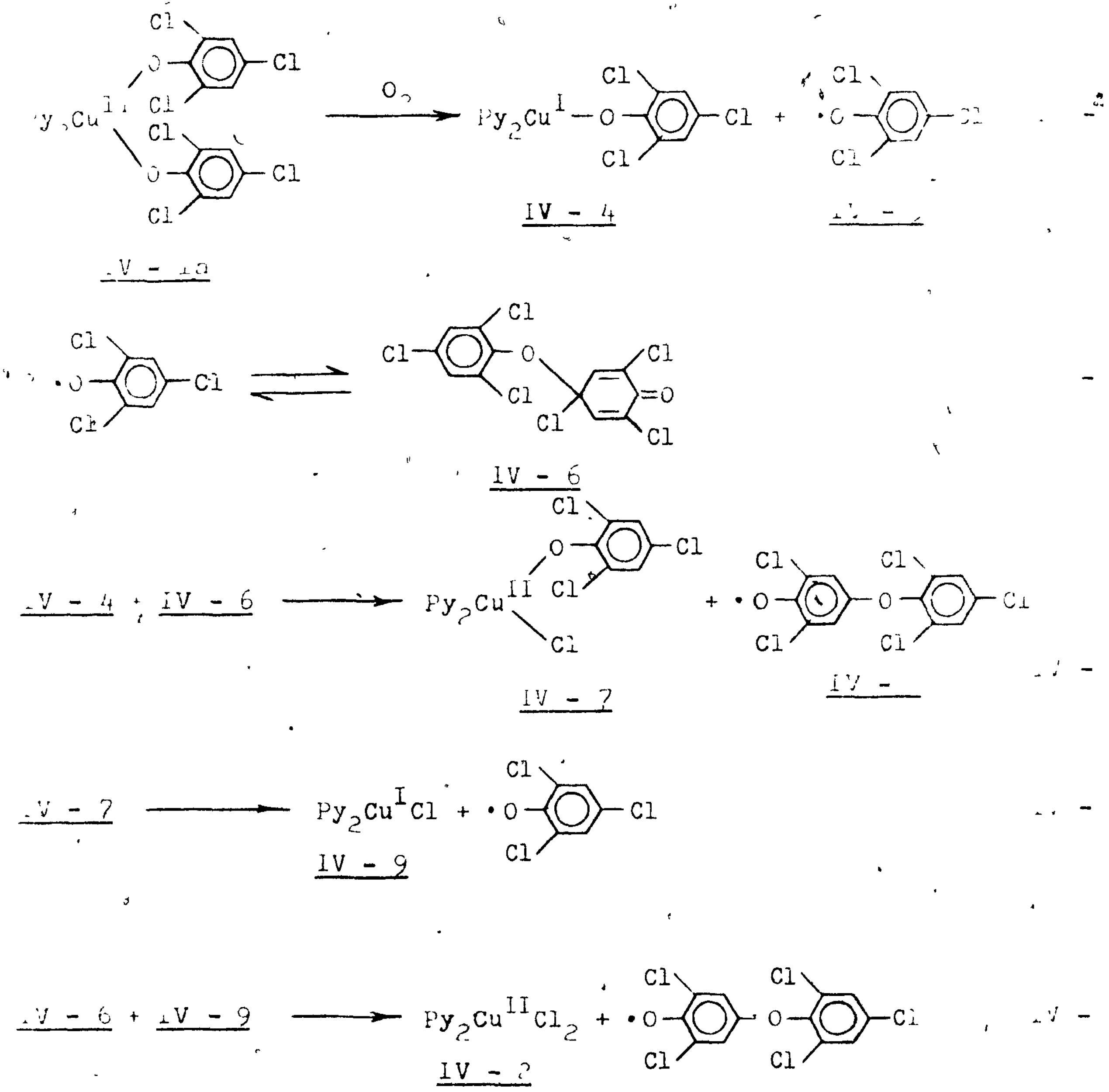
i) General Comments

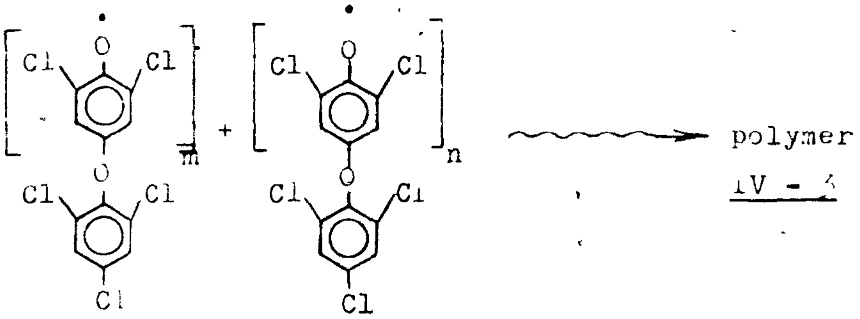
It has long been recognized that equation IV - 1 is rather idealized. Firstly, the final yield of copper(II) reaction product, IV - 2, never completely approaches the theoretical yield. This either suggests that not all of the phenoxocopper(II) complex has been decomposed; or that an additional hitherto undetected copper(II) reaction product exists. Secondly, the polymers, IV - 3, are well known to be branched. This has been clearly indicated by intrinsic viscosity(2) and by nuclear magnetic resonance studies(42). Similar findings were obtained by both techniques in this work, as evidenced in Table III - 11 and Figure III - 35. Even more important, these polymers have only modest number-average molecular weights (10^4 - 10^5), not essentially infinite molecular weights as required by the exact stoichiometry of equation IV - 1.

It would seem, therefore, that equation IV - 1 is only a rather poor first approximation to the actual reactants and products involved in the thermal decomposition of the phenoxocopper(II) complexes, IV - 1. In fact, under the best conditions of purity obtained in this work, the decomposition of complex IV - 1a exhibits an exceedingly long, perhaps infinite, induction period. This suggests the need for an initiator. There is no doubt that oxygen can function as an initiator. Reactions in air exhibit quite reproducible behaviour, unlike those carried out under vacuum.

ii) Reaction Scheme

It is highly unlikely that both phenoxo ligands in compound IV - 1a would be lost simultaneously. Compilation of the results of previous workers, as summarized in Section I for a variety of 2,6-disubstituted phenols, would suggest the series of reaction steps shown in equation IV - 2 to IV - 8.

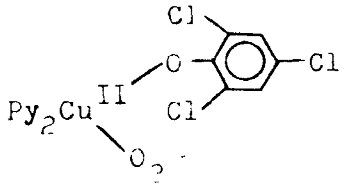




IV - 3

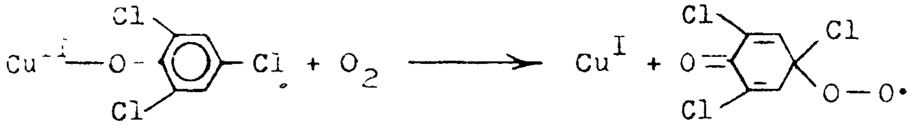
IV - 10

The initiation step in the thermal decomposition of phenoxocopper(II), IV - 1a, involves a ligand-to-metal charge transfer, resulting in a copper(I) complex, IV - 4, and a phenoxy radical, IV - 5(34). Oxygen may act as an initiator in this reaction step by reacting with starting material, to produce a phenoxy radical and a Cu-O_2 species, represented as compound IV - 11.



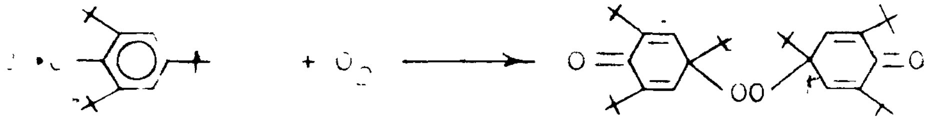
IV - 11

A more likely reaction, in view of the radical induced decomposition reaction to be discussed later, is the oxygen induced scission of the Cu-O bond, with formation of cyclohexadienoneperoxide, equation IV - 8.



IV -

The formation of such peroxides with phenoxy radicals is well established(37), equation IV - 9.

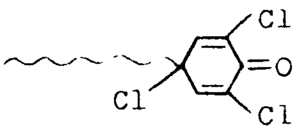


V -

Carbon-oxygen coupling of two phenoxy radicals results in quinol ether, IV - 6. This quinol ether can undergo chlorine atom transfer with IV - 4, resulting in the copper(II) complex, IV - 7, and a dimeric phenoxy radical, IV - 8. Compound IV - 7 can also undergo further decomposition by loss of a phenoxo ligand, producing the copper(I) species, IV - 9 and a phenoxy radical. Chlorine transfer between quinol ether and this copper(I) complex would give the dichlorocopper(II) precipitate, IV - 2.

Repetition of these reactions, accompanied by further reaction of the phenoxy radicals, either with monomeric phenoxy radicals or with other growing oligomeric phenoxy radicals via the quinone ketal mechanism, would eventually result in high molecular weight polymer.

Termination may result from direct coupling of two polymeric phenoxy radicals producing a dioxin molecule(68), or by simple equilibration of the carbon-oxygen coupling steps. In the latter case, ~~the~~ "heads" of the polymer chains would consist of quinol ethers, IV - 12.



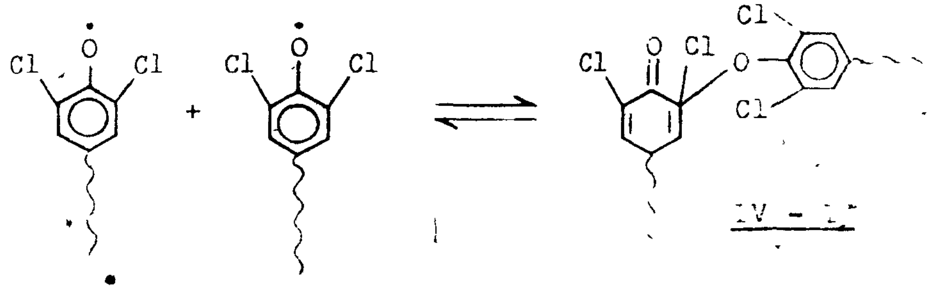
IV - 12

Infrared spectroscopy has revealed a small degree of terminal hydroxyl absorption. Evidence reported later in the discussion attributes this to trace amounts of trichlorophenol impurity in the phenoxocopper(II) starting material.

iii) branching

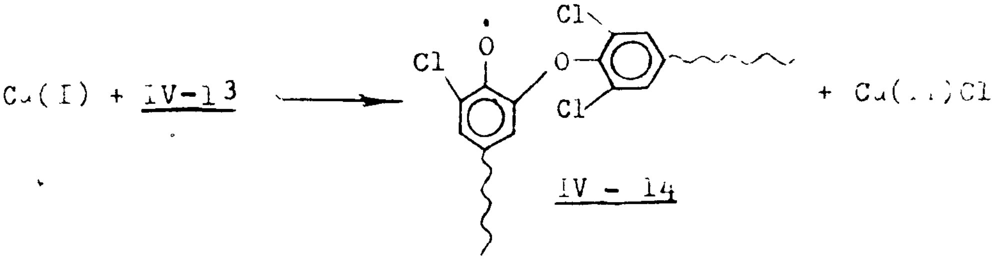
With trihalophenols, coupling can occur at any of the 2,4,6- positions(2), although there is some preference for coupling at the 4- position(9) when the halogens are identical. Coupling at the 2,6- positions results in branching, by the reactions shown in equations

IV - 10 and 11.



IV - 13

IV -



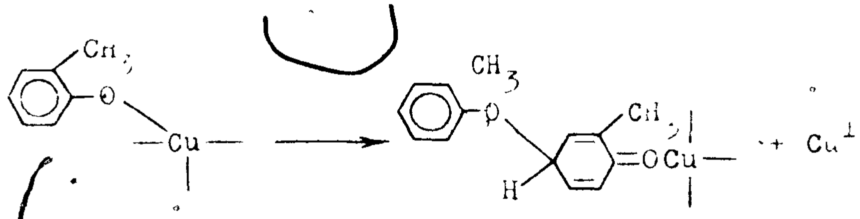
IV - 14

IV -

B. Present Findings

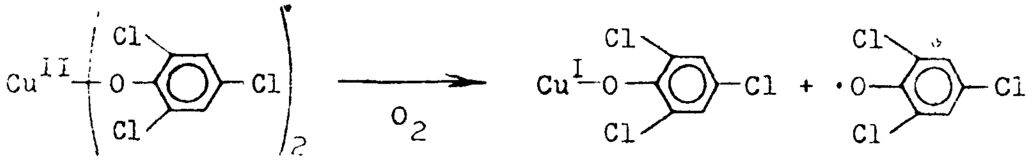
i) Spectrophotometric Results

Spectrophotometric observation of decompositions of trichlorophenoxocopper(II) at 22,500 cm^{-1} has thrown much light on several phases of the overall mechanism of reaction. The initial stage of the spectrophotometric curve suggests that decomposition of phenoxocopper(II) must be accelerated by the resulting formation of phenoxy radicals. If this were not so, the spectrophotometric decomposition plot would decrease linearly, and complete decomposition would require extensive reaction times. Hay and Endres(101) have suggested the direct attack of phenoxy radical at the 4- position of a phenoxo ligand on a phenoxocopper(II) intermediate, equation IV - 12.



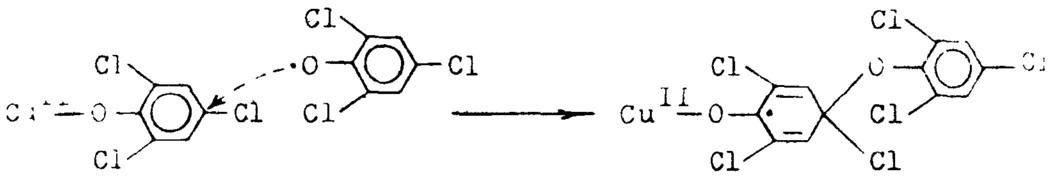
This postulate resulted from the finding that the oxidation of 2-methylphenol with Cu(I) and pyridine resulted in low molecular weight materials with presumably a great deal of coupling at the unsubstituted 6- position. On the other hand, with bulky amines, such as 2,6-dimethylpyridine, high molecular weight, although not completely linear, polymers were obtained. It was assumed that bulky neutral ligands prevented coupling at the 6- position.

The existence of an induction period in the spectrophotometric curve can be explained if the ligand-to-metal electron transfer does not occur spontaneously. In the presence of oxygen, a very slow oxygen induced reaction occurs, equation IV - 13.


IV - 1a IV - 4

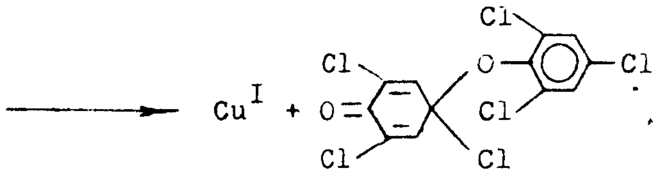
IV - 1

At the same time, any phenoxy radical produced in this reaction must couple rapidly with a phenoxy ligand to give quinol ether, IV - 6, equations IV - 14 and 15.


IV - 15

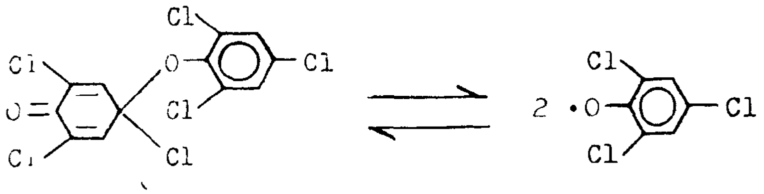
IV - 14

IV - 15


IV - 6

IV - 1

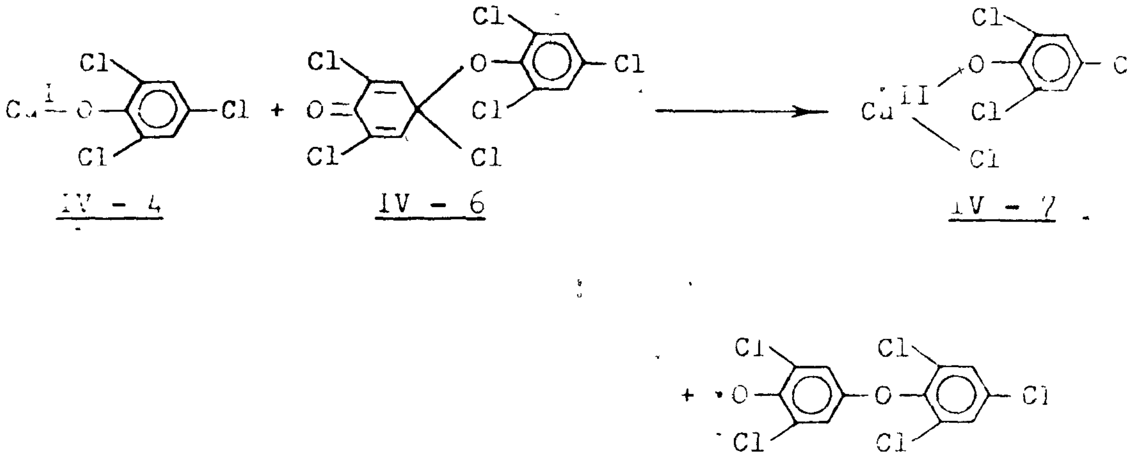
Since quinol ethers are now known to exist in equilibrium with their constituent radicals(63), the quinol ether can dissociate to two phenoxy radicals, equation IV - 16.



IV - 1

The net effect of this cycle, equations IV - 14 to IV - 16, is an induced decomposition of phenoxocopper(II) with a doubling of the radical concentration with each cycle. The decomposition of phenoxocopper(II) becomes more and more rapid as the concentration of phenoxy radicals continue to increase. Eventually, the rate of decomposition begins to fall off as the phenoxocopper(II) is consumed. As would be expected for this type of mechanism, the phenoxocopper(II) decomposes more rapidly at higher temperatures.

The appearance of a "hump" in the spectrophotometric curve suggests the formation of strongly absorbing intermediate compound. The most probable explanation would be quinol ether or compound IV - 7 (equation IV - 17).



IV - 4 IV - 6 IV - 7

IV - 1

Further reaction of this uncharacterized intermediate eventually leads to the final reaction products. Attempts to isolate this intermediate by chemical techniques have been unsuccessful. The existence of the uncharacterized chromophore presently precludes detailed kinetic analysis of the spectrophotometric curves.

