

**LOW-VALENT METAL COMPLEXES AS REDUCTIVE COUPLING  
AGENTS FOR SMOKE SUPPRESSION IN POLY(VINYL CHLORIDE)**

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A thesis

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The Faculty of the Department of Chemistry

The College of William and Mary in Virginia

In Partial Fulfillment

Of the Requirements for the Degree of

Master of Arts

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by

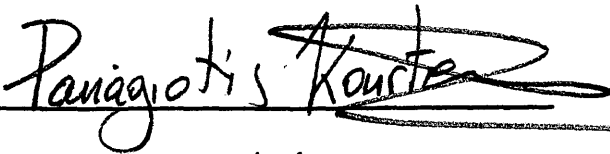
Panagiotis Ioannou Kourtesis

1996

# APPROVAL SHEET

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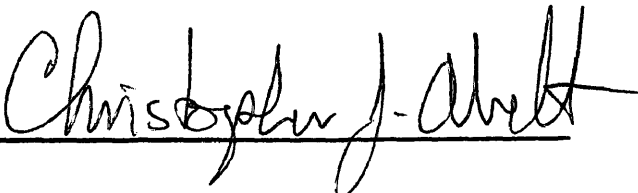
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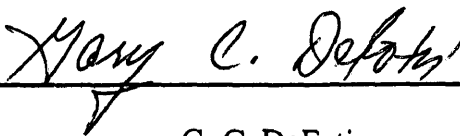
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## ABSTRACT

The role of metal additives in flame-retardancy and smoke-suppressancy in poly(vinyl chloride) (PVC) has been the center of scientific research for many years. Several proposed mechanisms have been suggested to explain the action of the metal additives during the pyrolysis of the polymer. Lewis-acid chemistry has been recognized as the important element of many of the proposed mechanisms for crosslinking of PVC during its pyrolysis. Nevertheless, cracking reactions occurring during a Lewis-acid catalysis can produce volatile hydrocarbons which, in turn, increase flame spread.

Late advances have demonstrated the use of zero-valent copper, in a reductive coupling mechanism, to produce coupling reactions of PVC model compounds and PVC itself. The aim of this investigation has been to explore the reductive coupling mechanism using a variety of low-valent transition metal additives (e.g. oxalates, formates, phosphites, hypophosphites and copper(I) precursor compounds) in hopes that a new and more effective class of PVC smoke suppressants might be uncovered.

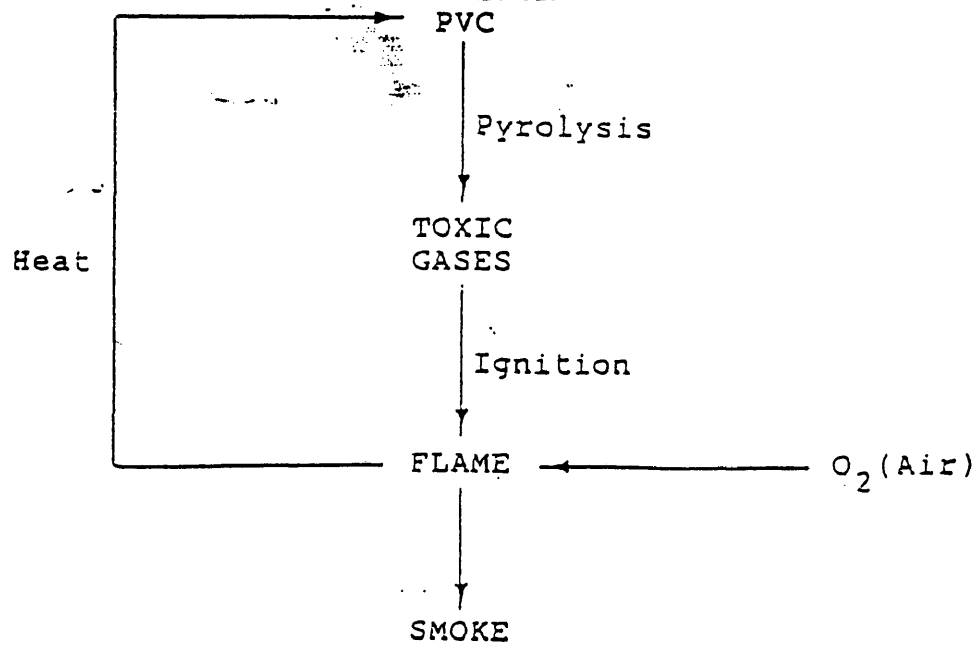
In the presence of several low-valent transition-metal additives, several benzyl and allylic chlorides model compounds, which represent structural defects in PVC, demonstrated the ability to reductively couple. The reduction of the metals in these additives was accomplished by pyrolysis, and experiments were conducted in both flowing and sealed systems. Substantial gelation of PVC was also demonstrated when these transition-metal additives were degraded in the presence of the polymer.

**LOW-VALENT METAL COMPLEXES AS REDUCTIVE COUPLING  
AGENTS FOR SMOKE SUPPRESSION IN POLY(VINYL CHLORIDE)**

## I. INTRODUCTION

### A. PVC and the Fire Hazard

Poly(vinyl chloride) (PVC),  $(-\text{CH}_2-\text{CHCl}-)_n$ , has been in the center of the scientific research for many years due to its extensive use by the chemical industry and its numerous applications in consumer products (e.g. in the automotive and construction industries).<sup>1,2</sup> Although PVC is a low-flammability polymer, upon pyrolysis, it will produce large amounts of toxic gases (e.g. HCl) and flammable vapors which burn to produce smoke (Scheme 1).<sup>1</sup> Therefore, numerous efforts have been made to alleviate this problem through the development of flame-retardancy and smoke-suppressancy additives for the polymer.

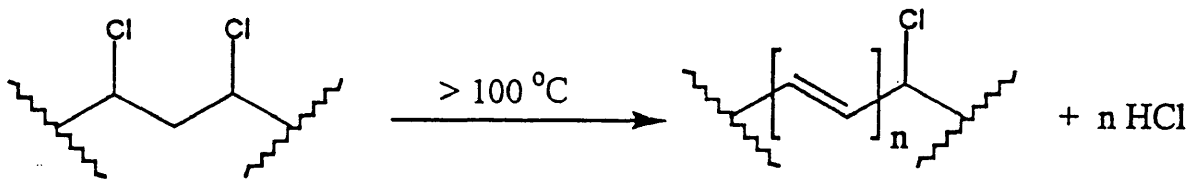


**Scheme 1. Combustion of PVC.**

## B. Thermal Instability of PVC

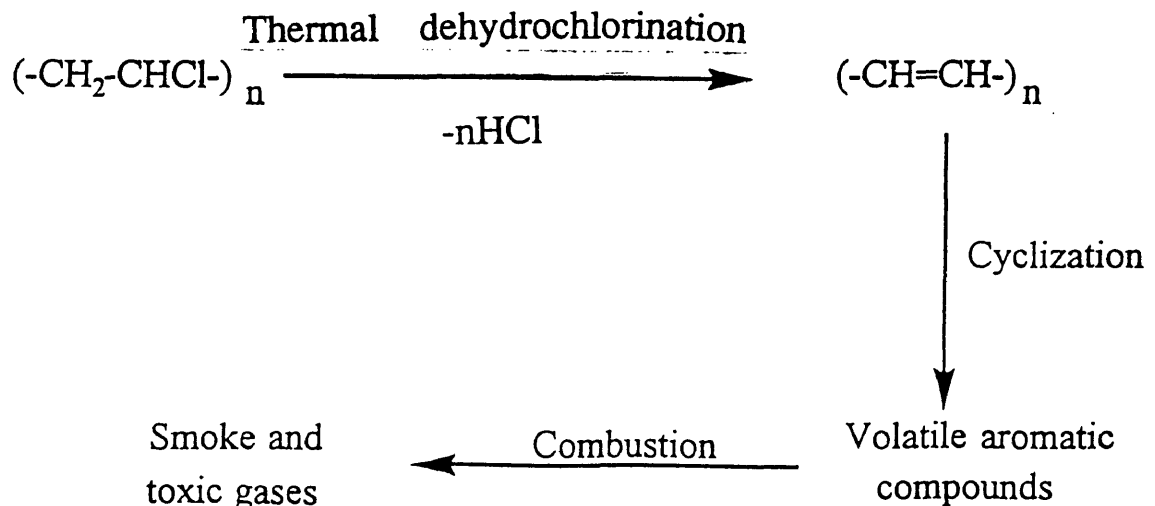
### Dehydrochlorination

The thermal instability of PVC results from facile dehydrochlorination and formation of conjugated polyene sequences which can take place at temperatures as low as 100-120 °C but typically occurs at over 200°C (scheme 2).<sup>3</sup> These conjugated polyene sequences can rearrange and decompose to produce volatile aromatic compounds capable



**Scheme 2. Dehydrohalogenation of PVC.<sup>3</sup>**

of smoke evolution according to scheme 3.<sup>4</sup>



**Scheme 3. Thermal Degradation of PVC.<sup>4</sup>**

Boettner, Ball and Weiss conducted thermal gravimetric analysis (TGA) which confirmed that two steps are involved in the thermal degradation of PVC (Figure 1).<sup>5</sup> According to the TGA curve shown in Figure 1, PVC experiences the first weight loss under 300°C. Further analysis confirmed evolution of HCl and unsubstituted aromatics (benzene, naphthalene, etc.) during this step. The second weight loss occurs at about

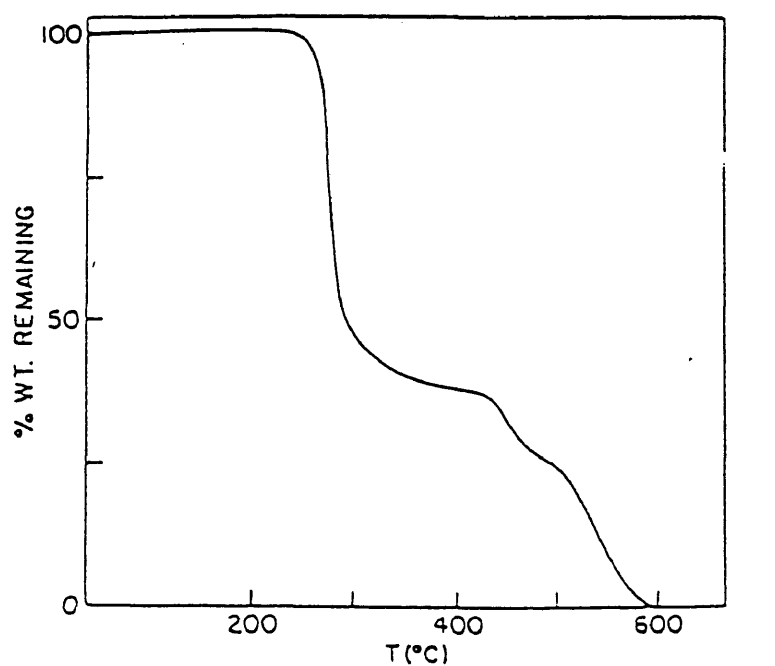
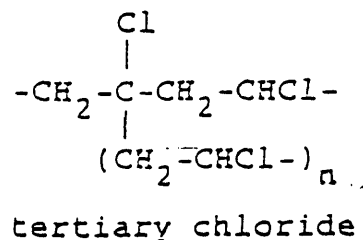
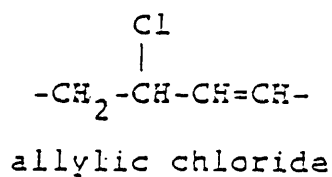


Figure 1. Weight loss vs Temperature profile of PVC.

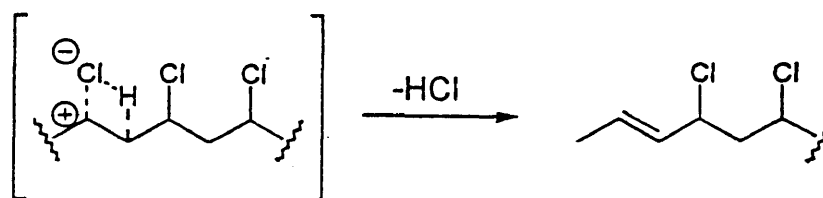
450°C and produces predominately substituted aromatics (toluene, methylnaphthalenes, etc.). Both unsubstituted and substituted aromatic compounds will readily burn to produce smoke. However, benzene appears to be the major contributor to flame and smoke evolution.

Labile defect sites in PVC are thought to be primary contributors to thermal instability. Dehydrochlorination may be initiated at such sites. These sites are created in the polymer during the polymerization process.<sup>3,6</sup> Various labile sites have been proposed: (1) unsaturated chain ends, (2) random unsaturation producing allylic chlorines, (3) branch points producing tertiary chlorines, and (4) oxygen, present as peroxide or carbonyl groups.<sup>3,6</sup> Some researchers believe that allylic chlorides have a more drastic effect on the initiation of dehydrochlorination than secondary or tertiary chlorides.<sup>7,8</sup>



However, other researchers consider tertiary chloride to be of prime importance.<sup>9,10</sup>

Recent experimental evidence by Boughdady et al. strengthens the proposal that both allylic and tertiary chlorides cause thermal dehydrochlorination of PVC which proceeds by a mechanism involving polar concerted transition states (Scheme 4).<sup>11</sup> However, other mechanisms for dehydrochlorination have been proposed.<sup>3,6</sup>



**Scheme 4. Concerted mechanism for PVC Dehydrochlorination.<sup>11</sup>**

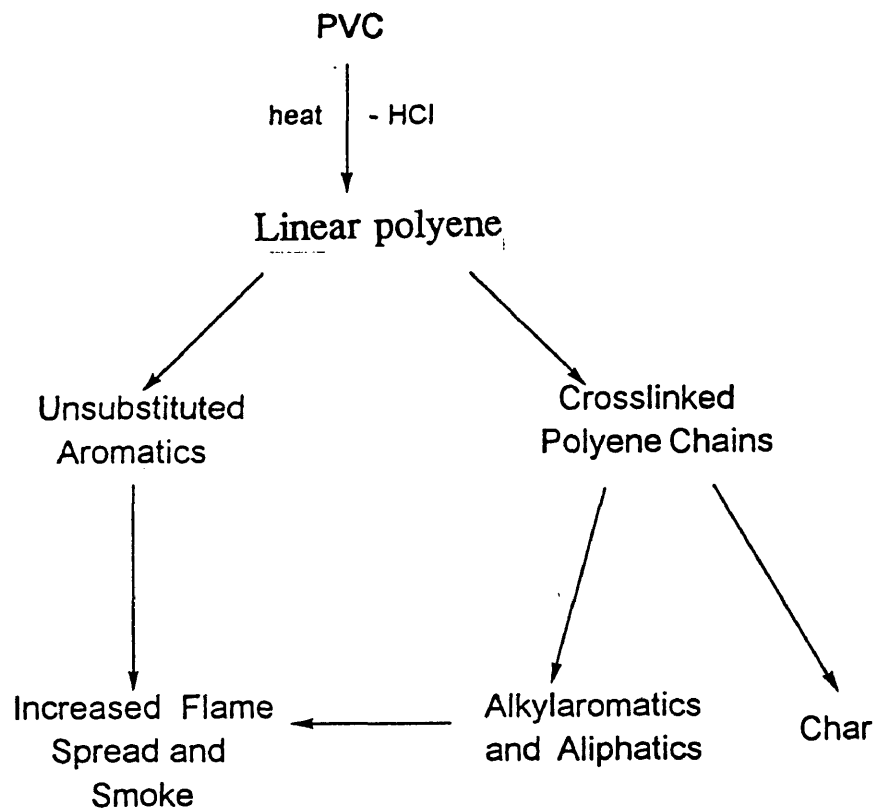
### C. Further Degradation of Polyene

There are two possible pathways that PVC may follow during its degradation. First, the polyene can undergo cyclization, producing volatile aromatic products such as benzene, styrene, naphthalene, xylene, toluene, biphenyl and many others.<sup>5</sup> These compounds will burn in the vapor phase, producing heat which, in turn, will promote further degradation of the PVC. Throughout this process, smoke and toxic gases are produced. Second, polyenes can also form crosslinks during degradation, a process in direct competition with the benzene formation. Crosslinked PVC can form either volatile aliphatics and alkyl-substituted aromatics<sup>12</sup> (promoting smoke and toxic gas evolution) or a thermally stable char residue.<sup>13</sup> A thermally stable char is desirable since it tends to cool the substrate, exclude O<sub>2</sub> necessary for pyrolysis, and reduce evolution of smoke and toxic gases.<sup>1</sup> A summary of the degradation of PVC is given in Scheme 5.

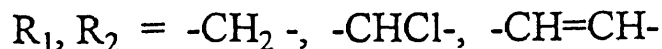
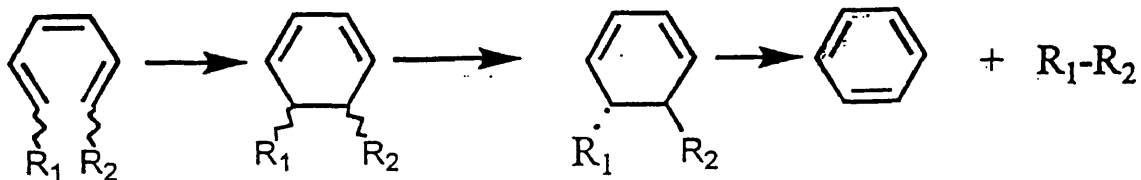
There has been extensive study of benzene formation during degradation of

PVC.<sup>1,5,14</sup> Benzene, the major source of smoke and toxic gas evolution during degradation of PVC, is produced through cyclization processes subsequent to the generation of the polyene sequences.<sup>14,15</sup>

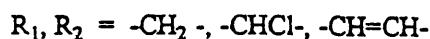
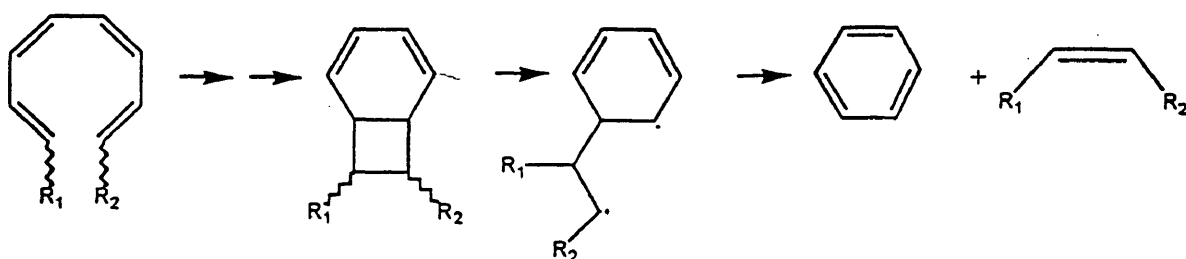
Two mechanisms have been suggested by Starnes and Edelson for the cyclization of conjugated polyene sequences producing benzene during thermolysis of PVC: the hexatriene mechanism (scheme 6) and the octatetraene mechanism (scheme 7).<sup>14</sup>



**Scheme 5. Thermal Degradation of PVC.**



**Scheme 6. Formation of Benzene by Hexatriene mechanism.<sup>14</sup>**



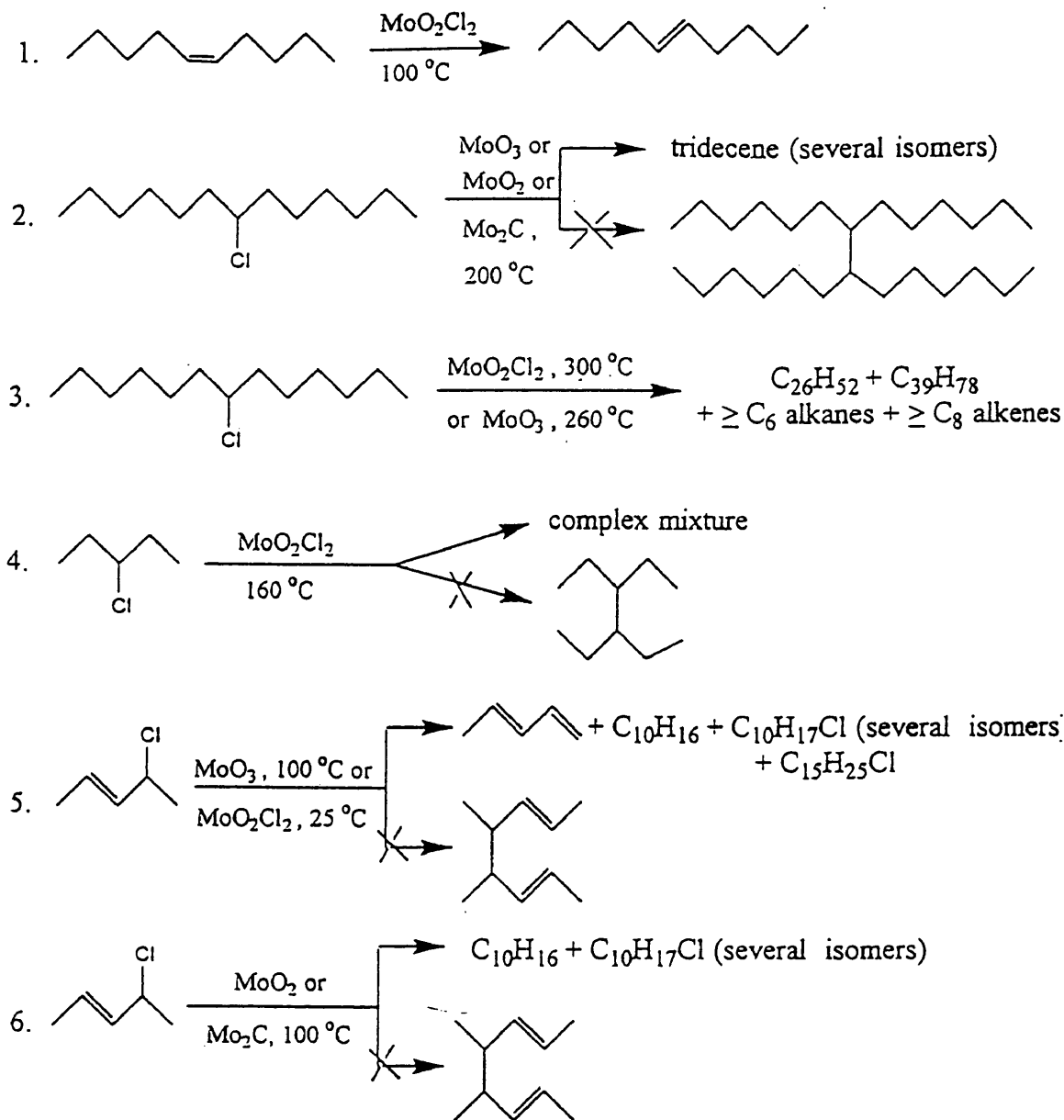
**Scheme 7. Benzene Formation by Octatetraene mechanism.<sup>14</sup>**

The hexatriene mechanism involves an intramolecular cyclization of three conjugated double bonds in the polymer backbone resulting into a cyclohexadiene structure. The only restriction is that the internal double bond must be *cis*. The cyclohexadiene structure is expected to subsequently rearrange into benzene through two C-C homolyses. The octatetraene mechanism differs in two ways from the hexatriene mechanism. Four conjugated double bonds are involved in the cyclization and both internal double bonds must be *cis*. The formation of benzene is also achieved through two C-C homolyses.

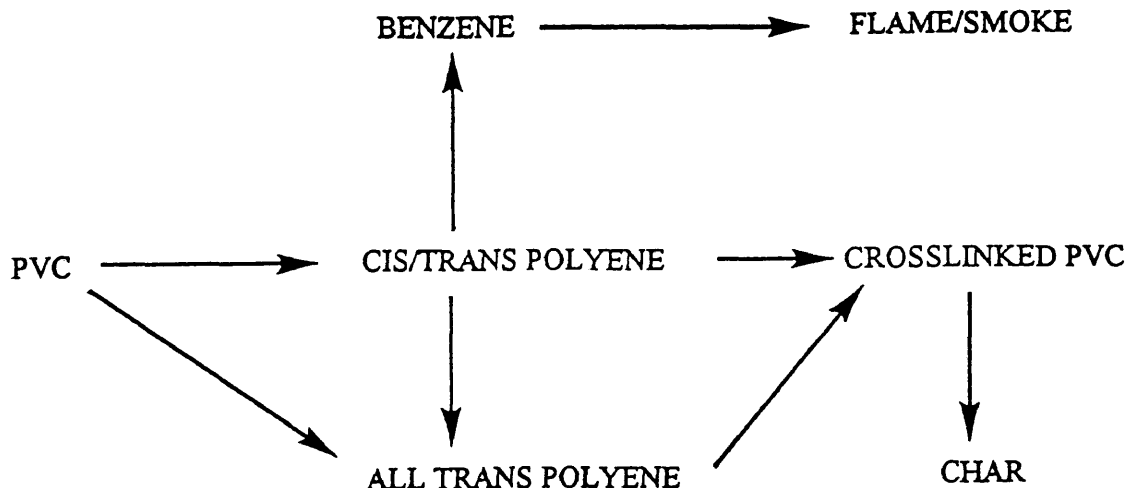
#### D. PVC and Smoke Suppression

One focus of current research is the search for effective smoke-suppressing compounds. Transition metal compounds, including chlorides and oxides, have been found to be among the most efficient smoke-suppressants.<sup>12,13</sup> Compounds of copper, iron, nickel, molybdenum, and bismuth are known to be efficient smoke suppressants in the condensed phase.<sup>16</sup> Effective smoke suppressants reduce the amount of flammable aromatics and smoke by promoting formation of a stable char. Char formation is the result of extensive crosslinking between polymer chains.

Many smoke suppressants currently in use contain Lewis acidic metal compounds, such as MoO<sub>3</sub>. Starnes and Edelson studied the effectiveness of MoO<sub>3</sub> in the degradation of PVC. Some of the PVC model compound reactions with MoO<sub>3</sub> uncovered by Starnes and Edelson are shown in Scheme 8.<sup>14</sup> When MoO<sub>3</sub> is pyrolyzed with PVC model compounds, the following competing take place: (a) dehydrochlorination (b) thermodynamically driven rearrangement of alkene segments from the *cis* to the *trans* arrangement (c) Friedel-Crafts alkylation of olefins leading to coupling and (d) cationic cracking at high temperatures (above 250-300 °C).<sup>17</sup> In the polymer itself, cationic char cracking would be expected to produce volatile, low molecular weight hydrocarbon fragments. Unfortunately, these will burn producing flame and smoke.<sup>18,19</sup> A summary of Lewis acid promoted PVC pyrolysis



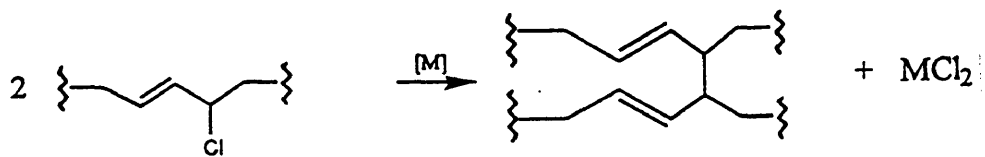
**Scheme 8. Model-compound Reactions with Molybdenum-containing Lewis acids.<sup>14</sup>**



**Scheme 9. Lewis acid Promoted Reactions during PVC Pyrolysis.<sup>14</sup>**

reactions is given in Scheme 9.<sup>14</sup>

Another theory which has been put forward to explain the smoke-suppressing action of  $\text{MoO}_3$  was proposed by Lattimer and Kroenke.<sup>12</sup> They proposed a reductive coupling mechanism according to Scheme 10. According to Lattimer and Kroenke,  $\text{MoO}_3$  can behave as a reductive coupling agent during the pyrolysis of PVC, producing crosslinks which in turn can lead to formation of a stable char. Reductive coupling of allylic halides has previously been demonstrated using low-valent metal compounds (*vide infra*).<sup>16</sup> However, model-compound experiments<sup>18-21</sup> have demonstrated that the reductive coupling mechanism does not operate or plays only a minor role in crosslink formation during the degradation of Mo(VI)-containing PVC. The reaction in Scheme 10 involves oxidative addition of R-Cl to the metal (see below). Molybdenum(VI) is in its highest available oxidation state and therefore cannot undergo further oxidation. Moreover, Lattimer and Kroenke propose that alkyl chloride sites in PVC may also undergo reductive coupling, a reaction for which there has been no literature precedent.

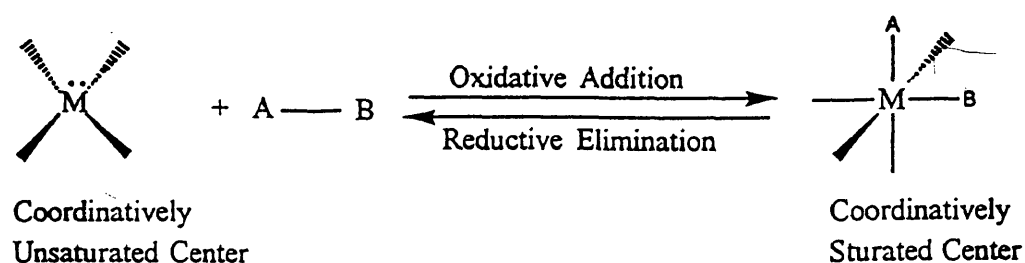


**Scheme 10. Reductive coupling of PVC.<sup>12</sup>**

Although reductive coupling of allylic chloride sites is doubtful as a mechanism for MoO<sub>3</sub> smoke suppression, it is nevertheless possible that low-valent metal compounds may promote this chemistry in the polymer. Hence, we decided to search for PVC crosslinking agents which would function despite inherently weak Lewis acidity. Metal compounds of this type would be expected to promote mild Lewis acid reactions such as dehydrochlorination, *cis/trans* isomerization and Friedel-Crafts alkylation, without promoting the cationic char cracking produced by stronger Lewis acids. Furthermore, low-valent metal compounds may also lead to reductive coupling crosslinking of PVC via oxidative addition and reductive elimination reactions.

