Effects of Copper and Molybdenum Oxides on the Pyrolysis of Model Compounds of Poly(vinyl Chloride)

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Synopsis

Numerous transition metal compounds can be added to poly(vinyl chloride) to decrease the smoke evolved during burning or smoldering conditions. Model compound pyrolysis experiments have been carried out to investigate the mechanisms by which smoke retarder additives function in PVC. Three models were used: 3-chloropentane, 2,4-dichloropentane, and 2,4,6-trichloroheptane. The additives MoO_3 and Cu_2O both enhanced the rate of dehydrochlorination and promoted the formation of crosslinked products (oligomers) during model compound pyrolysis, but their mechanistic pathways were found to be different. The choice of model compound also was an important influence in determining the observed decomposition pathways. While much of the pyrolysis chemistry can be explained by Lewis acid catalysis, other effects also appear to be important. The pyrolysis results are interpreted in terms of an "early crosslinking" mechanism of smoke retardation in PVC. In this mechanism the metal smoke retarder works primarily by catalytically promoting early crosslinking of decomposing PVC chains to yield char as a residue.

INTRODUCTION

Poly(vinyl chloride) (PVC) is inherently fire-retardant. When it is forced to burn, however, PVC behaves like most organic materials and evolves smoke. The combustion of benzene and other aromatic pyrolyzates is known to be an important source of this smoke. Active smoke retarders may be added to PVC to decrease the smoke evolved during burning or smoldering conditions. A large number of chemical compounds have been reported as smoke retarders for PVC, but in general the most effective additives are compounds of transition metals.[1] The more active smoke retarders change the thermal degradation pattern of the PVC and promote the formation of char.[1-3]

Several reports relating to the mechanisms by which smoke retarders function in PVC have appeared in the literature. In 1974, Iida, Nakanishi, and Gotō showed that SnO_2 and ZnO promoted the formation of aliphatics rather than benzene and other aromatics.[4] Smoke was not mentioned in this paper, however, and the first real mechanistic studies were conducted with ferrocene.[5,6] Lawson found that ferrocene promoted early dehydrochlorination and crosslinking in PVC, but no clear correlation between char formation and smoke reduction was found.[5] Lecomte et al. also studied ferrocene in PVC and found a linear correlation between benzene evolution and smoke generation, but again there was no clear correlation between smoke and char levels.[6]

In a followup study, Bert, Michel, and Guyot investigated a number of metal salts as smoke retarders in PVC.[7] These authors found a general correlation between benzene and smoke formation, but concluded that the linear relationship reported for ferrocene was not a universal phenomenon. They also concluded that "oxidation catalysis" was an important mechanism for smoke reduction which explains the afterglow or incandescence effect that is often observed in testing smoke-retarded PVC, particularly when larger quantities of material are burned.[7] The same workers in recent papers have expanded their oxidation catalysis arguments.[8-10] However, we believe experiments that do not give good correlations between char yield and smoke reduction usually can be explained by catalytic oxidation of the char to CO and CO_2. While Guyot, Michel, and co-workers believe that catalytic oxidation is an integral part of effective smoke retardation, other work, including our own, suggests that it is more likely a secondary effect.

Recent work at Bell Laboratories has concentrated on the functional role of molybdenum trioxide (MoO_3) as a smoke retarder in PVC.[11-14] The first Bell report contrasted Sb_2O_3 and MoO_3 as flame and smoke retarders for plasticized PVC.[11] It was concluded that while Sb_2O_3 works mainly through volatile chloride species in the vapor phase, MoO_3 works through condensed phase mechanisms. "Lewis acid" catalysis was proposed as an explanation for the smoke retarder action.[12-14] It was theorized that during dehydrochlorination, MoO_3 acts as a Lewis acid isomerization catalyst to favor the formation of trans alkene segments. These trans alkenes, which cannot undergo intramolecular cyclization to form aromatic hydrocarbons, are stable to higher temperatures where different mechanisms ensue to give aliphatic (less smoky) products.[12,13]

