# The Functional Role of Molybdenum Trioxide as a Smoke Retarder Additive in Rigid Poly(vinyl Chloride)

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## Synopsis

The most effective smoke retarders for poly(vinyl chloride) are compounds of transition metals, such as molybdenum trioxide. $MoO_3$ when added to a rigid PVC compound shows three general effects. First, smoke formation is reduced dramatically as measured either by the NBS smoke chamber test or Goodrich smoke–char test. Second, volatile aromatic pyrolyzate formation is also reduced dramatically. The "pure" conjugated aromatic compounds (particularly benzene and naphthalene) are reduced more than the "mixed" aliphatic–aromatic compounds (such as toluene). Third, char formation is effectively promoted. Based on results from studying $MoO_3$ (and other metal-based additives) in regular, perdeuterated, and syndiotactic PVC, we propose a "reductive coupling" scheme as the dominant mechanism to explain the smoke retarder action. In this mechanism the $MoO_3$ acts in the condensed phase to promote extensive crosslinking of the PVC polymer chains very early in the thermal degradation process. Specifically, the metal additive forms a redox catalyst system which promotes intermolecular crosslinking of polymer chains to form char, rather than the conventional degradation process which gives rise to aromatics and smoke.

## 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. Nonflammable fillers are sometimes added to PVC compounds in order to decrease the smoke. If the filler is inert, possessing no smoke retarder activity, it lowers smoke by diluting the organic content of the compound. Another way to decrease the smoke evolved from burning or smoldering PVC is to add an active smoke retarder. Such additive smoke retarders will reduce the smoke generated relative to burning the same compound without the smoke retarder.

A large number of chemical compounds have been reported as smoke retarders for PVC in both the patent and open literature. One of us (W.J.K.) has published an extensive review of the subject.[1] In general, the most effective smoke retarders are compounds of transition metals. The more active smoke retarders change the thermal degradation pattern of the PVC and promote the formation of char.[1]

Several reports relating to the mechanism by which smoke retarders function have appeared in the literature. In 1974, Iida, Nakanishi, and Gotō published a paper concerned with the evolution of aromatics on pyrolysis of PVC and the mechanism of pyrolysis.[2] Although smoke was not mentioned and was not a concern of these authors, their paper has smoke retarder implications. Iida et al. used a pyrolysis–gas chromatography (PY–GC) technique to study the py-

rolysis of PVC and PVC containing 10 wt % of $TiO_2$, $SnO_2$, ZnO, and $Al_2O_3$ in a helium atmosphere. They found that the $SnO_2$ and the ZnO favored the production of aliphatic hydrocarbons rather than benzene and other aromatics. Their data also indicated that the $TiO_2$ and $Al_2O_3$ were not nearly as effective as the $SnO_2$ and ZnO. Unfortunately, their data were very qualitative and the actual amounts of the pyrolyzates formed were unknown. We have found that $SnO_2$, ZnO, and certain titanium and aluminum oxides are in fact effective smoke retarders for PVC.[1] They appear to act in the condensed phase and promote the formation of char.

The first mechanistic studies regarding smoke retarders in PVC were conducted with ferrocene.[3,4] Lawson found that ferrocene increased char formation in PVC, but there was no clear correlation between char formation and smoke.[3] It was concluded that ferrocene "promotes early weight loss and crosslinking in PVC."[3] Ferrocene is rather volatile (unlike most other smoke retarder additives) and appeared to be active in both the vapor and condensed phases. The principal analytical techniques used by Lawson were NBS smoke chamber and Oxygen Index measurements, along with thermogravimetric analysis (TGA). The concentrations of individual pyrolyzates were not determined.

Lecomte et al. also studied ferrocene as a smoke retarder in PVC.[4] Using smoke data and TGA–GC, they concluded that "a linear correlation has been found between the amount of benzene evolved from the degradation (of PVC) and the amount of smoke generated by the combustion of the samples at temperatures higher than 500°C."[4] Although the correlation between smoke formation and benzene reduction with char formation was poor, it was proposed that ferrocene (or ferric chloride produced by reaction with HCl) "causes crosslinking of the polymer and then decreases the amount of benzene produced."[4]

In a followup study, Bert, Michel, and Guyot investigated a number of metal salts as smoke retarders in PVC.[5] The recipes used were simple mixtures of PVC with 1.5 or 3.0 parts smoke retarder. Experimental techniques used were TGA and dynamic combustion measurements of smoke, char, CO, and $CO_2$ in a tubular reactor. The following important conclusions were made:

(1) The "linear relationship" between smoke and benzene formation described earlier for ferrocene[4] is *not* a general phenomenon for all smoke retarders. A "general correlation" between benzene reduction and smoke reduction however, does exist.

