THE CHEMISTRY OF PHENOXOCOPPER COMPLEXES

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To Irène and Georges
for their unfailing love
and encouragement.

Pour qu'une chose soit
intéressante, il suffit de la
regarder longtemps.
Gustave Flaubert

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Ph.D. Chemistry

Patrick Van Gheluwe

Chemistry of Phenoxocopper Complexes

Abstract

The compounds Cu(I)OAr where OAr = alkyl or halo substituted phenoxide have been prepared in acetonitrile and their reactions with carbon tetrahalides were examined. Phenoxides unsubstituted in the ortho positions yield mainly tetraaryl orthocarbonates; triaryl orthoformates are produced with ortho substituted phenoxides or when the reaction is carried out in the presence of good hydrogen atom donors. A mechanism is proposed consistent with the production of intermediate CX_3 radicals which further react to produce trihalomethyl ethers, the precursors of the product ortho esters. The effect of carbon tetrahalides on the thermal decomposition of bis(amine)bis(trichlorophenoxo)copper-(II) complexes is discussed in the light of present knowledge. The previously proposed branching hypothesis concerning the polymers obtained from (trihalophenoxo)copper(II) complexes is reevaluated. To this end ^1H and ^{13}C spectra of a series of polymers obtained from mixed oxidation state copper complexes of 2,4,6-trichlorophenol were measured. The carbon-13 spectra are consistent with a polymer structure composed of 1,2 and 1,4-coupled units. The linewidth of the proton spectra shows a marked dependence on molecular weight and the relative proportion of 1,2 to 1,4-coupled units. The importance of the 1,2-coupled units in determining the overall flexibility of the polymer chain was indicated by preparing copolymers containing varying proportions of 1,2 to 1,4-coupled units and examining their nmr spectra.

Ph.D. Chimie

Patrick Van Gheluwe

Chimie des Complexes Phenoxo du Cuivre

Résumé

Les composés Cu(I)OAr (où OAr sont des phénolates alkyle- ou halogéno-substitués) furent préparés dans l'acétonitrile et leurs réactions avec les tétrahalogénures de carbone furent étudiées. Les phénolates non substitués en position ortho conduisent à des tétraphényle orthocarbonates. Des triphényle orthoformates résultent lorsque les phénolates sont substitués en ortho ou lorsque la réaction est éxécutée en présence de substances ayant des atomes d'hydrogène labiles. Un mécanisme est proposé s'accordant avec la production intermédiaire de radicaux CX_3 capables de former des éthers trihalogénométhylés. Ceux-ci sont les précurseurs des ortho esters. L'effet des tétrahalogénures de carbone sur la décomposition thermique des complexes bis(amine)bis(trichlorophénoxo)cuivre(II) est discuté à la lumière des connaissances acquises. L'hypothèse prévalant auparavant concernant le branchement des polymères obtenus à partir des complexes (trihalogénophénoxo)cuivre(II) est aussi réévaluée. A cette fin, les spectres ^1H et ^{13}C d'une série de polymères obtenus à partir de complexes (trichloro-2,4,6-phénoxo)cuivre à l'état d'oxidation multiple furent mesurés. Les spectres carbone-13 sont en accord avec une structure du polymère comprenant des unités couplés en 1,2 et en 1,4. La résolution des spectres de protons est fonction de la masse moléculaire ainsi que du rapport des unités couplés en 1,2 et en 1,4. La préparation de copolymères contenant différents rapports d'unités couplés en 1,2 et en 1,4 indiqua l'importance des unités couplés en 1,2 dans la détermination de la flexibilité de la chaîne macromoléculaire.

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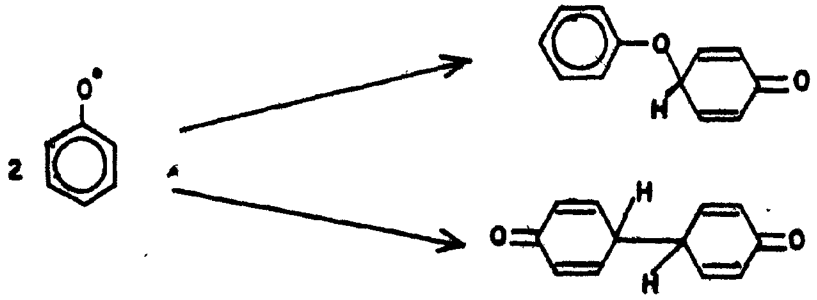
CHAPTER 1

1. GENERAL INTRODUCTION

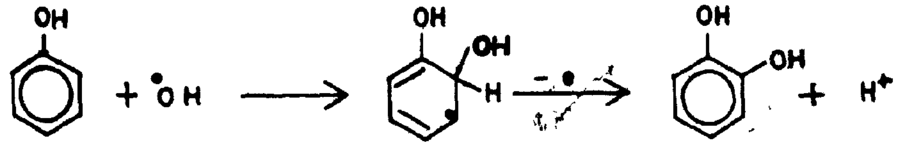
Oxidation of phenolic compounds as an area of organic chemistry has spread over the last few decades into a field of great technological applications and is highly relevant to the understanding of biochemical processes. Such diverse fields can be related to the extremely versatile oxidation-reduction system associated with phenols.

A number of plausible oxidative coupling mechanisms can be postulated depending on the particular conditions. Thus reactions can involve free radical intermediates or proceed via non-radical pathways.[1] The coupling of two free phenoxy radicals has become the more commonly accepted mechanism although this has not always been adequately justified (1).

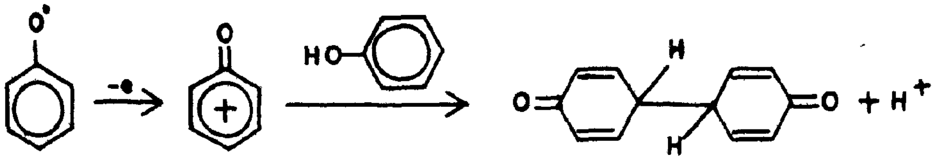


(1)

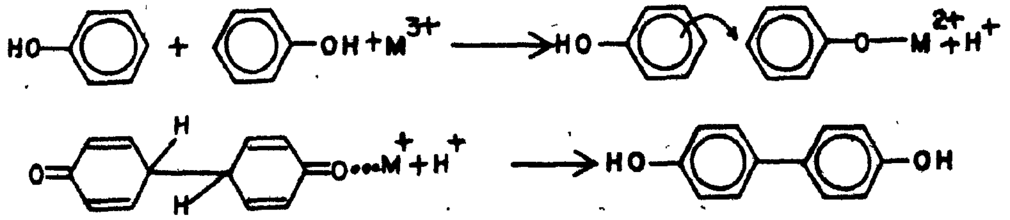
Another type of reaction which can be termed a homolytic aromatic substitution is depicted in (2).


(2)

The oxidation of phenoxy radicals to phenoxy cations followed by coupling with a phenolic moiety is representative of an ionic mechanism (3).


(3)

Non-radical pathways also rely on the intermediacy of phenoxy cations which can be produced by two electron oxidations of the phenol preceding an ionic reaction as in (3). Where the occurrence of a phenoxy cation is unreasonable on the basis of energetic requirements for the formation and stabilization of the intermediate, a concerted coupling and electron transfer mechanism can be devised (4).

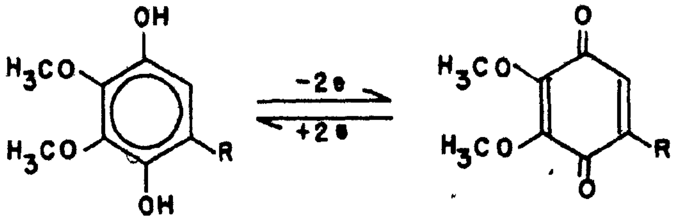

(4)

Such a diversity in mechanistic possibilities is responsible for the wide application received by phenol oxidation chemistry. Proper choice of the reaction conditions can often allow control over the course undertaken by the reactants.

Inhibition of autoxidation of lubricants and other organic compositions at moderately high temperatures is achieved through phenolic additives. The formation of stable aryloxy radicals terminates the free radical chains responsible for the degradation processes.

Development of catalytic systems capable of effecting a high yield coupling of various phenol monomers to poly(1,4-phenylene oxides) allowed the marketing of a whole new range of polymers.[2] Modification of these systems can induce exclusive formation of 4,4'-diphenoquinones. Hydrogenation to the corresponding biphenols completes the new synthetic route to these important bifunctional monomers for polyester and polyurethane synthesis.

The widespread occurrence of hydroxy-aromatic compounds throughout nature hints of the outstanding capability of a handful of enzymes having phenol-oxidase-like activity. These enzymes catalyze the elaboration of lignins, lignans, tannins and melanins, all products of oxidative polymerization.[3] Metabolism of aromatic compounds is accomplished by hydroxylation to mono or dihydric phenols, followed by oxidation to quinones and ring opening in later stages. In this way, many important metabolic regulators such as catecholamines, serotonin and tyrosine are synthesized and degraded.[4] The vitamins K as well as coenzyme Q seem to participate as electron carriers in terminal electron transport. Here again the hydroquinone-quinone equilibrium allows them to be elegantly included in the mitochondrial respiratory chains (5).[5]



(5)

In the field of phytochemistry intramolecular coupling of an appropriate phenolic intermediate can be used to generate at least ten percent of the 2000 known alkaloids.[6]

Phenol oxidation is easily accomplished by a multitude of reagents. For a particular substrate, product distribution is eminently dependent on the conditions and particularly the oxidant.[7] It is not the intent of the writer to review metal ion promoted oxidation of phenols since this has been done extensively in many recent reviews.[8] Rather the reader's attention is drawn to the outstanding ability of copper, and to a lesser extent iron, to catalyze oxidation of phenolic substrates. This particular focus finds its justification in a number of facts. Redox catalysis, be it of polymerization or telomerization, is everywhere dominated by the presence of copper.[9] Trace amounts of copper present as impurities can profoundly affect the product ratio or the course of a reaction.[10] Furthermore, the ubiquitous occurrence of copper and iron at the active sites in enzymes and oxygen carriers cannot be overstressed.[11] Nature, through evolution, has chosen these metals to be included from the very beginning in the most simple physiological processes through to the intricate systems of plant and animal metabolism.[12] Finally it is the object of the work presented here to obtain a better understanding of the participation of copper in phenol oxidation.

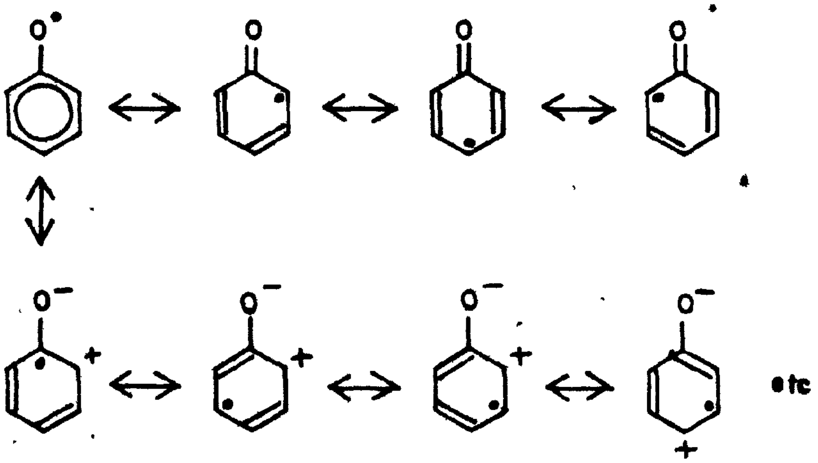
2. PHENOXY RADICALS

A. Development of the Field

The term phenoxy radical was coined by Pummerer fourteen years after Gomberg's controversial proposal of the triphenyl-methyl radical.[13] Soon afterwards, Hunter studying the decomposition of silver salts of trihalophenols, observed the appearance of transient blue colors. His interpretation of the process leading to the formation of polymer did not include the participation of radicals however.[14] In many instances at the turn of the century phenol chemistry seemed to afford compounds with peculiar properties, i.e., molecular weight, non-adherence to Beer's law and unusual reactivity remained difficult to explain. These anomalies were resolved by invoking the participation of phenoxy radicals in equilibria with dimeric products.[15] In the years to follow, phenol oxidation chemistry developed into a field of its own. The many monographs and reviews published in recent years serve to reflect the intense activity of numerous workers.[16] Although investigations concerning one electron oxidations and reductions involving metal ions still comprises a very extensive subject in a recent monograph, the production of aryloxy radicals and their reactions however no longer warranted inclusion in a separate chapter.[8c]

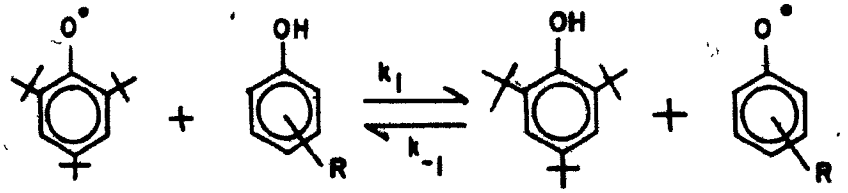
B. Reactivity of Phenoxy Radicals

The phenoxy radical itself is much more stable than its alkoxy counterpart. Delocalization of the unpaired electron to the o- and p-positions of the aromatic ring accounts for the increased stability.

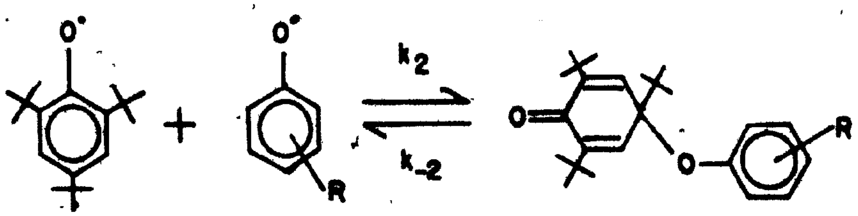


Coupling of these mesomeric radicals produces dimers which are formed through C-O, C-C but not O-O coupling. Formation of peroxides does not occur on account of their instability. C-O and C-C coupling occurs exclusively through the o- and p-positions although the unpaired electron density is non-zero at the C-1 and C-3 and C-5 positions. When the o- and p-positions are substituted by bulky groups there will be steric hinderance to dimerization. Consequently 2,4,6-trisubstituted radicals are much more stable than the phenoxy radical. The tri-t-butylphenoxyl radical is completely monomeric both in solution and in the solid state. The 2,4,6-triphenylphenoxyl radical likewise is completely disassociated in solution though it exists as its dimer in the solid state.[17] The greater tendency of the latter radical to exist as the dimer is attributed to the smaller steric requirements of the phenyl group thus allowing C-O coupling to occur in the p-position.

Much of what is presently known of the chemistry of phenoxy radicals stems from the independent discovery by Cook and Müller of the 2,4,6-tri-t-butylphenoxyl radical.[18] Reactions of the latter with a variety of simple substituted phenols affords products in good yields and are easily amenable to quantitative evaluation.[19] Spectrophotometric observation of the rate of disappearance of the blue 2,4,6-tributylphenoxy radical allowed the determination of the second order rate constants varying over a range of 10^4 demonstrating the high selectivity of this radical. The kinetic scheme consistent with the rate law is shown to be:



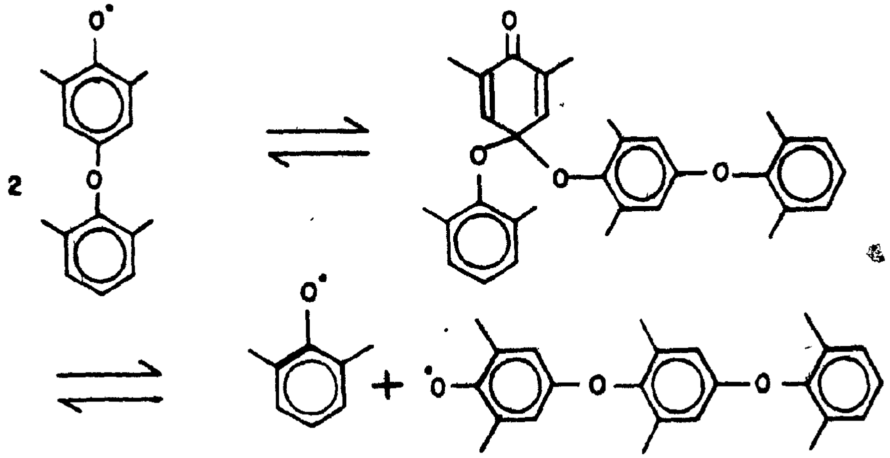
(6)



(7)

Hydrogen abstraction (6) is the rate determining step since a relatively large isotope effect was found ($k_H/k_D > 7.5$) and the wide variation in rates was attributed to the ability of the substituents to stabilize the radical intermediate.

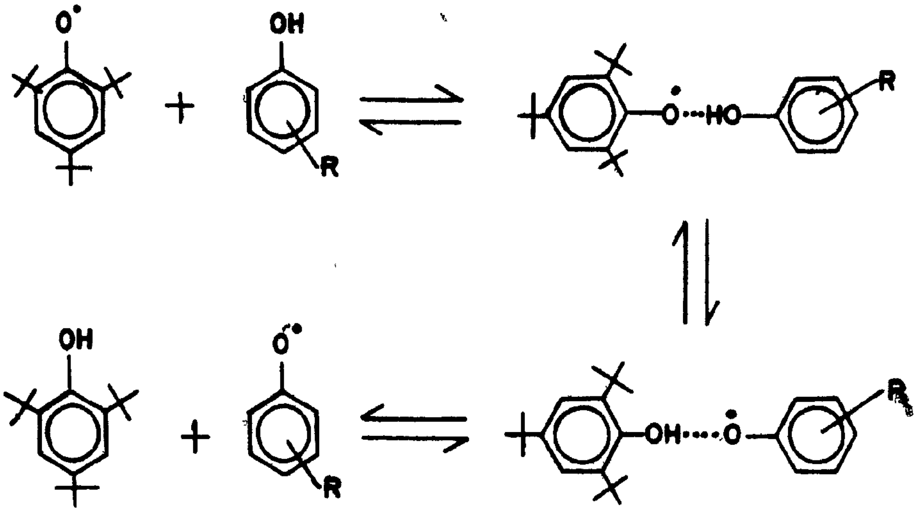
A thermochemical study of the same system allowed the estimation of the heats of formation of phenoxy radicals from the substituted phenols.[11] The results indicate that the enthalpy of the transfer reaction was dependent on the substituents and varied by about 8 kcal/mole. The equilibrium constant and the enthalpy for the reaction sequence (6-7) was also determined calorimetrically. Thus $k_1k_2/k_{-1}k_{-2}$ at 40° was $2.2 \pm 0.4 \times 10^8$ M^{-1} and the value for ΔH reaction was -20.3 ±0.5 kcal/mole and both are independent of substitution for m- and p-substituted phenols. The overall heats of reaction of o-dichloro and o-dimethylphenols are approximately equal but 5 kcal/mole less exothermic than the corresponding m- and p-substituted phenols. This difference is reportedly due to steric strain in the quinol ethers derived from di-ortho-substituted phenols. The presence of this strain energy has profound effects on the equilibrium position of reaction (7) resulting in extremely large values of k_{-2} for such quinol ethers. This observation has important bearing on the understanding of the fundamental polymerization process of phenoxy radicals, namely redistribution.[21] Xylenol and 2,6-dialkylphenol polymerization rests on the feasibility of the quinol ether formation-dissociation sequence (8):



(8)

Using different phenoxy radicals in presence of the 4-phenoxyphenoxy radical, redistribution was found to be markedly affected by the bulkiness of the ortho substituent on the monomeric phenoxy radical. When electron withdrawing substituents were present the process could be completely inoperative. For instance, 2,6-dichloro and 4-chlorophenols were not included in the polymer using a free radical initiated system.

Solvent effects in phenoxy radical chemistry are related mainly to their ability to form hydrogen bonds and subsequently to transfer hydrogen to the monomeric or polymeric radicals. When the absolute rate constants for hydrogen transfer of the tri-t-butylphenoxy radical with phenols in various solvent systems were determined, the data revealed that addition of acetonitrile or dioxane to the CCl_4 reference solvent led to decreased values of k_1 equal to 1/40th as large as those observed in pure CCl_4.[22] The relative magnitudes of these effects qualitatively parallel those which can be predicted from the ability of the added solvent to form hydrogen bonded complexes with phenols. Under these conditions the 2,4,6-tri-t-butylphenol radical must compete with the solvent in hydrogen bonding with the unhindered phenol to form the activated complex prior to the hydrogen atom transfer (9):



(9)

In a recent paper the values of the absolute rate and equilibrium constants for hydrogen transfer and termination of phenoxy radicals are summarized.[23] From these results the O-H bond dissociation energies for a large number of phenols are evaluated to be in the range 89.9 to 84.0±2.0 kcal/mole Following the activated complex theory, the higher transfer rates of phenols with the tri-t-butylphenoxy radical compared with similar rates of reaction of hydroperoxides and hydrocarbons are in line with the view that phenols are stronger hydrogen bonding acids towards oxy-radicals. The occurrence of a prior equilibrium hydrogen bonding step in the hydrogen transfer serves thus to explain the 6 to 10 fold lower rates observed for hydroperoxides. Larger rate differences, i.e., 10^4 to 10^5 are observed when the transfer reactions from O-H and C-H bonds are considered. In many instances such an equilibrium between reactants and a hydrogen bonded free radical activated complex has been invoked to explain the kinetic parameters of hydrogen transfer reactions.[24]

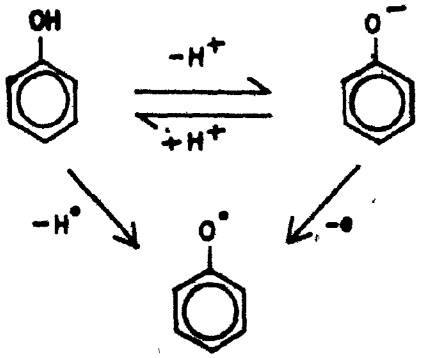
C. Reaction with Oxygen

Thus far the stability of phenoxyl radicals with respect to dimerization or cross coupling reactions in an inert atmosphere has been discussed. Significantly different orders of stability arise when the reaction with oxygen is considered. Thus, the 2,4,6-tri-t-butylphenoxy radical is decolorized in thirty minutes whereas eight hours are required to quench the 2,6-di-t-butyl-4-phenyl phenoxy radical.[25] 2,4,6-triphenylphenoxy radical solutions are completely stable to air.[17] These reactions lead to peroxides and generally occur by coupling through the 4-position with 2,4,6-trisubstituted radicals.

Phenoxy radicals bearing electron withdrawing substituents are believed to be more stable with respect to coupling with oxygen.[25] The fact that polymerizations of polyhalophenols can be effected in air has served to infer this. Unfavorable polar transition states in the reaction of phenoxy radicals with oxygen have also been invoked.[25] It would have been more elegant to explain this particular behavior of the reactivity of oxygen with phenoxy radicals by stressing the efficiency of the competing dimerization of two phenoxy radicals.

D. Preparative Methods

Formation of detectable amounts of phenoxy radicals can be achieved by various physical methods such as irradiation and photolysis.[27] For preparative purposes however, only chemical methods are suitable. In this case the process will require either homolytic cleavage of the O-H bond of the phenol or loss of an electron from the corresponding anion (10):

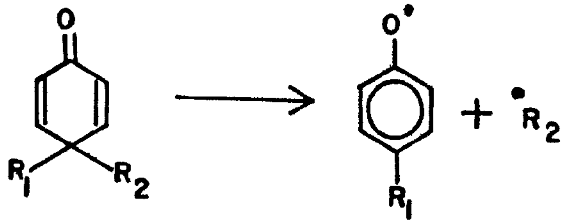


(10)

Perusal of the excellent tabulation presented by Musso[28] will allow an adequate choice of one electron oxidants and conditions for the oxidation of a particular substrate. However when high yields of dimeric or polymeric coupled products are required only a handful of reagents need to be considered.

Outstanding in this respect by its effectiveness is hexacyanoferrate(III) in alkaline solution. Use of a two-phase system consisting of the aqueous alkaline layer with an organic phase in which the products of oxidation are removed prevents their future oxidation. Heterogeneous systems consisting of a metal oxide (MnO_2, PbO_2, HgO, Ag_2O) in a polar or non-polar solvent, have also been applied with success.

Various methods based on dissociation of related cyclohexadienones can also be of use in some cases (11).[29] When one or two of the R substituents are phenoxy, then the process would generate two aryloxy radicals. If one or both of



(11)

the substituents are halogens, particularly bromine, the dissociation can be brought about by mercury.

Systems containing copper and an amine in presence of oxygen deserve separate treatment because of their more wide spread use as catalysts in the oxidative coupling polymerization of alkylphenols. Furthermore many oxidations of mono and dihydric phenols carried out under copper catalysis have been postulated as simple models for biological oxidation processes. These copper based systems, in contrast to the other reagents operating in a stoichiometric fashion, are remarkable for their catalytic properties.

E. Characterization of Phenoxy Radicals

Spectrophotometric characterization of aryloxy radicals has been useful for obtaining structural information. Good summaries of this data appear in various reviews.[30] The paramagnetism of tri-t-butylphenoxyl was confirmed by a Gouy determination of its susceptibility.[31]

Esr spectroscopy has given particularly useful information regarding the detailed structures of the aryloxy radicals and the mechanisms of phenol oxidation involving transient intermediates. The measured g-values for such radicals as the 2,4,6-tri-t-butylphenoxyl radical are close to that for the free electron ($g = 2.0023$)[32] Analysis of the hyper fine interactions in the various ^{17}O, ^{2}H and ^{13}C labelled radicals indicates that all the carbons in the ring as well as the oxygen show a spin density for the unpaired electron. The spin density is relatively higher on the oxygen and on the para-carbon. Unpaired electron density is low but nonzero on the C-1, C-3 and C-5 positions of the ring. This distribution of the spin density is in agreement with the chemical reactivity of phenoxyl radicals in that they undergo coupling reactions only at the ortho- and para-positions, the latter predominating.

F. Stable Aryloxy Radicals Used as Trapping Agents

The stability of these hindered radicals towards self-reaction or transfer to solvent has long been used for trapping transient alkyl, alkoxy or phenoxy radicals.[23,33] For this reason they are included in anti-oxidant formulations.

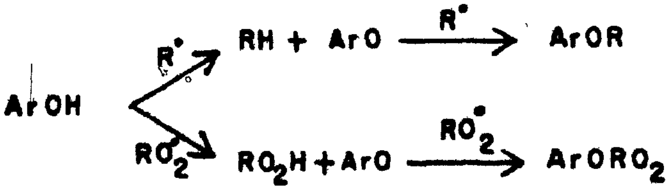
The term autoxidation applies to those spontaneous oxidations which take place with oxygen or air at moderate temperatures. The process follows a free radical induced chain mechanism for hydrocarbons (12-14):

$$R{-}H \xrightarrow{[I]} R^{\bullet} + H^{\bullet} \qquad (12)$$

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \qquad (13)$$

$$RO_2^{\bullet} + R{-}H \longrightarrow RO_2H + R^{\bullet} \qquad (14)$$

Inhibition of the free radical chain is achieved by reaction of the antioxidant phenols with the alkyl or alkylperoxy radicals to produce stable phenoxy radicals which can further trap other radical species (15,16):[34]



(15)

(16)

Reports on the interaction of simple aliphatic radicals with stable aroxyl radicals are rather scarce. Kinetic evidence tends to indicate however that tri-t-butylphenoxy radicals are efficient scavengers of radicals derived from benzoyl peroxide.[35] Similarly effective inhibition of polymerization of styrene or acrylonitrile has been accomplished.[35] The addition of a stable aryloxy radical to a reaction mixture undergoing a free radical process should thus afford a product mixture reflecting the free radical composition at that time.

3. THE RELEVANCE OF COPPER

A. Introduction

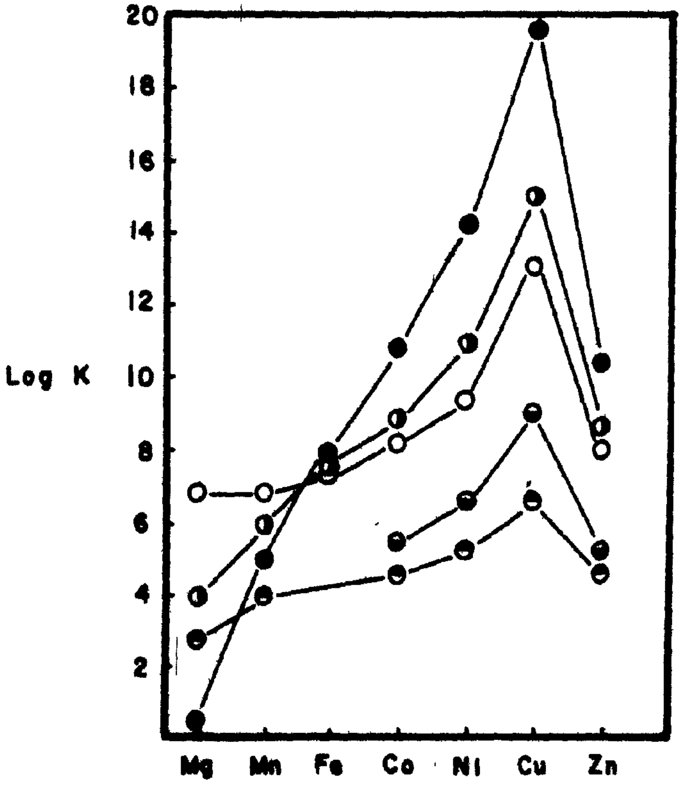
More than any other transition metals, copper and iron have found their way through the evolutionary drive into a whole array of biological systems. The reason for their prevalence is no doubt related to their superior complexing properties and their ability to undergo one-electron redox reactions at various redox potentials depending upon the ligand environment in which they exist.

Versatility in catalyzing redox reactions set copper and iron in the forefront at the time oxygen was accumulating in the atmosphere.[12] Copper however may have been quite scarce in the early aquatic environment as can be seen from the abundance scale.[37] The reason why

$$\mathrm{O > Si > Al > Fe > Ca > Na > K}$$
$$\mathrm{> Mg > Mn > V > Ni > Cu > Zn > Co}$$

uniquely useful copper proteins became available is most likely found in the superior chelating power of copper with oxygen, nitrogen and sulfur donor atoms of biological interest. This fact is clearly evidenced in Figure II.

FIGURE I.1 Logarithms of the stability constants of complexes between some M^{2+} ions and various bidentate ligands: ● ethylene diamine; ◐ glycinate; ○ salicylaldehyde; ⊖ salicylaldehyde-5-sulfonate; ◒ oxalate. Reproduced from 38.


Log K
20
18
16
14
12
10
8
6
4
2
Mg
Mn
Fe
Co
Ni
Cu
Zn

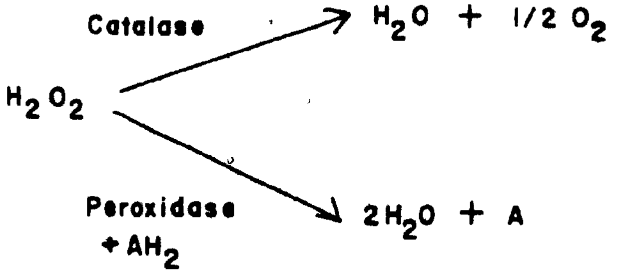
It can be seen that a fairly consistent pattern is followed by chelates of Mg(II) through to Zn(II) with the same bidentate ligands. The stability of chelates of the first transition series culminates with complexes of copper(II) then falls abruptly again in the case of zinc(II). The existence of such a series has become apparent from large amounts of data and can be explained by ligand field theory.

In order to use these ions efficiently and achieve an exquisite balance of physical and chemical properties, the first polymer-supported catalysts namely metalloproteins were evolved. These metal bearing macromolecules utilize most efficiently copper and iron as electron and oxygen carriers for oxygenation, hydroxylation, and other crucial metabolic reactions, including protection against deleterious oxygen by-products.

A number of copper proteins found in plant and animal systems possess an apparently unique enzymic superoxide dismutase activity.[39] The reaction catalyzed is dismutation of superoxide ion to molecular oxygen and hydrogen peroxide (17).

$$2H^{+} + 2O_2^{-} \xrightarrow[\text{Superoxide Dismutase}]{} H_2O_2 + O_2 \qquad (17)$$

The reactive superoxide ion is thus conveniently disposed of. The superoxide dismutase system is itself backed up by heme (iron protoporphyrin) enzymes that decompose hydrogen peroxide either to oxygen and water, as with catalase, or, with the aid of a hydrogen donor molecule to water and a dehydrogenated product as with peroxidases (18):

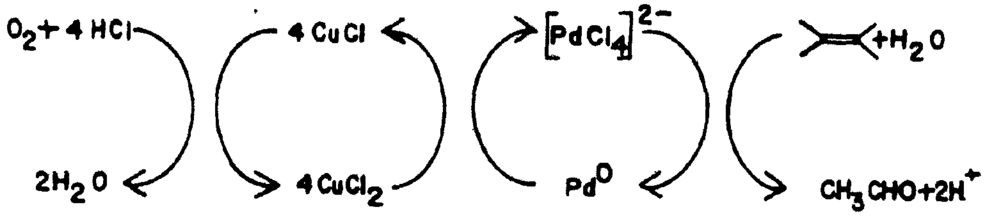


(18)

B. The Role of Metal Ions in the Autoxidation of Organic Substrates

Metal ions have many modes of action under oxidative conditions with organic substrates. Frequently the metal ion accelerates one or several of the steps in an autoxidation process; it may be the actual oxidant and in a later stage be reoxidized by oxygen.

The participation of metal ions may be required to generate a suitable catalytic species such as in the Wacker process. The latter case is exemplified by the oxidation of ethylene to acetaldehyde by tetrachloropalladate(II).[40] The process is rendered catalytic by use of copper(II) salts. Initial coordination of the olefin to palladium is followed by its oxidation to acetaldehyde and concomittant liberation of palladium metal. The complete catalytic chain is illustrated in scheme I where the copper system functions solely to regenerate the palladium(II) species and is not involved in the oxidation of the organic substrate.



SCHEME I

The autoxidation of organic compounds has already been briefly mentioned (Section 2, F). The radical chain carrying hydroperoxides are eminently susceptible to metal ion catalyzed decompositions. This intervention occurs following two different paths (19,20) according to the oxidation state of the metal ion.[41] The effect of added metal salts

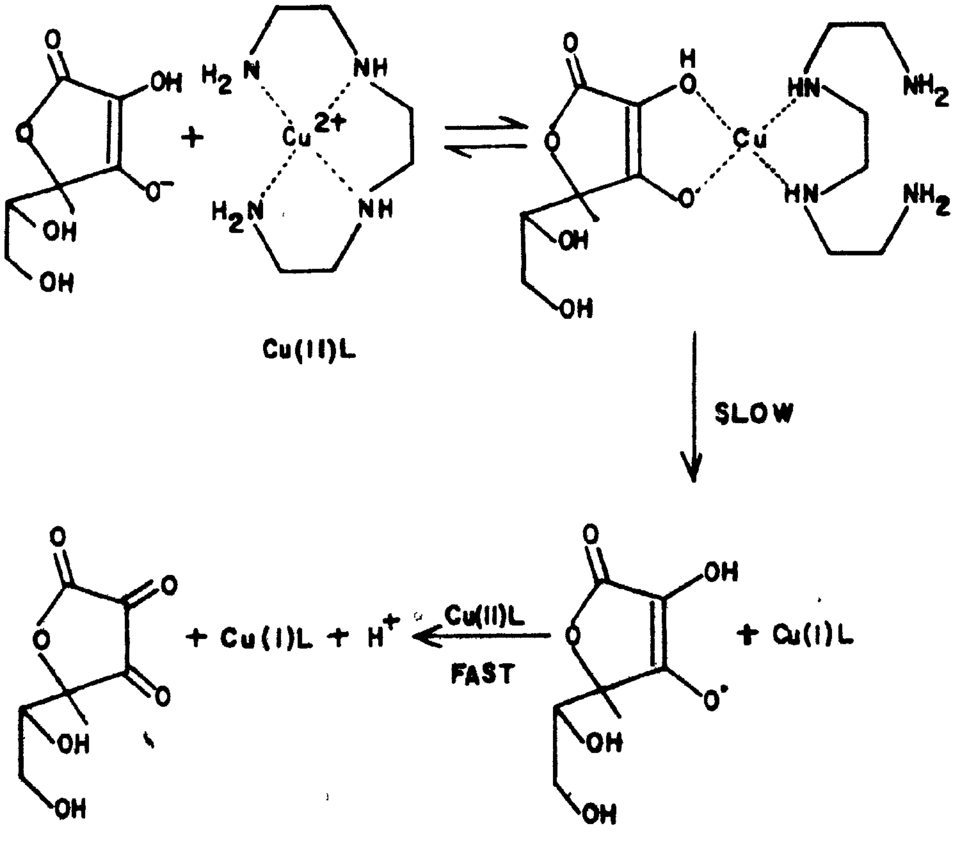
$$ROOH + M^{n+} \longrightarrow (HOM)^{n+} + {}^{\bullet}OR \qquad (19)$$

$$ROOH + M^{(n+1)+} \longrightarrow ROO^{\bullet} + M^{n+} + H^{+} \qquad (20)$$

is thus to initiate further radical chains, thereby increasing the overall rate of autoxidation. Use of larger quantities can however, in some cases inhibit peroxy radical transfer (21).

$$ROO^{\bullet} + M^{n+} \longrightarrow ROO^{-} + M^{(n+1)+} \qquad (21)$$

There is a large number of catalytic processes in which the substrate is coordinated to a readily reduced metal ion capable of oxidizing it to a radical. Subsequent reactions of this radical then lead to the products. The success of these reactions rests on the fact that the metal catalyst can easily oxidize the substrate by complex formation and further be reoxidized by atmospheric oxygen. The copper(II) chelate catalyzed autoxidation of ascorbic acid is an example of this general type (22-24).[42] The rate determining step



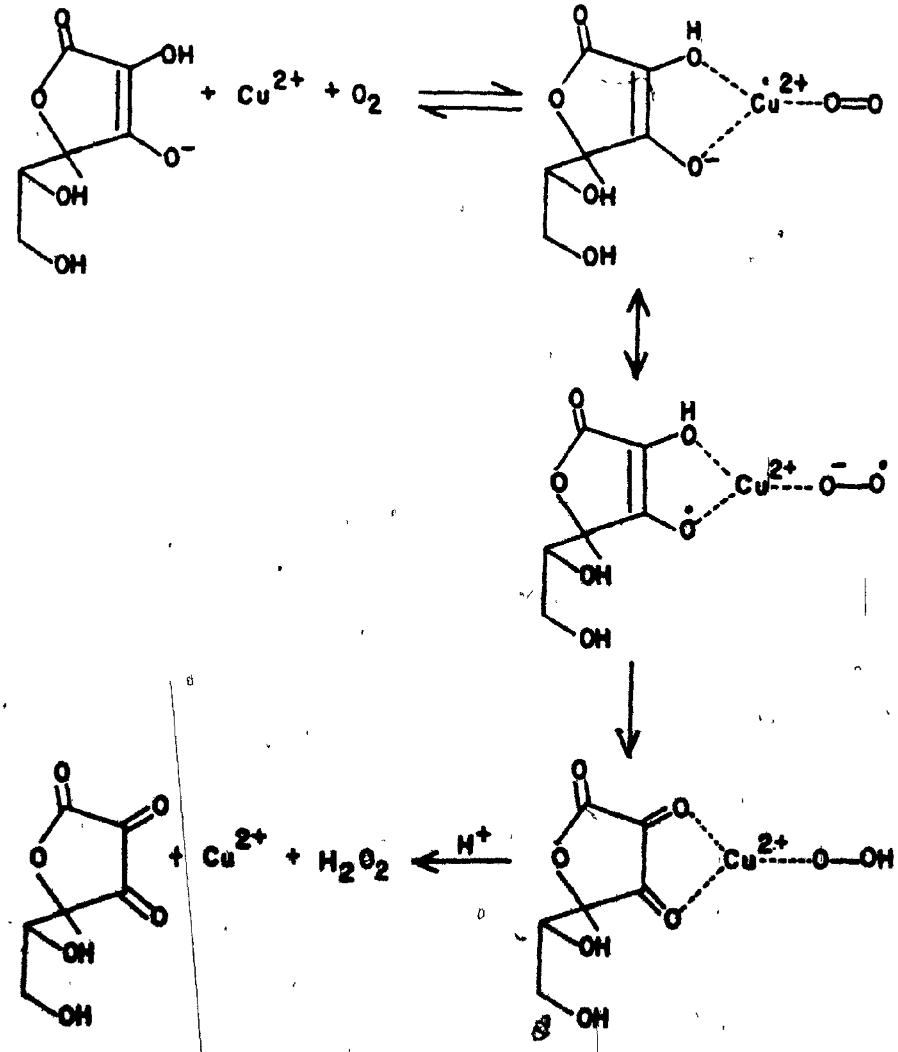
(22)

(23)

$$4\,Cu(I)L + O_2 + 4H^+ \longrightarrow 4\,Cu(II)L + 2\,H_2O \qquad (24)$$

appears to be the reduction of copper(II) to copper(I) and the formation of a semiquinone-like radical involving a single electron transfer. Rapid reoxidation of the copper(I) chelate by oxygen in the solution makes possible a relatively fast second electron transfer step to produce dehydroascorbic acid (24).[42]

The uncomplexed copper(II) ion catalyzed reaction surprizingly proceeds at an increased rate; 33.8×10^{1} M^{-1} sec^{-1} at pH 2.00 and 25° C compared to 0.09×10^{1} M^{-1} sec^{-1} for the chelate system under similar conditions.[43] In this case a more facile ionic pathway is thought to occur. The reaction was found to be first order with respect to ascorbate anion, copper(II) ion catalyst, oxygen concentration, and the reciprocal of the hydrogen ion concentration.[43] The mechanism under these circumstances is believed to take the following course (25,26).



(25)

(26)

The essential difference between (22-24) and (25-26) is that both oxidizing equivalents are delivered by two Cu^{2+} in the former, but in the latter the copper mediates transfer of two electrons from substrate to O_2 in a ternary complex.