## E. Oxidative Addition and Reductive Elimination Chemistry

Reductive coupling chemistry involves oxidative addition and reductive elimination steps. Scheme 11 demonstrates these processes: coordinatively unsaturated (<18-electron) metal complexes may undergo oxidative addition reactions, during which



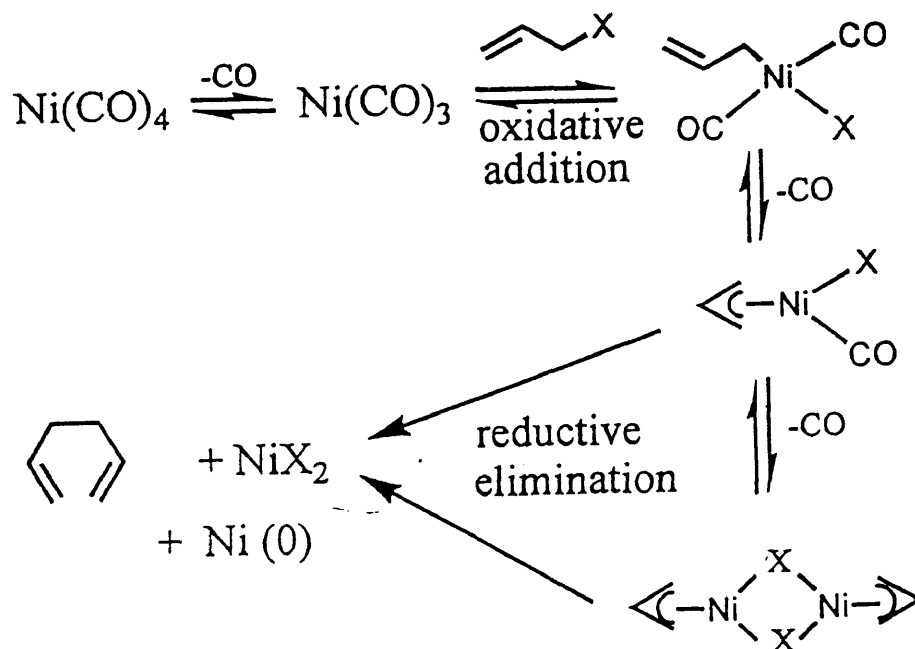
The substrates,  $\text{A} - \text{B}$ , can be  $\text{H} - \text{H}$ ,  $\text{H} - \text{X}$ ,  $\text{R} - \text{X}$ ,  $\text{RCO} - \text{X}$ ,  $\text{RCO} - \text{H}$  and many others.

### Scheme 11. General mechanism of Oxidative Addition and Reductive Elimination.

they gain ligands while formally losing electrons. Thus the metal is formally oxidized while the ligands are formally reduced. Coordinatively saturated (18-electron) metal complexes may undergo reductive elimination reactions, which are the microscopic reverse of oxidative addition. During a reductive elimination, the metal undergoes loss of ligands with acceptance of electrons. The departing ligands are oxidized and the metal is reduced.

A coordination site is opened during this process. Thus the requirements for oxidative addition are: low valent metal, coordinative unsaturation and a reducible substrate. The opposite requirements apply for reductive elimination.

Transition metals are stabilized by electron donation from ligands.  $\pi$ -Backbonding ligands, such as carbon monoxide, are especially apt to stabilize low metal oxidation states. A well-known example is the coordinatively saturated  $[\text{Ni}(\text{CO})_4]$ . Nickel carbonyl is known to couple allylic halides via the mechanism shown in Scheme 12.<sup>22</sup> Upon loss of a carbonyl group, an open coordination site is created. This site allows oxidative



Scheme 12. Coupling of Allylic halides with Nickel carbonyl.<sup>22</sup>

addition of an allylic halide. During oxidative addition, Ni(0) is oxidized to Ni(II). Subsequently, reductive elimination takes place with nickel being formally reduced, while the allyl ligands couple. Low valent metals can thus promote coupling of allylic halides through an oxidative addition and reductive elimination sequence since the metal can undergo oxidation. Since allylic halide sites are formed during the dehydrochlorination of PVC, it is conceivable that oxidative addition and reductive elimination may be useful in promoting reductive coupling of polymer chains in PVC. This would enhance char formation and thus lead to smoke suppression.

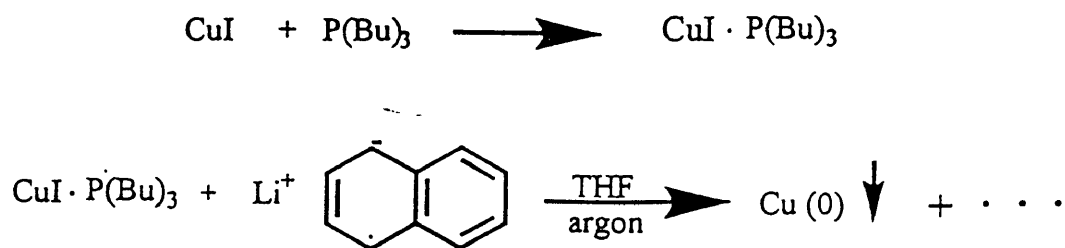
## F. Low-Valent Metal Additives and Smoke Suppression

In an effort to demonstrate PVC crosslinking through oxidative addition and reductive elimination, four steps need to be established: (1) generation of activated  $M(0)$  by well-established chemical methods (2) determination that  $M(0)$  causes reductive coupling of allylic chloride model compounds for degrading PVC (3) determination that  $M(0)$  causes the crosslinking of PVC itself (4) development of metal precursor compounds which will produce  $M(0)$  in PVC at combustion temperatures.

Copper-containing compounds have previously been shown to be highly effective as PVC smoke-suppressants.<sup>13</sup> This may be due to production of a high degree of crosslinking of the polymer.<sup>21</sup> Of course, the actual mechanisms of the coupling reactions that take place in degrading PVC are not entirely understood. Nevertheless, there are certain interesting features concerning the action of copper-containing compounds as smoke suppressants. Copper is a notoriously weak Lewis acid and it is also easily reduced. During pyrolysis, higher-valent copper compounds may be reduced to  $Cu(0)$  in the condensed phase of the polymer.<sup>12,16</sup> Copper produced under those conditions is expected to be highly reactive. Therefore, it is possible that PVC smoke suppression by copper additives may be due, at least in part, to reductive coupling chemistry. The mechanism of this reductive coupling may follow Scheme 10.

Some recent studies of the pyrolysis of PVC model compounds have been aimed to discovering the nature of copper-promoted intramolecular crosslinking. A number of

researchers<sup>17,21,23,24</sup> have thermolyzed PVC model compounds in the presence of copper compounds at temperatures ranging from 200 to 350 °C under anaerobic conditions. However, no reductive coupling products were detected. On the other hand, Jeng studied degradation of allylic chloride compounds with activated copper *metal*.<sup>25</sup> His results suggest that reductive coupling does take place under these conditions. Jeng produced activated copper metal by two different methods. Reduction of  $\text{CuI} \cdot \text{P}(\text{tBu})_3$  with lithium naphthalenide in ether solvent to give a finely divided (high-surface area) black copper powder suspended in the solvent (Scheme 13).<sup>26,27</sup> Thermal decomposition of copper(II) formate also produced a highly reactive copper film (Scheme 14).<sup>28</sup> The activated copper metal produced by these two techniques promoted rapid reductive coupling of allylic halides under very mild conditions. Since allylic chloride moieties are known to occur in both virgin and thermally degraded PVC samples,<sup>29,30</sup> these results suggested the possibility of activated metal promoting reductive coupling reactions among the PVC



**Scheme 13. Generation of High Surface Area Cu(0) by Chemical Reduction.**



**Scheme 14. Generation of Cu(0) by Thermal Decomposition of Copper(II) Formate.**

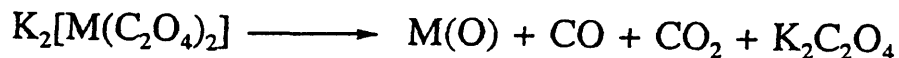
polymer chains as well. Reactions of activated copper with PVC itself in solution, as well as in the solid state were also found to promote extensive intramolecular crosslinking of PVC.<sup>25</sup>

Since copper metal appeared to be extremely promising as a crosslinking promoter, we sought to expand our study to investigate a variety of known zero-valent transition metals for reductive coupling activity. Metal carbonyls are a well-known class of metal(0) complexes. Upon thermal decomposition, these complexes lose carbon monoxide, depositing a metal film. Concurrent with the work herein, Bryant studied the reductive coupling effects of a variety of metal carbonyls.<sup>31</sup> He observed the production of shiny metal mirrors from  $\text{Co}_2(\text{CO})_8$ ,  $\text{Mo}(\text{CO})_6$ , and  $\text{Fe}_2(\text{CO})_9$ . Positive results were reported for reductive coupling of these metal additives with 3-chloro-1-butene. Although metal carbonyls readily provide active zero-valent metal which appears to promote the reductive coupling of thermally degrading PVC,<sup>31</sup> these compounds are quite unsuitable as potential polymer additives. This unsuitability relates to their toxicity and thermal instability. Therefore, we simultaneously explored other sources of low-valent metal.

The metals that were chosen for study were the first row transition elements: iron,

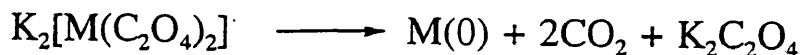
cobalt, nickel, and copper. These metals have the least negative reduction potentials of the first row transition metals; therefore, they exhibit greater stability in lower oxidation states. However (except for Au and Pt), zero-valent metal complexes are always thermodynamically unstable and would probably be useless as PVC additives. Therefore, precursor compounds which can generate zero-valent metal were sought as potential polymer additives. A promising pathway from higher-valent metal compounds to low-valent metal is offered via reductive elimination chemistry. Therefore, oxidizable ligands were chosen for use in metal precursor compounds.

Two major groups of metal precursor compounds were considered. The first group included compounds of oxalate and formate. The oxalate ligand is known to readily oxidize to carbon dioxide.<sup>32</sup> Nagase, Sato and Tanaka<sup>33</sup> reported the thermal analysis results for  $K_2[M(C_2O_4)]$  ( $M = Be(II), Mn(II), Co(II), Ni(II), Cu(II),$  and  $Zn(II)$ ) in the solid state. They conducted thermogravimetric (TG) and differential thermal analysis (DTA) studies, as well as measurement and analysis of evolved gas. They showed that the decomposition of the anhydrous complexes can be divided into two types: the complexes of  $Be(II), Mn(II),$  and  $Zn(II)$  (Scheme 15) produced metal oxide, carbon monoxide, carbon dioxide, and potassium oxalate; however, the complexes of  $Co(II), Ni(II),$  and  $Cu(II)$  (Scheme 16) produced metal(0), carbon dioxide and potassium oxalate. Therefore, it was reasonable to consider the late transition metal oxalate complexes, specifically iron, cobalt, nickel, and copper, as promising precursors to zero-valent transition metals.



M = Be, Mn, and Zn.

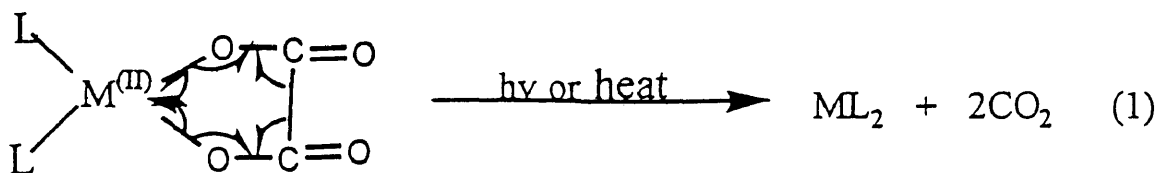
**Scheme 15. TG and DTA studies of metal oxalates.<sup>33</sup>**



M = Co, Ni, and Cu.

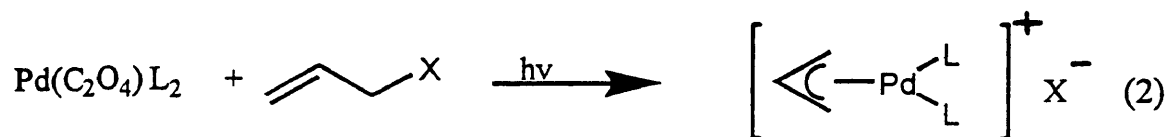
**Scheme 16. TG and DTA studies of metal oxalates.<sup>33</sup>**

Oxalate complexes are expected to undergo reductive elimination according to the following mechanism (reaction 1):

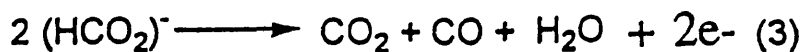


Experimental evidence has suggested that coordinatively unsaturated platinum(0) or palladium(0) species are produced on photolysis of  $\text{L}_2\text{M}(\text{C}_2\text{O}_4)$  (L = phosphines, M = Pd, Pt).<sup>32</sup>

Moreover, upon reaction of photogenerated  $\text{PdL}_2$  with allylic halide, oxidative addition of the allyl derivative occurs in high yield (reaction 2).<sup>34</sup> This demonstrates the ability of oxalate-generated metal(0) complexes to react stoichiometrically with allylic halides.



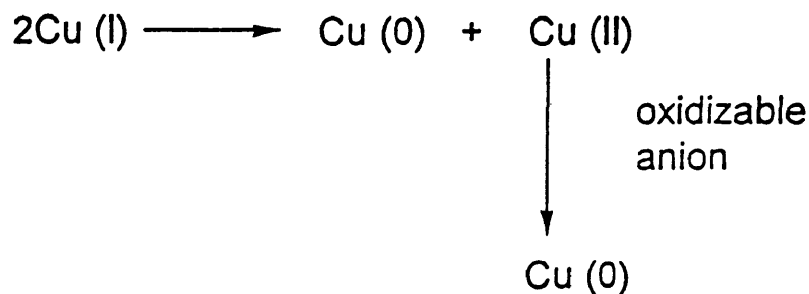
Formate ( $\text{HCO}_2^-$ ) was also considered as a promising oxidizable counterion for our late transition metal salts. Formate anion can be oxidized as shown in reaction (3).



In previous studies carried out in our laboratory, copper(II) formate<sup>25</sup> has proved to be a very successful metal precursor. Thus far, it is the only high-valent precursor compound which will form a metal film upon thermal decomposition under inert atmosphere. The resulting film has been shown to promote reductive coupling in allylic halide compounds.<sup>25</sup> Since copper(II) formate has yielded favorable results,  $\text{Fe}(\text{O}_2\text{CH})_2$ ,  $\text{Co}(\text{O}_2\text{CH})_2$ , and  $\text{Ni}(\text{O}_2\text{CH})_2$  were considered to be promising candidates as well.

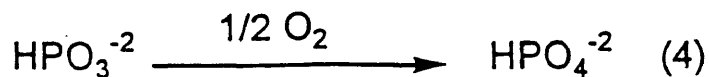
A second class of candidate metal precursors included copper(I) compounds. Copper(I) is metastable. Upon thermolysis copper(I) will disproportionate to copper(0) and copper(II) (Scheme 17). Since copper(I) readily disproportionates, donor ligands are needed to coordinate the metal in order to stabilize it. The use of oxidizable anions coordinating copper(I) would be advantageous, possibly leading to further reduction of

copper(II) produced during the disproportionation. Triphenylphosphine, formate and



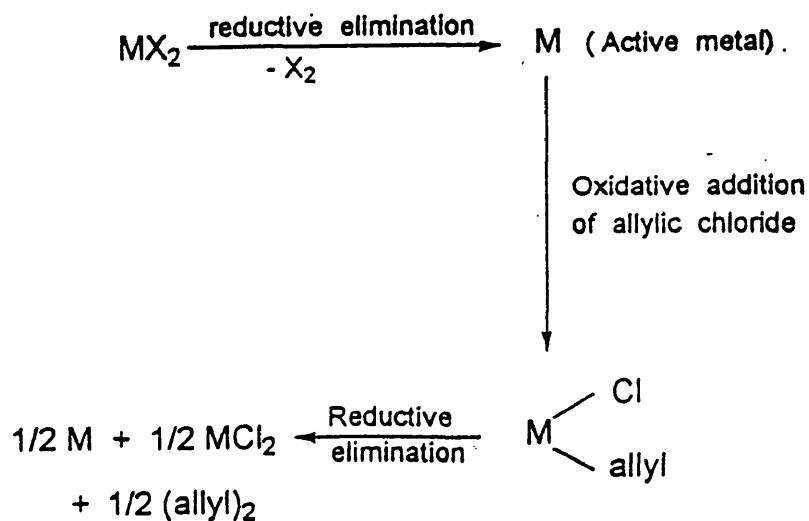
**Scheme 17. Disproportionation of Cu(I).**

borohydride were chosen to coordinatively stabilize Cu(I) while also serving as oxidizable anions which could reduce copper(II). Finally, metal phosphites and hypophosphites were also considered as promising coupling agents. The phosphite ( $\text{HPO}_3^{-2}$ ) and hypophosphite ( $\text{H}_2\text{PO}_2^-$ ) anions can be oxidized to the phosphate anion (reactions 4 and 5) and may also produce a glassy layer in the decomposing polymer further inhibiting smoke



evolution. Furthermore, aryl and alkyl phosphites are currently used as conventional flame retardants.<sup>35</sup>

With the addition of a reductive elimination step to generate low-valent metal *in situ*, we now propose a three-step mechanism for the reductive coupling of allylic chlorides shown in Scheme 18.



**Scheme 18. Reductive coupling of Allylic chlorides using a Metal Precursor compound.**

A variety of metal complexes containing iron, cobalt, nickel, and copper were explored as potential promoters of reductive coupling in PVC model compounds and PVC itself in hopes that a new and more effective class of smoke suppressants might be uncovered.

## II. EXPERIMENTAL SECTION

**A. General.** The PVC was purchased from Aldrich; it contained no additives and had a nominal inherent viscosity of 1.02.  $[\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}]$  (Johnson Matthey),  $[\text{CuC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}]$  (Pfaltz and Bauer),  $[\text{Ni}(\text{O}_2\text{CH}_2)_2 \cdot 2\text{H}_2\text{O}]$  (Alfa),  $[\text{Cu}(\text{O}_2\text{CH}_2)_2 \cdot 4\text{H}_2\text{O}]$  (Pfaltz and Bauer) were obtained from commercial sources.  $[\text{Co}(\text{O}_2\text{CH}_2)_2 \cdot 2\text{H}_2\text{O}]$  was already available having been prepared according to a literature method using cobalt metal.<sup>36</sup>  $[\text{Cu}(\text{NCCH}_3)_4](\text{BF}_4)^{37}$ ,  $[\text{Cu}(\text{PPh}_3)_3(\text{NCCH}_3)](\text{BF}_4)^{38}$  and  $[\text{Cu}(\text{PPh}_3)_4](\text{PF}_6)^{38}$  were available having been prepared according to the literature.

Reagents used for the synthesis of compounds were obtained from the following sources: (a)  $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$ ,  $[\text{CoSO}_4 \cdot 7\text{H}_2\text{O}]$ ,  $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ ,  $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$ ,  $\text{NiCO}_3$ , and  $\text{CuCO}_3$  were obtained from Fisher; (b)  $[\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}]$ , Iron powder, formic acid, triphenylphosphine,  $\text{NaBH}_4$ ,  $\text{H}_3\text{PO}_3$  were obtained from Aldrich; (c)  $[\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}]$  from Baker,  $\text{CoCO}_3$  from Alfa, and triphenylphosphite from Strem. Solvents were purified as follows: THF was distilled from benzophenone and sodium metal, acetonitrile was distilled from phosphorus pentoxide.

All experiments with PVC and model compound were carried out under argon except the sealed-ampule experiments, which were carried out under vacuum. Products of 4-chloromethylbiphenyl reaction studies were identified and quantified by GC/MS analyses, which were done with a Hewlett-Packard GC/MS System (Model 5988A) equipped with a fused-silica capillary column containing a 95:5 dimethyl: diphenylpolysiloxane mixture. All

other products of model compound studies were identified and quantified using a Hewlett-Packard GC/MS System (Model 5890 GC) with a Mass Selective Detector (Model HP5971) equipped with a Ultra-1 crosslinked methyl silicone gum fused-silica capillary. The carrier gas for both GC/MS instruments was helium. The FTIR spectra of coupling additives and polymer samples were recorded from KBr pellets with a Perkin-Elmer spectrometer, Series 1600. The TGA analyses of coupling additives and polymer samples were recorded with a Shimadzu Thermogravimetric Analyzer (Model TGA-50) connected to a WIN 486 computer via a Shimadzu Thermal Analyzer (Model TA-501). Melting point determinations of coupling additives were determined with a Thomas Hoover Unimelt capillary melting point apparatus.

Analyses of the iron oxalates were conducted for the percent metal, the percent oxalate ligand and the percent H<sub>2</sub>O. For the oxalate ligand, a sample of the compound was dissolved in 25 mL H<sub>2</sub>O and 15 mL of a 6M solution of H<sub>2</sub>SO<sub>4</sub> were added to it. The solution was heated to 80°C and immediately titrated with 0.0202M KMnO<sub>4</sub> solution. A ratio of 5:2 between C<sub>2</sub>O<sub>4</sub><sup>2-</sup> and MnO<sub>4</sub><sup>-</sup> was used to determine the weight percent of the oxalate ligands present in the compound. For the iron content, a literature procedure was followed.<sup>39</sup> For H<sub>2</sub>O, all samples were ground and dried at 105°C for 24 hours.

### **B. Reactions of 3-Chloro-1-butene with Metal Compounds.**

The metal oxalate or formate was introduced into a flame-dried 3-neck round-bottom flask

attached to a Drierite column. After the round-bottom flask had been purged with argon, the metal compound was decomposed by heating externally with a Bunsen burner. The apparatus was then allowed to cool to room temperature and a predetermined mole ratio of 3-chloro-1-butene was introduced with a syringe. The resultant suspension was filtered through celite and analyzed immediately by GC/MS after dilution with THF.

**C. Reactions of Cinnamyl Chloride with Metal Compounds.** The metal compound and cinnamyl chloride were introduced into a 40 mL glass ampule which was chilled in liquid nitrogen and immediately sealed under vacuum. The ampules were heated up either to  $200\pm 5^{\circ}\text{C}$  or to  $250\pm 5^{\circ}\text{C}$  for 1 hour and the reaction mixture was cooled, then diluted with THF and immediately analyzed by GC/MS.

**D. Reactions of Benzyl Chloride with Metal Compounds.** The metal compound and benzyl chloride were introduced into a 40 mL glass ampule that was chilled in liquid nitrogen and immediately sealed under vacuum. The ampules were heated up either to  $200\pm 5^{\circ}\text{C}$  or to  $250\pm 5^{\circ}\text{C}$  for 1 hour and the reaction mixture was cooled, then diluted with THF and immediately analyzed by GC/MS.

**E. Reactions of 4-Chloromethylbiphenyl with Metal Compounds.**

**1. Open System.** The metal compound, 4-chloromethylbiphenyl and hexadecane were introduced in a pear-shaped flask attached to a cold trap to capture volatile products. The hexadecane was used as an internal standard for quantization of the products by GC/MS. After the flask had been thoroughly purged with nitrogen, the flask was heated up by immersing it in a silicon oil bath at  $200\pm 2^{\circ}\text{C}$  for 10 minutes, then cooled. The reaction products were extracted with THF, filtered through celite and were immediately analyzed by GC/MS.

**2. Closed System.** The metal compound and 4-chloromethylbiphenyl were introduced in a 40 mL glass ampule which was chilled in liquid nitrogen and immediately sealed under vacuum. The ampules were heated up either to  $200\pm 5^{\circ}\text{C}$  or to  $250\pm 5^{\circ}\text{C}$  for 1 hour and the reaction mixture was cooled, then diluted with THF and immediately analyzed with GC/MS.

**F. PVC Gel Reactions.** A well ground mixture of metal compound and PVC (10:1 ratio by weight) was introduced in a 25 mL Erlenmeyer flask. After the flask had been thoroughly purged with nitrogen, the mixture was immersed in a Woods metal bath at  $200\pm 5^{\circ}\text{C}$  for 1 hour or at  $210\pm 5^{\circ}\text{C}$  for 1.5 hours. The resultant product was Soxhlet extracted with THF for 24 hours and subsequently dried in a vacuum oven at  $80^{\circ}\text{C}$ . The weight of the gel was determined and the percent gelation was calculated.

## G. Synthesis of Transition Metal Additives

### 1. Preparation of $[\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}]^{39}$

Ferrous ammonium sulfate (9.01 g, 23.04 mmol) was dissolved in 36 mL of water.  $[\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}]$  (6.01 g, 47.67 mmol) was added to the solution with continuous stirring. The yellow suspension that formed was heated for 15 minutes at 85°C to ensure completion of the reaction. After cooling the solution, the settled mixture was vacuum filtered and the collected yellow precipitate was washed with 95% ethanol and acetone. A bright yellow powder was the result (4.089 g, 22.73 mmol, 98.6% yield). The decomposition point was 225°C. Analysis for oxalate ligand, iron metal and  $\text{H}_2\text{O}$  gave the following results: 49.3% (theoretical 48.9%), 30.8% (theoretical 31.0%) and 6.28% (theoretical 10.01%) respectively. FTIR spectra gave the following results: 1661.5(s), 1359.0(s), 1317.9(s), 815.4(s)  $\text{cm}^{-1}$ .

### 2. Preparation of $\{\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}\}^{40}$

Ferrous ammonium sulfate (9.00 g, 22.95 mmol) was dissolved in 36 mL of water.  $[\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}]$  (5.999 g, 47.58 mmol) was added to the solution with continuous stirring. The yellow suspension that formed was heated for 15 minutes at 85°C to ensure completion of the reaction. After cooling the suspension, the excess water was removed from the settled

mixture using a pipet. The wet solid was washed three times with 5 mL portions of water, which was also removed using the same technique.  $[\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}]$  (5.999 g, 32.56 mmol) was dissolved in 18 mL of water and the solution was added to the wet yellow solid. The mixture was heated up to 80°C and 30 mL of a 30% hydrogen peroxide were added slowly. A red-brown mixture was formed and was heated up to 90°C.

Oxalic acid (1.530 g, 12.14 mmol) was dissolved in 12 mL of water and were added to the red-brown mixture. A bright green mixture was formed and it was allowed to cool down. 30 mL of 95% ethanol were added to the mixture to induce precipitation. The lime green, plate like crystals were collected with vacuum filtration and were washed with 50% aqueous ethanol and acetone (6.540 g, 13.30 mmol, 58.0% yield). The decomposition point was 290°C. Analysis for oxalate ligand, iron metal and  $\text{H}_2\text{O}$  gave the following results: 52.6% (theoretical 53.7%), 11.2% (theoretical 11.4%) and 9.97% (theoretical 10.98%) respectively. FTIR spectra gave the following results: 1710.0(s), 1684.4(s), 1397.7(s), 1273.0(s), 893.0(m), 804.5(s)  $\text{cm}^{-1}$ .

### 3. Preparation of $[\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}]$

Cobalt sulfate (9.068 g, 32.25 mmol) was dissolved in 36 mL of water.  $[\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}]$  (4.397 g, 34.88 mmol) was added to the solution which was heated at 90°C. A pink suspension was formed and was allowed to cool down. The mixture was vacuum filtered and the precipitate was washed with 95% ethanol and acetone. A pink powder was the product (5.709 g, 31.70 mmol, 99.1% yield). The decomposition point was 250°C. FTIR

spectra gave the following results: 1662.5(s), 1360.0(s), 1318.2(s), 816.1(s)  $\text{cm}^{-1}$ .

#### 4. Preparation of $\{\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3.5\text{H}_2\text{O}\}^{41}$

Oxalic acid (6.325 g, 50.17 mmol) and  $[\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}]$  (18.406 g, 99.90 mmol) was dissolved in 125 mL of boiling water.  $\text{CoCO}_3$  (6.318 g, 53.13 mmol) was slowly added to the solution in order to avoid excessive effervescence. The deep purple solution that was formed was cooled to 30°C and was kept at this temperature. To the continuously stirred purple solution,  $\text{PbO}_2$  (15.01 g, 62.77 mmol) and a uniform mixture of 6.25 mL of glacial acetic acid and 6.25 mL of water were added. The addition of the acid was done over a period of 15 minutes. The liquid was briskly stirred and left at a temperature of 30°C for 1 h for the oxidation to Co(III) to take place.

The deep green solution that formed was vacuum filtered and the filtrate was transferred to a beaker where 125 mL of 95% ethanol were added. The mixture was vacuum filtered again and the crystals that were collected were redissolved in 100 mL of cold water and 90 mL of 95% ethanol were added for recrystallization. After vacuum filtration, the deep green crystals were washed with 95% ethanol and acetone (9.882 g, 19.63 mmol, 36.9 % yield). The decomposition point was 145°C. FTIR spectra gave the following results: 1675.8(s), 1399.5(s), 1254.9(m), 904.7(m), 805.1(s)  $\text{cm}^{-1}$ .

### 5. Preparation of $\{K_4[Co_2(OH)_2(C_2O_4)_4] \cdot 3H_2O\}^{42}$

Potassium oxalate (12.499 g, 67.85 mmol) was dissolved in 40 mL of water at 100°C and  $[H_2C_2O_4 \cdot 2H_2O]$  (3.751 g, 29.75 mmol) was added to the solution.  $CoCO_3$  (3.501 g, 29.43 mmol) was added slowly to the boiling solution in order to control the effervescence. The solution was allowed to boil for 30 minutes and then it was filtered. The filtered solution was reheated to boiling temperature and  $[K_2C_2O_4 \cdot H_2O]$  (4.502 g, 24.44 mmol) was added. The solution was allowed to cool to 65°C and  $H_2O_2$  (15 mL, 20% by volume) was added within a 10 minute time interval keeping the temperature constant throughout the addition.

As soon as the addition was over, the suspension was cooled to room temperature and it was vacuum filtered. The crystals recovered were washed with cold water, a 1:1 mixture of 95% ethanol and water, and with 95% ethanol respectively. The orange crystals were allowed to dry at room temperature (3.351 gr, 4.63 mmol, 31.5% yield). The decomposition point was 150°C. FTIR spectra gave the following results: 1652.1(s), 1402.3(s), 1271.8(m), 1094.1(m), 810.8(s)  $cm^{-1}$ .

### 6. Preparation of $[NiC_2O_4 \cdot 2H_2O]$

Nickel nitrate (17.67 g, 60.08 mmol) was dissolved in boiling  $H_2O$  and  $[H_2C_2O_4 \cdot 2H_2O]$  (8.177 g, 64.80 mmol) was added to it. A pale blue precipitate appeared immediately. The suspension was vacuum filtered, washed with water, 95% ethanol and

finally with acetone. The crystals were air dried (10.92 g, 59.10 mmol, 97.2% yield). The decomposition point was 280°C.

### 7. Preparation of $\{K_2[Cu(C_2O_4)_2] \cdot 2H_2O\}$

Copper sulfate (6.201 g, 24.86 mmol) was dissolved in 12 mL of water at 90°C and  $[K_2C_2O_4 \cdot H_2O]$  (10.005 g, 54.30 mmol) was added to the solution. The bright blue solution that was formed was cooled in an ice bath and then vacuum filtered. The resulting blue crystals were washed with 95% ethanol and acetone (8.653 g, 24.45 mmol, 98.5% yield). The decomposition point was 265°C. FTIR spectra gave the following results: 1676.0(s), 1419.9(s), 1289.6(s), 1123.1(w), 897.4(w), 808.2(m)  $cm^{-1}$ .

