Macromolecules **1997,** *30,* 6957−6965

Low-Valent Metals as Reductive Cross-Linking Agents: A New Strategy for Smoke Suppression of Poly(vinyl chloride)

Robert D. Pike,* William H. Starnes, Jr.,* J. Paul Jeng, William S. Bryant, Peter Kourtesis, Christopher W. Adams, Scott D. Bunge, Yun M. Kang, Andrew S. Kim, J. Hana Kim, Jason A. Macko, and Charles P. O'Brien

Departments of Chemistry and Applied Science, College of William and Mary, Williamsburg, Virginia 23187-8795

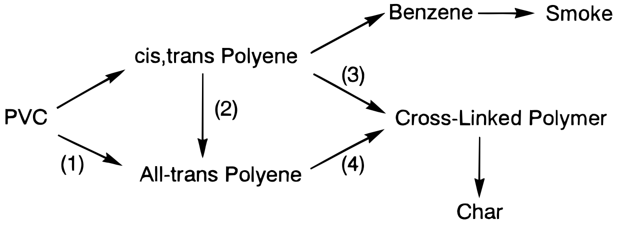
Received June 2, 1997; Revised Manuscript Received August 26, 1997⊗

ABSTRACT: Several types of additives that contain transition metals can promote the cross-linking of poly(vinyl chloride) (PVC) by a mechanism that apparently involves reductive coupling of the polymer chains. In solid PVC, the cross-linking occurs at 200 °C, and model-compound experiments show that it can be ascribed to the preferential reductive coupling of allylic chloride structures when the coupling agent is Cu(0). However, the concurrent coupling of other chloride moieties has not been entirely ruled out. The evidence for reductive coupling consists of rapid gel formation accompanied by substantial reductions (or minor changes) in the rates of total mass loss (as determined by thermogravimetric analysis), C═C formation (as observed by Fourier transform IR spectroscopy), and HCl evolution (as determined by acid−base titrimetry). Additives that promote the coupling process are sources of a zero- or low-valent metal upon pyrolysis. These additives include a number of transition-metal carbonyls, divalent formates or oxalates of the late transition metals, simple Cu(I) halides, and various complexes of Cu(I) containing phosphites or other ligands. Since the reductive coupling agents tend to have low acidities, they are not expected to promote the cationic cracking of char. Thus they are potentially attractive as replacements for the PVC smoke suppressants that stimulate cross-linking by acting as Lewis acids.

Poly(vinyl chloride) (PVC) is inherently flame retardant because of its high chlorine content. Thus it is widely used as an electrical insulator and for other applications in which flame spread must be minimized. Nevertheless, PVC is subject to pyrolysis reactions that ultimately lead to both smoke and flame. The mechanism of PVC pyrolysis has received a great deal of attention over the years,[1] and although some controversies remain, a relatively complete picture now can be presented. The initial step is dehydrochlorination, which occurs at temperatures as low as 100−120 °C and leads to the formation of conjugated polyene sequences.[1] The subsequent chemistry of these polyenes determines the fate of the pyrolyzing PVC. They can undergo cyclization reactions that lead to benzene and other aromatics.[2,3] These hydrocarbons burn in the vapor phase to generate smoke.[2,3] Moreover, the heat generated during this combustion tends to intensify the fire and facilitate the further pyrolysis of the polymer. If, on the other hand, the polyene segments can be induced to undergo cross-linking reactions, the intramolecular production of volatile aromatics will be limited, and a thermally stable char will result. Charring of polymers reduces the heat transmission and mass transfer that are associated with thermal degradation.[4] Thus, in the case of PVC, charring effectively retards the production of aromatic fuels, and the yield of char and the volume of smoke are in inverse proportion.[5]

Numerous chemical agents for PVC smoke suppression have been disclosed.[6] Many of those that appear to function primarily in the condensed phase are transition-metal compounds, particularly oxides and chlorides. Molybdenum(VI) oxide has received particular scrutiny with respect to its mode of smoke suppression.[2,5,7−10] On the basis of evidence from isotopic labeling studies and the behavior of small-molecule PVC models, a series of Lewis acid promoted pathways has been proposed for the thermal decomposition of PVC in the presence of MoO_3 or MoO_2Cl_2 (a product formed from MoO_3 and HCl).[8,9] These routes are summarized in Scheme 1.

Scheme 1

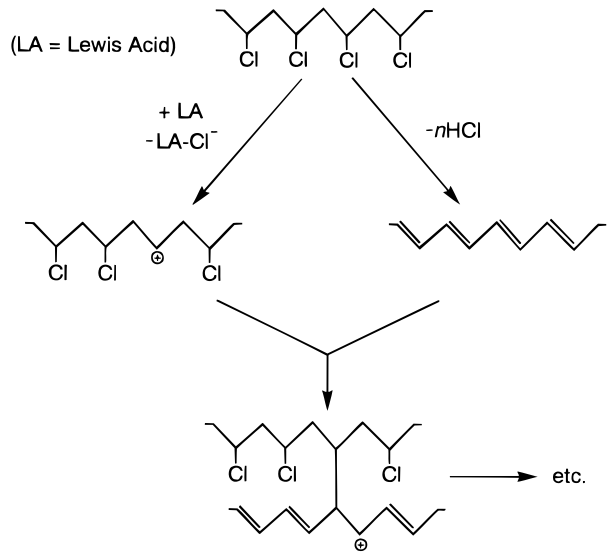


The smoke-suppression action of Mo(VI) could be due to its catalysis of at least three reaction types:[2,8] dehydrochlorination to form trans polyenes (step 1), cis-to-trans isomerization (step 2), and the cross-linking of polyene segments by Friedel−Crafts alkylation or Diels−Alder cyclization (step 3; step 4 also could be important if step 2 were reversible). The generation of a largely trans polyene will inhibit benzene formation, which requires at least one cis double bond.[2] Cationic (Friedel−Crafts) cross-linking could proceed according to Scheme 2. Lewis acid abstraction of chloride creates a carbocation that can alkylate a polyene. As was noted above, cross-linking is expected to decrease the amount of volatile hydrocarbon fuel produced by pyrolysis, while increasing the mass of solid char. Nevertheless, although MoO_3 showed flame-retardant and smoke-suppressant action in small-scale laboratory tests, large-scale experiments involving higher enthalpy inputs revealed a lack of such activity.[10]

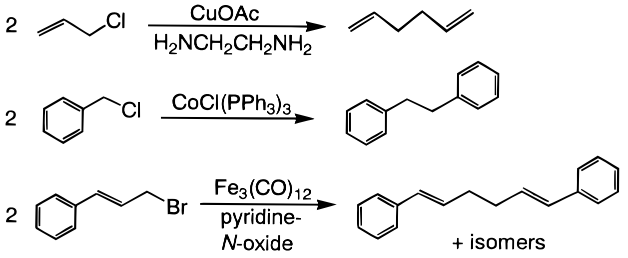
Model-compound reactions in the presence of MoO_3 led to rationalizations for these observations.[8,9] Molybdenum(VI)-promoted alkene isomerization and alkylation dominated at 200 °C. However, at higher temperatures, cationic cracking reactions also occurred, causing fragmentation of the models and their alkene products.

⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1997.