The enzyme ascorbic acid oxidase, however, seems to function by a radical mechanism similar to that illustrated in Equations (22-24). Oxygen is reduced to water and dehydroascorbic acid is obtained via two successive one-electron transfers, with intermediate formation of a free radical, which has been detected by esr.[44] Such a mechanism, proceeding through an intermediate radical, would not be expected to occur without resonance stabilization to the extent possible in the ascorbate radical.

When the available coordination sites of the metal ion are blocked by coordination with a chelating ligand, it is difficult to form a complex containing both oxygen and the substrate. Ternary complexes containing both substrate and activating agent have been frequently invoked to explain biological reactions occurring at the active site of metalloenzymes in recent years.[45,46] Ternary complexes are actually thermodynamically favored by a cooperative stabilization of the complex by the mixed ligands.[45] The first coordinated ligand will influence the type of ligand which may be coordinated at a further stage. This is an important aspect of metalloenzyme chemistry since the active site has to discriminate amongst the substrates available in the *in vivo* environment. The right enzyme has to coordinate the right substrate and ternary complexes achieve this high catalytic specificity. Furthermore the formation of a mixed ligand complex may be required in order to promote a reaction which is otherwise thermodynamically unfavorable. Such is the case in the oxidation via electron transfer of numerous metabolites. Phenols for example possess potentials at biological pH in the range of the oxygen potential and could thus not be oxidized *in vivo* by normal electron transfer without the risk of oxygen evolution. Indeed, recent investigations have demonstrated that indoleacetic acid is not oxidized by peroxidase as such.[46]. Rather the initiation of oxidative degradation requires the presence of oxygen, indoleacetic acid and enzyme in a ternary complex.

The kinetics of the oxidative polymerization of 2,6-xylenol with copper-amine complexes are also dominated by the involvement of ternary complex intermediates. Price[47] found that the rate of oxygen consumption is independent of xylenol concentration and yet depends on the structure of the phenol for xylenol analogues. This suggests that the rate controlling step for oxygen consumption and thus for oxidative coupling, is the reaction of oxygen with a copper-phenol complex.[47] Another kinetic investigation showed that the reaction exhibits Michaelis-Menten behavior and it was concluded that oxygen not only functions to recycle the catalyst, but promotes the catalytic action of the copper complex by being coordinated to the intermediate catalytic species.[48]

C. Phenol Oxidation by Metal Ions

Oxidation potentials of phenols have been estimated in various ways. These measurements are for the most part concerned with irreversible systems on account of the further fast reactions of the initially formed aryloxy radicals.[49] These values are thus not true thermodynamic redox potentials. However, it is claimed that halfwave potentials for irreversible phenol oxidations can be compared.[50] Within the frame of a same measuring system, the relative order adopted by the oxidation potentials reflects the more or less facile oxidation of the phenol (Table 1).

A large number of transition metal compounds have the necessary redox potential to effect the oxidation of phenols. Ferricyanide and ferriin (tris[1,10-phenanthroline]iron (III)), two substitutionally inert complexes represent typical one electron oxidants. They oxidize readily a number of organic compounds including phenols.[7,51] Numerous other high-valent metal complexes have been found to oxidize phenols by one or two electron transfer to radicals or phenoxonium cations.[8] None of these systems is suitable for maintaining a catalytic cycle by reoxidation of the lower valent ion by oxygen.

Although the redox potential of the O_2/H_2O system is

TABLE I.1

PHENOL OXIDATION POTENTIALS

Substituent	E (mV)			
none	1004[a]	920[b]		
4-NO$_2$	924[a]			
3-NO$_2$	855[a]			
2-NO$_2$	846[a]			
2,6-Me	760[b]			
2-Cl,4-Br	670[c]			
2,4-Cl	660[c]			
4-Cl	653[a]			
3-Cl	734[a]			
2-Cl	625[a]			
4-Me	543[a]	840[b]		
3-Me	607[a]	890[b]		
2-Me	556[a]	850[b]		
2,4,6-Ph	327[d]	211[e]		
2,4,6-(pOMe Ph)	244[d]	124[e]		
2,4,6-t-but	72[d]	-59[e]	690[b]	1024[f]

[a] J.C. Suatoni, R.E. Snyder, R.O. Clark, Anal. Chem., 33, 1894 (1961).

[b] G.E. Penketh, J. Appl. Chem., 7, 512 (1957).

[c] H.N. Simpson, C.K. Hancock, E.A. Meyers, J. Org. Chem., 30, 2678 (1965).

[d] Ref. 50.

[e] F.W. Stuber, K. Dimroth, Chem. Ber., 99, 258 (1966).

[f] B. Nickel, H. Mauser, M. Hezel, Z. Phys. Chemie Neue Folge, 54, 196 (1967).

very positive (+0.82 V at pH 7.0), oxygen in many cases is rather sluggish in effecting the reoxidation of the metal complex and thus maintaining a catalytic cycle. This is thought to be due to either the barrier in the electron receiving process of oxygen or the fairly low redox potential of the first reduction of oxygen (27,28).[52]

$$O_2 + H^+ + \bullet \rightleftharpoons HO_2^{\bullet} \qquad -0.32\text{ V at pH 1} \tag{27}$$

$$O_2 + \bullet \rightleftharpoons O_2^{\overset{\bullet}{-}} \qquad -0.45\text{ V at pH 7} \tag{28}$$

The problem of how O_2 is involved in such catalytic systems is of tremendous import to the field of biological oxygen activation but is not within the scope of the present outline. The chemical basis of this process has been well treated.[53] Let it suffice to say that the reduction of oxygen in model complexes is often associated with dinuclear centers capable of effecting a simultaneous two electron reduction or via the intermediacy of a ternary complex. The latter species would presumably stabilize a superoxide anion radical resulting from the otherwise unfavorable one electron reduction of oxygen.[54]

Complexes of copper are exceptional in that they undergo repeated oxidation reduction cycles in a chemically reversible way. The rapid generation of copper(II) by the facile oxidation of copper(I) with oxygen is observed in aqueous and organic media. The stoichiometry, kinetics and effect of ligands on this system have been examined.[55] Hexaaquoiron(II), on the other hand is only slowly oxidized[56] and hexacyanoferrate(II) is hardly oxidized at all. Many factors are involved in the reoxidation of catalysts by oxygen, spin conservation during the electron transfer and stabilization of the higher oxidation state appear to be the two dominating.[53]

Copper and iron containing enzymes possess the delicate balance of properties required to exhibit oxygen promoted regeneration of the high valent state. It has been suggested that one of the factors involved is a compromise in the geometries of both oxidation states.[57] The site of copper coordination would thus be intermediate between tetragonal and tetrahedral. In the case of iron, octahedral coordination is preferred by both oxidation states. The question of entasis, however, remains speculative even in the light of a recent demonstration that a tetrahedral environment about the copper ion facilitates the redox cycle.[58] The tetrahedral complex $[Cu^{II}(W_{12}O_{40})]^{6-}$ can be reduced to the corresponding copper(I) species. Aerial oxidation of the dark red solution of the copper(I) complex can be achieved. The redox process results only in small changes in the stereochemistry about the copper and no dissociation of the multidentate ligand occurs.[58]

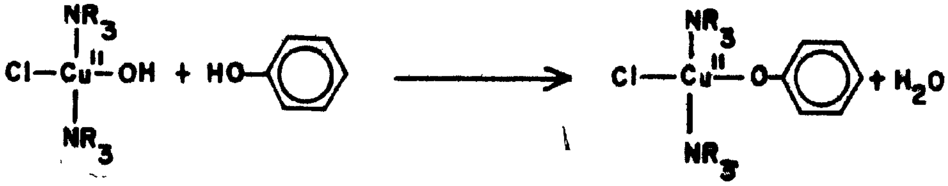
In the case of substrate oxidation, the question of precoordination at the metal center is one that is frequently difficult to answer. Coordination of the substrate manifests itself in the selectivity of the reaction. For example, in the oxidation of phenols, the regioselectivity exhibited by differing catalyst systems suggests that in some cases at least the reaction pathway is influenced by coordination. Oxidative coupling of 2,6-dimethylphenol may lead almost exclusively to carbon-oxygen or carbon-carbon coupled products depending on the nature of the ligands available in a copper catalyzed reaction.

Oxidations of xylenol promoted by reagents known to function via non-bonded electron transfer mechanisms, invariably afford a mixture of products. Oxidants with exchange-inert ligands, for example $[\mathrm{IrCl}_6]^{2-}$ and $[\mathrm{Fe(CN)}]_6^{3-}$,[7,59] undergo an initial bimolecular reaction with the phenol at a rate that approaches diffusion control. This is consistent with an extremely rapid outer-sphere mechanism and accordingly affords radicals that react with limited selectivity.

Early proposals for the oxidative polymerization mechanism of 2,6-xylenol were of the non-bonded type, i.e., polymer buildup was explained entirely by coupling of free radicals.[60,61]

Price first stressed the role of bonded phenoxy radicals in directing the mode of coupling during the oxidation of xylenol.[47] On the basis of observations made by Finkbeiner _et al._[62] and Hay,[63] that increases in the concentration of basic ligands promoted C-O coupling rather than C-C coupling, he proposed that "free" radicals are produced from highly coordinated catalysts and participate in the quinol-ether coupling mechanism to produce polymer through C-O coupling. The catalyst containing fewer coordinated basic ligands may not so readily release a "free" aryloxy radical. By remaining coordinated to copper(I) at oxygen, it will presumably undergo C-C coupling to give a diphenoquinone.

More recent discussions of data pertaining to this polymerization system tend to favor a mechanism whereby "free" phenoxy radicals generated in solution couple predominantly tail to tail.[64,65] This is reasonable in view of the esr evidence indicating high electron density in the para-position of phenoxyl radicals.[32] Initially the copper catalyst is visualized as coordinating the phenol monomer.[64] The phenoxide ion directly coordinated to copper then undergoes an electron transfer from oxygen to copper, to give a phenoxy radical, which remains coordinated to copper and then presumably undergoes carbon-oxygen coupling as shown (29,30). Further supporting evidence for this hypothesis comes from the observation that an increase in size of the ligand amine used in the oxidation of 2,6-dimethylphenol yields more carbon-carbon coupled products as well as decreasing the rate of polymerization.[60] Results presented in the present study, pertaining to the decomposition of halophenolatocopper(II) complexes tend to agree with a scheme affording polymer through attack at coordinated phenoxy moieties.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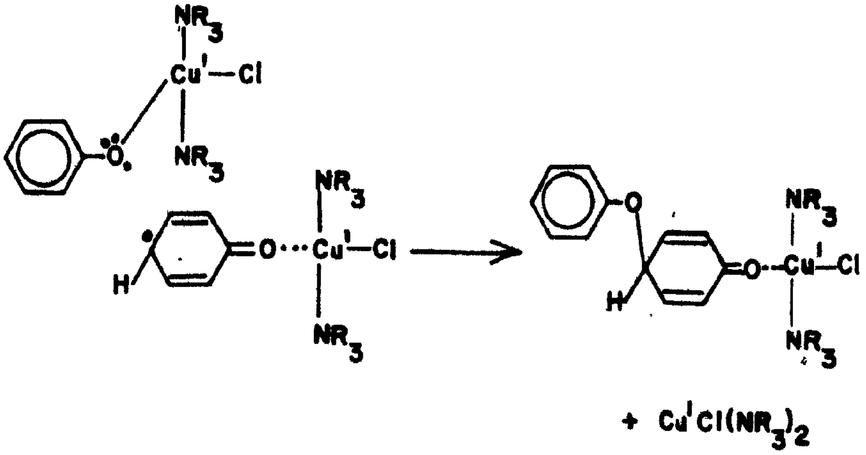

(30)

D. Present State of the Art in Copper Promoted Polymerization of Polyhalogenated Phenols

Synthesis of high molecular weight linear poly(halophenylene oxides) has been a long sought after goal. Historically Hunter prepared the first poly(halophenoxide) by decomposition of the corresponding silver salts in the presence of an oxidizing agent such as iodine and alkyl iodides.[66] Subsequently these polymers were shown to have a molecular weight in the range 2000-8000 and had rather low intrinsic viscosities compared to linear polymers of similar molecular weight.[67]

Patents claiming the preparation of linear poly(2,6-

dichloro-1,4-phenylene oxide) by peroxide initiated coupling of 2,6-dichloro-4-bromophenol have been issued. Poor characterization of these polymers lends doubt to claims of linearity.[68,69]

Polymers obtained from 2,4,6-trihalophenols are generally not exclusively 1,4-coupled. A recent investigation of the copper(II) promoted oxidative coupling of 2,4,6-tribromophenol concludes that the polymer is not linear.[70] The polymer prepared by Tsuruya has most likely a very low degree of polymerization considering its low intrinsic viscosity and the fact that the published nmr spectrum contains a broad peak attributed to the terminal OH. Examination of the phenyl region of the proton spectrum further eliminates the possibility of linearity since at least three peaks are prominent.

Oxidation of 2,4,6-trichlorophenol with MnO_2 or AgO or of its sodium salt in presence of iodine, affords polymers of modest molecular weight in the range 800-8000.[71] Although no characterization or discussion of the polymer structure was undertaken by these authors, it was believed to be linear.

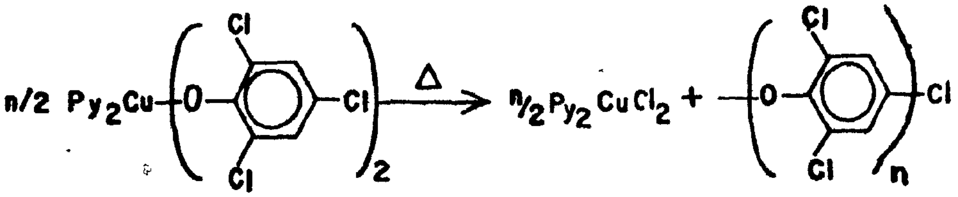
The original copper based catalytic systems for oxidative coupling of phenols have been to date the most successful. Polymerization has also been achieved, although with limited results, with compounds of cobalt, manganese and nickel, with alumina and with metal oxides.[72,77]

The oxidative coupling of phenols with copper(I) chloride based catalysts is very complicated. Although the overall mechanism is still not completely understood, the essential feature of the catalytic process is the copper(I)-copper(II) redox cycle. The copper(II) catalytic species oxidizes the phenolic monomers and oligomers, then is subsequently regenerated with oxygen. Detailed mechanisms including the role of oxygen in the copper system have been proposed.[47,67]

Using the copper(I)-amine-oxygen system, 4-halo substituted phenols are polymerized in a non-catalytic fashion. The polymers obtained starting with 4-bromo-2,6-dimethylphenol are identical with those prepared from 2,6-dimethylphenol itself.[67] The amount of oxygen absorbed is equivalent to the amount of copper present at which point the reaction stops. The copper(I) regenerated by oxidation of the phenols further abstracts halide from the quinol ether intermediate affording a copper(II) halo complex incapable of oxidizing the phenol.[67] Similarly polyhalophenols can be polymerized in a stoichiometric fashion in presence of an equivalent of a copper-pyridine complex. Presumably, it was proposed, this occurs by the intermediacy of bis(pyridine)bis(halophenoxo) copper(II) complexes. Such complexes have been prepared and thermally decomposed to polymer.[67]

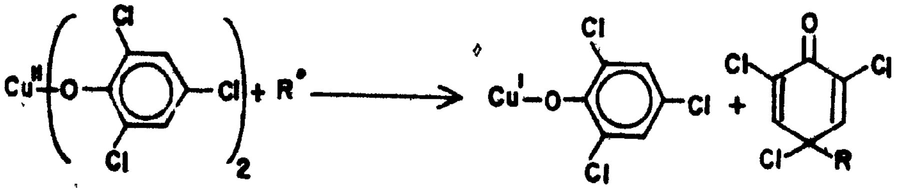
Most polymers obtained from the decomposition of the copper(II) phenolate complexes under a wide range of conditions were of modest molecular weight, the highest attained being 11,000.[67] Intrinsic viscosities were also low and attributed to branching of the polymers without further investigation. The belief, adopted rather blindly, that most polymers obtained from polyhalogenated phenols are branched has occasioned some disinterest in this type of polyether. However providing they could be obtained as linear polymers of high molecular weight, halogenated poly(phenylene oxides) have the potential for outstanding mechanical, chemical, electrical and thermal properties in addition to being extremely fire resistant.[78]

The mechanism of decomposition of bis(pyridine)bis(2, 4,6-trichlorophenoxo) copper(II) was investigated in this laboratory and it has been recognized that the stoichiometry proposed (31) for the reaction is rather simplified.[79] Indeed the polymers, in addition to being of finite molecular weight, were assumed to be branched, not uniquely 1,4-coupled.[80] The chemical equation is only a first approximation of the actual reactants and products involved in the thermal decomposition. This is particularly evident when the reaction is carried out in solvents capable of facile autoxidation. The occurrence of hydroperoxides in this case is conducive to a lowering of molecular weight and the appearance of novel μ_4-oxo-hexahalotetracopper(II) complexes.[79]



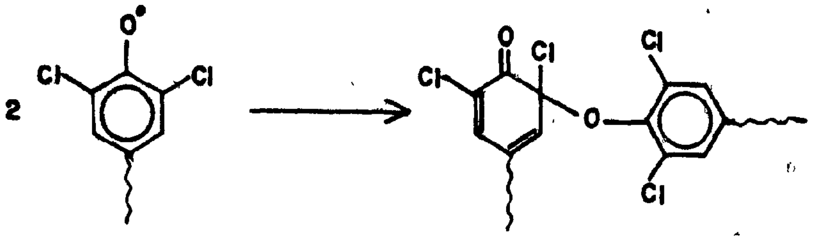
(31)

Experimental examination of the initial stages of the reaction indicated the presence of an induction period.[81] Samples prepared with careful exclusion of air did not decompose, suggesting that the initiation did not occur spontaneously by homolysis of the Cu-O bond as was earlier proposed.[67] Rather it became evident that initiation was induced by oxygen and other free radical initiators. The initial step thus consists of a rapid radical attack on the copper(II) complex producing non-radical products,[81] as shown in Equation (32). The initiating radical may be either oxygen or a radical initiator fragment. A number of direct and circumstantial facts agree with such an initiation process: cyclohexadienones are common products of phenol chemistry in the presence of free radicals;[82] free radical initiators greatly reduce the induction period;[81] no phenoxy radicals are evident in the solution until complete disappearance of the copper(II) complex as shown by esr.[81]



(32)

One important piece of experimental evidence which seemingly contradicts reaction (32) as the main propagation and initiation reaction is the failure to observe any variation of branching with conversion. If all radicals are rapidly trapped by copper(II) phenoxide, as suggested, there should be very little branching in the early stages of the reaction. Branching due to coupling of polymeric radicals as shown in (33), should only occur in the late stages of reaction as the



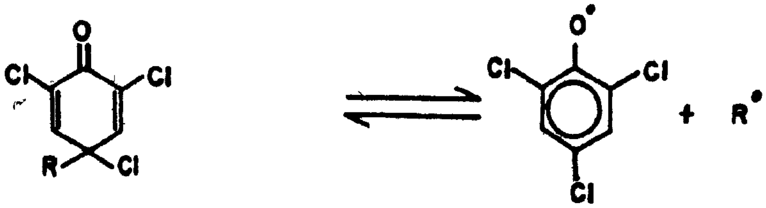
(33)

concentration of radicals begins to build up due to homolysis of quinol ethers and the depletion of copper(II) phenoxide. In fact no significant variation in branching as indicated by the pmr spectra of the polymers was detected over the whole range of molecular weights studied.

The low intrinsic viscosities of polymers obtained by dehalogenation of trihalophenoxides have long been associated with highly branched materials. In addition the ^1H nmr spectra of these polymers present a complex pattern of broad unresolved peaks[80] presumably resulting from restricted segmental motions in the branch units. One of the goals of the work presented here is a reevaluation of the actual polymerization mechanism. As it stands presently, the scheme presents the paradox of a reaction offering possible selectivity but leading to a product apparently devoid of regularity.

Another remarkable feature of the polymerization system using bis(trihalophenoxo)copper(II) complexes is the effect of carbon tetrahalide additives. Traces of carbon tetrachloride or of carbon tetrabromide greatly reduce the induction period without affecting the polymer molecular weight.[81] Halide from these promoters is however found associated with the final copper product. The mode of action has been discussed in detail and the fact that the copper product picks up halide from CX_4 clearly indicates that the interaction occurs primarily at the metal and does not interfere with the propagation.

The autoacceleration observed in the reaction must reflect an accelerating production of radicals, thus precipitating the disappearance of the copper(II)phenoxide starting complex via reaction (32). In absence of carbon tetrahalides, two reactions are conducive to an increase in the free radical concentration. Firstly it is known that quinol ethers as well as a number of other cyclohexadienone derivatives are thermally unstable towards dissociation to radicals (34, 35).[82] Secondly, radical regeneration can occur by halogen



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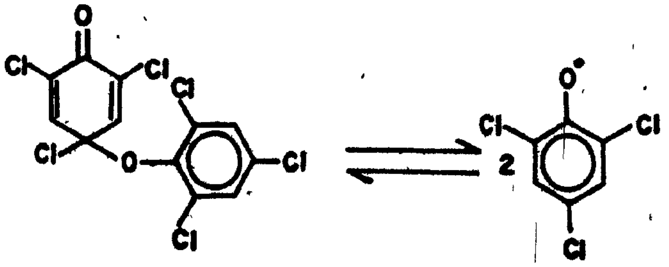
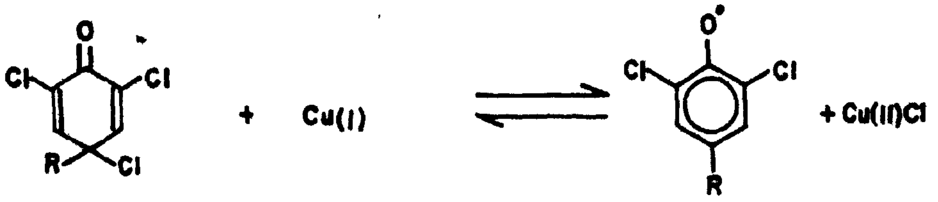


(35)

transfer from the cyclohexadienone or the quinol ether to the copper(II) species present (36,37). Reactions (34,35)



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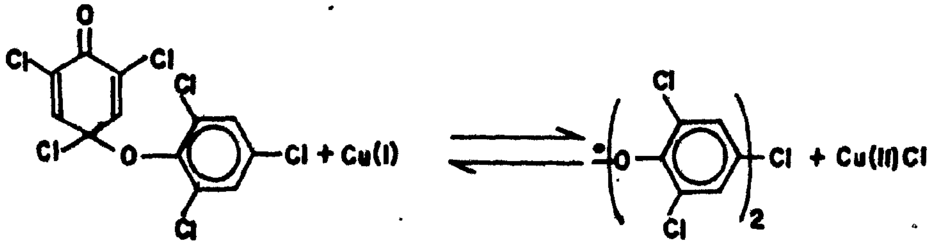
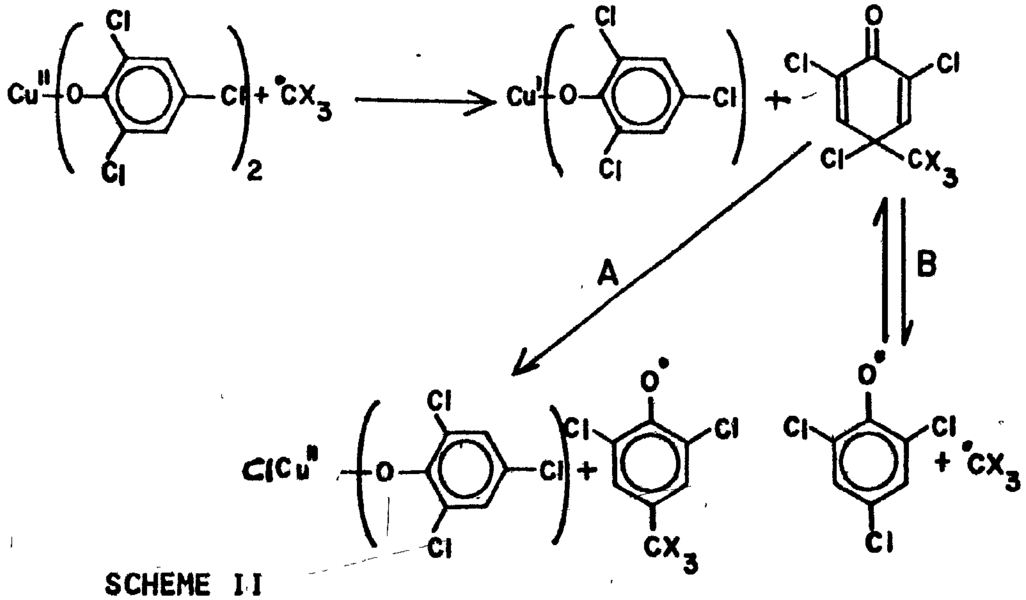


(37)

obviously provide an excellent radical chain branching process, doubling the available radicals for initiation and propagation.

In the presence of carbontetrahalides, there is competition between the cyclohexadienones and the additive to transfer halide to copper(I).[81] Using CBr_4 the amount of product Py_2CuBr_2 present following work up indicated a preference of copper(I) for the intermediate cyclohexadienones and not for the promoter. However the CBr_3 radicals that are produced seem to be very efficient in competing with copper(I) for halide abstraction from the 4-chlorocyclohexadienones. This conclusion stems from the fact that a substantial amount of $ClCBr_3$ is found in the product mixture and that there is no effect of the additive on the molecular weight of the polymer. Only traces of $HCBr_3$ and no C_2Br_6 were detected further indicating that chlorine abstraction is the ultimate fate of most of the $\cdot CBr_3$ radicals. It is thus at this stage that the effect of added carbon tetrahalides seems to be felt in rapidly producing large concentrations of phenoxy radicals capable of interaction with the starting complex. It could be argued that the trihalomethane radical itself could undergo phenoxo ligand transfer to produce the corresponding cyclohexadienone: Scheme II. If such were the case the trihalomethyl cyclohexadienone would undergo reaction following path A or B.



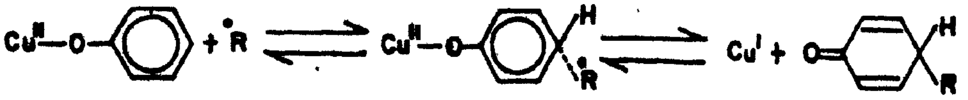
SCHEME II

Proceeding along path A would entail a diminution in polymer molecular weight which is not observed.[80] Should the trihalomethyl cyclohexadienone follow path B and generate two radicals this would correspond to a catalyzed production of 2,4,6-trichlorophenoxy radicals.

A considerable part of the present work is devoted to the interaction of copper(I) phenoxides and carbon tetrahalides. These studies were aimed at exploring the plausibility of the reactions represented in Scheme II in addition to mapping out the pathways followed by the free radicals produced. In order to eliminate a number of variables introduced by the presence of oxygen, and to clearly delineate the effect of carbon tetrahalides in these free radical processes, all systems were studied under anaerobic conditions.

E. Ligand Transfer as a Redox Process

The free radical initiation step discussed in the previous section is an example of electron transfer through an extended bridge and results in the transfer of a phenoxo ligand to the attacking radical (38).[83] Such a redox reaction is classified as bonded. Electron transfer can also occur by a non-bonded step and generate an onium ion (39). Classifying free radical redox reactions as bonded and non-bonded stems from the mechanistic conclusions concerning inorganic redox reactions. Electron transfer involving metal complexes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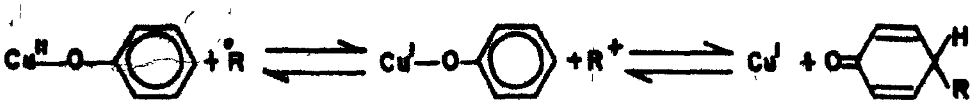

(39)

can take place via one of two transition states one termed outer-sphere, the other inner-sphere.[84]

The outer-sphere mechanism proceeds via an intermediate preserving intact the coordination shells of the two reagents. This essential criterion is represented by the following classical example (40):[85]

$$Fe(CN)_6^{4-} + IrCl_6^{2-} \longrightarrow Fe(CN)_6^{3-} + IrCl_6^{3-} \qquad (40)$$

This bimolecular reaction occurs with a second order rate constant of 1.2×10^5 M^{-1} sec^{-1} at 25° despite the substitution inertness of both reactants. Although no ligand-to-metal bond is broken in this process, some distortion of the inner shells must occur. The metal-ligand distances are certain to be affected by the valency change even though no bond is assumed to be formed between the reactants.

Inner-sphere electron transfer proceeds via a bridged activated complex in which contact between the oxidant and the reductant is maintained by a ligand bonded to both. A typical example of such a process is the oxidation of hexaaquochromium(II) by chloropentaamminecobalt(III) (41):[86]

$$Cr(H_2O)_6^{2+} + (NH_3)_5Cl\,Co^{2+} \longrightarrow \left[(NH_3)_5Co{-}Cl{-}Cr(H_2O)_5\right]$$

$$\longrightarrow Cr(H_2O)_5Cl^{2+} + Co^{2+} + 5\,NH_3 \qquad (41)$$

The rate constant for electron and ligand transfer is 6.0×10^5 M^{-1} sec^{-1}. The cobalt(III) and chromium(III) species are both slow to exchange their ligands making it possible to isolate the chlorochromium(III) complex. Use of isotopic ^{36}Cl enabled the demonstration that atom transfer had taken place. Actually ligand transfer is not necessarily required for an inner sphere process to occur, it merely allows for a more straightforward proof of the mechanism. In some cases the bridged complex is a true intermediate and may be detected in the medium by physical means.[87]

Radicals can participate in a similar manner in reactions with complex metal ions. Kochi has designated these as electron transfer (42) oxidations and ligand transfer (43) oxidations.[88]

$$R^{\bullet} + Cu^{2+} \longrightarrow R^{+} + Cu^{+} \qquad (42)$$

$$R^{\bullet} + CuCl^{+} \longrightarrow RCl + Cu^{+} \qquad (43)$$

The first of these corresponds to outer-sphere or non-bonded oxidation and the latter to inner-sphere or bonded oxidation

Electron transfer in this particular case essentially involves the oxidation of a radical to an -onium ion which undergoes subsequent reactions to stable products. The ease of oxidation will depend on the oxidation potential of both the radical and the oxidant. The ability of the substituents on the radical to stabilize the positive charge will determine its oxidation potential.

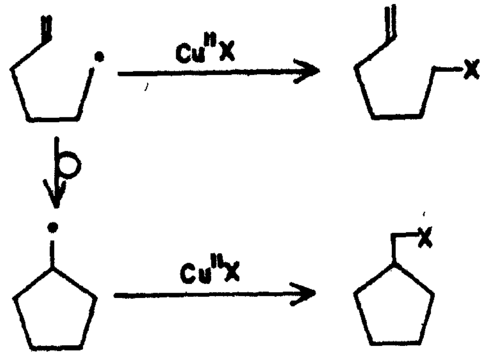
Electron transfer oxidations of radicals have been generally effected by Cu(II), Pb(IV), Co(III), Mn(III), Ce(IV) and Tl(III) coordinated to ligands via oxygen especially aquo and carboxylato complexes.[89] The principal products of the formation of carbonium ions from alkyl radicals are alkanes and alkyl derivatives. For example (44):

$$\mathrm{PhCH_2CH_2^{\bullet} + Cu^{II}(OAc)_2 \longrightarrow PhCH{=}CH_2 + PhCH_2CH_2OAc + H^+ + Cu^{I}OAc} \tag{44}$$

Both types of products have been well established as characteristic of carbonium ion intermediates generated by alternate routes.

Ligand transfer and the related electron transfer through an extended bridge are more pertinent to the work on copper phenoxides discussed herein. A greater part of the work to establish the ligand transfer mechanism has been carried out on alkyl radicals which can be oxidixed using Cu(II) and Pb(IV) complexes. The ligands transferred are halides Cl^- and Br^- as well as pseudohalides, cyanide, thiocyanate and azide.[90] Under these circumstances the oxidation of the 5-hexenyl radical can afford two products (45, 46). The chief distinction between electron-transfer and ligand-transfer is that the latter but not the former is relatively unaffected by electronic effects in the radical.

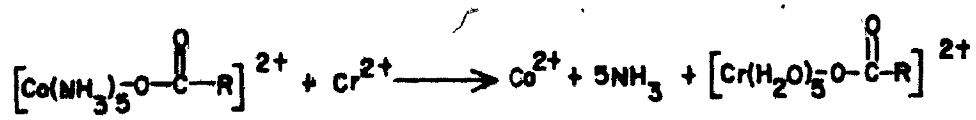
Organic bridging groups constitute an extension of the inner sphere redox reactions relying on coordination to a halide or pseudohalide bridge. Thus electron transfer can



(45)

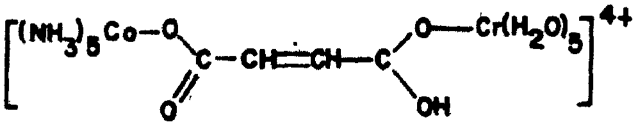
(46)

occur through suitable unsaturated ligands providing they possess a second donor group to allow coordination of the reductant. As an example the reduction of carboxylatopentaamminecobalt(III) complexes by chromium(II) can be cited (47).[91]



$$[\mathrm{Co(NH_3)_5{-}O{-}\overset{\overset{O}{\|}}{C}{-}R}]^{2+} + \mathrm{Cr}^{2+} \longrightarrow \mathrm{Co}^{2+} + 5\mathrm{NH_3} + [\mathrm{Cr(H_2O)_5{-}O{-}\overset{\overset{O}{\|}}{C}{-}R}]^{2+} \qquad (47)$$

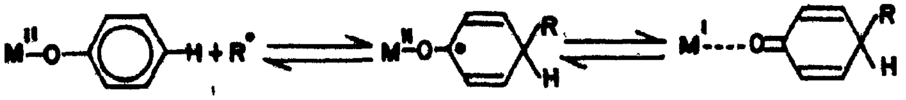
The group R is varied to include a range of saturated and unsaturated systems and substituents capable of coordinating Cr^{2+}. The results for acetato, butyrato and acid succinato all suggest a similar mechanism in which the chromous ion coordinates to the carbonyl group near the cobalt. The rate of methyl succinate is also similar. The succinate ion accelerates the rate somewhat. Striking rate increases are observed for oxalate, fumarate and maleate. They are attributed to easy coordination of the chromium(II) to the free carboxylate groups of these acids. The unsaturated nature of the ligands can then allow easy electron transfer to the cobalt such as in the fumarato intermediate (1).



(1)

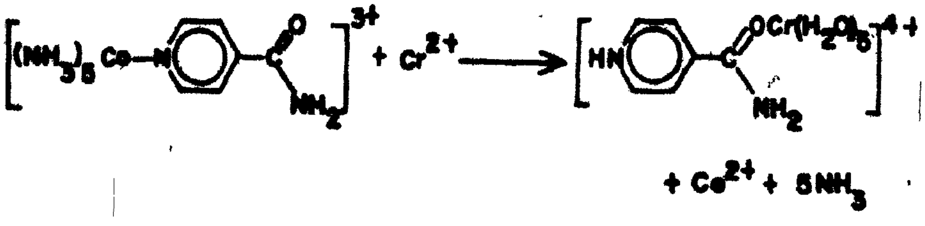
The entire process whereby the electron flows through the conjugated system is called resonance transfer.[92]

A special case of electron transfer through an extended bridge is represented by the remote attack of a radical on a coordinated ligand as depicted in (48). The postulated initiation and propagation steps for the decomposition



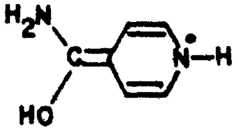
(48)

of $L_2Cu(OAr)_2$ complexes both bear a formal resemblance to the reaction illustrated in (48).[81] Very few examples of systems effecting oxidation of a radical through a conjugated ligand have been discovered although a number of coordinated radical intermediates have been proposed.[93] For example the reduction of isonicotinamide pentaammine cobalt(III) by chromium(II) proceeds as follows (49):

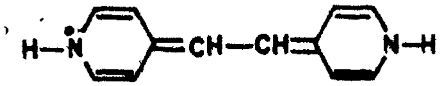


(49)

The site of attachment of the chromium(III) in the product establishes that the reductant attacks a remote position on the ligand. The available evidence indicates that this reaction proceeds by a radical ion intermediate. The electron transfer is initially to a low-lying unoccupied π orbital of the bridging ligand rather than to the cobalt-center. The fact that radicals such as (2) and (3) are readily formed



(2)



(3)

by reduction of the respective pyridinium ions has been cited as evidence for the preliminary generation of a radical center on the ligand. These in turn reduce external cobalt(III) centers.[94]

There are numerous instances in which added species have been found to accelerate electron transfer between two centers. A series of pyridine carboxylic acid derivative have been shown to undergo reduction by Eu(II) in a reversible manner to a pyridine derived radical.[95] The latter react with cobalt(III) by an inner-sphere process to regenerate the catalyst in its oxidixed form. Recently an induced electron transfer by remote attack of a hydroxyl radical at coordinated pyridine has been reported.[96] The intermediate, observable spectrophotometrically, is postulated to contain a radical ligand coordinated to cobalt(III) through the addition of the OH radical to the aromatic system.


(50)

The transient absorption decayed via first order kinetics to yield a stable product showing a rising absorption.

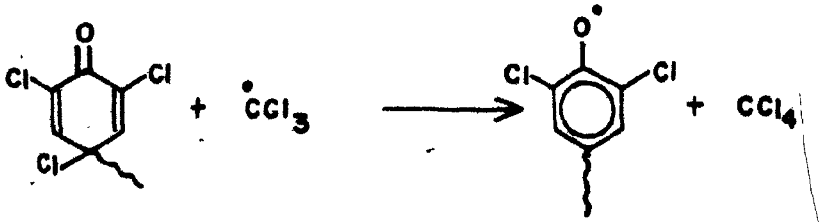
The work on reactions of copper(I) phenoxides with carbon tetrahalides described in the next chapter of this thesis was undertaken with the hope of obtaining more convincing evidence for the postulated radical abstraction of phenoxy ligands to yield cyclohexadienone derivatives such as depicted in (48).

CHAPTER II

1. SYNTHESIS AND GENERAL PROPERTIES OF COPPER(I) PHENOXIDES

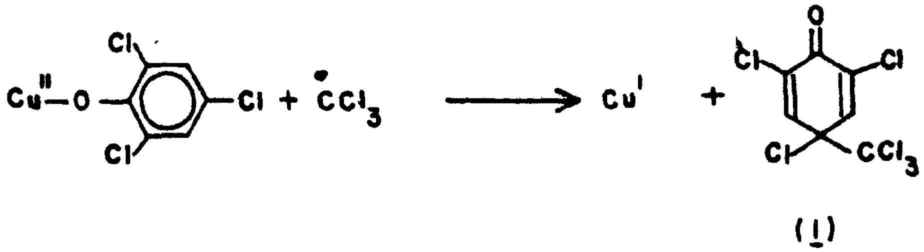
A. Introduction

In a study of the effect of typical radical transfer agents on the thermal decomposition of bis(pyridine)bis-(trichlorophenoxo)copper(II) complexes it was found that CX_4 additives reduced the induction period to a marked extent.[81] Evidence seemed to point to the intervention of trichloromethyl radicals when CCl_4 was used. This was thoroughly discussed in the previous chapter. It was clear from experimental evidence that some of the $\dot{C}Cl_3$ radicals participated in free radical chain propagation (1).

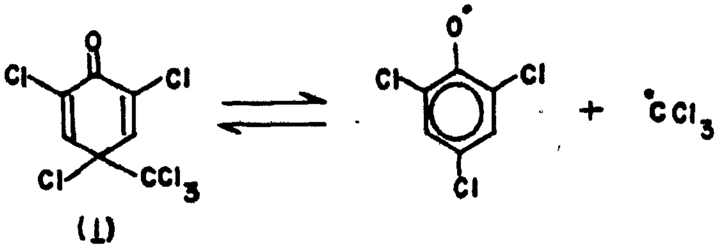


(1)

Whether the trihalomethyl radicals participate in actual initiation still remains uncertain. The postulated rapid attack of CCl_3 radicals at coordinated phenoxide (2) with ligand transfer to form a 4-trichloromethyl cyclohexadienone 1 seemed reasonable followed by the dissociative equilibrium (3). The latter step provides a chain branching mechanism and would



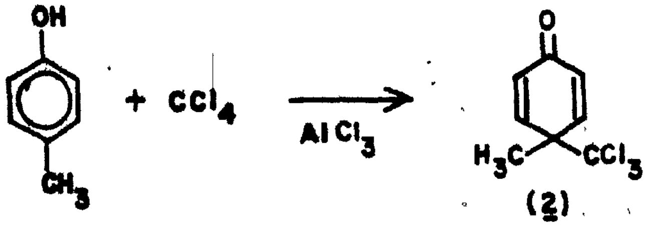
(2)



(3)

explain the drastic reduction of the induction period.

The cyclohexadienone (1) belongs to a class of known compounds isolable when alkyl substituents are present in the ring in addition to the 4-trichloromethyl group.[97] Zincke and Suhl showed that the reaction of p-cresol with CCl_4 and $AlCl_3$ gave 4-methyl-4-trichloromethyl-2,5-cyclohexadiene-1-one (2) in good yield.[97] The generality of the reaction has

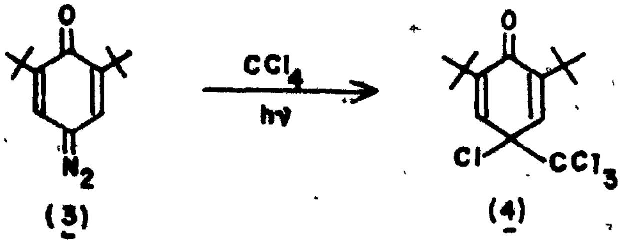


(4)

been explored[98] and it was found that only CCl_4 or CBr_4 could be used. The yields generally were low except when heavily alkylated phenols were used. Halogenated phenols gave only poor results and polyhalogenated phenols, such as 2,6-3,5-

dibromodichloro-p-cresol or tetrabromo-p-cresol, afforded the corresponding carbonate. In the present study the reaction of 2,4,6-trichlorophenol with CCl_4 and $AlCl_3$ similarly led to the isolation of the corresponding bis(2,4,6-trichlorophenyl)carbonate in good yield.