### 8. Preparation of $[Fe(O_2CH)_2 \cdot 2H_2O]^{36}$

Iron powder (6.007 g, 107.6 mmol) was added into a mixture of  $H_2O$  (240 mL) and aqueous  $HCO_2H$  (20 mL of 45% by volume). The mixture was allowed to boil for 2 hours until no further  $H_2$  gas production was apparent. More aqueous formic acid (10 mL, 45% by volume) was added to the suspension. Formic acid (10 mL, 45% by volume) was also poured into a filter flask. The solution was vacuum filtered into the filter flask containing the formic acid and the contents of the filter flask were allowed to boil under vacuum for 2 hours. After 2 hours, crystallization occurred. The suspension was cooled in an ice bath and

was vacuum filtered. Pale green crystals were collected and washed with 95% ethanol. The filtrate was further crystallized with 95% ethanol and was poured on top of the first crop of crystals for a second vacuum filtration. The pale green crystals were dried in a vacuum oven (16.33 g, 89.8 mmol, 83.6% yield). The decomposition point was above 300°C.

### 9. Preparation of $[\text{Cu}(\text{O}_2\text{CH})(\text{PPh}_3)_3]^{43}$

Triphenylphosphine (2.349 g, 8.96 mmol) was dissolved in 40 mL of 95% ethanol and  $[\text{Cu}(\text{O}_2\text{CH})_2 \cdot 4\text{H}_2\text{O}]$  (0.503 g, 2.20 mmol) was added to the solution. The solution was allowed to reflux for 15 minutes, by which time the color of the solution was discharged. (Triphenylphosphine acts as the reducing agent). The solution was allowed to cool and was concentrated *in vacuo* to half of its original volume. At this time, a white precipitate appeared. The suspension was vacuum filtered and the white crystals were washed with ethyl ether and dried *in vacuo* (1.820 g, 2.03 mmol, 92.4% yield). The decomposition point was 175°C.

### 10. Attempted preparation of $[\text{Cu}(\text{O}_2\text{CH})(\text{PPh}_3)_2]^{43}$

Copper(II) formate (0.500 g, 2.30 mmol),  $\text{PPh}_3$  (1.166 g, 4.46 mmol) and copper turnings (0.170 g, 2.67 mmol) were added to 40 mL of distilled acetonitrile and were allowed to reflux, under nitrogen, for 1 hour. The solution changed from blue color to deep

brown-black. The suspension was vacuum filtered through celite yielding a colorless solution. As soon as the mixture was filtered, the filtrate assumed a slight green color. The solution was immediately concentrated *in vacuo* leaving green crystals. The crystals were recrystallized from acetonitrile with ethyl ether and although the crystals collected had assumed a lighter green color, they were not white. The product is apparently too unstable in air when two triphenylphosphine ligands are coordinated with the metal instead of three.

#### 11. Attempted preparation of $[\text{Cu}(\text{O}_2\text{CH})(\text{P}(\text{OPh})_3)_3]$

Copper(II) formate (0.503 g, 2.23 mmol) and  $[\text{P}(\text{OPh})_3]$  (2.410 g, 7.77 mmol) were added to 40 mL of acetonitrile. The suspension was refluxed for 4 hours under nitrogen until the blue color had disappeared. The solution was concentrated under vacuum and an oily green liquid was obtained, indicating oxidation. Ethyl ether was added to the oil but no crystallization took place.

#### 12. Preparation of $[\text{Cu}(\text{BH}_4)(\text{PPh}_3)_2]$ <sup>44</sup>

Triphenylphosphine (1.049 g, 4.00 mmol) was dissolved in 50 mL of degassed chloroform. Cuprous chloride (0.099 g, 1.00 mmol) was added to the solution and the mixture was stirred under  $\text{N}_2$  for 30 minutes until most of the  $\text{CuCl}$  had dissolved. The solution was vacuum filtered and  $\text{NaBH}_4$  (0.076 g, 2.00 mmol) dissolved in 10 mL of 95% ethanol was added to the filtrate. The solution was stirred for 1 hour. 200 mL of 95%

ethanol were added to the solution which then was chilled in an ice bath until white needle-shaped crystals appeared. The suspension was vacuum filtered and the crystals collected were dissolved in chloroform. Upon addition of 95% ethanol, the colorless solution assumed a deep yellow color. The solution was allowed to cool down in an ice bath and within 20 minutes the solution had become colorless again. The crystals were collected by vacuum filtration. The filtrate recovered was concentrated to half its volume and allowed to cool in the freezer. More crystals precipitated (0.3180 gr, 0.53 mmol, 52.7% total yield). The decomposition point was 155°C.

### **13. Preparation of $[\text{Co}(\text{H}_2\text{PO}_2)_2]^{44}$**

A dilute solution of hypophosphorous acid (10 mL of a 50% solution diluted to 100 mL volume, 90.0 mmol) was slowly added with continuous stirring to an aqueous slurry of  $\text{CoCO}_3$  (6.956 g, 60.00 mmol). To prevent reduction of Co (II) to Co (0), it was necessary that cobalt carbonate be kept in excess and that the system be cooled in an ice bath as the reaction proceeded. Stirring was continued for 2 hours to ensure completion of the reaction. Excess  $\text{CoCO}_3$  and  $\text{CoO}$  were removed by gravity filtration and the solution was evaporated, on a hot plate, to induce crystallization. Purple crystals were produced which were dried under vacuum at 100°C (8.001 gr, 42.36 mmol, 94.1% yield). The decomposition point was between 250-270°C.

#### 14. Preparation of $[\text{Ni}(\text{H}_2\text{PO}_2)_2]^{44}$

A dilute solution of hypophosphorous acid (10 mL of a 50% solution diluted to 100 mL volume, 90.0 mmol) was slowly added with continuous stirring to an aqueous slurry of  $\text{NiCO}_3$  (6.947 g, 60.00 mmol). To prevent reduction of Ni (II) to Ni (0), it was necessary that nickel carbonate be kept in excess and that the system be cooled in an ice bath as the reaction proceeded. Stirring continued for 2 hours to ensure completion of the reaction. Excess  $\text{NiCO}_3$  and NiO were removed by gravity filtration and the solution was evaporated, on a steam bath, to induce crystallization. After the volume of the filtrate had been reduced to approximately 10 mL, it was placed in the refrigerator, where bright green crystals formed. The precipitate was vacuum filtered and the crystals recovered were dried under vacuum. During drying, the color of the crystals changed from bright green to a yellow-green color (8.062 gr, 42.72 mmol, 94.9% yield). The decomposition point was 220°C.

#### 15. Preparation of $[\text{Cu}(\text{H}_2\text{PO}_2)_2]^{44}$

A dilute solution of hypophosphorous acid (10 mL of a 50% solution diluted to 100 mL volume, 90.0 mmol) was slowly added with continuous stirring to an aqueous slurry of

$\text{CuCO}_3$  (7.415 g, 60.00 mmol). To prevent reduction of Cu (II) to Cu (0), it was necessary that copper carbonate be kept in excess and that the system be cooled in an ice bath as the reaction proceeded. Stirring was continued for 2 hours to ensure completion of the reaction. Excess  $\text{CuCO}_3$  and  $\text{CuO}$  were removed by gravity filtration. When crystallization of a portion of the filtrate obtained after the vacuum filtration was attempted on a steam bath, the solution turned from blue to brown indicating decomposition. 350 mL of 95% ethanol were added to the rest of the solution and it was chilled. Crystallization occurred, producing pale blue crystals. The crystals were vacuum filtered, washed with ethanol, acetone and ethyl ether. The solid was vacuum dried becoming a lavender color (4.821 g, 24.91 mmol, 55.4% yield). The decomposition point was 95°C.

## 16. Preparation of $\text{Co}(\text{HPO}_3)^{46}$

Molten  $\text{H}_3\text{PO}_3$ , in excess at 80°C, was reacted with  $\text{CoCO}_3$  (2.825 g, 23.75 mmol). The reaction was slow due to the fact that the mixture tended to solidify upon addition of the carbonate. The mixture was allowed to stir at 80°C for 3.5 hours. When the mixture was cooled to room temperature, it became a solid. This solid was suspended in minimal amount of 100% ethanol and was vacuum filtered. The purple crystals collected were washed with 100% ethanol, acetone, ethyl ether and were dried under vacuum. The crystals had now assumed a lavender-pink color. The crystals were refluxed with 95% ethanol for 48 hours in order to remove trapped  $\text{H}_3\text{PO}_3$  (3.112 g, 22.41 mmol, 94.3% yield). The decomposition point was 245°C.

### **17. Preparation of Ni(HPO<sub>3</sub>)<sup>46</sup>**

Molten H<sub>3</sub>PO<sub>3</sub>, in excess at 80°C, was reacted with NiCO<sub>3</sub> (2.968 g, 25.00 mmol). The reaction was slow due to the fact that the mixture tended to solidify upon addition of the carbonate. The mixture was allowed to stir at 80°C for 3.5 hours. After the mixture was cooled to room temperature, it became a solid which was suspended in minimal amount of 100% ethanol and was vacuum filtered. The yellow crystals collected were washed with 100% ethanol, acetone, ethyl ether and were dried under vacuum. The crystals had now assumed an even paler yellow color. The crystals were refluxed with 95% ethanol for 72 hours in order to remove trapped H<sub>3</sub>PO<sub>3</sub> after being vacuum dried (3.359 g, 24.22 mmol, 96.9% yield). The decomposition point was 245°C.

### **18. Attempted preparation of Cu(HPO<sub>3</sub>)<sup>46</sup>**

The compound was attempted to be synthesized using the above technique but, upon addition of CuCO<sub>3</sub>, a red color developed from the blue-green color of the mixture. It increased until, upon completion of carbonate addition, most of the mixture had assumed the red color. This indicated that the Cu(II) was being reduced to metallic Cu(0) by phosphorous acid.

### 19. Attempted preparation of $\text{Cu}(\text{O}_2\text{CH})^{36}$

Copper(II) formate (2.223 g, 9.90 mmol),  $\text{HCO}_2\text{H}$  (2.440 g, 53.00 mmol, 95-97% pure) and copper turnings (5.757 g, 90.59 mmol) were combined in acetonitrile (40 mL). The reactants were stirred under nitrogen for 64 hours, by which time the solution had become colorless. A colorless solution denoted the formation of the desired compound. The solution was then decanted from the flask containing the remaining copper turnings and vacuum filtered into stirred anhydrous, deoxygenated ether (200mL) which had been distilled from benzophenone and sodium metal in order to remove any water. The collected crystals were green in color indicating some oxidation. The product is apparently quite moisture and air sensitive. The lack of ancillary ligands is probably responsible for the sensitivity of copper (I) formate.

### III. RESULTS AND DISCUSSION

#### A. Synthesis and Characterization of Precursor Compounds

The metals that were chosen for study were the first row transition elements: iron, cobalt, nickel, and copper. These metals have the least negative reduction potentials of the first row transition metals; therefore, they exhibit greater stability in lower oxidation states. Precursor compounds which can generate zero-valent metal were sought as potential polymer additives. A promising pathway from higher-valent metal compounds to low-valent metal is offered via reductive elimination chemistry. Therefore, oxidizable ligands were chosen for use in metal precursor compounds.

Two major groups of metal precursor compounds were considered. The first group included compounds of oxalate and formate. The following compounds were synthesized:  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ ,  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{K}_2[\text{Co}(\text{C}_2\text{O}_4)_2] \cdot 3.5\text{H}_2\text{O}$ ,  $\text{K}_4[\text{Co}_2(\text{OH})_2(\text{C}_2\text{O}_4)_4] \cdot 3\text{H}_2\text{O}$ ,  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ , and  $\text{Fe}(\text{O}_2\text{CH})_2 \cdot 2\text{H}_2\text{O}$ . Their decomposition ranges are listed in Table 1.

A second class of candidate metal precursors included copper(I) compounds. Copper(I) is metastable and will thermally disproportionate to copper(0) and copper(II). The use of oxidizable anions coordinating copper(I) would be advantageous, possibly leading to further reduction of copper(II) produced during the disproportionation.

**Table 1**

**Decomposition Ranges of Oxalate and Formate  
Precursor Compounds**

Compound	Decomposition Range (°C)
$\text{FeC}_2\text{O}_4$	225-228
$\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$	290-293
$\text{CoC}_2\text{O}_4$	250-253
$\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$	145-148
$\text{K}_4[\text{Co}_2(\text{OH})_2(\text{C}_2\text{O}_4)]$	150-153
$\text{NiC}_2\text{O}_4$	270-290
$\text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2]$	265-268
$\text{Fe}(\text{O}_2\text{CH})_2$	190-210

Triphenylphosphine, formate, and borohydride were chosen to coordinatively stabilize Cu(I) while also serving as oxidizable ligands which could reduce copper(II). The following compounds were synthesized:  $[\text{Cu}(\text{O}_2\text{CH})(\text{PPh}_3)_3]$ ,  $[\text{Cu}(\text{BH})(\text{PPh}_2)]$ ,

$[\text{Cu}(\text{O}_2\text{CH})(\text{PPh}_3)_2]$ ,  $\text{Cu}(\text{O}_2\text{CH})$ , and  $[\text{Cu}(\text{O}_2\text{CH})(\text{P}(\text{O}(\text{Ph})_2)_2)]$ . Of the compounds synthesized, the three latter were not isolated. The reason was their instability in air which caused them to oxidize rapidly. The lack of ancillary ligands is probably responsible for the sensitivity of  $\text{Cu}(\text{O}_2\text{CH})$ . Even in the case of  $[\text{Cu}(\text{O}_2\text{CH})(\text{PPh}_3)_2]$ , the presence of only two triphenylphosphine ligands instead of three is probably the cause of its instability. The decomposition ranges of the isolated precursor compounds are listed in Table 2.

**Table 2**  
**Decomposition Ranges of Copper(I)**  
**Precursor Compounds**

Compound	Decomposition Range (°C)
$[\text{Cu}(\text{O}_2\text{CH})(\text{PPh}_3)_3]$	170-185
$[\text{Cu}(\text{BH}_4)(\text{PPh}_3)_2]$	145-165

Finally, metal phosphites and hypophosphites were also considered as promising coupling agents. The phosphite ( $\text{HPO}_3^{2-}$ ) and hypophosphite ( $\text{H}_2\text{PQ}^-$ ) anions can be oxidized to the phosphate anion and may also produce a glassy layer in the decomposing polymer, further inhibiting pyrolysis. The following compounds were synthesized:

$\text{Co}(\text{H}_2\text{PO}_2)_2$ ,  $\text{Ni}(\text{H}_2\text{PO}_2)_2$ ,  $\text{Cu}(\text{H}_2\text{PO}_2)_2$ ,  $\text{Co}(\text{HPO}_3)$ ,  $\text{Ni}(\text{HPO}_3)$ , and  $\text{Cu}(\text{HPO}_3)$ . Of the compounds selected to be synthesized, the latter was not isolated. Upon addition of  $\text{CuCO}_3$  to  $\text{H}_3\text{PO}_3$ , a red color developed from the blue-green color of the mixture indicating rapid reduction of copper(II) to copper(0) by phosphorous acid. The decomposition ranges of the isolated precursor compounds are listed in Table 3.

**Table 3**

**Decomposition Ranges of Metal Phosphite  
and Hypophosphite Precursor Compounds**

<b>Compound</b>	<b>Decomposition Range (°C)</b>
<b><math>\text{Co}(\text{H}_2\text{PO}_2)_2</math></b>	<b>250-270</b>
<b><math>\text{Ni}(\text{H}_2\text{PO}_2)_2</math></b>	<b>215-225</b>
<b><math>\text{Cu}(\text{H}_2\text{PO}_2)_2</math></b>	<b>80-85</b>
<b><math>\text{Co}(\text{HPO}_3)</math></b>	<b>240-250</b>
<b><math>\text{Ni}(\text{HPO}_3)</math></b>	<b>240-250</b>

## **B. Coupling Studies with Model Compounds and Metal Additives**

Four model compounds (3-chloro-1-butene, cinnamyl chloride, benzyl chloride, and 4-chloromethyl biphenyl) were used in order to investigate the possibility of a reductive coupling mechanism which may occur during pyrolysis of PVC. Allylic chlorides were chosen due to their high reactivity as well as their resemblance to active sites in PVC. Benzylic chlorides were also chosen due to their chemical reactivity similar to that of allylic chlorides. The benzylic chlorides were also chosen due to their relatively high molecular weights and boiling points. The boiling points of the model compounds were required to be at or above the decomposition points of the metal compounds.

## 1. Coupling Studies of 3-Chloro-1-butene with Metal Additives

Jeng reported coupling of 3-chloro-1-butene in the presence of high-surface-area copper produced from the reduction of  $\text{CuI} \cdot \text{PBU}_3$  by lithium naphthalenide.<sup>25</sup> The ability of 3-chloro-1-butene to reductively couple was the reason it was chosen as a model compound of allylic chloride structures in PVC.

Bryant synthesized the homocoupled product using lithium metal in diglyme as the coupling agent.<sup>31</sup> He reported the production of seven possible homocoupled product isomers with retention times of 0.659, 0.673, 0.751, 0.794, 0.971, 1.007, and 1.057 by GC/MS analysis (MW = 110 g/mol).

3-chloro-1-butene was injected into the GC/MS as a control to determine whether the model compound would couple in the absence of "coupling additives". None of the coupled products were observed. This result also eliminated the possibility of coupling occurring in the injection port during GC analysis.

8 different "coupling agents" were tested for coupling of 3-chloro-1-butene. The results are listed on Table 4. All metal additives were tested in the open (external flame) system (described in the Experimental section).

**Table 4**  
**GC Area Percentages of Pyrolysis Products from Metal**  
**Compounds and 3-Chloro-1-butene**

% Area

<b>Metal Compound</b>	<b>Weight Ratio</b>	<b>3-chloro-1-butene</b>	<b>Coupled product</b>	<b>All others</b>
<b>Time (min)</b>	<b>-----</b>	<b>0.638</b>	<b>0.751</b>	<b>----</b>
<b>FeC<sub>2</sub>O<sub>4</sub></b>	<b>1:3</b>	<b>0.0</b>	<b>0.0</b>	<b>100</b>
<b>Fe<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub></b>	<b>1:2</b>	<b>15.2</b>	<b>10.1</b>	<b>74.7</b>
<b>Fe<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub></b>	<b>1:3</b>	<b>23.9</b>	<b>3.4</b>	<b>72.7</b>
<b>Fe(O<sub>2</sub>CH)<sub>2</sub></b>	<b>1:3</b>	<b>44.7</b>	<b>4.6</b>	<b>50.7</b>
<b>CoC<sub>2</sub>O<sub>4</sub></b>	<b>1:2</b>	<b>17.6</b>	<b>1.9</b>	<b>80.5</b>
<b>CoC<sub>2</sub>O<sub>4</sub></b>	<b>1:3</b>	<b>0.0</b>	<b>0.0</b>	<b>100</b>
<b>K<sub>4</sub>[Co<sub>2</sub>(OH)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>4</sub>]</b>	<b>1:3</b>	<b>0.0</b>	<b>0.0</b>	<b>100</b>
<b>K<sub>3</sub>[Co(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]</b>	<b>1:3</b>	<b>23.7</b>	<b>3.0</b>	<b>69.1</b>
<b>Cu(O<sub>2</sub>CH)<sub>2</sub></b>	<b>1:2</b>	<b>77.7</b>	<b>20.1</b>	<b>2.2</b>
<b>NiC<sub>2</sub>O<sub>4</sub></b>	<b>1:3</b>	<b>0.0</b>	<b>0.0</b>	<b>100</b>

Among the metal additives tested, Cu(O<sub>2</sub>CH)<sub>2</sub> and Fe<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> gave the best yields for the coupled product of 3-chloro-1-butene (20.1% and 10.1% respectively). Figure 2

shows a representative chromatogram and mass spectrum for the peak observed by a GC/MS. Two interesting observations were made: (a)  $\text{Cu}(\text{O}_2\text{CH})_2$  gave the largest coupling product yield among all 8 metal additives tested while almost 80 percent of the starting material (3-chloro-1-butene) did not react and (b) the only coupled product was seen at 0.751 minutes while all other isomers were not observed. This coupled product is relatively unstable because the parent ion (110 m/z) is not observed.

The yields resulting from the rest of the metal additives tested were not as significant, but definitely support the idea of a reductive coupling mechanism through zero-valent transition metals.  $\text{FeC}_2\text{O}_4$ ,  $\text{K}_4[\text{Co}_2(\text{OH})_2(\text{C}_2\text{O}_4)_4]$  and  $\text{NiC}_2\text{O}_4$  proved to be extremely reactive with 3-chloro-1-butene (consuming all of the starting material) but producing no coupling product.

In conclusion, the results of the model-compound study of transition metals in the presence of 3-chloro-1-butene indicated that reductive coupling often did occur. These results support those obtained in Jeng's study of the reductive coupling of allylic chlorides via highly activated zero-valent copper metals as well as Bryant's study of the reductive coupling of allylic chlorides via transition metal carbonyls. Since allylic chloride structural defects are known to occur in both virgin and thermally degraded PVC, and since reductive coupling is shown to be a possible mechanism for allylic chlorides, this coupling reaction could lead to extensive crosslinking in PVC.

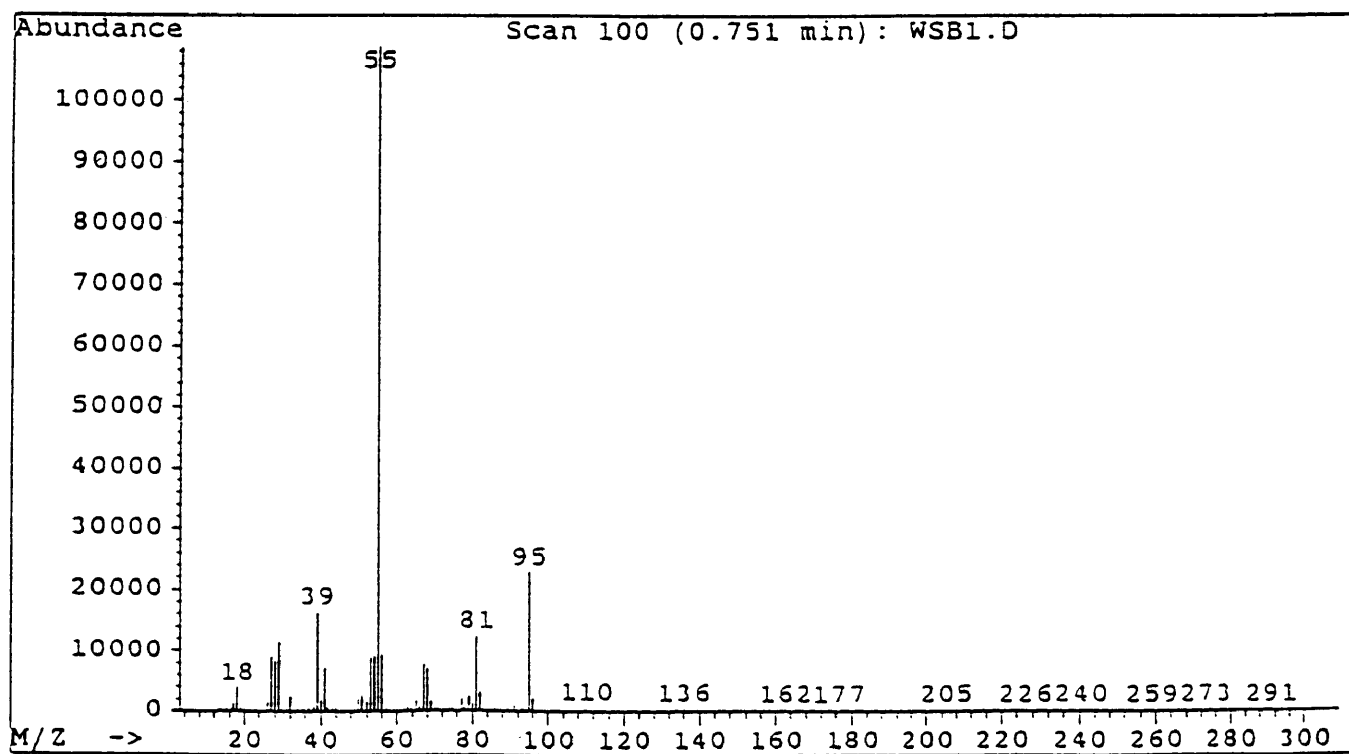
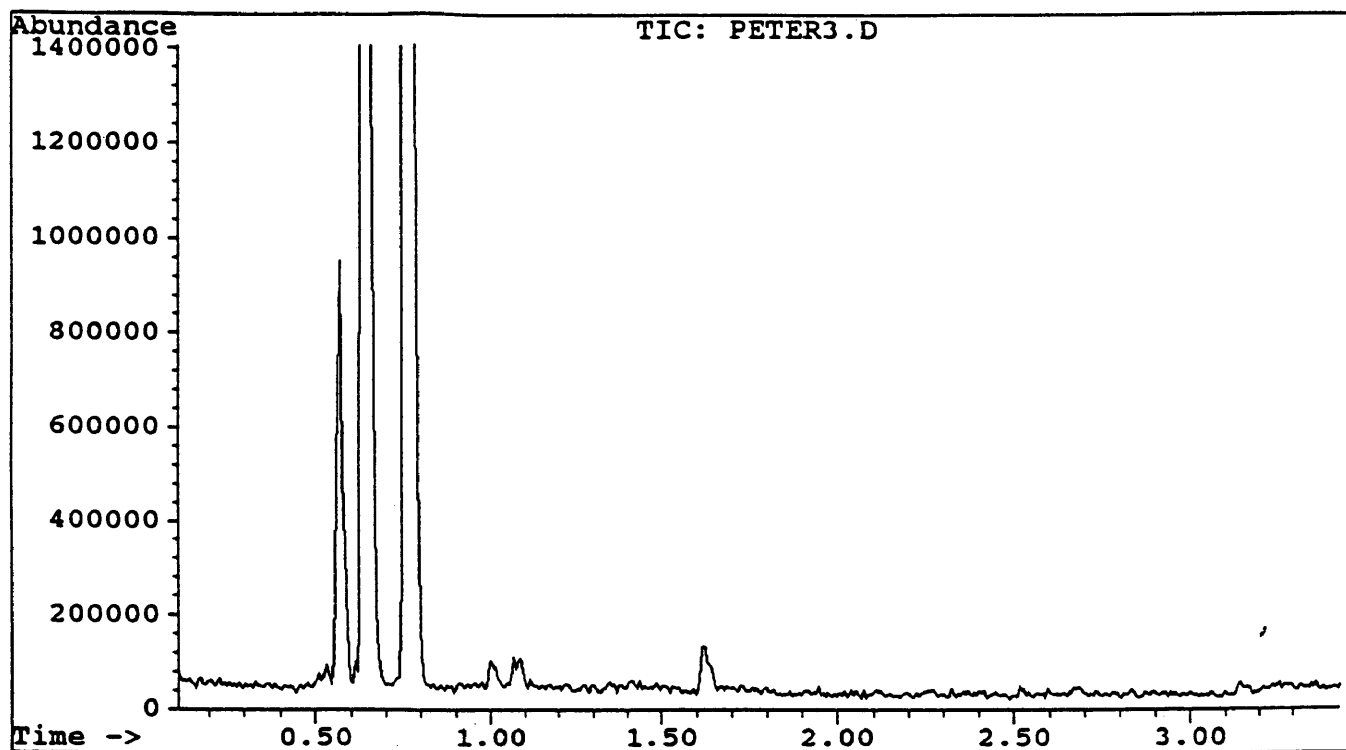


Figure 2. GC/MS data for the coupled product from Cu(II) formate and 3-chloro-1-butene.

## 2. Coupling Studies of Cinnamyl Chloride and Cinnamyl Bromide with Metal Additives

A variety of metal additives were tested for coupling of cinnamyl chloride and bromide as model compounds for PVC. Cinnamyl chloride has a relatively high boiling point compound (126 °C) and contains an allylic chloride functionality.

Cinnamyl chloride (Aldrich, 95% and Pfaltz and Bauer, 97%) and cinnamyl bromide (Aldrich, 97%) were injected into the GC/MS and the spectra were analyzed. The spectra indicated several peaks for all three compounds (Figures 3, 4, and 5 respectively) and gave purities of 92.0%, 81.0%, and 51.3% respectively. Sometimes, 97% cinnamyl chloride gave a spectrum which showed a peak corresponding to a dimeric species ( $m/z$  234)(Figure 6). This indicates the possibility of a coupling reaction taking place in the GC injection port.

Bryant reported the GC/MS spectra of the authentic coupled product with lithium and cinnamyl chloride (95%).<sup>35</sup> The retention times and the MS percent area yields of the three isomer peaks were the following: 8.47 min (46.6%), 9.06 min (1.4%), and 9.41 min (22.0%). Since the *trans* isomer is the most thermodynamically stable of the three isomers, the largest peak at 8.47 minutes can be assigned to this isomer.