The anomalously high absorbance at the end of reaction will be accounted for later in the discussion.

ii) Electron Spin Resonance Spectroscopy Results

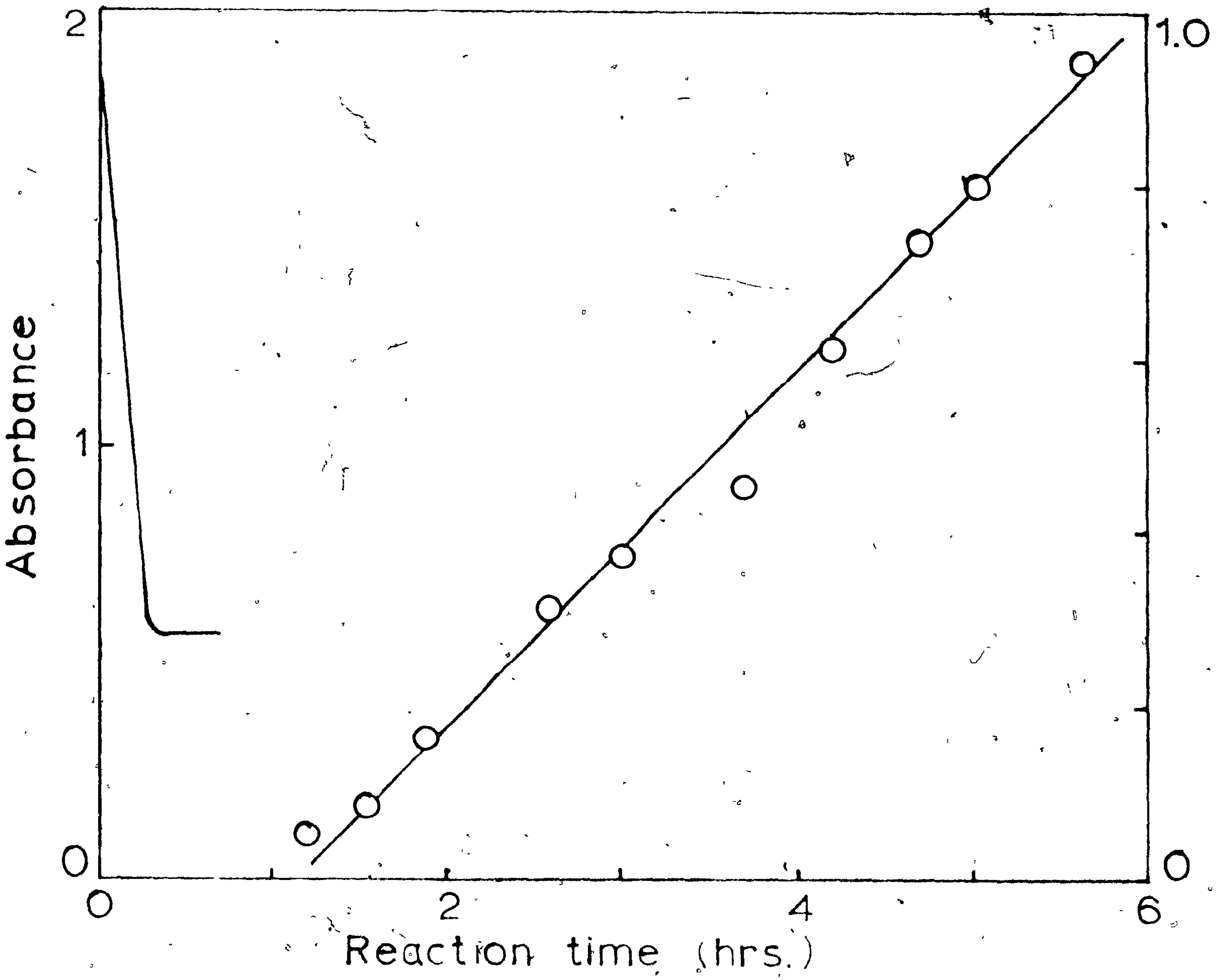
The observation of phenoxy radical during the reaction is of paramount importance in confirming the mechanism outlined above. Tsuruta, et al(42), have already reported the observation of a phenoxy radical signal at $g = 2.0056$ during the decomposition of trichlorophenoxo-hexamethylphosphoramide-copper(II) in the solid state at 120°C. This signal occurred on the high-field tail of the phenoxocopper(II) complex, reached a maximum intensity in about 25 minutes, and slowly diminished by 140 minutes. In the present work, compound IV - 1a, was decomposed in toluene in a quartz tube at 100°C.

The decomposition of IV - 1a featured the decay of the somewhat symmetrical phenoxocopper(II) absorption to give the asymmetrical signal of precipitated Py_2CuCl_2, IV - 2. At this stage a slight irregularity was detected at the high-field tail of the copper(II) signal. The signal level was increased in this region revealing a well defined singlet at $g = 2.007$ which continued to grow in intensity over an additional five hour period.

A comparison of the decomposition of phenoxocopper(II), IV - 1a, at 100°C taken photometrically at 22,500 cm^{-1} with the formation and increase in concentration of phenoxy radical is shown in Figure IV - 1. Compound IV - 1a has clearly decomposed almost completely long before there is a detectable quantity of phenoxy radical.

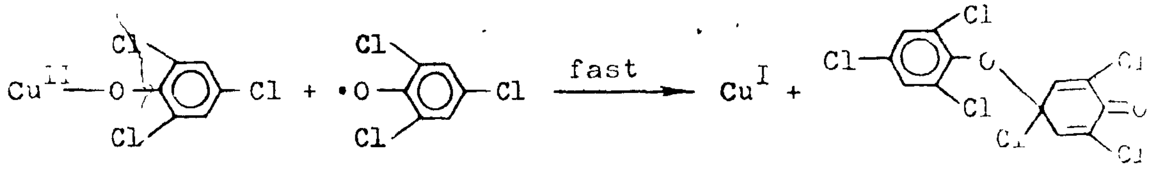
Figure IV - 1

Comparison of the Rate of Decomposition of $Py_2Cu(TCP)_2$ in Toluene at 100°C and the Rate of Formation of Phenoxy Radical


Absorbance
2
1
0
Relative intensity
1.0
0
Reaction time (hrs.)
0
2
4
6

Tsuruya, et al(42), reported the gradual disappearance of the phenoxy radical signal. A second decomposition of IV - 1a was performed in benzene at 70°C in the presence of a trace of carbon tetrachloride (the effect of carbon tetrahalides as initiator will be discussed below). This permitted an examination of complete reaction over a shorter time period. It was found, as with Tsuruya, et al(42) that the phenoxy radical signal quickly reached a maximum intensity then slowly decayed. Indeed, after five days at 100°C, the initial toluene run showed no apparent phenoxy signal. Similar results were obtained by Mahoney and Weiner(103) for the oxidation of 3,5-di-tert-butylphenol to dimer by photolysis.

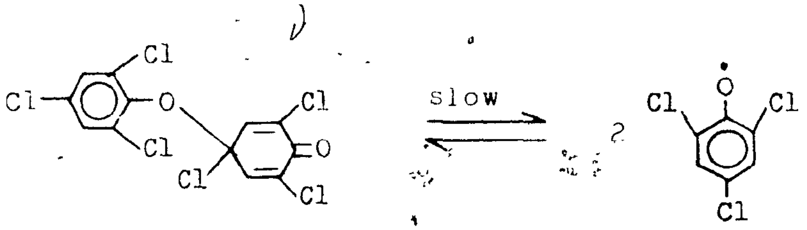
Other than actual detection of a phenoxy radical signal, the single most important observation for a mechanistic investigation is that this signal was not apparent until almost all of the phenoxocopper(II) complex had been consumed. If one assumes a rapid attack of phenoxy radical on phenoxocopper(II), IV - 1a, equation IV - 18, and a slow equilibration of quinol ether, IV - 6, with phenoxy radical, equation IV - 19, then a more precise interpretation of the spectra can be made.



IV - 1a

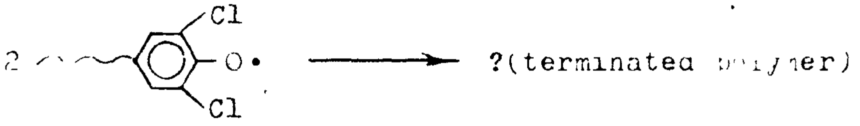
IV -

IV - 18

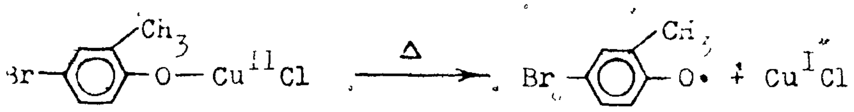


As soon as phenoxy radicals are produced by equation IV - 19, they react rapidly with phenoxocopper(II) generating quinol ether, equation IV - 18. Reaction IV - 18 is the initiation step, while reaction IV - 19 is the radical chain branching (autoacceleration) step.

Under these conditions, the steady state concentration of phenoxy radical is insufficient to be detected by electron spin resonance spectroscopy until almost all of the phenoxocopper(II) complex is consumed. Quinol ether, IV - 6, seems to be the most likely candidate for the intermediate chromophore. Once most of the phenoxocopper(II) is gone, the phenoxy radicals equilibrate and build up in concentration so as to be detectable by electron spin resonance spectroscopy. Coupling takes place to produce polymer and the phenoxy radical signal slowly disappears by some unspecified termination, equation IV - 20.

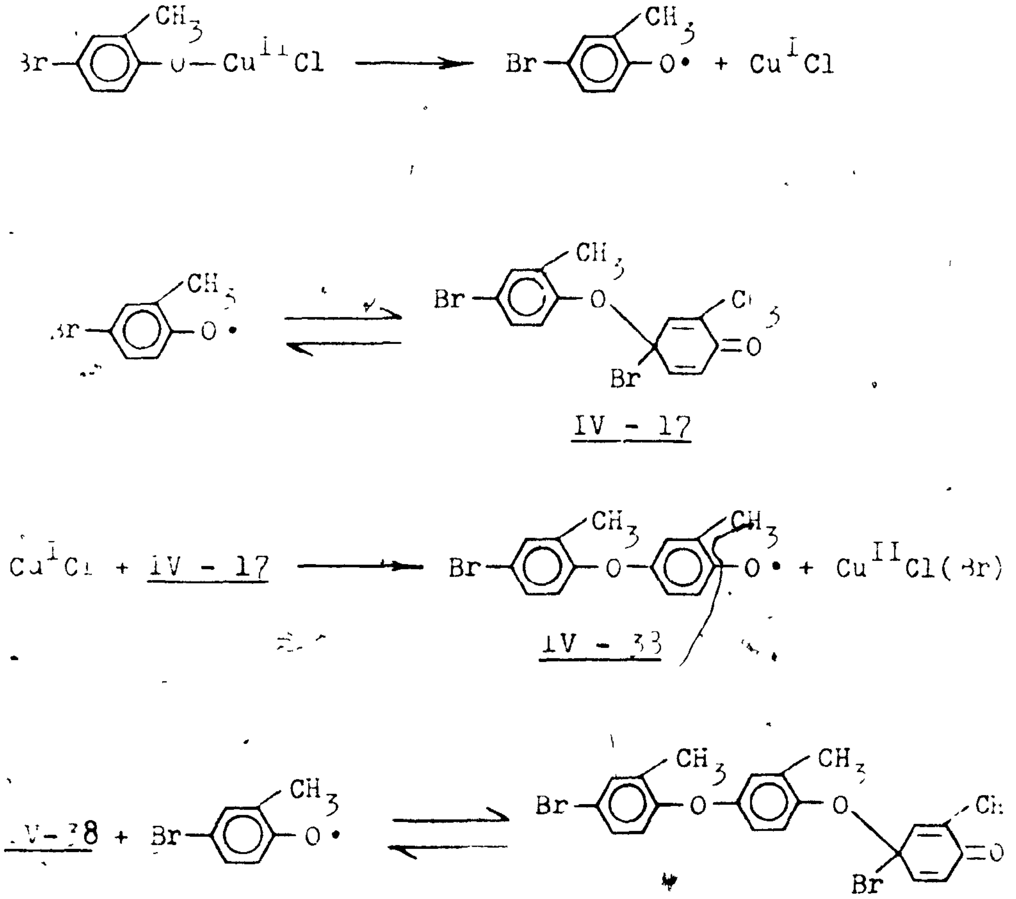


Kopylov and Pravednikov(39) have examined the thermal decomposition of 4-bromo-2-methylphenoxo-copper(II), IV - 16, in pyridine, by electron spin resonance spectroscopy. Initially, these authors noticed a decrease in intensity of the original phenoxocopper(II) signal. This was not accompanied by a corresponding formation of a phenoxy radical, equation IV - 21, as hoped.



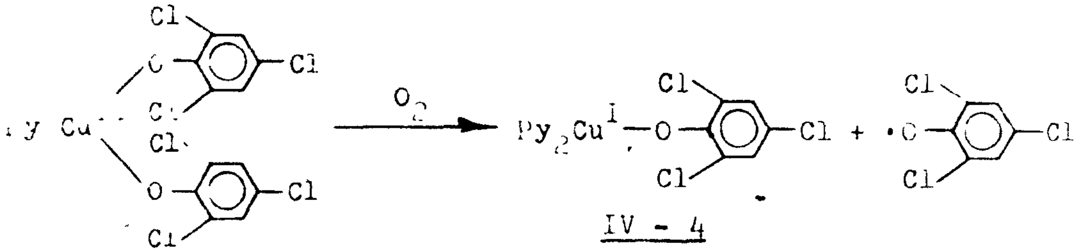
IV - 16

Prolonged heating resulted in a copper(II) spectrum of approximately the same intensity as the initial one. The shape of this absorption showed possible indication of the overlap of two signals; the narrow singlet of the phenoxy radical superimposed on the broad absorption of copper(II). With this information, they postulated the mechanism shown in equations IV - 22 to 25.



Since no definite phenoxy radical was observed, especially in the initial stages, it was assumed that reaction IV - 23 must be proceeding very rapidly. The rate of disappearance of the phenoxocopper(II) signal indicated that reaction IV - 22 was also rapid. Since any reactions after IV - 24 can be regarded as repetitious of IV - 23 and IV - 24, it was concluded that reaction IV - 24 was the rate controlling step.

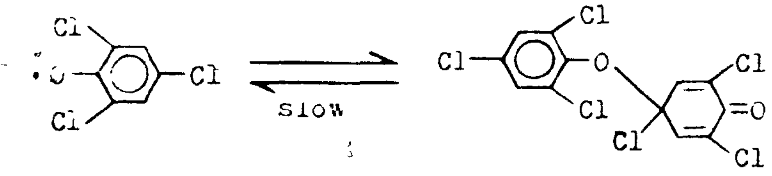
The interpretation of the electron spin resonance spectra for the decomposition of trichlorophenoxocopper(II), IV - 1a, is in agreement with mechanistic findings for the spectrophotometric results at 22,500 cm^{-1}, discussed in equations IV - 13 to 16. It is evident in both these cases that the equilibrium between quinol ether and a pair of phenoxy radicals, equation IV - 19, has a profound influence on reaction rate. The halogen atom transfer step, equation IV - 24, proposed by Kopylov and Pravednikov(39), may, or may not, be as important in determining the rate. The mechanism of reaction interpreted from electron spin resonance spectroscopy and spectrophotometric analysis is summarized in equations IV - 26 to 31.



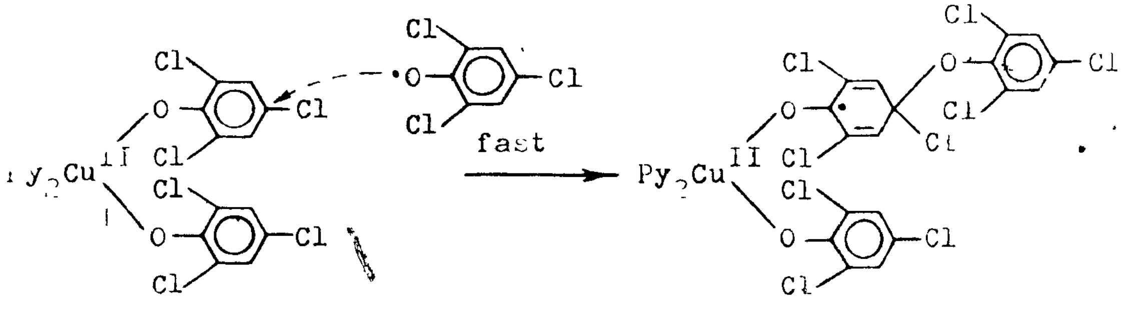
IV -

IV - 4

IV - 1a

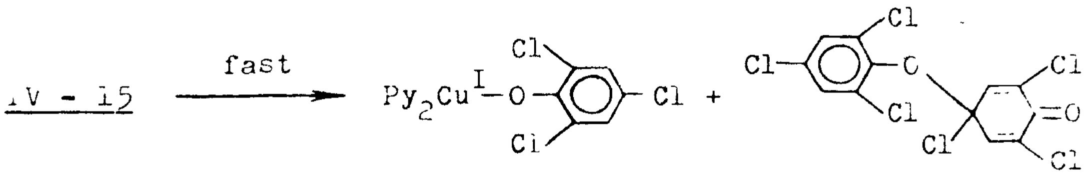


IV - 6



IV - 15

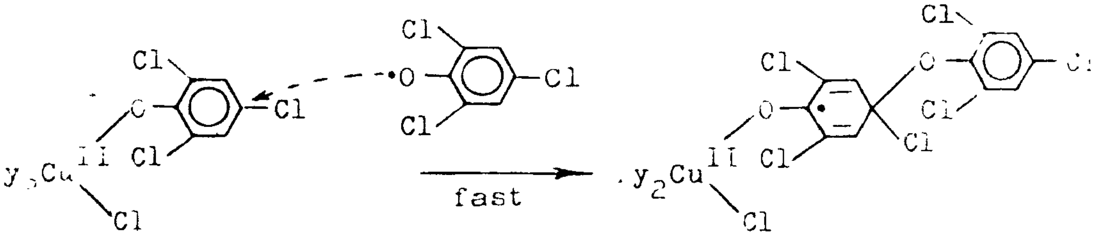
IV -



IV - 4

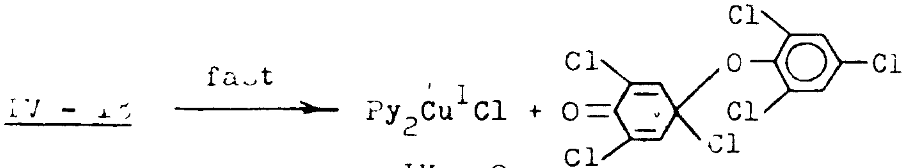
IV - 6

IV -



IV - 16

IV -



IV - 9

IV - 6

IV -

The relatively slow dissociation of quinol ether, equation IV -27, has been observed by Mahoney(63). The fact that radicals build up only AFTER <u>IV - 1a</u> has disappeared proves that radical dimerization is also slow compared to IV - 28 and that virtually all quinol ether arises from induced decomposition of phenoxocopper(II).

iii) Existence of μ_4-oxocopper(II) Complexes

The dihalocopper(II) precipitate, IV - 2, resulting from the decomposition of trichlorophenoxocopper(II), in benzene, was found to be admixed with approximately 3% total yield of golden, needle-shaped crystals. These analyzed as $Py_4Cu_4Cl_6O$, IV - 19, by X-Ray analysis, infrared spectroscopy, and molecular weight data. The existence of these crystals was initially believed to be due to impurities either in the starting material, IV - 1a, or as adventitious water. As a result, they were at first ignored. However, interest was revived when it was discovered, in the investigation of solvent on the number-average molecular weight of polymer, that in cumene as solvent, all of the copper-containing reaction product was IV - 19 and not IV - 2. Furthermore, when the decomposition of IV - 1a was carried out in benzene as solvent, but in the presence of an excess of hydroperoxide, the product copper complex was mostly IV - 19. The decomposition of phenoxocopper(II) using toluene as solvent resulted in a reaction product mixture containing approximately 15% IV - 19. This gold coloured μ_4-oxocopper(II) complex absorbs slightly at 22,500 cm^{-1} due to the tail end of an ultraviolet band, offering partial explanation for the "straw" colour of the final solution and the finite absorption at the end of the spectrophotometric decomposition study. This finite absorption is also due somewhat to the tail of an ultraviolet absorption from polymer.