Other syntheses of 4-trichloromethyl cyclohexadienones rely on photochemical methods. Photolysis of 3,5-di-t-butylbenzene-1,4-diazooxide (3) in carbon tetrachloride gave the cyclohexadienone (4), the product of carbon-chlorine insertion, in 91% yield (5).[99]



(5)

The 4-trichloromethyl cyclohexadienone (4) would seem to be quite stable since it had the proper elemental composition in addition to showing spectral properties in accord with the proposed structure.[99] Similar photochemical reactions carried out on phenols in the presence of chloroform or carbon tetrachloride allowed the isolation of modest amounts of trichloromethyl cyclohexadienones.[100] All of these stable cyclohexadienone species are usually alkylated on the ring; when halogens are substituted on the ring the stability of the latter compounds may be markedly reduced. Therefore cyclohexadienone ($\underline{1}$) may be expected to be a transient species and thus able to participate in the equilibrium illustrated in equation (3), if it is formed.

Assher and Vofsi[101] demonstrated that copper and iron halides in the presence of CCl_4 attain a pseudo equilibrium involving CCl_3 radicals (6). The latter reaction forms the basis of the widely used catalyzed addition of CCl_4 to olefins (7,8).

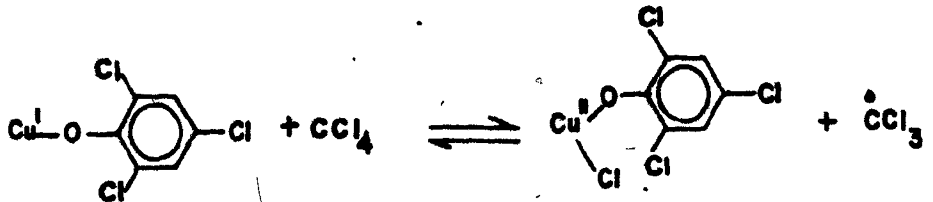
$$CuCl + CCl_4 \rightleftharpoons CuCl_2 + \dot{C}Cl_3 \tag{6}$$

$$\dot{C}Cl_3 + CH_2{=}CH_2 \longrightarrow Cl_3C{-}CH_2{-}\dot{C}H_2 \tag{7}$$

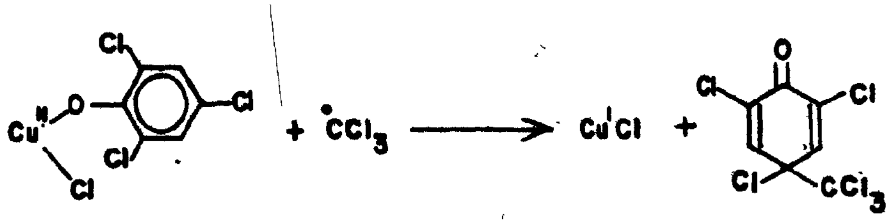
$$Cl_3C{-}CH_2{-}\dot{C}H_2 + CuCl_2 \longrightarrow Cl_3C{-}CH_2{-}CH_2{-}Cl + CuCl \tag{8}$$

If the analogue of reaction (6) could be carried out using copper(I) phenoxides it would provide an appropriate starting point for examining the fate of the CCl_3 radicals produced during the thermal decomposition of copper(II) phenoxides in the presence of carbon tetrachloride. One of the main goals of the present study was to investigate the possibility that cuprous phenoxides may react in a manner analogous to (6) and to study the products of reaction of CCl_3 radicals with phenoxocopper(II) species. In addition to providing a simple route to the synthesis of cyclohexadienones such reactions could also provide insight into the mechanism of some of the steps in the decomposition of phenoxocopper(II) complexes in the presence of CCl_4.

Since the pseudo equilibrium (6) is known to be established[101] it seemed reasonable to attempt to synthesize the intermediate trichloromethyl cyclohexadienone (1) according to reactions (9,10).



(9)



(10)

The realization of equations (9) and (10) would provide support for the plausibility of equation (2) and, depending on the fate of (1), demonstrate the mode of action of carbon tetrahalide additives.

B. Previous Reports of Copper(I) Alkoxides and Phenoxides

Intermediate copper(I) alkoxides and phenoxides have previously been thought to be involved in a variety of copper catalyzed reactions.[102-104] These reactions are variants of the Ullmann synthesis of biaryls (11).

$$2\,\mathrm{ArX} \xrightarrow[\text{Cu catalyst}]{} \mathrm{Ar{-}Ar} \qquad (11)$$

The name reaction also applies to the copper catalyzed condensation of aryl halides with phenoxide salts or aromatic amines to produce diaryl ethers or amines (12).

$$\mathrm{ArX} + \mathrm{MOAr'} \xrightarrow[\text{Cu catalyst}]{} \mathrm{Ar{-}OAr'} + \mathrm{MX} \qquad (12)$$

Copper, copper(I) oxide and copper(II) oxide catalyze reaction (12) as has been shown in a general evaluation of the method.[104] Recently it has been shown that the actual active species is a copper(I) phenoxide.[105]

Phenoxide and alkoxide derivatives of copper(I) have been prepared on various occasions[106,107] but owing to their instability they were poorly characterized. Cuprous methoxide prepared by reacting methanol with methyl copper(I) decomposed at room temperature to formaldehyde, methanol and elemental copper.[106] The presence of α hydrogen atoms was suggested to be the cause of the instability. Cuprous t-butoxide on the other hand, prepared to effect copper metallations could be sublimed at 170° under reduced pressure.[107]

A series of copper(I) phenoxides were prepared in a study of the reactivity of aryloxy copper(I) complexes with organic halides.[105] Under the conditions employed, condensation with bromo-benzene generally afforded modest amounts of the corresponding aryl ethers.

Whitesides obtained copper(I) alkoxides and phenoxides by heterogeneous reaction between dry, oxygen-free alcohols and halide-free methyl copper(I) at 0°.[108]

$$CuCH_3(s) + ROH \xrightarrow[0^\circ]{Et_2O} ROCu + CH_4 \qquad (13)$$

Most complexes with few exceptions were soluble in hydrocarbon solvents and could be precipiated from ether at -78° as light yellow solids. Characterization of the compounds rested solely on determination of the ratio of alkoxy to copper following hydrolysis. Reactions between alkyl halides and copper(I) alkoxides gave moderate yields of dialkyl ethers. The reaction with aryl halides afforded alkyl aryl ethers or diaryl ethers in good yields.

Cuprous alkoxides have been suggested as holding groups in mixed cuprate complexes R_1R_2 CuLi (R_1 = OR, R_2 = alkyl).[109] The substituted alkoxy group increases the stability of the organo cuprate and allows selective transfer of the alkyl substituent leading to an improved yield at a lesser cost of the alkyl transfer reagent.

The thermal decomposition of bis(pyridine)bis(trichlorophenoxo)copper(II) is believed to proceed via the intermediacy of trichlorophenoxocopper(I) complexes.[81] Although the not directly observed, the latter species represent a necessary postulate in an otherwise impossible redox reaction. A better understanding of the production and the ultimate fate of these transient copper(I) phenoxide species could be obtained through the preparation and study of the reactivity of a number of copper(I) phenoxides under controlled conditions.

C. Effect of Ligands and Solvents on the Stability of Copper(I) Phenoxides

Ligands have a profound effect on the stability of copper(I) complexes.[110] Soft ligands such as phosphines, arsines and sulfides stabilize copper(I) relative to copper(II) The copper(I) complexes are generally colorless and are stable to air, moisture and heat.[111] Most phosphine complexes in the phenoxide series can be derived from P_3CuCl* where the chloride ion is displaced by phenoxide with loss of one phosphine ligand. Thus sodium phenoxide and the corresponding thiophenoxide yield $P_2CuMC_6H_5$ (M = O,S). Sodium methoxide and ethoxide on the other hand yield copper metal and free phosphine indicating that the cuprous alkoxides are more difficult to stabilize. Reactivity of these phosphine copper(I) phenoxide complexes is drastically reduced by the soft ligands having an optimum combination of σ donor and π acceptor properties. Thus in oxidative reactions the phosphine rather than the copper is frequently oxidized.

Nitrile solvents are particularly attractive for carrying out reactions of copper(I) complexes.[112] Whilst the

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* P=triphenyl phosphine

cyanide solvent stabilizes the copper(I) state, it does not, like the phosphine, reduce the reactivity to a large extent. Acetonitrile for instance has been used to stabilize the lower oxidation state of copper in aqueous media with regard to disproportionation[113] and the complex $[(CH_3CN)_4Cu]Cl$ can be isolated.[114] Acetonitrile can in some cases induce the spontaneous reduction of copper(II) compounds to their copper(I) analogue.[103] This has been found in the present study to be true also for certain copper(II) phenoxide complexes. The addition of chelating ligands, favoring the copper(II) state, to copper(I) phenoxide solutions in acetonitrile does not lead to disproportionation to copper(II) phenoxide and elemental copper. This is an additional indication of the marked preference of the soft d^{10} copper(I) center for polarizable environments.

D. Reactions with Carbon Tetrahalides: Synthesis of Aryl Ortho Esters

Reactions of copper(I) phenoxides with CX_4 derivatives appear to have never been examined to date. The reactions reported herein thus represent a novel route to aryl ortho esters.[115] Alkyl halides however have been found to react with copper(I) phenoxides and alkoxides to afford the corresponding aryl or alkyl ethers.[108]

Aliphatic ortho esters have been widely studied;[116]

Their aryl counterparts however, remain curiosities. Tetraphenyl orthocarbonate first prepared in 1864[117] appears to be the only reported example of this class of compounds. Spiro orthocarbonates derived from catechols or glycols have been prepared,[115,118] but none of the methods involved made use of simple substitution on carbon tetrahalides.

Polyorthocarbonates were reported to be obtained in high yield by condensation of dichlorodiphenoxymethane with a series of dihydroxy compounds in the presence of an amine.[58] The intrinsic viscosities of these polymers were quite high in most cases, indicative of high molecular weights. Their infrared spectra exhibited a strong broad band at 1080 cm^{-1} which was attributed to the orthocarbonate structure.

Ferric chloride has been shown to catalyze chlorine substitution on CCl_4 by trihydroperfluoro alcohols (R_fCH_2OH) to produce the corresponding orthocarbonates: $(R_fCH_2O)_4C$ under anhydrous conditions.[120] Fluoroalcohol added to a water-ferric chloride-carbon-tetrachloride mixture produced the alcohol carbonate: $(R_fCH_2O)_2CO$ but no orthoformate: $(R_fCH_2O)_3CH$. These results are paralleled by observations made in the present work (Chapter II.A) concerning the reaction of 2,4,6-trichlorophenol with CCl_4 in presence of a different Lewis acid, $AlCl_3$.

2. RESULTS

A. Introduction

i. Preparation of Copper(I) Phenoxides

Synthesis of the phenoxides was generally accomplished by metathetical reaction between the sodium phenoxides and CuCl in acetonitrile solution at room temperature (14). In

$$\mathrm{NaOAr(s)} + \mathrm{CuCl} \xrightarrow[\mathrm{CH_3CN/N_2}]{} \mathrm{CuOAr} + \mathrm{NaCl(s)} \qquad (14)$$

every case the reaction led to a nearly colorless or straw-colored solution and sodium chloride was quantitatively recovered indicating that the above stoichiometry was observed. The sodium phenoxides were all prepared via reaction of sodium ethoxide with the appropriate phenol in absolute ethanol. Subsequent removal of the solvent by distillation followed by drying under high vacuum with applied heat afforded the white salts free of residual phenol.

ii. Oxidative Stability

The cuprous phenoxides like their sodium analogues are all easily oxidized by air and susceptible to hydrolysis. The extent to which they are affected is of course dependent on the phenoxy moiety, the less basic halogenated phenoxides presenting greater resistance to hydrolysis or oxidation. Pentachlorophenoxy and trichlorophenoxy complexes were noticeably more stable towards oxygen than alkylphenoxy complexes.

iii. Thermal Stability

Under inert atmosphere, solutions of copper(I) trichlorophenoxide prepared as outlined above, can be refluxed for extended periods in acetonitrile without any sign of decomposition. Copper(I) alkylphenoxide complexes appear to be of comparable stability. Whitesides[108] reported copper(I) 2,6-dimethylphenoxide to be stable below 200°. It is safe to assume that under the conditions employed herein, such decompositions do not present an important completing process.

iv. Phosphine Copper(I) Complexes

Due to difficulties in handling of the copper(I) phenoxides in acetonitrile solution, phosphine derivatives of the copper(I) complex were briefly examined. There was reason to believe[110] that the phosphine copper(I) phenoxides would be easier to handle due to their greater resistance to hydrolysis and oxidation. Unfortunately their reactivity was much reduced.

Coordination of triphenylphosphine to copper(I) trichlorophenoxide rendered it considerably less reactive towards CCl_4 at room temperature. Bis(triphenylphosphine)trichlorophenoxocopper(I) (5) was obtained by chloride exchange on P_3CuCl (P: triphenylphosphine) with sodium trichlorophenoxide following the method of Reichle,[110] or by direct reaction of triphenylphosphine, CuCl and sodium trichlorophenoxide in refluxing acetonitrile. The stoichiometry of the compound was established to be similar to those obtained by Reichle[110] by its pmr spectrum (($CDCl_3$; δ 7.40 (S,2H), 7.70 (m, 30H)) (IR, KBr disc: 1470, 1325, 1250, 860 cm^{-1}). This compound presents the advantage of being relatively stable to air and moisture. The complex (5) slowly decomposed on standing in chloroform solution. Refluxing in benzene containing CBr_4 and 10 equivalents of sodium trichlorophenoxide afforded polymer in 71% yield of theoretical.

Although the chemistry of these triphenyl phosphine complexes generally resembled their uncoordinated congeners, they were not studied any further due to their low reactivity.

B. Reactions of Copper(I) Phenoxides with Carbon Tetrahalides: Synthesis of Phenyl Ortho Esters

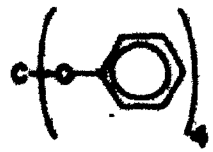
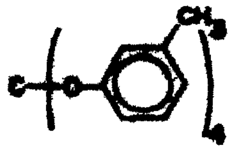
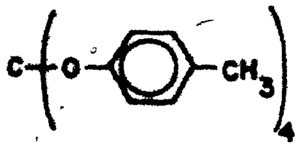
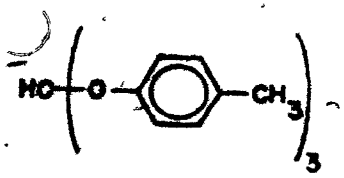
Reactions were carried out by addition of an excess of degassed CCl_4 to a freshly prepared solution of the copper(I) phenoxide in acetonitrile. Stirring at room temperature was continued until fading of the dark color had occurred. Filtration of the acetonitrile to remove the NaCl produced during the preparation of the copper(I) phenoxide followed by evaporation of the solvent under reduced pressure afforded an off-white solid mass. Extraction of the latter with CCl_4 left behind CuCl, recoverable quantitatively. Evaporation of the CCl_4 extract and treatment of the product with ethanol afforded crystalline ortho esters. A list of products prepared in this manner is given in Table II.1,(page 64) with a summary of their characteristic properties.

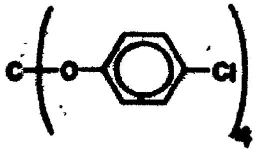
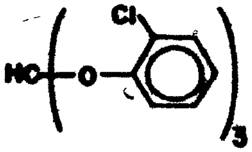
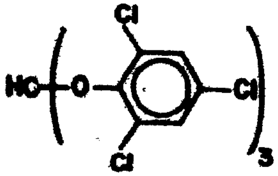
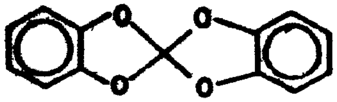
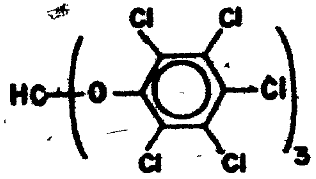
The fact that CuCl was isolated quantitatively from the reaction mixture suggested that the process could be made catalytic. This was verified by using a ten-fold excess of the sodium phenoxide to CuCl in presence of the required amount of CCl_4. Quantitative yields of ortho esters were still isolated albeit at the expense of a slower reaction.

Physical methods allowed the identification of the isolated ortho esters. ^1H nmr spectra (Table II.1, page 64), were all in agreement with the proposed structures. Infrared spectra of the compounds dispersed in KBr present essentially the same features as those of the starting phenols. The distinguishing characteristics are the complete absence of an O-H stretch in the 3600-3200 cm^{-1} region and the appearance of a new broad intense band at ca. 1050 cm^{-1} in the case of orthoformates and at ca. 1100 cm^{-1} for orthocarbonates. These characteristic bands are presumably associated with the $-CO_3$

TABLE II.1

PROPERTIES OF ISOLATED ORTHO ESTERS

	m/e (abundance)	pmr	mp
	291(4) 228(1) 214(62) 170(28) 154(1) 77(100)	7.75 (m)	95 (lit. 96-98°)[115]
	333(100) 256(2) 242(3) 198(6) 182(16) 91(70)	7.50 (m 16H) 2.55 (s 12H)	84-85
	333(100) 256(1) 242(2) 198(4) 182(5) 91(23)	7.20 (s 16H) 2.35 (s 12H)	101
	333(1) 242(3) 227(76) 198(4) 107(100) 91(73)	7.10 (s 12H) 6.50 (s 1H) 2.40 (s 9H)	104

	m/e (abundance)	pmr	mp
	393(28) 282(2) 238(3) 222(3) 111(100)	7.98 (d 8H) 7.80 (d 8H)	129-130
	393(100) 282(4) 266(4) 247(3) 222(2) 111(44)	7.75 (m)	177
	439(9) 404(100) 196(36) 179(27)	7.60 (s 6H) 7.20 (s 1H)	165-167
	228(100) 120(34) 92(68) 64(60)	7.20 (s)	109 (lit. 109°)[115]
	555(1) 539(1) 291(1) 263(1) 247(2) 78(100)	7.30 (s)	224-226

and CO_4 structures in these compounds. Mass spectra of ortho esters are characterized by the complete absence of a parent peak. The base peak however is frequently due to the trisubstituted ion $[C(OAr)_3]^+$. This is the case with the cresyl derivatives. Some orthoformates and orthocarbonates give mass spectra where the base peak is that corresponding to the phenol moiety $[OAr]^+$.

The behavior of copper(I) phenoxide compounds prepared and reacted *in situ* fell into two categories dependent on the ease of oxidation of the phenol, i.e. alkylphenoxides and polyhalophenoxides. In the case of phenols having a low oxidation potential the reaction was very rapid affording a short-lived transient blue species rapidly going to dark brown. At this stage the dark color faded more or less rapidly, depending on the ease of oxidation of the phenol, to a nearly colorless solution. Orthocarbonates could be isolated from these solutions in high yields when phenoxides having unhindered ortho positions were used. Substitution in the ortho position may prevent the reaction from attaining the tetraaryl orthocarbonate stage. In these cases trisubstitution of carbon tetrahalides was often found to occur and the main product was then a triarylorthoformate $(ArO)_3CH$ (Table II.1). For instance 2,4,6-trichlorophenol under appropriate conditions consistently gave the orthoformate. No evidence for the presence of traces of the corresponding orthocarbonate was found.

The isolation of triarylorthoformate esters is not only related to steric hindrance around the carbon being substituted, but can also be traced to the presence of protic compounds during the reaction. When the reaction of 4-methylphenoxocopper(I) with CCl_4 was first carried out, reagent grade acetonitrile (containing 0.3% water) was used without purification. The product of such reactions consistently contained substantial amounts of 4-methylphenylorthoformate in addition to the corresponding orthocarbonate.

Further studies indicated that the deliberate introduction of protic substances to the reactant mixture also led to increased amounts of the orthoformate products. It became evident that these additives either produced reductants as is the case when water is present, or acted as reductants themselves.

Copper(I) phenoxides of polyhalogenated phenols such as 2,4,6-trichlorophenol or pentachlorophenol underwent the same initial sequences of color changes when reacted with carbon tetrahalides as did the low oxidation potential phenoxides. However the dark red-brown solutions obtained did not fade in the usual manner. Seemingly the reaction stops at this point and is not pushed any further by addition of excess CCl_4. This solution is moderately stable in air and, providing the proper conditions are present, is capable of producing either ortho ester compounds or polymer. These reactions are discussed in more detail in Section 5 of this chapter and in Chapter III.

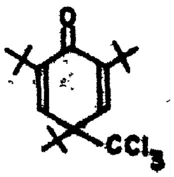
Copper(I) ethoxide prepared in acetonitrile was quite stable in solution. However, reaction with CCl_4 was highly exothermic. This may have been detrimental to the survival of the complex since the organic fraction obtained following workup was a complex mixture of carbonyl and ortho ester containing products. This is to be expected in view of the thermal sensitivity of copper(I) alkoxides carrying hydrogen atoms.[108] Two pathways are followed during the thermal decomposition of copper(I) alkoxides. The dominant pathway seems to be the generation of alkoxy radicals by Cu-O bond fission, the other being hydride elimination to form an intermediate copper(I) hydride and the corresponding aldehyde.

C. Reactions of Copper(I) 2,4,6-tri-t-butylphenoxide and Related Systems

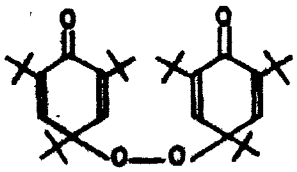
An outstanding property of the tri-t-butylphenoxide ligand is its ability through one electron oxidation to form a stable radical. Providing oxygen and good hydrogen donors are excluded, this radical is indefinitely stable in solution and in the solid state. Dimerization is precluded by the presence of bulky t-butyl substituents in the ortho and para positions. However in the presence of another radical rapid coupling can occur between the two species. This feature lends itself to the execution of a number of interesting reactions. Indeed, the free radical distribution at the intermediate stages of a reaction will be reflected in the product distribution resulting from the coupling of the radicals present with the tri-t-butylphenoxyl radical, if it can be produced *in situ*.

Ortho esters are not expected from the reaction of copper(I) tri-t-butylphenoxide with CCl_4. The nature of the phenol would not allow the formation of such sterically crowded compounds. However the reaction was investigated since it would most likely lead to the formation of the stable tri-t-butylphenoxyl radical and possibly trap a transient CCl_3 radical.

Copper(I) tri-t-butylphenoxide in acetonitrile under nitrogen reacted rapidly with an excess of CCl_4 to provide mainly 2,4,6-tri-t-butyl-4-trichloromethyl-2,5-cyclohexadien-1-one (6), as the major product and 4,4'-di(2,4,6-tri-t-butylphenol)peroxide (7), as a minor product. Evaporation of the acetonitrile and excess CCl_4 allowed quantitative recovery of CuCl after extraction of the mass. Evaporation of the extract afforded the crude product. The 4-trichloromethylcyclohexadienone (6) was separated from the minor component by recrystallization from aqueous ethanol. The chlorine isotopic ratio in the mass spectrum of compound (6) is in agreement with the presence of the trichloromethyl group in a number of fragments. Furthermore



(6)



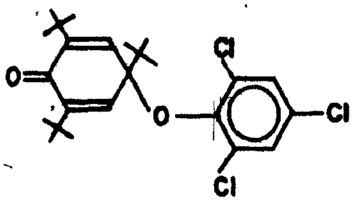
(7)

the infrared spectrum was indicative of the presence of the chlorinated 4-substituent by virtue of the appearance of a triple band system centered at 800 cm^{-1} not present in tri-t-butylphenol. A strong double band at 1645 and 1665 cm^{-1} was consistent with the presence of a cyclohexadienone carbonyl.[99] Compound (6) gave a satisfactory analysis.

No hexachloroethane could be found amongst the reaction products. Chloroform was however identified by V.P.C. in the solvent evaporated from the reaction mixture. This observation correlates with the observed presence of a small amount of peroxide (7). Loss of CCl_3 radicals through hydrogen abstraction from solvent would leave an excess of tri-t-butylphenoxyl radicals which upon workup would react with oxygen to form peroxide.

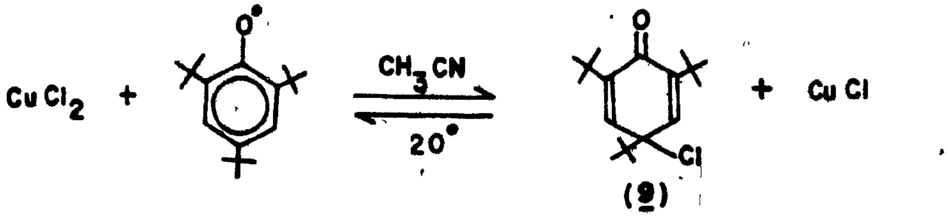
The cuprous chloride catalyzed reaction of sodium tri-t-butylphenoxide with CCl_4 also leads to the formation of the 4-trichloromethylcyclohexadienone (6). After five hours under similar conditions to the stoichiometric reaction, 65% of compound (6) was present. Heating the mixture to reflux did not lead to increased conversion nor did it cause deterioration of the mixture.

Further evidence for the production of trichloromethyl radicals during the reactions of copper(I) phenoxides with CCl_4 was gained by performing the reaction in presence of the 2,4,6-tri-t-butylphenoxyl radical itself. Cuprous trichlorophenoxide was prepared in the usual manner in acetonitrile under inert atmosphere. To this was added a benzene solution of the phenoxyl radical followed by an excess of CCl_4. The product isolated from this reaction contained the 4-trichloromethyl cyclohexadienone (51% based on phenoxyl radical). The remainder of the product mixture contained the peroxide (7), some quinol ether (8) and tri-t-butylphenol. No 2,4,6-trichlorophenyl orthoformate was detected in the mixture.


(8)

A number of other reactions were investigated in relation to the previous reaction. The aim was to use the tri-t-butylphenoxyl radical as a means of studying ligand transfer by a number of copper(II) complexes. Cupric chloride is a typical ligand transfer agent, transferring chloride to free radicals in solution.[121] When the reaction of cupric chloride and the tri-t-butylphenoxyl radical was carried out, the expected 4-chloro-2,4,6-tri-t-butyl-2,5-cyclohexadien-1-one (9) was isolated in 70% yield. The properties of the yellow crystalline material compared with those of the known compound prepared by reaction of chlorine with the radical.[122]

The reversibility of reaction (15) was verified by adding solid cuprous chloride to an acetonitrile solution of the 4-tri-butyl cyclohexadienone. The originally yellow



(15)

solution immediately assumed a dark-green color. An infrared spectrum of the organic material recovered from this solution showed the presence of tri-t-butylphenol peroxide (7), resulting from the reaction of the product tri-t-butylphenoxyl radical with air.

The possibility of ligand transfer with the red-brown complex resulting from the copper(I) trichlorophenoxide/CCl_4 system was also examined. It was mentioned in Section B that the reaction of copper(I) polyhalophenoxides produced a red-brown solution containing little ortho ester compound. The complex present at this stage closely resembles copper(II) trichlorophenoxide in color and in its IR spectrum. The product of the reaction of copper(I) trichlorophenoxide with CCl_4 is expected to be a chloride containing copper(I)—copper(II) trichlorophenoxide. This will be further discussed in Section E. It is thus possible for the isolated red-brown complex to transfer either chloride or phenoxide. Reaction of this complex with the tri-t-butylphenoxyl radical followed by an aerobic workup of the reaction mixture afforded a quantitative yield of the peroxide (7) and complete recovery of the starting complex. Similarly no ligand transfer was observed using bis(pyridine)bis(trichlorophenoxo)copper(II), copper(II) acetate, copper(II) methoxide, copper(II) (chloro)-methoxide or copper(II) thiocyanate.

D. Reactions of Copper(I) Polyhalophenoxides with CCl_4

As stated above, 2,4,6-trichlorophenoxide and pentachlorophenoxide complexes of copper(I) in acetonitrile react instantaneously with CCl_4 giving an intense red-brown solution. At room temperature the reaction stops at this point. Heating the mixture induces a rapid decomposition to polymer which precipitates out of solution. The polymers isolated from these systems are discussed in the next chapter. Similarly if the solvent is stripped from the reaction mixture and the resultant red-brown solid is heated, polymers can be extracted from the residues.

A workup of these red-brown solutions by evaporation under high vacuum and trapping of the volatiles at liquid nitrogen temperature allowed the detection of chloroform in the condensate by V.P.C. Extraction of the residue with either hexanes, ether or CCl_4 afforded a small amount of 2,4,6-trichlorophenyl orthoformate or pentachlorophenyl orthoformate. These compounds were characterized on the basis of their IR (strong bands at 1050 cm^{-1}), ^1H nmr and mass spectra. The isolated yields of these ortho esters were about 10% based on starting phenoxide.

E. Nature of the Complexes Obtained from Copper(I) Polyhalophenoxide/CCl_4 Systems

i. Presence of Coordinated Halide

The reaction of polyhalophenoxo complexes of copper(I) with carbon tetrahalides was believed to proceed by halide abstraction. A labile halide analysis on the resulting complex ought thus to allow the stoichiometry of the reaction to be established. Two methods were applied to this end, a gravimetric analysis and the Fajans precipitation titration.[123a,b]

Gravimetrically determined chloride represented 8.9% of the weight of complex. The titration results indicated 8.98% chloride content. The trichlorophenol recovered after hydrolysis and extraction represented 59.6% of the weight of complex.

The presence of a Cu-X bond in this complex was further demonstrated by its facile exchange with sodium phenoxides and concomittant quantitative precipitation of NaX. These experiments however did not allow the estimation of the amount of X present since the newly formed complexes were unstable and decomposed in solution. Polymers were obtained when halogenated sodium phenoxides were reacted with the mixed oxidation state complex. In every case in the presence of CCl_4, an amount of NaCl equivalent to the amount of sodium phenoxide introduced was found after the reaction. Under similar conditions in presence of CCl_4 the addition of alkylphenoxides to the mixed oxidation state complex led to the formation of ortho esters of the halophenol and to various coupling products depending on the nature of the added phenoxide.

ii. Presence of Mixed Oxidation States

Reactions of copper(I) or copper(II) phenoxides are often characterized by the transitory appearance of intensely colored solutions. It is evident in the initial stages of these reactions, where redox processes are implied, that both oxidation states are present. This is thought to be the case when reactions of polyhalophenoxides with carbon tetrachloride lead to their characteristic dark-red brown color. An analysis of the copper(I)/copper(II) ratio in these intensely colored complexes was thus of some interest.

Following a procedure similar to that adopted by Kochi[124] the copper(I) in the system was analyzed as CuCl after hydrolysis under nitrogen atmosphere of a weighed amount of complex with 5N HCl in acetonitrile/water solution. Results of these analyses are summarized in Table II.2.

The difficulty in these analyses rests essentially with the removal of contaminants from the relatively unstable complexes. Upon standing in the solid state, polymers are

TABLE II.2

RESULTS OF ANALYSES OF TWO COMPLEXES OBTAINED FROM CUPROUS POLYHALOPHENOXIDES

		Cu(I)TCP/CCl_4	Cu(I)PCP/CCl_4
Approximate stoichiometry		[CuTCP] [CuCl] [CuClTCP]	[CuPCP] [CuCl] [CuClPCP]
Molecular weight		654.5	792.0
Cu(I)	calc.	19.40	16.04
	found	19.78	11.18
Cu(total)	calc.	29.11	24.05
	found	26.68	23.83
Phenoxide	calc.	60.04	66.99
	found	59.6	68.5
Cl^-	calc.	10.85	8.96
	found	8.98	
C	calc.	22.00	18.18
	found	17.37	17.46
H	calc.	0.61	0.00
	found	1.01	0.55
Cl	calc.	43.39	53.79
	found	43.85	53.50

generated as well as phenols resulting from hydrolysis. Furthermore, the stoichiometry of the complex is impaired by the presence of extra cuprous chloride introduced through the formation of orthoformates. This can be circumvented to some extent by performing the reactions under the best conditions of moisture exclusion thus preventing hydrolysis of the sodium phenoxide to the phenol which is the precursor of the ortho ester contaminants.

iii. Interaction Complexes of Defined Stoichiometry

The complexes isolated from the reactions discussed in this section are generally obtained as amorphous powders. In the hope of obtaining a crystalline complex isolable from acetonitrile, various ratios of copper(I) to copper(II) trichlorophenoxides were mixed in solution.

Addition of one and two equivalents of copper(II) trichlorophenoxide to an acetonitrile solution of copper(I) trichlorophenoxide afforded stable solutions from which could be obtained amorphous powders having a similar appearance to the products obtained from the CCl_4 reactions. The relative stability of these solutions was indicative of complex formation between the two copper phenoxides since addition of copper(II) trichlorophenoxide to acetonitrile containing no copper(I) species results in immediate decomposition and concomitant precipitation of polymer. Refluxing under nitrogen atmosphere of these solutions containing the mixed oxidation complexes yields polymer only following a lengthly induction period. In presence of CCl_4 however, polymerization was induced much more rapidly.

Similarly mixtures of copper(II) trichlorophenoxide and CuCl are stable up to a mole ratio of 3:1. Excess copper(II) phenoxide spontaneously induces the precipitation of polymer from the acetonitrile solutions.

Addition of common ligands to these copper(I)/copper(II) trichlorophenoxide solutions either led to decoloration in cases where copper(I) directed donors were introduced, or to crystallization of known copper(II) phenoxide complexes when chelating ligands were used.

The possibilities of reduction or disproportionation are not to be eliminated when ligands are introduced into these copper(I)/copper(II) phenoxides. The oxidation state of a complex is highly dependent on its environment[125] and a redox equilibrium can be directed either way by use of an appropriate ligand. Such considerations are to be eliminated at least in the case where tetramethylethylenediamine was added. No metallic copper was found with the product and the amount of $TMEDCu(TCP)_2$ isolated corresponded roughly to the amount of copper(II) trichlorophenoxide initially present.

The effect of dilution on these mixed oxidation state complexes is also worthy of comment. Beyond a certain dilution these interaction complexes, as well as the products obtained from the copper(I) polyhalophenoxide/CCl_4 reactions, show signs of extensive dissociation. Beer's law is not observed and the characteristic intense red-brown color progressively fades upon dilution going to a definite brown color. The solution at this point is no longer clear and slowly deposits polymer. The aforementioned observations point to weak copper(I)-copper(II) interactions prevailing in the solid state and in concentrated solutions, but in dilute solution the copper(I) and copper(II) species express their individual chemistries.

iv. Effect of Reductant Additions

It will be recalled that during the synthesis of orthocarbonates the presence of water in the reaction medium resulted in the appearance of orthoformates. It was suggested that this was caused by the adventitious production of free phenols. The latter, by virtue of their facile hydrogen atom donating ability, could act as reducing agents during the reaction. In order to test this possibility a number of confirmatory reactions were performed.

The 4-methylphenyl orthocarbonate producing reaction was examined in the presence of one equivalent of added p-cresol. Thus CCl_4 was added to a mixture of the copper(I) phenoxide and the phenol. The workup afforded a crystalline product containing the excess phenol as well as orthocarbonate and orthoformate in a 2:1 ratio. In contrast the product of a reaction carried out using moist (0.3% water) solvent contained the ortho esters in a roughly 10:1 ratio whereas under rigorously anhydrous conditions only orthocarbonate was detected.

The reaction of copper(I) 2,4,6-trichlorophenolate with CCl_4 carried out under similar conditions in presence of one equivalent of added trichlorophenol also produced an increased amount of trichlorophenyl orthoformate. In this case the yield of ortho ester was 44% based on starting phenoxide. This represents a substantial increase from the roughly 10% usually isolated under normal conditions.

2,6-dimethylphenol which is a much better reducing agent than trichlorophenol, achieves complete bleaching of the red-brown copper(I) trichlorophenoxide/CCl_4 reaction product within one hour. A small amount of 2,2',6,6'-tetramethyldiphenoquinone was recovered from the acetonitrile solvent. The organic fraction contained coupled products of xylenol as well as trichlorophenyl orthoformate isolable in 44% yield after removal of phenols by sublimation.

Addition of ascorbic acid to the product resulting from the copper(I) trichlorophenoxide/CCl_4 reaction led to complete bleaching of the dark-colored solution within one hour. A substantial amount of the reducing agent was recovered indicating that only a fraction of the total copper was in the higher oxidation state. Crystalline trichlorophenyl orthoformate was isolated in 40% yield after the removal of the parent phenol by sublimation.

3. EXPERIMENTAL

A. General

Solvents were reagent grade and used as such unless specified. Dry hydrocarbon solvents were obtained by distillation under inert atmosphere from sodium benzophenone dianion immediately prior to use. Dry acetonitrile was stored over molecular sieves following reflux and distillation from calcium hydride. Methanol and ethanol were dried by distillation from sodium under nitrogen before use. Inorganic compounds were reagent grade and used as such unless otherwise noted. Pure cuprous chloride was prepared following a published procedure[126] and was kept in an evacuated flask.

Melting points were determined on a Gallenkamp block in open capillary tubes and were corrected. Proton magnetic resonance spectra were recorded on a Varian T-60 instrument using internal tetramethylsilane (TMS) unless otherwise stated. Chemical shifts are given in the δ scale in parts per million (ppm). Infrared spectra were obtained on a Perkin Elmer 257 spectrophotometer. Mass spectra were obtained on an AEI-MS-902 mass spectrometer at 70 eV using a direct insertion probe.

B. Preparation of Sodium Phenoxides, a Typical Example

Absolute ethanol was distilled from sodium. To 150 ml of this dry solvent in a distillation setup was added 2.300 g of sodium. When the metal had dissolved, phenol (9.45 g, slight excess) was dissolved in the sodium ethoxide solution. The solvent was distilled off until appearance of solid material. The residual solvent was pulled off on a vacuum line followed by heating to 90° for 16 hours at 10^{-3} torr to remove excess phenol. The white cake of sodium phenoxide was then ground to a fine powder in a glove bag and sealed in a number of small tubes. This procedure was used for the preparation of all sodium phenoxides used in this work.

C. Preparation of Copper(I) Phenoxides and Reaction with CCl_4: Isolation of Phenyl Ortho Esters

i. Copper(I) Phenoxide

A dry 200 ml two neck flask was filled with 100 ml acetonitrile which was degassed by bubbling nitrogen through the solvent. Sodium phenoxide (10.82 g; 93.3 m moles) was added and the suspension was stirred under inert atmosphere prior to the addition of CuCl (9.23 g; 93.3 m moles). Stirring was continued under rigorous exclusion of air until the precipitate was finely divided indicating complete consumption of sodium phenoxide. CCl_4 (9 ml; 4 fold-excess) was then injected into the suspension resulting in instant darkening of the mixture which was then left stirring overnight. The clear off-white solution was then filtered to remove sodium chloride (5.4 g; theoretical 5.4 g) and evaporated to yield a white solid. Extraction of the acetonitrile soluble fraction with CCl_4 left behind CuCl (9.2 g; theor. 9.2 g). The extract contained essentially pure tetraphenyl orthocarbonate (by nmr). It was recrystallized from absolute ethanol to yield 4 g of pure product (45%), mp: 95°, (lit. 96-98°).[115]

ii. Copper(I) 4-methylphenoxide

CuCl (2.28 g) and sodium p-cresolate (3.00 g) were mixed in 100 ml acetonitrile following the same procedure as in Section i). CCl_4 (10 ml) was injected and darkening resulted. Over a period of a few minutes the solution progressively lightened and after 12 hours had gone colorless. Workup of the reaction mixture as outlined previously allowed the quantitative isolation of sodium chloride (1.33 g) and cuprous chloride (2.18 g). The crude organic product (2.87 g; quantitative) was quite pure 4-methylphenyl orthocarbonate (by nmr). Recrystallization from ethanol gave a product of mp: 101°.

iii. Copper(I) 3-methylphenoxide

Essentially the same procedure was used with copper(I) 3-methylphenoxide to yield 3-methylphenyl orthocarbonate (mp: 85-86° from absolute ethanol).

iv. Copper(I) 2-methylphenoxide

Sodium o-cresolate (10.8 g) and cuprous chloride (9.9 g) were stirred together in 100 ml acetonitrile. Injection of 10 ml CCl_4 resulted in immediate reaction giving the usual dark suspension. After stirring overnight the color had faded somewhat and workup was effected as usual. Filtration of the reaction mixture yielded polymer in addition to NaCl. Cuprous chloride was recovered quantitatively. The organic fraction contained a brown solid admixed with a sticky material. Although attempts to work up this mixture were not successful, the infrared spectrum of the material did indicate the presence of ortho esters by the broad band appearing in the 1050-1100 cm^{-1} region.

v. Copper(I) 4-methoxyphenoxide

An acetonitrile suspension of sodium 4-methoxyphenolate (9.25 g; 71.2 m moles) and CuCl (6.3 g; 63.6 m moles) was reacted with an excess of carbon tetrachloride. The dark-colored solution did not fade overnight but was worked up to give quantitative recovery of CuCl and 7.3 g of an oil containing largely the phenol and phenol derived coupled products.

vi. Copper(I) 4-chlorophenoxide

Sodium 4-chlorophenoxide (7.5 g) and cuprous chloride (4.95 g) were stirred together in acetonitrile (100 ml) under inert atmosphere. Carbon tetrachloride (5 ml) was added and the usual color transitions were observed overnight. Workup and recrystallization from absolute ethanol afforded the 4-chlorophenyl orthocarbonate in 42% yield, mp:124-125 .

vii. Copper(I) 2-chlorophenoxide

Sodium o-chlorophenoxide (1.00 g) and cuprous chloride (0.64 g) were reacted together in acetonitrile (30 ml). Addition of CCl_4 (5 ml) resulted in a dark suspension going to a pale brown supernatant after 36 hours stirring. The crude product obtained (0.44 g) following evaporation and extraction with CCl_4 contained a substantial amount of phenol in addition to the orthoformate. The isolated crystalline white solid (0.12 g) represented a yield of 14%, mp:177°.

viii. Dicopper(I) Catecholate

Disodium catecholate was prepared via the sodium ethoxide method and obtained as a tan-colored amorphous solid indicating that little oxidation had taken place during its preparation. The sodium salt (7.71 g; 50 m moles) was suspended in 80 ml acetonitrile under nitrogen and cuprous chloride was introduced (9.90 g; 100 m moles) giving a straw-colored solution tion with a white precipitate. Carbon tetrachloride (20 ml) was then injected resulting in a dark green-black suspension with evolution of heat. The mixture was stirred overnight and then thrown into sufficient water to allow extraction with methylene chloride. The viscous oil obtained from the dried (Na_2SO_4) extract was deposited on a Florisil column and eluted with CH_2Cl_2 affording essentially pure diphenylspiro orthocarbonate in roughly 50% yield. Recrystallization from absolute ethanol affords white needles mp:109°, (lit. 109°).[115]

ix. Copper(I) 2,6-dimethylphenoxide

Cuprous chloride (9.9 g) and sodium xylenolate (14.4 g) were stirred in 100 ml acetonitrile into which 10 ml CCl_4 were injected. The reaction occurred very rapidly, the initial brown color fading within a few minutes. Workup of the products yielded tetramethyldiphenoquinone (40%), dimethylphenol (40%) and an unidentified oil (20%).

x. Copper(I) 4-methylphenoxide, Reaction in Wet Acetonitrile

The procedure followed was exactly that outlined in paragraph ii, of this section except that reagent grade acetonitrile containing 0.2-0.3% water was used as solvent.