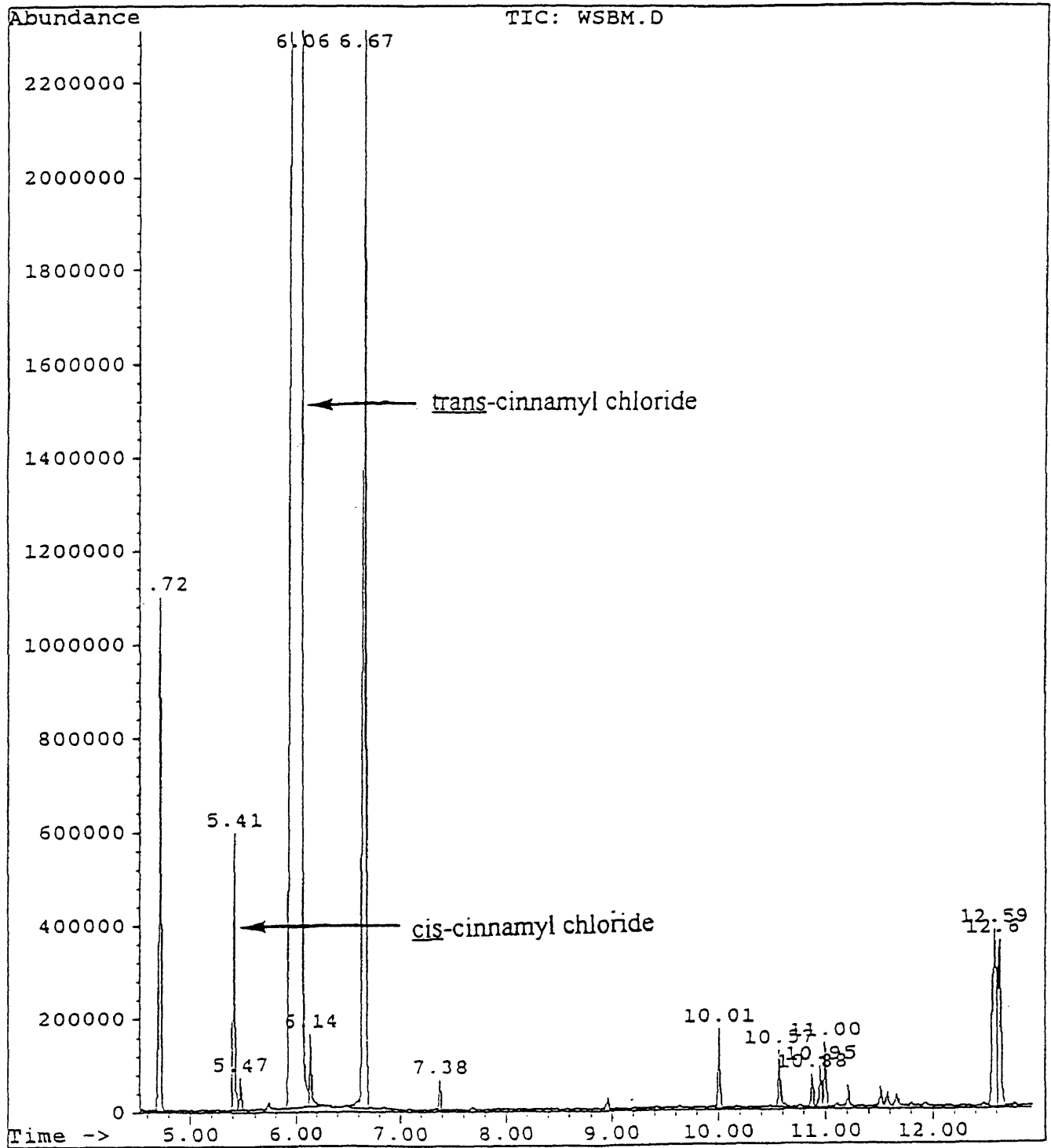


Figure 3. GC chromatogram of 95% Cinnamyl Chloride.

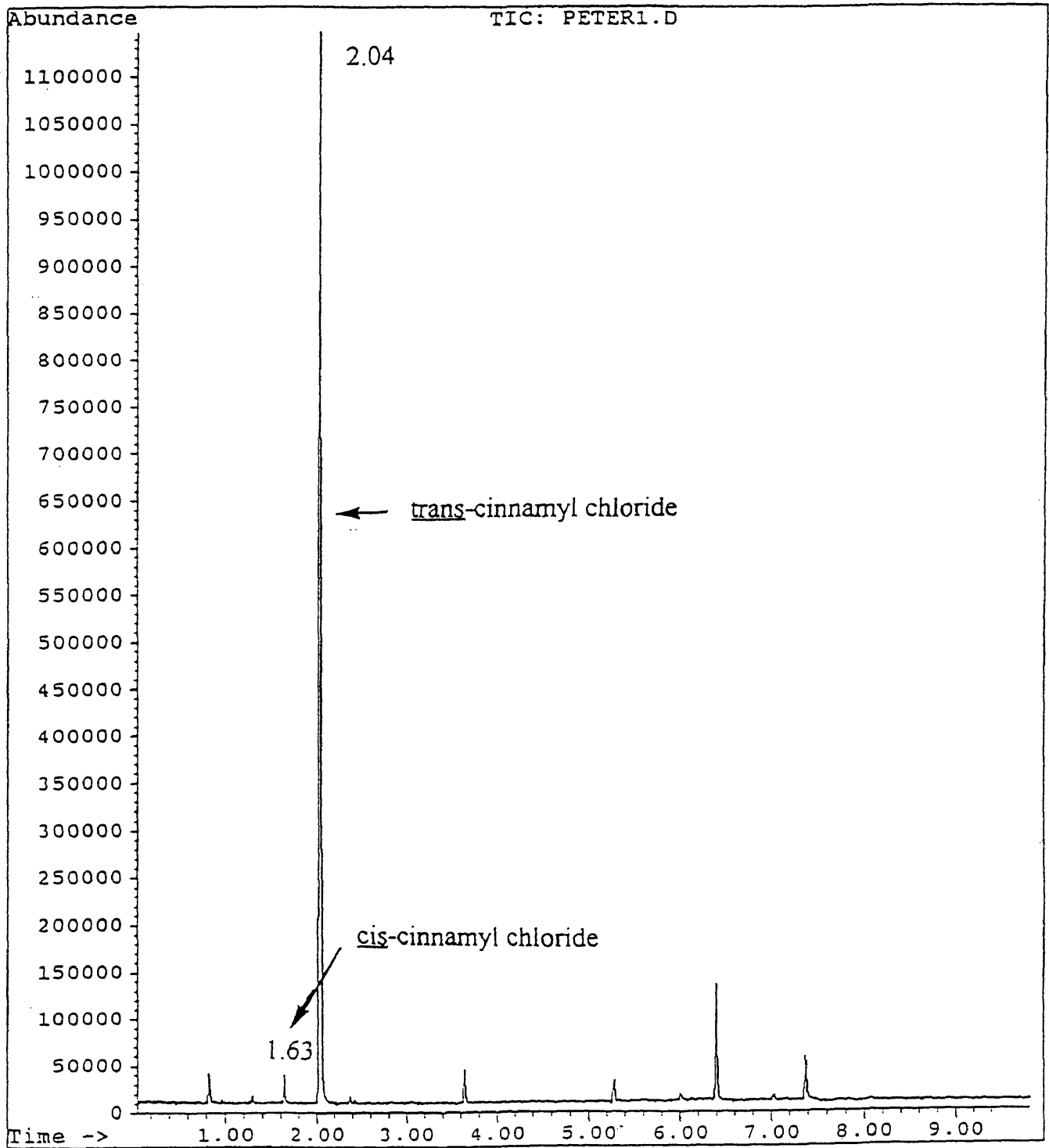


Figure 4. GC chromatogram of 97% Cinnamyl Chloride.

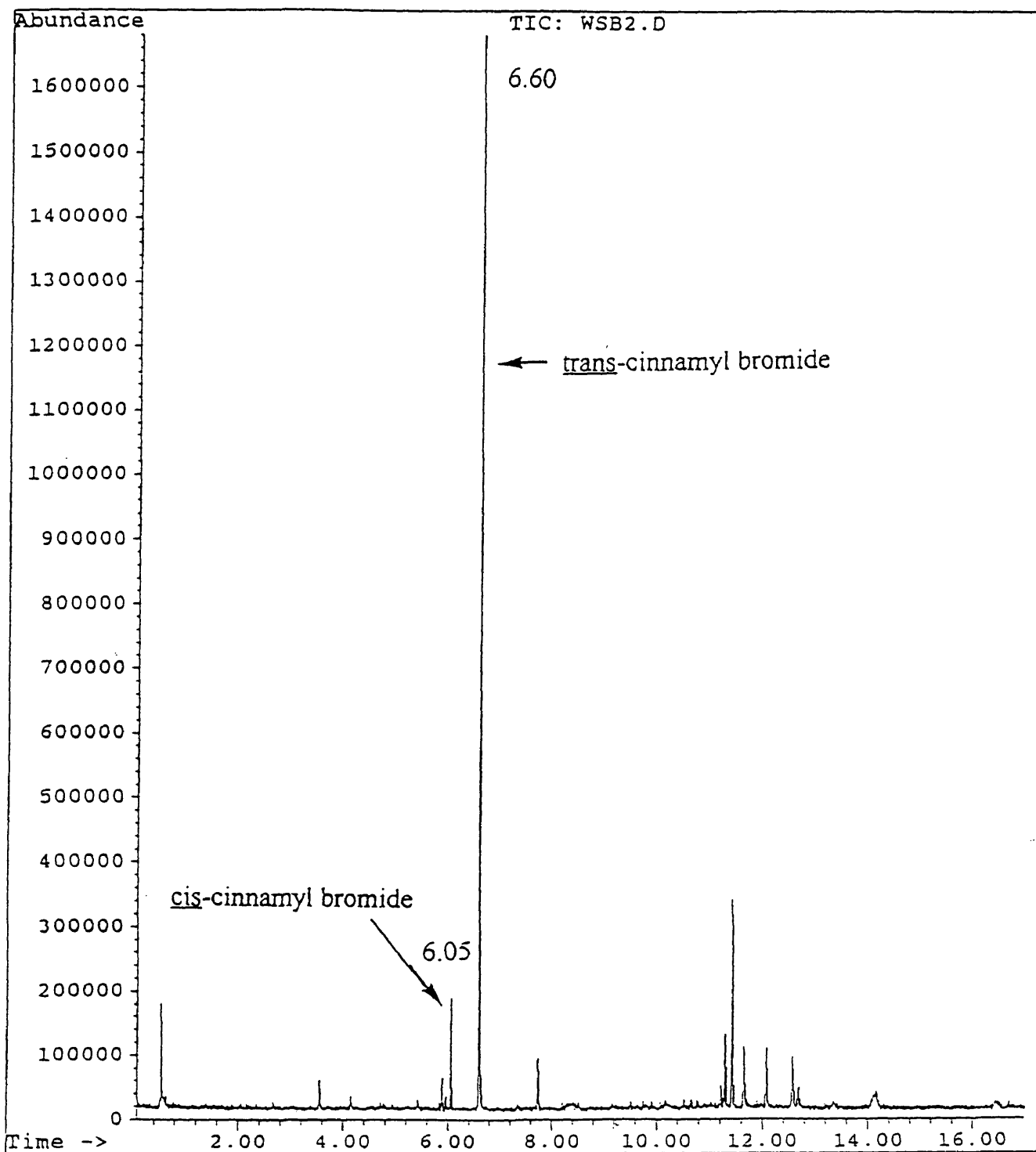


Figure 5. GC chromatogram of 97% Cinnamyl Bromide.

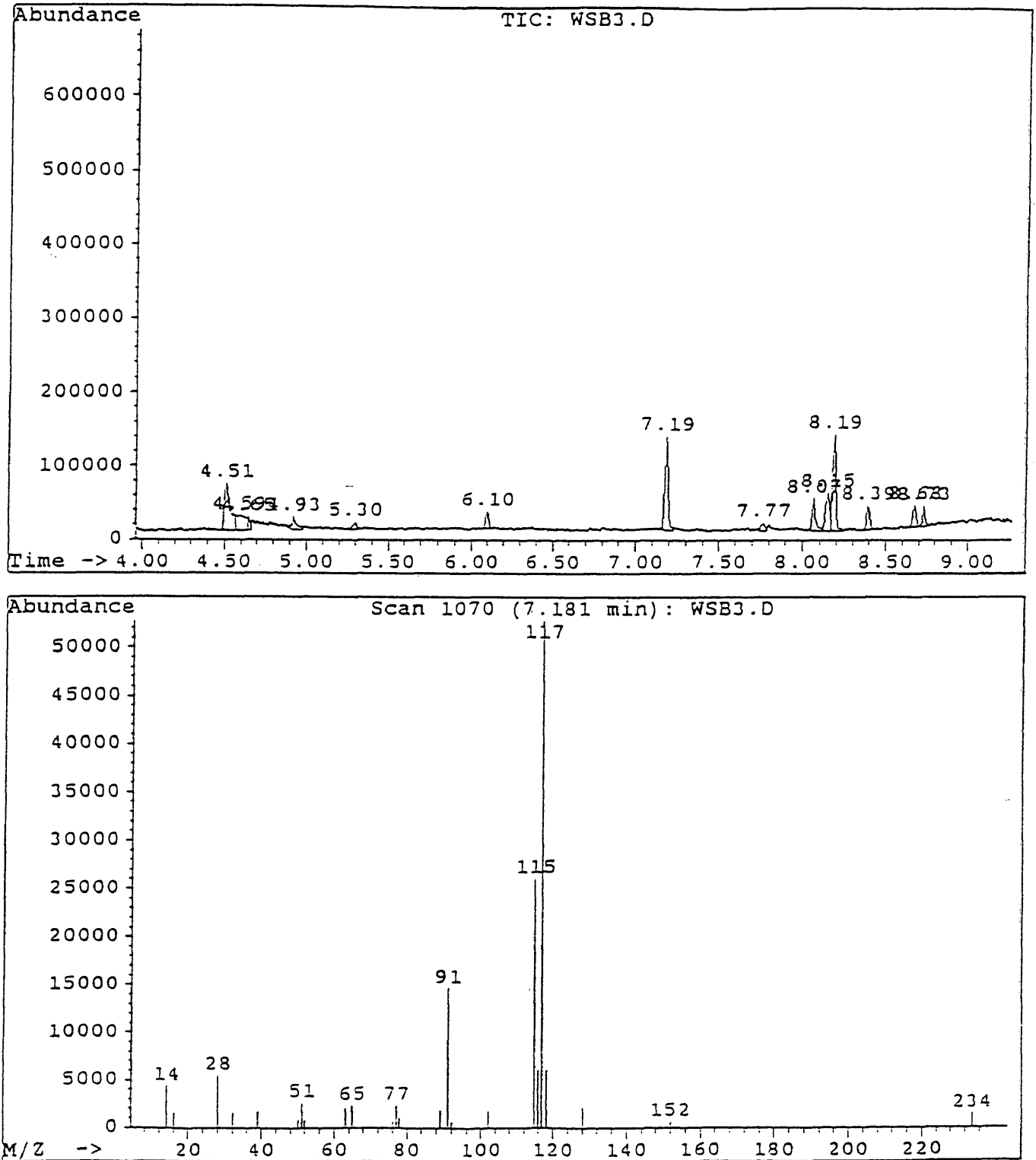


Figure 6. Partial GC chromatogram of 97% Cinnamyl Chloride.

The GC/MS data obtained from the degradation of metal compounds with both cinnamyl chloride (95%, and 97%) and cinnamyl bromide (97%) proved to be very difficult to interpret. Massive fragmentation and rearrangement of the model compound in the presence of the metal compounds typically prevented the realistic interpretation of the spectra. Even the observation of the dimeric product for some of the metal compounds was suspect due to the observation of occasional autodimerization of the model compound itself in the GC injection port. Therefore, the study of this model compound was aborted.

### **3. Coupling Studies of Benzyl Chloride with Metal Additives**

Benzyl chloride (Aldrich, 99%) was used as a model compound for defects in PVC. A benzylic chloride was chosen due to its similar chemical reactivity to that of an allylic chloride. Moreover, its higher boiling point (179 °C) permitted studies at somewhat higher temperatures.

The authentic dimer which would result from the reductive coupling was obtained from Aldrich (bibenzyl, 99%) and its GC retention time was established. The MS showed a parent ion peak of 182 m/z while its base peak was 91 m/z (half that of the coupled product). Figure 7 shows the GC/MS for bibenzyl. The thermolysis reactions involving a metal precursor and benzyl chloride were carried out in a closed system (sealed evacuate ampule).

The analysis results for the benzyl chloride experiments are shown in Table 5.

The typical chromatogram from the closed system reaction products of metal compounds and benzyl chloride can be divided, according to retention time, into three regions: i) 1-3 min, ii) 6-8 min, and iii) 11-12 min. The first region contains low-molecular-weight compounds such as toluene (1.1 min), and unreacted benzyl chloride (3.0-3.1 min). The second region contains products from Friedel-Crafts chloroalkylation. The third region contains products from Lewis acid oligomerization. A representative chromatogram is shown in Figure 8 (for copper(II) formate and benzyl chloride).

A few interesting observations can be made from Table 5. The compounds which were decomposed at 250°C appeared to have reacted more efficiently with benzyl chloride than the compounds decomposed at 200°C. The only compound which produced coupling product was copper (II) formate (16.7 area percent, Figure 8). The results for copper (II) oxalate (Figure 9) and copper(I) formate triphenylphosphine (Figure 10) showed a very high percent area yield of the starting material (80.9% and 83.6% respectively). This indicates the low reactivity of those compounds with the starting material. The last two compounds on Table 5 ( $\text{FeCl}_3$  and  $\text{ZnCl}_2$ ) are strong Lewis acids. The chromatogram for  $\text{FeCl}_3$  (Figure 11) indicates extensive production of oligomers while the starting material has completely reacted.

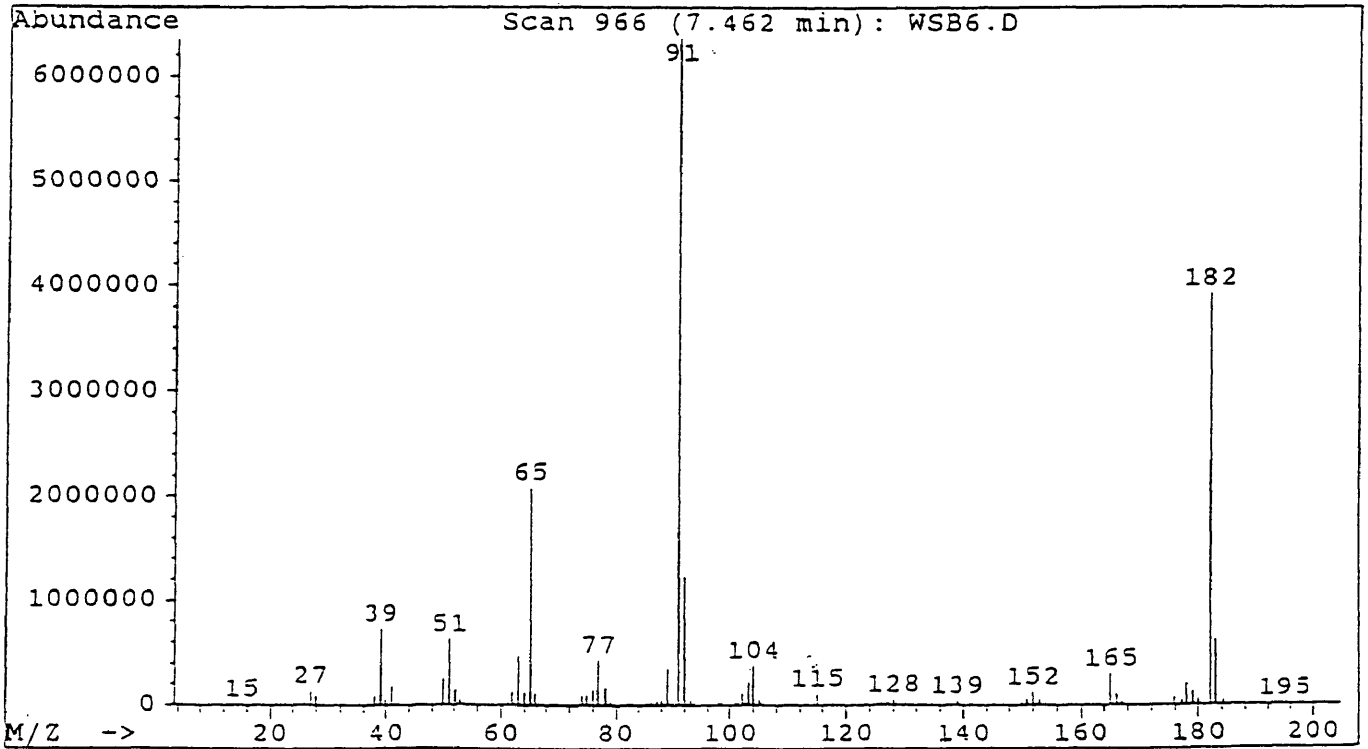
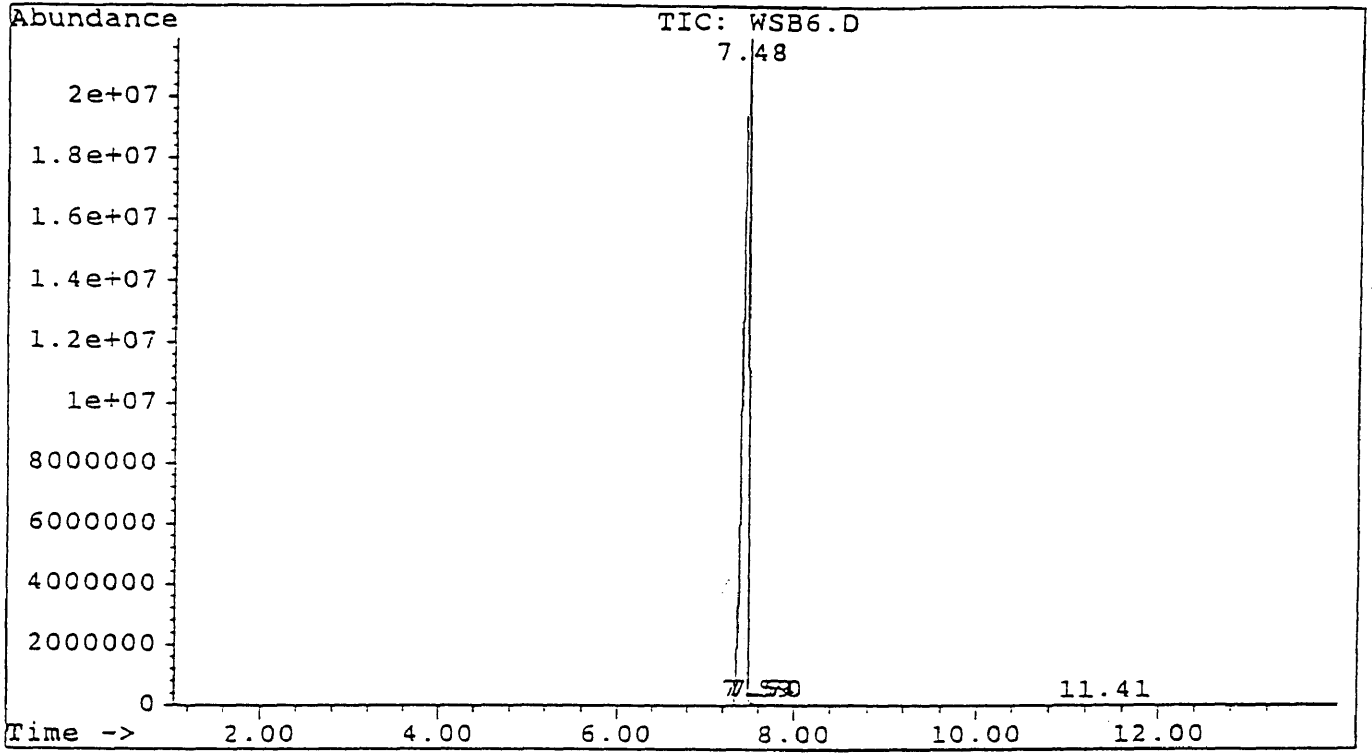
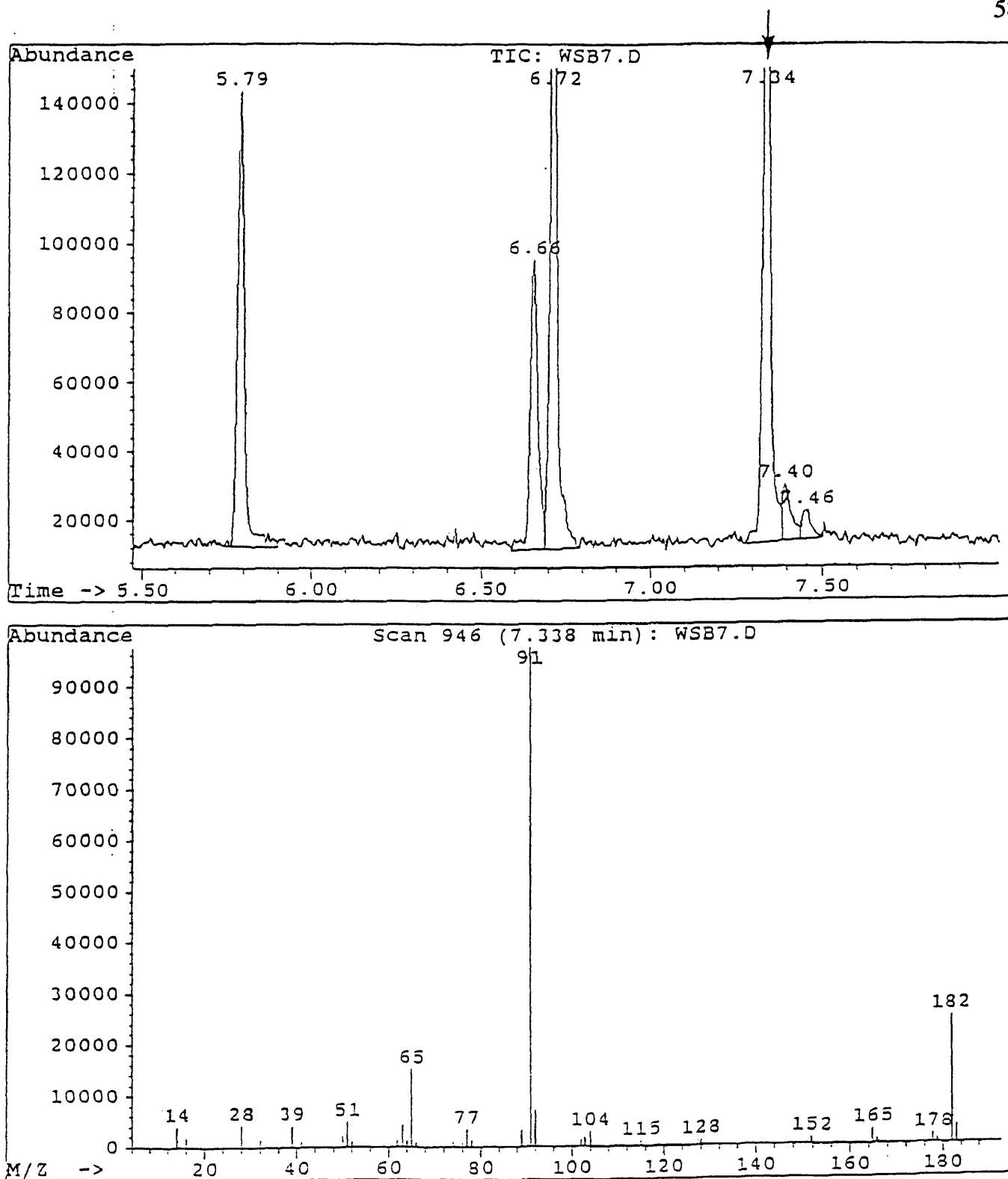


Figure 7. GC/MS results for Bibenzyl.



**Figure 8. GC/MS results for thermolysis products from Cu(II) formate and Benzyl Chloride.**

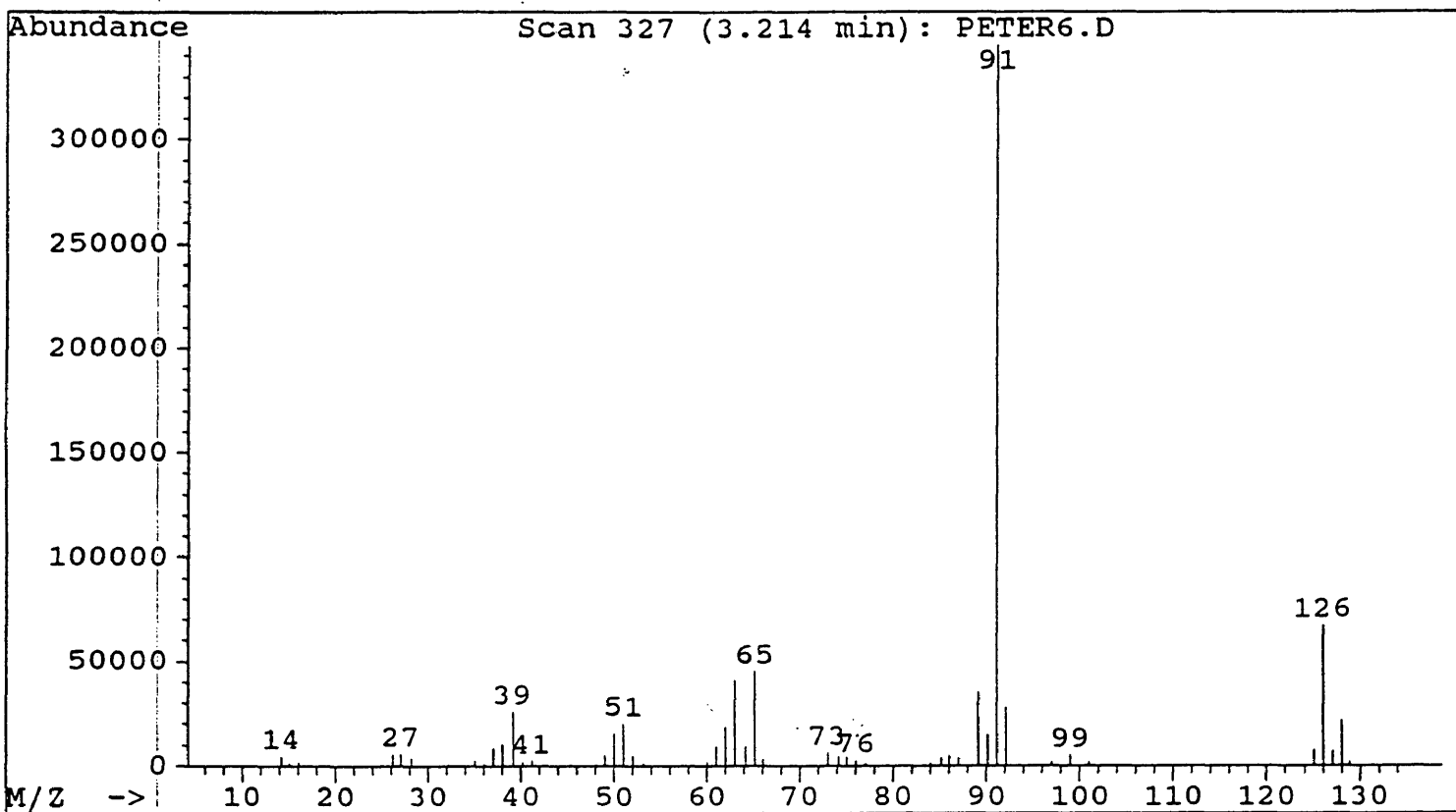
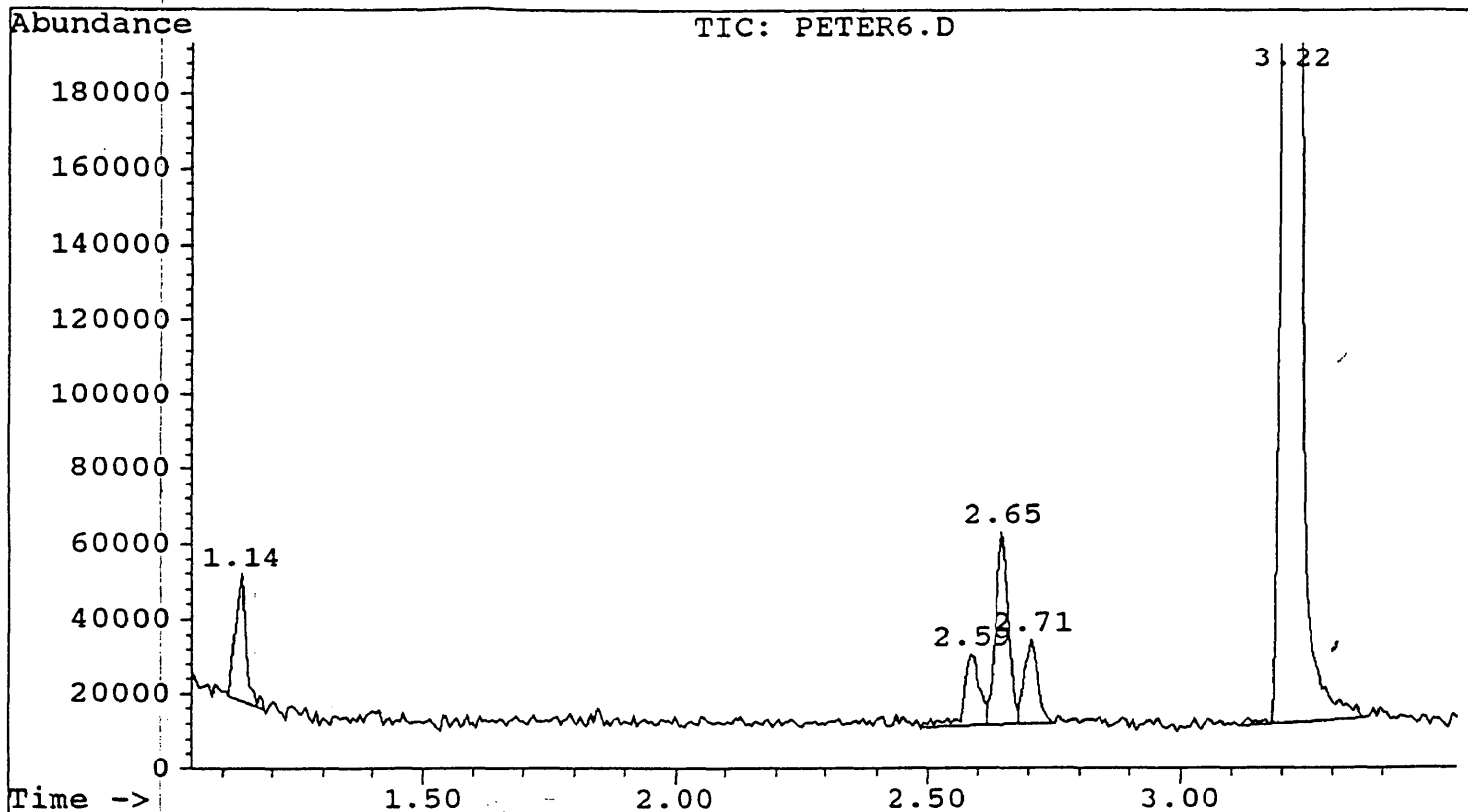


Figure 9. Partial GC/MS results for thermolysis products from Cu(II) oxalate and Benzyl Chloride.