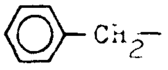
The trends observed for the dependence of yield of μ_4-oxocopper(II) on solvent strongly indicate that <u>IV - 19</u> was a product associated with solvent autoxidation. Autoxidation, shown in equations IV - 32 and 34(113), is preferred in cumene as opposed to toluene(113-115), and is likely non-existent in benzene. The resulting hydroperoxide, <u>IV - 20</u>, can then decompose to give an hydroxyl radical, <u>IV - 22</u>, as in equation IV - 35.

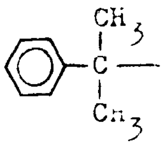
$$RH + I\cdot \longrightarrow R\cdot + IH$$ IV - [illegible]

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$ IV - [illegible]

$$RO_2\cdot + RH \longrightarrow ROOH + R\cdot$$ IV - [illegible]

$$ROOH \dashrightarrow RO\cdot + \cdot OH$$ IV - [illegible]

where R =  for toluene

 for cumene

In the case of reactions in benzene, the small amount of $Py_4Cu_4Cl_6{\cdot}O$ produced possibly results from direct reaction of a copper(I) species with molecular oxygen, perhaps along the line suggested by Finkbeiner, *et al.* (31), shown in equations IV - 36 and 37. A distinct odour of pyridine in the solution after decomposition helps support this proposal.

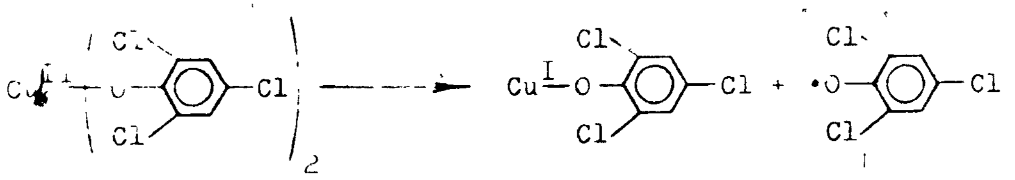
$$2\ \mathrm{Py\,Cu^{I}Cl} + 1/2\ \mathrm{O_2} \longrightarrow \mathrm{Py_2CuCl_2{\cdot}CuO} + \ \mathrm{Py} \qquad \text{IV -}$$

IV - [illegible]

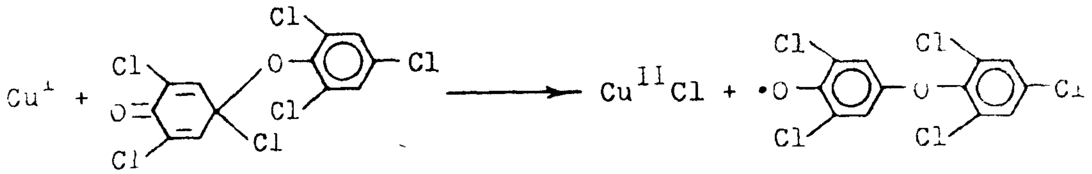
$$\mathrm{Py_2CuCl\ {\cdot}CuO} + 2\ \mathrm{Py_2CuCl_2} \longrightarrow \mathrm{Py_4Cu_4Cl_6{\cdot}O} + \ \mathrm{Py} \qquad \text{IV -}$$

IV - 2 IV - 1[illegible]

The most likely first step in the decomposition of phenoxocopper(II) is a homolytic dissociation as shown in equation IV - 38. Apparently this reaction does not occur spontaneously, but may be induced by such species as oxygen, radical initiators and carbon tetrahalides (cf. preceeding section). If copper(I) intermediates are produced in the decomposition, they will be subject to competitive oxidation either by phenol-derived oxidants, as shown in equation IV - 39, or by added initiator species.



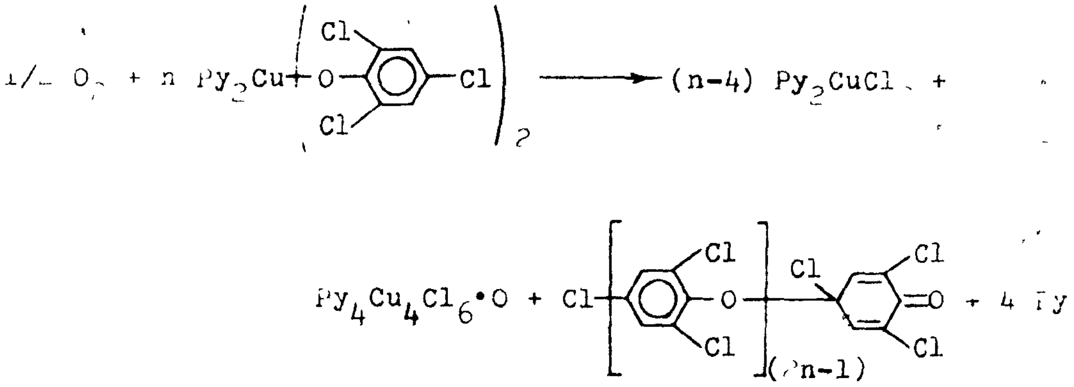
- IV -



IV -

Oxidations, as in equation IV - 39, will eventually produce <u>IV - 2</u>, but introduction of an oxide, or hydroxide, ligand during oxidation by oxygen, or hydroperoxide resulting from the autoxidation of solvent, will produce <u>IV - 19</u>.

The formation of compound <u>IV - 19</u> as an additional reaction product in the decomposition of <u>IV - 1a</u> contradicts the exact stoichiometry of equation IV - 1, suggesting an alternate overall reaction scheme shown in equation IV - 40.



IV -

The much greater reluctance of IV - 1c to yield a μ_4-oxocopper(II) complex is presumably due to the lower reactivity of bromocopper(I) species towards oxidation, and a greater selectivity with respect to the appropriate analogue of reaction IV - 39. Bromophenoxocopper(II) complexes decompose much more readily than their chloro-analogues and this presumably reflects a greater facility for reaction IV - 38.

Both IV - 1g and IV - 1h are difficult to decompose in solution, and in the presence of oxygen, or hydroperoxides, yield intractable products. It seems very likely that the neutral ligands become involved in an autoxidative sequence in these cases to give polymerized complexes as products. The decomposition of IV - 1g in the presence of CCl_4, although probably still a radical chain process, does not involve oxygen and side reactions of the ligand are less serious. Ethylamine complexes of copper(II) are often oxidatively unstable(94).

The μ_4-oxocopper(II) complexes containing triphenylphosphine oxide, dimethylformamide and dimethylsulphoxide were also successfully prepared. All of the μ_4-oxo compounds obtained in this work, with the exception of the one containing ethylamine as neutral ligand, have been reported previously(76,78,82,94). Their structures have been established either crystallographically, or by infrared spectroscopy in the region of 588 - 516 cm^{-1}.

It appears that the decomposition of halophenoxocopper(II) complexes may provide a fairly general route to the preparation of μ_4-oxocopper(II) derivatives. The two exceptional circumstances seem to be:

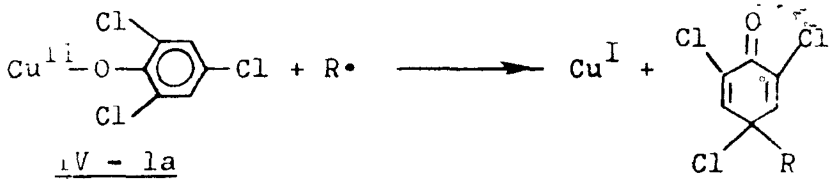
a) when the neutral ligand is sensitive to attack by free radicals, and

b) when the neutral ligand is weakly attached.

iv) Effect of Free Radical Initiators

The addition of peroxide, hydroperoxide or azo free radical initiators to a solution of phenoxocopper(II) greatly enhances the decomposition rate, Figure III - 27. The effectiveness of nonhydroperoxide initiators follows their ease of decomposition and no initiator fragments appear in product copper complexes with such initiators. This favours the hypothesis that these initiators function by rapid attack in coordinated phenoxide, as in equation IV - 41, rather than by attack at copper.

✓

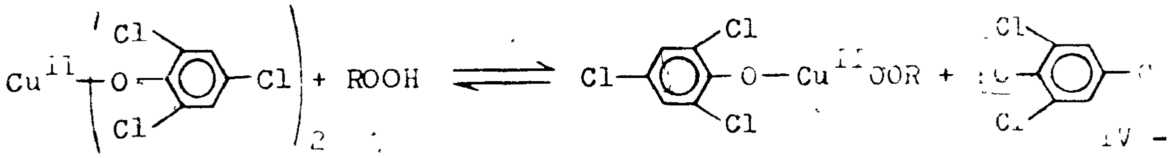


IV - 1a

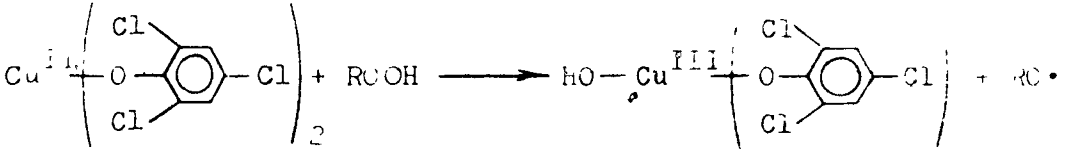
IV - 41

Subsequent loss of these initiator fragments would regenerate initiator radicals and produce phenoxy radicals. White has detected initiator fragments on the terminal rings of oligomers prepared from the oxidation of 2,6-dimethylphenol with benzoyl peroxide as oxidants(23). No initiator fragments were detected in the polymers prepared for this thesis.

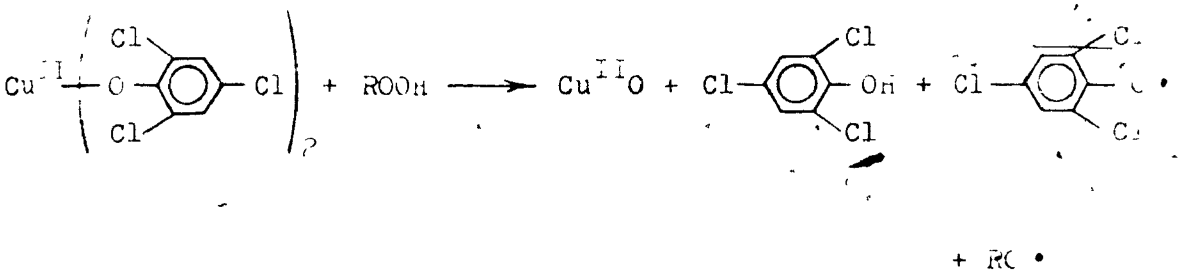
The nature of the copper reaction products, Table III - 12, suggest that hydroperoxides function by attack at copper. The extremely rapid decomposition rate of trichlorophenoxocopper(II) in the presence of hydroperoxides, as manifest by the very rapid fall in absorbance in Figure III - 27, are out of line with their ease of homolytic dissociation relative to the other initiators examined(102). At least two plausible explanations for the initial rapid reaction of hydroperoxides present themselves. On the one hand, a simple acid-base solvolysis of phenoxide by hydroperoxide, equation IV - 42, may lead to rapid reduction in the concentration of the copper(II) phenoxide chromophore.


IV -

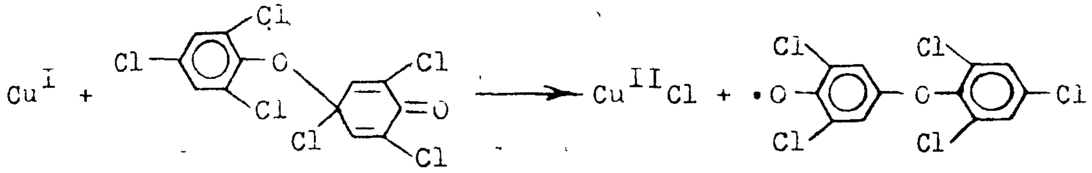
On the other hand, a rapid electron transfer reaction may cause oxidation of copper(II) according to equation IV - 43.


IV -

In either case, the copper complexes produced are unlikely to have a significant lifetime and would in fact decay to a common product, giving the overall stoichiometry of equation IV - 44.



Since the μ_4-oxo-μ-hexahalotetracopper(II) nucleus has the stoichiometry $3CuCl_2 \cdot CuO$, the reaction of IV - 1a with hydroperoxides, as exemplified by equations IV - 42 to 44, cannot be occurring to the exclusion of the reaction in equation IV - 45. It is clear that a great deal of additional information is required before a definitive understanding of these reactions is achieved.



IV - 45

Since both toluene and cumene can be autoxidized to hydroperoxides, much of the chemistry discussed above can be applied to these solvents. Both solvents gave more rapid decomposition of phenoxocopper(II) than benzene as solvent, as shown in Figure III - 18. Benzene is not expected to autoxidize. Both toluene and cumene resulted in a greater yield of μ_4-oxo complex, IV - 19. Cumene had the most dramatic effect, and cumene would be more readily autoxidized than toluene.

The reduction of induction period with successive increasing concentrations of benzoyl peroxide as free radical initiator additive supports the findings, reported earlier in the discussion, for a radical chain mechanism. The high levels of initiator required reflect the slowness of the chain propagation processes, compared, for instance, to vinyl polymerization.

v) Molecular Weight Data

Some polymer molecular weight data is summarized in Table IV - 1. From this, as well as from Figures III - 4 and III - 6, polymer growth clearly proceeds by a series of discrete reaction steps, in a manner similar to that shown in Figure I - 1 for 2,6-dimethylphenol.

Figures III - 5 and III - 6 show a comparison of decomposition rate *versus* polymer molecular weight. It is obvious that polymer growth continues long after all of the phenoxocopper(II) complex has been decomposed. Similar results were obtained for the oxidative coupling of 2,6-dimethylphenol(27), as shown in Figure IV - 2. The extent of reaction, in this case the oxidation of phenol by autoxidized copper(I) salts, is measured by oxygen consumption. This was possible since, from equation I - 1, it is clear that the total amount of oxygen consumed after complete reaction is proportional to the initial concentration of 2,6-dimethylphenol. The term "reaction completion" in both cases implies a stage where after dramatic change in oxygen consumption or yield of copper(II) precipitate, IV - 2, a relatively stable point is reached.

TABLE IV - 1

Effect of Various Parameters on $\overline{M}_n$

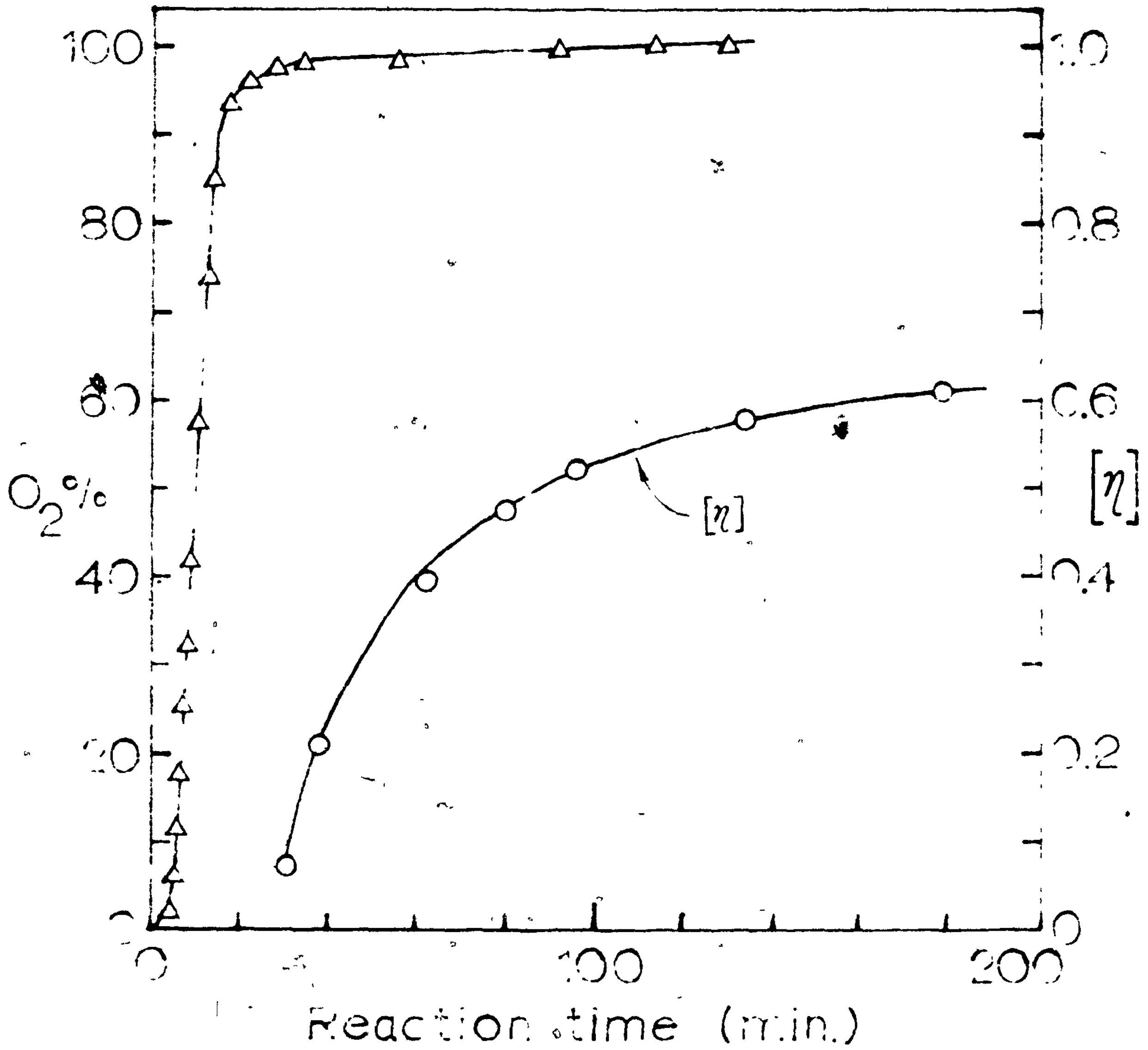
(Reaction Temp. 70°C)

Solvent	Conc. (g/l)	Reaction time (hrs.)	$\overline{M}_n \times 10^4$
benzene	50	2	0.8
benzene	50	2.5	2.5
benzene	50	3	3.4
benzene	50	4	4.7
benzene	50	6	5.5
benzene	50	12	6.1
benzene	50	24	6.9
benzene	50	48	7.9
benzene	40	48	7.0
benzene	30	48	5.9
benzene	20	48	4.6
benzene	10	48	2.5
toluene	50	24	3.9
cumene	50	24	1.3

Figure IV - 2

Relation Between Oxygen Uptake and Viscosity of Polymer Produced in the Autoxidation of 2,6-Dimethylphenol with Cu(I) at Room Temperature*

* Reproduced from Reference(27)


100
80
60
40
20
0
O2%
1.0
0.8
0.6
0.4
0.2
0
[η]
[η]
0
100
200
Reaction time (min.)

both spectrophotometric and electron spin resonance spectroscopy studies have concluded that any phenoxy radicals will initially induce further decomposition of phenoxocopper(II), equation IV - 18. Although carbon-oxygen coupling can be occurring, this reaction is slow compared to IV - 18. Extensive polymer growth would not be apparent until most of the phenoxocopper(II) has been consumed. A comparison of results in Figures I - 1 and IV - 2 for 2,6-dimethylphenol indicate similar results. In Figure IV - 2, the two extreme readings for intrinsic viscosity at reaction times of 30 minutes and 175 minutes are also represented as the final two readings in Figure I - 1. It is quite clear in this reaction that extensive polymer growth does not occur until most of the phenol has been oxidized by copper(II).