Conventional workup afforded a crude organic product containing some phenol. The ratio of orthocarbonate to orthoformate in this mixture was 10:1, as determined by nmr after removal of the residual phenol by sublimation.

D. Reactions Involving Tri-t-butylphenol, Tri-t-butylphenoxide and Tri-t-butylphenoxyl

i. Copper(I) Tri-t-butylphenoxide

1.291 g (4.55 m moles) of sodium tri-t-butylphenoxide was suspended in 30 ml acetonitrile under nitrogen atmosphere. Cuprous chloride (0.450 g; 4.55 m moles), was introduced and the mixture was stirred until a uniform precipitate was obtained. Carbon tetrachloride (5 ml) was injected causing the mixture to go from yellow to green to blue at which point no further changes were observed. Evaporation of the mixture afforded a greenish mass which was extracted to yield a brown oil. Cuprous chloride was quantitatively recovered after the extraction. Recrystallization of the crude material affords the 4-trichloromethylcyclohexadienone (6) 1.38 g, 80% as a pale yellow crystalline powder, mp: 71-72°, (lit. 68-71°).[130]

Analysis: calc. for:

$C_{19}H_{29}OCl_3$ (379.4); C:60.10; H:7.64; Cl:28.04,
found C:59.16; H:8.05; Cl:26.93,
pmr (CCl_4) δ 1.90 (s 27H); 7.35 (s 2H)
ir (KBr) 1660, 1640 cm^{-1}, cyclohexadienone carbonyl.[99]

The compound, 4,4'-di(2,4,6-tri-t-butylphenol) peroxide 7 was isolated as a minor product from the mother liquor as pale yellow needles, mp: 145-146°, (lit. 147-148°).[122]

pmr (CCl_4) δ 1.45 (s, 9H), 1.90 (s, 18H), 7.05 (s, 2H)
ir (KBr) 1670, 1650, 1365, 980 cm^{-1}

A catalytic reaction was carried out using sodium tri-t-butylphenoxide (0.700 g; 2.46 m moles) and CuCl (0.025 g; 0.25 m mole) in 40 ml acetonitrile with excess CCl_4. After 5 hours stirring at room temperature 65% conversion to the 4-trichloromethylcyclohexadienone was estimated by pmr.

ii. Copper(I) 2,4,6-trichlorophenoxide/CCl_4 Reaction Carried out in Presence of the 2,4,6-tri-t-butylphenoxyl Radical

A copper(I) trichlorophenoxide solution was first prepared by reacting cuprous chloride (0.5 g; 5 m moles) with sodium trichlorophenoxide (1.1 g; 5 m moles) in acetonitrile (15 ml). The reaction flask was fitted with a Schlenk filter containing a 1 cm layer of Celite. The phenoxyl radical was prepared according to a literature procedure[122] by stirring tri-t-butylphenol (2.00 g; 7.6 m moles) in benzene (100 ml) with manganese dioxide (6 g) in a 250 ml two-necked flask with a syphon to the Schlenk filter. After one hour stirring the benzene solution containing the blue radical was directly transferred under pressure of nitrogen to the Schlenk filter and filtered into the copper(I) trichlorophenoxide solution. Carbon tetrachloride (3 ml) was injected producing a red-brown solution which was kept stirring under inert atmosphere for one hour. Evaporation of the volatiles gave a very dark solid which was extracted with pentane. Evaporation of the latter extract afforded an oil which crystallized on standing and contained mainly 4-trichloromethylcyclohexadienone (6), 1.5 g (51% based on tri-t-butyl phenol). Compound (6) was identified by comparison of its ir and nmr spectra with those of the known compound. The remainder of the product consisted of the tri-t-butylphenoxylperoxide (7) and a small amount of quinol ether (8) mp: 117-118°, (lit. 127-129°).[82]

ir (film) 1670, 1650, 1440, 1370, 1250, 945, 800 cm^{-1}

pmr (CCl_4) δ 1.65 (s,18H), 1.75 (s,9H), 7.50 (s,2H), 7.63 (s,2H).

iii. Ligand Transfer to the 2,4,6-tri-t-butylphenoxyl Radical

(a) With Cupric Chloride

The blue radical was prepared by stirring in benzene (100 ml), 2.62 g (10 m moles) of the phenol and 12 g MnO_2. This suspension was filtered under nitrogen atmosphere directly into an acetonitrile solution of anhydrous cupric chloride (2.0 g; 14.8 m moles). Initially the blue color of the radical was discharged on contact with the green cupric chloride solution and upon completion of the filtration a dark solution was obtained. Filtering this reaction mixture afforded a small amount of cuprous chloride. Evaporation of the filtrate left a black sticky solid which was extracted with hexanes yielding a brown oil, 2.2 g. This mixture contained 70% of 4-chloro-2,5,-cyclohexadien-1-one (9) mp:89-90°, (lit. 94-96°).[122]

ir (film) 1665, 1645, 1370, 920 cm^{-1}

pmr (CCl_4) δ 1.60 (s,9H), 1.79 (s,18H), 7.10 (s,2H)

20% of 4-hydroxy-2,5-cyclohexadien-1-one was also found in this product mixture and was shown to be a by-product of the phenol oxidation reaction over MnO_2. The reason for its appearance was not investigated. A blank reaction which was run under the same conditions except for omission of $CuCl_2$ afforded a product mixture after letting the blue solution react with air, containing approximately 80% peroxide and 20% of the 4-hydroxyquinone. mp:125-127°, (lit. 133-134°, 113-125°).[127,122]

ir (film) 3510, 1662, 1645, 1635, 1365, 970 cm^{-1}

pmr (CCl_4) δ 1.55 (s,9H), 1.80 (s,18H), 2.05 (s,1H),
7.00 (s,2H).

(b) <u>With Bis(pyridine)bis(trichlorophenoxo)copper(II)</u>

The radical was prepared as in (a) and filtered directly into a solution of the copper complex (1.574 g, 2.56 m moles) in 10 ml benzene. Overnight the solution had not changed color. A short reflux did not induce any reaction. Aerobic workup by evaporation of the benzene and extraction with hexane left unchanged copper complex (1.420 g). The ir spectrum of the recovered compound was identical to that of an authentic sample of the bis(pyridine) complex.[128] The hexane fraction afforded a dark crystalline solid identified as impure peroxide (7).

(c) With the Reaction Product of the Copper(I) Trichlorophenoxide/CCl_4 Reaction

The dark red-brown complex was prepared by reacting CuCl (0.450 g; 5 m moles) and sodium trichlorophenoxide (1.100 g; 5 m moles) in 40 ml acetonitrile with carbon tetrachloride (10 ml). The mixture was filtered to remove NaCl and evaporated to remove excess CCl_4 yielding 1.63 g of the dark complex. This was redissolved in 40 ml acetonitrile and added to a benzene solution (100 ml) containing 10 m moles of the blue phenoxyl radical. After two hours no significant color changes occurred and the mixture was worked up as in the previous reaction. The copper complex was quantitatively recovered and the hexane soluble material consisted solely of the peroxide (7).

E. Copper(I) Polyhalophenoxides

i. Copper(I) 2,4,6-trichlorophenoxide

Sodium trichlorophenoxide (1.100 g; 5 m moles) was suspended in acetonitrile (30 ml) under nitrogen. Cuprous chloride (0.450 g; 5 m moles) were then added and the mixture was stirred till the remaining precipitate was uniformly dispersed. Slight oxidation produced a faint yellow color in the solution. Carbon tetrachloride (5 ml; 10-fold excess) was then injected resulting in the appearance of a transient blue color which immediately faded to leave a dark red-brown solution. After stirring for one hour the acetonitrile solution was filtered affording 0.3 g of NaCl. Evaporation of the filtrate afforded a dark red-brown amorphous solid. Extraction of the latter with ether or carbon tetrachloride afforded variable amounts (approximately 10%) of trichlorophenyl orthoformate. The extracted solid had an infrared spectrum essentially the same as that of the bis(2,4,6-trichlorophenoxo)copper(II) complex.[128]

ii. Copper(I) Pentachlorophenoxide

A suspension of sodium pentachlorophenoxide (1.44 g; 5 m moles) in 30 ml acetonitrile was reacted with cuprous chloride (0.455 g; 5 m moles) till the precipitate was uniformly dispersed. Carbon tetrachloride (5 ml) was injected, resulting in a slow reaction without the appearance of the usual transient blue color. After 24 hours stirring the solution had attained a dark red-brown color and was filtered to remove NaCl (0.41 g). This precipitate was found to contain 0.12 g of material extractible with toluene and reprecipitated with methanol, mp 224-226°. The infrared spectrum of this compound contained essentially four bands: 1400, 1365, 1040, 720 cm^{-1}. The identity of the white microcrystalline solid was confirmed by mass spectrometry to be the pentachlorophenyl orthoformate, Table II.1, page 64. Evaporation of the acetonitrile filtrate gave a dark purple solid having an infrared spectrum consistent with a copper pentachlorophenoxide complex.

iii. Analysis of Products from the Carbon Tetrachloride Reaction

(a) Gravimetric Analysis for Chloride[123a]

A fresh sample of the copper(I) trichlorophenoxide/CCl_4 reaction product was prepared as outlined in E.i. and dried under vacuum. An accurately weighted amount (0.4-0.6 g) of the complex was then hydrolyzed with 50 ml dilute nitric acid and extracted with ether to remove the phenol. The aqueous phase was then scrupulously recovered in a beaker and silver nitrate solution was added till no further precipitation occurred. The silver chloride precipitate was digested by bringing the solution to boil. After cooling the

AgCl precipitate was transferred to a constant weight porous glass filter, washed with distilled water and dried at 110°. The results of a duplicate analysis averaged to 8.9% chloride content.

(b) Fajans Precipitation Titration for Chloride[123b]

A silver nitrate solution was prepared by dissolving approximately 17.0 g of the salt in distilled water and completing to 1 litre. Standard sodium chloride solution (25 ml; 0.0965 N), was pipetted into a 500 ml Erlenmeyer flask and made up to approximately 100 ml by adding distilled water. Dilute dextrin solution (25 ml; 1%; 10% ethanol/water), was added with ten drops of sodium dichlorofluoresceinate (0.1%) imparting a yellow color with green fluorescence to the mixture. A triplicate titration with the $AgNO_3$ solution to a pink end point allowed its exact titer to be determined (0.098 N).

Samples of approximately 0.7 g of the red-brown copper(I) trichlorophenoxide/CCl_4 reaction product were accurately weighed into three 125 ml Erlenmeyer flasks, dissolved in a minimum of acetonitrile and hydrolyzed with dilute nitric acid. The hydrolysates were extracted with ether and the aqueous phases quantitatively transferred to three 500 ml conical flasks. The three solutions were completed to approximately 100 ml with distilled water. Ethanolic dextrin and ten drops of sodium dichlorofluoresceinate were added and the pH was then adjusted to 4-5 with solid sodium carbonate. Titration was performed with the standard $AgNO_3$ solution to a pink end point. The average of the three determinations gave a chloride content of 8.98%.

(c) Evaluation of the Copper Content in the Mixed Oxidation State Complexes[124]

Approximately 0.2 g of the complex was accurately weighed in a 100 ml three-neck flask fitted with a calomel reference electrode and a platinum electrode. The middle neck was closed with a rubber septum receiving a nitrogen inlet and outlet and the burette. The system was flushed with nitrogen and a small amount of acetonitrile was added to dissolve the complex followed by 30 ml of 5N HCl. The stirred hydrolyzed mixture was then titrated with 0.072 N ceric sulfate in 1N H_2SO_4 (standardized against ferrous ammonium sulfate). The change in potential was measured using an Orion Research pH meter model 701 in the mV mode. When the end point was reached the burette was changed and the solution was then titrated for total copper using 0.197 N stannous chloride in 5N HCl (standardized against ceric sulfate). End points were determined by interpolation on the volume/mV data recorded from the millivoltmeter. Results expressed as % copper(I) and % total copper are found in

Table II.2, page 75.

(d) Analysis of Phenoxide Content

Evaluation of the phenoxide content of the copper(I)/ CCl_4 trichlorophenoxide and copper(I) pentachlorophenoxide/ CCl_4 reaction products was done during the chloride analysis (Section E.iii.a). The dark red-brown complexes were hydrolyzed followed by extraction with ether as was previously outlined. Each extract was individually dried with anhydrous sodium sulfate and quantitatively transferred to a weighed Erlenmeyer flask. The ether solvent was removed on a rotary evaporator and the weight of phenol was obtained by difference and converted to percent phenoxide content of the original sample. These results are included in Table II.2, page 75.

iv. Reaction of the Copper(I) Trichlorophenoxide/ CCl_4 Reaction Product with Sodium Phenoxides

(a) Sodium Trichlorophenoxide

Cuprous chloride (0.452 g) and sodium trichlorophenoxide (1.000 g) were stirred together in 20 ml acetonitrile. CCl_4 (2 ml), was injected and the reaction was left for one hour. The solution was filtered to remove sodium chloride (0.255 g, theor. 0.268 g). To the filtrate another addition of sodium trichlorophenoxide was made (1.000 g). After 12 hours stirring the suspension had become colorless. Filtration afforded 1.326 g of colorless precipitate which was extracted with toluene. Filtration of the toluene yielded 0.340 g of sodium chloride and after precipitation from methanol 0.980 g of polymer were recovered, 68% based on total phenoxide. The acetonitrile fraction contained a mixture of cuprous and cupric chlorides as well as a small amount of trichlorophenyl orthoformate.

(b) Sodium Tri-t-butylphenoxide

The copper(I) trichlorophenoxide/CCl_4 reaction was performed as in paragraph (a). Sodium tri-t-butylphenoxide (1.291 g, 1 eq) was then added to the red-brown mixture; the surface of the sodium salt immediately became blue. After completion of the reaction the red-brown mixture was evaporated to a dark solid which was extracted with hexanes. Evaporation of the solvent afforded 2.1 g of a brown oil. Infrared and pmr spectra of this crude product showed it to contain mainly the 4-trichloromethyl cyclohexadienone (<u>6</u>) and minor quantities of trichlorophenyl orthoformate and trichlorophenol as well as a small amount of a 2-substituted cyclohexadienone. Chromatography on Florisil eluting with CCl_4 afforded in the first fractions 1.5 g of (<u>6</u>), 87% based on the starting tri-t-butylphenoxide.

V. Mixed Oxidation State Complexes of Defined Stoichiometry

Copper(I) trichlorophenoxide was prepared as usual in acetonitrile and one equivalent bis(trichlorophenoxo)copper(II) was added to the colorless suspension. The resulting red-brown solution was refluxed for one-half hour without any apparent change. Addition of 2 ml CCl_4 to the refluxing solution induced immediate polymerization. Separation of the polymer by filtration and removal of the sodium chloride (0.267 g) afforded 1.880 g pure polymer after reprecipitation, 87% based on phenoxide introduced. Similar results were observed when the copper(I) to copper(II) ratios in solution were 1:2 and 1:3. When four equivalents of copper(II) trichlorophenoxide were added to the copper(I) trichlorophenoxide solution in the manner described above, spontaneous polymerization resulted without addition of CCl_4.

To a mixture of cuprous chloride (0.113 g) and sodium trichlorophenoxide (0.250 g) in acetonitrile (8 ml) was added copper(II) trichlorophenoxide (1.04 g; 2 eq to copper(I)). To this stable dark solution was added dry tetramethylethylene diamine (0.528 g; 4 eq. to copper(I)) and stirring was continued overnight. Filtration afforded crystals of tetramethylethylenediaminebis(trichlorophenoxo)copper(II) which gave an infrared spectrum identical to that of an authentic sample.[128]

vi. Reactions of Copper(I) Phenoxides with Reducing Agents

(a) The Reaction of Copper(I) 4-methylphenoxide with One Equivalent of 4-methylphenol and CCl_4

4-methylphenol (0.497 g; 4.6 m moles) and the corresponding sodium salt (0.598 g; 4.6 m moles) were suspended in 30 ml acetonitrile under nitrogen. Cuprous chloride was added (0.455 g; 4.6 m moles) and the colorless suspension was stirred prior to the injection of CCl_4 (3 ml). The resulting dark brown solution slowly faded producing a colorless supernatant with a slightly greenish precipitate. Filtration followed by evaporation of solvent and extraction with carbon tetrachloride afforded 0.933 g of crude organic product. Cuprous chloride was quantitatively recovered. Residual cresol (0.768 g) was sublimed out of the oil and the ratio of 4-methylphenyl orthocarbonate to orthoformate in the remaining mixture (0.165 g) was 2/1 as determined by pmr.

(b) Reaction of Copper(I) Trichlorophenoxide with CCl_4 and One Equivalent of Trichlorophenol

Sodium trichlorophenoxide (1.000 g, 4.6 m moles) and trichlorophenol (0.905 g, 4.6 m moles) were suspended in 30 ml acetonitrile under nitrogen. Cuprous chloride (0.455 g, 4.6 m moles) was added and the stirring resumed till the precipitate appeared finely divided. CCl_4 (3 ml) was injected producing the usual color changes. Workup of the reaction product as in paragraph (a) afforded 0.86 g of crude product from which residual phenol was removed by sublimation. The crude crystalline trichlorophenyl orthoformate (0.40 g) thus obtained represented 44% of theoretical mp 163°.

(c) Reduction of the Copper(I) Trichlorophenoxide/CCl_4 Reaction Product with Xylenol

Sodium trichlorophenoxide (1.00 g), cuprous chloride (0.455 g) and CCl_4 (3 ml) were reacted in acetonitrile (30 ml). Xylenol (0.576 g; 1 eq to copper) was then added to the red-brown solution. After one hour the color had completely faded. The sodium chloride was filtered off together with some tetramethyldiphenoquinone (0.300 g). Cuprous chloride was quantitatively recovered following extraction of the evaporated filtrate with carbon tetrachloride. The crude organic fraction (1.1 g was a mixture of trichlorophenyl orthoformate, trichlorophenol and xylenol. Crude orthoformate was obtained (0.49 g; 44%) by removal of the phenols by sublimation.

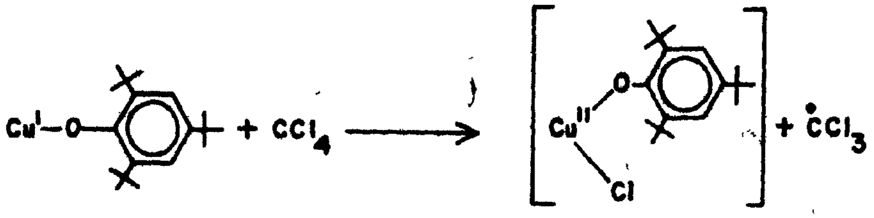
(d) Reduction of the Copper(I) Trichlorophenoxide/CCl_4 Reaction Product with Ascorbic Acid

The copper(I) trichlorophenoxide reaction was performed as above in (c) and ascorbic acid (0.880 g; 1 eq to copper) was added. Within one hour the reaction mixture was bleached. Filtration separated the sodium chloride and a large amount of unreacted ascorbic acid (sparingly soluble in CH_3CN). Removal of the solvent from the filtrate produced a white sticky mass which was extracted with CCl_4. The CCl_4 insoluble material (1.036 g) contained the cuprous chloride and dehydroascorbic acid, the oxidation product. The crude organic extract (0.911 g) contained free phenol and trichlorophenyl orthoformate. Removal of the phenol by sublimation and recrystallization of the residue afforded 0.364 g (40%) of pure ortho ester.

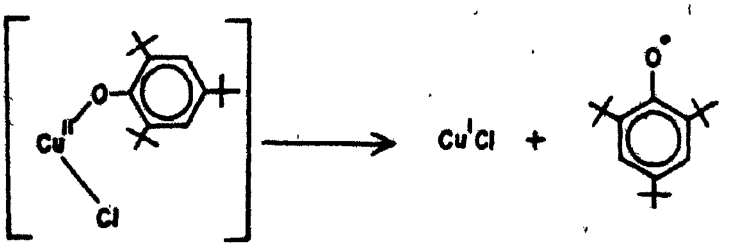
4. DISCUSSION

A. Formation of Trihalomethyl Radicals

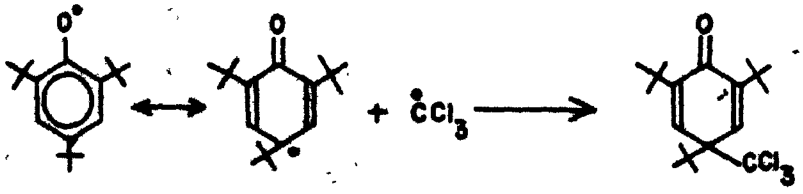
Previous studies of reactions of CuCl with CCl_4 have furnished strong evidence for production of CCl_3 radicals.[9b,101,129] The foregoing observations concerning the reactions of cuprous phenoxides with carbon tetrahalides also point to the involvement of trihalomethyl radicals. The isolation of a 4-trichloromethyl cyclohexadienone from the reaction product of copper-(I) tri-t-butylphenoxide is most convincing in this regard. A three-step process can be proposed as a likely route to the main product (<u>6</u>) (16-18).



(16)



(17)



(6)

(18)

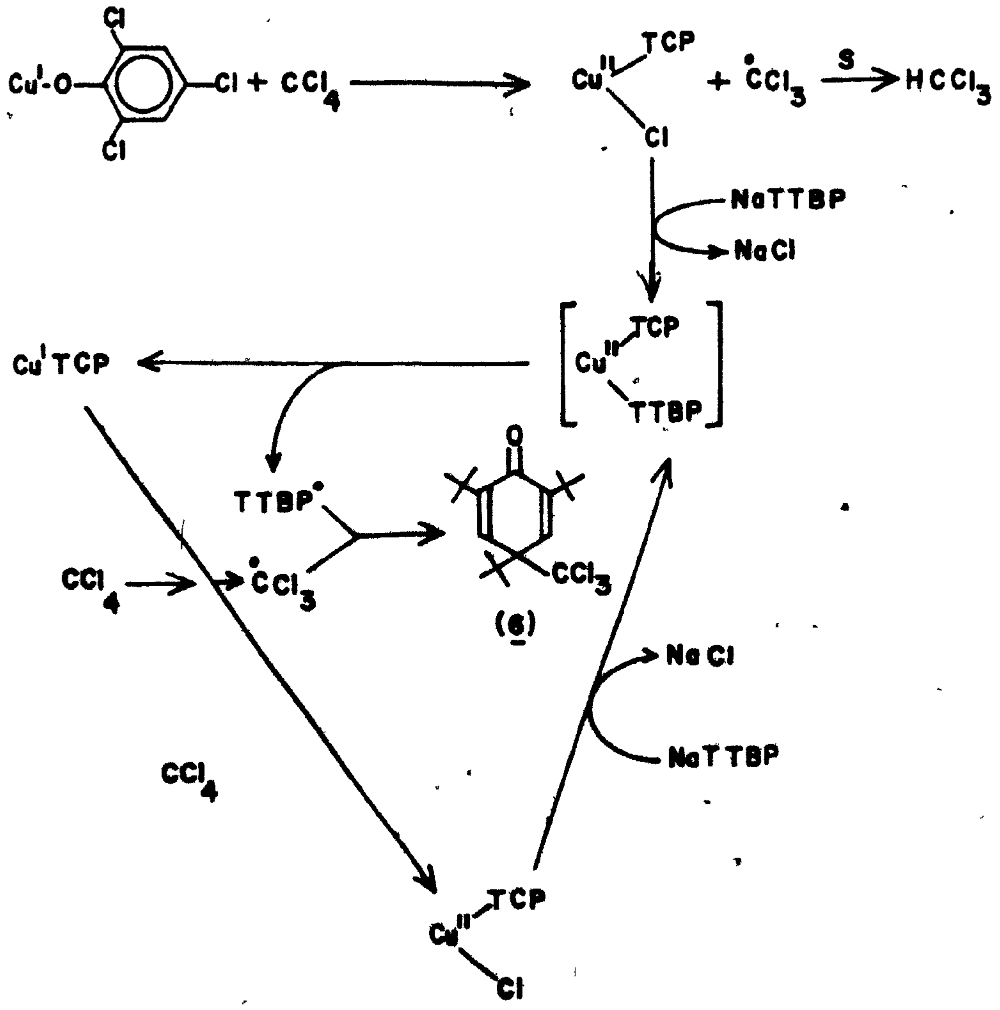
The primary reaction produces the trichloromethyl radical and an intermediate copper(II) (halo)phenoxo complex. The latter is expected to be extremely susceptible to homolytic dissociation in acetonitrile on account of the low oxidation potential of the coordinated phenoxide (Table I.1, Chapter I), thus rapidly producing the tri-t-butylphenoxyl radical. In the last step, coupling of the two radical species would produce the observed product. The 4-trichloromethyl cyclohexadienone had been reported previously as the product of irradiation of tri-t-butylphenol in carbon tetrachloride solvent.[130]

The fact that the solution upon completion of the reaction, contains excess of the stable blue phenoxyl radical is an indication that some of the more reactive CX_3 radicals have been lost in secondary processes. Reaction (16) unfortunately produces the more reactive species first (CCl_3) which most likely undergoes a hydrogen atom transfer from solvent to yield chloroform at a rate approaching diffusion control.[131] The second order rate constant for termination of CCl_3 radicals is nearly diffusion controlled (0.5×10^8 1 $mole^{-1}$ sec^{-1}).[132] However no hexachloroethane was identified in any of the present systems. Once reaction (17) has produced a substantial concentration of the stable tri-t-butylphenoxyl radical, reaction (18) can efficiently compete with hydrogen abstraction from solvent.

Reaction of copper(I) trichlorophenoxide with carbon tetrachloride in presence of the blue tri-t-butylphenoxyl radical also leads to the formation of the 4-trichloromethyl cyclohexadienone (6). The yield in this case was substantially reduced presumably because of a dilution effect when the benzene solution of the radical was introduced thus favoring hydrogen abstraction by the trichloromethyl radicals.

The most efficient system for trapping the transient CCl_3 radicals is no doubt that relying on the addition of sodium tri-t-butylphenoxide to the cuprous trichlorophenoxide/ CCl_4 reaction product. In this case the isolated yield of pure (6) attained 87%. This result is consistent with the fact that the stable radical is generated before the more reactive species is produced, Scheme (I) (TCP: trichlorophenoxide, TTBP and $TTBP^{\bullet}$: tri-t-butylphenoxide and the corresponding radical).

The system illustrated in Scheme (I) is thus capable of catalytically producing (6), the catalyst being the (chloro)-phenoxocopper(II) complex of which for sake of brevity only the reacting ligands are shown. Metathetical substitution of chloride on the product by the sodium salt affords the unstable bis(phenoxo)copper(II) complex which spontaneously dissociates to copper(I) trichlorophenoxide and a tri-t-butylphenoxyl radical. Rapid reaction of the copper(I) phenoxide with CCl_4 generates a CCl_3 radical and the catalytic species.

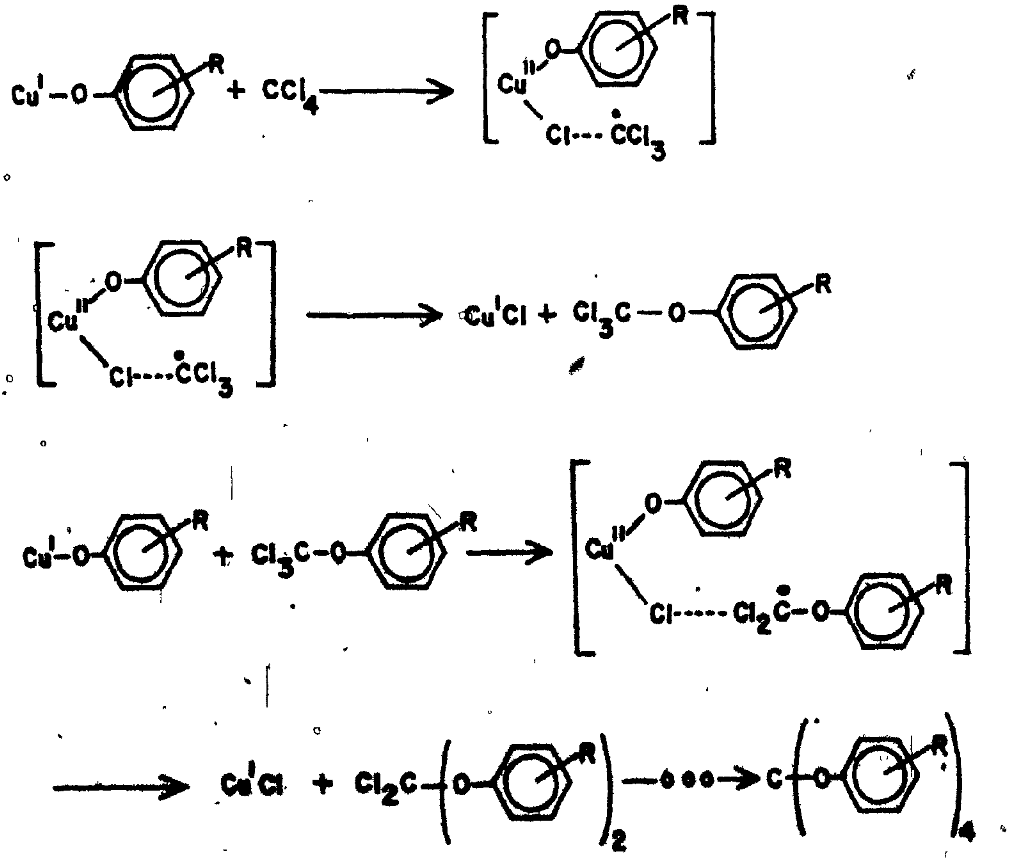


SCHEME I

The observed compound is then formed by coupling of the two radical species.

B. The Mechanism of Ortho Ester Formation

Copper(I) phenoxides capable of producing ortho esters presumably also rely on the formation of tri-halomethyl radicals. The reaction sequence can be visualized as occurring in a cage containing the CCl_3 radical and the unstable copper(II) phenoxide. The production of the C-O coupled trichloromethyl ether depends on the rapid dissociation of the copper(II) phenoxide before the CCl_3 radical can escape the cage to react with the medium, Scheme (II).



(19)

(20)

(21)

(22)

SCHEME II

The orthocarbonates ultimately produced indicate that the intermediate chloromethyl ethers are recycled through the reaction sequences (21,22). Furthermore the observation that ortho esters are the sole products of these reactions even in the presence of excess CCl_4 leads to the conclusion that further reaction of the chloromethylaryl ethers with the copper(I) species must be faster than the corresponding reaction with CCl_4. If the contrary were true a mixture of chloromethyl intermediates $Cl_{3-n}C(OAr)_n$ would be the observed product.

Alternatively, ortho esters could result from the direct nucleophilic substitution of the trichloromethyl ether by phenoxide anion. Although such a possibility would seem unlikely since sodium phenoxides in acetonitrile were found unable to substitute either chloroform or carbon tetrachloride at reflux, it has been shown that dichlorodiphenoxymethanes are considerably more reactive towards substitution by sodium phenoxides.[115]

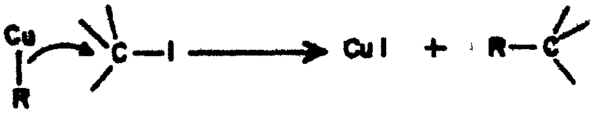
The attack of the polar pyramidal CCl_3 radical[133] at the oxygen is in line with the expected higher electron density in this position.[32] The alternative possibility of attack by the radical at the ring to yield a 4-trichloromethyl cyclohexadienone has to be rejected. Such compounds are known,[98] stable, isolable species and are, with the exception of the tri-t-butylphenoxide reaction, not found with the final product.

The question whether CCl_3 attacks a coordinated phenoxide or a free phenoxy radical still remains largely speculative. Phenoxides carrying ortho methyl substituents were found not to yield ortho esters. 2-methylphenoxide and 2,6-dimethylphenoxide both gave coupled products consistent with the production of free phenoxy radicals. On the other hand, 3-methyl and 4-methylphenoxides both underwent clean ortho ester producing reactions consistent with attack at coordinated phenoxide. The 2-chlorophenoxide and 2,4,6-trichlorophenoxide both gave low yields of orthoformates again suggesting attack on coordinated phenoxide since the copper(II) complexes of these species do not spontaneously decompose to radicals. The steric requirements of the methyl and chloro groups are in both cases roughly equal. It thus seems that if the first collision is unfavorable to chloromethyl ether formation, the phenoxide may dissociate from the copper center and undergo self-coupling reactions. This is a much favored process in the case of alkylphenoxides whereas the higher oxidation potential halophenoxides would be expected to remain coordinated.

It is relevant at this point to note the steric requirements for ortho ester formation. By means of space filling models it is easy to demonstrate that the tri-t-butylphenoxyl radical is unable to undergo C-O coupling with a CCl_3 radical. The oxygen is well enclosed within the two ortho-t-butyl groups. In the case of 2-chloro and 2,4,6-trichlorophenol it is easy to build the tri-phenoxymethyl radicals. However introduction of a fourth 2-chlorophenoxy unit is clearly feasible only for a limited number of conformations. Introduction of a fourth tri-chlorophenoxy unit in the latter case is completely impossible due to excessive crowding around the central carbon. The only possible termination step for these tri-phenoxymethyl radicals is thus hydrogen abstraction from solvent to form the corresponding orthoformates.

C. Copper(I) Phenoxides as Nucleophiles

It is well known that copper(I) can promote reactions involving nucleophilic displacements.^{103} Reactions of organocuprates with alkyl halides are dominated by trends consistent with a mechanism for carbon-carbon bond formation which involves an S_N2 displacement at the carbon of the alkyl halide.^{134} However the actual nucleophile was not specified in the scheme proposed (23).

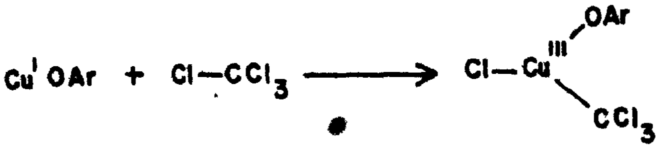


(23)

Copper(I) phenoxides exhibit some typical nucleophilic behavior since chloroform and methylene chloride are markedly less reactive than carbon tetrachloride or tetrabromide. The reaction with methyl iodide is also rather slow. The lower reactivity of copper(I) pentachlorophenoxide towards CCl_4 would also agree with the nucleophilic nature of these cuprous phenoxides.

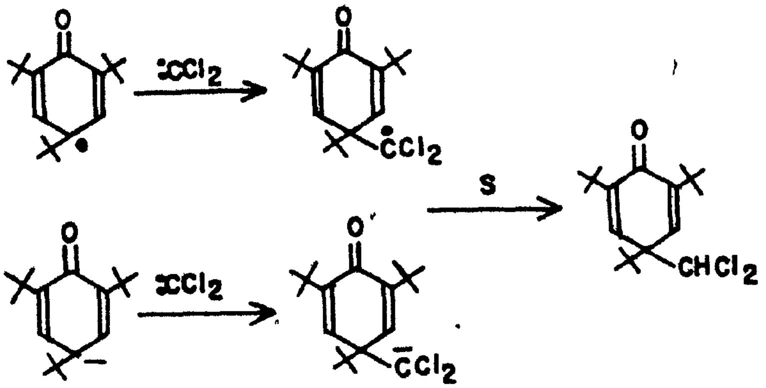
A more recent discussion[135] concerning organocuprate reagents from the view point of redox potentials of the nucleophile and the electrophile would tend to favor a free radical mechanism in cases where the electrophile is sufficiently oxidizing. Under these circumstances, addition occurs via an initial electron transfer to the electrophile followed by a coupling step of the radical with the oxidized form of the cuprate reagent rather than by direct nucleophilic addition.

An oxidative addition mechanism can also be considered. Such reactions are quite common with d^{10} and d^8 transition metal complexes.[136] A two electron process would entail the formation of a copper(III) complex (24).[137] A two electron transfer to carbon tetrachloride would also result in the formation of a trichloromethyl carbanion, an untenable hypothesis in the light of the present experimental evidence, although organomercury derivatives containing CCl_3 carbanion substituents are known.[138] These compounds are thermally unstable and have been shown to be carbene precursors.[138] The carbanion is known to rapidly disproportionate to chloride



$$\mathrm{Cu^{I}OAr} + \mathrm{Cl{-}CCl_3} \longrightarrow \mathrm{Cl{-}Cu^{III}(OAr)(CCl_3)} \qquad (24)$$

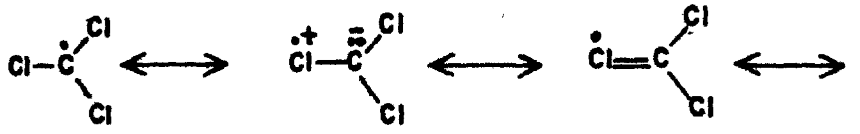
ion and dichlorocarbene.[139] The carbene in the presence of phenoxides or even phenoxy radicals would rapidly generate Reimer-Tieman-type products (25). Furthermore, the reaction of copper(I) trichlorophenoxide with carbon tetrachloride carried



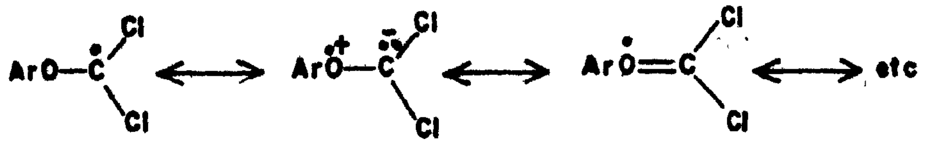
(25)

out in presence of cyclohexene, a good carbene trapping agent[140] and only moderately reactive towards trichloromethyl radicals, gave the usual red-brown complex. Chromatography of the volatile products of this reaction showed the presence of chloroform but no dichloronorcarane.

The fact that chloroform can be observed as a product from these reactions definitely demonstrates that the primary process is the production of trichloromethyl radicals possibly through a one-electron oxidative addition to the copper(I) phenoxide. The generation of trihalomethyl radicals by a one-electron transfer such as illustrated in reactions (16) and (19) would seem to be most consistent. Such reactions of alkyl halides with transition metal complexes undoubtedly proceed by a free radical mechanism.[141] The difference in reactivity between the rather unreactive X_nCH_{3-n} and the much more reactive CX_4 is probably related to steric effects as a result of increased encumbrance in tetrahalomethanes. Carbon tetrachloride and carbon tetrabromide have chain transfer constants much greater than those for chloroform or methylene chloride.[142] Furthermore, α-chlorine atoms are effective in causing stabilization of chloromethane radicals.[143] This would favor the formation of a trichloromethyl radical over the corresponding dichloro and monochloromethyl radicals.



(26)

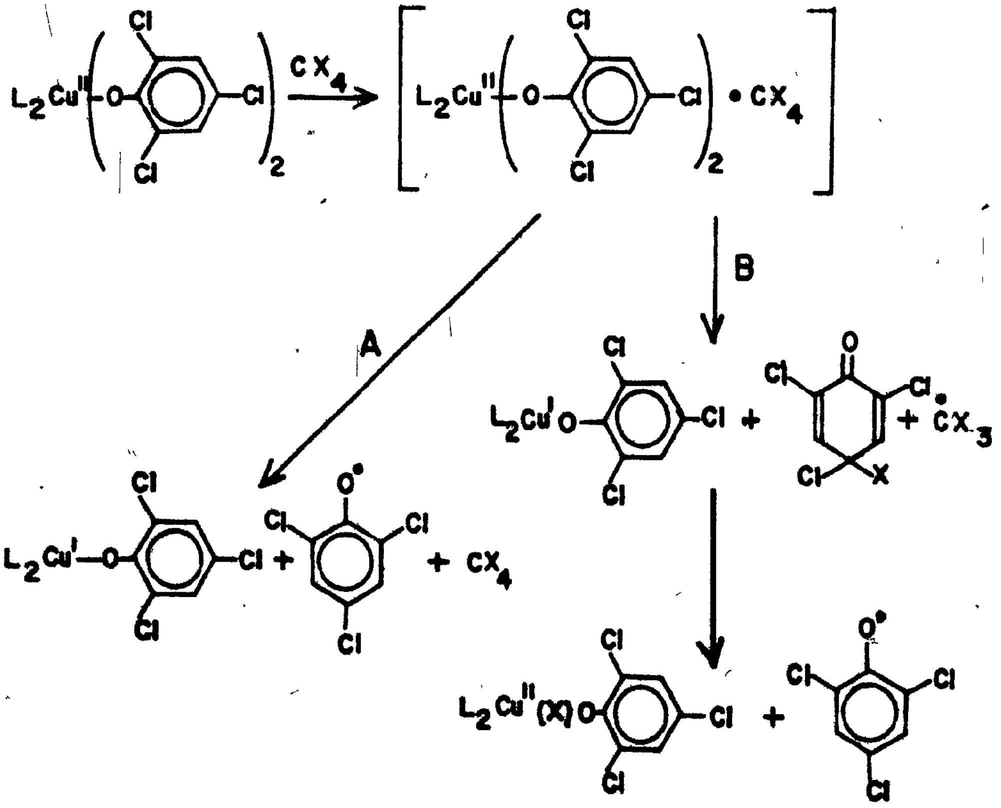


(27)

Such a situation would also explain the higher reactivity of the intermediate trichloromethyl ethers compared to carbon tetrachloride.