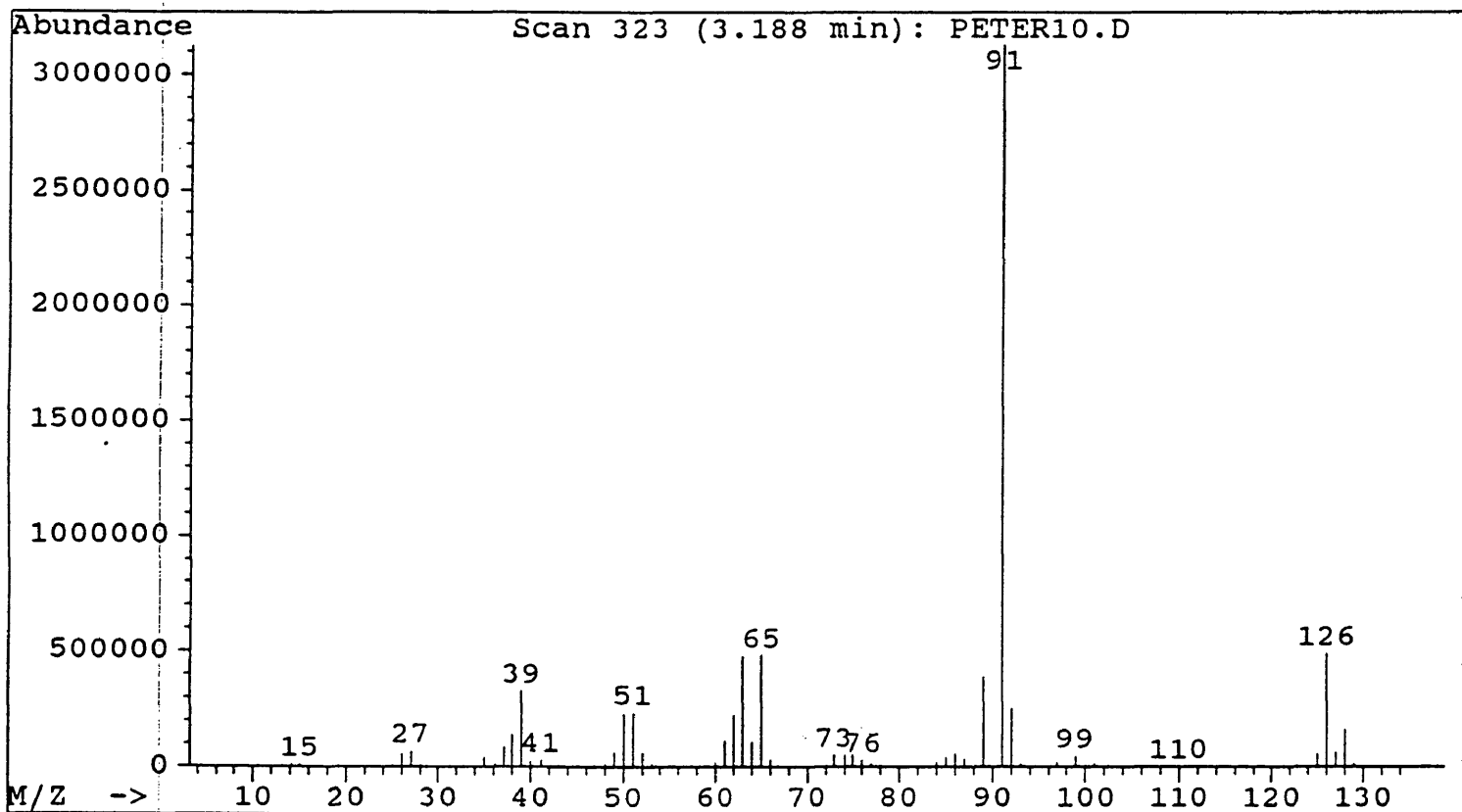
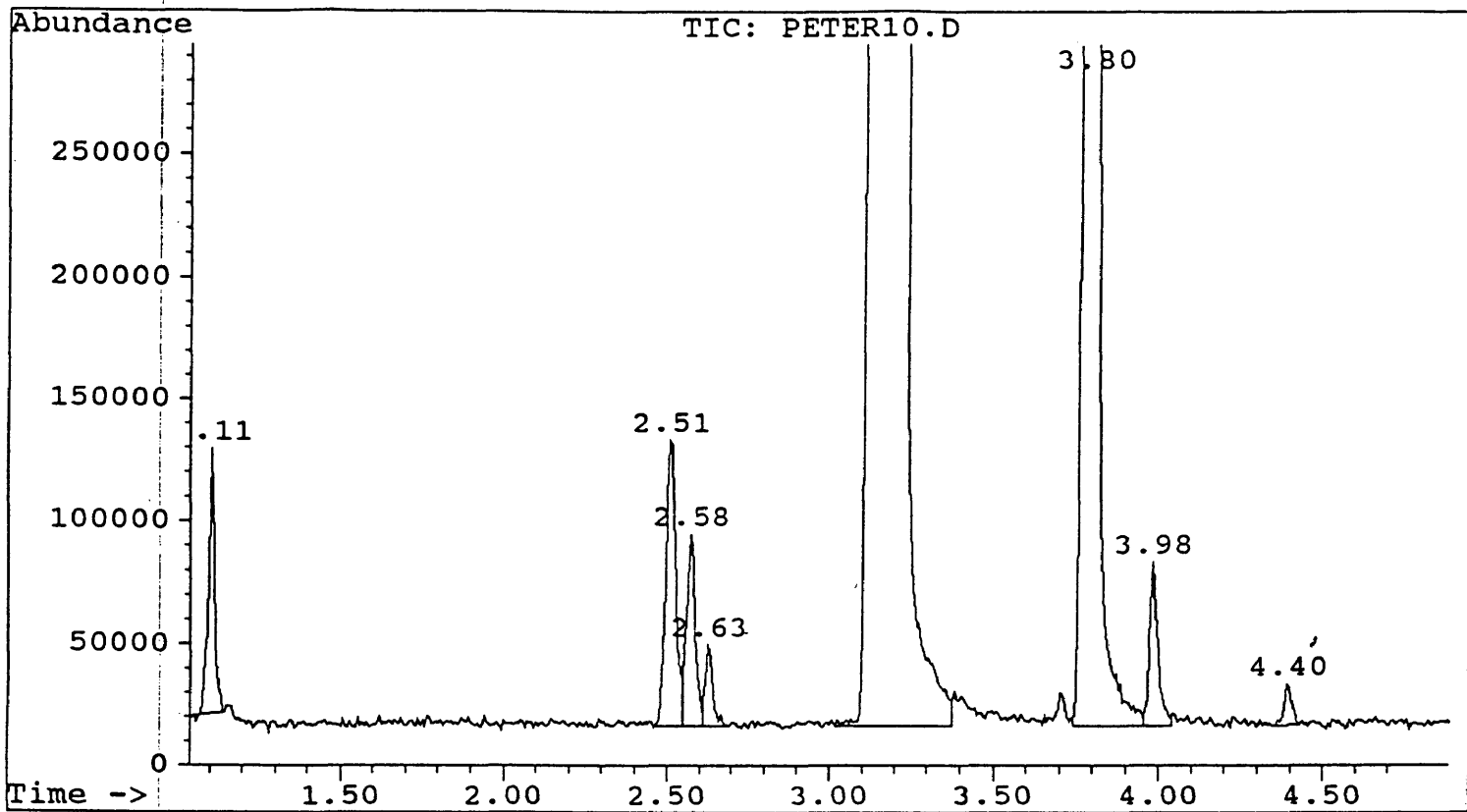


Figure 10. Partial GC/MS results for the thermolysis products of Cu(I) formate triphenylphosphine and Benzyl Chloride.

**Table 5**  
**GC Area Percentages of Pyrolysis Products from Metal**  
**Compounds and Benzyl Chloride**

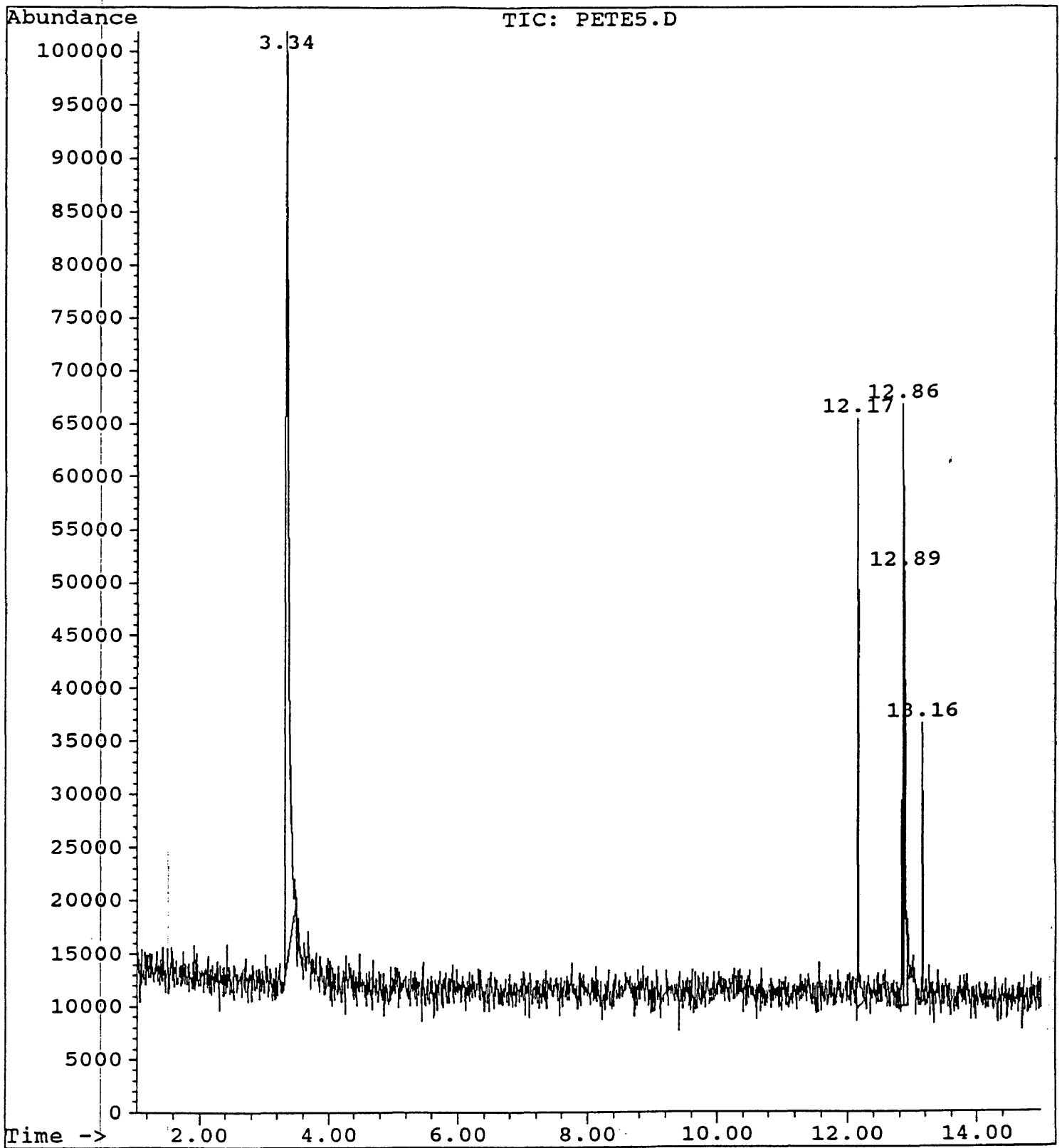
% Area

<b>Metal Compound</b>	<b>PhCH<sub>2</sub>Cl</b>	<b>Tolu-ene</b>	<b>Ph<sub>2</sub>CH<sub>2</sub></b>	<b>Biben- zyl</b>	<b>All other</b>
<b>Time (min)</b>	<b>3.1</b>	<b>1.1</b>	<b>6.8</b>	<b>7.5</b>	<b>----</b>
<b>FeC<sub>2</sub>O<sub>4</sub>*</b>	<b>0.0</b>	<b>20.5</b>	<b>20.8</b>	<b>0.0</b>	<b>58.7</b>
<b>CoC<sub>2</sub>O<sub>4</sub>*</b>	<b>2.4</b>	<b>44.2</b>	<b>16.3</b>	<b>0.0</b>	<b>37.1</b>
<b>CuC<sub>2</sub>O<sub>4</sub></b>	<b>80.9</b>	<b>2.9</b>	<b>1.6</b>	<b>0.0</b>	<b>14.6</b>
<b>NiC<sub>2</sub>O<sub>4</sub>*</b>	<b>10.0</b>	<b>30.3</b>	<b>23.7</b>	<b>0.0</b>	<b>36.0</b>
<b>Fe<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub></b>	<b>15.3</b>	<b>0.4</b>	<b>5.2</b>	<b>0.0</b>	<b>79.1</b>
<b>K<sub>3</sub>[Fe (C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]*</b>	<b>5.2</b>	<b>1.7</b>	<b>4.7</b>	<b>0.0</b>	<b>88.4</b>
<b>Cu(O<sub>2</sub>CH)<sub>2</sub></b>	<b>34.6</b>	<b>3.5</b>	<b>2.7</b>	<b>16.7</b>	<b>59.2</b>
<b>Cu(O<sub>2</sub>CH)<sub>2</sub> (PPh)<sub>3</sub></b>	<b>83.6</b>	<b>0.3</b>	<b>0.0</b>	<b>0.0</b>	<b>16.1</b>
<b>FeCl<sub>3</sub></b>	<b>59.2</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>40.8</b>
<b>ZnCl<sub>2</sub></b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>100</b>

\* Reactions were conducted at 250 °C for 1 hour.

All other reactions were conducted at 200 °C for 1 hour.

In summary, the results of the model-compound study of transition metals in the presence of benzyl chloride suggested the possibility of reductive coupling in the presence of suitable precursor compounds (copper(II) formate). The unsuitability of certain precursor compounds (either strong Lewis acids or relatively unreactive compounds like copper(II) oxalate and copper(I) formate triphenylphosphine), as well as the temperature at which the reactions were conducted, demonstrated the high selectivity of the reaction. The addition of other more suitable low-valent transition metal precursors to the list of possible reductive coupling agents could significantly clarify the possibility of reductive coupling in the polymer.



**Figure 11. GC/MS results for thermolysis products from FeCl<sub>3</sub> and Benzyl Chloride.**

#### 4. Coupling Studies of 4-Chloromethylbiphenyl with Metal Additives

A higher-boiling point benzylic chloride, 4-chloromethylbiphenyl, was chosen so that higher temperature studies could be conducted without extensive volatilization of the model compound. Bryant synthesized the authentic coupling product via the Wurtz reaction using sodium metal.<sup>36</sup> Chromatographic retention time and MS fragmentation pattern are shown in Figure 12.

All reactions of 4-chloromethylbiphenyl were run in an open system, as described in the Experimental section. The experimental results for the thermolyses of 4-chloromethylbiphenyl are shown in Table 6. 4-Chloromethylbiphenyl alone was thermolyzed at 200 °C for 1 hour as a control. Figure 13 shows that no coupling product was observed, and that the largest peak represented the starting material (4.65 min, 65.8 area %).

From Table 6, a few interesting observations can be made. The thermolysis of  $\{K_3[Co(C_2O_4)_3]\}$  and  $\{K_4[Co_2(OH)_2(C_2O_4)_4]\}$  with 4-chloromethylbiphenyl gave approximately the same results. Figures 14a,b and 15a,b show the GC/MS data from these two reactions respectively. The peaks at 2.33 min represent the reduced product, 4-methylbiphenyl (m/z 168). This compound was probably the result of the quenching of the reaction mixture containing benzylic cation. The peaks at 3.39 min represent the internal standard, hexadecane (m/z 226). The peaks at 4.60 min represent the starting material (m/z 202). The peaks at 17.71, 17.98, 20.04, and 21.92 minutes are higher

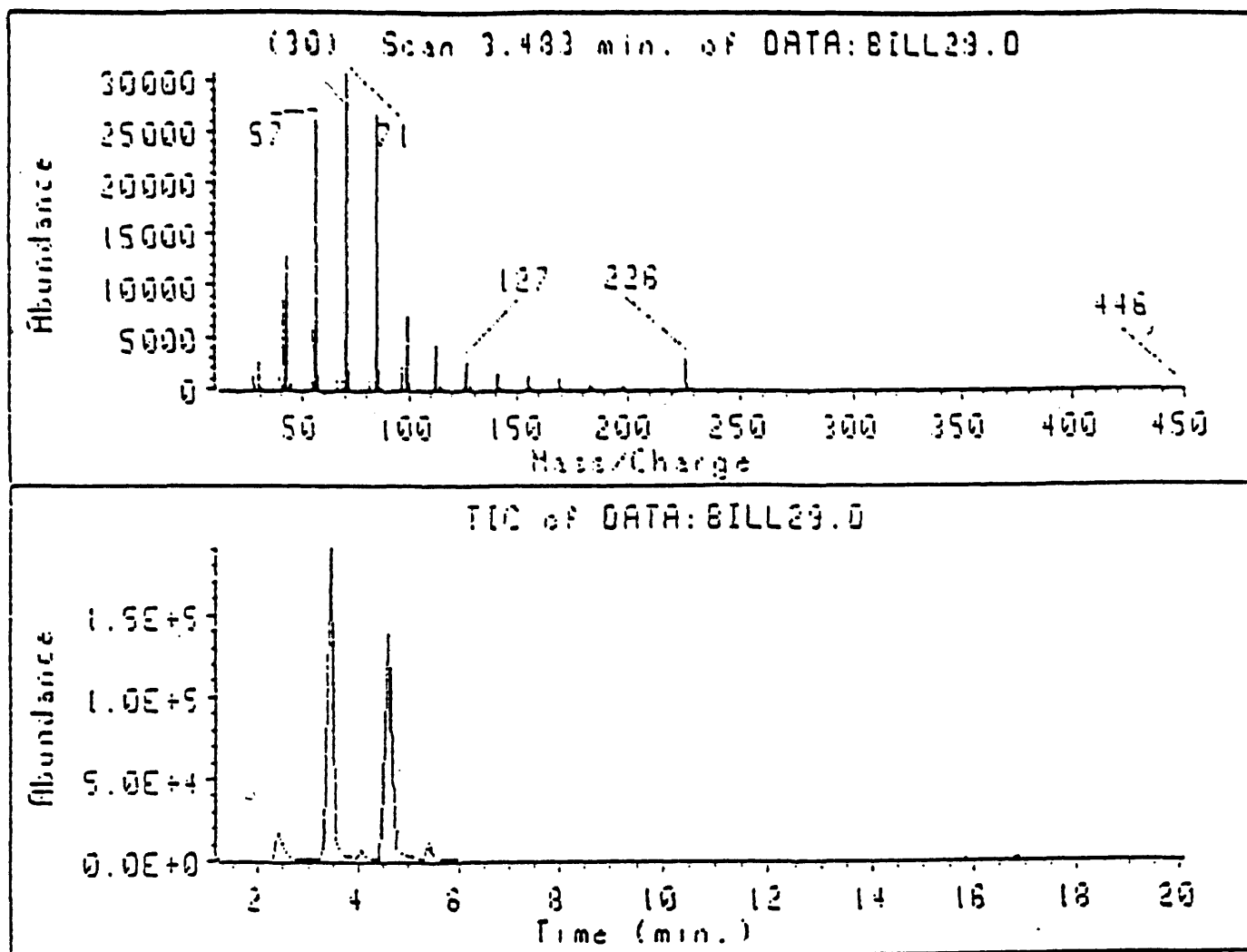
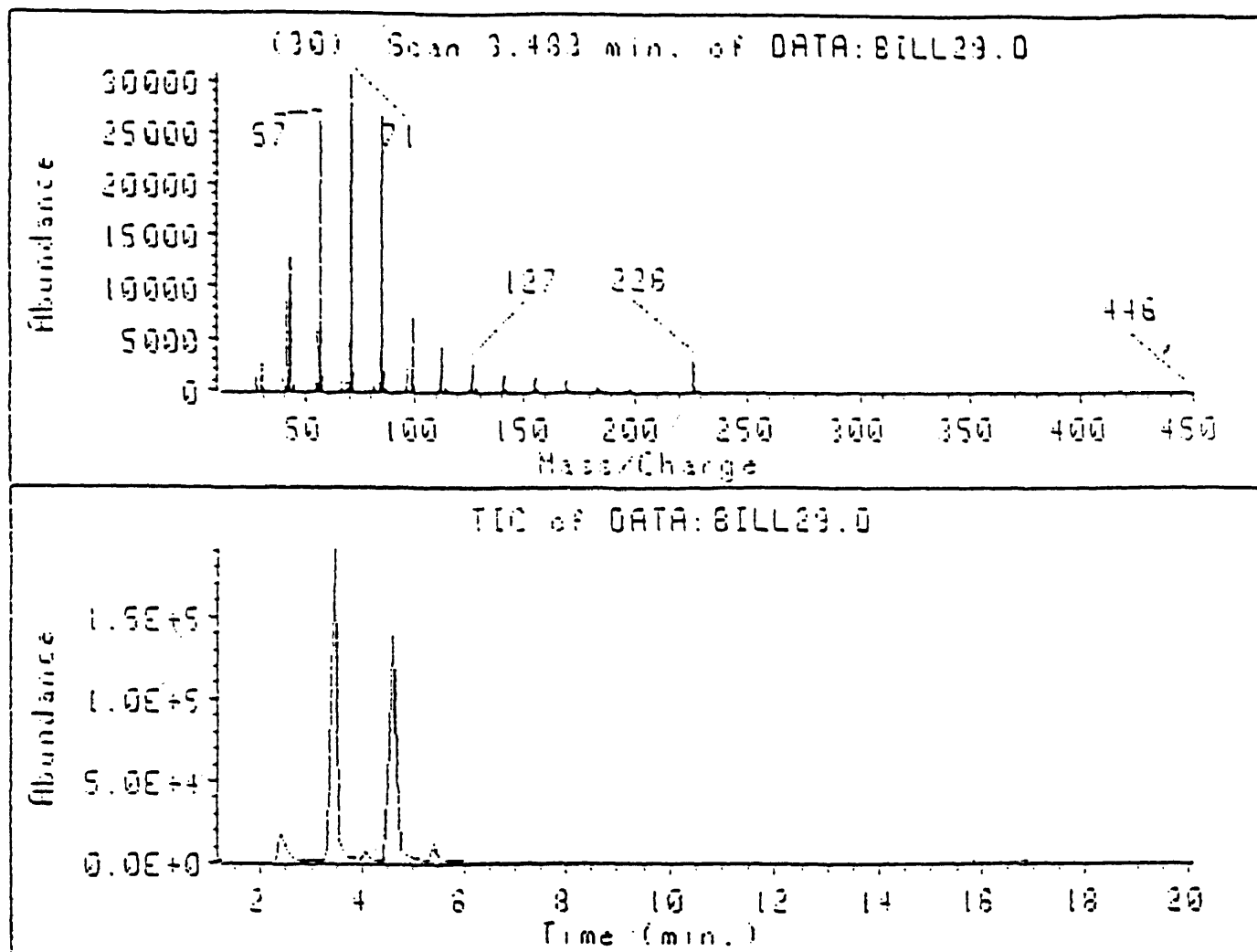


Figure 12. GC/MS results for 4-chloromethylbiphenyl.