The relationship between polymer molecular weight and phenoxocopper(II) concentration, shown in Figure III - 17 and represented in equation IV - 46, is not understood, and necessitates further investigation.

$$\overline{M}_n = k\left[Py_2Cu(TCP)_2\right]^{\frac{1}{2}} \qquad \text{IV - 46}$$

However, the square root dependency of phenoxocopper(II) concentration in this relationship perhaps reflects the generation of two phenoxy radicals from each molecule of <u>IV - 1a</u>.

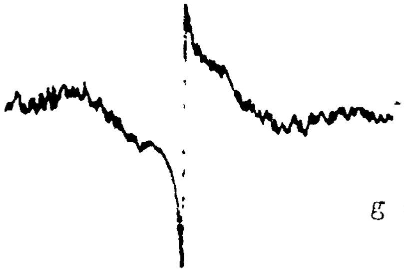
Ideally the plot should pass through the intercept. The fact that it does not, can be explained simply by errors in the experimental values due to leakage through the membrane. Under these circumstances, the resulting values are higher than the recognized true values.

The finite values of polymer molecular weight, rather than the values expected by the exact stoichiometry of equations IV - 1 or IV - 40, can be accounted for by equilibration of the carbon-oxygen coupling steps.

Obviously, considerable research needs to be conducted on the number-average molecular weight of polymers resulting from the decomposition of IV - 1a, in order to determine their dependence on reaction conditions and relevance to the overall mechanism of reaction.

vi) "Trapped" Phenoxy Radicals

The presence of a faint electron spin resonance singlet at $g = 2.007$, IV - 23, for terminated polymer suggests the existence of trapped" phenoxy radicals.



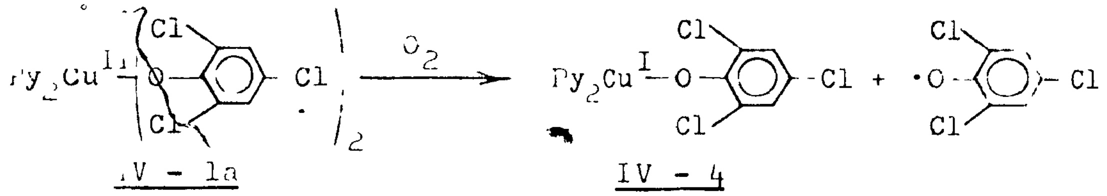
IV - 3

This offers additional support for the equilibrium character of the carbon-oxygen coupling steps, as reported in Section I. The presence of these "trapped" radicals would account for the rather broad nuclear magnetic resonance absorptions of polymers resulting from the decomposition of IV - 1a. Tsuruya, et al(42), reported the existence of a weak, complex electron spin resonance signal which remained unchanged for several days for polymer prepared from trichlorophenoxo-hexamethylphosphoramide-copper(II).

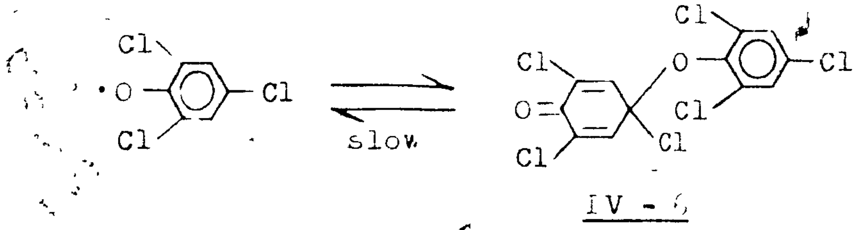
vii) Summary of Mechanistic Results

A summary of the overall mechanism is shown in equations IV - 47 to 62. Equations IV - 47 to 56 describe the decomposition of phenoxocopper(II), IV - 1a, to phenoxy radicals and copper reaction products, IV - 2 and

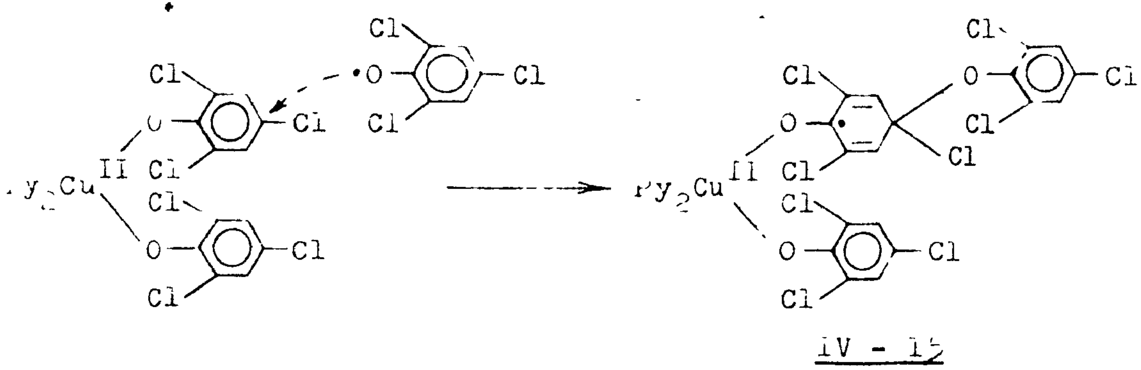
Decomposition of Phenoxocopper(II)



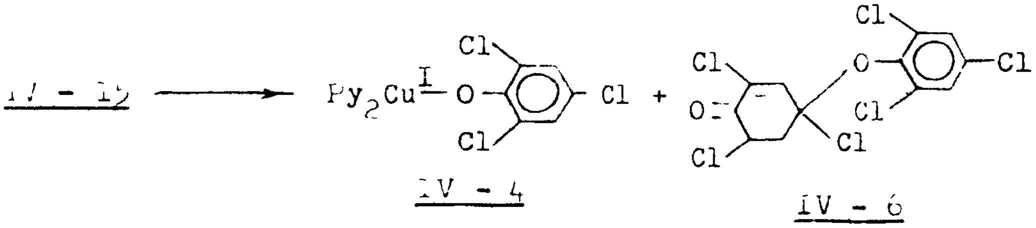
IV - 47



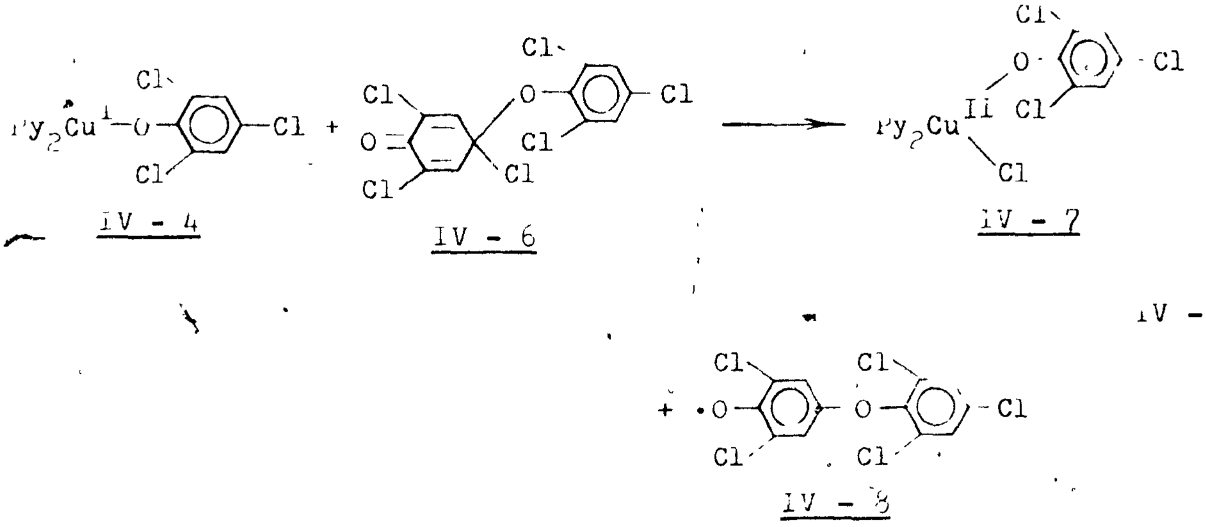
IV - 48



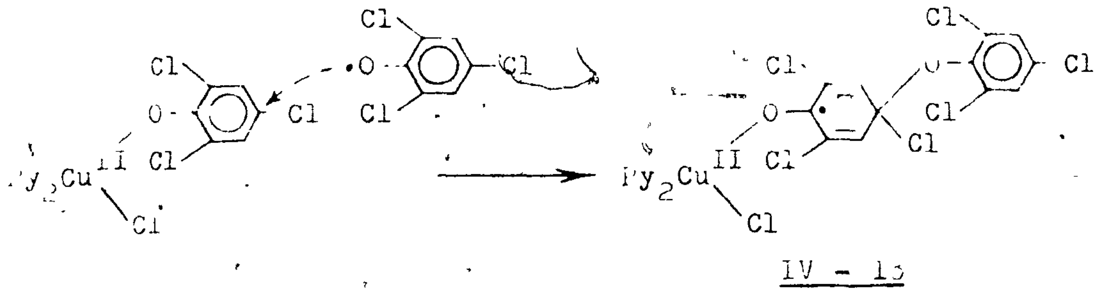
IV - 49



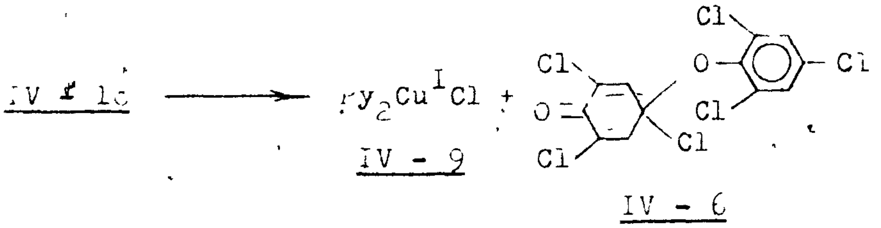
IV - 50



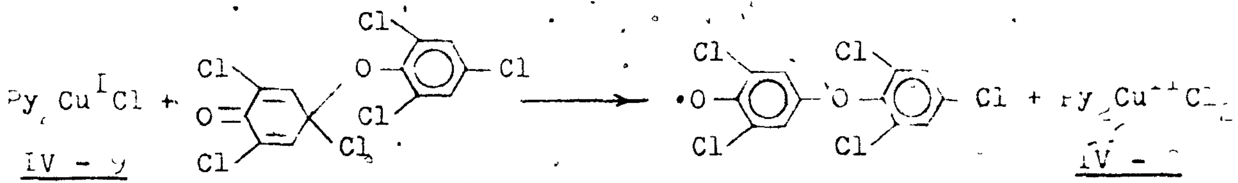
IV - 51



IV - 52



IV - 53



IV - 54

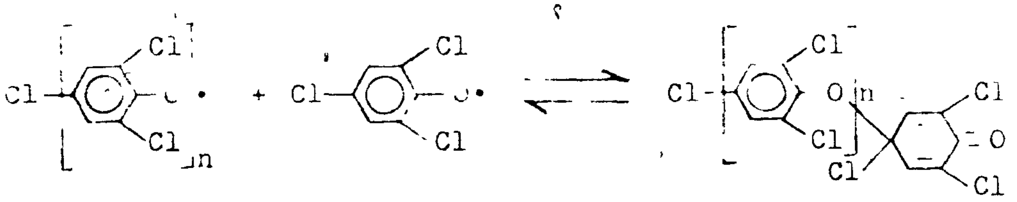
$2\ Py_2Cu^{I}Cl + 1/2\ O_2 \longrightarrow Py_2CuCl_2{\cdot}CuO + 2\ Py$ IV - [illegible]

IV - 9

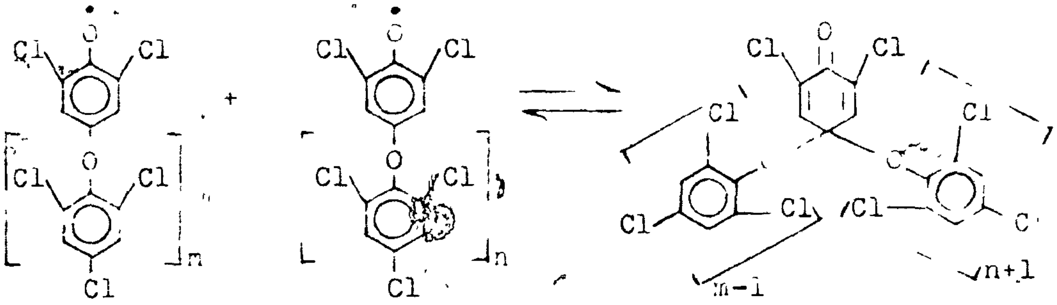
$Py_2CuCl_2{\cdot}CuO + 2\ Py_2CuCl_2 \longrightarrow Py_4Cu_4Cl_6{\cdot}O + 2\ Py$ IV - [illegible]

IV - 2 IV - 19

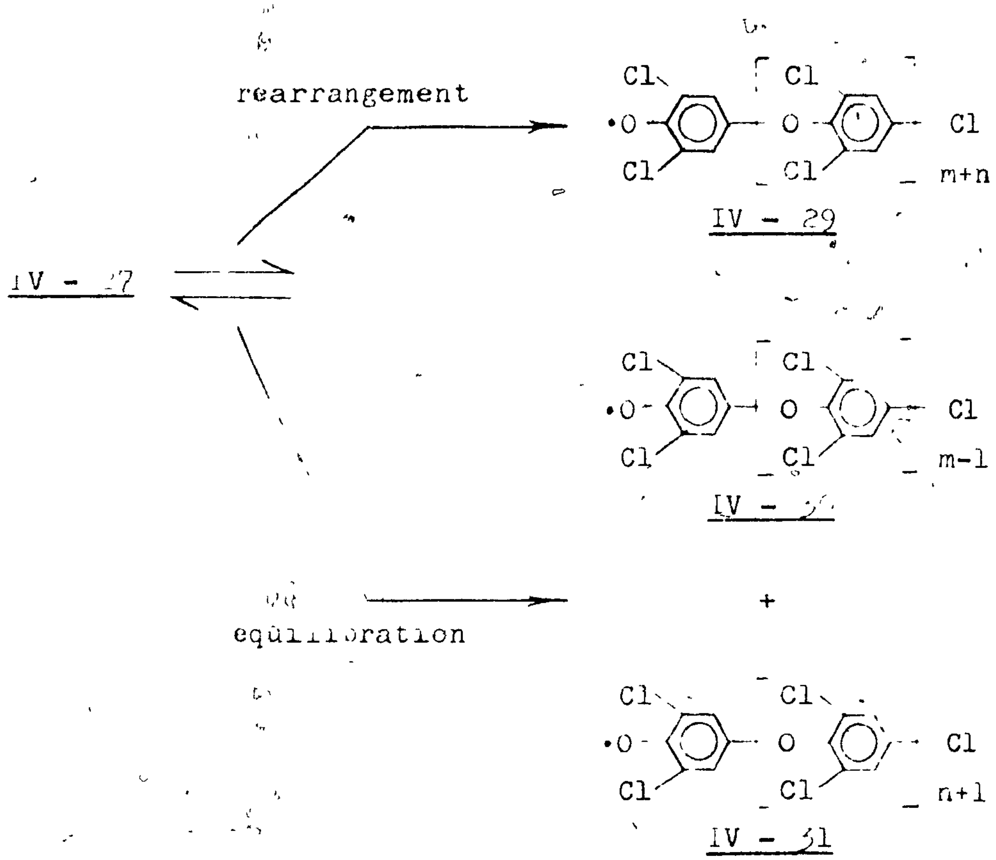
Polymer Growth



IV - 24 IV - [illegible]



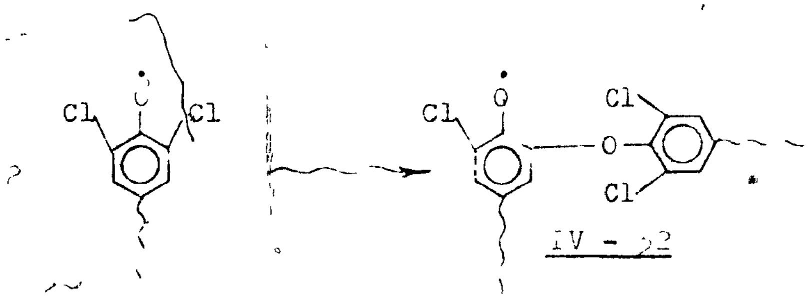
IV - 25 IV - 26 IV - 27 IV - [illegible]



IV - 59

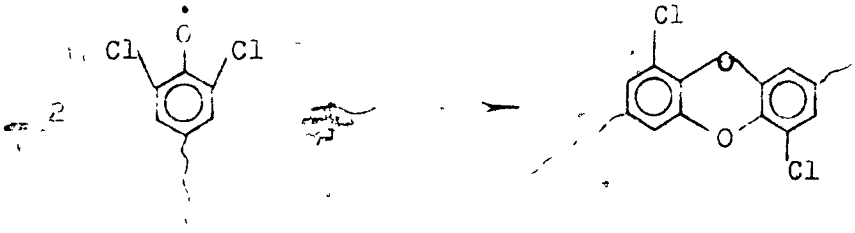
IV - 60

Branching



IV - 61

Termination



IV - 62

IV - 19. Addition of free radical initiators strongly enhance this stage of reaction, as reflected either in the rate of decomposition or in the copper reaction products. Equations IV - 57 to 61 represent the chain growth steps. These steps are identical to those summarized in Section I. Polymer growth continues long after all of IV - 1a has been decomposed. Branching, equation IV - 61, occurs by attack of phenoxy radical at the 2,6- positions. Termination results either by equilibration, leaving a terminal quinol ether, or by dioxin formation, equation IV - 62.

IV - 3 Carbon Tetrahalide as Initiator

The increase in yield of μ_4-oxocopper(II), IV - 19, from the decomposition of IV - 1a, in the presence of hydroperoxides, could possibly result from the ready formation of a copper(II) hydroxide intermediate, IV - 34, equation IV - 63.

$$Cu^{I} + ROOH \longrightarrow \underset{\text{IV - 34}}{Cu^{II}OH} + RO\cdot \qquad \text{IV - 63}$$

Unfortunately, it was impossible to isolate any intermediate complexes.