(2) Smoke formation appears to occur *after* the dehydrochlorination process. Since the evolution of benzene is "concomitant with the dehydrochlorination, it is probable that the smoke is not directly related to the benzene formation."

(3) The most effective smoke retarder additives are "precursors of oxidation catalysts which cause incandescent combustion of the solid residue with low smoke production."[5]

(4) The efficiency of a particular additive depends on (a) its ability to disperse well in PVC, (b) its reaction with HCl, and (c) its ability to form oxidation catalysts.

Bert, Michel, and Guyot[5] mainly attempted to correlate a large amount of experimental data and did not discuss smoke retarder mechanisms per se.

Recent work at Bell Laboratories has concentrated on the functional role of

molybdenum trioxide ($MoO_3$) as a smoke retarder in PVC.[6–8] The first of the Bell Laboratories' reports, by Lum,[6] contrasted $Sb_2O_3$ and $MoO_3$ as flame and smoke retarders for plasticized PVC. The principal investigative technique used was "laser microprobe analysis,"[9] a form of direct pyrolysis–mass spectrometry. Lum concluded that while $Sb_2O_3$ works mainly through volatile chloride species in the vapor phase, $MoO_3$ works through "condensed-phase mechanisms and heterogeneous reactions."[6] Lum's conclusions were based principally on the following observations regarding *plasticized* PVC:

(1) $MoO_3$ catalyzes the dehydrochlorination of PVC, i.e., HCl evolution occurs at lower temperatures and at increased rates.

(2) $MoO_3$ reduces the evolution of benzene, "the major fuel species from PVC."[6]

(3) $MoO_3$ reduces the evolution of volatile hydrocarbon species from the polymer plasticizer component.

Lum was not specific on what condensed-phase reactions might occur, but he did speculate on the nature of the proposed heterogeneous reactions: "Evolution of benzene and toluene from the polymer is inhibited by a chemisorption process apparently involving the formation of relatively stable $\pi$-arene complexes with $MoO_3$."[6]

The second article from Bell Laboratories, by Edelson et al., reported that $MoO_3$ behaves anomalously as a fire and smoke retarder for *plasticized* PVC.[7] The anomalous behavior was an inconsistency between small-scale and large-scale laboratory tests of $MoO_3$ in a plasticized PVC compound formulated for use as wire and cable insulation. The large-scale test was the ASTM E-84 Surface Flame Spread of Materials Test performed in a Steiner tunnel. The PVC insulated cables were supported just below the ceiling of the tunnel. Edelson et al. found that $MoO_3$ was ineffective in limiting flame spread. They also said, "Qualitative observations showed that $MoO_3$ greatly reduced the amount of char formed in our Steiner Tunnel tests."[7] We presume this is relative to the wire cables which contained $Sb_2O_3$ and no $MoO_3$. It is interesting to note that compared to $Sb_2O_3$, $MoO_3$ gave a larger residue (char) in the TGA experiments reported by Edelson et al., in both nitrogen and air.[7]

In this second report, Edelson et al. apparently refute Lum's earlier contention[6] that $MoO_3$ forms $\pi$ complexes with aromatic decomposition products of PVC. Instead they propose that $MoO_3$ acts as a Lewis acid to promote the formation of trans polyene segments during dehydrochlorination of the PVC chains. These proposed trans polyenes, "being unable to cyclize and split off benzene, are stable to higher temperatures, at which a different mechanism obtains to give aliphatic products."[7] This implies that aliphatic products are formed in preference to aromatics. The aliphatics burn more completely (i.e., they give less smoke), and the observed reduction in char is due to the increased formation of volatile aliphatic pyrolyzates.

The most recent report from Bell Laboratories is by Starnes and Edelson.[8] It is an interpretive review of the mechanism of benzene formation during PVC pyrolysis. The "intramolecular cyclization" scheme for benzene formation[10,11] is nicely summarized with numerous references, and the "Lewis acid" mechanism for benzene reduction[7] is explained in detail.

A most revealing statement made by Starnes and Edelson is: "Since abundant evidence exists to show that benzene combustion is also the major source of smoke

during the burning of the polymer, the smoke-suppressant action of $MoO_3$ must be related to the ability of this oxide to reduce the benzene yield."[8]  This is a key revelation that never has been stated so clearly in the chemical literature.