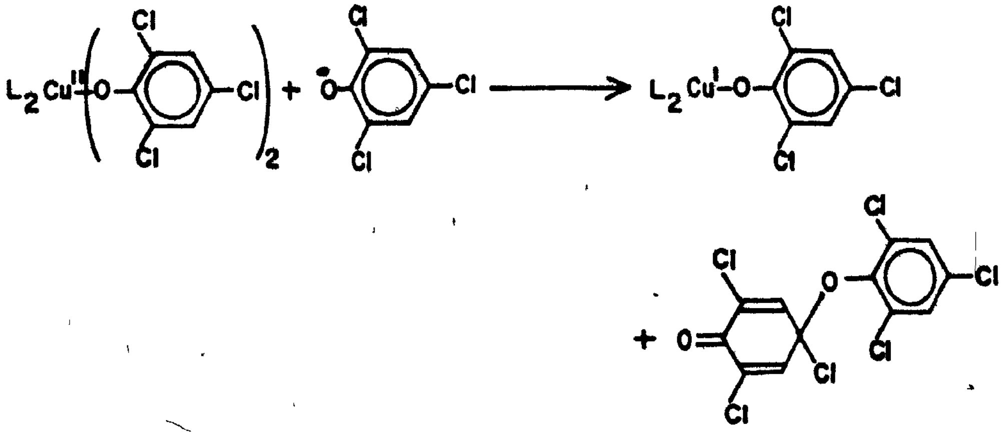
D. Carbon Tetrahalides as Initiators in the Thermal Decomposition of Bis(amine)bis(phenoxo)copper(II) Complexes

Previous observations by Carr and Harrod[81] concerning the effect of CX_4 additives on the thermal decomposition of the bis(amine)bis(trichlorophenoxo)copper(II) complexes stress the drastic diminution of the induction period. The fact that the reaction is free radical initiated calls for a scheme whereby carbon tetrahalides react with the phenoxo-copper(II) complex to produce free radical species capable of entering a propagation process. Such an initiation could possibly rely on the formation of an intermediate charge transfer complex which could presumably undergo either of two pathways leading to the formation of the initial monomeric phenoxy radicals (28A, B).



(28)

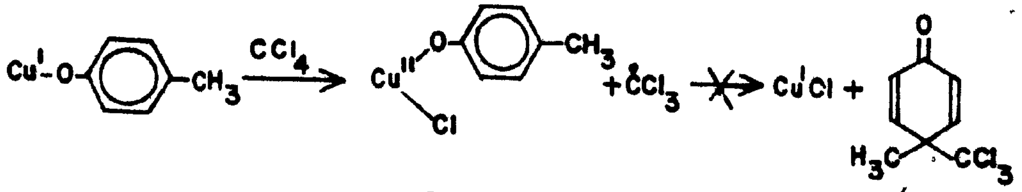
Both routes produce phenoxy radicals, directly as in the case of pathway (28A), or indirectly as in pathway (28B). The CX_4 additives thus reduce the induction period by initiating the reaction through the rapid production of trichlorophenoxy radicals. The latter can then enter into a propagation step (29) to produce non-radical products as previously suggested.[81]



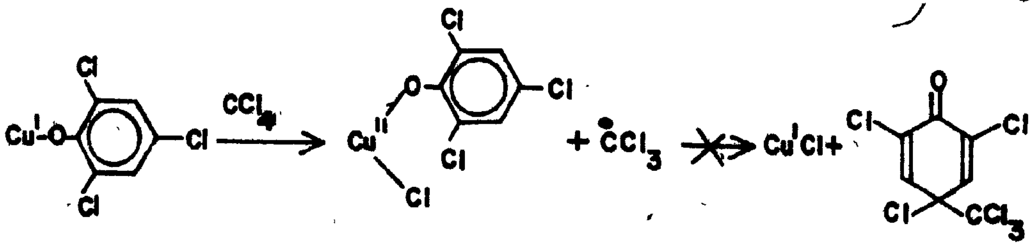
(29)

Following the onset of initiation and the primary propagating steps, copper(I) phenoxides begin to accumulate in the system. The results presented thus far in this work have clearly demonstrated the extreme reactivity of carbon tetrahalides with copper(I) phenoxides. It can thus be questioned whether the CX_4 additives, in addition to initiating the reaction, may not also behave as promoters in the propagation step.

The experimental evidence presented herein concerning reactions of copper(I) phenoxides with carbon tetrahalides has definitely eliminated the previously proposed possibility[81] of phenoxy ligand transfer to trichloromethyl radicals to produce cyclohexadienone compounds (30,31).



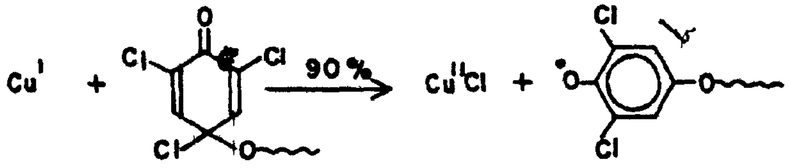
(30)



(31)

It can thus safely be assumed that a reaction such as depicted on the right-hand side of equation (31) is not contributing to the depletion of the phenoxocopper(II) species in a propagation reaction analogous to that illustrated in equation (29).

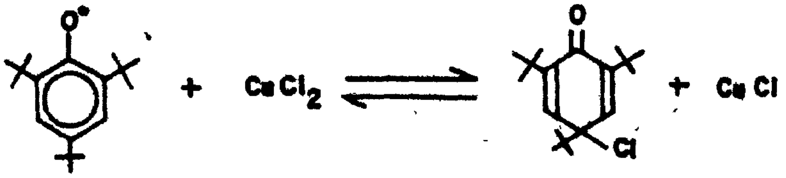
The production of trihalomethyl radicals during the thermal decomposition in the presence of CX_4 additives is minimal. When the reaction was carried out in the presence of a tenfold excess of carbon tetrabromide[81] only ten mole percent of Py_2CuBr_2 was admixed with the final Py_2CuCl_2 product. Such a low value for the bromine content in this copper by-product demonstrates the higher reactivity of copper(I) phenoxides towards quinol ethers relative to carbon tetrahalides (32,33).



(32)

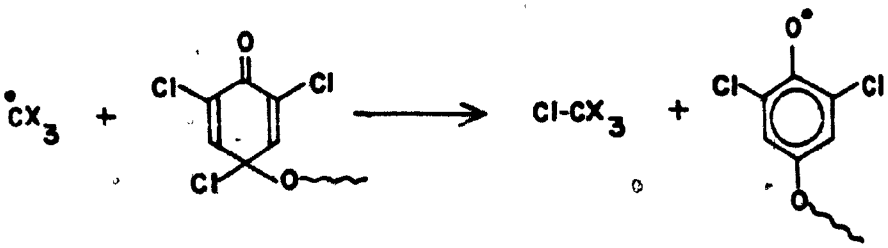
$$Cu^{I} + CX_4 \xrightarrow{10\%} Cu^{II}X + {}^{\bullet}CX_3 \qquad (33)$$

The fact that 4-chloro-4-phenoxy cyclohexadienones are efficient in competing with carbon tetrahalides in transferring a halide to copper(I) is supported in two ways by the present findings. Firstly, the ortho ester forming reaction relies on the increased reactivity towards copper(I) of chloromethyl ethers relative to carbon tetrahalides, (Section 4.B). Secondly, it has been found that the ligand transfer reaction (34) is reversible, demonstrating the possibility of chloride abstraction from 4-chlorocyclohexadienones, (Section 2.C).



(34)

The fact that 10% of the copper(I) produced in the system reacts with the CX_4 additive to produce a CX_3 radical requires that the latter be as efficient as copper(I) in abstracting halide from the quinol ethers (35).



(35)

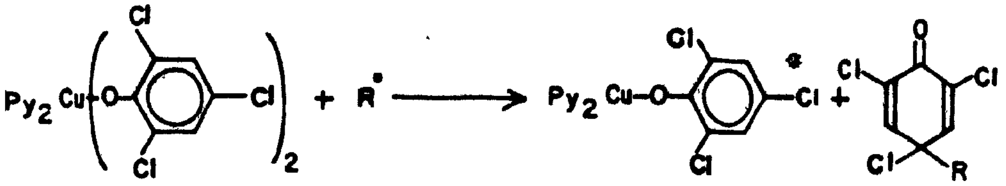
This argument stems from the observation that polymer molecular weight is insensitive to the presence of CX_4 additives.[80] Reaction (32) regenerates the necessary phenoxy radicals for the propagation to occur. Loss of copper(I) through reaction with carbon tetrahalides would result in early chain termination and thus decreased molecular weights.

It can thus be concluded that carbon tetrahalides function primarily as initiators in the thermal decomposition of the phenoxocopper(II) complexes. Furthermore, the evidence presented eliminates the possibility of any drastic promoting effect on the propagation step.

E. Ligand Transfer to Tri-t-butyl-phenoxyl Radical

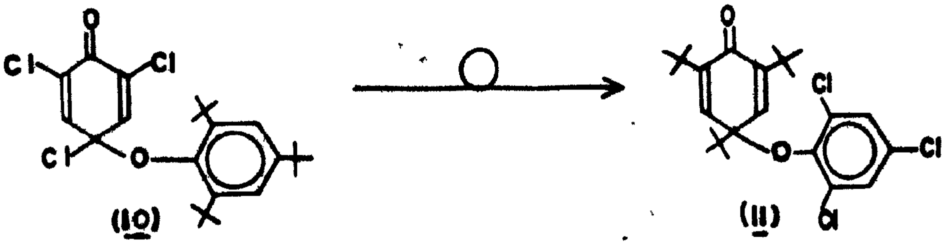
The series of reactions of the tri-t-butylphenoxyl radical with a number of copper(II) containing compounds was originally undertaken to obtain a better understanding of the initial step in the thermal decomposition of the bis(pyridine)bis(trichlorophenoxo)copper(II) complex, particularly the importance of the ligand transfer reaction[81]. Unfortunately reactions such as

(36), where $R^{\bullet}$ is the tri-t-butylphenoxyl radical, were hampered it seems by an inherent drawback of the radical, its high steric hindrance at the oxygen and on the ring. The



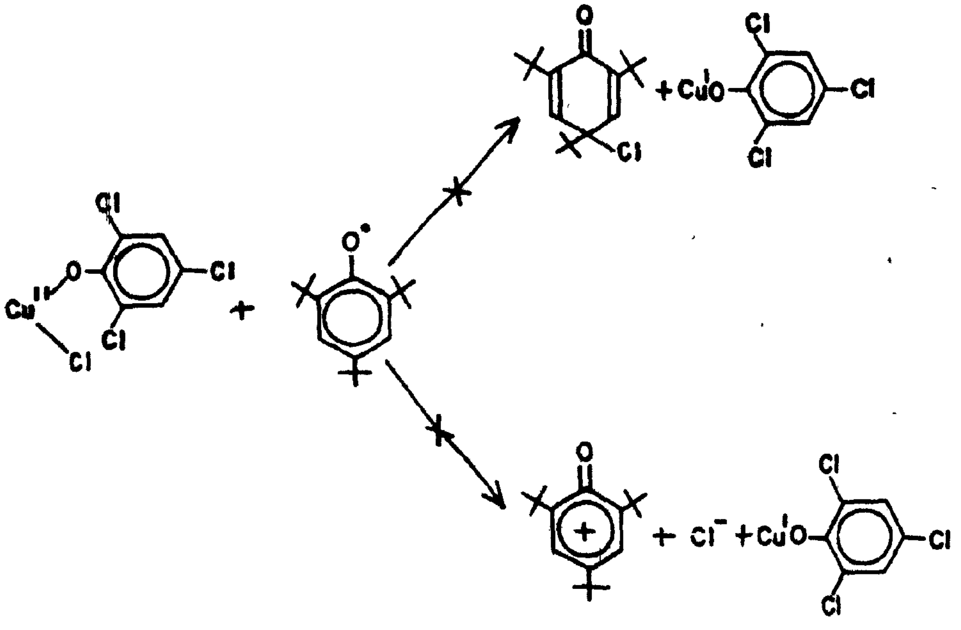
(36)

expected 4-chloro-4-tri-t-butylphenoxy cyclohexadienone (10) was not observed. Had it formed and were it dissociatively unstable (37), the 4-t-butyl-4-(2,4,6-trichlorophenoxy)cyclohexadienone (11) would have been obtained. The latter compound can be isolated following simultaneous oxidation of tri-t-butylphenol and trichlorophenol over manganese dioxide.[82]



(37)

The only ligand observed to be transferred was chloride and for that matter only from cupric chloride. The copper(I) trichlorophenoxide/CCl_4 reaction product left the radical unchanged, demonstrating that even in that compound it cannot approach the copper center close enough to undergo a non-bonded electron transfer (38). Oxygen containing ligands coordinated to copper



(38)

are known to promote this type of oxidation of free radicals.[121] It could be argued that the red-brown complex is a polynuclear species in which the chloride ligands are bridging groups thus making them less accessible to bridge with the phenoxyl radical prior to electron transfer.

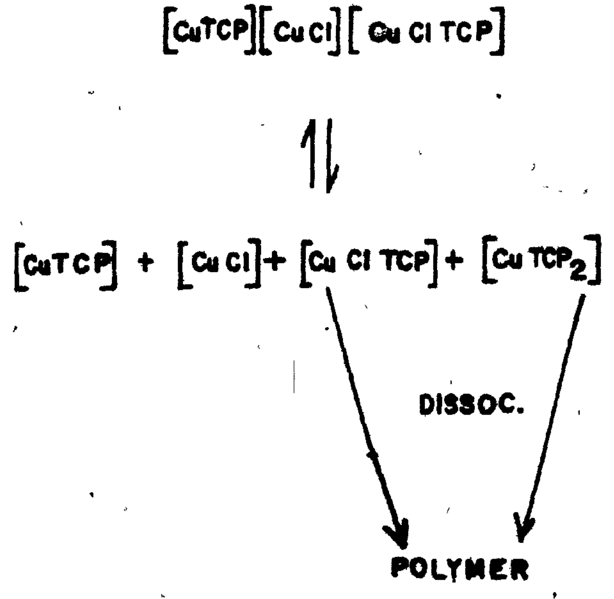
F. The Nature of the Products Obtained from Copper(I) Polyhalophenoxide/CCl_4 Systems

2,4,6-trichlorophenol and pentachlorophenol both have higher oxidation potentials than alkyl phenols. This may be in part the reason why the corresponding copper(I) phenoxides do not attain complete reaction with CCl_4 to yield ortho esters under normal conditions. The forward reaction in the system studied by Vofsi and his co-workers for the addition of CCl_4 to olefins in the presence of CuCl was found to be rather slow at room temperature.[101,129] Furthermore, quasiequilibrium was attained at 1.5% conversion. These results tend to indicate that the reaction of copper(I) phenoxides with carbon tetrachloride would attain an equilibrium before total consumption of the copper(I) species. If the very slow forward reaction in Vofsi's system is the reason for incomplete conversion, this is obviously not the case with copper(I) phenoxides. Here it can be postulated that complexation of the unreacted cuprous phenoxide with the copper(II) phenoxide product produces a mixed oxidation state polynuclear complex which cannot undergo further reaction with CCl_4. The stability of this complex with respect to homolytic dissociation of the copper(II) phenoxide moiety, relative to the alkylphenoxy analogues, is assured by the combined effect of stabilization by the copper(I) moiety and the higher oxidation potential of the coordinated halophenoxides.

The intensely colored mixtures obtained from these reactions contain both oxidation states of copper in a ratio close to 2:1 for Cu(I):Cu(II). Such mixed oxidation state complexes are well-known and generally possess characteristic dark colors.[144,145] The observations made on the dark products of the present reactions tend to support the hypothesis that they are polynuclear copper complexes which dissociate relatively easily. Many copper(I)[146] and copper(II)[147] clusters have been characterized and although it is speculative to propose the existence of polymeric phenoxo copper complexes in acetonitrile such a hypothesis provides a relatively simple and consistent explanation for the properties of these solutions.

Over the last few years a considerable body of information has accumulated pertaining to the propensity of copper to form mixed valence clusters.[148-151] Particularly relevant to the compounds being discussed herein is the isolation of a purple complex formed by the reaction of copper(II) and D-penicillamine.[150] The intensely colored compound was shown to be an anionic Cu(I)/Cu(II) cluster, $[\mathrm{Cu(II)}_6\mathrm{Cu(I)}_8\mathrm{(D\text{-}Pen)}_{12}\mathrm{Cl}]^{5-}$, by X-ray diffraction. In this complex and other polynuclear mixed valence complexes,[148,149] mercaptides often serve as bridging groups stabilizing the copper(I) moiety whereas the amino acid residues will serve to stabilize the copper(II) units.[150] The outstanding property of these clusters is that copper(II) mercaptides can exist in the presence of copper(I) in spite of the fact that reduction of the higher oxidation state would normally occur with simultaneous disulfide formation. The analogy can be drawn with the copper(I) halophenoxide/CCl_4 reaction products. The inclusion of copper(II) phenoxide within a cluster also containing copper(I) phenoxide can similarly result in stabilization of the copper(II) species relative to homolytic dissociation. It is relevant to note that chloride[148] and phenolate[151] ligands have also been found to participate as bridging groups between copper nuclei.

The solutions containing the product from the polyhalophenoxo copper(I)/CCl_4 reactions decompose on dilution. Addition of acetonitrile solvent to these dark-colored solutions causes them to discolor and cloud with the eventual precipitation of polymer. Heating the dark solutions also leads to the formation of polymer following a short induction period. The effects of heat are possibly manifold, however, the two foregoing observations can be cited to support the existence of a dissociative equilibrium. Assuming the probable stoichiometry for the complex as established by analysis (Table II.2), the following equilibrium can be postulated (39).



(39)

Copper(II) species are prone to dissociate in acetonitrile.[103] This has been found to be true for unligated copper(II) trichlorophenoxide (Section E.iii). This amorphous compound when put in contact with acetonitrile, spontaneously generates polymer. By analogy the chloro(trichlorophenoxo)copper(II) species formed in the dissociative equilibrium (39) is believed to also be responsible for the appearance of polymer when the intensely colored solutions are either diluted or heated.

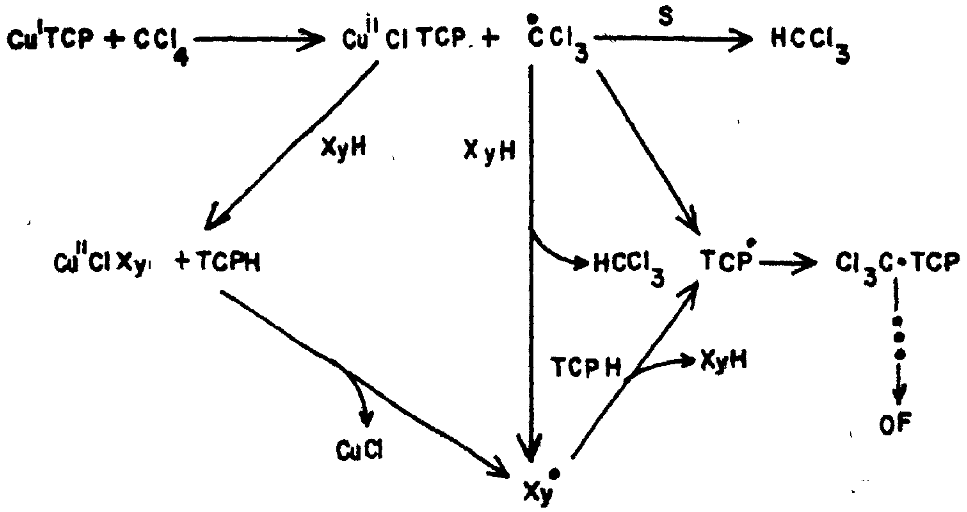
An equilibrium such as illustrated in (39) is further supported by the fact that the addition of copper(I) species to these solutions tends to stabilize the mixture and increase the induction period for decomposition at reflux.

The species obtained by the addition of copper(II) trichlorophenoxide to solutions of either cuprous chloride or copper(I) trichlorophenoxide in acetonitrile (Section E.iii) are likely to be similar to that depicted on the left-hand side of equilibrium (39). It was found in these experiments that copper(II) species in acetonitrile can be stabilized towards disproportionation if copper(I) is present. There is however a 3 Cu(II)/Cu(I) threshold beyond which spontaneous appearance of polymer is observed. The products obtained by mixing in acetonitrile solution copper(I) and copper(II) phenoxide complexes as outlined, behave similarly to the copper(I) halophenoxide/CCl_4 reaction products with respect to dilution and heating.

The amount of ionic halide was determined by two different analytical procedures (Section 3.E.iii, (a) and (b)). The occurrence of chloride in the dark complexes is to be expected if the reaction with CCl_4 follows a one electron oxidative addition to copper(I) leading to the formation of a trichloromethyl radical. The ultimate fate of the latter where copper(I) polyhalophenoxides are concerned, is hydrogen abstraction from solvent to yield chloroform.

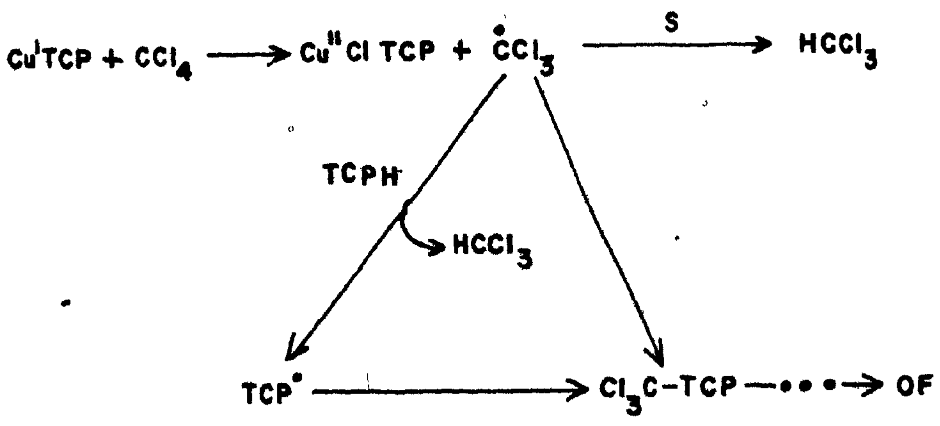
It was also demonstrated that coordinated halide would undergo metathetical reactions with sodium phenoxides (Section 3.E.iv). These reactions were not amenable to quantification in terms of the amount of labile halide present since the dark complex acted as a catalyst for the polymerization of the added sodium phenoxide. The amount of NaCl recovered from the reaction product was in accord with the quantity of sodium phenoxide initially introduced.

The intermediate nature of the products from the copper(I) polyhalophenoxide/CCl_4 reactions, in the sense that they have the potential to resume reaction to produce ortho esters, was demonstrated by carrying out a number of reactions in the presence of reducing agents. Tri-t-butylphenol, xylenol and ascorbic acid all bleached the dark mixed Cu(I)/Cu(II) trichlorophenoxide complex to regenerate cuprous chloride and produce the corresponding orthoformate of the polyhalophenol. In Scheme III, xylenol is used to illustrate a possible mode of action of these hydrogen donors (TCP: trichlorophenolate, XyH: Xylenol, OF: trichlorophenyl orthoformate).



SCHEME III

A modification of Scheme III would also allow an explanation for the occurrence of roughly 10% orthoformate in the product of the copper(I) polyhalophenoxide/CCl_4 reactions. Small amounts of free polyhalophenol could be inadvertently introduced in the reaction medium through hydrolysis of the sodium phenoxides during weighing. Such a situation would result in the presence of variable amounts of free phenols and consequently yield aleatory quantities of halophenyl orthoformates. In Scheme IV, trichlorophenol behaves as a reductant by transferring hydrogen atoms to the initially formed trichloromethyl radicals. The newly generated phenoxy radical can then react with other trichloromethyl radicals to form the trichloromethyl ether and eventually the corresponding trichlorophenyl orthoformate as described earlier (c.f., page 106).



SCHEME IV

The sequence illustrated in Scheme IV is supported by the observation that the copper(I) trichlorophenoxide/CCl_4 reaction, when carried out in the presence of one equivalent of added trichlorophenol (Section 2.E.iv), led to a substantial increase in the yield of isolated ortho ester.

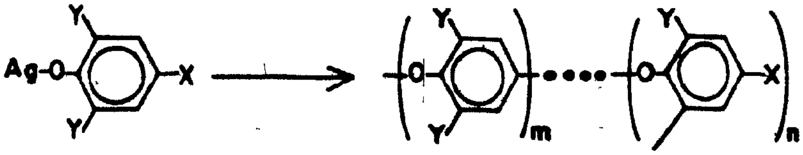
The essential difference between Schemes III and IV rests with the ability of xylenol to coordinate and ultimately reduce the copper(II) species. In the case of the trichlorophenol the latter cannot be expected to be a better reducing agent than the phenoxide already coordinated. Rather here, it is proposed that it acts as a transfer agent competing with solvent to transfer a hydrogen atom to the CCl_3 radicals to produce chloroform and trichlorophenoxy radicals. The latter would subsequently in a radical-radical reaction with the CCl_3 species yield the trichloromethyl ether precursors of the orthoformates.

CHAPTER III

I. INTRODUCTION

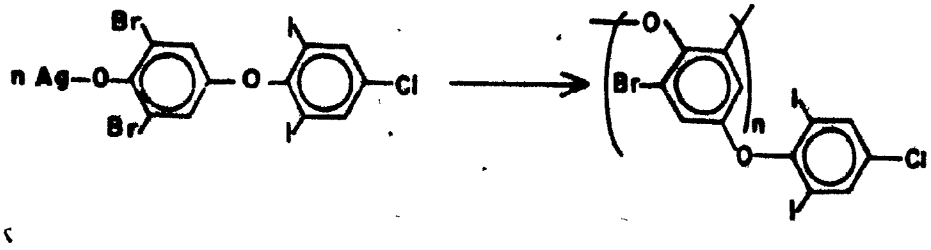
A. Polymers from Trihalophenols, the Branching Hypothesis

Hunter[153] first isolated poly(halophenylene oxide) polymers as a result of the thermal decomposition of silver halophenoxides. He indicated that two types of enchainment were present on the basis of chemical analysis results (1).



(1)

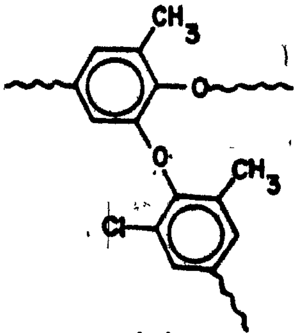
It was also established that iodine was displaced somewhat more readily than bromine, which in turn was more reactive than chlorine and that para halogen reacted more readily than ortho halogen. Furthermore Hunter believed that only halogen in a ring carrying a free ionisable phenol group could be displaced (2).[154]



(2)

Serious doubt can be cast on the structure proposed for this polymer in view of the present knowledge concerning the oxidative coupling of halophenoxides (Chapter I).[155]

In a first detailed study of the decomposition of 2,4,6-trihalophenoxide complexes under a variety of conditions to poly(halophenylene ethers), the term branched polymer was used to describe the products.[67] Even though the molecular weight of a poly(dichlorophenylene oxide) is of the order of 10,000, its intrinsic viscosity is always approximately 0.05 dl/g. By way of comparison, poly(2,6-dimethylphenylene oxide) of molecular weight 10,000 has an intrinsic viscosity of 0.30 dl/g. Similar arguments were applied by Hay[156] when he found that the oxidative polymerization of 2-chloro-6-methylphenol gave high molecular weight polymer with a lower than expected intrinsic viscosity. Analysis of the polymer also showed loss of chlorine (10-15%) during the polymerization. Branch points such as (1) were assumed in this instance.



(1)

The branched structure of polyhalophenoxide polymers was further supported when their ^{1}H nmr spectra were first published. Tsuruya[157] thermally decomposed the hexamethylphosphoramide copper(II) complex of 2,4,6-trichlorophenol and isolated the product polymer. The ^{1}H nmr spectrum of the trichlorophenol polymer shows overlapping broad peaks. This indicated, it was presumed, an additional substitution mode to the expected linear mode and could possibly be attributed to substituent branches in the 2,6 positions. Similar poorly resolved and complex spectra were observed for the polymers obtained from other copper(II) trichlorophenoxide systems.[80] On the other hand polymers having a high proportion of 1,4-coupled units gave remarkably sharper spectra. For instance the products obtained from the thermal decomposition of 2,6-dichlorophenoxide copper(II) complexes containing a 4-bromo or 4-iodo substituent, afforded ^{1}H nmr spectra featuring a sharp singlet attributed to the 2,6-dichloro-1,4-phenylene oxide unit. A smaller doublet at lower field than the singlet and its counterpart partially obscured by the singlet were assigned to minor branched structures.

The polymer obtained by the oxidative coupling of 2,4,6-tribromophenol in the presence of copper in acetonitrile produced a ^{1}H nmr spectrum consisting of a number of sharp peaks.[158] A linear structure would entail an nmr spectrum consisting of a singlet. However at least four peaks are prominent in addition to a few minor features thus indicating, as the authors stressed, that ortho bromine had also been eliminated. The high resolution of these peaks as well as the presence of a band attributed to the proton of an OH end group tend to indicate that the product is a polymer of low molecular weight. The modest degree of polymerization was further substantiated by an observed low intrinsic viscosity (0.02 dl/g).

Infrared spectroscopy has been of limited value in determining the structure of poly(phenylene oxides). However, in one particular case, branching in poly(1,4-phenylene oxide) was possibly demonstrated by infrared spectroscopy.[159] An absorption at 970 cm^{-1} was assigned to side chain substitution by phenoxy units after the examination of the infrared spectra of model compounds. A polymer containing 5% of 1,2-coupled units did not present any marked difference in its vibration spectrum when compared to a completely 1,4-coupled polymer.

Very little data is thus at hand to permit a clear assignment of the actual structure of the polymers obtained from 2,4,6-trihalophenols. The probes available do indicate that the enchainment mode is quite different in both the linear polymer obtained from 4-bromo-2,6-dichlorophenol and the branched polymer obtained from trichlorophenol.

Branching as such remains a simple hypothesis to explain the peculiar spectral and solution properties of the polymers obtained from trihalophenols. In this section a new look is taken at a number of poly(halophenylene oxides) obtained from the copper(I) systems described in the previous chapter as well as from various other copper complex systems. Physical measurements have been undertaken on these polymers in hope of attaining a better understanding of their microstructure.

B. The Relationship Between Intrinsic Viscosity and Molecular Weight for Poly(halophenylene oxides)

i. Introduction

The viscosity of a dilute polymer solution is associated with the frictional resistance of the molecules in motion with respect to each other in the solvent medium.[160] The size and shape of the molecules are most important in determining the magnitude of the effect. Other factors, such as the possibility of forming hydrogen bonds, the presence of charges on the macromolecule, as well as the effect of solvent on the secondary structure are also important factors affecting the viscosity of a polymer solution.

For a series of linear homologous polymers it has been recognized[160] that the intrinsic viscosity is directly proportional to a power of the molecular weight:

$$[\eta] = K\ M^{a}$$

K and a are dependent on the type of polymer, the solvent and the temperature. They are empirically determined from the intercept and the slope of a log-log plot of intrinsic viscosity versus molecular weight.

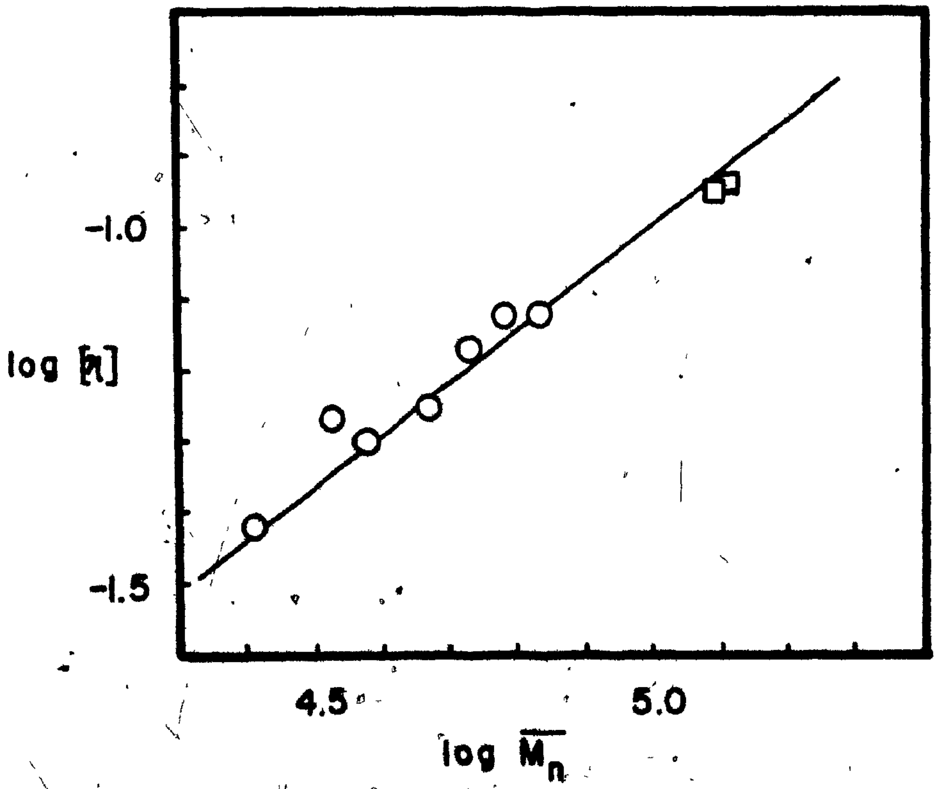
Molecular weights are commonly determined by measuring a colligative property of the polymer thus yielding a number-average molecular weight, and intrinsic viscosities are obtained by extrapolation to zero concentration of an η_{sp}/c versus c plot, where concentration is expressed in g/dl.

A branched molecule extends over a smaller average volume in solution than a linear molecule of the same molecular weight. In other words, the time-average distribution of segments about the center of gravity of a molecule depends on chain structure. Other factors being equal, a branched molecule has a more compact distribution than a linear molecule. Thus a change in branching degree for a comparable molecular weight would show up in the double logarithmic plot of intrinsic viscosity versus molecular weight. It is expected that a slower increase in $[\eta]$ vs M_n will be observed for a branched polymer.

ii. Mark-Houwink Plots for Linear and Non-Linear Poly(halophenylene oxides)

The molecular weight-viscosity data obtained by Carr and Harrod[80] can be used to construct the plot shown in Figure III.1. It can be seen that data points for polymers which have been shown to have a linear enchainment fall on the same line as the data pertaining to polymers believed to be branched.

FIGURE III.1. Intrinsic viscosity-molecular weight relationship for poly(chlorophenylene oxides) in CH_2Cl_2 at 25°. ○: non-linear polymer, ☐: linear polymer. Data taken from 80.


-1.0
-1.5
log [η]
4.5
5.0
log $\overline{M_n}$

The slope and intercept respectively yield values for a: 0.67 and for K: 4.27×10^{-5}. The values for these constants agree with those obtained from poly(2,6-dimethylphenylene oxide) under a variety of conditions as shown in Table III.1. Although it may seem that the value for K is rather low for the halo polymers, it is known that K is very sensitive to the molecular weight distribution,[161] especially if the molecular weight data is obtained on unfractionated samples using $\overline{M_n}$ rather than $\overline{M_w}$. The values for K would tend to diminish if less polydisperse samples are used or if weight average molecular weight data are used to construct the Mark-Houwink plot. This factor may be the cause of the low K values in the present case since G.P.C. curves of a few typical polymers obtained from these systems indicated that the polymers have fairly narrow molecular weight distributions.

Temperature on the other hand affects the K and a values to a lesser extent.[161] For $a > 0.70$, K becomes essentially independent of temperature. Furthermore, measurements on poly (2,6-xylenol) in toluene, chloroform and chlorobenzene have shown that the unperturbed dimension of the chain-coil of this polymer is relatively small and does not vary appreciably in the solvents used.[162]

Similar plots can be obtained for other data existing in the literature.[67,156,157] These are illustrated for the chlorinated and brominated poly(phenylene oxides) in Figure III.2. The supporting data for these plots, along with the

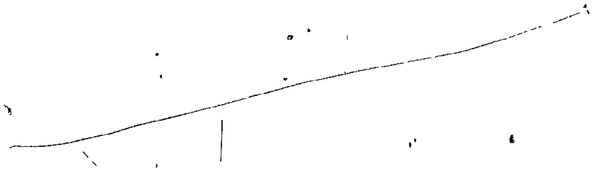
TABLE III.1

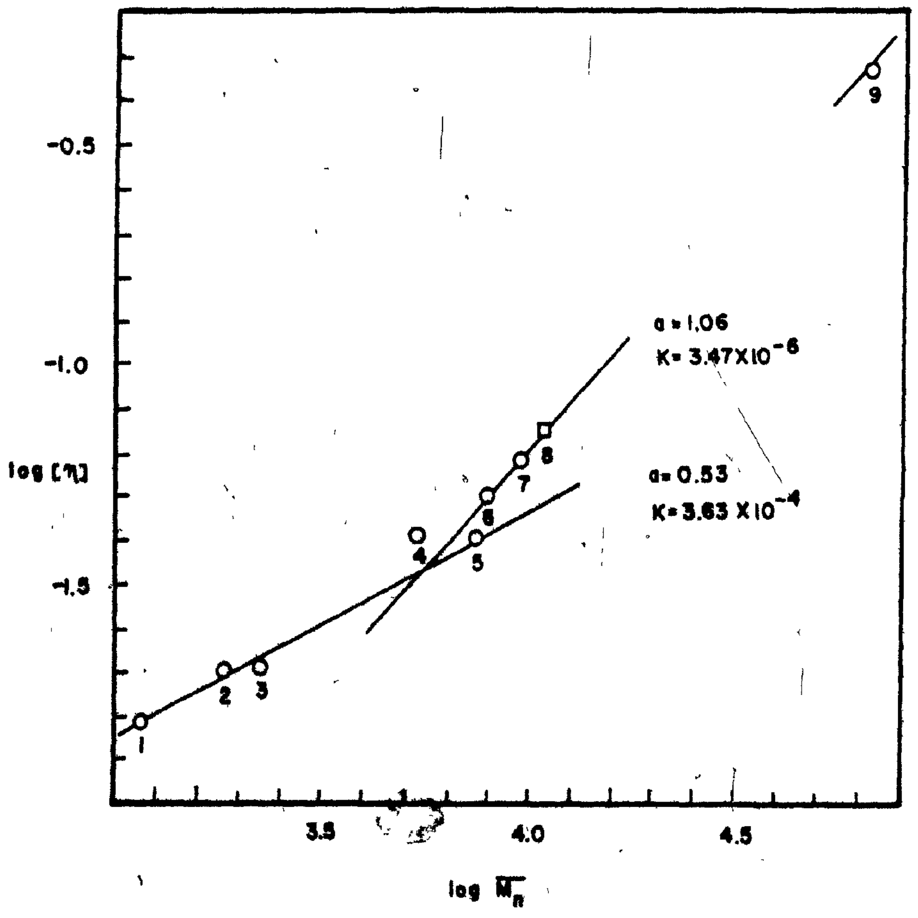
VISCOSIMETRIC COEFFICIENTS K AND a FOR POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

Solvent	T (°C)	K ($x10^4$)	a	Reference
Toluene	25	2.85	0.68	183
Chlorobenzene	25	3.78	0.66	183
Chloroform	25	4.83	0.64	183
Carbon tetrachloride	25	7.55	0.585	184
Benzene	25	2.60	0.69	184
(a)		3.80	0.73	63
Benzene	29.4	4.66	0.70	185

(a) No solvent or temperature was specified.

FIGURE III.2. Intrinsic viscosity-molecular weight relationship for halogenated poly(phenylene oxides). Supporting data in Table III.2.

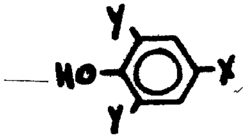




-0.5
-1.0
-1.5
log [η]
3.5
4.0
4.5
log $\overline{M}_n$
1
2
3
4
5
6
7
8
9
a = 1.06
K = 3.47 X 10^{-6}
a = 0.53
K = 3.63 X 10^{-4}

TABLE III.2

SUPPORTING DATA FOR FIGURE III.2

Data Point Number			Polymerization Technique (a)	$[\eta]$ $(\frac{dl}{g})$[b]	$\overline{M}_n$	Reference
	X	Y				
1	pentachloro		A	0.015	1,200	67
2	Br	Br	C	0.02	1,900[c]	158
3	Br	Br	B	0.02	2,300	67
4	Br	Br(3-OMe)	A	0.04	5,500	67
5	Br	Br	A	0.04	7,500	67
6	Cl	Cl	A	0.05	8,000	67
7	Cl	Cl	B	0.06	9,600	67
8[d]	Br	Cl	B	0.07	11,000	67
9	H	Cl,Me	D	0.47	71,000	156

[a] A: thermal decomposition of the silver phenolate; B: thermal decomposition of the bis(pyridine)bis(phenoxo)copper(II) complex; C: cupric nitrate catalyst in CH_3CN at room temperature; D: copper/pyridine catalyst at room temperature.

[b] Intrinsic viscosities in $CHCL_3$ at 25°.

[c] Molecular weight determined in this laboratory.

[d] Because of the nature of the monomer this polymer is expected to be linear.[80]

origin of the polymers are listed in Table III.2.

The values for K and a of the chlorinated polymer series (6,7,8,9) are somewhat out of line when compared with the values for the poly(2,6-dimethylphenylene oxide) listed in Table III.1. However, within the error limits normally assumed for viscosimetric data, the points fit a straight line to an excellent degree. The coincidence of the data point corresponding to polymer (9) with the curve is most likely fortuitous. The chemical composition of this polymer is different in that one of the chlorines in the monomer is replaced by a methyl group. For the brominated polymers the K and a constants assume normal values. The low value for a is in line with the behavior expected since in the low molecular weight range (mostly less than 10^4), a becomes 0.50 irrespective of the solvent.[163]

The remarkable feature of the plot pertaining to the chlorinated polymers in Figure III.2 is the colinearity of the data point 8 for a linear polymer with the data points of polymers considered to be branched. This, and the previously cited similar behavior of data originating from an independent laboratory (Figure III.1), led to the questioning of the branching hypothesis. The behavior observed for these linear and so-called "branched" polymers is at variance with that expected in the intrinsic viscosity-molecular weight relationship. In extreme cases, highly branched polymers exhibit intrinsic viscosities independent of molecular weight.[160] On the other hand the presence of short chain branches has little effect on the solution viscosities of polymers. In this case the linearity of the Mark-Houwink plots would be quite well preserved, but the nmr spectra would not show gross differences for polymers considered to be branched and polymers known to be linear. At most, short chain branches would show up as a few additional resonances associated with the increased number of chain ends. This is not so in the present case since the so-called branched polymers yield drastically different spectra compared to those obtained from linear polymers.[80]

The foregoing discussion of existing data pertaining to poly(halophenylene oxides) led to the conclusion that the structure of these polymers needed to be reexamined. The accepted branching hypothesis, although largely in agreement with the nmr spectra and the fact that the so-called branched polymers yield brittle films, clearly does not explain the intrinsic viscosity-molecular weight relationships.