Another possible smoke retarder explanation that was proposed in subsequent Bell reports was the crosslinking of decomposing polymer chains, as by Diels–Alder cyclizations or Friedel–Crafts (Lewis acid) alkylations.[12,13] This crosslinking would promote the formation of nonvolatile residues (char) in the decomposing polymer. Unfortunately, the crosslinking possibility was not emphasized in these early reports,[12,13] because no clear correlations between smoke reduction and char formation had yet appeared in the literature. It has been our experience, however, that effective smoke retarders for PVC are always effective char formers as well.[1-3] Often workers also have come to recognize the strong correlation between smoke reduction and increased char yield.[15,16] In fact, early crosslinking in thermally decomposing PVC containing metal additives has been recently verified experimentally.[17] It is now clear that in cases where poor correlations of smoke vs. char were reported, the char had been oxidized by metal residues to CO and CO_2 as a direct consequence of the experimental combustion conditions and/or PVC composition.

It has been our contention that "early crosslinking" of the decomposing polymer chains is the *principal* mechanism by which effective metal-based smoke retarders work in PVC.[1-3] This early crosslinking produces these generally observed effects: (1) smoke formation is reduced; (2) volatile aromatic pyrolyzate formation is reduced; (3) volatile aliphatic pyrolyzate production is increased; and (4) char formation is promoted. These effects have been observed for numerous metal additives, including compounds of

molybdenum, copper, iron, nickel, and bismuth.[1-3] Lewis acid effects are certainly important in promoting crosslinking for many, if not all, metal-based additives. In fact, recent model compound experiments by Starnes et al. yielded products that were consistent with Lewis-acid-catalyzed dehydrochlorination and crosslink formation.[14] There still does not seem to be a clear correlation between Lewis acidity and smoke retarder effectiveness, however,[1-3] so that other mechanisms are also possible. For example, we have proposed reductive coupling as one alternative pathway.[2]

A recent trend in research in this area has been the pyrolysis of model compounds to help distinguish among the various proposed smoke retarder mechanisms. In a preliminary report, Starnes et al. pyrolyzed several small chlorine-containing hydrocarbons in the presence of various molybdenum compounds.[14] The main conclusions reached were that (1) no evidence to support reductive coupling reactions was found, (2) Lewis acid catalysis provided the major (if not the only) reaction pathways, and (3) Lewis acid processes such as oligomerization and haloalkylation can lead to crosslinking of thermally decomposing PVC chains.

In examining the Starnes et al. report,[14] we developed two principal reservations to their work. First, the choice of model compounds was limited. Starnes et al. chose one alkene, two alkanes containing a single secondary chlorine atom, and two alkenes containing an allylic chloride structure. None of these compounds is able to "unzip" to form a polyene chain that can cyclize intramolecularly as does PVC.[12,18] Second, most of the reactions reported were carried out between 100°C and 200°C.[14] These may not be reasonable thermal degradation temperatures for modeling the combustion of smoke-retarded PVC.

In an extension of the work reported by Starnes et al.,[14] we have carried out pyrolysis studies with three model compounds—3-chloropentane, 2,4-dichloropentane, and 2,4,6-trichloroheptane. Closed tube pyrolysis experiments were carried out with two common smoke retarder additives, molybdenum trioxide and copper(I) oxide. Overall, the roles of the molybdenum and copper additives showed some similarities, but distinct differences were also apparent. The choice of model compound was also important in effecting various decomposition pathways. Based on results from these experiments, we summarize our current understanding of the role of metal-based smoke retarders in PVC.

EXPERIMENTAL

Model Compounds and Additives

The 3-chloropentane (3-CP) was obtained from Alfa Products and used as received. Gas chromatography–mass spectrometry (GC–MS) analysis showed mostly 3-chloropentane, a few percent 2-chloropentane, and a trace of 2-pentene, the dehydrochlorination product.

The 2,4-dichloropentane (24-DCP) was synthesized in two steps. First, 2,4-pentanedione was reduced with sodium borohydride to 2,4-pentanediol. Second, the diol was reacted with phosphorus trichloride to yield 24-DCP. GC analysis revealed ~60% meso and ~40% racemic forms.