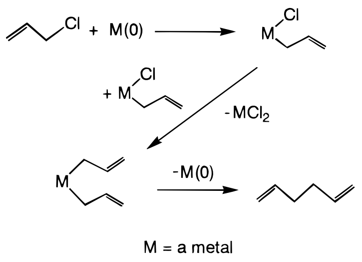
S0024-9297(97)00774-2 CCC: $14.00



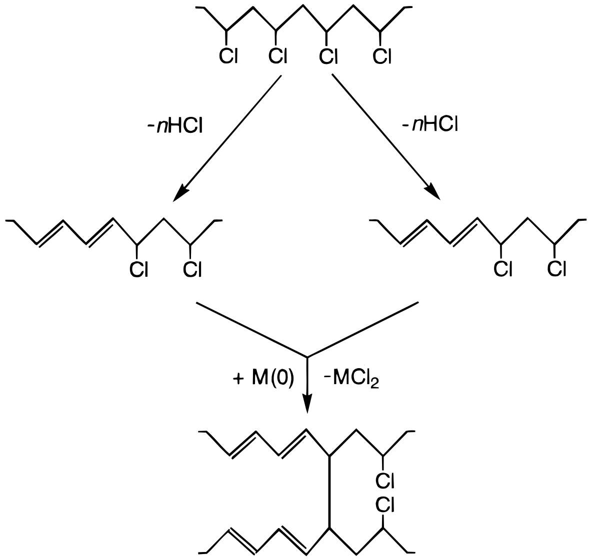
Scheme 2



Scheme 3[11b–d]



Scheme 4



Scheme 5

This result is consistent with the observation that the ratio of volatile aromatics to aliphatics decreases sharply when PVC is pyrolyzed with MoO_3 at high temperatures.[5] As fuels, aliphatic hydrocarbons are superior to aromatics, and they produce less smoke. Therefore, cationic cracking of PVC polyene residues during a fire would be expected to increase and improve the fuel available in the vapor phase and thus decrease the smoke while increasing the flame spread. These effects were, in fact, observed with MoO_3-containing PVC during large-scale tests.[10] Hence it appears that while limited Lewis acidity is useful for reducing smoke from PVC, strong acidity may actually worsen the problem of flame.

Acid-catalyzed cross-linking is not the only metal-promoted coupling reaction that has been considered as a possible mechanism for PVC smoke suppression. Several years ago, a number of transition-metal-containing additives were suggested to promote "reductive coupling" reactions in the pyrolyzing polymer.[5] The reductive homocoupling of simple allylic and benzylic halides, promoted by low-valent organometallic complexes, actually is well-known (for examples, see Scheme 3).[11] Moreover, several workers have demonstrated that suspensions of highly active metal(0) powder also promote allylic, benzylic, and (in some cases) alkyl and aryl halide reductive coupling.[12] The mechanism of these coupling reactions (Scheme 4) may involve oxidative addition of the organic halide to the metal center, a process that increases the oxidation state of the metal by two units: 0 → II (or I → III if the starting metal is univalent). Bimolecular ligand exchange then would give rise to a metal dihalide and a metal dialkyl. The latter species should readily undergo reductive elimination to yield the starting metal and a C−C bond. However, an alternative mechanism for reductive coupling has been suggested by Ebert et al.,[12c] and mechanisms involving free-radical intermediates also might be operating in certain cases.

Scheme 5 illustrates the hypothetical reductive coupling process in PVC under pyrolysis conditions. Allylic chloride groups are present in the degrading polymer.[1] They represent the sites of dehydrochlorination where polyene growth occurs.[1b] Reductive coupling of allylic chlorides on adjacent polymer chains would create cross-links. Additionally, since the allylic chloride functionalities would be removed by the coupling, that process would stop the propagation of dehydrochlorination along both chains.

In 1981 Lattimer and Kroenke[5] suggested that reductive coupling might account for the smoke-suppression activity of MoO_3 in PVC. This possibility was shown to be unimportant, however, by later work which revealed that MoO_3 behaves primarily as a Lewis acid coupling agent.[7−9] There are a number of reasons why this additive is an unlikely reductive coupling promoter. As was noted already, reductive coupling should inhibit PVC dehydrochlorination. However, MoO_3 greatly increases the rate of evolution of HCl, as expected for a Lewis acid.[8] Secondly, Mo(VI) is not an oxidizable species and therefore cannot directly promote reductive coupling. Thermal reduction of Mo(VI) would be necessary in order for reductive coupling to take place. Finally, none of the model compound studies using MoO_3 or MoO_2Cl_2 has provided conclusive evidence for the occurrence of reductive coupling reactions.[7−9] Hence, it appears that Lewis acid chemistry is dominant for this metal oxide. Likewise, Lewis acid smoke suppression has been claimed for compounds of high-valent iron and for some other metal salts.[13]

Although the substances just referred to apparently do not function via reductive coupling, there are other

PVC additives that may promote such a reaction. Two studies that examined a wide variety of potential smoke suppressants for PVC showed copper compounds to be one of the most effective classes[6a] (or, in fact, the single most effective class[6b]) of transition metal salts. Moreover, copper(II) compounds were shown to suppress benzene production greatly during PVC pyrolysis,[14] and a recent XPS study provided evidence for significantly enhanced cross-linking of PVC in the presence of Cu_2O at temperatures as low as 200−300 °C.[15] If acid catalysis were indeed of prime importance, then all of these results would be quite surprising in view of the relatively weak Lewis acidities of Cu(I) and Cu(II). Thus, for copper compounds, another cross-linking mechanism, such as reductive coupling,[5] seems to be required. It should be noted, however, that model-compound studies have shown that although copper salts do not readily catalyze either cis/trans alkene isomerization or cracking reactions,[16] they do act as weakly acidic catalysts for Friedel−Crafts alkylation.[7,16b]

For several reasons, some of which were given above, reductive coupling agents should offer a number of advantages over strictly Lewis acid based smoke suppressants. As may be seen in Scheme 5, each reductive coupling cross-link would halt simultaneously the growth of two polyene sequences. The resulting inhibition of dehydrochlorination would slow the degradation of the polymer. In fact, isolated allylic chloride defect sites might be attacked, stabilizing the polymer against the earliest stages of thermal degradation. Nonallylic sites conceivably could couple to some extent as well, and such reactions also would retard dehydrochlorination if they involved tertiary chloride (which is thermally labile[1a,c,d]) or the cross-coupling of thermally stable and thermally labile C−Cl groups. The shorter polyene segments resulting from allylic coupling would serve to restrict the amounts of benzene and other aromatics generated during pyrolysis. Furthermore, metal additives which were readily reducible, and thus might act as reductive coupling agents, would typically be weak Lewis acids. Therefore, while they might promote some beneficial Friedel−Crafts cross-linking,[7,16b] they would not be likely to catalyze char cracking.

In general, good candidate reductive coupling agents would be expected to possess the following attributes: (i) The metal should have relatively low electrochemical activity. In other words, the metal ion should be relatively easy to reduce to the zero oxidation state. (ii) The metal should be present in a low oxidation state in the additive compound. Alternatively, the metal complex should possess oxidizable ligands. These could generate low- or zero-valent metal by means of thermal reductive elimination. (iii) The temperature at which the metal was reduced would, of course, have to be well above those of polymer processing. (iv) Finally, the additive should be inexpensive and colorless (if possible), and it should not impart adverse properties to the polymer formulation.

Prior to the present work (portions of which have been described elsewhere[17]), studies involving copper compounds and other additives had provided little, if any, evidence for the reductive coupling of model chlorides or PVC itself. Nevertheless, Cu(II) was known to be readily reducible to Cu(I) ($\Delta G° = -15$ kJ mol^{-1}) or Cu(0) ($\Delta G° = -66$ kJ mol^{-1}),[18] and thus it was conceivable that the smoke-suppressant activity shown by both Cu(II) and Cu(I) stemmed from a combination of weak Lewis acidity and the ability to promote reductive coupling reactions.

Objective and Approaches

The goal of the current study was to identify metal additives that could promote reductive coupling in thermally degrading PVC and were essentially nonacidic. In order to reach this objective, experiments were carried out with both the polymer and appropriate model substances. In keeping with the preceding discussion, the criteria used to establish reductive coupling of the polymer itself were the rapid formation of cross-linked resin (insoluble gel) accompanied by *decreases* (or minor alterations) in the rates of total mass loss (as determined by thermogravimetric analysis (TGA)), C═C formation (as determined by Fourier transform IR (FTIR) spectroscopy), and HCl evolution (as determined by acid−base titrimetry). These criteria contrast markedly with those for Lewis acid promoted cross-linking, which are gelation in conjunction with major *increases* in the rate of mass loss and in the rates of production of double bonds and HCl.