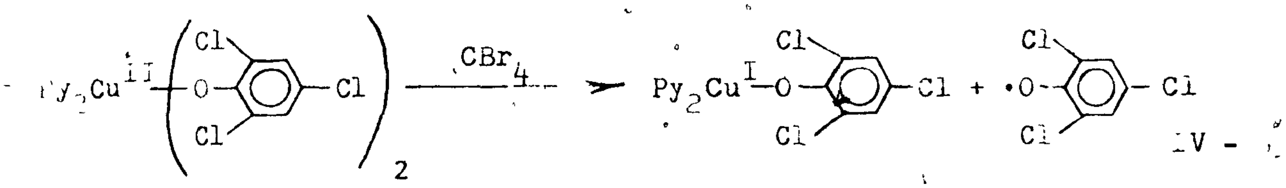
Carbon tetrahalide is known to react with copper(I), resulting in copper(II) halide and carbon trihalide radical(105,106), equation IV - 64.

$$\mathrm{Cu^{I} + CX_4 \longrightarrow Cu^{II}X + \bullet CX_3} \qquad \text{IV - 64}$$

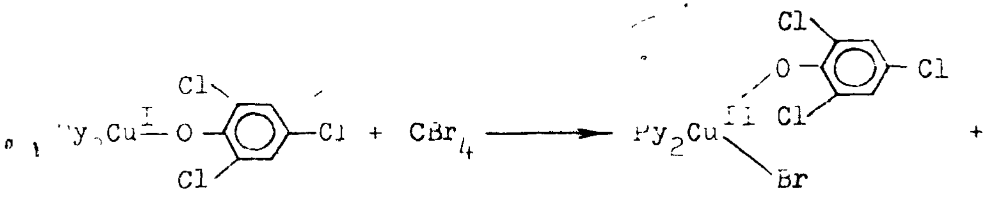
Generation of dibromocopper(II) during the decomposition of trichlorophenoxocopper(II), IV - 1a, in the presence of carbon tetrabromide, would suggest the existence of copper(I) intermediates. It would also offer some support for reaction IV - 50. Indeed, the addition of a 10:1 molar ratio of carbon tetrabromide to IV - 1a, in benzene, resulted in a seven mole per cent production of bromide in the copper reaction product.

Unexpectedly, the addition of carbon tetrahalide to a solution of phenoxocopper(II) greatly enhanced its decomposition.

An interpretation of these results is shown in equations IV - 65 to 67.

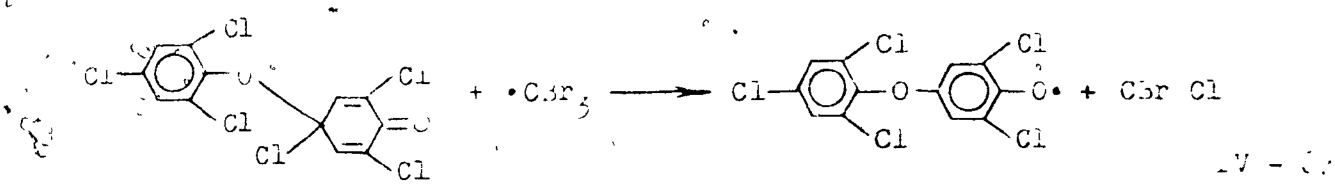


IV - [illegible]



IV - 35

IV - [illegible]

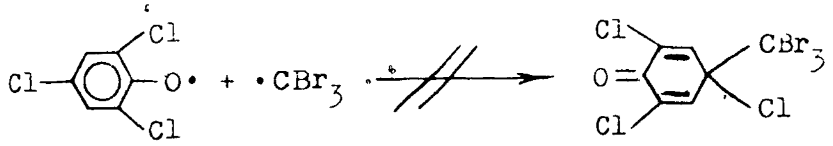


IV - [illegible]

IV - [illegible]

Reactions IV - 62 and 64 occur in conjunction with reactions IV - 50 to 57. Decomposition of IV - 35 by further loss of phenoxo ligand eventually results in dibromocopper(II).

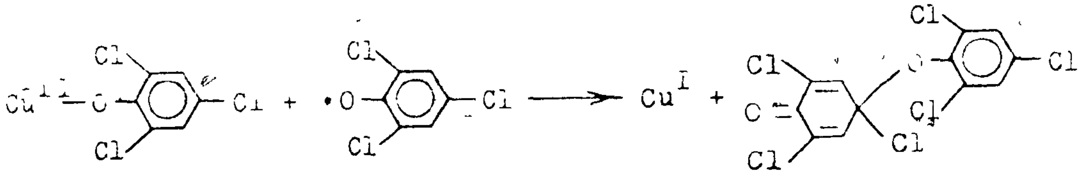
The absence of bromide in the resulting polymer, and the lack of change of its molecular weight due to the presence of carbon tetrahalide, rules out the possibility of equation IV - 66.



IV - 68

The existence of carbon tribromide radical should be reflected in the formation of CBr_3Cl, IV - 36, if equation IV - 67, holds true. Analysis by gas chromatography-mass spectrometry of the reaction products remaining in solution after removal of polymer, for the decomposition of IV - 1a in benzene in the presence of a 10:1 molar ratio of carbon tetrabromide to IV - 1a, affirmed the presence of IV - 36. However, for reaction with a 1:1 molar ratio of carbon tetrabromide to IV - 1a, no CBr_3Cl was detected. Instead dichlorobenzene, IV - 37, was obtained. In order to permit passage of benzene/methanol through the detector, the signal intensity had to be reduced. A sufficient quantity of time was required to readjust the intensity to a level where any solute could be detected. An additional peak, "c", in Figure III - 30 was observed, but this appeared before complete readjustment had been made. As a result, this peak was not analyzed by mass spectrometry. Later interpretation of the mass spectral data, in our laboratory, revealed its importance. At least one additional reaction product needed to be determined in order to account for the unexpected formation of dichlorobenzene. Melting point analysis of the white powder remaining after evaporation of the solvent (benzene/methanol), suggested the presence of tribromomethane. This compound would be expected to appear in the region of uncharacterized peak in Figure III - 30.

In excess carbon tetrabromide, the reaction shown in equation IV - 65 is strongly promoted. The resulting generation of phenoxy radical leads to a rapid build up of quinol ether, equation IV -69.



IV - 69

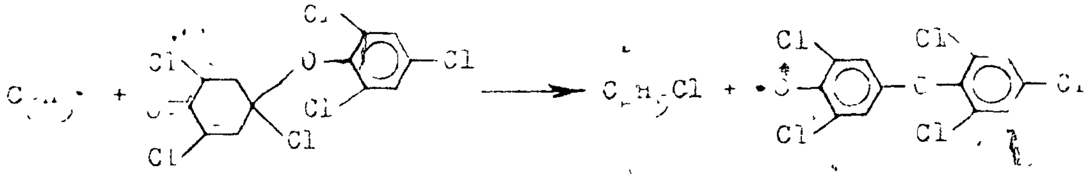
The carbon tribromide radical produced from equation IV - 65 could react readily with quinol ether, IV - 67, as evidenced by the reaction products. The absence of reaction IV - 67 with a 1.1 molar ratio of carbon tetrabromide radical could perhaps be accounted for by the correspondingly slower build up of quinol ether; decreasing the probabilty of this compound coming in contact with carbon tribromide radical. This latter compound would therefore react with the solvent, benzene, through hydrogen extraction, equation

IV - 70.

$$\cdot CBr_3 + C_6H_6 \longrightarrow CHBr_3 + C_6H_5\cdot \qquad IV - 70$$

The ability of carbon trichloride radicals to abstract allylic hydrogen to yield chloroform has been studied in some detail(106,107). Carbon trichloride radical was found to be only slightly reactive with benzene(108), but carbon tribromide radical was found to be more than a hundred fold more reactive with vinyl monomers than carbon trichloride radical(108,109).

Reaction of phenyl radical with quinol ether, equation IV - 71, would result in chlorobenzene.



IV - 71

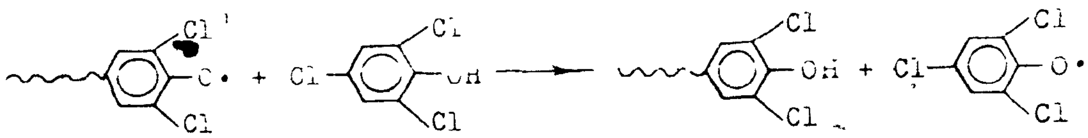
Chlorobenzene could then react further with carbon tribromide radical and quinol ether to give dichlorobenzene. Kharasch, et al(110-112), have reported the addition of carbon trichloride radical to olefinic double bonds in competition with hydrogen extraction. Clearly, more research needs to be conducted to determine a definite mechanism of decomposition in the presence of small amounts of carbon tetrabromide. A more careful work-up of the reaction products would perhaps reveal both chlorobenzene and benzene addition products as well as the compounds already characterized.

Decomposition of IV - 1a in the absence of carbon tetrahalide showed no evidence of any chlorinated benzene.

IV - 4 Effect of Trichlorophenol Additive

Throughout this research, several batches of phenoxocopper(II), IV - 1a, were prepared. Each batch was sufficient to complete several runs. It was found that the number-average molecular weight of polymer, prepared under identical reaction conditions, varied from batch-to-batch. However, the dependence of polymer molecular weight on reaction variables (ie., concentration of IV - 1a, reaction time, solvent, temperature, etc.), observed in one set of runs for one batch, were also apparent for a similar set of runs with another batch. No other reaction conditions were affected by changing the batch of phenoxocopper(II). The effect on molecular weight was attributed to some impurity in phenoxocopper(II) which had not been completely removed by recrystallization. The quantity of this contaminant would vary somewhat with each new preparation of starting material. Investigation of the technique of synthesis suggested trichlorophenol as the most likely candidate for impurity.

Addition of trichlorophenol to a solution of phenoxocopper(II) was found to decrease the number-average molecular weight of polymer, Figure III - 33. From this plot, it is apparent that only a trace quantity of trichlorophenol is required to cause a dramatic reduction in molecular weight. Infrared spectra of the polymers obtained in the presence of trichlorophenol additive indicate terminal hydroxyl groups. The concentration of these hydroxyl groups increase proportionately with increasing amounts of trichlorophenol added. In fact, polymer prepared in the absence of additive (ca., spectrum a), Figure III - 34), shows some indication of hydroxyl absorption, supporting the proposal of trichlorophenol contaminant. Trichlorophenol can redistribute with polymeric phenoxy radicals, equation IV - 72.



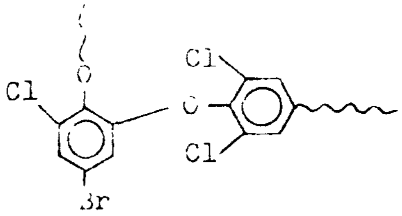
IV - 72

Addition of further trichlorophenol monomer shifts the equilibrium, favouring lower molecular weight polymers. This finding offers additional support for the equilibrium nature of the carbon-oxygen coupling steps.

The effect of trichlorophenol on molecular weight could also account for the corresponding effect of solvent, Table IV - 1. For the solvents examined, molecular weight reduction became more prominent with the ability of solvent to autoxidize to hydroperoxide. From equation IV - 44, reaction of hydroperoxide with phenoxocopper(II), IV - 1a, produces trichlorophenol. At least part of the molecular weight reduction in this case is, however, attributable to formation of μ_4-oxocopper(II) complex.

IV - 5 Polymer from Bis(4-bromo-2,6-dichloropenoxo)bis(pyridine)copper(II)

It was hoped that decomposition of 4-bromo-2,6-phenoxocopper(II), IV - 1b, would produce exclusively linear polymer, by virtue of the greater reactivity of the 4-bromide, relative to chlorine. The polymer was found to contain one bromide atom for an average of every sixth "mer". Correspondingly, the copper reaction product mixture featured just over four bromides for every chloride. The slight discrepancy between the two observations is due to the assumption that the polymer is entirely linear. The nuclear magnetic resonance spectrum of polymer prepared from IV - 1b indicates some branching, as shown in Figure III - 35. The intense peak at 7.3 ppm. is most likely due to the protons from the units with 1,4- linkage. The doublet at 8 ppm. would then be due to the protons from 1,6- linkage in IV - 37 for the unit containing bromide. The two small peaks between 6.5 and 7.0 ppm. could be accounted for by branching.



IV - 37

The polymer prepared from IV - 1b in benzene at room temperature likely has a number-average molecular weight much greater than 160,000 and could be obtained as a tough, clear film by evaporation from hot toluene. However, some branching was still evident by nuclear magnetic resonance. No crystallinity was indicated by X-Ray analysis.

Stamatoff(74) had reported the formation of linear polyphenylene ether from 4-bromo-2,6-dichlorophenol, using benzoyl peroxide as oxidant. This polymer contained a 1.1 weight per cent of bromide. Linearity was confirmed by nuclear magnetic resonance, but no further information was provided. A small degree of coupling at the ✓ 2,6- positions, IV - 37, would account for bromide retention while conserving the linearity. Repetition of the experimental procedure reported by Stamatoff(74) in our laboratory resulted in a polymer which gave a nuclear magnetic resonance spectrum identical to the polymer produced by decomposition of IV - 1b.

V - SUGGESTIONS FOR FURTHER WORK

The work described in this thesis has answered a few questions regarding the decomposition of phenoxocopper(II) to polyphenylene ether. On the other hand, it has merely scratched the surface of the total chemistry involved. Further work along the lines reported in this thesis could perhaps confirm many of the remaining hypotheses relating to the overall mechanism of oxidative coupling phenols to polymer.

1. Little physical proof has been offered on the intermediate compounds involved in the decomposition of phenoxocopper(II).

    i) The oxidation of trichlorophenol in the presence of tri-_tert_-butylphenoxy radical resulted in the formation of quinol ether(63). Quinol ethers are postulated as intermediates in the carbon-oxygen coupling mechanisms. Isolation of a quinol ether in the presence of the above radical would confirm their existence as intermediates.

    ii) The nature of the various copper-containing intermediates, in the decomposition of phenoxocopper(II), needs to be investigated further, with the hopes of their possible isolation and characterization.

2. Further research needs to be carried out utilizing the various reaction conditions and various additives reported in this thesis.

3. Reactions along the lines reported in this thesis with other phenoxo-metal complexes, by changing the metal, phenol or neutral ligand would perhaps provide mechanistic information not obtainable with bis(trichlorophenoxo)bis(pyridine)copper(II).

4. The possibility of performing kinetic measurement should be considered, perhaps photometrically or by electron spin resonance spectroscopy.

5. More research could be conducted with the hopes of obtaining linear, crystalline poly(2,6-dihalophenylene ether).

6. Further research should be carried out with the polymers prepared from trichlorophenoxocopper(II) in hopes of determining the dependence of molecular weight on the various reaction conditions.

7. Further studies on the use of phenoxocopper(II) in the

synthesis of μ_4-oxocopper(II) complexes could be investigated.

VI - CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

This research constitutes the first detailed systematic investigation of the mechanism of decomposition of phenoxocopper(II), in solution, to polyphenylene ether. The phenoxocopper(II) complex most frequently used was bis(trichlorophenoxo)bis(pyridine)copper(II).

The decomposition was found to involve an induction period, but this could be reduced somewhat by the presence of oxygen, free radical initiators, or carbon tetrahalides. The reaction was found to proceed through the generation of phenoxy radicals, as was evidenced by electron spin resonance spectroscopy. Interpretation of the experimental results of decomposition, utilizing ultraviolet-visible spectrophotometry and electron spin resonance spectroscopy, permitted a detailed mechanism to be postulated. This was supported by an investigation of the reaction products.

The decomposition of phenoxocopper(II) under various reaction condition (ie. temperature, concentration, and solvent), as well as the addition of free radical initiators, carbon tetrahalides or trichlorophenol, lent additional support for these mechanistic proposals.

Oxygen or hydroperoxides were found to generate μ_4-oxocopper(II) complexes as side reaction products. Suitable adjustment of reaction conditions led to formation of these complexes as the sole copper-containing reaction product. Reactions under similar conditions with phenoxocopper(II), utilizing several other neutral ligands, provided a unique method for the synthesis of μ_4-oxocopper(II) complexes.

Bis(4-bromo-2,6-dichlorophenoxo)bis(pyridine)copper(II) was decomposed at room temperature in benzene, resulting in high molecular weight, nearly-linear polymer.

VII - INFRARED SPECTRA

Table VII-1

Infrared spectra of phenoxo-metal complexes

Complex	Absorption frequency (cm^{-1})																
sodium trichlorophenolate[a]		1525		1450			1310	1240	1220	1180				855	780	740	
copper(II) trichlorophenolate[a]		1530			1435			1265		1130				845	810 790	750	
$Py_xCo(TCP)_2$	1610	1560 1530	1480	1450	1440	1390	1315	1250	1220 1215	1185 1160	1075	1045 1020	960	890 880 860	810 790	760 735	700
$Py_2Ni(TCP)_2$	1605	1560 1525	1480	1460	1445	1390	1315	1250	1230 1215	1180 1155	1075 1065	1045 1020	960	880 870 860	810 795	760 750 740	705 695
$Py_2Cu(TCP)_2$[b]	1605	1565 1530	1489	1455	1445	1390	1310	1250	1215	1185 1160	1075	1045 1020 1000	965	895 885 870 855	810 795	770 760 735	705
$Py_2Cu(Cl_2BrP)_2$	1605	1560 1520	1485	1455	1445 1420	1380	1305	1250	1215	1185 1160	1075	1050 1020	950	865	795	760 745 735 725 715	705 695
$Py_2Cu(TBP)_2$	1605	1555 1520	1485	1455	1445 1410	1380	1310 1305	1250	1220	1180 1160	1075	1050 1020	955	890 880 865	770	730 720	705 695
$Py_2Cu(TIP)_2$	1605	1535 1490	1450	1425	1410	1360	1305	1245	1215	1170 1155	1070	1045 1020	965	880 870 860	765	735	705 695
$(NH_3)_2Cu(TCP)_2$[b]	1620 1605	1530		1450	1420	1390	1300 1295	1250 1235		1190 1135 1125				865	810 795	750 735	700

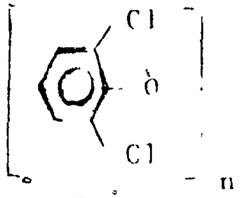
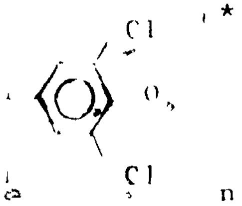
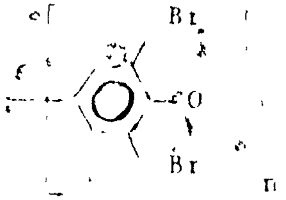
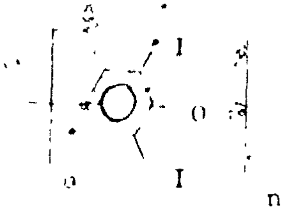
Complex	Absorption frequency (cm^{-1})																
$(C_2H_5NH_2)_2Cu(TCP)_2$[b]	1600	1565 1530		1455	1420 1410	1385 1380	1300 1290	1245	1220	1185 1175	1070	1050 1040		895 885 880 860	810 800	750 730	
$(DMF)_xCu(TCP)_2$	1640	1570 1550 1535	1500	1450		1390 1370	1310 1285	1250		1185 1135 1120	1065			860 855	815 805	760 735	705
$(DMSO)_xCu(TCP)_2$		1560 1540		1440		1385	1305	1270 1240		1130		1020 985	950 935	865	815 800	760	
$(TMED)Cu(TCP)_2$		1560	1525	1460	1420	1385	1310 1295 1285	1250	1230	1180 1120 1100	1070	1045 1020 1005	950	875 860	805 790	770 750 735	
$(TMED)Cu(Cl_2BrP)_2$		1560	1525	1460	1425	1385	1315 1300 1285	1250		1185 1125 1105	1080	1045 1025 1005	955	865 860	810 795	770 745	715

a) ref. (34)

b) agrees with ref. (34)

Table VII-2

Infrared Spectra of Various Polyphenylene Ethers

Polymer	Absorption frequency (cm^{-1})																
	1605	1560	1495	1450	1410	1250	1210	1145	1120	1085	1035	1010	960	920	865 850	825 810	770
 *	1600	1520	1480	1445	1405	1240	1200 1185	1130	1115	1070	1030	1005	945	910	860 845	825 810	
	1595	1560	1470	1430	1370	1235	1190	1115		1070 1055		1005		925	865 800	770 750	705
	1580	1550	1455	1410	1360	1225	1180	1110		1050		1005		900	870 860	790	720

* polymer prepared from $Py_2Cu(Cl_2BrP)_2$

Table VII 3

Infrared data for various dihalo- and μ_4-oxo-copper (II) complexes*

Complex	Absorption frequency (cm^{-1})																
$(C_5H_5N)_2CuC\ell_2$ [a]	1605 1599	1572	1490	1449	1366	1242	1220	1154	1080 1065	1044	1020 1011	951	876	762	690	648	
$(C_5H_5N)_4Cu_4C\ell_6\cdot O$	1605 1599	1572	1488	1449	1362	1242	1219	1158 1148	1070	1050	1020 1010	960	890	772 768 762	705 700	665	576 [b]
$(C_5H_5N)_2CuBr_2$ [a]	1605 1598	1572	1490	1449	1366	1240	1220	1161 1156	1082 1075	1049	1021 1015	950	875	762	692	650	
$(C_5H_5N)_4Cu_4Br_6\cdot O$	1605 1598	1570	1486	1444	1368	1239	1219	1156 1150	1072	1049	1021 1015	955	890	772 770 764	702 698	650	535 [b]
$[(C_6H_5)_3PO]_2CuC\ell_2$	1590 1575		1485	1436 1397	1332 1313	1277	1190 1185 1170	1155 1140 [c] 1115	1090 1084 1070	1029	1000 984 975	931	869 864 854	760 754	728 700		
$[(C_6H_5)_3PO]_4Cu_4C\ell_6\cdot O$	1590		1484	1433 1396	1340 1318	1262	1194 [d] 1180	1120 [d] 1100	1070	1035	1001 975	935	860	768 760 753	730 700		535
$(C_2H_5NH_2)_4Cu_4C\ell_6\cdot O$		1572	1468	1450 1395	1360		1198		1068	1045			892 805			650	582
$[(CH_3)_2N\cdot CHO]_4\ Cu_4C\ell_6\cdot O$	1635		1492	1430	1366	1250		1115		1059	1009				710		580 [b]

*Data cited for spectra in KBr pellets.