The synthesis of 2,4,6-trichloroheptane (246-TCH) has been previously reported.[19-21] A four-step procedure was used. The first step involved the acidic rearrangement of 3-acetyl-6-methyl-2,4-pyrandione (dehydroacetic acid) to yield 2,6-dimethyl-4-pyrone. The method was that of King et al.,[22] which is a modification of the method of Arndt et al.[23] In the second step, the pyrone was ring opened with barium hydroxide to yield 2,4,6-heptanetrione. The third step involved the hydrogenation of the trione over a ruthenium catalyst to give 2,4,6-heptanetriol. The final step was reaction with thionyl chloride to yield 246-TCH. The final product was distilled twice. GC–MS analysis revealed no appreciable impurities.

Metal oxide additives included molybdenum trioxide (MoO_3) and copper(I) oxide (Cu_2O). Both were obtained from the Fisher Scientific Co. (Certified Reagent grade) and used as received.

Pyrolysis Procedures

Standard borosilicate glass melting point capillary tubes (Fisher Scientific Co.) were used. The tubes were loaded with ∼5.0 μL of the appropriate model compound using a 10-μL syringe. The tubes were purged with argon prior to sealing.

For experiments with the metal oxides, a different procedure was used. The capillaries were weighed and then filled completely with either MoO_3 or Cu_2O. When the oxide was removed, the walls of the tubes remained uniformly coated with the oxide. The upper half of the tubes was then cleaned with a small wooden cleaning stick. The tubes were then reweighed. Typically, ∼0.5 mg of oxide remained. The tubes were then loaded with the proper amount of liquid model compound and sealed as previously described.

Pyrolyses were conducted in a muffle furnace heated to the test temperature. A nickel boat was placed in the oven and heated until the equilibrium temperature was reached. The sealed tube was then dropped into the boat and heated for the appropriate length of time. Each tube was quenched to room temperature by removing the boat from the furnace and then removing the tube from the boat.

Initial pyrolysis experiments were conducted under the following conditions: 5 min at 300°C, 15 min at 300°C, 5 min at 350°C, and 5 min at 550°C. The most suitable conditions to assure decomposition of the chloroalkane and to minimize fragmentation of the primary pyrolyzates were either 15 min at 300°C or 5 min at 350°C. All of the data reported herein were obtained by pyrolyzing for 5 min at 350°C.

Analysis of Pyrolyzates

The cooled capillary tubes were scored with a file and broken just prior to analysis. About 20 μL dichloromethane was added directly to each tube as an extraction solvent. The solutions were analyzed by glass capillary gas chromatography [$(GC)^2$] and by $(GC)^2$-mass spectrometry. A Varian 3700/ CDS 111 GC with flame ionization detector was used for semiquantitative $(GC)^2$ analysis. The column was a 50-m SP2100 fused silica type, pro-

grammed from 50°C to 260°C at 4°C/min after a 2-min hold on injection. $(GC)^2$–MS was conducted with a Varian 3700/Finnigan MAT 311A/Finnigan Incos 2400 system. A 45-m SP2100 glass capillary column was used with the same temperature program described above. Pyrolyzates were identified by their 70 eV electron impact mass spectra.

Analysis of the most volatile pyrolyzates (C_1–C_7) was carried out by headspace-GC–MS. The scored, but unbroken, pyrolysis tubes were placed in standard 24 cm³ headspace vials (Perkin-Elmer Corp.) with an agate ball. The sealed headspace vial was then shaken gently until the agate ball broke the pyrolysis tube. The headspace was sampled with a gas-tight 10 mL syringe after equlibrating the vial at 90°C. GC–MS was conducted with a 2 m × 2 mm ID glass Poropak QS column, programmed from 50°C to 210°C at 8°C/min after a 2-min hold on injection.

RESULTS

Four types of pyrolysis experiments were run with each of the three model compounds:
1. Neat model compound (no additive).
2. Model compound plus 9 or 20 pph (parts per hundred) MoO_3.
3. Model compound plus 10 or 20 pph Cu_2O.
4. Model compound plus 10 pph MoO_3 and 10 pph Cu_2O.

The resulting pyrolyzate mixtures (pyrolysis at 350°C for 5 min) were generally quite complex, and only the general features will be reported here.

3-Chloropentane Experiments

Pyrolysis of 3-CP at 350°C yielded little reaction; only a trace of 2-pentene was observed in addition to the starting material. Cu_2O tended to accelerate the dehydrochlorination somewhat, producing at least three isomeric pentenes. Trace levels of dimeric products (decenes, $C_{10}H_{20}$) were also produced.