Experimental Section

General Information. The PVC was obtained from Aldrich; it contained no additives and had a nominal inherent viscosity of 1.02. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Organic model compounds for PVC were purchased from Aldrich and used as received. Copper powder (99.999%) and copper(I) iodide (Aldrich), copper(II) formate and nickel(II) formate (Pfaltz and Bauer), the metal carbonyl complexes (Strem), and the metal chlorides (Aldrich or Fisher) were obtained from the indicated commercial sources. All formate, oxalate, and chloride salts were dried in a vacuum oven at 100 °C prior to use. They then were analyzed by TGA (*vide infra*) for residual water content. Metal additive (9.1 wt %, 1 part by weight) and PVC (10 parts by weight) were mixed by grinding in a liquid-nitrogen-cooled mortar. All experiments involving PVC or model compounds were carried out under argon. The high-purity copper powder was stored and handled in an argon-filled drybox.

Instrumentation. Thermogravimetric studies were conducted by using a Shimadzu TGA-50 instrument or a Seiko DT-TGA 200 apparatus under a flowing nitrogen atmosphere (50 mL/min). Three protocols were used: (i) 200 °C isothermal for 1 h for PVC-additive mixtures; (ii) 10 deg/min to 200 °C, then 1 h isothermal to determine the hydration of metal compounds; and (iii) 5 deg/min to 900 °C to investigate the thermal degradation of metal compounds. All gas chromatography/mass spectrometry (GC/MS) analyses were carried out with a Hewlett-Packard Model 5890/5971A instrument equipped with a fused-silica capillary HP-1 column. The FTIR spectra were recorded on a Perkin-Elmer spectrophotometer, Series 1600. Dehydrochlorination rates of PVC specimens were determined by acid−base titrimetry performed with a Brinkmann Metrohm 702 SM Titrino automatic titration device. Flame atomic absorption spectroscopy (AAS) was carried out with a Perkin-Elmer 1100B spectrophotometer, and decomposition points were determined with a Thomas Hoover Meltemp apparatus.

Synthesis of Complexes. Copper(I) chloride and bromide were freshly prepared by the reaction of $CuCl_2$ or $CuBr_2$ with Cu in aqueous HCl or HBr. The copper(I) phosphite and phosphine complexes were made according to literature methods.[19] The acetonitrile complex $[Cu(NCCH_3)_4]PF_6$ also was synthesized by using a published procedure,[20] and the novel benzonitrile analog $[Cu(NCPh)_4]PF_6$ was prepared in analogous fashion. All of the copper(I) complexes were analyzed for copper content by digestion in 6 M HNO_3, followed by atomic absorption analysis. The synthesis yields and the results of the AAS determinations are shown in Table 1. Iron(II) formate was prepared according to a literature method.[21] The metal oxalate salts were obtained as precipitates by mixing aqueous solutions of oxalic acid and the appropriate metal(II) sulfate or nitrate. All of the metal oxalates, formates, and carbonyls, as well as the copper(I) complexes, were tested for decomposition point by using a capillary melting point technique.

Table 1. Analytical Data for Copper(I) Complexes

complex	yield, %	% Cu theory	% Cu by AAS
$[Cu(NCCH_3)_4]PF_6$	47	17.1	16.9
$[Cu(NCPh)_4]PF_6$	59	10.2	10.1
$[Cu(P(OCH_3)_3)_4]BF_4$	81	9.8	9.8
$[Cu(PPh_3)_4]PF_6$	77	5.1	5.8
$[CuCl(PPh_3)]_4$	90	17.6	17.9
$[CuCl(P(OPh)_3)]_4$	95	15.5	15.1
$[CuBr(P(OPh)_3)]_4$[a]	96	14.0	13.6
$[CuI(P(OPh)_3)_2]$	75	7.8	8.2
$[CuCl(P(OPh)_2(O^iDec))]_4$[a]	68	13.4	13.2
$[CuBr(P(OPh)_2(O^iDec))]_4$[a]	66	12.3	12.7
$[CuCl(P(OPh)(O^iDec)_2)]_4$[a]	70	11.8	11.9
$[CuBr(P(OPh)(O^iDec)_2)]_4$[a]	65	10.9	10.8
$[CuCl(P(O^iDec)_3)]_4$[a]	63	10.6	10.7
$[CuBr(P(O^iDec)_3)]_4$[a]	65	9.8	9.6

[a] Tetrameric formulation not confirmed.

Determination of Polymer Gel. Gel yields were obtained as the weight percentages of the PVC-additive residue after pyrolysis. The residue was weighed, subjected to overnight Soxhlet extraction with THF, and reweighed after drying at 60 °C under vacuum. The extraction, drying, and weighing procedures then were repeated in order to ensure complete removal of residual soluble PVC.

Preparation of Activated Copper(0) Slurry.[12b,c] All glassware used in the following procedure was flame-dried. Under argon, $[CuI(P^nBu_3)]_4$ (3.93 g, 10 mg-atom of Cu) was dissolved in THF or ethyl ether (10 mL) at 0 °C. Lithium naphthalenide solution in THF (10 mL, 11 mmol) then was introduced by syringe. After about a minute, a dark brown suspension of activated copper had formed. Removal of excess lithium naphthalenide proceeded as follows: The freshly prepared Cu(0) slurry (5 mL, 2.5 mmol) was transferred to an argon-filled centrifuge tube. Ethyl ether (5 mL) was added, and the tube was shaken and then ultracentrifuged at 3200 rpm for 3−5 min. After removal of the ether via syringe, the process was repeated.

Reactions of Activated Copper Slurry with Model Organic Halides. A model organic halide (2.5 mmol) or a mixture of two such halides (1.25 mmol of each) was injected into the centrifuge tube containing the Cu(0) slurry at 0 °C under argon. The resultant mixture was agitated continuously at constant temperature for 5 min. It then was analyzed immediately by GC/MS.

Reactions of Activated Metal Film with Model Organic Halides. Copper(II) formate or another appropriate metal compound was introduced into a flame-dried 100-mL round-bottom flask equipped with a Drierite column. After the flask had been thoroughly purged with dry argon, the compound was decomposed by heating externally with a Bunsen flame. Complete decomposition was indicated by the formation of a metal mirror in many cases. The residue was cooled to room temperature and then treated with a model organic halide or an equimolar mixture of two such halides, which was added by syringe. After 1 min of reaction, the mixture was diluted with THF and immediately analyzed by GC/MS.

Reactions of Activated Copper Slurry with PVC in Solution.[17a] Activated copper slurry (20 mg-atom) in THF (15 mL), derived from the reduction of $[CuI(P^nBu_3)]_4$, was added by syringe to a refluxing solution of PVC (2.00 g, 32 mmol of monomer units) in the chosen solvent (35 mL for THF, 50 mL for the other solvents). In all of the experiments except those where THF was the only solvent used, the THF was allowed to boil off quickly at the start of the heating period. After the reflux period, the insoluble fraction was separated by decantation or filtration, and the gel percentage was determined by the standard extraction procedure described above.

Thermal Degradation of Solid PVC Samples. An intimate mixture of PVC (1.00 g, 16 mmol of monomer units) and additive (0.100 g) was prepared by grinding at liquid nitrogen temperature. The mixture was placed under flowing argon and maintained at 200 ± 2 °C for 1 h. Then the gel percentage was determined by the extraction procedure described above. Thermolysis residues which had not been extracted with THF were used to prepare mulls for FTIR analysis. After the residue had been reground at liquid nitrogen temperature, a portion of it (0.032 g) was mulled with mineral oil (0.18 g). A sample (0.025 g) of the resulting mull then was placed between NaCl plates and analyzed. Samples being analyzed for acidic vapor evolution were swept with argon at a rate of 50 mL/min in order to transfer the gaseous effluent into water, which was titrated continuously with 0.010 N NaOH in order to maintain a pH of 7.0.