[a] Agrees with Ref. (92).

[b] Agrees with Ref. (82). Data cited for nujol mull on KBr plates.

[c] Agrees with Ref. (93) for P=O stretch at 1142 cm^{-1}.

[d] Agrees with Ref. (79) for P=O stretch.

TABLE VII 4

Far-infrared data for various dihalo and μ_4-oxo-copper(II)

Complex	Absorption frequency (cm^{-1})									
$(C_5H_5N)_2CuCl_2$[a]			291	268		235	202		178	
$(C_5H_5N)_4Cu_4Cl_6.O$					$\underbrace{247}$		$\underbrace{202}$			
$(C_5H_5N)_2CuBr_2$[a]				267	255		205	194†		128
$(C_5H_5N)_4\cancel{Cd}_4Br_6.O$						$\underbrace{220}$,	$\underbrace{200}$		$\underbrace{166}$,	$\underbrace{135}$
$[(C_6H_5)_3PO]_2CuCl_2$	330	300	289	267				189	168	
$[(C_6H_5)_3PO]_4Cu_4Cl_6.O$			293		$\underbrace{257}$,	$\underbrace{234}$		$\underbrace{195}$,	$\underbrace{170}$	
$(C_2H_5NH_2)_2CuCl_2$[b]		313		263	250†			186		
$(C_2H_5NH_2)_4Cu_4Cl_6.O$				$\underbrace{270}$			$\underbrace{209}$			
$[(CH_3)_2N.CHO]_4Cu_4Cl_6.O$					$\underbrace{240}$			$\underbrace{194}$		
$[(CH_3)_2SO]_4Cu_4Cl_6.O$					$\underbrace{240}$			$\underbrace{186}$		

*Data cited for nujol mull on polyethylene plates.

For all μ_4-oxo complexes, bracket under absorption indicated broad band.

† Shoulder

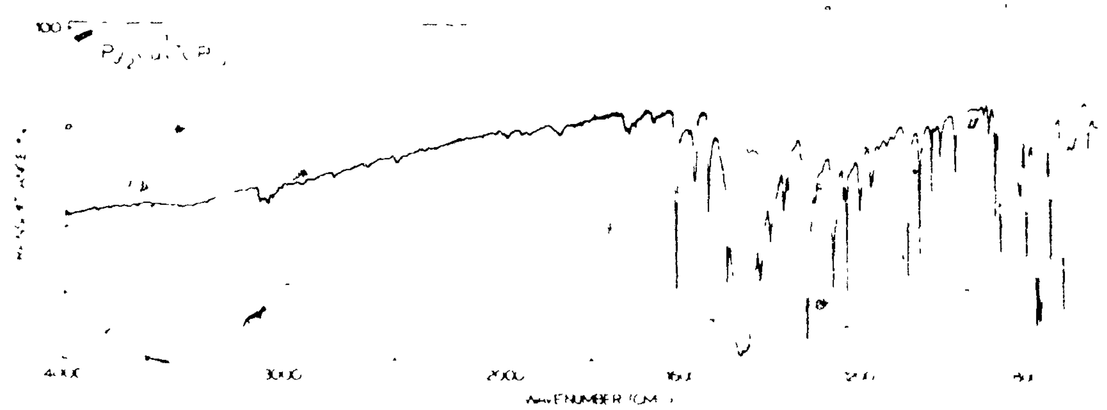
[a] Agrees with Ref. (92)

[b] Reproduced from Ref. (94)

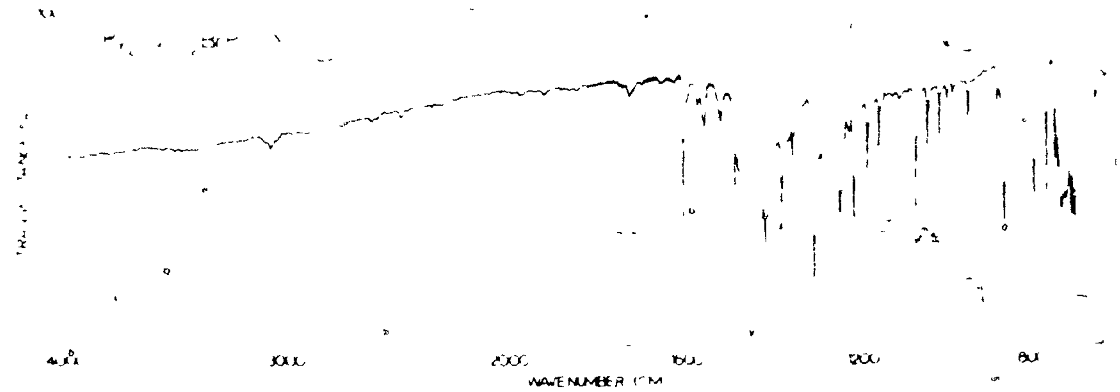
FIGURE VII - 1

Infrared Spectra of Various Phenoxocopper(II) Complexes.

a)


100
4000
3000
2000
1600
1200
800
WAVENUMBER (CM⁻¹)

b)


4000
3000
2000
1600
1200
800
WAVENUMBER (CM⁻¹)

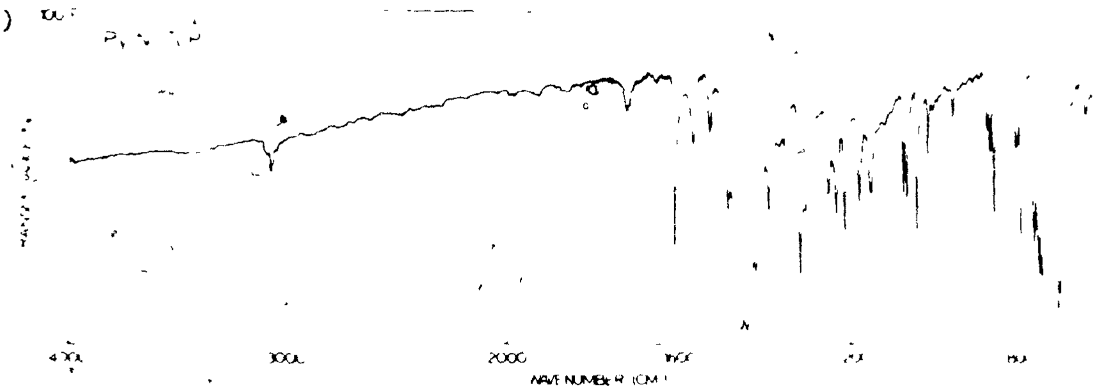
c)


100
WAVENUMBER

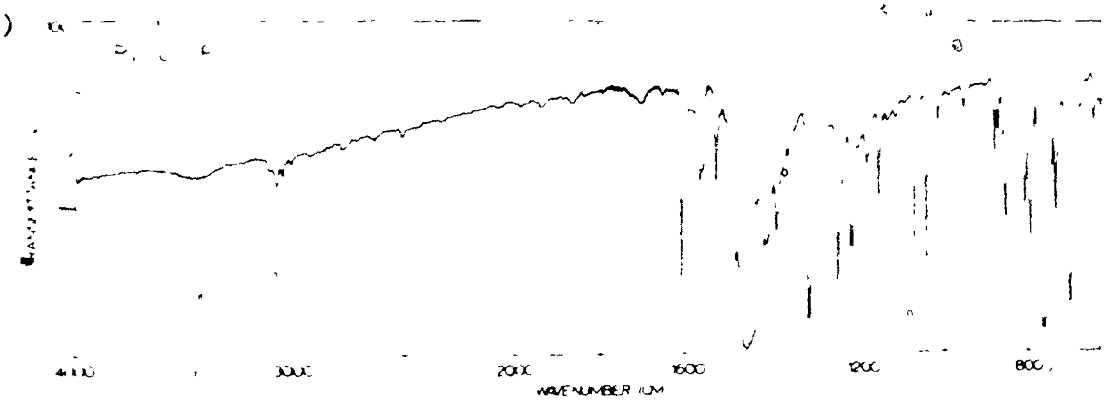
d)


4000
3000
2000
1600
1200
800
WAVENUMBER (CM⁻¹)

e)


4000
3000
2000
1600
WAVENUMBER (CM⁻¹)

f)


4000
3000
2000
1600
1200
800
WAVENUMBER (CM

g)


2000
WAVENUMBER

h)

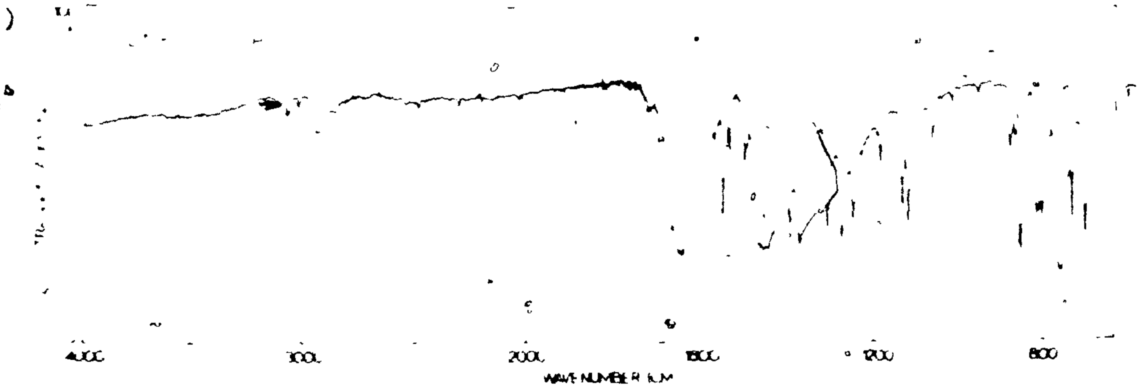
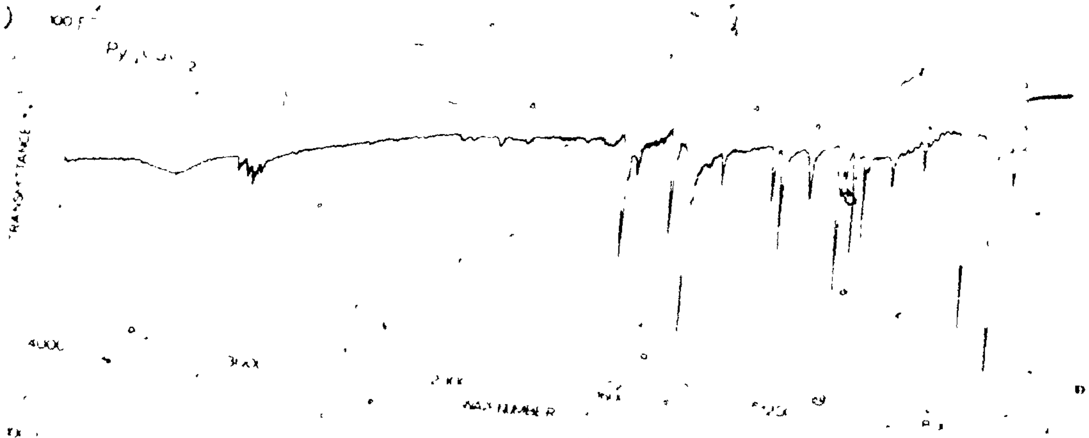

4000
3000
2000
1600
1200
800
WAVENUMBER (CM

FIGURE VII - 2

Infrared and Far-Infrared Spectra of Various Dihalogenocopper(II) Reaction Products.

a)


100
TRANSMITTANCE
4000
2000
WAVENUMBER

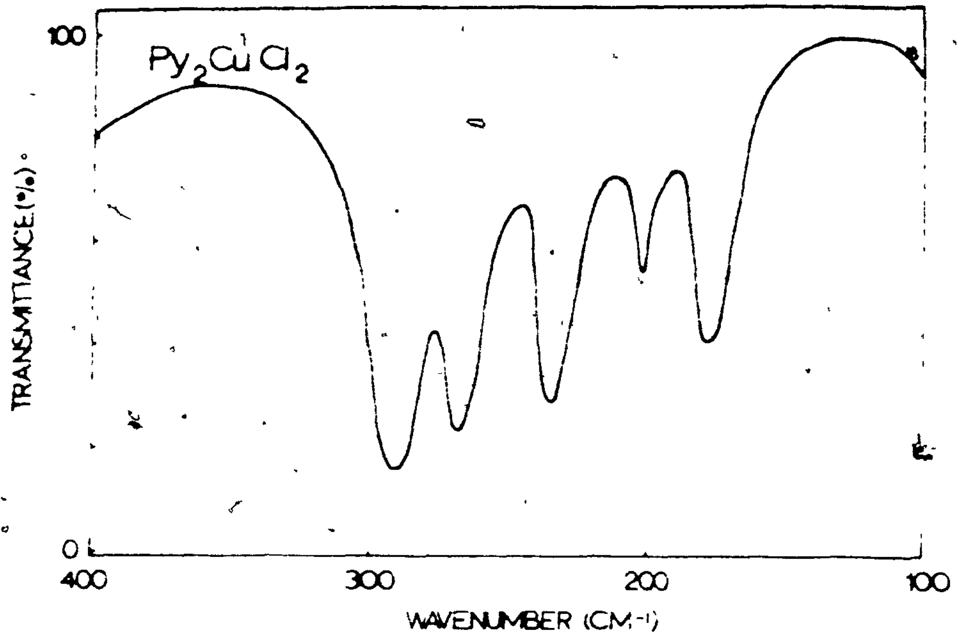
b)


4000
3000
2000
WAVENUMBER (CM
1600
1200
800

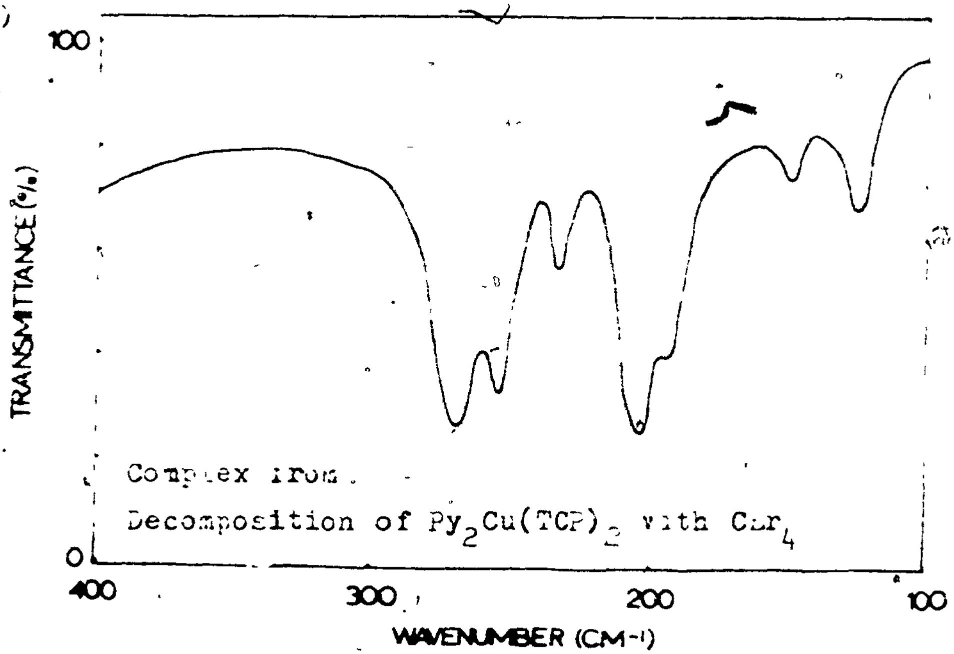
c)


100
TPP
4000
2000
WAVENUMBER

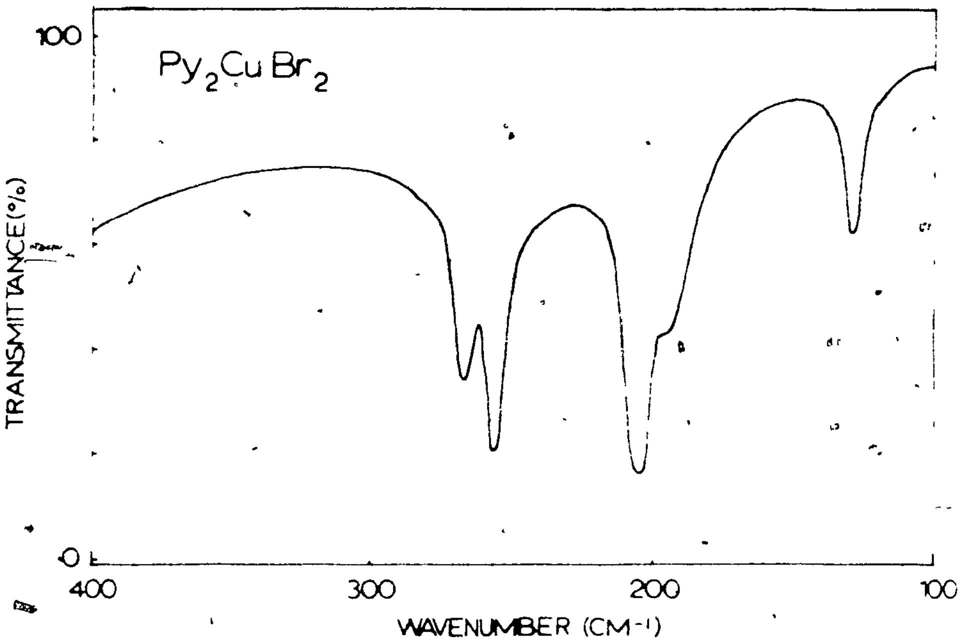
d)