2. RESULTS

A. Polymers from Copper(I) Trichlorophenoxide Systems

i. Introduction

During the course of investigations concerning reactions of copper(I) phenoxides, it was found that polyhalophenoxo copper(I) complexes did not undergo complete reaction with carbon tetrachloride. Unexpectedly, the effect of heat on the resultant dark solutions was to precipitate polymer rather than to push the reaction to completion to afford ortho esters. On first examination the product polymers seemed to exhibit much simpler ^{1}H nmr spectra, possibly indicating the formation of a new type of polymer as result of a stereoregulating effect of the polynuclear copper complex. This reasoning prompted an investigation of a number of reaction parameters in an effort to delineate the factors affecting the structure of these polymers.

ii. Thermal Decomposition of the 2,4,6-trichlorophenoxo Copper(I)/CCl_4 Reaction Product

The preparation of cuprous phenoxides and their reaction with carbon tetrachloride have been described in a previous section (Chapter II.2.D).

The addition of variable amounts of carbon tetrachloride

(0.2-2.0 equivalents) to the cuprous trichlorophenoxide prior to heating has no effect on the yield nor on the structure of the isolated polymer, Table III.3. The slight variation (±10%) observed in the yields of isolated polymers is related to the difficulty encountered during the separation of the polymer from the sodium chloride. The precipitate recovered from the thermal decomposition containing both products was extracted with a solvent for the polymer and filtered. The extreme fineness of the sodium chloride resulted in frequent clogging of the filter and variable losses of polymer during work-ups.

There seemed to be a limiting minimum amount of CCl_4 required for the induction of polymerization. For instance, the addition of less than 0.10 equivalent of added CCl_4 did not succeed in inducing polymerization. Also, a solution of 2,4,6-trichlorophenoxocopper(I) in acetonitrile containing no carbon tetrachloride could be kept at 70° for extended periods under nitrogen without any signs of decomposition.

iii. Preparation of Mixed Oxidation State Complexes $[Cu(I)TCP]_n[Cu(II)TCP_2]_m$ and their Thermal Decomposition

The title compounds (TCP: 2,4,6-trichlorophenoxide) were obtained as dark red/brown amorphous powders by mixing cuprous chloride and sodium trichlorophenoxide in acetonitrile followed by the required amount of copper(II) trichlorophenoxide, filtering the sodium chloride and stripping the solvent. All

TABLE III.3

POLYMER YIELDS FROM 2,4,6-TRICHLOROPHENOXOCOPPER(I) (0.23M) IN THE PRESENCE OF CCl_4

CCl_4 Equivalents	T (°C)	Time	Yield (%)
0.05	73	5 hrs	a
0.10	70	5 hrs	-
0.20	70	instantaneous	66
0.50	80	instantaneous	75
1.00	80	instantaneous	59
2.00	65	instantaneous	66

[a] Solution was brought to 90° without any change.

mixed oxidation state complexes had infrared spectra similar to that of unligated copper(II) trichlorophenoxide.[128] No acetonitrile was ligated in any of the samples, as was easily demonstrated by the absence of an i.r. absorption at 2260 cm^{-1} corresponding to the nitrile stretch of the solvent.

Samples of the complexes were weighed in a flask and decomposed either in refluxing acetonitrile (81°) or toluene (110°). The acetonitrile reactions were homogeneous initially but precipitated polymer during reaction. In toluene, the complexes were insoluble but the polymer went into solution. The results along with some characteristics of the polymers are summarized in Table III.4.

All the samples decomposed smoothly in the refluxing solvent. One exception was observed with the complex $[Cu(I)TCP]_{10}[Cu(II)TCP_2]$ in refluxing acetonitrile which after six hours had not undergone any observable decomposition. Carbon tetrachloride was thus injected in order to induce decomposition. Another exception was the spontaneous decomposition of the $Cu(II)TCP_2$ complex in acetonitrile. This matter has already been treated previously (Chapter II.2.E).

Polymers obtained from the decomposition in acetonitrile had lower molecular weights and accordingly lower intrinsic viscosities. In toluene higher molecular weights were observed. These trends correlated with the observation that the ^1H nmr spectra became progressively more complex as molecular weight increased. This will be discussed in the next section.

TABLE III.4

POLYMERS OBTAINED BY THERMAL DECOMPOSITION OF $[Cu(I)TCP]_m[Cu(II)TCP]_n$

Cu(I)/Cu(II)	Polymer Identification	Solvent	Yield (%)	$\overline{Mn}$	$[\eta]$[a]
10	$TCP10_A$	CH_3CN[b]	89	5,900	0.041
10	$TCP10_T$	Toluene	81	-	-
5	$TCP5_T$	Toluene	77	-	-
2[c]	$TCP2_A$	CH_3CN	79	-	0.041
1	$TCP1_A$	CH_3CN	83	-	0.042
1	$TCP1_T$	Toluene	72	32,600	0.090
0.5	$TCP0.5_A$	CH_3CN	-	-	0.042
0	$TCP0_A$	CH_3CN[d]	94	13,300	0.049

[a] Intrinsic viscosities in $CHCl_3$ at 25° ± 0.02°.

[b] Sample did not decompose after 6 hours at 81°, CCl_4 was added to induce decomposition.

[c] $Cu(I)TCP/CCl_4$ reaction product, filtered to remove NaCl, evaporated to remove CCl_4 and decomposed in CH_3CN.

[d] Spontaneous decomposition in acetonitrile at room temperature.

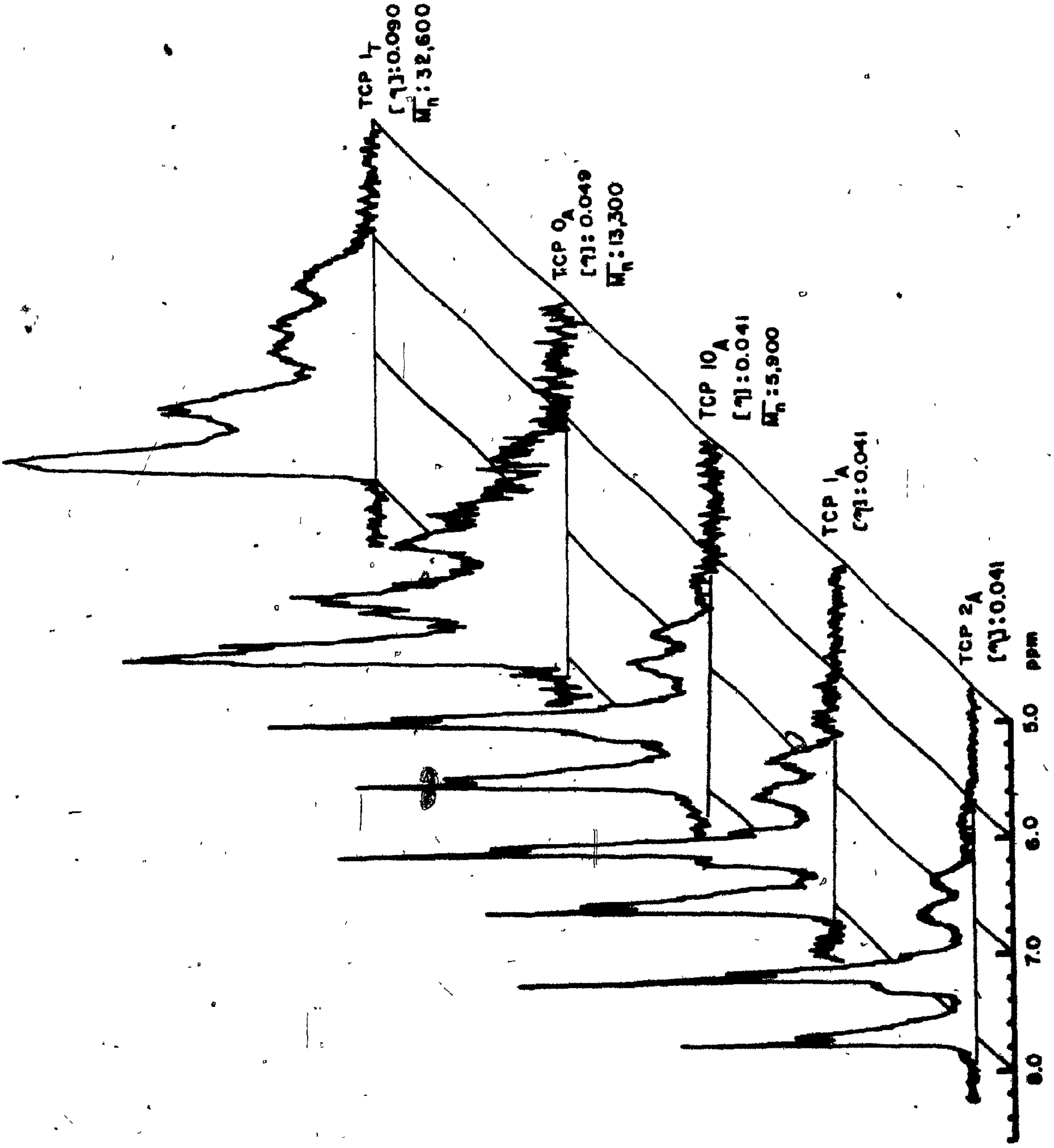
iv. ^{1}H nmr Spectra of the Polymers Obtained from the Copper(I) Trichlorophenoxide Systems, Comparison with Intrinsic Viscosity and Molecular Weight Data

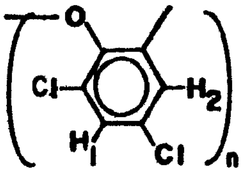
The thermal decomposition in two different solvents of the series of mixed oxidation state complexes containing varying ratios of copper(I) to copper(II) led to the isolation of a number of polymers having molecular weights spanning an order of magnitude. A fair range of intrinsic viscosities was also observed.

Comparison of these polymer characteristics with the ^{1}H nmr they afforded (Figure III.3) immediately stressed the drastic effect of increasing molecular weight on the overall linewidth of the proton spectra. The effect is so marked for these poly(chlorophenylene oxides) that it can be questioned whether all the polymers in this series have the same microstructure. It is with this possibility in mind that a ^{13}C nmr study was undertaken, the results of which are described below (Section C).

Examination of the spectra obtained from the low molecular weight polymers also brought up the question of whether the "doublets" observed at low field were associated with a possible ortho enchainment as shown in (2). Such a possibility could account for the observation of two types of resonances associated with two types of protons coupled meta. The veracity, however, of such a postulate is rather doubtful because of the non-converging slant in the doublets and also

FIGURE III.3. Comparison of ^{1}H nmr spectra with intrinsic viscosity-molecular weight data for a series of polymers obtained from mixed oxidation state complexes. Identification of polymers is given in Table III.4.


TCP 1$_T$
[η]:0.090
$\overline{M}_n$:32,600
TCP 0$_A$
[η]: 0.049
$\overline{M}_n$: 13,300
TCP 10$_A$
[η]: 0.041
$\overline{M}_n$: 5,900
TCP 1$_A$
[η]: 0.041
TCP 2$_A$
[η]: 0.041
ppm
5.0
6.0
7.0
8.0



(2)

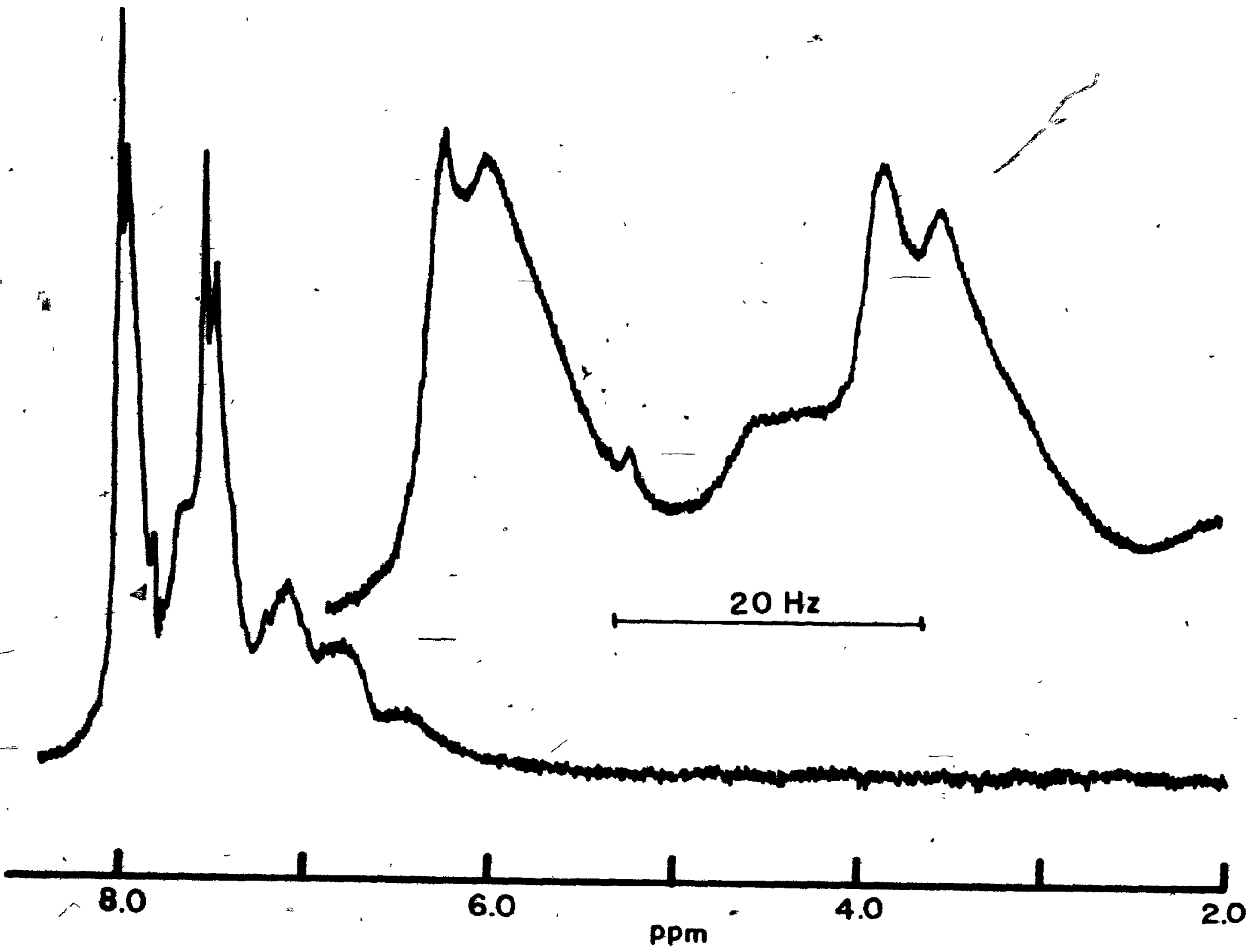
because of unequal broadening of the two single bands constituting the "doublets". An expansion of the aromatic region under question (Figure III.4) did not allow a clear cut decision to be made since the separation is very close to the limits of resolution. The low field and high field "doublets" had respectively a separation of 2.8 and 4.0 Hz. Other structural possibilities in accord with the ^{1}H nmr spectra will be discussed in Section 4.

v. ^{1}H nmr Spectra at Elevated Temperatures

An increase in temperature of the sample solution containing the polymer often brings about an enhancement in the resolution of the nmr spectra. Lines become sharper because of the combined effects of higher segmental mobility and lower solution viscosity.

Four polymers were examined in tetrachloroethylene at temperatures as high as 119°. In all cases no improved resolution of the proton spectra was obtained. The polymers investigated were: (origin (temp.)), linear high molecular

FIGURE III.4. ^{1}H nmr spectrum of a low molecular weight polymer, expansion of the low field doublets.


20 Hz
8.0
6.0
4.0
2.0
ppm

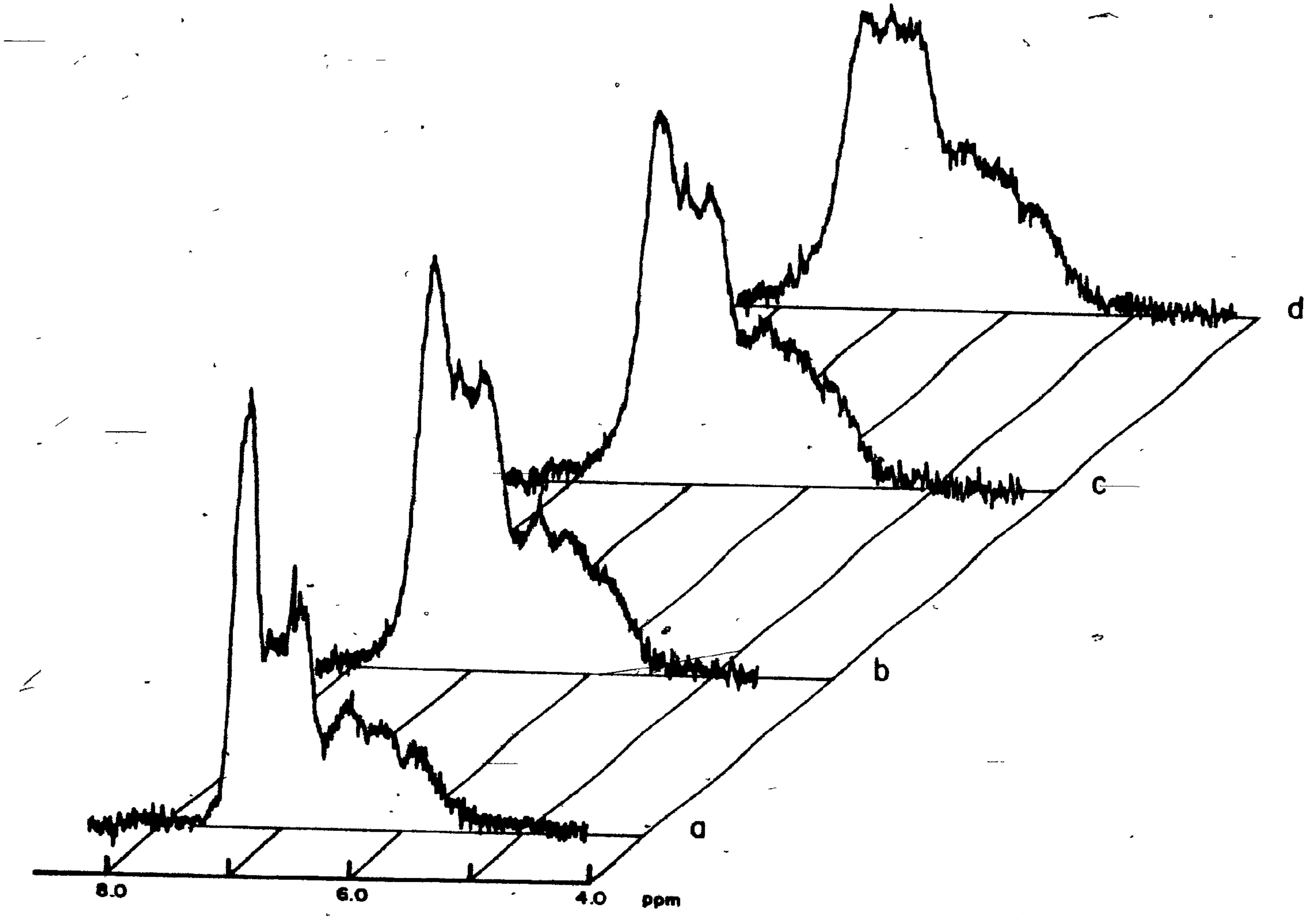
weight polymer from bis(pyridine)bis(4-bromo-2,6-dichlorophenoxo)copper(II) (105°); "branched" polymer from bis(2,4,6-trichlorophenoxo)copper(II) decomposed in acetonitrile (119°); "branched" high molecular weight polymer from bis(pyridine)-bis(2,4,6-trichlorophenoxo)copper(II) (105°); low molecular weight polymer from [Cu(I)TCP] [Cu(II)TCP_2] decomposed in acetonitrile (118°).

vi. ^{1}H nmr Spectra in the Presence of Paramagnetic Materials

The effect of paramagnetic materials on the proton spectrum of "branched" polymers was examined in hope of obtaining either better resolution or additional information as to the nature of their microstructure. Contact interactions may result in drastically changed chemical shifts and ultimately broadened resonances. The effect arises through the fluctuating field produced by the unpaired electron which has a moment in the order of 10^3 greater than the nuclear moment.[164] The local magnetic field experienced by a proton due to the presence of an unpaired electron, falls off as an inverse cube power of distance.

A typical polymer yielding a broad proton spectrum was thus examined in the presence of increasing amounts of added tris(acetylacetonato)chromium(III). It was observed (Figure III.5) that as the concentration of the paramagnetic material

FIGURE III.5. Effect of tris(acetylacetonato)-chromium(III) on the ^{1}H nmr spectrum of a high molecular weight "branched" polymer. Polymer concentration: 17% (w/v) in tetrachloroethylene; reagent concentration: a) 0; b) 5.7×10^{-3} M; c) 1.2×10^{-2} M; d) 1.7×10^{-2} M.


d
c
b
a
8.0
6.0
4.0
ppm

is increased, only the low field resonance is broadened and ultimately collapsed. The other features in the spectrum remain essentially unaffected. Similar broadening was observed with tris(acetylacetonato)iron(III).

B. High Molecular Weight Polymers from Bis(pyridine)bis(trihalophenoxo)copper(II) Systems

i. Introduction

The above speculation concerning the possible ortho-enchainment (1,2-coupling as opposed to 1,4-coupling) for the low molecular weight polymers, prompted a search for likely means of producing a truly 1,2-coupled polymer. The success attained in the isolation of poly(2,6-dichloro-1,4-phenylene oxide) by use of copper(II) complexes containing the 4-bromo-2,6-dichlorophenoxo monomer[80] suggested that a similar reaction should be tried using copper(II) complexes derived from 2-bromo-4,6-dichlorophenol. The orthobromophenol and the corresponding copper complex are easily prepared by established procedures.[128]

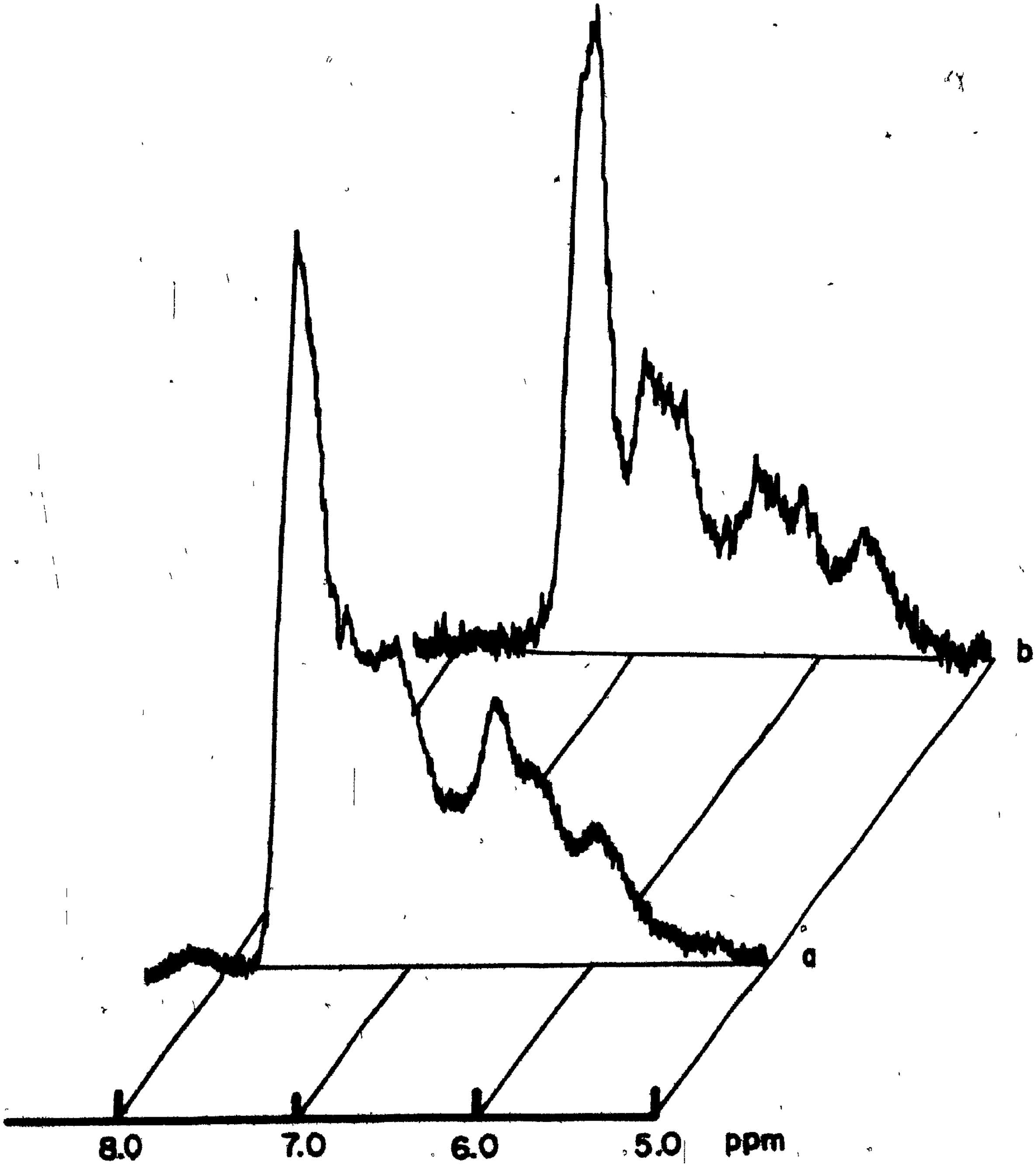
Copolymers were also prepared with the intent of obtaining additional structural information by comparison of their nmr spectra with those of polymers already isolated, particularly by comparison with the ^{13}C spectra of a series of polymers obtained from trichlorophenol which tended to suggest that these polymers might be constituted of 1,2 and 1,4-coupled units. In order to test this possibility co-decompositions of two different bis(pyridine)bis(phenoxo)-copper(II) complexes were undertaken. Copolymers were obtained by virtue of the near equivalence of the oxidation potential of the two different halophenoxo ligands.

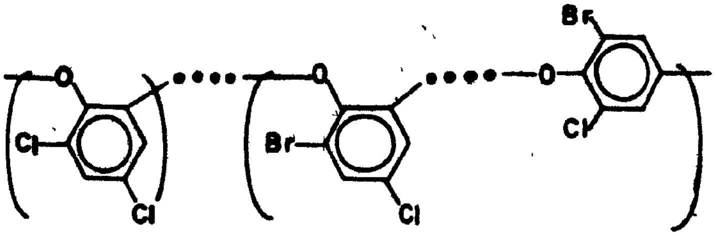
ii. Preparation and Thermal Decomposition of Bis(pyridine)bis(2-bromo-4,6-dichlorophenoxo)copper(II)

The monomer ligand was prepared by direct bromination of 2,4-dichlorophenol and the copper(II) complex was easily obtained as dark brown needles by following established procedures.[128] The polymer obtained by thermal decomposition at elevated temperature had a similar ^{1}H nmr spectrum to a polymer obtained by decomposition of the same complex in toluene at room temperature in the presence of carbon tetrachloride.

Complete analysis of both the high temperature and low temperature polymers showed that a considerable amount of bromine had been retained, thus eliminating the possibility that these polymers are completely 1,2-coupled. Rather, the structure, on the basis of the chemical analyses, appears to be a mixture of 1,2 and 1,4-coupled units (3), where $1.5 > x/y > 1$. A more precise estimation is unreasonable considering the difficulty in obtaining an accurate Cl/Br ratio by chemical analysis in a product where the two halides are present simultaneously.

FIGURE III.6. ^{1}H nmr spectra of the polymers obtained from bis(pyridine)bis(2-bromo-4,6-dichlorophenoxo)copper(II): a) and from bis(pyridine)bis(2,4,6-trichlorophenoxo)copper(II): b) 80.


b
a
8.0
7.0
6.0
5.0
ppm



(3)

The ^{1}H nmr spectrum had the same features as those obtained from polymers resulting from the decomposition of bis(pyridine)bis(trichlorophenoxo)copper(II) under similar conditions, Figure III.6.

The intrinsic viscosity of the high temperature polymer was somewhat low (0.044 dl/g in toluene at 25°) and this remains unexplained. Both polymers afforded brittle films when cast from solution.

iii. Decomposition of Bis(pyridine)bis(4-bromo-2,6-dichlorophenoxo)copper(II) with Bis(pyridine)bis(2-bromo-4,6-dichlorophenoxo)copper(II) and with Bis(pyridine)bis(2,4,6-trichlorophenoxo)copper(II)

In one case the 4-bromo- and the 2-bromo-complexes were decomposed together in refluxing toluene. In the second case the 4-bromo and 2,4,6-trichlorophenoxo complexes were codecomposed in toluene at room temperature in the presence of added carbon tetrachloride. Both reactions lead to straw colored solutions which had deposited pale green bis(pyridine)bromochlorocopper(II). The copolymers were isolated from the toluene solutions in a yield greater than 90% in both cases.

The first copolymer, obtained from the high temperature reaction contained approximately 18% bromine which is consistent with a composition close to $((C_6H_2O\ Cl_2)_{1.5} \cdots (C_6H_2O\ ClBr))_n$ for the units. The intrinsic viscosity of this copolymer was quite high (0.062 dl/g, $CHCl_3$ @ 25°C) in accord with its relatively high molecular weight (58,000). The latter values applied to the Mark-Houwink plot (Figure III.1) for poly(halophenylene oxides) yield a point coinciding with the curve.

As a general rule, the composition of a polymeric substance is not homogeneous as far as molecular weights are concerned. However, a fractionation of the product polymer was carried out in order to ascertain that the polymer was truly a copolymer and not a mixture of two different polymers, a linear and a non-linear one, obtained from the two complexes. The fractionation experiment here relies on the lesser solubility of the linear polymer relative to the non-linear polymer.[80] This was performed on a dilute methylene chloride solution of the polymer by adding methanol till the appearance of a permanent turbidity. The suspension was then centrifuged to remove each fraction prior to addition of more non-solvent.

Each of the fractions was examined by ^1H nmr spectroscopy and no variation in the appearance of the spectra from one sample to another was observed. A typical spectrum of one of the fractions is shown in Figure III.7a. Furthermore, a ^{1}H nmr spectrum of a mixture of the linear and non-linear homopolymers did not yield the spectrum observed for the copolymer (Figure III.8). Such behavior has also been observed for a copolymer of 2,6-dimethylphenol and 2,6-diphenylphenol where the ^{1}H nmr spectrum of the copolymer had distinct features not observed in a spectrum of a mixture of the two homopolymers.[165]

The ^{1}H nmr of the copolymer has a striking resemblance to those spectra obtained from the low molecular weight polymers although the former spectrum is slightly more broadened. An additional broad peak of low intensity which was not apparent in the spectra of the low molecular weight polymers is now apparent to the high field end of the spectrum.

The second copolymer, obtained in a similar way, but by adding carbon tetrachloride to allow the reaction to proceed at room temperature, gave a ^{1}H nmr spectrum essentially similar to that of the first copolymer (Figure III.7b). No further characterization was carried out on this polymer but it may be assumed that its molecular weight was fairly high considering the poor solubility in common solvents.

FIGURE III.7. ^{1}H nmr spectra of two copolymers obtained from the decomposition of bis(pyridine)bis(4-bromo-2,6-dichlorophenoxo)copper(II): a) with bis(pyridine)bis(2-bromo-4,6-dichlorophenoxo)copper(II) (1:1, refluxing toluene); b) with bis(pyridine)bis(2,4,6-trichlorophenoxo)copper(II) (1:1, toluene/CCl_4, room temperature).

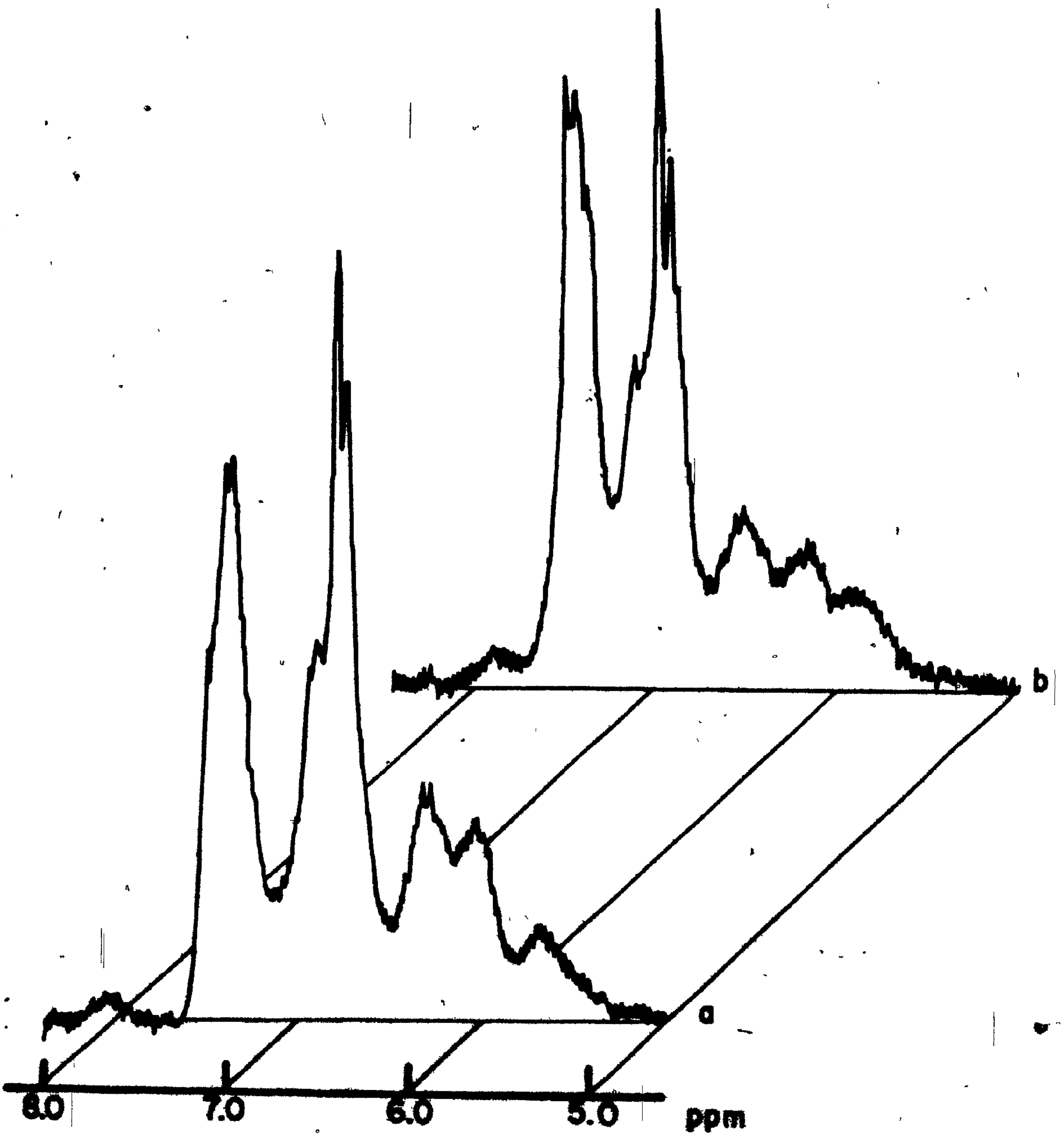
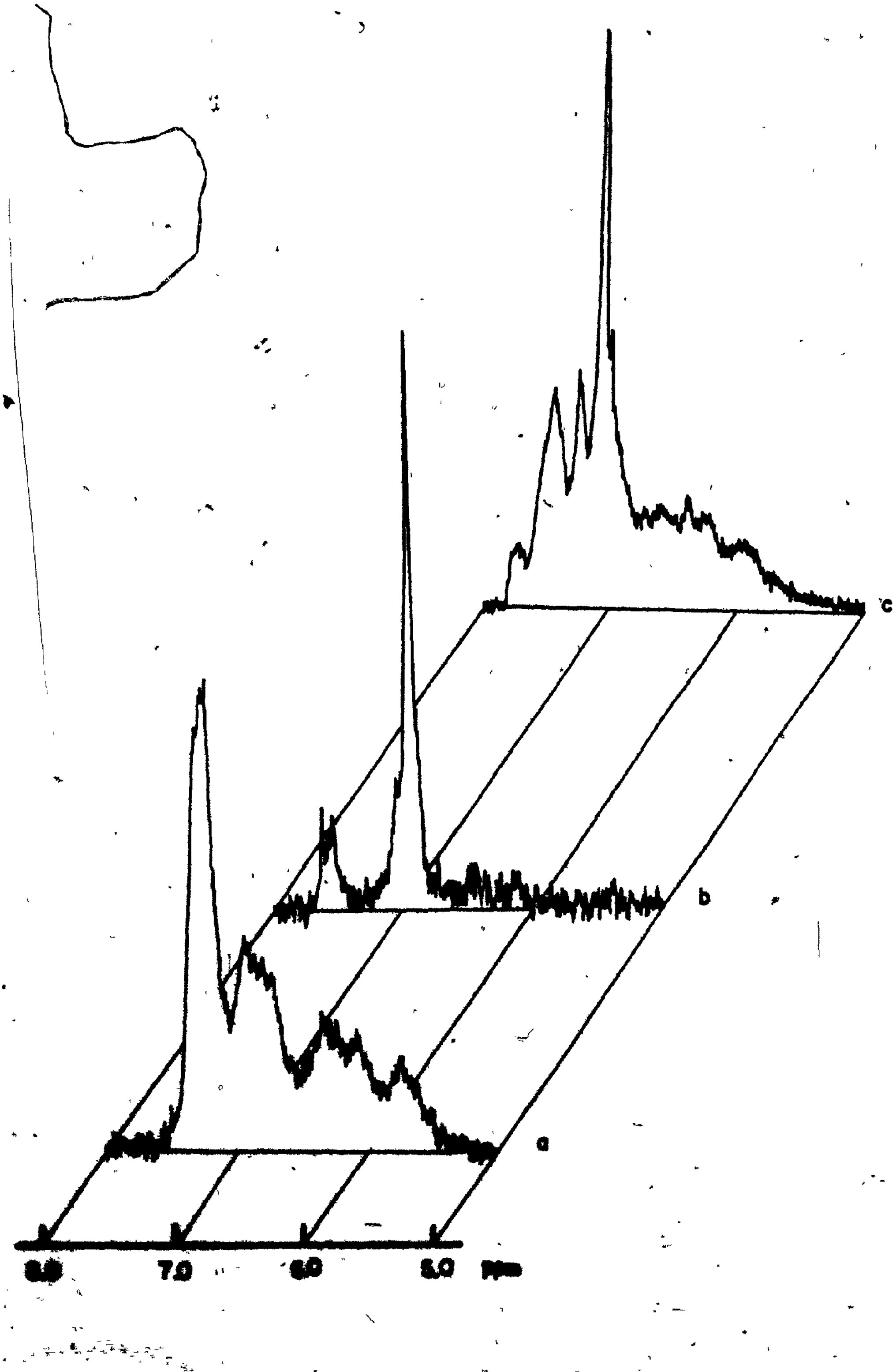

b
a
8.0
7.0
6.0
5.0
ppm

FIGURE III.8. ^1H nmr spectra of: a) non-linear homopolymer; b) linear homopolymer; c) mixture of a) and b): (1:1 by weight), solvent: CS_2/TMS.


c
b
a
8.0
7.0
6.0
5.0
ppm

C. ^{13}C nmr Spectra of Poly(halophenyleneoxide) Polymers

i. Introduction

Because of their complexity and in some cases their drastically broadened appearance, the proton spectra presented herein have been of little use in determining the microstructures of the polymers prepared in this work. Interpretation has only been possible in the case of "linear" 1,4-coupled polymers, where the expected spectrum is observed. With the intent of obtaining additional structural information on the polymers prepared during the course of this work, carbon-13 spectroscopy was resorted to.

The general tendency of ^{13}C spectra of polymers to be less sensitive than ^{1}H spectra to relaxation broadening, the very substantial sensitivity of ^{13}C chemical shifts to conformational changes[166] and to steric effects[167] and the wide window for the observation of ^{13}C chemical shifts (200 ppm as compared to 10 ppm for protons) suggested that this technique could be particularly useful in the examination of the primary and secondary structures of polymers.[168]

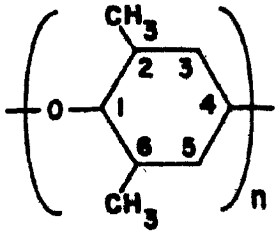
The wide application of ^{13}C nmr has been largely dependent on the introduction of Fourier transform techniques. This has been necessary to overcome a number of difficulties inherent in the ^{13}C nucleus, notably its low sensitivity relative to the proton (1.59%) and its low natural abundance (1.1%). Where polymers are concerned, other drawbacks associated with the low concentrations required in order to maintain a suitable viscosity of the solution have to be dealt with.

These drawbacks are partly overcome by multiple scanning with the result of an increased signal to noise ratio. Furthermore decoupling of the protons, in addition to greatly simplifying the spectra, further enhances the intensity of the spectra by collapse of the multiplet structure and by the Nuclear Overhauser Effect. The maximum enhancement attainable is approximately a factor of 3 and is critically dependent on the functionality of the carbon and is thus highly variable for carbons within the same molecule. The variable magnitude of the NOE destroys the simple relationship between the resonance intensity and the number of ^{13}C nuclei. Hence carbon-13 spectra cannot be used in a quantitative manner as easily as ^{1}H spectra.