Table 2. Coupling of Organic Halides by Activated Copper Slurry

substrate(s)	product(s)	yield(s), %[a]
3-chloro-1-butene	C_8H_{14}[b]	16 ± 2
2-chlorobutane	C_8H_{18}	5 ± 2
1-chlorobutane	C_8H_{18}	<1
4-bromooctane	$C_{16}H_{34}$	6 ± 2
1-bromohexane	$C_{12}H_{26}$	3 ± 1
p-methylbenzyl chloride	$C_{16}H_{18}$	20 ± 3
benzyl bromide	$C_{14}H_{14}$	12 ± 3
3-chloro-1-butene/1-chlorobutane	C_8H_{14}[b]	6 ± 3
	C_8H_{16}[b]	4 ± 2
	C_8H_{18}	<1
3-chloro-1-butene/4-bromooctane	C_8H_{14}[b]	9 ± 1
	$C_{12}H_{24}$[b]	2 ± 1
	$C_{16}H_{34}$	<1
3-chloro-1-butene/1-bromohexane	C_8H_{14}[b]	12 ± 3
	$C_{10}H_{20}$[b]	3 ± 1
	$C_{12}H_{26}$	<1

[a] GC area percentages based on amount(s) of starting substrate(s); mean values from duplicate runs. [b] Mixture of several isomers.

Results and Discussion

Reductive Coupling of Model Compounds and PVC Using Activated Metals. High-surface-area copper metal suspensions were produced in THF or ethyl ether by the lithium naphthalenide reduction of $[CuI(P^nBu_3)]_4$.[12b,c] The coupling of organic halides was tested by using these slurries after their air-free washing to remove residual lithium naphthalenide. The organic coupling products were analyzed by GC/MS, and the results are shown in Table 2. It may be noted that the secondary allylic chloride and the benzylic halides were coupled to form homodimers, while the saturated alkyl halides showed less reactivity of this type. Moreover, when the allylic halide and the alkyl halides were allowed to react together, the homocoupled product from the allylic substrate predominated. These results are consistent with previous observations by other workers.[12c] Isomeric product distributions suggested the occurrence of rearranging allylic intermediates in our coupling reactions.

High-surface-area copper also was generated as a film by heating solid, anhydrous copper(II) formate to >200 °C under flowing argon.[22] Films prepared in this way appeared as copper mirrors. Metal mirrors also were formed by the thermal decomposition of some metal carbonyls. The metal films produced in this manner were found to couple allylic and benzylic halides in the absence of solvent. These results are presented in Table 3.

Since allylic chloride groups were known to be present in both virgin and thermally degraded PVC,[1] the above results suggested that activated zero-valent metals could promote interchain reductive coupling reactions leading to cross-linking of the polymer. Therefore, PVC cross-linking experiments were carried out with copper metal slurries. Solutions of PVC were prepared in a number of solvents having boiling temperatures of 66−

Table 3. Coupling of Organic Halides by Activated Metal Films

metal precursor (mol/[mol of substrate(s)])	substrate(s)	product(s)	yield(s), %[a]
$Cu(O_2CH)_2$ (1.0)	3-chloro-1-butene	C_8H_{14}[b]	20 ± 2
$Cu(O_2CH)_2$ (1.0)	1-chloro-2-butene	C_8H_{14}[b]	30 ± 3
$Cu(O_2CH)_2$ (1.0)	*trans*-4-chloro-2-pentene	$C_{10}H_{18}$[b]	24 ± 2
$Cu(O_2CH)_2$ (1.0)	*p*-methylbenzyl chloride	$C_{16}H_{18}$	21 ± 2
$Cu(O_2CH)_2$ (1.0)	benzyl bromide	$C_{14}H_{14}$	14 ± 3
$Cu(O_2CH)_2$ (1.0)	3-chloro-1-butene/*trans*-4-chloro-2-pentene	C_8H_{14}[b]	26 ± 1
		C_9H_{16}[b]	12 ± 3
		$C_{10}H_{18}$[b]	24 ± 2
$Mo(CO)_6$ (0.25)	3-chloro-1-butene	C_8H_{14}[b]	6[c]
$Co_2(CO)_8$ (0.22)	3-chloro-1-butene	C_8H_{14}[b]	6[c]
$Mn_2(CO)_{10}$[d] (0.14)	3-chloro-1-butene	C_8H_{14}[b]	7[c]

[a] GC area percentages based on amounts of starting substrate(s); mean values from duplicate runs, except as noted. [b] Mixture of several isomers. [c] Single run. [d] No mirror formed.

Table 4. Gel Yields from PVC Treated with Copper Slurry in Solution[17a]

solvent	temp, °C	time, h	gel, %[a]
THF	66 ± 2	2.0	79 ± 2
anisole	155 ± 2	2.0	92 ± 2
o-dichlorobenzene	174 ± 2	2.0	88 ± 2
phenyl ether	257 ± 2	0.5	90 ± 2

[a] Mean values from duplicate runs.

257 °C. Into each was injected a suspension of copper in THF that had been produced by the lithium naphthalenide method. The extent of cross-linking in the PVC residue was measured as the insoluble (gel) portion of the polymer after Soxhlet extraction with THF. The results, shown in Table 4, confirmed that PVC was extensively cross-linked by the active copper suspensions, even at 66 °C. Significantly, copper-free control experiments performed at each temperature gave no cross-linking whatsoever. A copper(0) suspension also was produced by refluxing a suspension of copper(II) formate in phenyl ether. Dissolved PVC showed 69% gelation after 15 min in the resulting mixture.

Cross-Linking of PVC Using Low-Valent Metal Precursor Compounds. Taken together, the foregoing results strongly suggested that high-surface-area oxide-free copper and other metals could promote the reductive cross-linking of allylic chloride moieties in PVC, both in solution and in the solid state. It was realized, however, that zero-valent metals which were simply blended with the polymer not only would cause difficulties with processibility but also were not likely to function well as smoke suppressants, because such metal powders were prone to surface air oxidation, which has a strong passivating effect. Therefore, potential PVC smoke suppressants were sought among compounds that could decompose thermally to liberate a free metal. Since PVC cross-linking was desirable only in the event of pyrolysis, a viable additive would have to generate the metal only at elevated temperatures.

Several classes of metal precursors were considered for use. Certain ligands, most notably carbonyl, are known to stabilize zero-valent metal centers. However, metal carbonyl complexes tend to be toxic and volatile, and they decompose at relatively low temperatures (<200 °C) to release toxic and flammable carbon monoxide gas. A second class of complexes consisted of divalent formates and oxalates of the late transition metals. Unlike oxalate and formate salts of the main group and early transition metals, which decompose to produce metal oxides, the later transition metal salts have been shown by thermal analysis to undergo reductive elimination to yield zero-valent metals according to reactions such as eqs 5 and 6.[23] A third metal precursor strategy involved the use of ligated copper(I) salts. Copper(I) undergoes the disproportionation reaction 7

$$MC_2O_4 \rightarrow M + 2CO_2(g) \tag{5}$$

$$M(O_2CH)_2 \rightarrow M + CO_2(g) + H_2O(g) + CO(g) \tag{6}$$

$$2Cu(I) \rightarrow Cu(II) + Cu(0) \tag{7}$$

($\Delta G° = -35$ kJ mol^{-1})[18] to give copper(II) and copper(0) as products. Nevertheless, the relative stability of the copper(I) center is strongly influenced by the choice of ligands.

To capitalize upon metal-releasing strategies such as those of reactions 5−7, a number of metal formate and oxalate salts and several copper(I) complexes were prepared or purchased. A variety of metal chloride salts also were evaluated for comparison, because such compounds do not readily undergo reductive elimination and therefore were not expected to produce low-valent metals under our conditions. The metal compounds, where appropriate, were dried under vacuum and tested for residual water content by TGA and for approximate decomposition temperature with a capillary melting point apparatus. Decomposition temperatures for metal carbonyls, formates, and oxalates and for copper(I) complexes are included in Table 5.

Mixtures of PVC with each of the metal compounds were prepared by grinding at low temperature. Each of the mixtures was subjected to two screening tests. The first of these involved solid state thermolysis at 200 °C under flowing argon, followed by extraction with THF in order to determine the gel content of the polymer residue. Gelation results are presented in Table 5. Although desirable for a more realistic simulation of PVC pyrolysis during combustion, thermolysis temperatures above 200 °C were not useful, because at such temperatures the control sample underwent extensive gelation.