Py$_2$CuCl$_2$
100
0
TRANSMITTANCE (%)
400
300
200
100
WAVENUMBER (CM^{-1})

e)


100
0
TRANSMITTANCE (%)
400
300
200
100
WAVENUMBER (CM^{-1})
Complex from
Decomposition of Py$_2$Cu(TCP)$_2$ with CBr$_4$

f)


Py$_2$CuBr$_2$
100
0
TRANSMITTANCE (%)
400
300
200
100
WAVENUMBER (CM^{-1})

g)

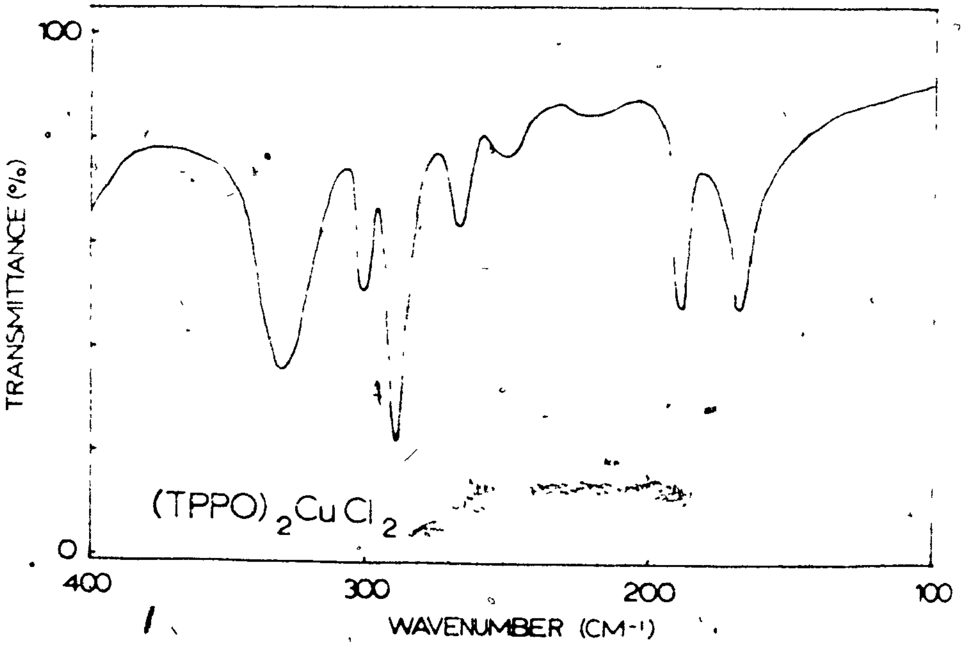
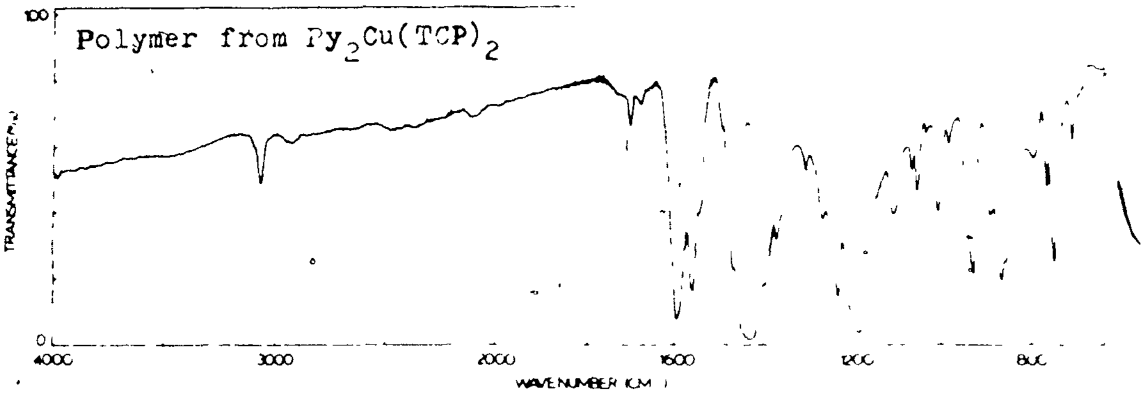

100
0
TRANSMITTANCE (%)
(TPPO)$_2$CuCl$_2$
400
300
200
100
WAVENUMBER (CM^{-1})

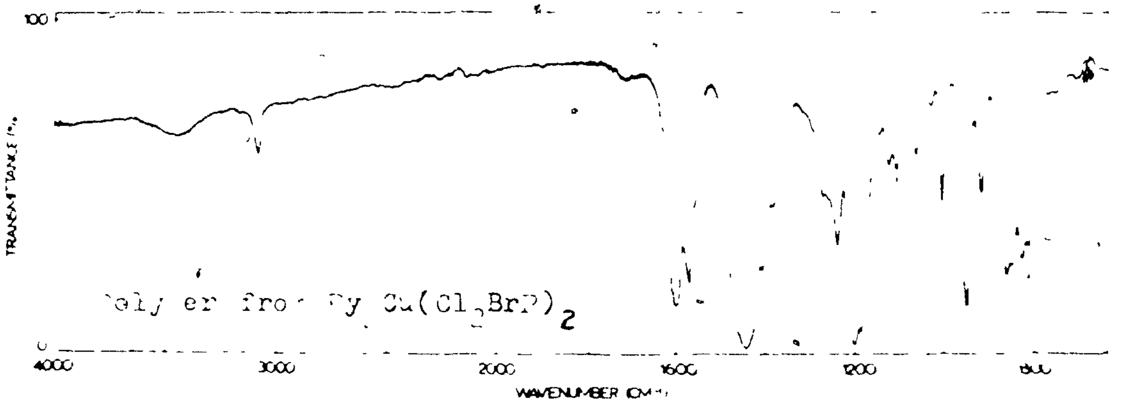
FIGURE VII - 3

Infrared Spectra of Polymer Reaction Product from the Thermal Decomposition of Various Phenoxocopper(II) Complexes.

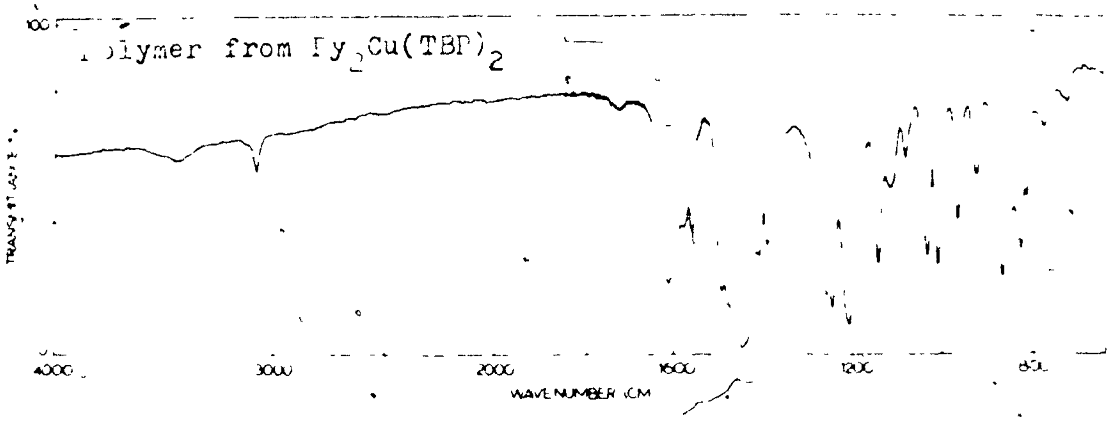
a)


Polymer from Py$_2$Cu(TCP)$_2$
100
TRANSMITTANCE (%)
0
4000
3000
2000
1600
1200
800
WAVENUMBER (CM⁻¹)

b)


Polymer from Py$_2$Cu(Cl$_2$BrP)$_2$
100
TRANSMITTANCE (%)
0
4000
3000
2000
1600
1200
800
WAVENUMBER (CM⁻¹)

c)


Polymer from Py$_2$Cu(TBP)$_2$
100
TRANSMITTANCE (%)
4000
3000
2000
1600
1200
800
WAVENUMBER (CM⁻¹)

d)

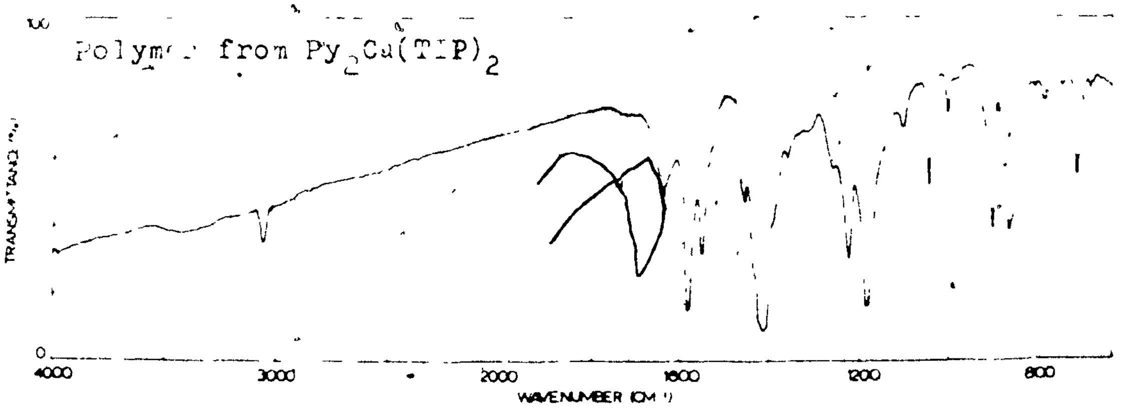
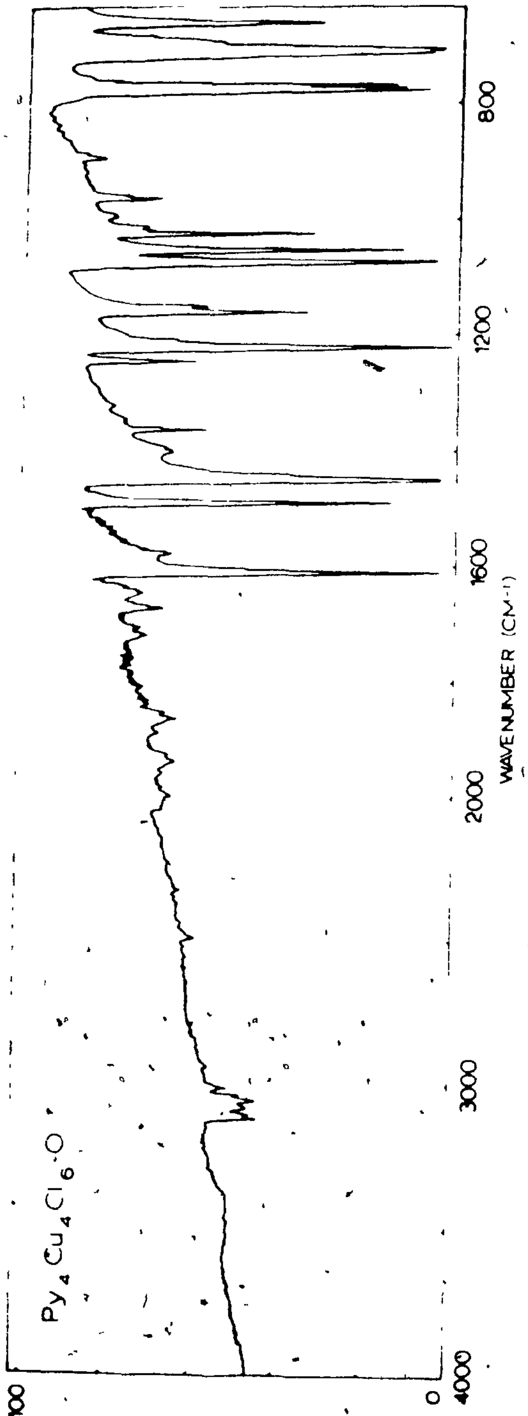
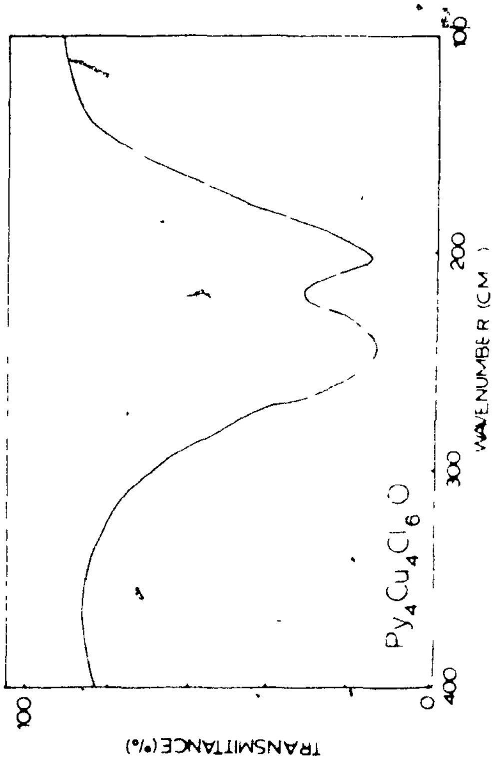

Polymer from Py$_2$Cu(TIP)$_2$
100
TRANSMITTANCE (%)
0
4000
3000
2000
1600
1200
800
WAVENUMBER (CM⁻¹)

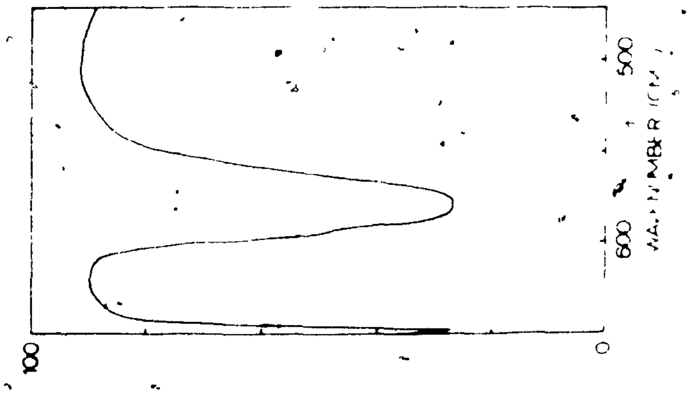
FIGURE VII - 4

Infrared and Far-Infrared Spectra of Various
μ_4-oxo-hexa-μ-halotetra-copper(II) Complexes.

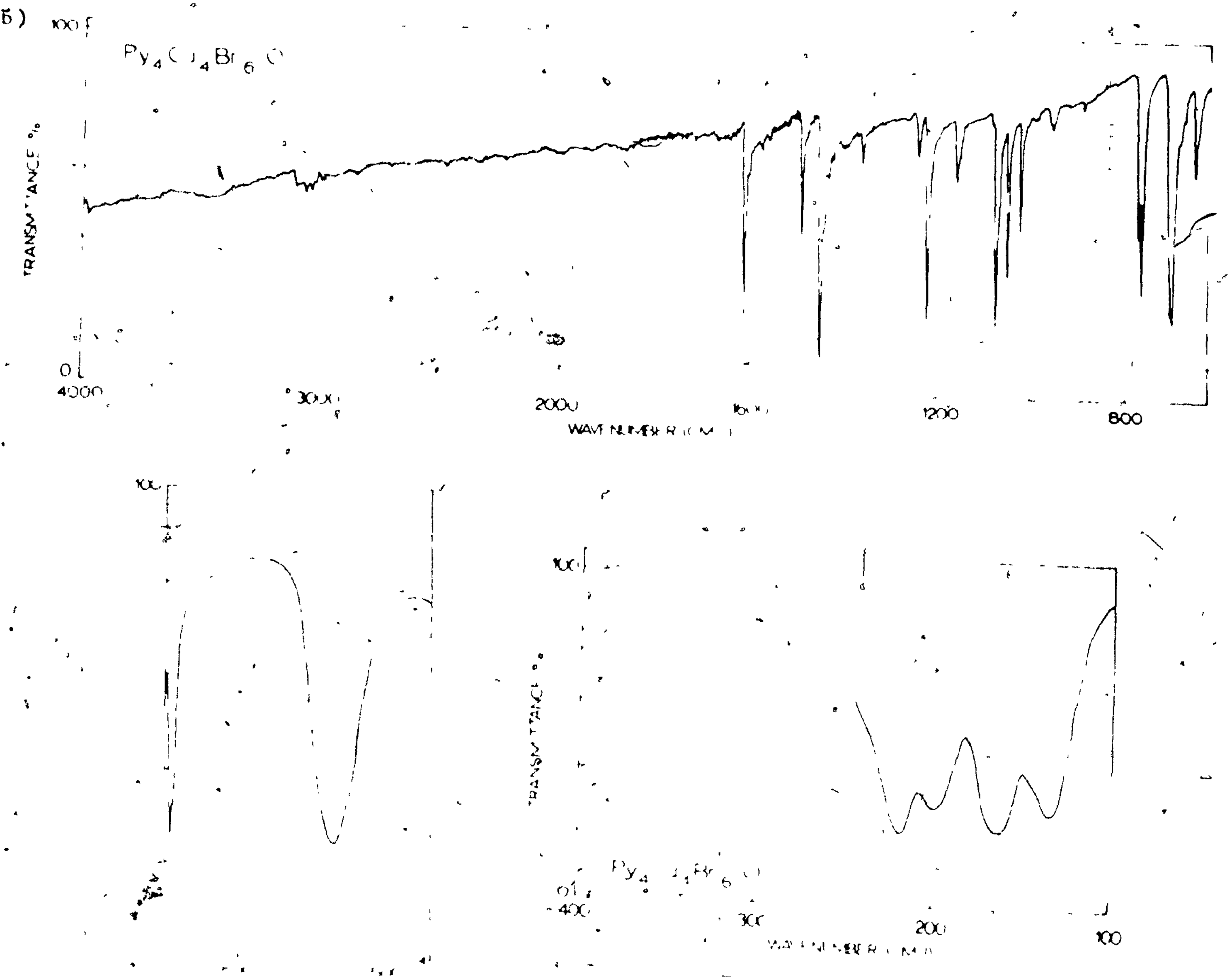
a)


Py$_4$Cu$_4$Cl$_6$O
TRANSMITTANCE (%)
100
0
4000
3000
2000
1600
1200
800
WAVENUMBER (CM-1)