MoO_3, on the other hand, promoted the formation of numerous dimeric products. The most abundant dimers were of the composition $C_{10}H_{20}$ or $C_{10}H_{21}Cl$. These species are the types expected from Lewis acid oligomerization or chloroalkylation. Aromatic dimers of the composition $C_{10}H_{14}$ (C_4-benzenes) were also present, as were diene species ($C_{10}H_{18}$). Only a trace of saturated dimer ($C_{10}H_{22}$) was observed. Overall, then, the principal pyrolyzates can be explained by Lewis acid reactions (dehydrochlorination, oligomerization, chloroalkylation). Some aromatization and C—C bond scission products were observed, but these were relatively much less abundant than the other pyrolyzates.

The MoO_3/Cu_2O/3-CP pyrolysis products were very similar to the products formed by MoO_3 alone. This is not surprising, since Cu_2O by itself produced little reaction other than dehydrochlorination. The distributions of dimeric products for the metal-catalyzed pyrolyses of 3-CP are summarized in Table I.

TABLE I
Distributions of Dimeric Products for 3-Chloropentane Pyrolyses[a]

Formula	MW	Control	MoO_3	Cu_2O	MoO_3/Cu_2O
$C_{10}H_{14}$	134	nd[b]	15	nd	18
$C_{10}H_{18}$	138	nd	15	nd	15
$C_{10}H_{20}$	140	tr[c]	69	tr	67
$C_{10}H_{21}Cl$	176				
$C_{10}H_{22}$	142	nd	1	nd	tr

[a] Determined from FID–(GC)[2] peak intensities.
[b] nd = not detected.
[c] tr = trace.

2,4-Dichloropentane Experiments

Pyrolysis of 24-DCP yielded chloropentene (two principal isomers) and pentadiene (mostly the 1,3 isomer). Traces of dimeric products ($C_{10}H_{16}$) were also observed. The starting material was the largest component in the reaction mixture.

Cu_2O promoted dehydrochlorination and oligomerization. Major peaks were from pentadienes (C_5H_8), chloropentenes (C_5H_9Cl), and starting material ($C_5H_{10}Cl_2$). Dimers of three molecular formulas were observed, and they were all relatively abundant—$C_{10}H_{14}$ (C_4-benzenes), $C_{10}H_{16}$ (Lewis acid dimers), and $C_{10}H_{18}$ (coupling dimers?). Trimers of the composition $C_{15}H_{24}$ were also fairly abundant. Although MW204 ($C_{15}H_{24}$) is consistent with Lewis acid oligomerization, the mass spectra suggest that these trimers are aromatic (C_9-benzenes). Finally, there were traces of products arising from C—C bond cleavage (i.e., species with carbon numbers other than 5, 10, or 15). These apparently result from cationic cracking.

MoO_3 promoted numerous reactions—dehydrochlorination, aromatization, C—C bond cleavage, and chain segment saturation. Almost all of the higher mass products were aromatic hydrocarbons with saturated side groups. Only low molecular weight aliphatics were observed ($\leq C_8$), and these were mostly saturated. Alkyl-substituted benzenes covering every carbon number from C_7 to C_{15} were observed, with C_{10} (dimers) being the most abundant.

The $MoO_3/Cu_2O/24$-DCP pyrolysis products showed the influence of both molybdenum and copper, but molybdenum was dominant. Both aromatic and aliphatic oligomers were produced, but the aromatics were considerably more abundant. The distributions of dimeric products for the 24-DCP pyrolyses are summarized in Table II.

2,4,6-Trichloroheptane Experiments

The largest component in the reaction mixture from pyrolysis of 246-TCH was the starting material. Dehydrochlorination products were also observed—dichloroheptanes, chloroheptadienes, heptatrienes, and toluene. Several dimers were also observed, most having the composition $C_{14}H_{20}$, but a few with the formula $C_{14}H_{22}$.