The second screening test was isothermal TGA during 1 h at 200 °C under nitrogen. Mass losses of PVC at this temperature are mostly the result of dehydrochlorination.[24] However, sample mass losses due to the escape of volatile ligands from the metal compounds also were expected. The mass loss values in Table 5 have been corrected for the latter effect. Characteristic isothermal TGA traces of additive-free PVC and PVC blended with several copper and iron additives are overlaid in Figure 1. The metal-free control sample showed no significant gelation or mass loss upon pyrolysis for 1 h at 200 °C. A number of additives showed a combination of extensive PVC gelation and low polymer mass loss (after correction for ligand dissocia-

Table 5. Polymer Gelation and Thermogravimetric Mass Loss Results for Thermally Degraded PVC/(Metal Additive) Samples (after 1.0 h at 200 °C under N_2, 9.1% additive)

metal additive	decomp temp,^{a} °C	gelation replicates	mean gel yield, %, ± av dev from mean	mass loss, % (corrected)^b
no additive		2	<5	1.3
$Co_2(CO)_8$	52	3	73 ± 2	3.4
$Fe_2(CO)_9$	100	5	75 ± 6	13.4
$Mn_2(CO)_{10}$	152	3	68 ± 2	2.8
$Mo(CO)_6$	150	6	67 ± 7	3.1
$W(CO)_6$	169	6	79 ±10	3.4
$FeCl_2{\cdot}1.8H_2O$		5	56 ± 7	8.8
$FeCl_3{\cdot}3.1H_2O$		7	68 ±10	31.8
$NiCl_2{\cdot}0.6H_2O$		3	16 ± 6	2.9
$CuCl_2{\cdot}0.3H_2O$		3	82 ± 4	4.4
$CuBr_2{\cdot}5.3H_2O$		2	61 ± 4	1.8
$ZnCl_2{\cdot}0.2H_2O$		2	56 ± 0	36.0
$SnCl_2{\cdot}3.3H_2O$		2	53 ± 3	33.2
$Fe(O_2CH)_2{\cdot}1.9H_2O$	230	3	50 ± 4	0.2
$Ni(O_2CH)_2$	261	3	18 ± 4	−2.6
$Cu(O_2CH)_2$	199	6	83 ±10	−0.5
$Fe(C_2O_4)$	225	2	85 ± 4	5.4
$Co(C_2O_4)$	250	2	42 ± 1	−2.8
$Ni(C_2O_4){\cdot}0.2H_2O$	280	3	18 ± 9	−2.9
$Cu(C_2O_4){\cdot}0.8H_2O$	~300	2	58 ± 2	−2.8
CuCl		4	83 ± 7	2.6
CuBr		2	90 ± 2	2.1
CuI		4	87 ± 3	1.4
$[CuCl(PPh_3)]_4$	248	2	75 ± 1	20.8
$[Cu(PPh_3)_4]PF_6$	242	2	47 ± 1	44.0
$[Cu(NCCH_3)_4]PF_6$	160	3	83 ± 7	0.3
$[Cu(NCPh)_4]PF_6$	165	2	78 ± 1	0.5
$[Cu(P(OCH_3)_3)_4]BF_4$	238	4	52 ± 1	1.6
$[CuCl(P(OPh)_3)]_4$	285	7	73 ± 3	−0.9
$[CuBr(P(OPh)_3)]_4$	251	2	65 ± 4	−1.0
$CuI(P(OPh)_3)_2$	167	2	58 ± 0	−1.2
$[CuCl(P(OPh)_2(O^iDec))]_4$	249	3	84 ± 4	2.7
$[CuBr(P(OPh)_2(O^iDec))]_4$	260	3	76 ± 8	3.4
$[CuCl(P(OPh)(O^iDec)_2)]_4$	239	2	74 ± 6	2.5
$[CuBr(P(OPh)(O^iDec)_2)]_4$	255	2	72 ± 3	1.5
$[CuCl(P(O^iDec)_3)]_4$	249	2	75 ± 3	0.6
$[CuBr(P(O^iDec)_3)]_4$	251	3	72 ± 5	3.3
Cu (99.999%)		2	81 ± 2	1.7
$P(OPh)_3$		3	26 ± 7	0.2
$P(OPh)_2(O^iDec)$		3	58 ± 2	0.4
$P(OPh)(O^iDec)_2$		3	50 ± 9	−0.1
$P(O^iDec)_3$		2	58 ± 5	4.0
PPh_3		2	44 ± 2	43.5

[a] Capillary melting point values, uncorrected. [b] Mean values from duplicate runs in most cases. Correction by subtraction of mass of the volatile portion of the additive (0−9.1%) from the raw datum. After correction, some mass loss values were negative, as shown.

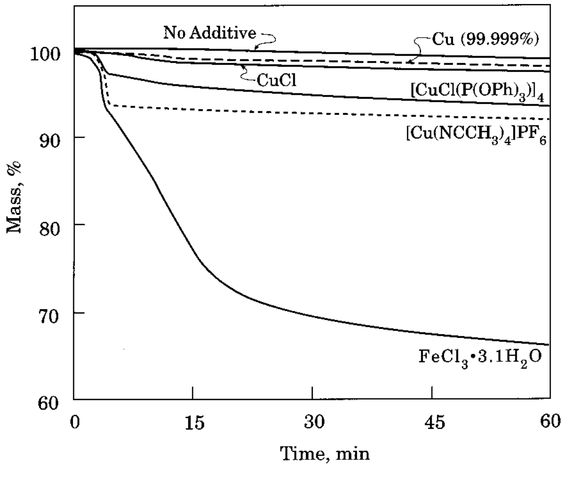


Figure 1. Isothermal thermogravimetric mass loss profiles for thermally degrading PVC/(metal additive) samples (during 1.0 h at 200 °C under N_2, 9.1% additive).

tion) during 1 h at 200 °C. This behavior was taken as evidence for the promotion of reductive cross-linking. Alternatively, PVC gelation coupled with significant dehydrochlorination was considered to be diagnostic of cross-linking induced by a Lewis acid.

The metal carbonyl complexes caused gelation at 200 °C. The TGA results at this temperature demonstrated that, among the carbonyls tested, only $Fe_2(CO)_9$ produced a significant decrease in mass. Although these compounds are not viable polymer additive candidates, their cross-linking activity provides strong support for the reductive coupling mechanism, since these complexes of zero-valent metals have minimal Lewis acidities.

Many of the transition and post-transition-metal(II) chlorides produced moderate amounts of gel under the test conditions. However, in these cases, very significant losses of polymer mass tended to accompany gel formation. The better metal chloride cross-linking agents usually caused the greatest amounts of dehydrochlorination, but the copper(II) halides were notable exceptions to this trend. Copper(II) is not a potent Lewis acid, and its reduction to Cu(I) and even Cu(0) is favored thermodynamically, especially at low oxygen partial pressures (see above).[18] Hence, even with copper(II) additives, the experimental evidence strongly suggests the occurrence of reductive coupling.

The simple formate and oxalate salts of Cu(II), Ni(II), Co(II), and Fe(II) (except for $Co(O_2CH)_2$) were evaluated for possible reductive coupling activity. Unlike the Lewis acidic metal chlorides, these oxalates and formates were expected to require significant amounts of additive decomposition in order to function as cross-linking agents, since here the requisite low-valent metal would be generated by the thermal reductive elimination of ligands, as in reactions 5 and 6. As is indicated in Table 5, several of these compounds ($Cu(C_2O_4)$, $Ni(C_2O_4)$, $Co(C_2O_4)$, and $Ni(O_2CH)_2$) decompose at ≥250 °C. Those additives produced relatively low degrees of cross-linking at 200 °C. Nevertheless, the value of 58% for $Cu(C_2O_4)$ (~300 °C (dec)) again points to cross-linking activity for copper(II) salts that is surprisingly high. The oxalates and formates having decomposition temperatures in the range of 200−230 °C were generally the more effective cross-linking agents, and of the oxalates and formates tested, only $Fe(C_2O_4)$ caused a significant loss of polymer mass.