**Figure 13. GC/MS data for control run with neat 4-chloromethylbiphenyl.**

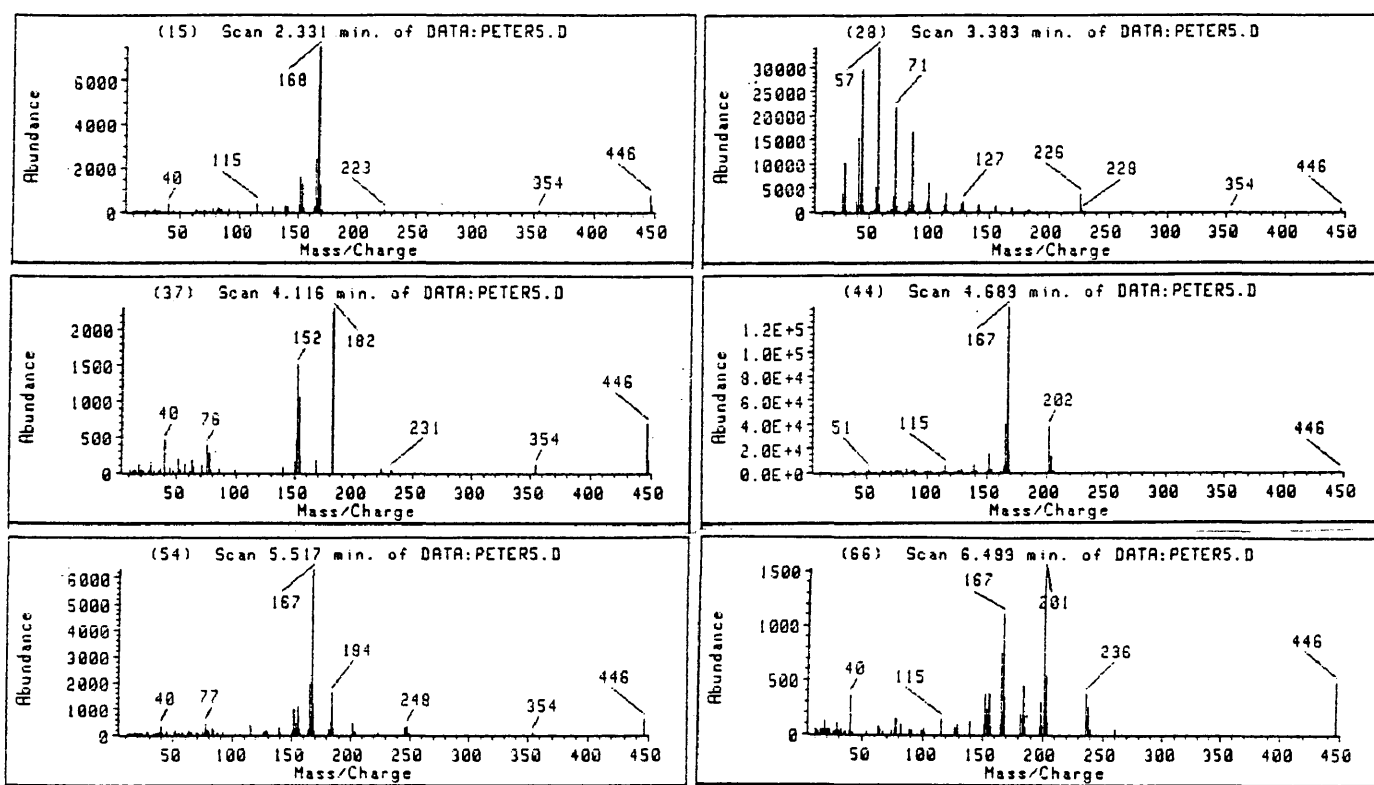
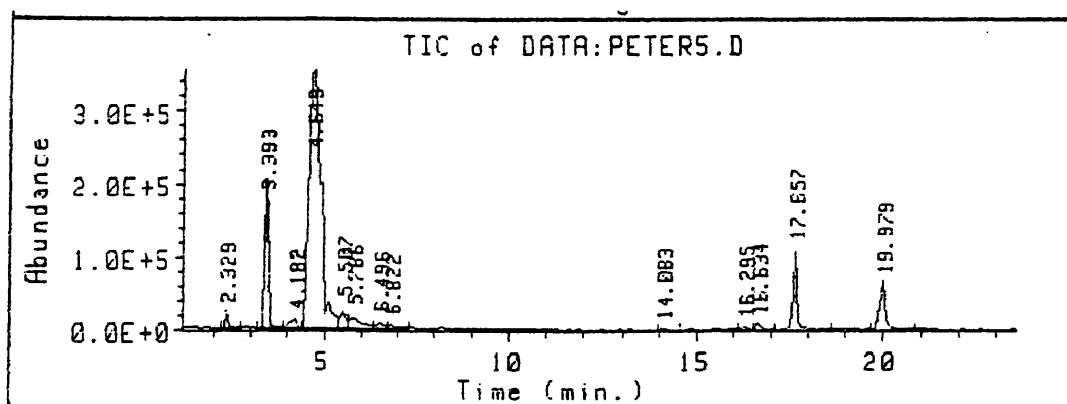
**Table 6**

**GC Area Percentages of Pyrolysis Products from Metal  
Compounds and 4-Chloromethylbiphenyl (Open System)**

% Area

<b>Model Compound</b>	<b>4-Methyl biphenyl</b>	<b>Hexadecane</b>	<b>4-Chloro methyl biphenyl</b>	<b>Coupled Product</b>
<b>Time (min)</b>	<b>2.32</b>	<b>3.40</b>	<b>4.60</b>	<b>16.10</b>
<b>Control</b>	<b>1.1</b>	<b>12.3</b>	<b>65.8</b>	<b>0.0</b>
<b>K<sub>3</sub>[Co (C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]</b>	<b>0.9</b>	<b>12.6</b>	<b>59.0</b>	<b>0.3</b>
<b>K<sub>4</sub>[Co<sub>2</sub>(OH)<sub>2</sub> (C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]</b>	<b>0.9</b>	<b>6.0</b>	<b>64.8</b>	<b>0.0</b>
<b>Cu(H<sub>2</sub>PO<sub>2</sub>)<sub>2</sub></b>	<b>4.1</b>	<b>13.1</b>	<b>7.8</b>	<b>5.3</b>
<b>Cu powder</b>	<b>1.6</b>	<b>19.6</b>	<b>61.0</b>	<b>4.8</b>
<b>Cu(O<sub>2</sub>CH)<sub>2</sub></b>	<b>4.9</b>	<b>45.1</b>	<b>19.6</b>	<b>5.0</b>

molecular weight oligomers which might have been produced by Friedel-Crafts attack of the benzylic cation at aryl sites. The only difference in the results of these two metal compounds was in the ability of the former to couple, producing a small area percent



**Figure 14a. GC/MS data for pyrolysis products from  $K_3[Co(C_2O_4)_3]$  and 4-chloromethylbiphenyl.**

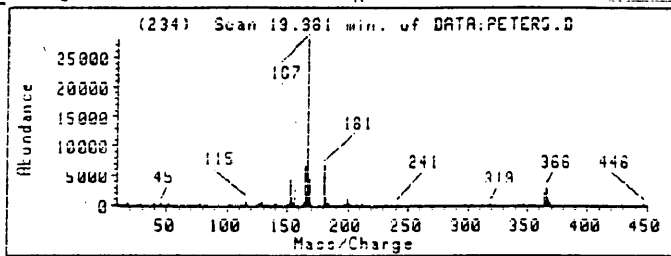
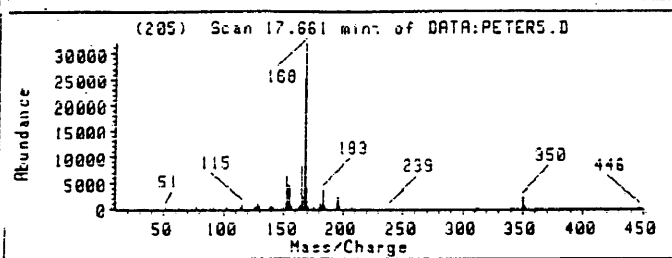
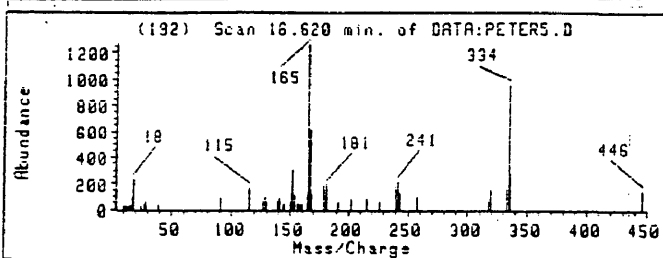
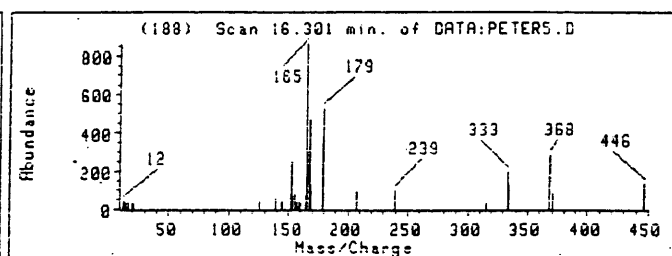
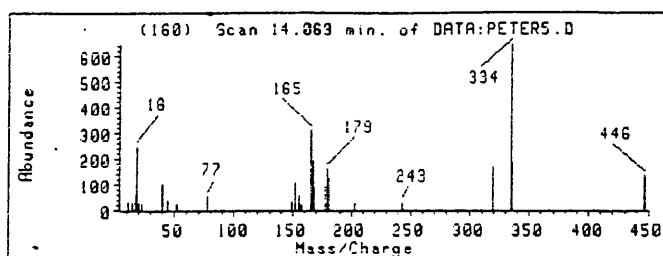
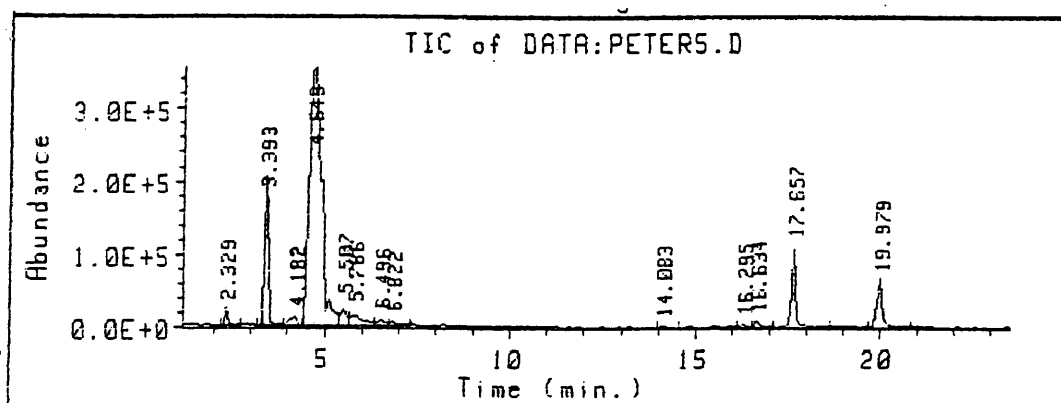


Figure 14b. GC/MS data for pyrolysis products from  $K_3[Co(C_2O_4)_3]$  and 4-chloromethylbiphenyl.

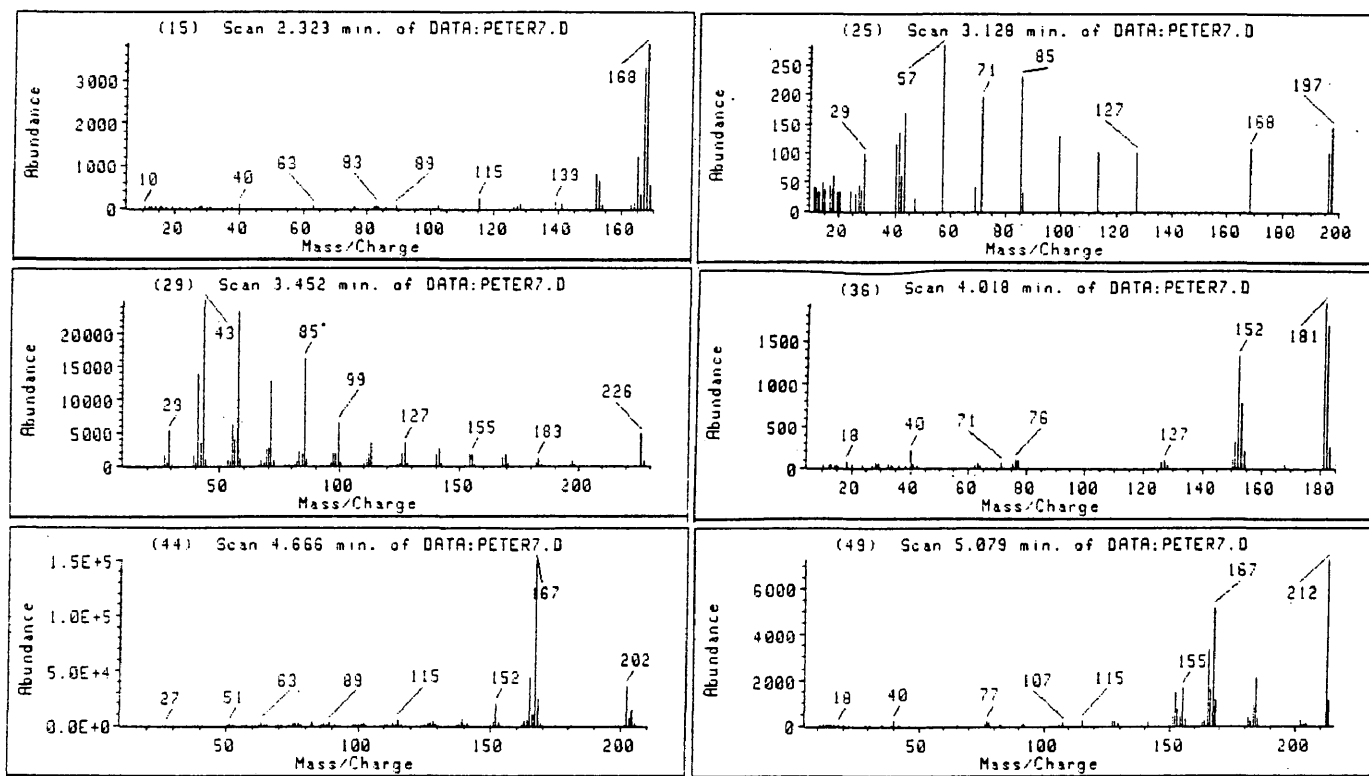
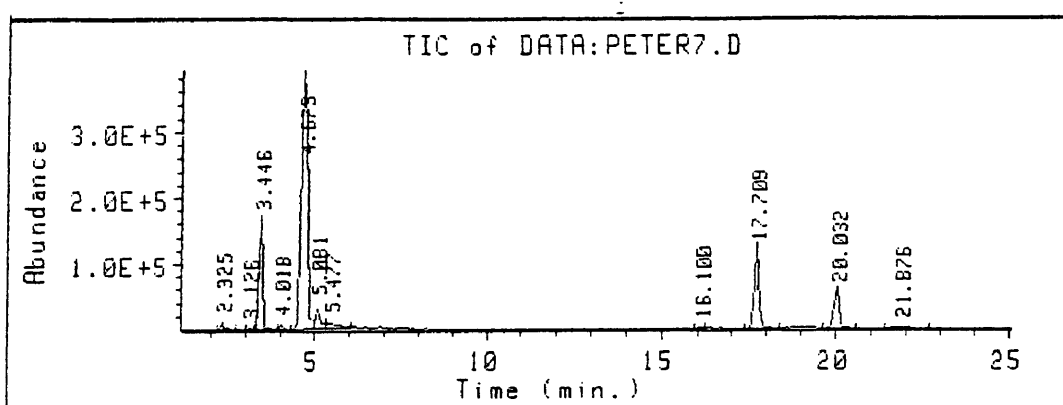
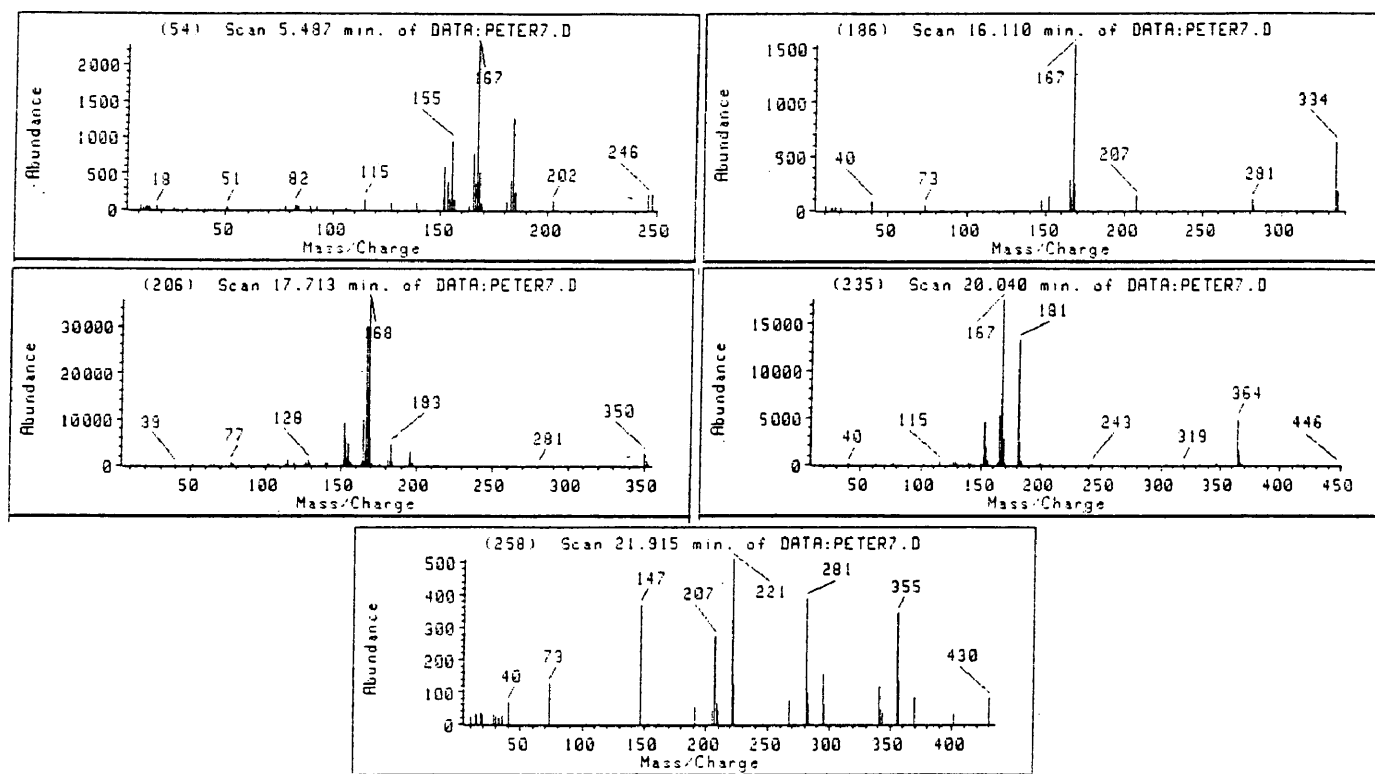
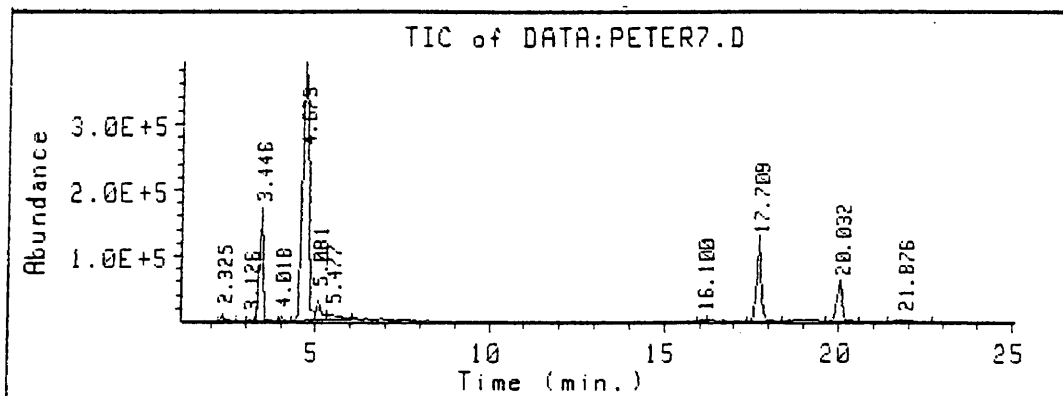


Figure 15a. GC/MS data for pyrolysis products from  $K_4[Co_2(OH)_2(C_2O_4)_4]$  and 4-chloromethylphenyl.



**Figure 15b. GC/MS data for pyrolysis products from  $K_4[Co_2(OH)_2(C_2O_4)_4]$  and 4-chloromethylbiphenyl.**

yield (16.10 min, 0.3 area % by GC/MS). Copper (II) hypophosphite gave the highest area percent yield (5.3% by GC) with recovery of only a small amount of the starting material (7.8 % area by GC) (Figure 16a,b). This suggests the possibility of an easily oxidized ligand which enabled the metal to readily reduce to Cu(0), promoting reductive coupling.

Cu powder (Aldrich, 99.999%) demonstrated lower area percent yield of the coupled product than copper hypophosphite (4.8% by GC) with much recovery of the starting material (61.0 area % by GC) (Figure 17). Like the results of the copper powder, the GC/MS results of copper(II) formate and 4-chloromethylbiphenyl showed peaks for the reduced product(4-methylbiphenyl), the internal standard, unchanged starting material, and the coupled product (Figure 18).

The results of the model-compound study of transition metals in the presence of 4-chloromethylbiphenyl suggest the possibility of a reductive coupling mechanism in the presence of a suitable precursor compound with easily oxidizable ligands that will readily reduce the low-valent metal to metal(0). The extensive study of this reaction with other low-valent metal precursors was not possible due to the continuation of the investigation of gellation studies with metal additives in the solid state.

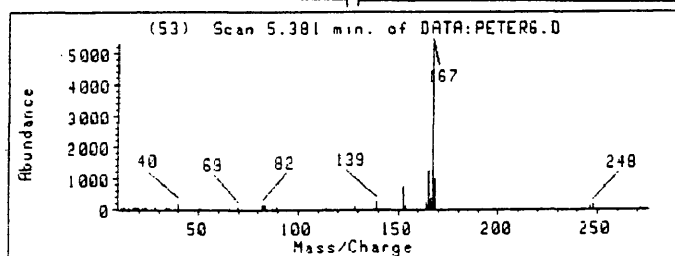
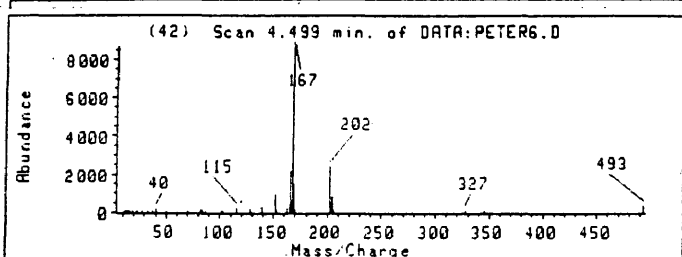
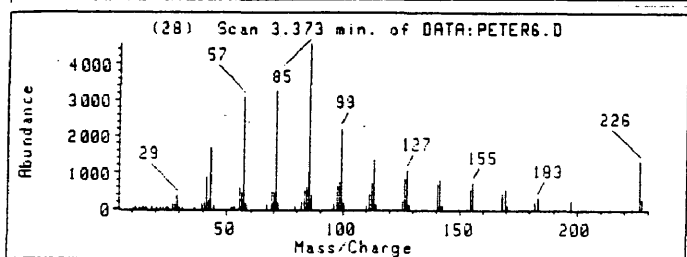
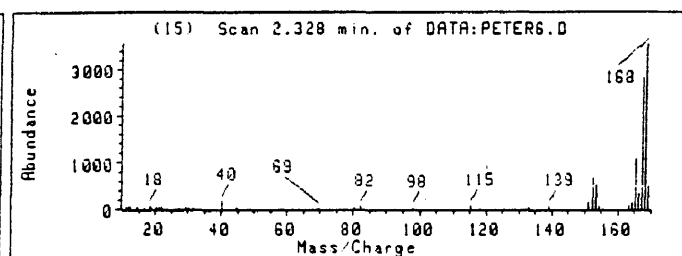
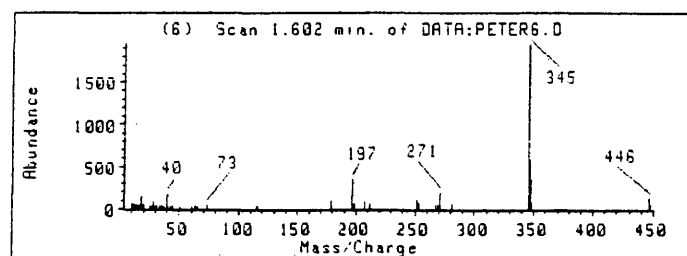
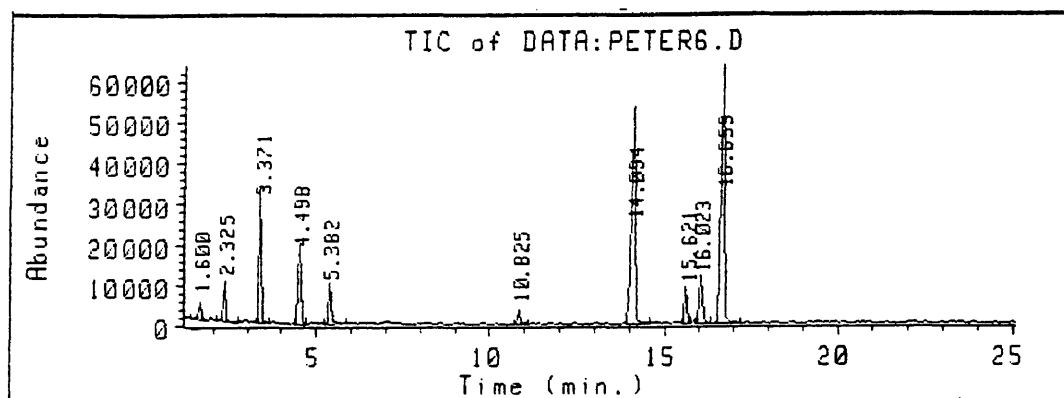
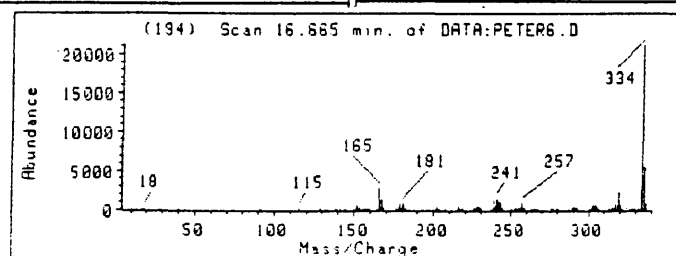
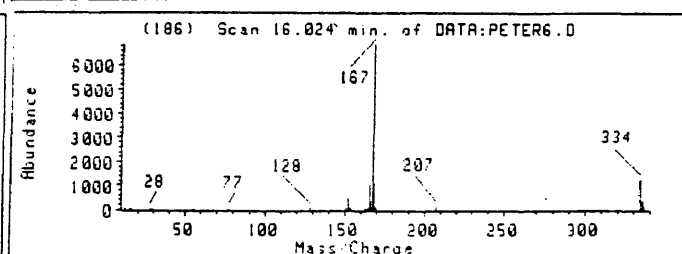
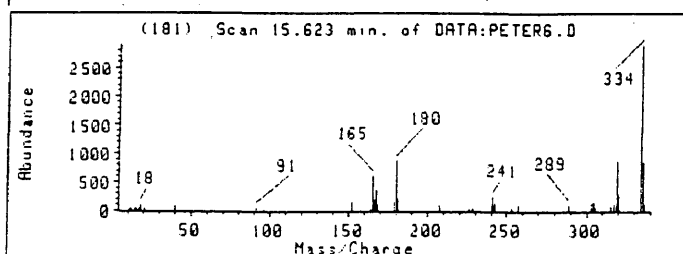
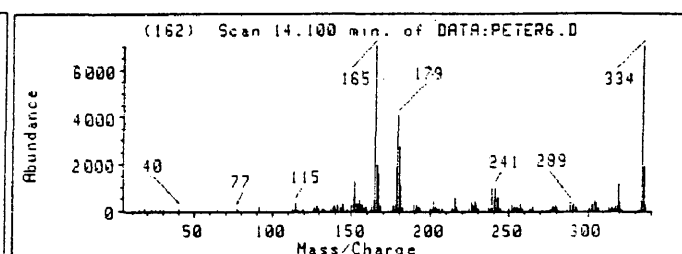
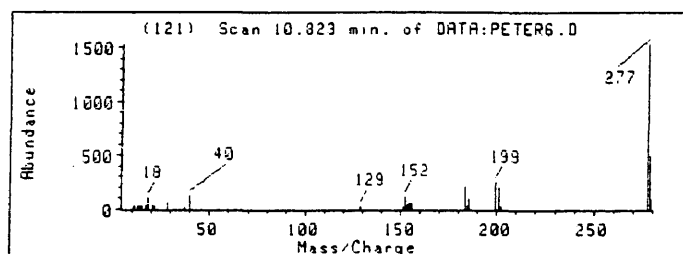
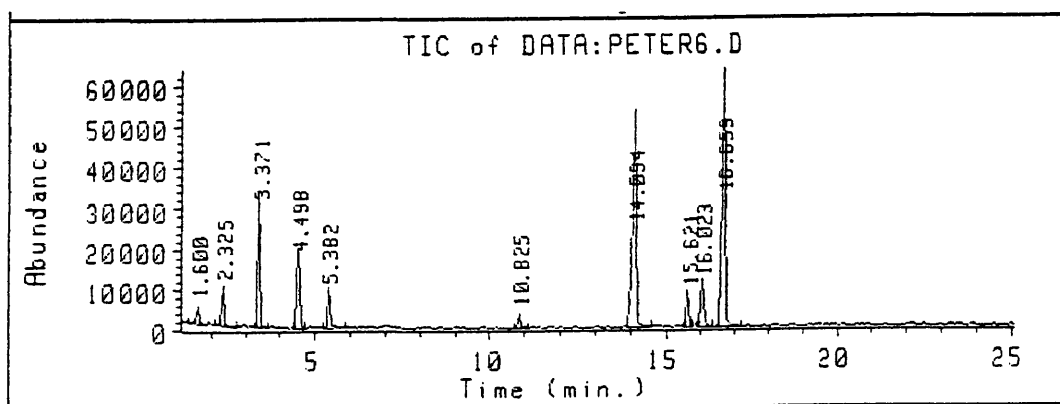


Figure 16a. GC/MS data for pyrolysis products from  $\text{Cu}(\text{H}_2\text{PO}_2)_2$  and 4-chloromethylbiphenyl.



**Figure 16b. GC/MS data for pyrolysis products from  $\text{Cu}(\text{H}_2\text{PO}_2)$  and 4-chloromethylbiphenyl.**

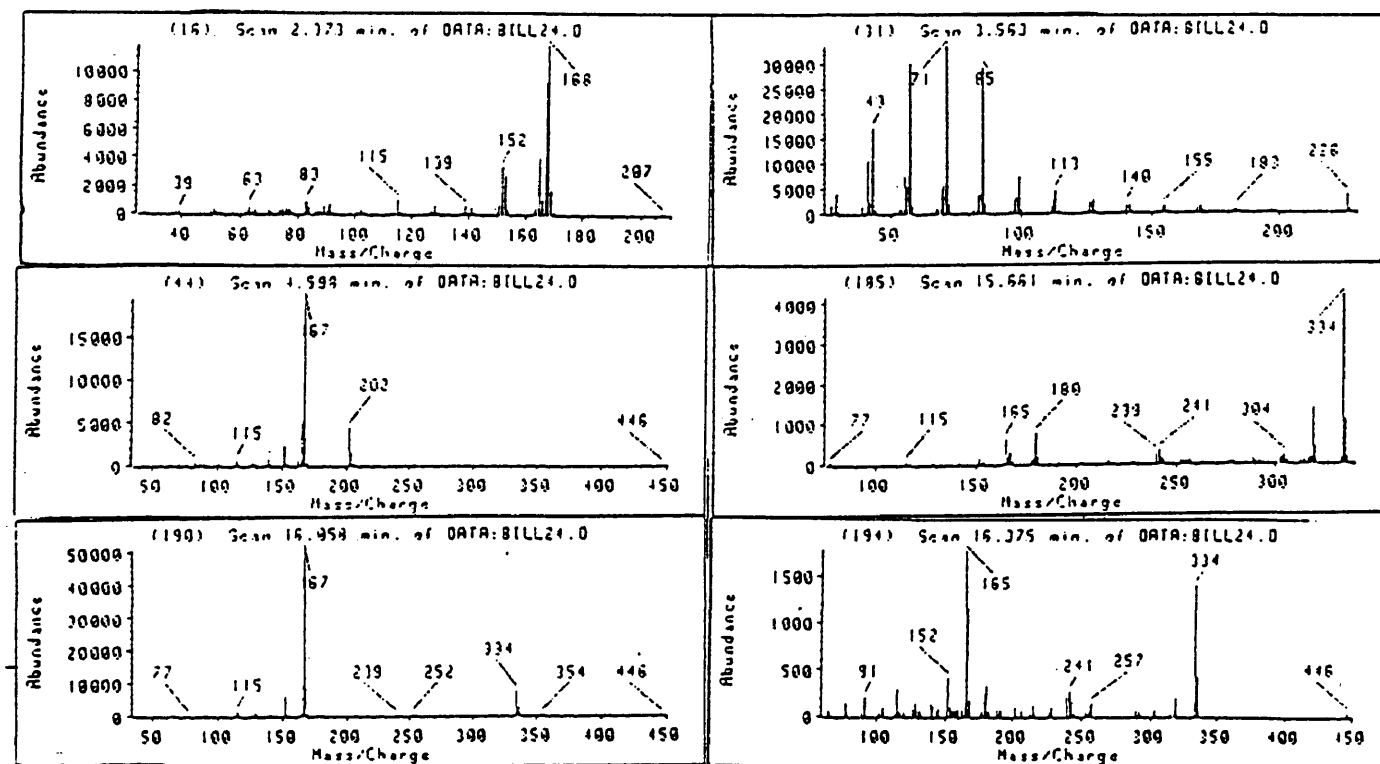
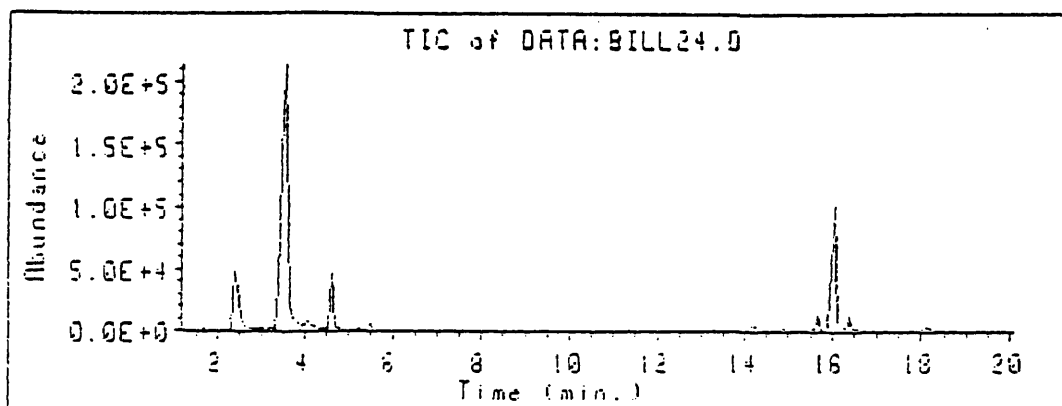


Figure 17. GC/MS data for pyrolysis products from copper powder and 4-chloromethylbiphenyl.