TABLE II
Distributions of Dimeric Products for 2,4-Dichloropentane Pyrolyses[a]

Formula	MW	Control[b]	MoO$_3$	Cu$_2$O	MoO$_3$/Cu$_2$O
C$_{10}$H$_{14}$	134	nd[c]	100	41	87
C$_{10}$H$_{16}$	136	tr[d]	nd	31	nd
C$_{10}$H$_{18}$	138	nd	nd	28	12
C$_{10}$H$_{20}$	140	nd	nd	nd	1

[a] Determined from FID–(GC)^2 peak intensities.
[b] Only traces of dimers were present in the control pyrolyzate.
[c] nd = not detected.
[d] tr = trace.

Cu$_2$O promoted extensive dehydrochlorination and dimerization. The dimers formed were mostly of the formula C$_{14}$H$_{20}$ (Lewis acid type), but dimers of the composition C$_{14}$H$_{22}$ were also observed. Aromatization and C—C bond cleavage products were very low in abundance.

MoO$_3$ promoted the formation of a wide variety of products, but no class of pyrolyzates tended to dominate. A number of low molecular weight aliphatics (C$_1$ to at least C$_{10}$) was produced. Most of these hydrocarbons were saturated and either straight chained or methyl branched. Several chloroalkanes (C$_1$–C$_7$) were also detected. Unsaturated dimers (C$_{14}$H$_{20}$ and C$_{14}$H$_{22}$) were fairly prominent. Alkyl-substituted benzenes (with C$_1$–C$_7$ saturated side groups) and naphthalenes (C$_3$–C$_6$ side groups) were also produced in fair abundance. From the mass spectra it was clear that methyl and ethyl side groups were abundant in most of the substituted aromatics. Still higher molecular weight aromatics were found by direct probe EI–MS analysis of the MoO$_3$/246-TCH pyrolyzate. These included alkyl-substituted anthracenes/benzopyrenes. (Molecular formulas for these polynuclear aromatics were confirmed by high resolution accurate mass measurements.) From this wide assortment of products, it is clear that molybdenum promoted several types of reactions: dehydrochlorination, aromatization, structural isomerization, C—C bond cleavage (due to cationic cracking and/or metathesis), and chain segment saturation.

The MoO$_3$/Cu$_2$O/246-TCH mixture showed a combination of effects, and, interestingly, copper products dominated. That is, aliphatic dimers were large, and aromatics were relatively low in abundance. The dimer distributions are given in Table III.

TABLE III
Distributions of Dimeric Products for 2,4,6-Trichloroheptane Pyrolyses[a]

Formula	MW	Control	MoO$_3$	Cu$_2$O	MoO$_3$/Cu$_2$O
C$_{14}$H$_{16}$[b]	184	nd[c]	62	nd	19
C$_{14}$H$_{18}$	186	nd	nd	1	nd
C$_{14}$H$_{20}$	188	95	23	83	67
C$_{14}$H$_{22}$	190	5	15	16	13

[a] Determined from FID–(GC)^2 peak intensities.
[b] C$_4$-substituted naphthalenes.
[c] nd = not detected.

DISCUSSION

The series of model compound experiments can be discussed from a number of viewpoints. We will consider three: (1) Lewis acid versus reductive coupling, (2) molybdenum vs. copper, and (3) model compound effects.

Lewis Acid vs. Reductive Coupling Mechanisms

A principal purpose of model compound experiments reported by Starnes et al.[14] was to test Lewis acid[12,13] vs. reductive coupling[2] mechanisms for chloroalkane oligomerization (crosslinking). In principle, appropriate model compound experiments should be able to distinguish the two mechanisms in a straightforward manner. For example, the pyrolysis of 3-chloropentane (3-CP) is illustrated in Scheme I:
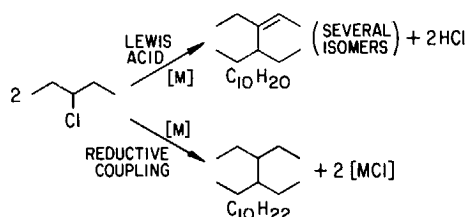
Lewis acid effects would produce dimeric species with the formula $C_{10}H_{20}$, while coupling would produce $C_{10}H_{22}$. Starnes et al.[14] found no oligomers with molecular weights expected for coupling products in any of their experiments. Both our studies and those of Starnes et al. included 3-CP as one of the model compounds. From Table I it is clear that only a trace of the "coupling" product ($C_{10}H_{22}$) was formed from 3-CP in our experiments; this is consistent with Starnes et al.[14]