Copper(I) complexes may prove to be the most attractive group of coupling agents considered here. They lack undesirable color, and the thermal stability of their copper(I) center may be adjusted through the judicious selection of ligands. We examined the use of halide, phosphine, phosphite, and nitrile ligands. The simple Cu(I) halides, CuCl, CuBr, and CuI, gave excellent PVC gel yields with very low polymer mass losses at 200 °C. Such was also the case for the acetonitrile and benzonitrile solvent-supported complexes of $CuPF_6$.

Organophosphites are used routinely as stabilizers for PVC and other polymers.[6c,25] Hence, their incorporation into smoke-suppressant Cu(I) complexes appeared to be a natural extension of current additive technology. The following P(III) compounds were chosen for current study: PPh_3, $P(OCH_3)_3$, $P(OPh)_3$, $P(O^iDec)_3$, $P(OPh)(O^iDec)_2$, and $P(OPh)_2(O^iDec)$ (^iDec = 8-methylnonyl). The free phosphine and phosphite ligands were tested in the absence of copper for promotion of PVC gelation and mass loss. Results obtained by TGA indicated that triphenylphosphine was sufficiently basic to catalyze the dehydrochlorination of the polymer, resulting in a serious loss of mass. However, the mass losses caused by most of the phosphites were negligible, perhaps because these substance reacted irreversibly with HCl to form nonvolatile products. The free phosphites promoted low to moderately high gel yields at 200 °C.

The phosphine and phosphite complexes of Cu(I) were readily prepared in organic solvents of low polarity. All of the phosphite complexes were good to excellent PVC gel formers at 200 °C. However, as anticipated from the tests with the free ligand, the PPh_3 complexes caused unacceptable polymer mass losses, as determined by TGA. The phosphite complexes of CuCl and CuBr are considered to be especially promising as reductive coupling agents because of their ability to cause relatively high degrees of gelation with minimal losses of mass.

Solid state structures of tetrahedral[26] $[Cu(PPh_3)_4]^+$ and "cubane" tetramer[27] $[CuCl(PPh_3)]_4$ were determined previously by single crystal X-ray diffraction. Our cuprous complexes of $P(OPh)_3$ were highly crystalline, but the new isodecyl phosphite complexes remained as oils, despite efforts to induce their crystallization. X-ray structure studies[28] of $[CuCl(P(OPh)_3)]_4$ crystals grown from different solvent combinations revealed two isomorphic structures, both of which featured a Cu_4Cl_4 cubane core analogous to that of $[CuCl(PPh_3)]_4$.[27]

Gelation−Time Profiles. Gelation of PVC in the presence of a number of additives was studied further as a function of thermal degradation time. Solid PVC samples containing additives, as well as a control, were pyrolyzed for varying lengths of time at 200 °C. The samples then were quenched thermally, and polymer gelation was measured. The resulting data are plotted in Figures 2 and 3. Although the control sample gelled only slowly, the high-purity copper powder and all of the copper-based additives produced rapid and extensive gelation. Gelation due to the organophosphites alone or to the Lewis acidic iron chlorides was neither as rapid nor as copious as that induced by low-valent copper.

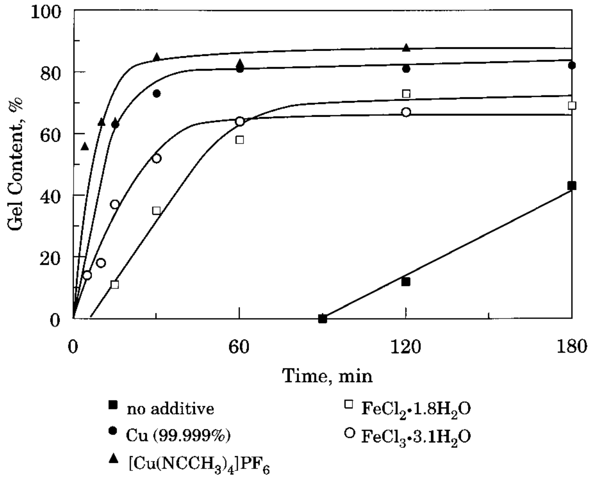


Figure 2. Gelation profiles of thermally degrading PVC/(metal additive) samples (at 200 °C under argon, 9.1% additive).

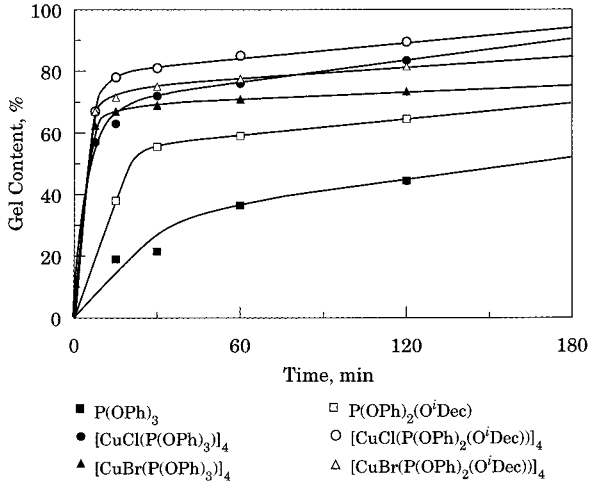


Figure 3. Gelation profiles of thermally degrading PVC/(metal additive) samples (at 200 °C under argon, 9.1% additive).

Evolution of Volatile Acid. Figure 4 shows the volatile acid evolution from PVC and PVC−(metal additive) samples during thermal degradation at 200 °C. Reductive coupling is expected to limit HCl evolution from pyrolyzing PVC, because the inserted cross-links will block dehydrochlorination (*vide supra*). On the other hand, Lewis acid additives are known to promote dehydrochlorination.[1c,d,2] Hence, it was significant mechanistically to find that the copper additives either reduced or increased only slightly the rate of dehydrochlorination, as compared to that of the additive-free control, while at the same time strongly promoting gelation (see Table 5 and Figures 2 and 3). The production rate of acidic vapors was somewhat higher for $[CuBr(P(OPh)_3)]_4$ than for CuBr. Thus, HCl vapor generation apparently was enhanced slightly by this additive. The [copper(II) formate]/PVC mixture produced an initial burst of acidic vapor which probably can be attributed to formic acid and/or CO_2 resulting from metal formate decomposition. Thereafter, the acid evolution rate was comparable to that of the control.

Table 6. Thermogravimetric Decomposition Results for Copper Complexes

complex	temp, °C	product	wt % (theory)	wt % (actual)
$[CuCl(P(OPh)_3)]_4$	225−305	CuCl	28	27
	370−500	Cu	17	15
$[CuBr(P(OPh)_3)]_4$	230−310	CuBr	32	32
	450−570	Cu	14	14
$[CuCl(P(OPh)_2(O^iDec))]_4$	160−350	CuCl	20	22
$[CuCl(P(OPh)(O^iDec)_2)]_4$	160−330	CuCl + ?	17	22
$[CuCl(P(O^iDec)_3)]_4$	205−275	CuCl + ?	15	23
$CuI(P(OPh)_3)_2$	195−265	CuI	24	24
	490−665	(sublimation)	0	2
$[Cu(NCCH_3)_4]PF_6$	90−215	$[Cu(NCCH_3)_2]PF_6$	78	78
	215−280	$CuPF_6$	56	56
	280−340	CuF	22	22
$[Cu(NCPh)_4]PF_6$	90−310	$CuPF_6$	34	32
$Cu(O_2CH)_2$	190−230	Cu	41	45

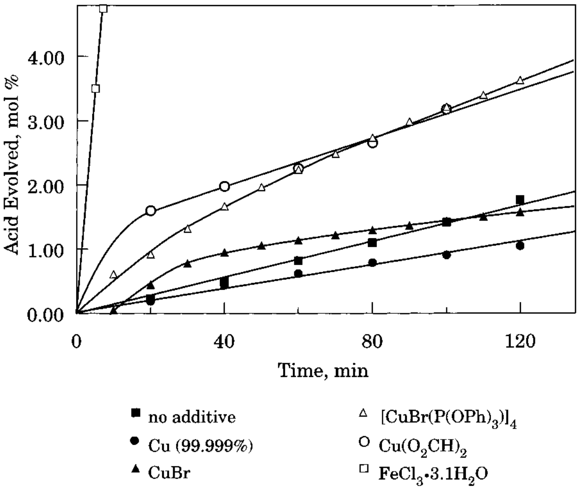


Figure 4. Volatile acid evolution from thermally degrading PVC/(metal additive) samples (at 200 °C under argon, 9.1% additive).