From the above studies,[1-8] it is evident that the mechanisms of volatile pyrolyzate formation from the thermal decomposition of PVC play a key role in determining the effectiveness of smoke retarder additives.  Condensed phase additives clearly function by altering the mechanisms by which volatile pyrolyzates are formed.  The first step in PVC thermal decomposition is dehydrochlorination.  Loss of HCl leaves as a residue a conjugated polyene structure that can undergo further pyrolysis to yield a vast array of hydrocarbon products.[12-17] The most abundant volatile pyrolyzate from PVC (other than HCl) is benzene. Deuterium labeling experiments using pyrolysis–gas chromatography–mass spectroscopy (PY–GC–MS) have shown that benzene formation is the result of intramolecular cyclization of the polyene chain rather than by crosslinking between neighboring PVC/polyene chains.[10,11]  We also have shown that other "pure conjugated" aromatic pyrolyzates (e.g., styrene, naphthalene, biphenyl, and anthracene) are formed mainly by intramolecular cyclization.[11]  "Mixed" aromatic–aliphatic pyrolyzates (e.g., toluene, indene, methylnaphthalene) are formed at least partially via intermolecular (crosslinking and/or hydrogen transfer) mechanisms.  Low-molecular-weight aliphatic pyrolyzates (e.g., ethylene and propylene) are also formed via the more complex intermolecular pathways.[11]  Effective smoke retarders function by altering or interfering with the mechanisms by which these volatile pyrolyzates normally form.

In this report, we describe the results of experiments designed to elucidate the mechanism by which molybdenum trioxide functions as a smoke retarder additive in rigid PVC.  The principal investigative techniques used are the NBS smoke chamber and Goodrich smoke–char[1] tests, pyrolysis–gas chromatography (PY–GC), and PY–GC–mass spectroscopy (PY–GC–MS).  Our results indicate that $MoO_3$ primarily functions by promoting crosslinking of PVC/polyene chains early in the thermal degradation process.  This early crosslinking results in a large decrease in volatile aromatic pyrolyzate formation and a concomitant increase in the formation of char.  These results are shown to be inconsistent with recent smoke retarder mechanisms described in the literature.[6-8]  Our results are interpreted in terms of a new "reductive coupling" mechanism which we feel best explains the dominant role of the smoke retarder.

## EXPERIMENTAL

### Smoke, Char, and Volatile Pyrolyzate Tests

A simple rigid PVC compound was used in these studies.  It contained 100 parts Geon 103EP-F76 ($\bar{M}_n = 6.2 \times 10^4$ and $\bar{M}_w = 1.2 \times 10^5$), 2 parts dibutyltinthioglycolate stabilizer, and 2 parts Microthene 510 polyethylene lubricant. The smoke retarded compound used had the same composition with the addition of 5 parts molybdenum trioxide ($MoO_3$).  The compounds were milled on a clean 6-in. (15 cm) rolling rubber mill.  The mill temperature was about 160°C.  After milling, the stock was pressed into thin sheets (15 × 15 × 0.064 cm; 6 × 6 × 0.025 in.) or else into ACS sheets (15 × 15 × 0.19 cm; 6 × 6 × 0.075 in.).  The molding operation consisted of pressing the preheated sheets in the appropriate mold

for about 4 min at ~165°C. The pressed samples were quickly cooled by removing the mold from the press.

The samples for pyrolysis–flame ionization–gas chromatography (PY–FID–GC) were cut from the center of the 0.064-cm-thick sheets. In practice, a 15-cm strip just under 1 mm thick was removed and cut into 1- to 2-mm pieces. This gave samples for PY–FID–GC which weighed 1–2 mg. For PY–GC–mass spectroscopy, somewhat smaller samples (weight ~0.1 mg) were used. The samples for the NBS smoke chamber were also cut from the 0.064-cm sheets. They were 7.32 × 7.32 × 0.064 cm (2.88 × 2.88 × 0.025 in.). One sample was cut from each 0.064-cm sheet. The Goodrich smoke–char[1] samples were made from 15 × 1.3 cm (6 × 0.5 in.) strips cut from the center of each of the 0.190-cm sheets. One piece 1.3 × 1.0 × 0.19 cm (0.5 × 0.38 × 0.075 in.) was cut from each strip.

Two laboratory tests were used for determining the relative amounts of smoke formed when PVC samples are forced to burn. One of these is the NBS smoke chamber test (flaming mode), and the other is the Goodrich smoke–char test.[1]

Pyrolyses were carried out at 550°C in dry helium atmospheres. Identification of pyrolyzates was carried out (PY–GC–MS) with a Varian MAT 311A mass spectrometer system. This consisted of a CDS model 100 pyroprobe (platinum coil probe), a Varian 3700 digital gas chromatograph, a Varian MAT 311A double-focusing mass spectrometer, and a Finnigan INCOS 2400 data system. Pyrolyzate identifications were made by examination of the electron impact fragmentation patterns. Two gas-chromatographic columns were used. Lower-boiling pyrolyzates were separated on a 4 m × 2 mm i.d. glass 80/100 mesh Porapak PS column, programmed from 40 to 200°C at 4°C/min after an initial 4-min hold. Higher-boiling pyrolyzates were separated on a 4 m × 2 mm i.d. glass 3% Dexsil 300 on 100/120 mesh Supelcoport column, programmed from 50 to 300°C at 5°C/min after an initial 4-min hold. Distributions of pyrolyzates were similar to those reported previously.[12–17]