For 2,4-dichloropentane (24-DCP, Table II) Lewis acid dimers are $C_{10}H_{16}$ and coupling dimers are $C_{10}H_{18}$. Products of the formula $C_{10}H_{18}$ were observed with Cu_2O, but not with MoO_3. Starnes et al. did not use 24-DCP, but they did conduct experiments with 4-chloro-2-pentene, a dehydrochlorination product of 24-DCP. No coupling products were observed in pyrolyses of 4-chloro-2-pentene with added MoO_3 or MoO_2Cl_2.[14] This is consistent with our findings for MoO_3 (Table II).

For 2,4,6-trichloroheptane (246-TCH, Table III) products with the coupling composition ($C_{14}H_{22}$) were observed for both MoO_3 and Cu_2O additives. Starnes et al.[14] did not use this model compound.

The presence of dimers at the molecular weights expected for coupling products (Tables II and III) provides evidence that some reductive coupling may have occurred for both molybdenum and copper catalysts. It is recognized, however, that normal (Lewis acid) dimers were more abundant (generally considerably more abundant) in every case for which a comparison can be made. Thus coupling reactions only can be relatively minor contributors to the overall crosslinking chemistry.

Finally, it should be pointed out that the presence of dimers with the correct molecular weights for coupling products does not prove that coupling

reactions have actually taken place. Other mechanisms could be responsible for hydrogen addition to dimers. For example, when aromatization occurs during pyrolysis, extra hydrogen becomes available to the system. This hydrogen may be added to olefinic segments of the pyrolyzate.

Molybdenum vs. Copper

Although both molybdenum and copper oxides promoted dehydrochlorination and oligomerization in our model compound experiments, the mechanistic pathways were significantly different. Cu_2O generally promoted simple oligomerization reactions, forming dimers that are explainable by Lewis acid processes. With MoO_3, however, additional pathways were present—aromatization, C—C bond cleavage, and chain segment saturation. In pyrolyses with both MoO_3 and Cu_2O present, molybdenum-catalyzed products were dominant for 3-CP and 24-DCP, while copper-catalyzed products were more prominent for 246-TCH.

The MoO_3–Cu_2O combination is known to be weakly synergistic in terms of smoke retardation in PVC.[1] Two possible explanations for synergistic effects were proposed in earlier studies.[2] One is that the molybdenum and copper *interact* (as a redox couple) to give a more effective redox catalyst system for promoting crosslinking. The second theory is that the molybdenum and copper each promote *different types* of crosslinking reactions, so that the overall effect of the combination is synergistic. Our model compound experiments indicate that at least the latter explanation may be operative. On the other hand, we have no clear evidence either for or against the first possibility (redox interaction). The presence of a *strong* Mo–Cu interaction seems to be excluded, since we did not observe different products in the mixed MoO_3–Cu_2O pyrolyses than were observed with the two additives alone. Also, in earlier work,[3] the ultimate fates of the molybdenum and copper oxides during combustion of PVC did not change when the two oxides were combined. No mixed Mo–Cu compounds were observed. It would be useful to investigate an Mo–Cu system that exhibits stronger synergism to see if an interactive redox effect can be observed.

Model Compound Effects

Our results show that the metal additives behave somewhat differently depending on the model compound chosen. We believe that 246-TCH is the best readily synthesized model for PVC, since it can "upzip" during pyrolysis to form a polyene chain with three alternating double bonds. This chain can then intramolecularly cyclize to form an aromatic ring.[12,18] None of the other model compounds used by us or Starnes et al.[14] can do this. The 246-TCH was unique among the models used in its ability to form condensed aromatic systems (naphthalenes, pyrenes, benzopyrenes, and others) with the MoO_3 catalyst. Thus 246-TCH can form aromatic structures both intra- and intermolecularly, while the other models cannot.

Our two-chlorine model (24-DCP) readily formed aromatic dimers (Table II) with *both* MoO_3 and Cu_2O. The intermediates could be Lewis acid or Diels–Alder in nature. Apparently after "normal" dimers ($C_{10}H_{16}$) are

formed, there is a strong driving force to lose two hydrogen atoms and produce aromatic (C_4-benzene) isomers.