The iron(III) chloride additive caused a highly elevated rate of acid evolution that indicated very strong promotion of the dehydrochlorination.

Infrared Spectra. Additional support for the reductive coupling mechanism of PVC gelation was obtained by infrared spectroscopy. Portions of several PVC IR absorption spectra are shown in Figure 5. Nonpyrolyzed (virgin) PVC showed no appreciable absorption in the region of 1600 cm^{-1}, indicating a very low concentration of C═C groups. An additive-free control sample which had been thermolyzed for 1 h at 200 °C showed only a trace of unsaturation in this spectral region. This result is consistent with the negligible amount of HCl loss from additive-free PVC at 200 °C that was indicated by TGA. The spectra of thermolysis residues from PVC blended with $[CuBr(P(OPh)_3)]_4$, $[Cu(NCCH_3)_4]PF_6$, Cu, $FeCl_3{\cdot}3.1H_2O$, and $FeCl_2{\cdot}1.8H_2O$ also are shown in Figure 5. Although each of these substances was a relatively effective gelation agent (see Table 5), the copper additives gave much less evidence of C═C in the polymer residue. Since reductive coupling is expected to halt dehydrochlorination, for the reasons discussed above, the IR results provide further strong support for the operation of this mechanism with low-valent copper additives.

TGA of Copper Additives. The decomposition behavior of several copper-based additives was studied by TGA under N_2. Although gravimetric analysis could not provide direct evidence for Cu(I) disproportionation, the results in Table 6 and Figure 6 revealed some interesting thermal behavior. The $P(OPh)_3$ complexes of CuCl and CuBr showed two distinct mass losses. The first occurred around 200−300 °C and corresponded to loss of the phosphite ligands. A second mass loss in the region of 350−600 °C corresponded to the reductive elimination of Cl_2 or Br_2. On the other hand, the CuCl complexes of alkyl-bearing phosphites showed only a single mass loss which left a residue having a somewhat higher mass than that of CuCl alone. Interestingly, the decomposition of $[Cu(NCCH_3)_4]PF_6$ caused the loss of acetonitrile (in two steps) followed by the loss of PF_5 to

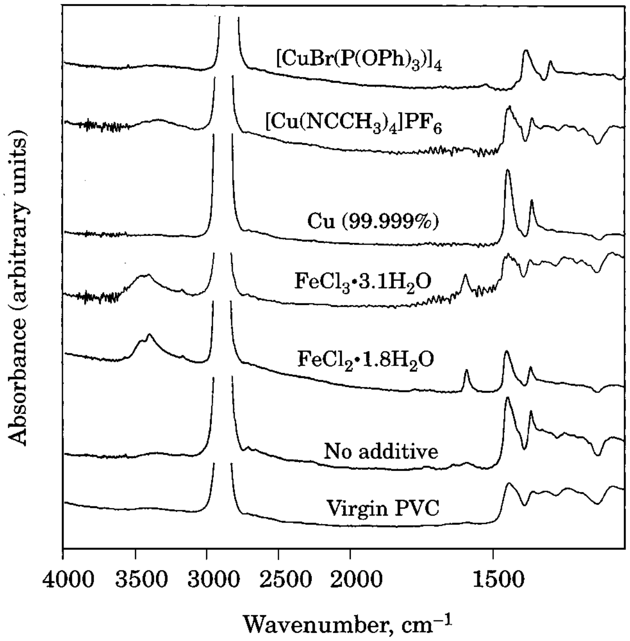


Figure 5. Infrared spectra of thermally degraded PVC/(metal additive) samples (after 1.0 h at 200 °C under argon, 9.1% additive).

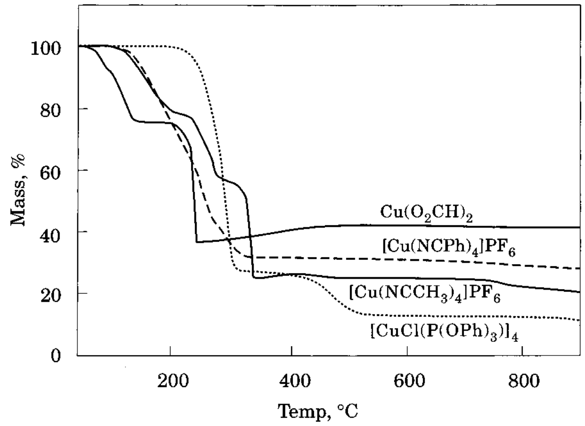


Figure 6. Thermogravimetric mass loss profiles of copper compounds (under N_2).

give a mass corresponding to that of CuF. In contrast, $[Cu(NCPh)_4]PF_6$ did not expel PF_5. It is evident from these studies that many complexes of CuX (X = halide) are indeed able to generate Cu(0) under low-oxygen pyrolysis conditions. Moreover, it is likely that Cu(0) is formed by disproportionation even at lower temperatures.

Conclusions

Zero- and low-valent transition metals and transition-metal complexes have been shown to cause the reductive coupling of small allylic halides. Likewise, sources of low-valent metal have produced extensive gelation of PVC at 200 °C in the solid state and at even lower temperatures in solution. Unlike the behavior observed for Lewis acidic metal chloride additives, the cross-linking caused by low-valent metal compounds is characterized by exceedingly rapid onset, minimal polymer mass loss and acidic vapor generation, and little evidence of C═C formation. These observations point to a mechanism for PVC cross-linking that does not entail acid catalysis but is very likely to involve reductive coupling. Coupling at allylic sites accounts for the available facts, but nonallylic coupling might be occurring as well.

For technological viability, smoke suppressants for PVC must not cause extensive cross-linking at the temperatures and times that are used to process the polymer. Reductive coupling agents that are able to meet this requirement could eventually become attractive for use in commercial PVC products.

Acknowledgment. We are indebted to the GenCorp Foundation and the International Copper Association for partial support of this research. We also thank the Dover Chemical Corp. for supplying the organophosphites.

References and Notes

(1) (a) Starnes, W. H., Jr.; Girois, S. *Polym. Yearbook* **1995**, *12*, 105. (b) Starnes, W. H., Jr.; Wallach, J. A.; Yao, H. *Macromolecules* **1996**, *29*, 7631. Correction: *Macromolecules* **1997**, *30*, 676. (c) Iván, B.; Kelen, T.; Tüdös, F. In *Degradation and Stabilization of Polymers*; Jellinek, H. H. G., Kachi, H., Eds.; Elsevier: New York, 1989; Vol. 2, Chapter 8. (d) Hjertberg, T.; Sörvik, E. M. In *Degradation and Stabilisation of PVC*; Owen, E. D., Ed.; Elsevier: New York, 1984; Chapter 2.

(2) Starnes, W. H., Jr.; Edelson, D. *Macromolecules* **1979**, *12*, 797.

(3) Lattimer, R. P.; Kroenke, W. J. *J. Appl. Polym. Sci.* **1980**, *25*, 101.

(4) Camino, G.; Costa, L.; Luda di Cortemiglia, M. P. *Polym. Degrad. Stab.* **1991**, *33*, 131.

(5) Lattimer, R. P.; Kroenke, W. J. *J. Appl. Polym. Sci.* **1981**, *26*, 1191.

(6) (a) Bert, M.; Michel, A.; Guyot, A. *Fire Res. (Lausanne)* **1977/78**, *1*, 301. (b) Kroenke, W. J. *J. Appl. Polym. Sci.* **1981**, *26*, 1167. (c) Troitzsch, H. J. In *Plastics Additives Handbook*, 4th ed.; Gächter, R., Müller, H., Eds.; Hanser/Gardner: Cincinnati, OH, 1993; Chapter 12.