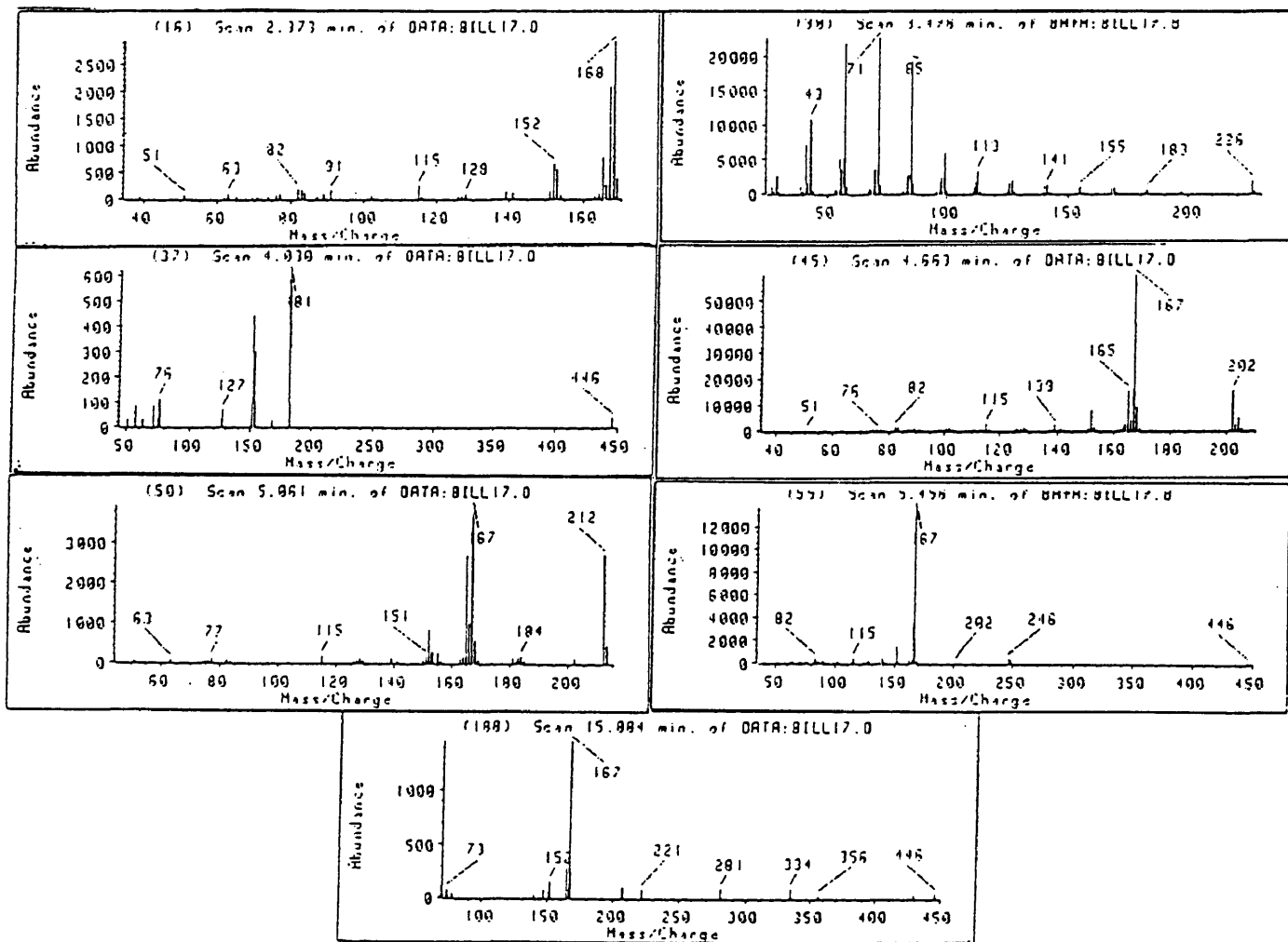
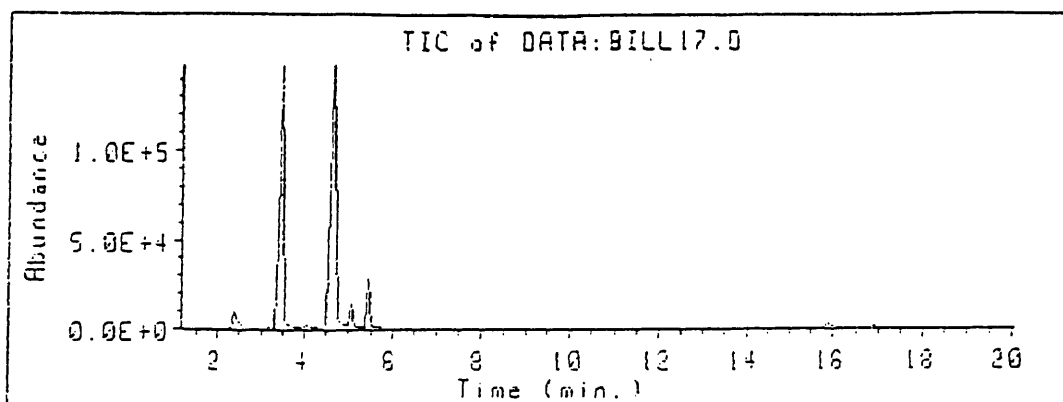


Figure 18. GC/MS data for pyrolysis products from copper(II) formate and 4-chloromethylbiphenyl.

### **C. Gelation Studies of PVC with Metal Additives in the Solid State.**

The thermal degradation of PVC with metal additives was studied in order to evaluate the gelation promotion effectiveness of various metal compounds. Jeng previously studied PVC gelation with copper additives in the solid state.<sup>16</sup> He observed that both high purity copper powder (99.999%) and copper formate caused rapid gel formation. In the case of copper formate, gelation seems to have been caused by the activated Cu(0) that was produced during the degradation of the mixture. Metal oxalates, formates, phosphites and hypophosphites as well as copper(I) precursor additives were tested in a similar manner.

According to the decomposition ranges of the different metal additives, the gelation experiments were conducted at either  $200 \pm 5$  °C for 1 hour or at  $210 \pm 5$  °C for 1.5 hours. Two conditions had to be met during the selection of the thermolysis conditions: it was essential to choose the appropriate temperature and time settings which would ensure decomposition of the metal additives. However, conditions which would cause the decomposition of virgin PVC had to be avoided. Therefore, a variety of temperatures and time combinations were tested using a PVC control. Under the more severe conditions, the PVC control showed a high degree of gelation (Table 7). A 1.5 hour thermolysis at  $210 \pm 5$  °C was deemed to be the most rigorous condition which could be used for additive/PVC testing.

All the metal additives with decomposition ranges at or below 200 °C were thermolyzed at  $200 \pm 5$  °C for 1 hour. The metal additives with decomposition ranges

well above 200 °C were degraded at 210±5 °C for 1.5 hours. The results of these gelation studies are presented in Tables 8 and 9. After completion of each degradation reaction, the sample residue appeared as a black char. Once gelation has occurred, the degraded sample becomes insoluble. The degraded samples were Soxhlet extracted

**Table 7**

**% Gel Formation for PVC Control Reactions**

**% Gel**

<b>Temp. (°C)</b>	<b>Time (min)</b>	<b>Run 1</b>	<b>Run 2</b>
<b>200</b>	<b>60</b>	<b>&lt;5</b>	<b>0</b>
<b>210</b>	<b>90</b>	<b>21</b>	<b>25</b>
<b>225</b>	<b>60</b>	<b>65</b>	<b>63</b>
<b>250</b>	<b>60</b>	<b>64</b>	<b>67</b>
<b>250</b>	<b>10</b>	<b>57</b>	<b>55</b>
<b>275</b>	<b>10</b>	<b>70</b>	<b>72</b>
<b>300</b>	<b>60</b>	<b>71</b>	<b>75</b>

**Table 8****Gel Contents of PVC Thermolyzed with Metal Compounds****(10% added to PVC)****[All reactions conducted at  $200 \pm 5$  °C for 1 hour]****[^ Denotes incomplete decomposition]****% Gel**

<b><u>Metal Additive</u></b>	<b><u>Run</u></b>	<b><u>Run 2</u></b>	<b><u>Run 3</u></b>	<b><u>Run 4</u></b>	<b><u>Run 5</u></b>	<b><u>Decomp.</u></b>
	<b><u>1</u></b>					<b><u>T °C</u></b>
<b>none</b>	<b>&lt;5</b>	<b>0</b>				
<b><math>K_3[Co(C_2O_4)_3]</math> ^</b>	<b>29</b>	<b>25</b>				<b>145</b>
<b><math>K_4[Co_2(OH)_2(C_2O_4)_4]</math></b>	<b>50</b>	<b>49</b>				<b>150</b>
<b><math>Ni(H_2PO_2)_2</math></b>	<b>46</b>	<b>16</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>215-225</b>
<b><math>Cu(H_2PO_2)_2</math></b>	<b>75</b>	<b>88</b>	<b>37</b>	<b>67</b>		<b>95-100</b>
<b><math>Cu(BH_3)(PPh_3)_2</math></b>	<b>55</b>	<b>99</b>	<b>55</b>			<b>145-165</b>
<b><math>Cu(O_2CH)(PPh_3)_3</math></b>	<b>98</b>	<b>81</b>	<b>38</b>	<b>38</b>		<b>170-185</b>
<b><math>Cu(O_2CH)_2</math></b>	<b>84</b>	<b>97</b>	<b>95</b>			<b>198-200</b>
<b><math>[Cu(NCCH_3)_4](BF_4)</math></b>	<b>74</b>	<b>90</b>	<b>43</b>	<b>71</b>		<b>157-162</b>
<b><math>[Cu(PPh_3)_3(CH_3CN)](BF_4)</math></b>	<b>49</b>	<b>48</b>				<b>165-219</b>
<b><math>[Cu(PPh_3)_4](PF_6)</math> ^</b>	<b>48</b>	<b>46</b>				<b>223-237</b>

**Table 9****Gel Contents of PVC Thermolyzed with Metal Compounds****(10% Added to PVC)****[All reactions conducted at  $210 \pm 5$  °C for 1.5 hours]****[ ^ Denotes incomplete decomposition]****% Gel**

<u>Metal Additive</u>	<u>Run</u> 1	<u>Run</u> 2	<u>Run</u> 3	<u>Run</u> 4	<u>Decomp.</u> T °C
none	21	25			
$\text{Cu}(\text{C}_2\text{O}_4)$ ^	100	100			>300
$\text{Ni}(\text{C}_2\text{O}_4)$ ^	93	93			270-290
$\text{Co}(\text{C}_2\text{O}_4)$ ^	66	86	92		250
$\text{Fe}(\text{C}_2\text{O}_4)$ ^	93	97			225
$\text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2]$	79	85			265
$\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ ^	69	96	66		290
$\text{Fe}_2(\text{C}_2\text{O}_4)_3$ ^	69	78			295
$\text{Cu}(\text{O}_2\text{CH})(\text{PPh}_3)_3$	55	40	62		170-185
$\text{Cu}(\text{BH}_4)(\text{PPh}_3)_2$	41	41			145-165
$\text{CoHPO}_3$ ^	81	90			240-250
$\text{NiHPO}_3$ ^	100	100			240-250
$\text{Co}(\text{H}_2\text{PO}_3)_2$	59	66			250-270
$\text{Ni}(\text{O}_2\text{CH})_2$	46	44			260-263
$\text{Co}(\text{O}_2\text{CH})_2$ ^	55	15	37	46	>300
$\text{Fe}(\text{O}_2\text{CH})_2$	74	56	48		170-240?

with THF. Although undegraded PVC dissolves in a number of solvents, gelled PVC becomes insoluble in all common solvents. In this way, all non-crosslinked PVC was removed from the sample during the Soxhlet extraction, leaving only gelled PVC. Gelation results from intramolecular crosslinking of the polymer and therefore is diagnostic for crosslinking.

The results in Tables 8 and 9 suggest that a variety of metal additives could potentially be excellent crosslinking promoters. Simple oxalates of all four metals under study (Fe, Co, Cu, and Ni) produced a high percent gelation of the polymer. Specifically, all  $\text{MC}_2\text{O}_4$  additives produced  $\geq 90\%$  gelation results, with copper(II) oxalate showing the best result (100%). The complex oxalates showed a variety of results with copper(II) complex salt having the best gelation value (83%). Most of the metal formate additives produced moderate gelation (around 50%) with copper(II) formate giving the highest value (96%). Phosphites and hypophosphites gave a range of results which tended to be above 80% gel formation, with nickel phosphite producing 100% gelation. In examining trends for individual metals, copper additives demonstrated, overall, a greater ability to produce gelation than additives of iron, cobalt and nickel.

Copper(I) additives produced some very interesting results. Copper(I) additives with oxidizable ligands were expected to produce  $\text{Cu}(0)$  in two ways (*vide supra*). Therefore, we might expect a higher percent gelation of the polymer when oxidizable ligands are present. The results indicate that only  $[\text{Cu}(\text{NCCH}_3)_4](\text{BF}_4)$  (which has no readily oxidizable ligands) produced a high percent gelation yield (75-90%) while

$[\text{Cu}(\text{O}_2\text{CH})(\text{PPh}_3)_3]$ ,  $[\text{Cu}(\text{BH}_4)(\text{PPh}_3)_2]$ ,  $\{[\text{Cu}(\text{PPh}_3)_3(\text{NCCH}_3)](\text{BF}_4)\}$ , and  $\{[\text{Cu}(\text{PPh}_3)_4](\text{PF}_6)\}$  produced moderate gelation (around 50%). A reason for the low percent gelation of  $[\text{Cu}(\text{PPh}_3)_4](\text{PF}_6)$  is probably incomplete decomposition. Therefore, at higher temperatures, we should expect a higher percent gelation yield.

Nevertheless, at higher temperatures, as shown in Table 7, PVC gelation is extensive (for temperatures between 225 and 300 °C it's between 64 and 75 percent). Thus it is impractical to evaluate metal-induced gelation at higher temperatures.

Thermogravimetric analyses (TGA) of the PVC samples blended with a variety of metal additives (Figures 19, 20, and 21) further suggested that these additives may serve as potential fire retardants and smoke suppressants for PVC by promoting crosslinking via the reductive coupling mechanism. From Figures 19, 20, and 21, a few interesting observations can be made. When the metal additives are degraded in air, they showed weight loss corresponding to the production of zero-valent metal and then a weight recovery reflecting production of the metal oxide.

Therefore, when metal additive was mixed with undegraded PVC in a 1 to 10 weight ratio prior to degradation in air, the final weight loss was less than that for the PVC control sample. Furthermore, the addition of the metal additives to PVC enhanced weight loss at lower temperatures.

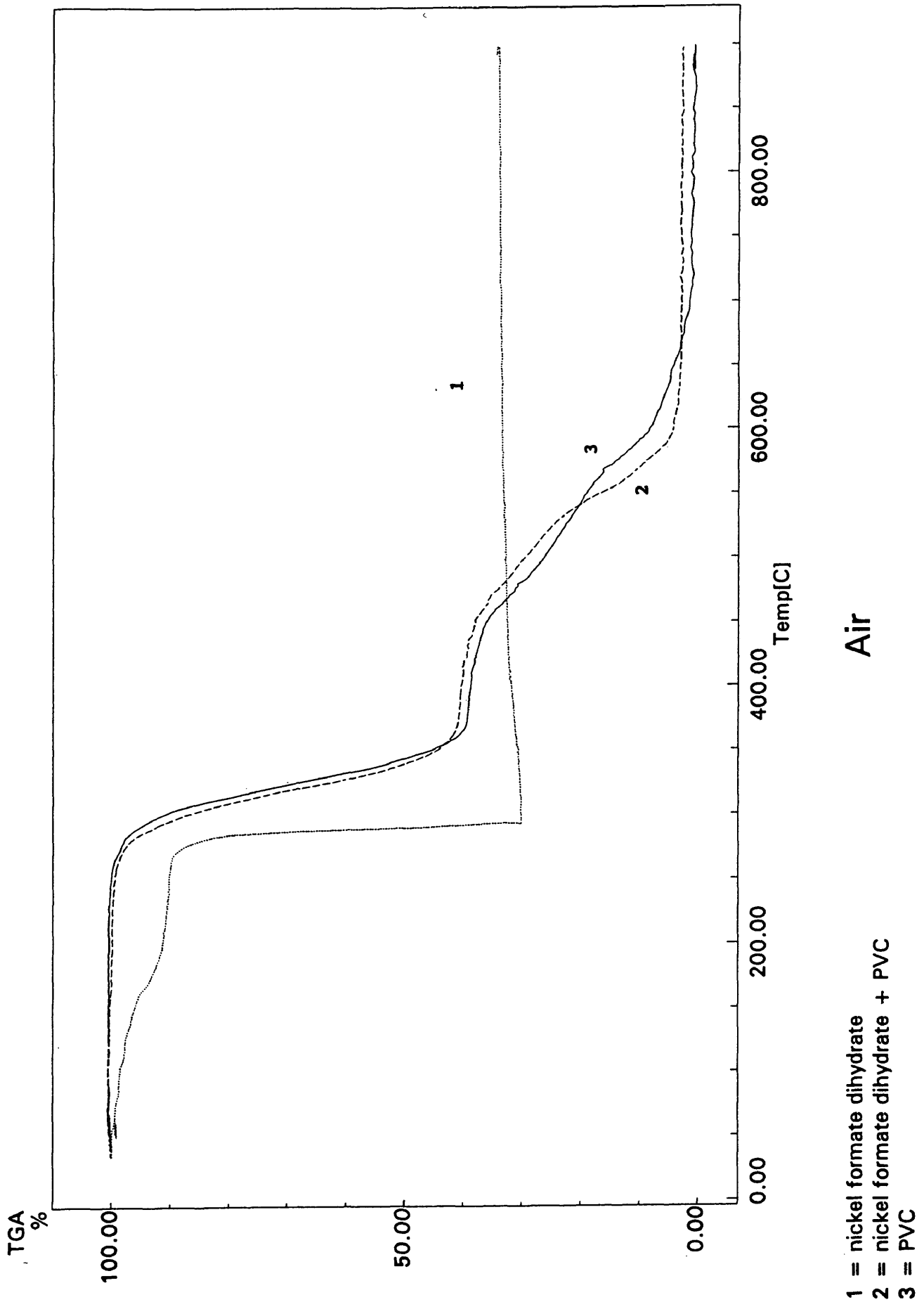


Figure 19. Thermogravimetric analyses of PVC blended with copper(II) formate dihydrate.

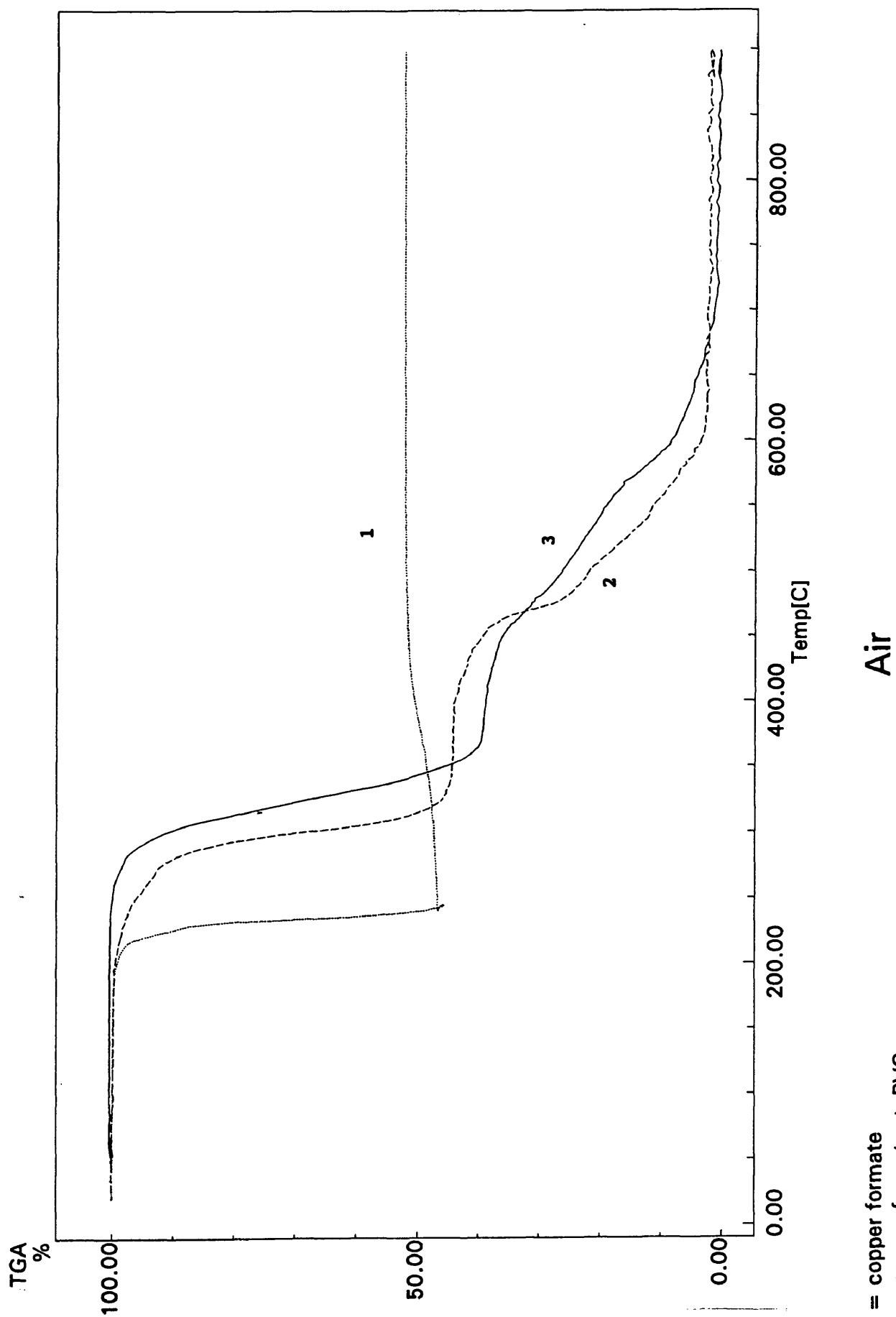


Figure 20. Thermogravimetric analyses of PVC blended with copper(II) formate.

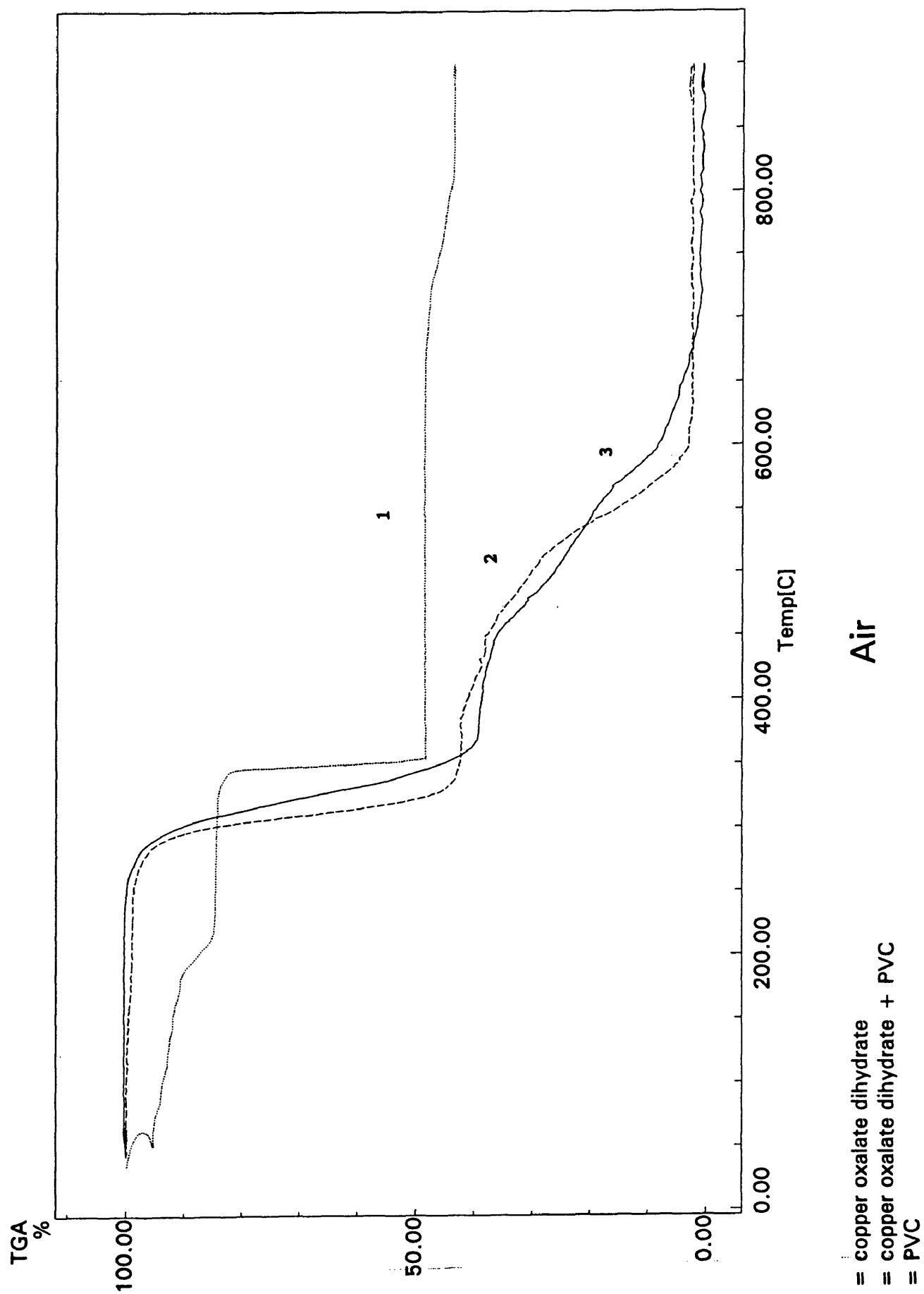


Figure 21. Thermogravimetric analyses of PVC blended with copper(II) oxalate dihydrate.

Infrared spectra of PVC sample residues were taken after thermal degradation for one hour at 200 °C under argon. Figure 22 shows a comparison between a PVC control sample degraded without additives and those degraded with various iron additives. The most noteworthy region of the spectra was the C=C region (1600-1640  $\text{cm}^{-1}$ ). This polyene band originates from the dehydrochlorination of the polymer. This band is absent from virgin PVC, even after thermolysis. This was expected since virtually no gelation occurs upon thermolysis of the was control PVC. The PVC sample which was blended with  $\text{Fe}_2(\text{CO})_9$  (an Fe(0) complex) and thermolyzed showed extensive crosslinking but the IR spectrum showed virtually no increase in the C=C band. In the reductive coupling mechanism, coupling halts growth of 2 polyene chains thus producing relative few C=C bonds. In the Friedel-Crafts mechanism, crosslinking halts the growth of only one chain, while the other one may still grow, producing C=C bonds. Therefore, the presence of Fe(0) may have promoted reductive coupling of the polymer. The PVC sample that was thermolyzed with iron (II) formate showed moderate crosslinking in the gelation study, but also showed essentially no increase in the C=C band. This may again be the result of reductive coupling of the polymer promoted by Fe(0). On the other hand, although the sample containing  $\text{FeCl}_2$  also showed moderate crosslinking after degradation, it showed a large C=C band in the IR spectrum. This suggested Lewis acid promotion of extensive dehydrochlorination. Crosslinking in this sample was probably of Friedel-Crafts type. The same observations can be made for copper and nickel additives in Figures 23a,b and 24 respectively.