There appears thus far to be only one report of a ^{13}C spectrum of a poly(phenylene oxide).[169] Poly(2,6-dimethyl-1,4-phenylene oxide) produced the expected carbon-13 spectrum exhibiting five resonances corresponding to the five types of carbon present in the unit. (Table III.5.) A polymer obtained in low yield by the high temperature oxidative coupling of 2,6-xylenol produced a complicated ^{13}C spectrum most likely resulting from the presence of end groups since the polymer had a molecular weight of only 1,300. Branching was also proposed to account for some of the additional peaks in

TABLE III.5

^{13}C CHEMICAL SHIFTS FOR POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE) IN CDCl$_3$[169]

	ppm (rel.TMS)
C_1	154.8
$C_{2,6}$	132.6
$C_{3,5}$	114.5
C_4	145.5
CH_3	16.5

the spectrum.

ii. Comparison of ^{13}C Spectra of Low Molecular Weight and High Molecular Weight "Non-Linear" Polymers

The low molecular weight polymer studied was the product of the thermal decomposition of the copper(I)trichlorophenoxide/CCl_4 reaction product in acetonitrile whereas the high molecular weight polymer was the product of the thermal decomposition of the bis(pyridine)bis(trichlorophenoxo)copper(II) complex in benzene.

Immediately apparent in the carbon-13 spectra (Figure III.9) is the much greater broadening observed in the spectrum of the high molecular weight polymer in spite of the much greater number of scans (58,895 as compared to 7,331 for the low molecular weight polymer.) All of the features are essentially similar in the spectra of both polymers indicating that the low molecular weight polymer has the same microstructure as the high molecular weight analogue. The chemical shifts of these two polymers are included in Table III.6.

All of the resonances in the spectrum of the high molecular weight polymer are considerably broadened, particularly the resonances in the carbon bonded to chlorine region. Reduction of resonance intensity as well as broadening is a common occurrence where quadrupolar nuclei are bound to

FIGURE III.9. ^{13}C nmr spectra of high a) and low b) molecular weight poly(dichlorophenylene oxide); $CDCl_3$; ppm downfield from TMS.

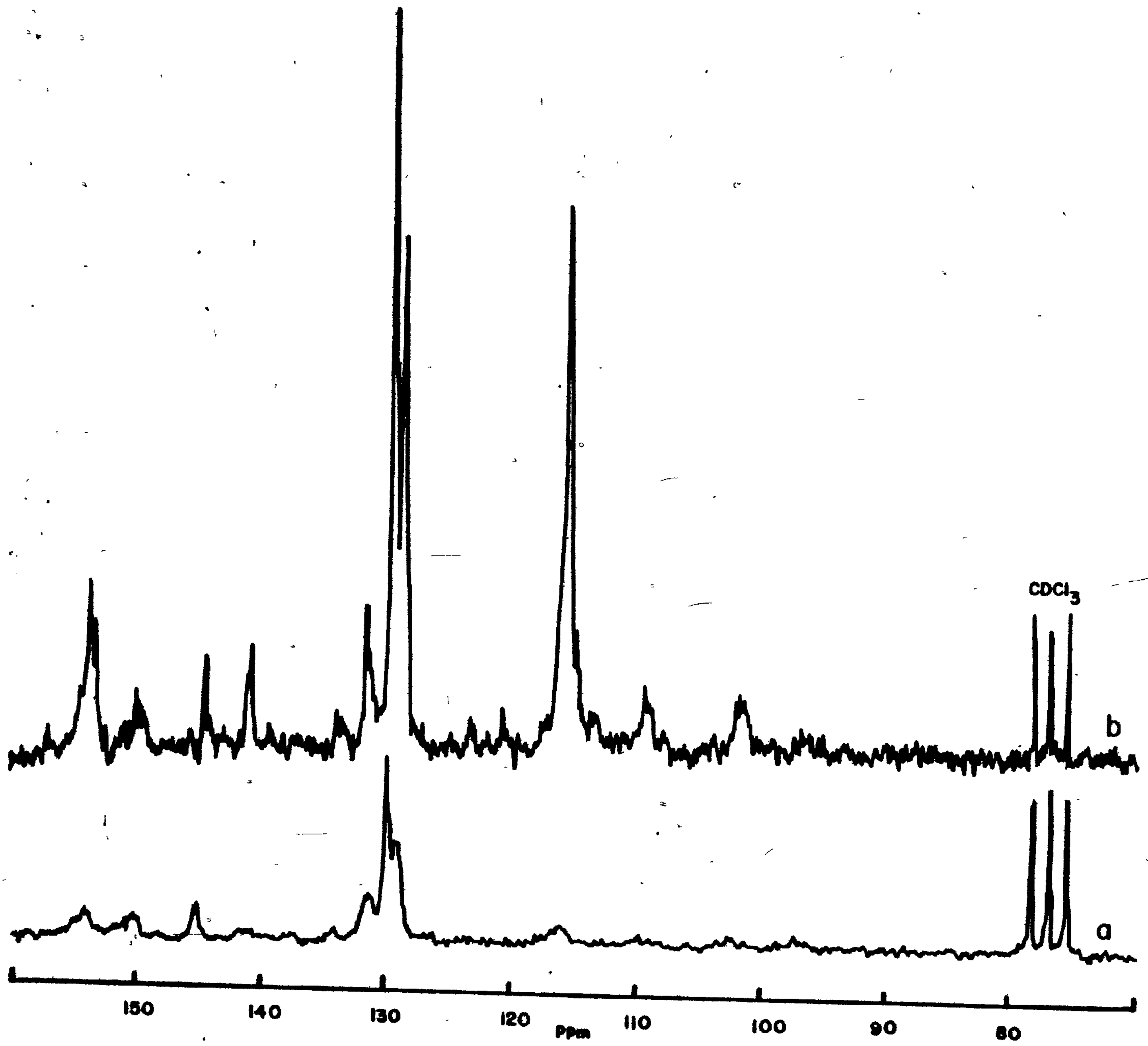

CDCl$_3$
b
a
150
140
130
120
ppm
110
100
90
80

TABLE III.6

^{13}C CHEMICAL SHIFTS OF HIGH AND LOW MOLECULAR WEIGHT POLY(DICHLOROPHENYLENE OXIDES)

Polymer Origin[a]	TYPE OF CARBON									
	C-O				C-H			C-X		
Cu^{I}TCP/CCl$_4$	154.5	150.0	145.1	141.5	132.0	130.3	129.4	116.2	109.8	101.5
Py$_2$CuTCP$_2$	154.5	150.2	145.5	141.5	132.0	130.3	129.4	116.2	109.8	101.8

[a] TCP: 2,4,6-trichlorophenoxide; Py: pyridine.

carbon.[168] Broadening is also observed for the two high field resonances in the low molecular weight spectrum. However, the peak at 116.8 ppm is, for the latter polymer, remarkably sharp and intense.

iii. Comparison of ^{13}C Spectra of the Polymers Obtained from 2,4,6-trichlorophenol and from 2-bromo-4,6-dichlorophenol with the Linear Polymer from 4-bromo-2,6-dichlorophenol

The ^{13}C spectrum of the 1,4-coupled polymer (Figure III.10b) exhibits four bands in accord with a unit containing two types of carbon bound to oxygen, one type of carbon bound to hydrogen and one type of carbon bound to chlorine.

The two "non-linear" polymers had molecular weights of the order of 10^4 and exhibited considerably broadened resonances in contrast to the linear polymer with a molecular weight of the order of 10^5, emphasizing the low segmental mobility in the former polymers. The number of accumulated scans required to achieve reasonable resolution in the spectra of the "non-linear" polymers was as much as ten times greater.

A compilation of all the resonances observed in the three spectra is given in Table III.7. It can be seen that those peaks corresponding to the linear units are also present in the spectra of both "non-linear" polymers. The origin of the other bands present in the spectra of the latter polymers will be treated in the discussion.

FIGURE III.10. ^{13}C spectra of polymers: a) from 2-bromo-4,6-dichlorophenol(48,992 scans); b) linear poly(2,6-dichloro-1,4-phenylene oxide)(5,809 scans); c) from 2,4,6-trichlorophenol(58,895 scans).

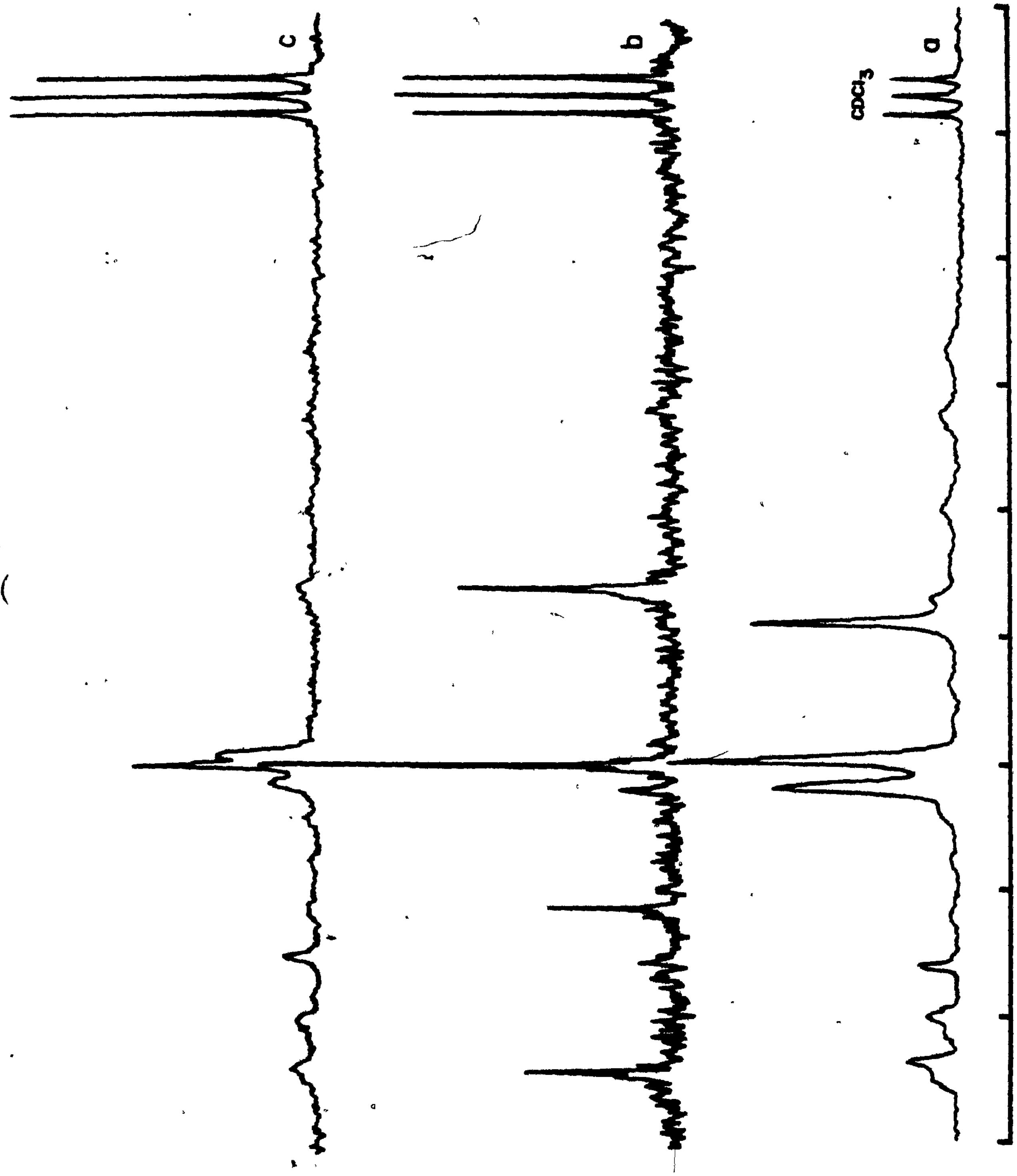

c
b
a
$CDCl_3$
80
90
100
110
ppm
120
130
140
150

TABLE III.7

^{13}C CHEMICAL SHIFTS FOR TWO NON-LINEAR POLYMERS COMPARED WITH THOSE OBSERVED FOR THE LINEAR POLYMER (PPM DOWNFIELD FROM TMS)

Polymer Origin	TYPE OF CARBON									
	C-O				C-H			C-X		
2,4,6-trichlorophenol	154.5	150.2	145.5	141.5	132.0	130.3	129.4	116.2	109.8	101.8
4-bromo-2,6-dichlorophenol	154.6			141.6		130.3		116.3		
2-bromo-4,6-dichlorophenol	154.2	150.1	145.8	141.6	132.2	130.0	118.6	116.4	110.0	102.1

The sharp band occurring at 118.6 ppm in spectrum (a), (Figure III.10), can be attributed to the carbon carrying bromine in this polymer. Carbons bound to bromine in phenols typically give rise to bands at about 112 ppm. The relatively intense peak is to be expected since this polymer is composed of roughly one bromine containing unit for every three units.

Another divergence of spectrum (a) from spectrum (b) is the absence of the band at 129.4 ppm in the former spectrum for a carbon carrying hydrogen.

iv. Comparison of ^{13}C Spectra of Copolymer, Linear and Non-Linear Polymers

All of the spectra are presented in Figure III.11. It can be seen that the copolymer has combined all the features of the linear and non-linear polymers. A number of peaks which were originally quite broad in the spectrum of the non-linear polymer (b) have become much sharper in the spectrum of the copolymer (a). The higher resolution of these peaks is definitely an indication of copolymer formation. The inclusion of 1,4-coupled units in the non-linear polymer structure has then most likely favored increased segmental mobility and consequently improved the overall resolution of the spectrum. A compilation of the chemical shifts for these three polymers is presented in Table III.8.

FIGURE III.11. ^{13}C spectra: a) copolymer obtained from 2-bromo-4,6-dichlorophenol and 4-bromo-2,6-dichlorophenol (25,100 scans); b) polymer from 2-bromo-4,6-dichlorophenol (48,892 scans); c) linear polymer from 4-bromo-2,6-dichlorophenol (5,809 scans); d) polymer from 2,4,6-trichlorophenol (58,895 scans); e) copolymers obtained from 2,4,6-trichlorophenol and 4-bromo-2,6-dichlorophenol (55,326 scans).

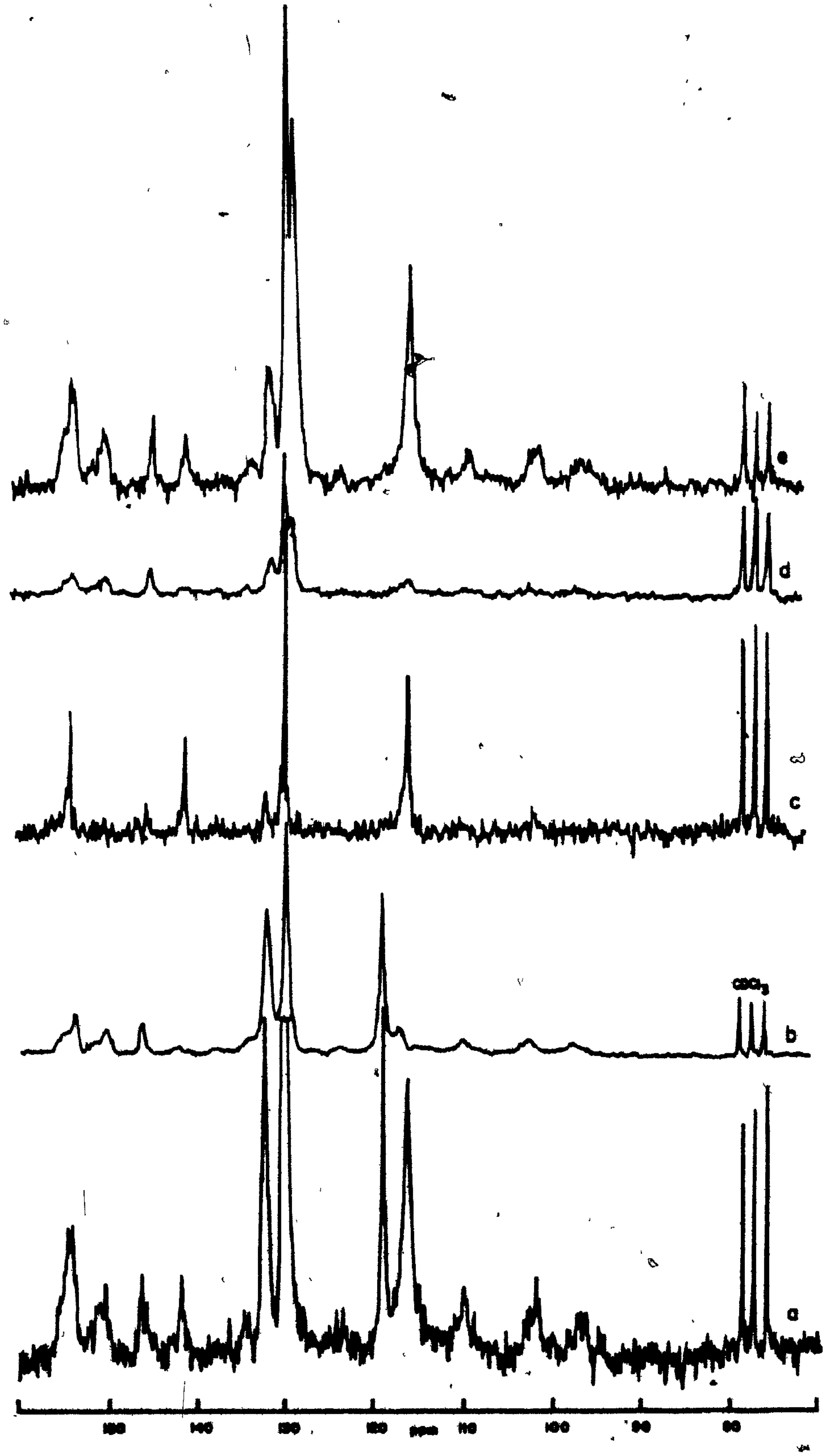

e
d
c
CDCl$_3$
b
a
150
140
130
120
ppm
110
100
90
80

TABLE III.8

CARBON-13 CHEMICAL SHIFTS FOR THE COPOLYMERS AND THE CORRESPONDING HOMOPOLYMERS

Polymer Origin	CARBON TYPE										
	C-O				C-H		C-X				
Copolymer a)	154.5	150.3	146.3	141.6	132.2	130.1	118.9	116.1	109.9	101.9	96.8
4-homo-2,6-dichlorophenol	154.6			141.6		130.3		116.3			
2-bromo-4,6-dichlorophenol	154.2	150.1	145.8	141.6	132.2	130.0	118.6	116.4	110.0	102.1	97.5
2,4,6-trichlorophenol	154.5	150.2	145.5	141.5	132.0	130.3	129.4	116.2	109.8	101.8	
Copolymer e)	154.3	150.5	145.4	141.5	132.2	130.3	129.4	116.1	109.8	102.0	97.0

3. EXPERIMENTAL

A. General

The preparation of solvents and reagents was outlined in a previous section (Chapter II.3) and the reactions were carried out with the usual precautions specified therein.

The purification of polymers was generally accomplished by dissolving the material in toluene, filtering and reprecipitation in a large volume of methanol containing a small amount of concentrated HCl. All the polymers were dried under high vacuum at 120° overnight. This was usually sufficient to remove all traces of residual toluene.

i. Molecular Weight Data

Most of the polymers obtained in this work had molecular weights less than 20,000. Number-average molecular weights were thus obtained by vapor pressure osmometry using a Hewlett-Packard 301A instrument. The calibration was accomplished by using polystyrene ($\overline{M_n}$ 10,300, $\overline{M_w}/\overline{M_n}$:1.10) supplied by Pressure Chemical. Toluene used at 25° was found to be a satisfactory solvent in all cases.

Since the method is based on a colligative property of these dilute solutions, the error tends to be greater in the higher molecular weight range. For molecular weights in the order of 10^3, the expected error is about 1%,[170] in the order of 10^4 the error becomes roughly 10%.

For molecular weights above 20,000, membrane osmometry was used. The determinations were made by employing a Hewlett-Packard 302 High Speed Membrane Osmometer. The instrument was operated at 25° using toluene as solvent.

ii. Viscosimetric Data

Intrinsic viscosities were conveniently obtained by using a Ubbelohde dilution viscometer having run through times of 436.8 sec. and 250.0 sec. at 25° for toluene and chloroform respectively. The initial more concentrated solution (roughly 5% w/v) was filtered through a medium pore glass frit and transferred to the scrupulously clean viscometer. Similarly, filtered solvent was used for the dilutions. All measurements were carried out at 25.00±0.02°

iii. ^{1}H nmr Spectra

Proton spectra of the polymers were obtained on a Varian T-60 instrument at 35° and 60 MHz. The solvent most commonly used was carbon disulfide unless otherwise indicated. All spectra are reported in parts per million (ppm) downfield from internal TMS. Solution viscosity presented a problem for polymers of high molecular weight, whereas low molecular weight polymers allowed the preparation of concentrated solutions. The attainable concentration, within the limits of a reasonable solution viscosity, was rather low for polymers having either a high molecular weight and/or a high proportion of linear enchainment. Low molecular weight polymers typically were run at concentrations up to 20% without the adverse viscosity effects.

The effect of temperature variation on the proton spectra was examined by employing a Varian A-60 instrument with a Varian-4060 probe heater attachment. Polymer samples were dissolved in either $CDCl_3$ or tetrachloroethylene, the latter being preferred because of its high boiling point (121° as compared to 61° for the former). High viscosity was not of concern here and solutions were made as concentrated as could be obtained without being turbid. These viscous solutions were then sealed in thick walled nmr tubes (5 mmOD; 3 mmID) and tested in an oil bath in the temperature range to be employed. Probe temperatures were obtained with an ethylene glycol sample tube and by measuring the peak separation.

iv. ^{13}C Spectra

The carbon-13 spectra were recorded on a Bruker WH90 22.63 MHz pulsed Fourier transform instrument equipped with a Nicolet BNC-12 computer having 4K real data points. The sample temperature was 30°. The spectra were obtained on roughly 10% solutions of the polymer in deuterated chloroform which is also the frequency lock for the instrument. All chemical shifts are reported in ppm downfield from internal TMS. The spectra are proton decoupled using broad band irradiation (5W).

v. Infrared Spectra

All polymer spectra were obtained in the range 4,000-625 cm^{-1} using a Perkin Elmer 257 instrument. Samples were dispersed in compressed KBr disks. High molecular weight linear polymers could also be run as films cast from solution.

B. Polymers from Copper(I) Trichlorophenoxide Systems

i. Thermal Decomposition of Copper(I) Trichlorophenoxide in the Presence of Variable Amounts of Added Carbon Tetrachloride

Solutions of Copper(I) trichlorophenoxide (0.23 M) were prepared in acetonitrile (50 ml) under nitrogen by reacting cuprous chloride (1.13 g; 11.4 m moles) and sodium trichlorophenoxide (2.50 g; 11.4 m moles). The required amount of carbon tetrachloride for one equivalent was 1.1 ml; fractions or multiples thereof were thus injected as indicated in Table III.3. Following injection of CCl_4 the solutions were heated resulting in immediate bleaching of the darkly colored solutions with concomitant precipitation of polymer. The crude polymer was filtered, extracted with toluene and the finely divided NaCl was removed by filtration. This latter procedure somewhat decreased the yields of polymer due to frequent clogging of the filter by the finely divided salt. The polymer containing filtrate was then added to a large volume of methanol. The precipitated polymers were dried for several hours under reduced pressure (1 torr, 120°C) prior to weighing.

ii. Preparation of Mixed Oxidation State Complexes $[Cu(I)TCP]_m[Cu(II)TCP_2]_n$ and their Thermal Decomposition

The complexes were prepared by mixing in dry acetonitrile (30 ml) the indicated quantities of reagents (Table III. 9) and stirring till the precipitate was uniformly dispersed. Filtration of the sodium chloride followed by removal of the solvent and drying under vacuum afforded the complexes as dark red-brown amorphous powders.

A quantity of the complex was then weighed into a flask and refluxed under nitrogen in either acetonitrile or toluene (30 ml) until complete decomposition had occurred as judged by the loss of color. In the case of acetonitrile the product polymer was directly filtered out of the solution, redissolved in toluene (10 ml) and reprecipitated in methanol. For the toluene reactions, the solution was filtered to

TABLE III.9

PREPARATION OF $[Cu(I)(TCP)]_m[Cu(II)TCP_2]_n$ IN ACETONITRILE

CuCl (g)	NaTCP (g)	$Cu(II)TCP_2$ (g)	Cu(I)/Cu(II) (molar)
0.451	1.000	✓ 2.079	1
0.451	1.000	0.208	10
0.451	1.000	0.416	5
0.451	1.000	1.040	2
0.225	0.500	2.079	0.5

remove the insoluble copper products and the filtrate was concentrated to approximately 10 ml before being added dropwise to methanol. All polymers were dried by heating under high vacuum prior to weighing. Yields reported in Table III. 4, are based on the theoretical dichlorophenoxide ($C_6H_2OCl_2$) content of each complex.

iii. ^1H nmr Spectra at Elevated Temperatures

The samples for the variable temperature study were prepared as follows. A fairly concentrated but not too viscous solution of the polymer was prepared in tetrachloroethylene (1 ml). This solution was filtered over Celite into a small flask and concentrated. The viscous solution was then sealed into a thick-walled nmr tube, placed in an oil bath and tested up to the boiling point of the solvent. No phase separation was observed for any of the samples in the temperature range investigated.

iv. ^1H nmr Spectra in the Presence of Paramagnetic Materials

A portion of the polymer obtained from Cu(I)TCP Cu(II)-TCP_2 by decomposition in refluxing toluene was weighed (0.084 g) and dissolved in tetrachloroethylene (0.5 ml) contained in an nmr tube. The tube containing the solution was then weighed prior to running its nmr spectrum. Small amounts of tris(acetylacetonato)chromium(III) were introduced into the tube which was then weighed. Between each addition of paramagnetic material the conditions on the nmr instrument remained unchanged.

C. High Molecular Weight Polymers from Bis(pyridine)bis(trihalophenoxo)copper(II) Systems

i. Preparation of 2-bromo-4,6-dichlorophenol

An aqueous solution (150 ml) of potassium bromide (24.0 g; 0.2 mole) and bromine (16.0 g; 0.1 mole) was added dropwise with vigorous stirring to 2,4-dichlorophenol (32.6 g; 0.2 mole) in a minimum of alcohol. As the bromine reagent was added the product began to precipitate out. Stirring was continued for an hour and the slurry was cooled in ice prior to filtering. The solid product was taken up in hexanes and washed with aqueous sodium bicarbonate followed by water. The hexane layer was dried over anhydrous sodium sulfate and concentrated. The product crystallized out upon cooling as white needles: (89%), mp:65-66°, (lit. 64° (171)); pmr ($CDCl_3$), 5.85(s,1H), 7.20(d,1H), 7.35(d,1H).

ii. Preparation and Thermal Decomposition of Bis(pyridine)bis(2-bromo-4,6-dichlorophenoxo)copper(II)

The complex was prepared by following the literature[128] procedure for the isolation of similar compounds. An aqueous solution (100 ml) of sodium hydroxide (2.33 g; 58 m moles) and 2-bromo-4,6-dichlorophenol (14.1 g; 58 m moles) was added dropwise to a vigorously stirred aqueous solution (300 ml) of cupric sulfate pentahydrate (7.30 g; 29 m moles) and pyridine (4.60 g; 4.7 ml; 58 m moles). The complex precipitated out as a pale brown powder. The slurry was filtered, washed with water and dried on the filter overnight. The friable lumps were taken up in toluene (100 ml) containing pyridine (3 ml), filtered through Celite and concentrated (60 ml). Hexanes were added (300 ml) and cooling afforded brown needles (14.0 g; 70%).

The complex (3.00 g) was weighed into a flask and toluene was added (20 ml). The dark solution was kept at 70° overnight. Upon completion of the reaction a pale yellow solution was obtained along with a green precipitate (1.33 g). The toluene filtrate afforded white polymer (1.43 g; quantitative) following reprecipitation in methanol; $[\eta]$: 0.044 dl/g toluene, 25°.

A similar decomposition effected at room temperature in toluene (20 ml) on the same complex (3.00 g) in the presence of CCl_4 (2 ml) afforded 1.26 g of polymer (90%) and 1.37 g of copper by-product.

Since coupling had not occurred exclusively in ~~the~~ ortho position the copper by-product accordingly contained both chlorine and bromine: C:36.52, N:8.41, H:3.07, Br:18.80,

POLYMER ANALYSES

	C	H	O	Cl	Br
Toluene 70°	38.70	0.89	8.77	24.60	26.37
Toluene 23°	39.43	1.16	10.08	27.70	21.86
Calc. for: $(C_6H_2OCl_2)$- (C_6H_2OClBr)	39.29	1.09	8.73	21.82	29.06
$(C_6H_2OCl_2)_{1.5}$ (C_6H_2OClBr)	40.29	1.13	8.95	31.76	17.87

Cl:13.18. The nmr spectra of the polymers are presented in the results section.

iii. Decomposition of Bis(pyridine)bis(2-bromo-4,6-dichlorophenoxo)copper(II) with Bis(pyridine)-bis(4-bromo-2,6-dichlorophenoxo)copper(II)

The title complexes were weighed in a flask (1.5 g of each) and toluene was added (20 ml). The dark solution was refluxed overnight yielding a straw colored solution and a green precipitate (1.42 g). The copolymer was recovered by reprecipitation in methanol (1.54 g, quantitative).

Fractionation was carried out by dissolving 0.912 g of the copolymer in methylene chloride (90 ml). Methanol (12 ml) was added to the stirred solution till a persistent turbidity was obtained. The suspension was then equally divided amongst a number of tubes and centrifuged. The supernatant solutions were then recombined in the fractionation vessel while the polymer was recovered from the tubes by redissolving in CH_2CI_2. Evaporation of the latter solvent afforded a first fraction (0.417 g). Four other samples were similarly obtained. A ^1H nmr spectrum of each of these five samples was taken and found to be exactly superimposable on the nmr spectrum of the initial copolymer.

COPOLYMER ANALYSIS

	C	H	O	Cl	Br
Found	41.16	1.10	9.61	30.08	18.24
Calc. for $(C_6H_2OCl_2)_{1.5}$-(C_6H_2OClBr)	40.29	1.13	8.95	31.76	17.87

iv. Decomposition of Bis(pyridine)bis(2,4,6-trichlorophenoxo)copper(II) and Bis(pyridine)bis(4-bromo-2,6-dichlorophenoxo)copper(II)

The trichlorophenoxo complex (1.20 g, 2 m moles) and the 4-bromo complex (1.38 g, 2 m moles) were dissolved in toluene (20 ml), carbon tetrachloride was added (2 ml) and the solution was stirred at room temperature for 42 hours. The supernatant liquid had become straw-colored and the pale-green bromochlorobis(pyridine)copper(II) complex was filtered out (1.27 g). The copolymer was isolated by adding the toluene filtrate to methanol (600 ml) containing concentrated HCl (1 ml). The dried copolymer (1.18 g, 94%) had an ^1H nmr spectrum similar to that of the preceding copolymer (Figure III.7).

COPOLYMER ANALYSIS

	C	H	O	Cl	Br
Found	46.72	1.39	10.46	41.77	trace
Calc. for ($C_6H_2OCl_2$)	44.72	1.24	9.94	44.10	–

4. DISCUSSION

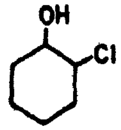
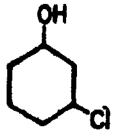
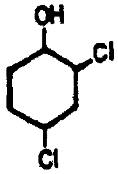
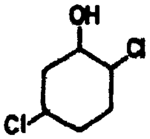
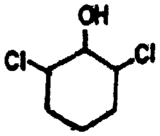
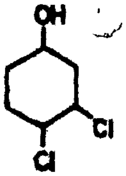
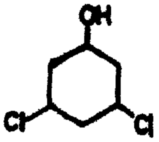
A. ^{13}C Spectra of High and Low Molecular Weight Polymers Structural Elucidation

The ^{1}H nmr spectra of polymers obtained from 2,4,6-trichlorophenol with two different copper complex systems showed a gradual degradation of resolution with increasing molecular weight. It could be argued that, notwithstanding the molecular weight effect, the different conditions employed in obtaining these polymers had led to different modes of enchainment and thus to variation in the ^{1}H nmr spectra. A comparison of the ^{13}C nmr spectra of both high and low molecular weight polymers clearly demonstrates that both are composed of similar units (Figure III.9). Both spectra contain the same number of peaks in the three regions associated with the three types of carbon bound to oxygen, hydrogen and chlorine. The relative intensities, however, in both spectra are not equivalent. Such an observation may in part be related to relaxation phenomena dependent on segmental mobility or overall tumbling.

A tentative assignment of the carbon-13 spectrum obtained from a low molecular weight "non-linear" polymer (Figure III. 9b) to a structure containing 1,2 and 1,4-coupled units can be made. This is achieved by comparison with the chemical shift data for a number of chlorinated phenols (Table III.10)

TABLE III.10

^{13}C CHEMICAL SHIFTS FOR CHLORINATED PHENOLS
(PPM DOWNFIELD FROM TMS; SOURCE: JEOL ^{13}C FT NMR SPECTRA VOL. 4)

Phenol	C-1	C-3	C-5	C-4	C-2	C-6
	151.2	129.0	128.3	121.3	119.9	116.3
	155.3	134.9	130.7	121.6	116.0	113.9
	153.2	129.6		126.1	116.8	
	149.5	128.2	128.0	125.1	120.0	116.7
	151.8	129.5	133.8	121.6	118.3	116.6
	147.8	128.2		121.1	121.1	
	154.1	132.9	130.9	124.4	117.5	115.3
	155.4	135.5		121.1	114.1	

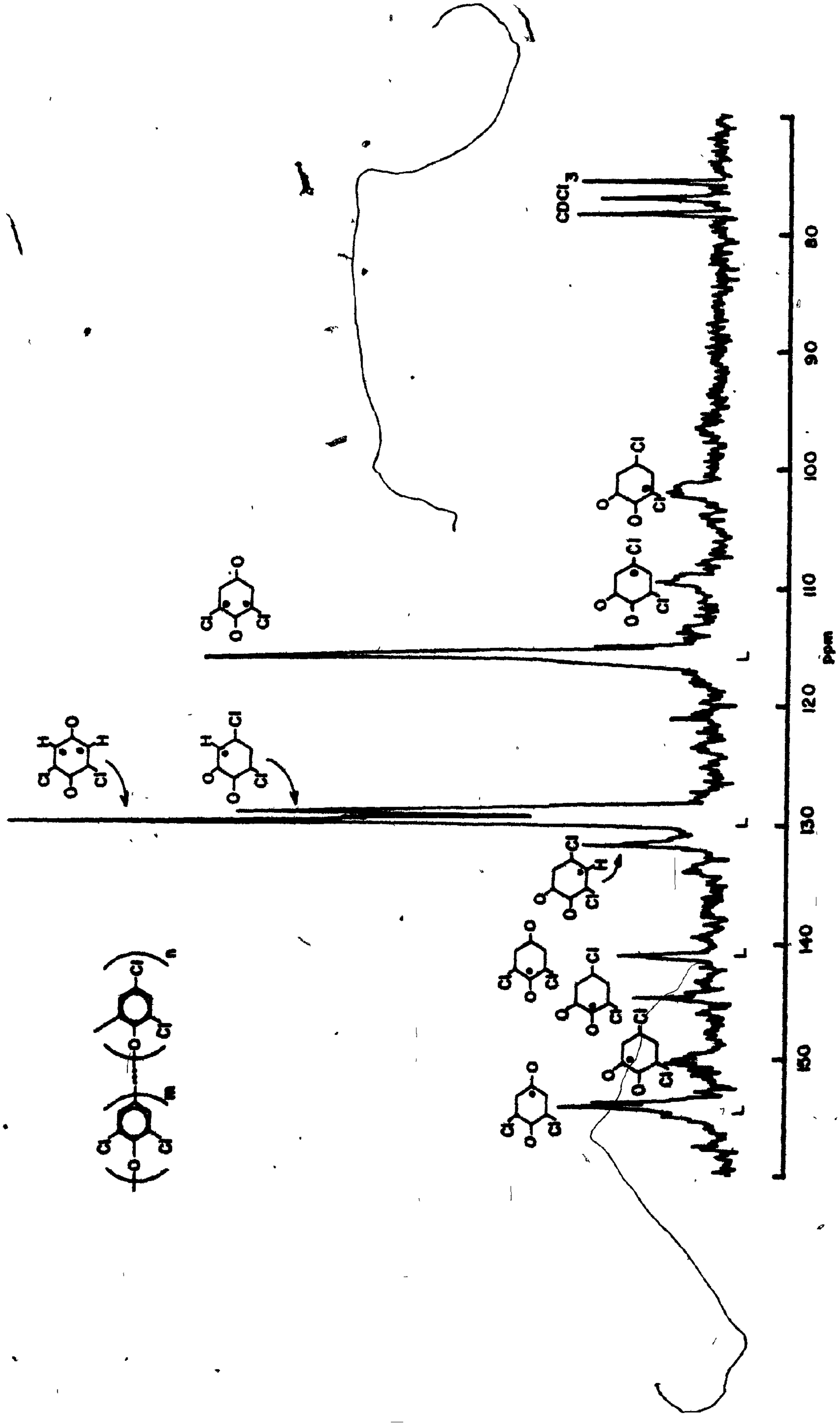
and by assuming reasonable additivity of chlorine substituent effects[172] as well as by using the well established effect of an ethereal oxygen substituent on ortho and para shieldings.[173,174]

It can be seen (Figure III.12) that all the prominent features of the spectrum can be assigned to a particular carbon of the ortho and para coupled polymer. Four of the peaks could unequivocally be assigned since they are present in the spectrum of the linear polymer. The six other resonances agree fairly well with the trends observed in the chlorinated phenols. A more rigorous assignment would of course require the preparation of model compounds particularly the eight possible triads.

As molecular weight increases, the carbon-13 spectrum of these polymers displays broadened peaks although the effect is not as marked as for the proton spectra. A few additional broad peaks also begin to rise above the noise. The occurrence of the latter can possibly be related to locked-in structures because of the increasing difficulty experienced by the high molecular weight chain in reorienting all its segments. Anisotropic shielding of certain segments thus results in the appearance of new resonances. This will be discussed further below (Section 3.C).

It cannot be ascertained at the moment if the broadening observed in the proton and carbon-13 spectra as molecular weight is increased, is not in part related to a variation

FIGURE III.12. Assignment of the ^{13}C nmr spectrum obtained from a non-linear polymer from 2,4,6-trichlorophenol.


CDCl$_3$
80
90
100
110
120
130
140
150
ppm
Cl
O
H
m
n

in the relative proportion of 1,2 to 1,4-coupled units. The carbon-13 spectra clearly indicate that no new units are present in the high molecular weight polymer by comparison with a spectrum of a similar low molecular weight polymer. Unfortunately, due to the non-quantitative nature of the peak areas because of dipolar broadening and the variable magnitude of the NOE, the ratio of ortho to para coupled units cannot be compared in both spectra of Figure III.9.

The carbon-13 spectrum of the polymer obtained from 2-bromo-4,6-dichlorophenol (Figure III.10a) shows that this polymer has essentially the same microstructure as the products discussed above. A new peak, however, is apparent at 118.6 ppm and is beyond doubt attributable to a carbon bound to bromine. The occurrence of this peak is to be expected since the analytical results reveal that the polymer contains 26% bromine. The peak observed at 129.4 ppm in the polymers obtained from trichlorophenol is absent in the spectrum of the 2-bromophenol polymer and also in the spectrum of the copolymer obtained with the 4-bromophenol (Figure III.11). It is possible that this may be the result of a change in chemical shift of this carbon in units where bromine is present. The resonance of this carbon may well be overlapping with the 132.2 ppm peak which is considerably more intense in spectrum (a) as compared to the same resonance in spectrum (b).

The carbon-13 spectrum of the copolymer obtained from

2-bromo-4,6-dichlorophenol and 4-bromo-2,6-dichlorophenol (Figure III.11a)) clearly emphasizes the importance of 1,4-coupled units for improving segmental mobility. All of the peaks in this spectrum are considerably sharper than those of the corresponding "non-linear" homopolymer (Figure III.10a) at the expense of a lesser number of scans.

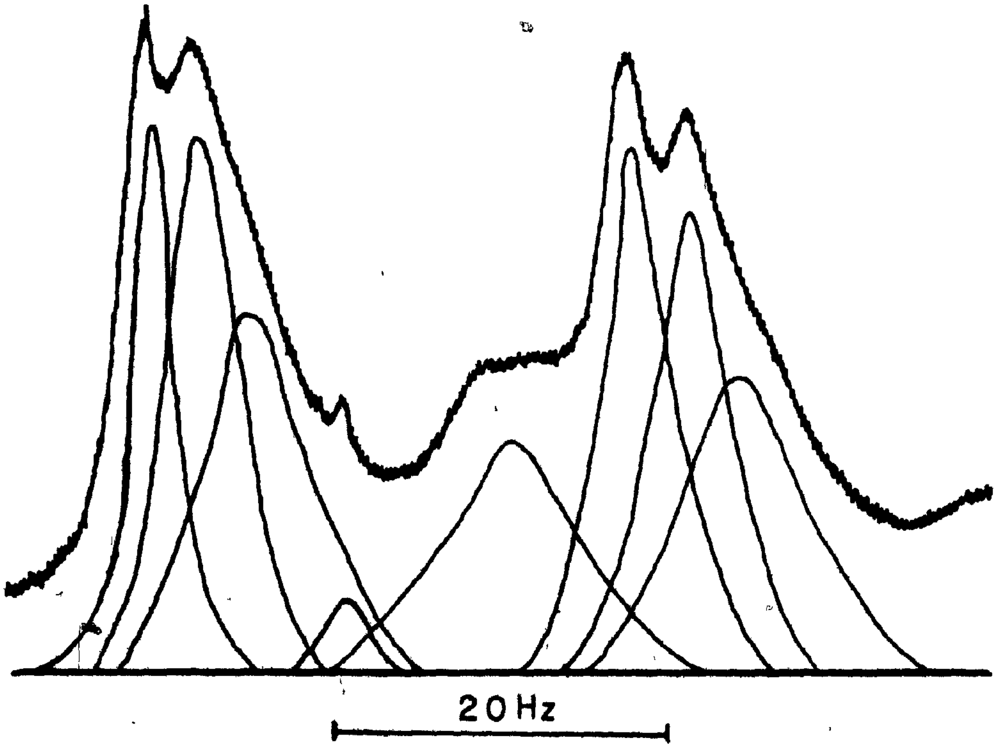
Thus the ^{13}C data would tend to favor a random enchainment of 1,2 and 1,4-coupled units for these polymers. They will thus subsequently be referred to as "1,2-1,4-coupled" polymers.