(7) Lattimer, R. P.; Kroenke, W. J.; Getts, R. G. *J. Appl. Polym. Sci.* **1984**, *29*, 3783.

(8) (a) Starnes, W. H., Jr.; Wescott, L. D., Jr.; Reents, W. D., Jr.; Cais, R. E.; Villacorta, G. M.; Plitz, I. M.; Anthony, L. J. In *Polymer Additives*; Kresta, J. E., Ed.; Plenum: New York, 1984; p 237. (b) Starnes, W. H., Jr.; Wescott, L. D., Jr.; Reents, W. D., Jr.; Cais, R. E.; Villacorta, G. M.; Plitz, I. M.; Anthony, L. J. *Org. Coat. Appl. Polym. Sci. Proc.* **1982**, *46*, 556.

(9) Wescott, L. D., Jr.; Starnes, W. H., Jr.; Mujsce, A. M.; Linxwiler, P. A. *J. Anal. Appl. Pyrol.* **1985**, *8*, 163.

(10) Edelson, D.; Kuck, V. J.; Lum, R. M.; Scalco, E.; Starnes, W. H., Jr.; Kaufman, S. *Combust. Flame* **1980**, *38*, 271.

(11) (a) Corey, E. J.; Semmelhack, M. F. *J. Am. Chem. Soc.* **1967**, *89*, 2755. (b) Kawaki, T.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3130. (c) Nakanishi, S.; Oda, T.; Ueda, T.; Otsuji, Y. *Chem. Lett.* **1978**, 1309. (d) Yamada, Y.; Momose, D. *Chem. Lett.* **1981**, 1277. (e) For a detailed mechanistic discussion, see: Hegedus, L. S.; Thompson, D. H. P. *J. Am. Chem. Soc.* **1985**, *107*, 5663.

(12) (a) Chao, C. S.; Cheng, C. H.; Chang, C. T. *J. Org. Chem.* **1983**, *48*, 4904. (b) Ebert, G. W.; Rieke, R. D. *J. Org. Chem.* **1988**, *53*, 4482. (c) Ginah, F. O.; Donovan, T. A., Jr.; Suchan, S. D.; Pfennig, G. R.; Ebert, G. W. *J. Org. Chem.* **1990**, *55*, 584. (d) Yanagisawa, A.; Hibino, H.; Habaue, S.; Hisada, Y.; Yamamoto, H. *J. Org. Chem.* **1992**, *57*, 6386.

(13) (a) Carty, P.; Metcalfe, E.; White, S. *Polymer* **1992**, *33*, 2704. (b) Carty, P.; White, S. *Polymer* **1995**, *36*, 1109. (c) Lum, R. M.; Seibles, L.; Edelson, D.; Starnes, W. H., Jr. *Org. Coat. Plast. Chem.* **1980**, *43*, 176.

(14) (a) Ballistreri, A.; Foti, F.; Maravigna, P.; Montaudo, G.; Scamporrino, E. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3101. (b) Ballistreri, A.; Montaudo, G.; Puglisi, C.; Scamporrino, E.; Vitalini, D. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1397. (c) Matsusaka, K.; Sugimoto, Y.; Murakami, I. *Polym. Commun.* **1985**, *26*, 371.

(15) Tu, H.; Wang, J. *Polym. Degrad. Stab.* **1996**, *54*, 195.

(16) (a) Starnes, W. H., Jr.; Huang, C.-H. O. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (1), 527. In this paper, the data for Cu_2O and CuO should be interchanged. (b) Huang, C.-H. O.; Starnes, W. H., Jr. In *Proceedings, 2nd Beijing International Symposium on Flame Retardants*; Yuxiang, O., Ed.; Geological Publishing House: Beijing, 1993; p 168.

(17) (a) Jeng, J. P.; Terranova, S. A.; Bonaplata, E.; Goldsmith, K.; Williams, D. M.; Wojciechowski, B. J.; Starnes, W. H., Jr. *ACS Symp. Ser.* **1995**, *No. 599*, 118. (b) Starnes, W. H., Jr.; Jeng, J. P.; Terranova, S. A.; Bonaplata, E.; Goldsmith, K.; Williams, D. M.; Wojciechowski, B. J. In *Proceedings, 5th Annual BCC Conference on Flame Retardancy*; Business Communications Co.: Norwalk, CT, 1994; Chapter 2. (c) Starnes, W. H., Jr.; Pike, R. D.; Bryant, W. S.; Jeng, J. P.; Kourtesis, P. In *Proceedings, Additives '95 Conference*; Executive Conference Management: Plymouth, MI, 1995; Chapter 17. (d) Pike, R. D.; Starnes, W. H., Jr.; Bryant, W. S.; Jeng, J. P.; Kourtesis, P. In *Proceedings, 6th Annual BCC Conference on Flame Retardancy*; Business Communications Co.: Norwalk, CT, 1995; Chapter 11. (e) Starnes, W. H., Jr.; Pike, R. D.; Bryant, W. S.; Kourtesis, P.; Macko, J. A.; O'Brien, C. P. In *Proceedings, Additives '96 Conference*; Executive Conference Management: Plymouth, MI, 1996; Chapter 7. (f) Starnes, W. H., Jr.; Pike, R. D.; Bunge, S.; Kang, Y.; Kim, A.; Macko, J. A.; O'Brien, C. P. In *Proceedings, Additives '97 Conference*; Executive Conference Management: Plymouth, MI, 1997; Chapter 20. (g) Pike, R. D.; Starnes, W. H., Jr.; Adams, C. W.; Bunge, S. D.; Kang, Y. M.; Kim, A. S.; Kim, J. H.; Macko, J. A.; O'Brien, C. P. In *Proceedings, 8th Annual BCC Conference on Flame Retardancy*; Business Communications Co.: Norwalk, CT, 1997; in press.

(18) Shriver, D. F.; Atkins, P.; Langford, C. H. *Inorganic Chemistry*, 2nd ed.; Freeman: New York, 1994, pp B4ff. The $\Delta G°$ values in this reference are useful for comparison purposes, although they are uncorrected for ligand type, concentration, and temperature.

(19) (a) Nishizawa, Y. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1170. (b) Cotton, F. A.; Goodgame, D. M. L. *J. Chem. Soc.* **1960**, 5267. (c) Costa, G.; Reisenhofer, E.; Stefani, L. *J. Inorg. Nucl. Chem.* **1965**, *27*, 2581. (d) Jardine, F. H.; Rule, L.; Vohra, A. G. *J. Chem. Soc. A* **1970**, 238.

(20) Kubas, G. J. *Inorg. Synth.* **1990**, *28*, 68.

(21) Rhoda, R. N.; Fraioli, A. V. *Inorg. Synth.* **1953**, *4*, 159.

(22) Körösy, F. *Nature* **1947**, *160*, 21.

(23) (a) Dollimore, D.; Griffiths, D. L. *J. Therm. Anal.* **1970**, *2*, 229. (b) Mu, J.; Perlmutter, D. D. *Thermochim. Acta* **1981**, *49*, 207. (c) Górski, A.; Kraśnicka, A. *J. Therm. Anal.* **1987**, *32*, 1243. (d) Gallagher, P. K. *Thermochim. Acta* **1993**, *214*, 1.

(24) (a) Boettner, E. A.; Ball, G.; Weiss, B. *J. Appl. Polym. Sci.* **1969**, *13*, 377. (b) Ballistreri, A.; Foti, S.; Montaudo, G.; Scamporrino, E. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1147.

(25) Gugumus, F. In *Plastics Additives Handbook*, 4th ed.; Gächter, R., Müller, H., Eds.; Hanser/Gardner: Cincinnati, OH, 1993; Chapter 1.

(26) Engelhardt, L. M.; Pakawatchai, C.; White, A. H.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1985**, 125.

(27) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1065.

(28) Carpenter, G. B.; Pike, R. D.; Starnes, W. H., Jr. Unpublished results.

MA9707749