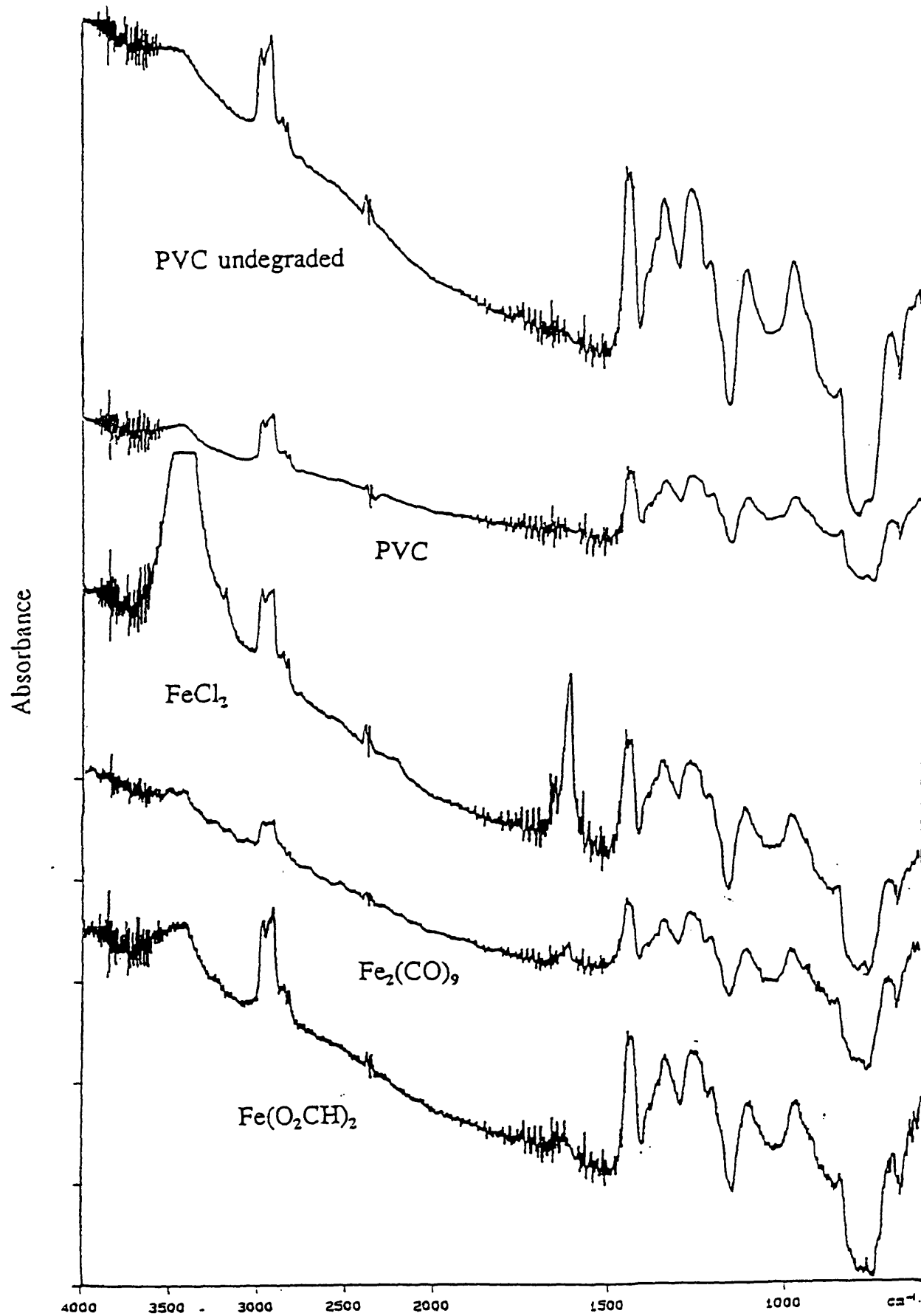


Figure 22. IR spectra for PVC degraded in the presence of iron additives.

Infrared spectroscopy of the chars has also demonstrated that, although the simple metal oxalates and formates of iron, cobalt, nickel, and copper did not fully decompose during degradation, they nevertheless caused significant gelation (Figures 25, 26, 27, and 28). The undegraded coupling agent produced strong IR absorptions. These were removed by washing the char sample with dilute acid. Therefore, under burning conditions, where decomposition will be more complete,  $MC_2O_4$  compounds may prove to be very effective smoke suppressants.

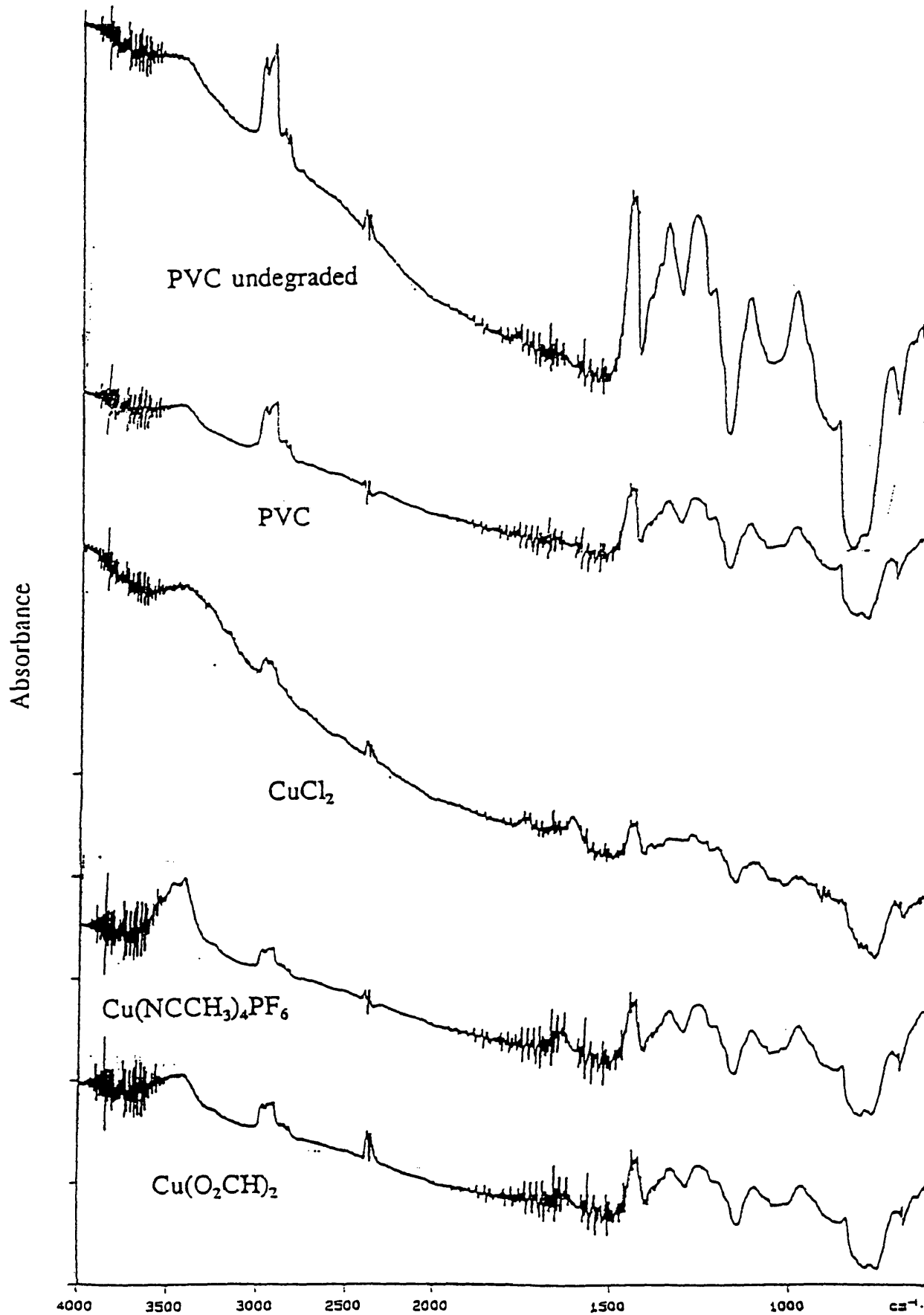


Figure 23a. IR spectra for PVC degraded in the presence of copper additives.

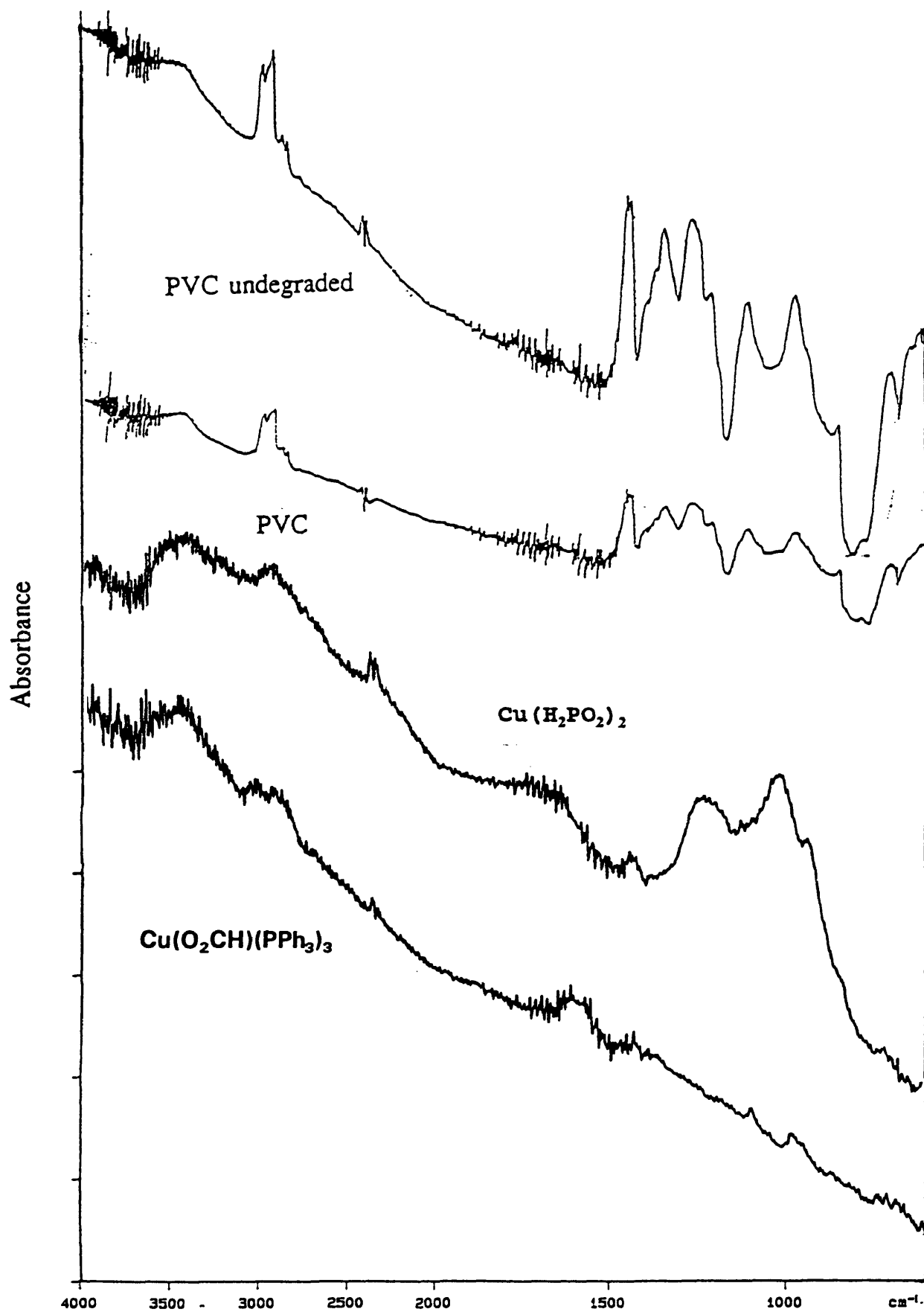


Figure 23b. IR spectra for PVC degraded in the presence of copper additives.

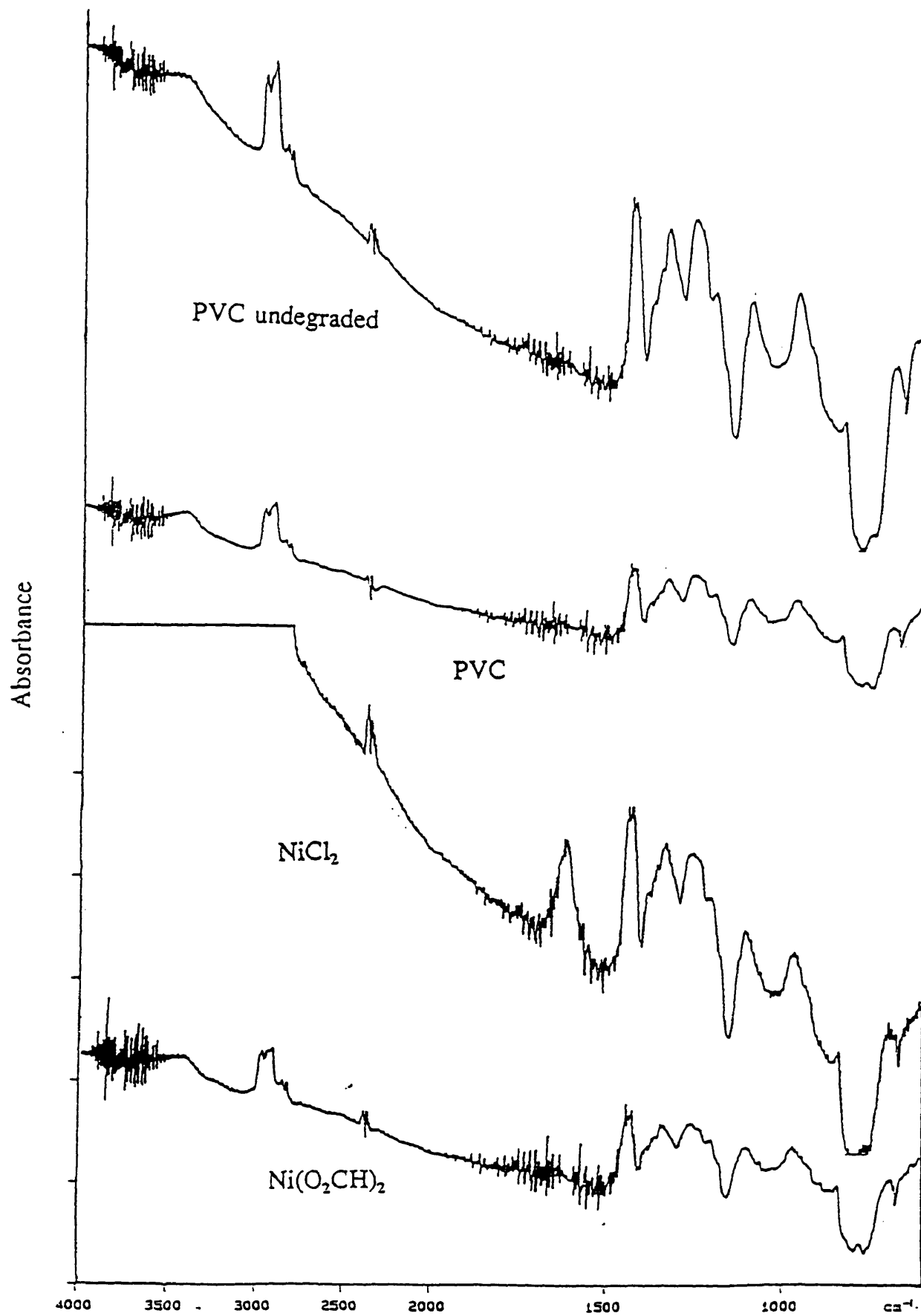


Figure 24. IR spectra for PVC degraded in the presence of nickel additives.

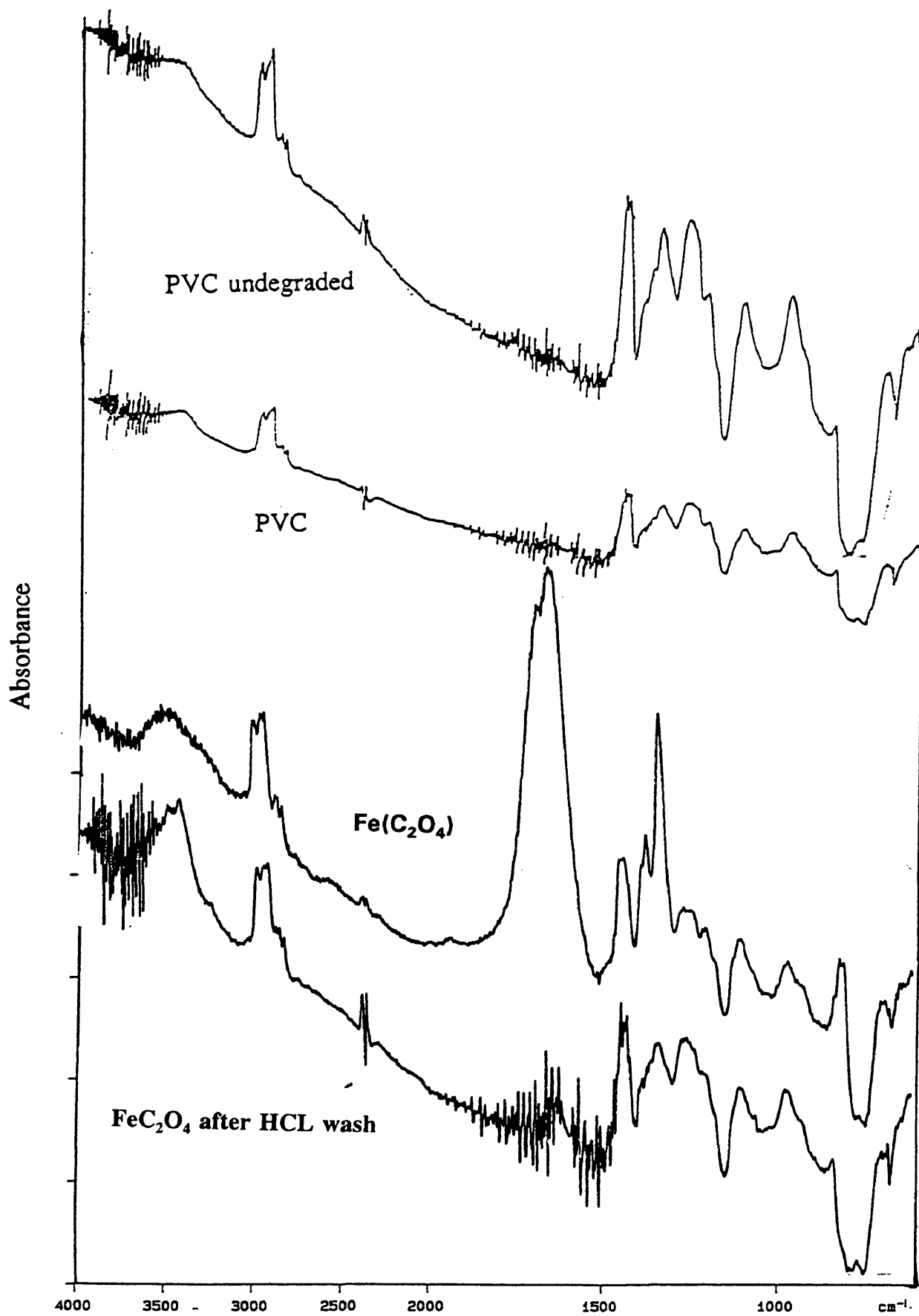


Figure 25. IR spectra for PVC degraded in the presence of ferrous oxalate.

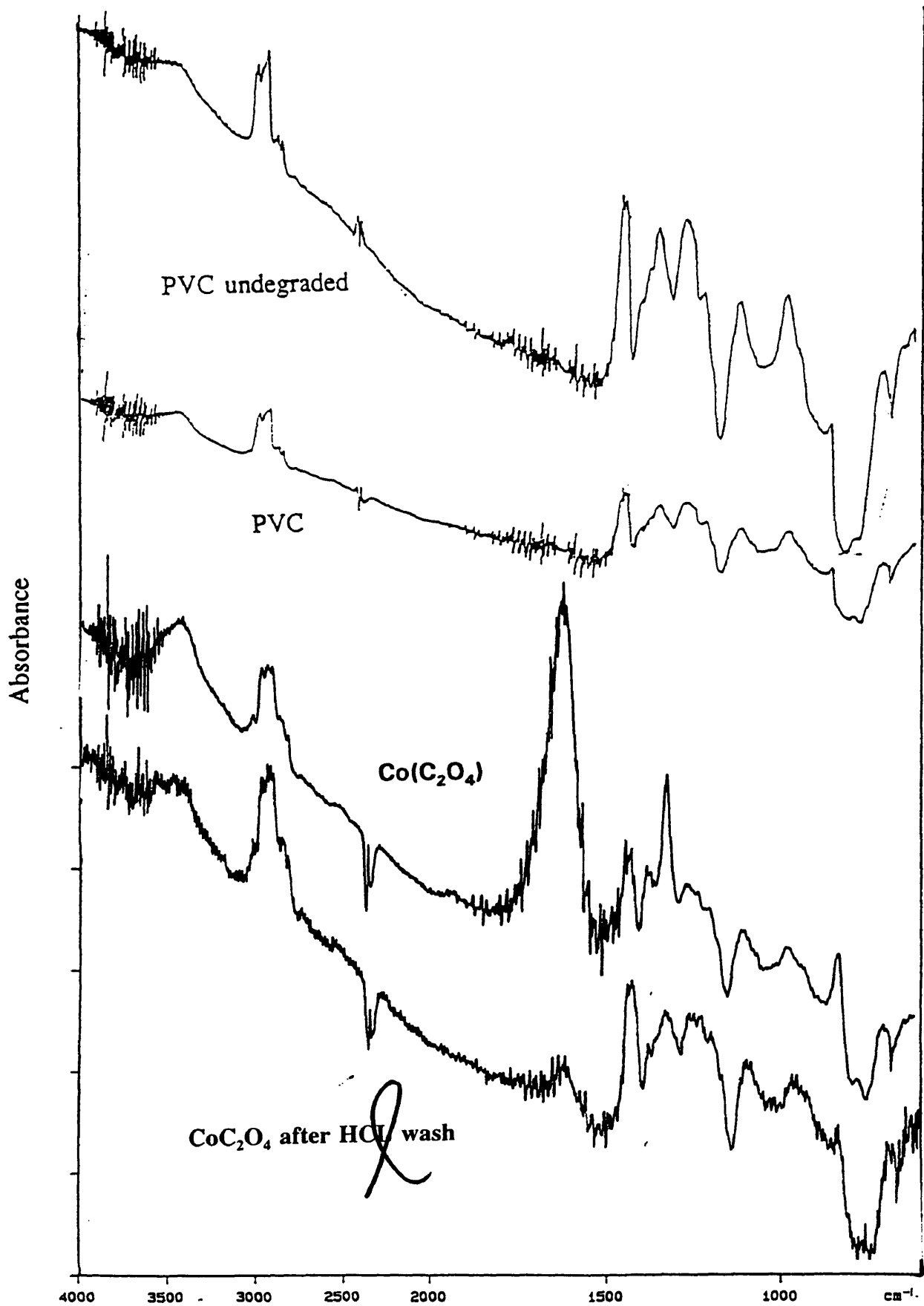


Figure 26. IR spectra for PVC degraded in the presence of cobalt oxalate.

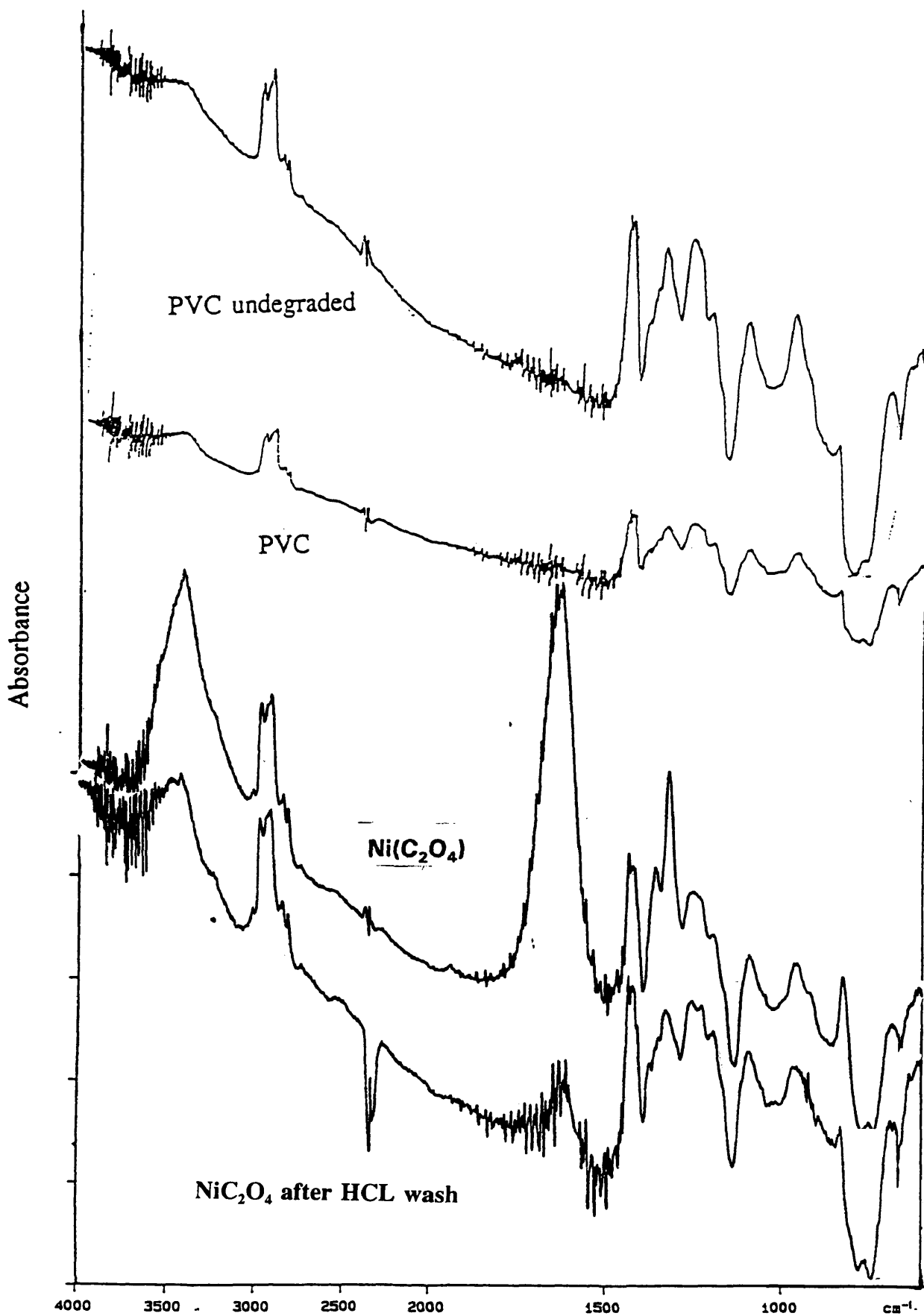


Figure 27. IR spectra for PVC degraded in the presence of nickel oxalate.

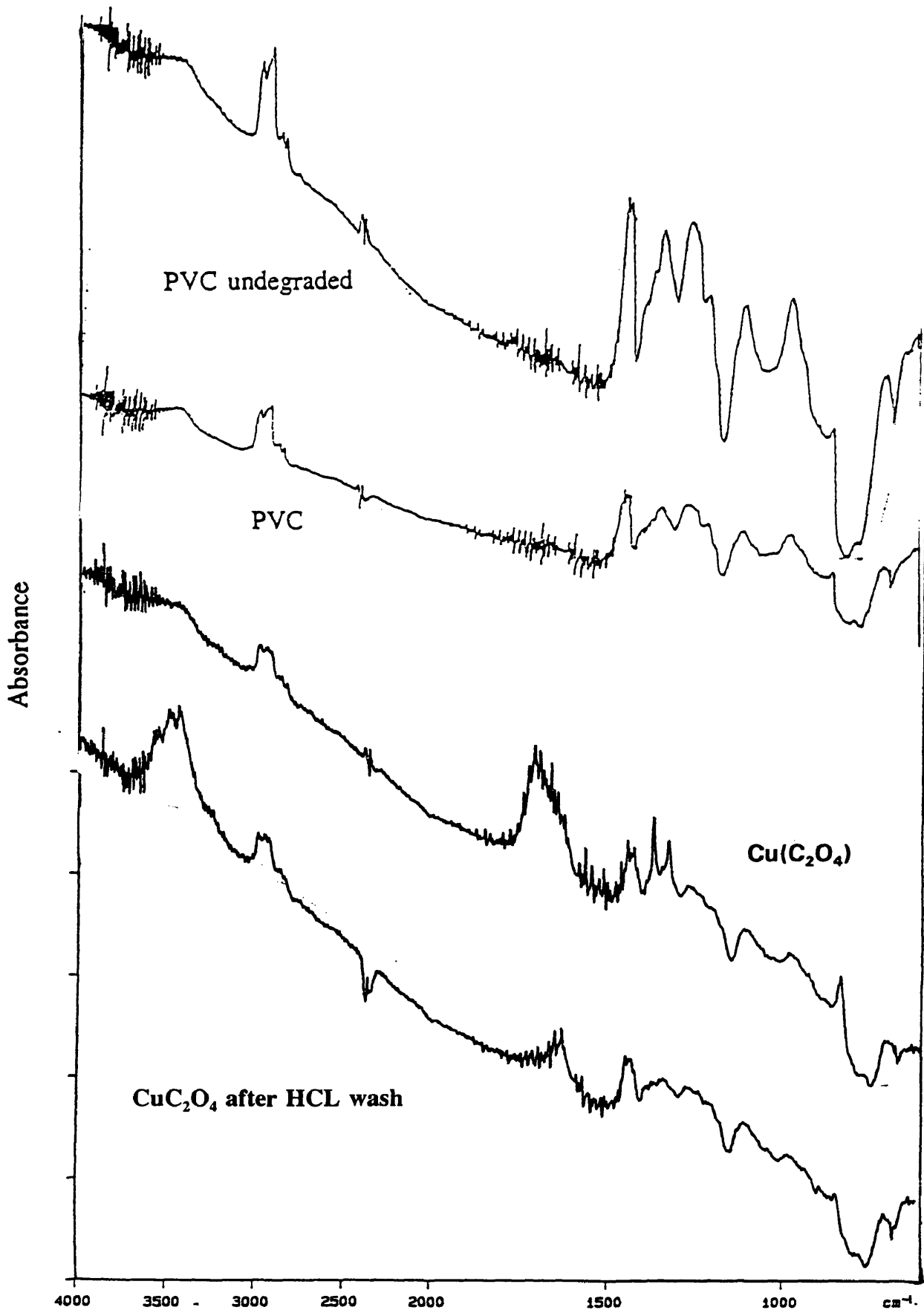


Figure 28. IR spectra for PVC degraded in the presence of copper oxalate.

## IV. CONCLUSIONS

In the presence of several low-valent transition-metal additives, benzylic and allylic chloride model compounds, which represent structural defects in PVC, demonstrated the ability to reductively couple. The reduction of the metals in these additives was accomplished by pyrolysis, and experiments were conducted in both open and sealed systems.

Substantial gelation of PVC was also demonstrated when these transition-metal additives were degraded in the presence of the polymer. Of particular interest are several formate [ $\text{Cu}(\text{O}_2\text{CH})_2$ ,  $\text{Fe}(\text{O}_2\text{CH})_2$ ], oxalate [ $\text{Fe}(\text{C}_2\text{O}_4)$ ,  $\text{Co}(\text{C}_2\text{O}_4)$ ,  $\text{Cu}(\text{C}_2\text{O}_4)$ ,  $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ ], phosphite and hypophosphite [ $\text{Co}(\text{H}_2\text{PO}_2)_2$ ,  $\text{Cu}(\text{H}_2\text{PO}_2)_2$ ,  $\text{NiHPO}_3$ ], and Cu(I) [ $\text{Cu}(\text{O}_2\text{CH})(\text{PPh}_3)_3$ ,  $\text{Cu}(\text{BH}_4)(\text{PPh}_3)_2$ ] low-valent precursor compounds.

This investigation, suggests that, in some cases, the reductive coupling mechanism could be a possible pathway for the crosslinking of the polymer. Still, further studies with other low-valent transition metal precursors are needed to further support this interpretation.

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## Vitae

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