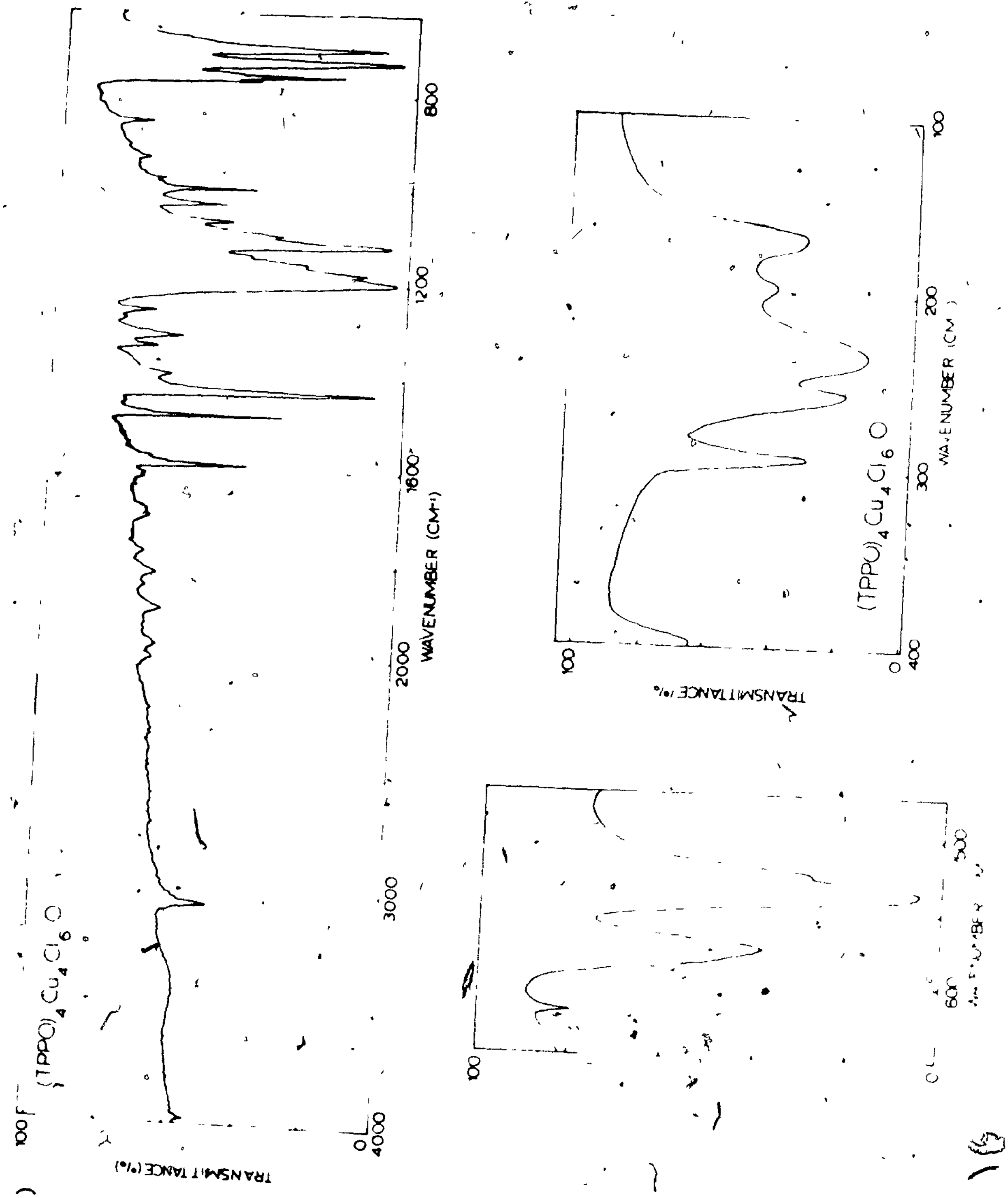

Py$_4$Cu$_4$Cl$_6$O
TRANSMITTANCE (%)
100
0
400
300
200
100
WAVENUMBER (CM-1)


100
0
600
500
WAVENUMBER (CM-1)

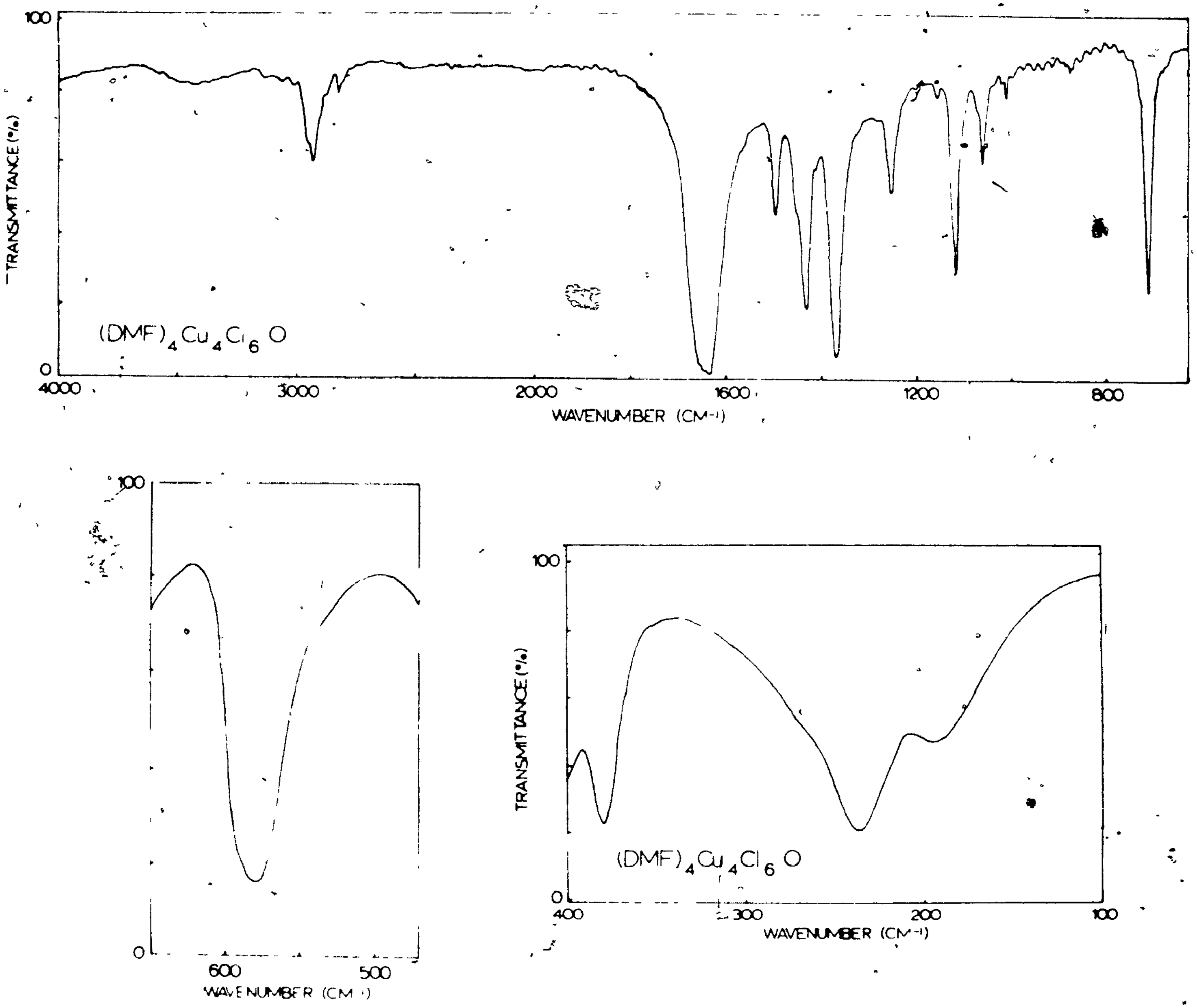
b)


100
Py4Cu4Br6O
TRANSMITTANCE %
0
4000
3000
2000
1600
1200
800
WAVE NUMBER (CM-1)
100
100
TRANSMITTANCE %
0
400
Py4Cu4Br6O
300
200
100
WAVE NUMBER (CM-1)

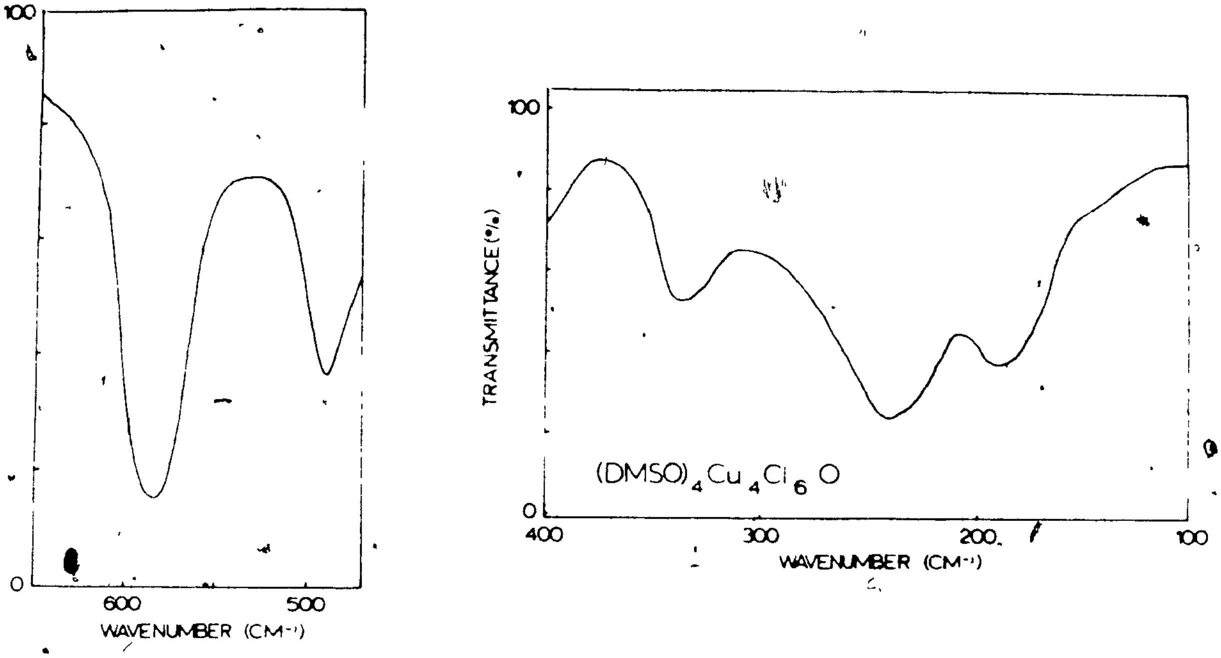
c)


(TPPO)$_4$Cu$_4$Cl$_6$O
TRANSMITTANCE (%)
100
0
4000
3000
2000
1800
1200
800
WAVENUMBER (CM^{-1})
(TPPO)$_4$Cu$_4$Cl$_6$O
TRANSMITTANCE (%)
100
0
400
300
200
100
WAVENUMBER (CM^{-1})
100
0
600
500

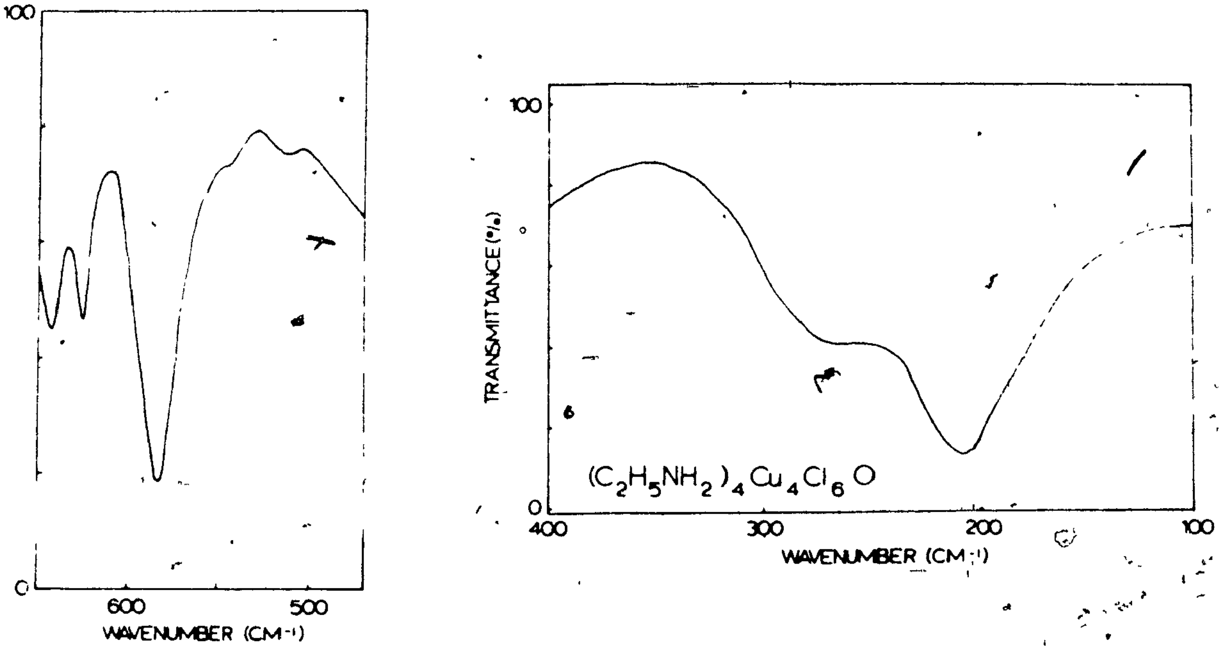
d)


100
0
TRANSMITTANCE (%)
(DMF)$_4$Cu$_4$Cl$_6$O
4000
3000
2000
1600
1200
800
WAVENUMBER (CM^{-1})
100
0
600
500
WAVENUMBER (CM^{-1})
100
0
TRANSMITTANCE (%)
(DMF)$_4$Cu$_4$Cl$_6$O
400
300
200
100
WAVENUMBER (CM^{-1})

e)


100
0
600
500
WAVENUMBER (CM⁻¹)
100
0
TRANSMITTANCE (%)
(DMSO)₄Cu₄Cl₆O
400
300
200
100
WAVENUMBER (CM⁻¹)

f)


100
0
600
500
WAVENUMBER (CM⁻¹)
100
0
TRANSMITTANCE (%)
(C₂H₅NH₂)₄Cu₄Cl₆O
400
300
200
100
WAVENUMBER (CM⁻¹)

VIII - APPENDICES

Supporting Data for Figures

FIGURE III - 1

Yield of Copper(II) Reaction Products at Various Reaction Times for a Series of Decompositions of $Py_2Cu(TCP)_2$ in Benzene at 84.5°C Under Vacuum.

		Run I	Run II	Run III	Run IV
vessel #1*	reaction time	3 hrs.	30 hrs.	48 hrs.	48 hrs.
	wt. complex	0.71	0.75	0.83	0.66
vessel #2	reaction time	½ hr.	3½ hrs.	2¾ hrs.	3 hrs.
	wt. complex	0.91	0.85	0.87	0.87
vessel #3	reaction time	½ hr.	1 hr.	1½ hrs.	1½ hrs.
	wt. complex	0.95	0.93	0.92	0.85

FIGURE III - 2

Yield of Copper(II) Reaction Products with Time in the Decomposition of $Py_2Cu(TCP)_2$ in Benzene at 84.5°C Under Vacuum.

Reaction time	Wt. complex
½ hr.	0.01*
1 hr.	0.01*
2½ hrs.	0.86
2¾ hrs.	0.41
3 hrs.	0.87
3½ hrs.	0.76

* greyish powder

FIGURES III - 3 and III - 4

Data on Reaction Products vs Time in the Decomposition of $Py_2Cu(TCP)_2$ in Toluene at 84.5°C.

Reaction Time (hrs.)	Yield of Cu(II) Complex (gms.)*	$\bar{M}_n$
0.25	none	--
0.50	0.41	
0.75	0.47	
1.	0.62	7600
1.5	0.69	8500
2.	0.76	12000
2.5	0.80	
3.	0.79	
3.5	0.82	
4.	0.79	
4.5	0.84	12000
5.	0.87	
18.	0.87	15000

* theoretical yield of Py_2CuCl_2 = 0.95 gms.

FIGURES III - 5 and III - 6

Data on Reaction Products vs Time in the Decomposition of $Py_2Cu(TCP)_2$ in Benzene at 71°C.

Reaction Time (hrs.)	Wt Cu(II) Complexes* (gm)	$\bar{M}_n$
1.	none	--
2.	0.29	8000
2.5	1.74	26,700
3.	2.20	34,000
4.	2.17	47,500
6.	2.26	54,500
12.	2.26	61,000
24.	2.21	69,500
48.	2.31	79,000

* theoretical 100% yield Py_2CuCl_2 = 2.35 gm.

ⲧ molecular weights obtained by VPO.

FIGURE III - 8

Absorbance at 22,500 cm^{-1} vs Concentration of $Py_2Cu(TCP)_2$ in Benzene.

Conc x 10^3	Absorbance
0.035	0.03
0.069	0.08
0.138	0.15
0.276	0.31
0.405	0.46
0.540	0.63
0.552	0.64
0.614	0.71
0.689	0.79
0.768	0.89
0.810	0.93
0.864	1.00
0.960	1.11
1.08	1.25
1.20	1.40
1.35	1.57
1.50	1.74
1.60	1.86
1.70	1.94

FIGURE III - 14

2,4,6-Trichlorophenoxy Radical Signal at Various Reaction Times in the Decomposition of $Py_2Cu(TCP)_2$ in Benzene at 71°C in the Presence of CCl_4.

Reaction Time (min.)	Peak Height (arbitrary units)
25	0.15
30	0.32
35	0.45
38	0.79
40	0.85
45	0.92
60	0.75
65	0.70
80	0.60
95	0.65
110	0.49
125	0.42
180	0.31

FIGURES III - 16 and III - 17

Polymer Molecular Weight at Various Concentrations of $Py_2Cu(TCP)_2$ in Benzene at 71°C.

Conc. (g/l)	$Conc.^{\frac{1}{2}}$ $(moles/l)^{\frac{1}{2}}$	$\bar{M}_n$
10	0.128	25,000
20	0.181	45,500
30	0.221	58,500
40	0.255	70,000
50	0.285	79,000

FIGURE III - 28

Effect of Induction Period at Various Concentrations of Benzoyl Peroxide

Initiator/$Py_2Cu(TCP)_2$ (molar ratio)	Induction Period (min.)
0	64
0.05	52
0.08	22.4
0.1	16.2
0.1	15
0.2	9.2
0.3	5.4
0.5	3.8
1.0	2.0

FIGURES III - 30 to III - 32

Mass Spectra of Various Compounds

dichlorobenzene		CBr_3Cl		CBr_4	
M/e	R.I.	M/e	R.I.	M/e	R.I.
146	100	207	100	251	100
148	64	209	67	253	98.5
111	39.8	205	42.7	249	34
113	12.5	79	22.8	255	31.8
150	10.4	81	22.1	172	25.6
		128	18.8	79	23.0
		129	14.5	93	22.4
		126	14.2	173	14.9
		91	13.0	81	22.7
		93	13.0	91	22.6
		211	13.0	170	13.4
		127	11.2	174	13.2
		130	4.2	171	7.8
		172	4.2	80	2.7
		131	3.3	175	7.3
		170	2.1	81	2.6
		174	2.1	92	2.3
		78	3.2	94	2.3
		80	3.2	332	trace
		82	3.2		
		251	2.7		
		253	2.4		
		287	trace		

FIGURE III - 33

Effect of the Addition of Trichlorophenol on Polymer Molecular Weight.

Weight Trichlorophenol (gm)	$\bar{M}_n$
0.	44,000
0.25	18,100
0.50	11,350
0.75	7,650
1.00	7,600

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