In contrast to 24-DCP and 246-TCH, our one-chlorine model (3-CP) produced relatively little aromatic product. The C—C bond cleavage and chain segment saturation normally promoted by MoO_3 also was greatly reduced. Lewis acid dimerization was the dominant feature with MoO_3/3-CP, while Cu_2O produced only a small catalytic effect during pyrolysis. The lack of conjugated double bonds after dehydrochlorination apparently precluded much of the interesting chemistry observed for the two- and three-chlorine models.

SMOKE RETARDER MECHANISMS

Based on our studies and recent publications from other laboratories, the following overall summary seems valid. Transition metal-based smoke retarders work primarily by promoting crosslinking of decomposing PVC chains to yield char as a residue. This conclusion is consistent with the fact that good char formation–smoke reduction correlations have been reported for numerous systems.[1-3,15,16] Furthermore, benzene and other volatile aromatics, which can burn to form smoke, are formed almost exclusively from noncrosslinked segments of the decomposing PVC chains.[3,14,24] Thus the more effective a metal additive is at forming a crosslinked network, the better its smoke-retarding performance will be. This crosslinking must begin very *early* in the thermal decomposition process, since benzene evolution in PVC occurs nearly concurrently with dehydrochlorination.[25] Early crosslinking in decomposing PVC containing metal additives has been recently verified experimentally.[17]

The crosslinked network that leads to char is evidently composed of condensed aromatic structures that thus far have not been characterized in any detail. From our experiments with MoO_3 and 246-TCH, it appears that, as the condensed aromatic network forms, the remaining olefinic segments tend to become saturated. These saturated chain segments lead to the increased formation of volatile aliphatic pyrolyzates that is observed during pyrolysis of smoke-retarded PVC.[2,3] Volatile aromatic pyrolyzate formation is reduced, since crosslinking inhibits intramolecular cyclization reactions, which lead to isolated "benzenoid" structures.[18,26] Pure conjugated aromatics (such as benzene and naphthalene) are reduced more than aromatics with alkyl substituents (such as toluene and xylenes).[2,3] The formation of alkyl-substituted aromatics represents a balance between two factors, the availability of (1) isolated aromatic rings and (2) saturated side-chain segments. The former are less abundant with smoke retarder present, while the latter are more abundant.

It is now clear that various smoke retarders can crosslink the decomposing polymer by somewhat different mechanisms. Our model compound experiments show, for example, that MoO_3 and Cu_2O catalyze somewhat different reactions during chloroalkane pyrolysis. Lewis acid effects are certainly important for many, if not all, metal-based additives.[12-14] The most important Lewis acid effects appear to be enhanced dehydrochlorination and oligomerization (crosslinking). Other Lewis acid effects for which model

compound experiments provide evidence are cationic cracking, structural isomerism, and chloroalkylation. It has been proposed that Lewis acid *cis-trans* isomerism is a key factor in PVC smoke retardation,[12,13] but in our opinion this theory has not yet been conclusively verified experimentally. Some evidence has been presented to indicate that molybdenum additives can promote the formation of *trans* double bonds in model compounds,[14] but more work is necessary to determine if this is a principal factor in the overall mechanism of smoke retardation.

Despite the importance of Lewis acid effects in metal-catalyzed PVC smoke retardation, there does not seem to be a clear correlation between Lewis acidity and smoke retarder effectiveness.[1,2] Thus other effects are also operative. Reductive coupling reactions now appear to make only minor contributions to the overall process. Our MoO_3/246-TCH results indicate that molybdenum, at least, has a multifaceted role which may include metathesis and dehydrogenation (leading to aromatization) in addition to Lewis acid effects.

A final point is that many of the transition metal-based additives have the *secondary* effect of promoting oxidation of char to CO and CO_2.[6-9] That is, the same additive that promotes the formation of char acts to use it up in a competing reaction. Catalytic oxidation is important to combustion, since it is exothermic and contributes heat to support further combustion. It is now clear that most experiments that do not give good correlations between char yield and smoke reduction can be explained by oxidation of the char to CO and CO_2. While it has been proposed that catalytic oxidation is an *integral* part of effective smoke retardation, we believe it is a secondary effect.

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