B. Proton Spectra

In spite of the relative simplicity of the proton spectra for the low molecular weight polymers (Figure III.3), their assignment to the 1,2-1,4-coupled structure is not possible. Particularly frustrating is the absence of the typical doublet of doublets expected for two AB protons coupled meta in the 1,2-unit. Collapse of the AA'BB' pattern has also been observed in the proton spectra of para substituted aryl orthocarbonates (Chapter II). Both these occurrences may be related to the proximity of the aromatic rings in both the polymer and the ortho ester. If the two protons in the ortho-coupled unit assume the same chemical shift and constitute a singlet, four peaks corresponding to the four possible triads containing a central 1,2-coupled unit should be observed. In addition four peaks corresponding to the inclusion of a 1,4-coupled unit in four triads should also be observed.

Obviously there is considerable overlap in the proton spectra of these low molecular weight polymers. Only four sharp peaks and two broad ones to high field with possibly a third broad peak appearing as a shoulder to the low field of the central resonance are observed. An expansion of the low field part of the spectrum in Figure III.4 reveals that the four sharp peaks may actually be the result of a greater number of superimposed peaks. The non-symmetry of the envelope as well as the unequal separation (2.8 and 4.0 Hz) in the two doublets would tend to support the multiple resonance hypothesis. A rigorous curve resolving analysis could reveal the exact constitution of this spectrum. However a freehand breakdown (Figure III.13), on the expanded spectrum clearly shows that at least eight resonances can be resolved in the low field region. This of course is not sufficient to account for the expected number of lines for all the possible triads. Four triads containing a central 1,4-coupled unit yielding four singlets, and four triads containing a central 1,2-coupled unit yielding doublets of doublets separated by roughly 0.2 ppm and with a meta coupling constant of 1-2 Hz could in principle lead to sixteen resonances for a total of twenty possible peaks. Clearly the number of possible resonances is far too great to be resolved over such a small

FIGURE III.13. Resolution of the low field ^{1}H nmr resonances of the expanded spectrum (Figure III.4) for a low molecular weight polymer.


20 Hz

chemical shift range. As they stand, these deceptively simple proton spectra remain beyond interpretation.

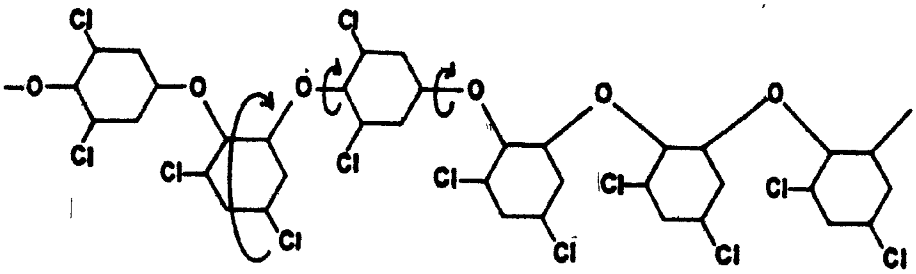
Segmental mobility is rather restricted in the 1,2-1,4-coupled polymer. When the degree of polymerization attains 35, broadening of the proton spectra becomes apparent; at DP: 80, the spectra become a mass of overlapping peaks. The inclusion of a greater number of 1,4-coupled units seems to favor overall flexibility of the chain. The copolymer resulting from the two bromophenols has a DP of 360 and its proton spectrum (Figure III.7a) assumes the same features as those of a low molecular weight polymer. The carbon-13 spectrum (Figure III.11) further demonstrates that it contained no new structural units that were not already present in the 1,2-1,4-coupled polymers. In addition this copolymer fitted the intrinsic viscosity-molecular weight relationship established for poly(halophenylene oxides) (Figure III.1).

The rigidity in the polymer chain is then most likely associated with the 1,2-coupled units which prevent the chain segments from undergoing rapid reorientation with a consequent elimination of dipolar broadening. As the number of 1,4-coupled units increases in the copolymer, the proportionally shorter 1,2-coupled blocks become more mobile, being included within the flexible 1,4-coupled segments. The rigid 1,2-coupled blocks then begin to exhibit nmr spectra of the same kind as those observed for low molecular weight "nonlinear" polymers. The effect of the 1,4-coupled units can thus be likened to a hinge, breaking up the rigid 1,2-1,4-coupled polymers into shorter blocks which can then move more freely as units.

C. Broadening Phenomena in the Proton Spectra of 1,2-1,4-coupled Polymers

The ^1H nmr spectra of the 1,2-1,4-coupled polymers suggest that there may be considerable constraint on free rotation at the aryl ether bonds. Hindrance may explain the appearance of greatly spread resonances or even lead to the appearance of peaks in excess of the number expected, particularly in the case of proton spectra. In order that a single sharp resonance line be observed from chemically equivalent nuclei along the polymer chain, each must sustain a similar magnetic field. This can only be achieved if there is complete freedom of rotation through rapid segmental motion of the polymer chain. However, in the majority of cases where polymer molecular weight was above 13,000, notwithstanding proper solvent conditions and increased temperatures, the linewidth was still much greater than that observed in the spectra of low molecular weight 1,2-1,4-coupled polymers. ^{13}C spectra in contrast seem to be little affected by dipolar interactions not averaged to zero by the motions of the chain. This has also been observed for other polymers.[175]

Severe restriction in segmental mobility of the 1,2-1,4-coupled polymer coils is most certainly related to a high proportion of 1,2-coupled units in the chain. The linear 1,4-coupled units on the other hand can be visualized as long bonds capable of undergoing relatively facile rotation.



The inclusion of a greater number of these units in a 1,2-1,4-coupled polymer enchainment results in improved mobility for the 1,2-coupled units. It can be seen by inspection of models that the latter cannot undergo crankshaft-like reorientation without displacing a larger part of the molecule.

The effects on nmr spectra of hindered rotation in aryl ethers[176] and in thyroxine analogue[177] has been investigated. When preferred conformations are imposed by substitution of the ortho positions in one ring, forcing one ortho proton of the other ring over the electron cloud of the adjacent ring, the resonance of the latter is observed to be shifted upfield. Furthermore, calculations[178] on the secondary magnetic field due to the ring current in benzene suggest that aromatic groups in polymers will significantly perturb the chemical shifts of the neighboring protons. Thus a combination of ring current effects and restricted segmental mobility will ultimately result in considerable overlap of the peaks through chemical shift dispersion.

The extreme rigidity of the coiled structure of these polymers is further emphasized by the inability of increased temperatures to bring about greater resolution in their proton spectra. A variable temperature study was done on a series of polymers exhibiting broadened proton spectra, with the result that no effect was observed on the overall resolution of the spectra for temperatures as high as 120°. Under these conditions viscosity was certainly reduced thus favoring Brownian tumbling. It has then to be concluded that internal relaxation mechanisms were not affected and are thus the cause of line broadening.

The fact that rigidity in these polymers is associated with linewidth also leads to the conclusion that the locked in structure must be disordered. This stems from the fact that it has been observed that a smaller number of conformations in a highly rigid structure can still result in narrow nmr bands.[179] The sharp bands observed in the nmr spectrum of an optically active poly(isocyanate), shown to adopt a rigid helical structure, cannot arise from higher segmental mobility. Rather, the fewer allowed conformational states was thought to be a better explanation. In contrast, a homologous racemic polymer, also adopting the helical form, displayed a considerably broadened nmr spectrum.[179]

The foregoing arguments concerning the possibility of an immobilized coil structure for the 1,2-1,4-coupled polymers lead to further speculation as to the nature of this secondary structure. The peak on the low field side of the proton spectra of the high molecular weight 1,2-1,4-coupled polymers is invariably sharper and also more intense. This could presumably be related to the fact that the protons corresponding to this resonance are actually on the outside of the polymer coil. If this is the case then through proper relaxation mechanisms they are expected to resonate at a more defined frequency, thus resulting in better resolution. The protons giving rise to the other much less intense and also broader resonance envelopes are presumably buried within the polymer coil. This reasoning is somewhat substantiated by the fact that the low field, sharper resonance is greatly affected by the introduction of increasing amounts of tris-(acetylacetonato)chromium(III). The low field peak progressively broadens while the other features in the spectrum remain unchanged. The sharp peak is also very readily saturated.

If adventitious paramagnetic species were the cause of the broad ^{1}H nmr spectra observed in the present study it could be argued that part of the reason for poor resolution is due to the presence of free radical chain ends in the polymer. This was ruled out by running esr spectra on a number of the high molecular weight polymers. Although unpaired spins were present, their concentration was barely within the limits of detection. In addition, it would be difficult to conceive that a high molecular weight linear polymer containing some living chain ends could afford a well resolved spectrum whereas a similar polymer having a different structure would give a broadened spectrum as a result of unterminated chain ends.

The effect on the nmr spectra of increasing molecular weight of these polymers (assuming no concurrent changes in microstructure) are possibly many-fold. For instance a mixture of two poly(dimethyl siloxane) polymers having molecular weights in the orders of 10^3 and 10^6 in benzene gave two distinguishable peaks separated by 2 Hz in a spectrum taken at 220 MHz.[180] The possibility of chemical shift dispersion through polydispersity of the sample is rather remote in the present system considering the modest molecular weights. Another effect related to molecular weight pertains to conformational changes of the chain as a function of chain length. This is reflected in a molecular weight threshold for the ordering of poly(ethylene) and poly(ethylene glycol).[181,182] If this were the case for poly(dichlorophenylene oxides), the change in the secondary structure would occur in the range 6,000-13,000 where marked broadening is observed in the proton spectra.

The arguments presented in this Chapter thus tend to support the idea that the formerly so-called "branched" polymers are actually copolymers of 1,2-1,4-coupled units.

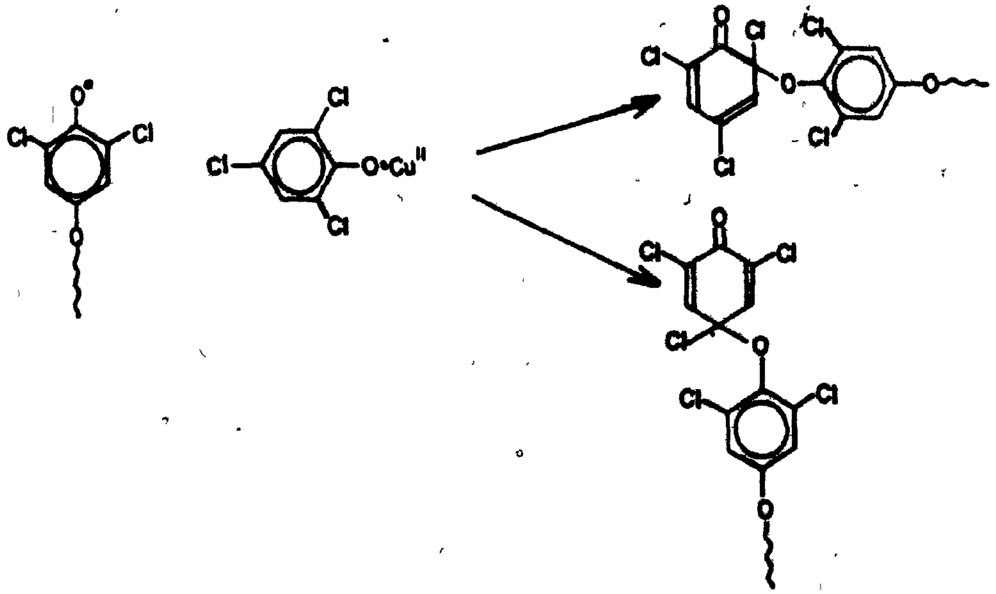
Evidence provided by proton and ^{13}C nmr spectra supports the fact that inclusion of a high proportion of the ortho-coupled units in these polymers has an unfavorable effect on their segmental mobility. Conversely, when copolymers containing an increased number of para-coupled units are prepared, their properties indicate an improvement in the mobility of the chain. Higher temperatures had no observable effect on the resolution of the proton spectra indicating that macroscopic viscosity has only a limited influence on the relaxation properties. Rather, it is believed that it is the local viscosity in the immediate neighborhood of each segment which is responsible for the broadness of the spectra.

CHAPTER IV

1. CONCLUSIONS

A. Reevaluation of the Mechanism of the Thermal Decomposition of Phenoxocopper Complexes

In a first detailed study of the thermal decomposition of trihalophenoxocopper(II) complexes, Carr and Harrod[81] observed that the ^{1}H nmr spectra of the product polymers were invariant with the degree of polymerization. Branching in the polymer chain was thought to be the cause of the broadened proton spectra. This hypothesis however is difficult to reconcile with a propagation mechanism involving displacement at coordinated phenoxide by polymeric phenoxy radicals (1)



(1)

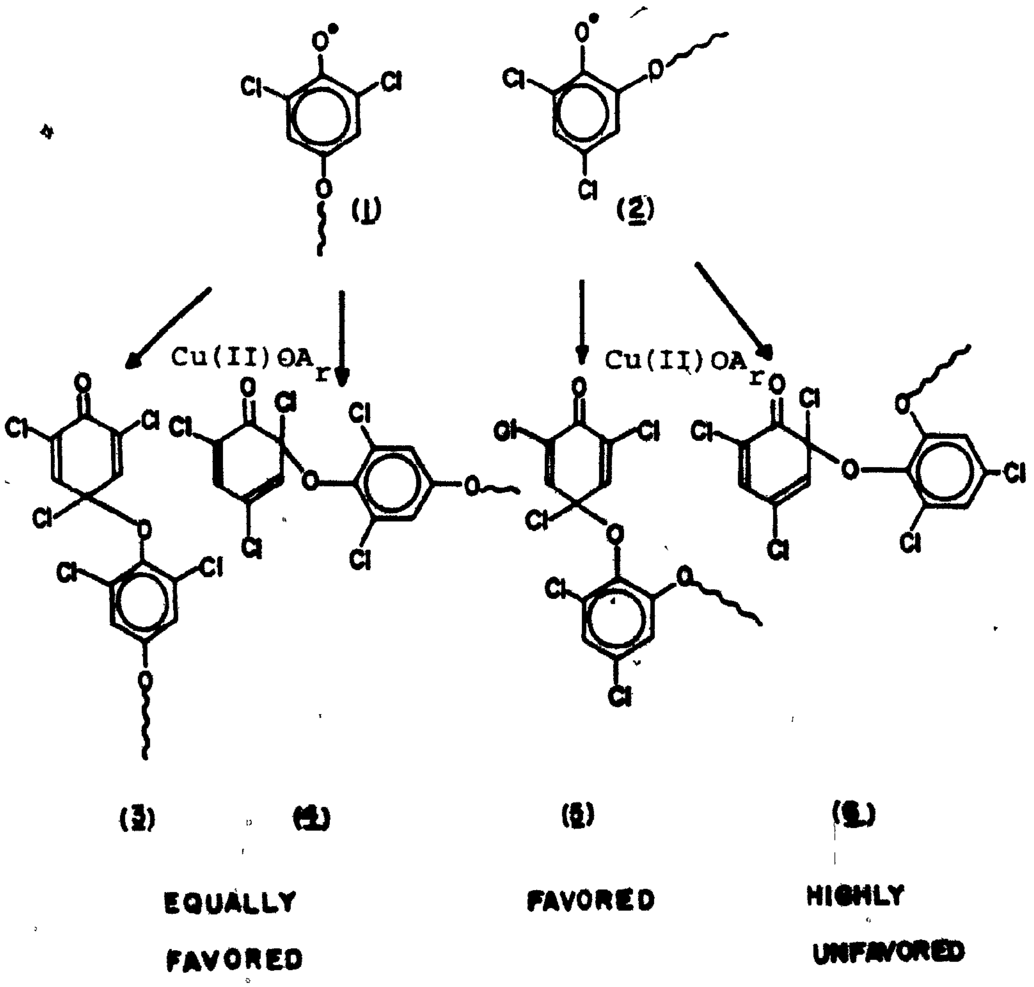
The coupling step illustrated in equation (1) clearly does not lead to branching.

The findings outlined in the present work indicate that the anomalous ^{1}H nmr spectra are not related to a high degree of branching but rather result from the presence of 1,2-coupled units in the polymer chain. This conclusion removes the above mentioned anomaly and can be completely accommodated by the previously proposed mechanism.

The conclusion that the polymers contain both 1,2 and 1,4-coupled units raises a number of questions related to the regioselectivity of coupling. None of the presently existing data allows an estimation to be made of the relative amounts of 1,2 and 1,4-coupled units in any of the polymers. Furthermore, circumstantial evidence tends to support the idea that the ligand transfer depicted in equation (1) is not subject to selectivity imposed by the nature of the copper(II) phenoxide complex. In particular the use of bulky amine ligands on the bis(amine)bis(trichlorophenoxo)copper(II) complex did not result in any measurable variation in the nature of the product polymer as expected for a mechanism where the regioselectivity is influenced by coordination to the metal center. An example of apparent influence of amine ligands on the outcome of an oxidative coupling reaction is provided by the Hay copper/amine catalyst for the polymerization of xylenol.[67] In this case it was shown that the ratio of C-O to C-C coupling was markedly affected by the steric demands of the amine coordinated to the copper.

If coordination of the phenoxide to the copper center does not introduce selectivity, the question then remains whether selectivity can result from the stereochemical demands of the attacking phenoxy radicals. A monomeric phenoxy radical would be expected to be quite reactive and thus rather unselective in a coupling step affording either an ortho or para-coupled dimer.

The head of a polymeric radical can have either of two substitution modes (Scheme I) each of which will have different

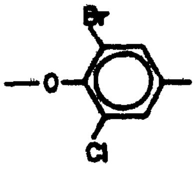


SCHEME I

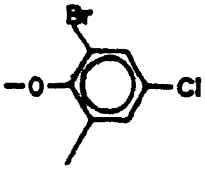
steric requirements and thus produce a new polymer radical with a particular substitution mode. Examination of models shows that coupling is likely to lead to only a limited number of more or less favored sequences.

A living chain ending in a 1,4-coupled unit (Scheme I(1)) is expected to be less selective in that the oxygen carrying the unpaired electron is less sterically crowded. Again, an examination of models shows that the latter can easily approach all of the coupling positions at the coordinated phenoxide. Ortho and para coupling are then more or less equally favored to yield (3) and (4). A different situation prevails when the radical end of the chain is a 1,2-coupled unit (Scheme I(2)). Here the terminal oxygen is much more obstructed by the adjacent phenoxy substituent than by a chlorine and is expected to prefer coupling to the para position of the coordinated phenoxide to yield (5) rather than (6). This steric preference makes a sequence of two units coupled through the 1,2-positions very unlikely.

Furthermore, if there is a bias towards o-coupling in the absence of large steric hindrance the aforementioned effects would lead to an alternating copolymer of 1,2 and 1,4-coupled units. Although there is no direct evidence to support a regular alternating structure, it is tempting to believe that the removal of only about half of the bromine during the polymerization of 2-bromo-4,6-dichlorophenol is a consequence of such sterically enforced alternation. A resolution of this question could perhaps be achieved by a ^{13}C nmr analysis designed to distinguish between the units (7) and (8). By virtue of the expected greater reactivity of the brominated



(7)



(8)

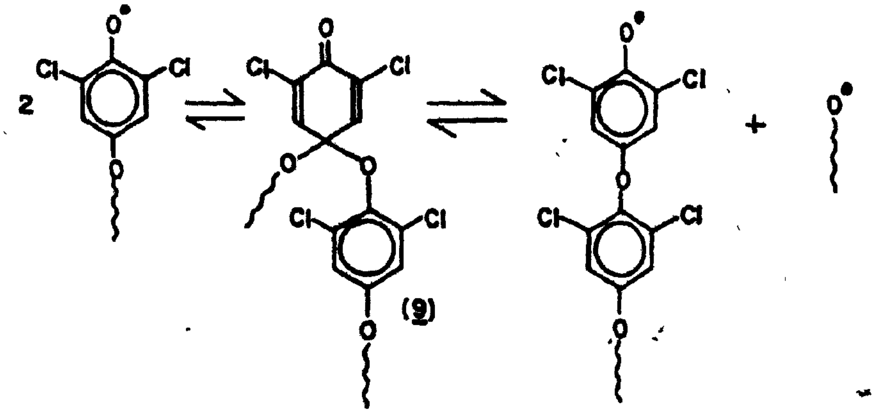
position in the monomer and the foregoing arguments an alternating copolymer would contain brominated units (7) but not (8).

A further problem which was inadequately explained by the mechanism of Carr and Harrod[81] is the approximate doubling of the polymer molecular weight subsequent to the removal of most of the copper from the reaction by precipitation as Py_2CuCl_2. How this increase in molecular weight occurs and whether the reactions accompanying it can lead to asperities, such as branch units, in the polymer is currently poorly understood.

Furthermore, one has to resist the temptation of a too liberal comparison of the coupling schemes of the widely investigated xylenol oxidative coupling reaction with those proposed for the coupling of trihalophenols. There exist fundamental differences between both systems which should not be overlooked. Firstly the former reaction is a catalytic process where the oxidizing capability of the system is preserved by the nature of the copper catalyst in the presence of oxygen whereas the latter reaction discussed in this work is a stoichiometric system containing a finite oxidizing capability. Secondly the nature of the alkyl phenol will allow the intermediate 4-hydro-4-phenoxy-2,5-cyclohexadienones to undergo tautomerization to a phenolic chain end and thus potentially to regenerate a live polymer; the analogous 4-chloro-4-phenoxy-2,5-cyclohexadienones are incapable of such a rearrangement.

Certain features of both these polymerization reactions have been interpreted in terms of the so called "redistribution reaction".[21] In the case of xylenol polymerization, redistribution was proposed to explain the molecular weight surge observed in the later stages of the reaction.[155] Harrod and Carr briefly cited redistribution as a possible explanation for the slow, near doubling of molecular weight in the trichlorophenoxide polymerization, following complete precipitation of the copper halide complex.

Redistribution[21] occurs through the coupling of two polymeric phenoxy radicals to form a quinone ketal (9) which can revert by dissociation to the original radicals or break down to one polymeric radical containing one more unit and another containing one less monomer unit (2). Formally this does not produce an increase in molecular weight since the number of molecules does not change. The net result if (2) proceeds to the right is that long chains have become longer while short chains have become shorter leaving unchanged the number average molecular weight.

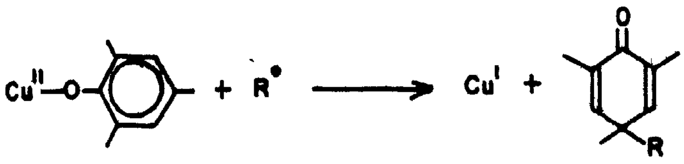


(2)

However the molecular weight distribution has changed.

A more plausible way of increasing the molecular weight relies on the formation of a new bond between two polymeric phenoxy radicals. The following discussion will show how this can be effectively accomplished in a coupling scheme in agreement with existing data.

According to the previously proposed mechanism for initiation and propagation[81], the polymer chain ends are of four possible different kinds, two at the initial and two at the terminal positions. The initial position may be either a non phenoxyl group R- originating from the initiator, or a trichlorophenoxyl unit arising from initiation of a chain by a monomeric phenoxyl radical. The terminal positions may be either a trichlorocyclohexadienone or a phenoxyl radical (3-5).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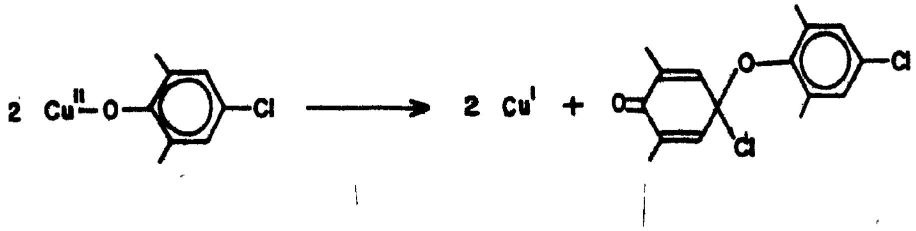
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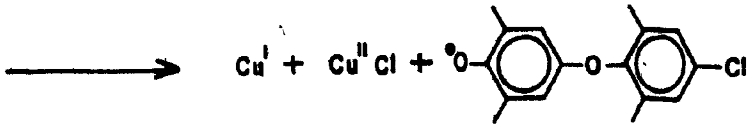
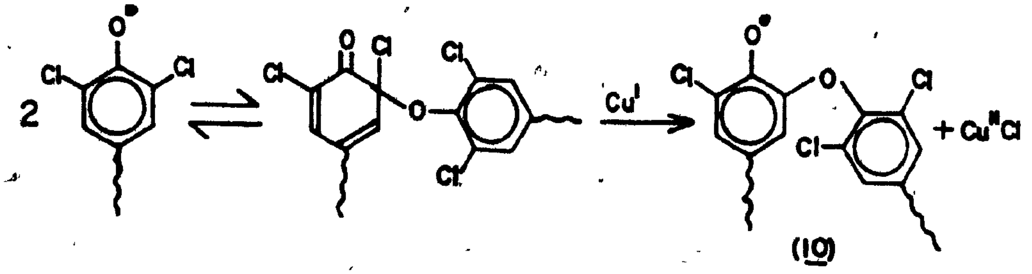

(5)

The amount of residual Cu(I) in the system can easily be shown to be the sum of the concentrations of terminal cyclohexadienyl groups and the initial trichlorophenoxyl groups in the polymer chains if one ignores the occurence of side reactions.

Following the depletion of all the copper(II) trichlorophenoxide, an increase in phenoxy radical concentration is detected in the system by esr.[81] This presumably results from chloride extrusion from the cyclohexadienyl terminal ends by the copper(I) accumulated, equation (5). At this time the polymer molecular weight[80] has reached a value of ca. 4×10^4 and coupling of these chains could in effect achieve the observed near doubling of the molecular weight (6).



(6)

As long as there is copper(I) available, these coupling reactions do not represent termination steps and the product radical polymer chains (10) could undergo further bond forming steps. The radical decay in the system follows a slow exponential with time[81] possibly reflecting the increased difficulty of the live ends in finding a suitable coupling position. Cyclization could also be envisaged in a termination step affording a dioxin bridge as has previously been proposed.[188]

If the polymer chain (10) were to couple another live chain this would result in the introduction of a branch point in the resulting polymer. Although branching could occur in these later stages of the polymerization, this does not detract from the essential argument of Chapter III that branching is not a major factor determining the properties of these polymers. The number average molecular weight[80] at the time "all" the copper in the system has precipitated is roughly $4x10^4$. If we then couple two polymer chains as depicted in equation (6) the resulting polymer will have a DP of 500. One branch point in a chain containing 500 units is hardly enough to alter its fundamental properties.

B. Halogenated Poly(phenylene oxides), Future Prospects

It has been recognized[64] that the very high thermal capabilities of poly(2,6-dimethyl-1,4-phenylene oxide) could not be utilized for extended periods because of autoxidation reactions involving the methyl groups. The preparation of linear polymer containing 2,6-dichloro substituents could thus represent a definite improvement in this line. The difluoro analogue however would possibly present even greater thermal and fire retardancy properties. Unfortunately, at the moment no convenient synthesis is available for the preparation of adequate amounts of 2,6-difluorophenol.

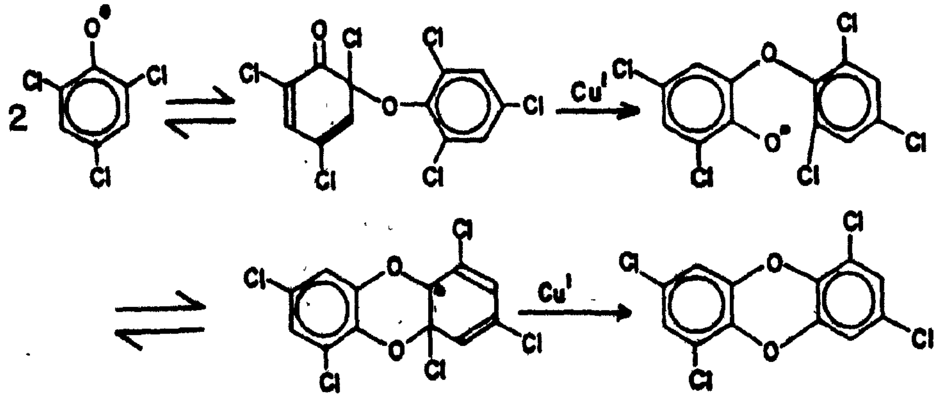
High molecular weight linear poly(2,6-dichloro-1,4-phenylene oxide) can be obtained by the present coupling system. This material combines outstanding properties such as thermal stability confered by the aromatic character of the polymer and fire retardancy associated with the halogen substituents.

It was shown in the present study that the presence of 1,2-coupled units in the 1,4-coupled chain led to inferior mechanical properties which were previously attributed to branching. The poor physical properties of these polymers can be associated with the stiffness of the polymer backbone as was discussed in the previous chapter. Where the proportion of the 1,2-coupled units attains one third of the total segments in the chains, the polymer no longer yields flexible films. The lack of segmental mobility occasioned by the presence of a high proportion of ortho-coupled units furthermore adversely affects the resolution of the proton spectra and to a lesser extent the carbon-13 spectra.

Exclusively 1,2-coupled polymers, let alone of high molecular weight, can not be obtained by placing a better halogen leaving group in the 2-position of the coordinated phenoxide. This observation tends to stress the importance of reactivity at the ring particularly the regioselectivity as discussed in the previous section. Because of the restrictions imposed by the copper chemistry effecting the coupling of the halogenated phenols, the only possible substituents which may be envisaged as better nucleofuges are pseudohalides. Whether improved results can be obtained with these remains doubtful for the moment since the efficacy of the leaving group relies on the low Ar-X bond strength. In this regard little improvement is likely beyond that attained with the 4-iodo substituent.

In the realm of polymer syntheses from halogenated phenols the possible occurence of a dangerous side reaction needs to be stressed. Coupling of halogenated phenols presents the possibility of generating dibenzo dioxins[189] a class of compounds notoriously toxic to living organisms. Toxicity is strikingly dependent on the number and position of the chloro substituents. Although no ill effects of the poly(dichlorophenylene oxides) have so far been observed, the possible presence of trace amounts of these compounds should be kept in mind.

Dibenzo dioxins (11) may arise from reaction (7), a variant of which has also been mentioned as a possible radical termination for the coupling of trihalophenols.[188] The very low radical concentration during the initial stages of the thermal decomposition of copper(II) phenoxides[81] suggests a very rapid reaction of phenoxyl radicals at coordinated phenoxide. This would tend to suppress both the radical dimerization and cyclization steps until the copper(II) phenoxide reaches a very low level.



(11)

(7)

The possibility that these polymers may generate dioxins on thermal degradation will also likely prevent their widespread practical use.

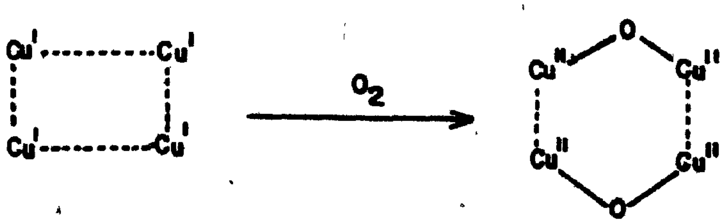
C. Polynuclear Copper Complexes

One of the remarkable features of copper ions is their ability to cluster and form mixed oxidation state complexes thus achieving islands of stability on the redox scale. The chemistry of halophenoxocopper(I) complexes described in this work seems to be influenced by the occurrence of polynuclear species. For instance, copper(II) trichlorophenoxide normally decomposes in acetonitrile, generating phenoxy radicals which couple to form polymer but in the presence of copper(I) it can be stabilized. This behavior indicates that in solution the copper species are in the form of polynuclear complexes bridged by either chloride or phenoxide ligands.

Copper clusters are widespread in biological systems. The haemocyanins responsible for oxygen transport in the blood of mollusks are known to contain a number of polynuclear copper centers which are the active sites for oxygen binding. Many biological systems in which copper occurs have more than one metal atom in them and these are coupled in oxidation-reduction reactions. Under these conditions clustering will allow the generation of mixed oxidation states in controlled release and trapping of redox equivalents. In biological systems the environment about the metal clusters often comprizes a number of polarizable ligands which are capable of inducing at the metal centers low lying charge transfer states favoring rapid electron exchange. Mixed ligand coordination furthermore induces cooperative stabilization of the substrate adducts and will tune the redox potential to a precise value allowing highly selective redox reactions to be performed.

There are reasons to suspect that clustering may also lead to a greater selectivity because it obviates the need to generate free radicals. Although the occurrence in biological systems of species carrying unpaired electrons has been recognized, their formation is energetically demanding and their high reactivity often is conducive to deleterious side reactions. Multicenter electron transfer to a substrate (oxidative addition) followed by intramolecular ligand transfer which is equivalent to a reductive elimination, will introduce enhanced selectivity without the need to implicate free radical chemistry. By combining two principles that have figured largely in the present work, namely: ligand transfer to phenoxide within a polynuclear copper complex an interesting model for dioxygen activation and selective hydroxylation may be evolved. Schematically this is represented in equations (8-10).

The difficulty in transferring oxygen containing ligands is well recognised.[89] The possibility of transferring $HO^{\bullet}$ will be maximized by coordination of the copper to highly polarizable ligands which are expected to raise the redox potential of copper(II).[190] It is interesting to note that a number of copper proteins seem to fit such a situation,



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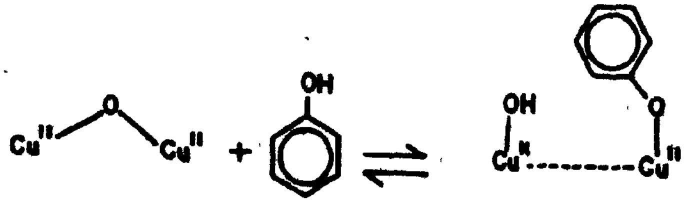
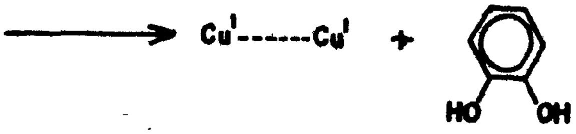


(9)



(10)

especially the "blue" proteins, where the ligands seem to be mercaptide and imidazole.[148,149]

The design and demonstration of a practical model based on the above speculation is an interesting challenge for the future.

CHAPTER V

CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

A number of copper(I) phenoxides were prepared and their reactions with carbon tetrahalides were studied. The generality of the reaction was demonstrated and it represents a novel route for the isolation of aryl ortho esters.

A mechanism for this reaction was proposed involving trihalomethyl radicals. The occurrence of the latter was verified by appropriate trapping experiments. The knowledge concerning the fate of these trihalomethyl radicals was applied in a reevaluation of the effect of CX_4 additives on the thermal decomposition of bis(amine)bis(trihalophenoxo)-copper(II) complexes.

Carbon-13 spectroscopy was for the first time applied to the examination of poly(halophenylene oxides) and allowed the determination of their microstructure as a copolymer of 1,2 and 1,4-coupled units.

The effect of increasing molecular weight of poly(halophenylene oxides) on the appearance of their proton spectra was examined and found to lead to gradual deterioration of the resolution. The peak broadness in the proton spectra was also shown to be related to the relative proportion of 1,2 to 1,4-coupled units, the 1,2-coupled units being responsible for the reduction in the segmental mobility of the chain.

Copolymers incorporating a higher proportion of 1,4-coupled units were prepared. These copolymers were found to yield better resolution in the proton and carbon-13 spectra.

CHAPTER VI

SUGGESTIONS FOR FURTHER WORK

The reactions of copper(II) phenoxides with CCl_4 could be examined under various conditions. For instance the cage hypothesis could be put to the test by adding CCl_4 to boiling acetonitrile solution of the copper(I) phenoxide. The higher temperature would be expected to cause the breakdown of the cage with the consequent appearance of phenoxy radical coupling products at the expense of ortho esters. The effect of varying the solvent should be inspected, particularly the copper(I) trichlorophenoxide/CCl_4 reaction should be carried out in pyridine.

A series of copper(I) phenoxides should be screened in a reaction with chlorotrifluoromethane in hope of preparing trifluoromethylaryl ethers.

An examination of the controlled oxidation of dicopper(I) catecholate might shed further light on the controversial[152] matter concerning oxygen incorporation during the cleavage of 1,2-dihydroxyphenols to yield cis-muconic acid derivatives.

The chemistry of ortho esters should be examined, particularly the possibility of obtaining a high selectivity in substitution reactions at the ring. This could lead to the preparation, following hydrolysis, of phenols otherwise unobtainable by conventional methods.

The 4-trichloromethyl-2,4,6-tri-t-butylcyclohexa-2,5-dien-1-one (II.6) was found to possess anti-inflammatory and anti-microbial properties in a biological screening. A number of other compounds in this class should thus be prepared and tested in hope of finding more potent congeners. In order to achieve this goal, proper phenolic synthons will have to be chosen by consideration of the stability of the corresponding phenoxy radicals as well as their capability to couple the trichloromethyl radical at the ring rather than at the oxygen. In the light of the present findings, only phenols carrying bulky substituents in the ortho positions would be appropriate.

GPC could be used in a conventional way to study the polymerization kinetics now that branching is no longer a factor.

In order to verify the microstructure of the 1,2-1,4-copolymer, additional experiments would need to be undertaken. Carbon-13 spectroscopy is possibly the most powerful tool at hand in this regard. Firstly, a rigorous assignment of all the peaks in the spectrum should be attempted by the examination of undecoupled and partially proton decoupled spectra. Secondly, the preparation of model oligomeric compounds, although a rather time consuming enterprise, might possibly shed further light on the ^{13}C and ^{1}H nmr spectra. Lastly, a study of the thermal degradation of the polymers either directly in the mass spectrometer[186] or by gas chromatography of the pyrolyzates[187] could allow an evaluation of the randomness of the copolymer.

In the realm of new polymer syntheses, another attempt could be made at obtaining a completely 1,2-coupled polymer. This can possibly be achieved by the preparation and oxidative coupling of 2,6-dichloro-4-fluorophenol. The 4-fluoro substituent is expected to be an unfavorable leaving group relative to the two ortho chlorines because of its high bond dissociation energy. The monomer can easily be prepared by thermal decomposition of the diazonium tetrafluoroborate of the corresponding 4-amino-2,6-dichlorophenol.

The orthocarbonate-forming reaction could be used as the basis for the preparation of a whole new line of polymers. For instance, using bisphenols and carbon tetrachloride, crosslinked poly(orthocarbonates) could possibly be isolated.

APPENDICES

A. COPPER PHENOXIDE COMPLEXES

COMPOUND	WAVENUMBER (CM^{-1})											
$Cu(TCP)_2$		1570	1550	1445	1390	1320	1270		1135	855	820 800	760
$Py_2Cu(TCP)_2$	1605	1565	1530	1450	1390	1310	1250	1210	1070	865 850		765 755
$Py_2Cu(2\text{-}BrDCP)_2$	1610		1525	1450	1385	1310	1245	1215	1070	860 855		770 760
$Py_2Cu(4\text{-}IDCP)_2$	1610	1555		1450	1380	1310	1250	1220	1080	870	795	770
$Cu(TCP)/CCl_4$ reaction product		1560	1540	1435	1380		1265	1215	1115	850	810 800	755
$Cu(TCP)\cdot Cu(TCP)_2$		1565	1545	1440	1390		1270	1245	1130	855	815 800	755

TCP: 2,4,6-trichlorophenoxide; 2-BrDCP: 2-bromo-4,6-dichlorophenoxide;

4-IDCP: 4-iodo-2,6-dichlorophenoxide;

B. POLY(HALOPHENYLENE OXIDES)

ORIGIN	WAVENUMBER (CM^{-1})										
$Py_2Cu(4\text{-}BrDCP)_2$	1600	1575 1560	1440	1240	1200	1000	945	910	860	820	
$Py_2Cu(TCP)_2$	1600	1575 1560	1440	1240	1200	1000	950	910	860	820	
$Py_2Cu(4\text{-}IDCP)_2$	1600	1570 1550	1440	1240	1200	1010	955	915	865	830	
$Py_2Cu(2\text{-}BrDCP)_2$	1605	1575 1560	1430	1245	1210	1005	945	910	860		780
copolymer TCP/4-BrDCP	1605	1575 1560	1450	1245	1200	1005	950	910	855	820	
copolymer 2BrDCP/4-BrDCP	1605	1575 1560	1445	1240	1205	1005	950	915	865	820	790 765
$Cu(I)TCP/CCl_4$	1600	1585	1445	1240	1200	1005	950	915	860	820	

ORIGIN	WAVENUMBER (CM^{-1})										
$Cu(II)(TCP)_2/CH_3CN$	1600	1575 1560	1450	1245	1205	1005	950	915	860	820	
$TBP/Cu(NO_3)_2/CH_3CN$	1600	1565	1435	1235	1195			920	860 850		765 745

C. ARYL ORTHO ESTERS

COMPOUND*	WAVENUMBER (CM^{-1})									
phenyl OC	1600 1595	1495		1300		1195	1180	1095	1010		910
3-methylphenyl OC	1610 1585	1490	1460		1245		1140	1090	1000		920
4-methylphenyl OC	1615 1590	1515	1385	1290		1205 1180		1110	1025		820
4-methylphenyl OF	1615 1590	1510	1390	1290		1215 1180		1080	1020		820
2-chlorophenyl OF		1485	1450	1290 1280		1220		1105	1060 1040		760
4-chlorophenyl OC		1485				1215 1205	1120	1080	1015		830
2,4,6-trichlorophenyl OF	1575 1560		1450 1390 1380		1240			1050		860	825 810

COMPOUND*	WAVENUMBER (CM^{-1})								
pentachlorophenyl OF		1395	1360	1240		1040		795	720
diphenylspiro OC	1485			1230	1185	1105	1000	760 740	

*OC: orthocarbonate; OF: orthoformate;

D. 2,4,6-TRI-T-BUTYL-2,5-CYCLOHEXADIEN-1-ONE DERIVATIVES

4-SUBSTITUENT	WAVENUMBER (CM^{-1})								
2,4,6-trichlorophenoxy	1670 1650	1550	1460 1440	1395 1385 1370	1250	1000	945	800	745
trichloromethyl	1665 1645	1485 1470		1405 1395 1370	1285 1250			825 805 785	
chloro	1665 1645	1490 1470		1370 1360	1250 1225 1205	1160	940 920	885 850 820	760 750
hydroxy	3515 1665 1645 1635	1485 1470		1365 1340		1160	1000 970	885 820	770 750
disubstituted peroxy	1670 1650	1485 1465		1395 1365 1340	1270 1250	1165	975	885 825 815	750

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