Semiquantitative analysis of pyrolyzates was carried out by flame ionization–gas chromatography (PY–FID–GC). The same CDS 100 pyroprobe was used for sample introduction, and the chromatograph was a Varian 3700 with data acquisition via a Varian CDS 111 microprocessor. Pyrolyses were carried out for 20 sec at 550°C (helium atmosphere) using the fastest temperature rise time available on the pyroprobe. Pyrolyses were carried out in Pyrex sample tubes open at one end; a plug of glass wool was used to hold the polymer sample in place. The same column packings described above (Porapak PS and Dexsil 300) were used for PY–FID–GC, except that in this case the packings were contained in 0.318 cm (0.125 in.) stainless steel tubing.

### Perdeutero-PVC Pyrolyzate Tests

Two PVC samples were used. The "normal" PVC sample was Geon 103EP-F76 prepared by suspension polymerization at 50°C. (This was the same PVC sample used for the smoke, char, and volatile pyrolyzate tests described in the previous section.) The perdeutero-PVC samples (DPVC) was prepared by the suspension polymerization of $C_2D_3Cl$ (reported deuterium enrichment 97.3%) at 50°C. GPC-derived parameters were $\overline{M}_n = 1.9 \times 10^5$ and $\overline{M}_w = 3.9 \times 10^5$.

Pyrolysis experiments were carried out using the same PY–GC–MS system

described above.   Field ionization (FI) was used for PY–GC–MS runs in which isotopic abundances were to be measured.   The techniques used were the same as those described previously.[11]

## RESULTS AND DISCUSSION

### Smoke and Char Formation

The model PVC compounds (with and without $MoO_3$) were examined in the flaming mode of the NBS smoke chamber, and also in the Goodrich smoke–char test (Table I).   Char formation was determined from the smoke–char test and is expressed as percent BC, backbone char.[1]   BC is that part of the PVC in a sample which would remain after complete dehydrochlorination.

It is clear from Table I that addition of $MoO_3$ to the PVC compound causes a marked reduction in smoke in either of the two tests used.   At the same time the percent backbone char increases by a factor of about three over the "control" sample.   This dual phenomenon of smoke reduction and increased char formation is very typical of numerous smoke retarder systems studied in our laboratory (including compounds of many transition metals such as copper, iron, and nickel).[1]   Our experience indicates, in fact, that good smoke retarders are always good char formers in NBS smoke chamber and smoke–char tests.

### Volatile Pyrolyzate Formation

The pertinent semiquantitative PY–FID–GC results for the $MoO_3$–PVC model compound are given in Table II.   Relative peak areas of several key pyrolyzates (or groups of pyrolyzates) are listed.   Total aliphatics, total aromatics, and total chlorine-containing hydrocarbons are also listed.

Several general effects can be noted from the data of Table II.   First, while aromatic compounds predominate in the volatile pyrolyzates from the control compound, their formation is greatly reduced in the $MoO_3$ sample.   Aliphatic pyrolyzate formation increases rather dramatically, by a factor of about 2.   The relative amount of chlorine-containing pyrolyzate also increases, but the total

TABLE I
Smoke Reduction and Char Formation for PVC–$MoO_3$ Compounds

| PVC Compound[a] | $MoO_3$, phr | $D_m/g$[b] | $S_{PVC}$[c] | % BC[d] |
|---|---|---|---|---|
| Model Compound | — | 62.4 ± 9.0[e] | 108. ± 25. | 9.1 ± 3.4 |
| Model Compound | 5 | 30.3 ± 5.4 | 70. ± 5. | 30.8 ± 1.7 |
| 103EP-F76 | — | — | 64. ± 5. | 9.4 ± 0.3 |
| 103EP-F76 | 10 | — | 31. ± 1. | 39.0 ± 4.6 |

[a] The tin-stabilized model compound was prepared using conventional milling and hot pressing techniques as described in the experimental section.   The 103EP-F76 compounds, containing only PVC or PVC and $MoO_3$, were prepared by grinding the ingredients under liquid $N_2$ and pressing into pellets at room temperature.

[b] NBS smoke chamber (flaming mode) smoke number per gram PVC in the sample.

[c] Smoke–char test smoke number per gram PVC in the sample.

[d] Percent backbone char (see text) from smoke–char test.

[e] Errors given are standard deviations from multiple runs.

TABLE II

A. Relative Abundances of Selected Pyrolyzates at 550°C

| Pyrolyzate | Relative abundance[a] |
|---|---|
| $C_1$–$C_3$ aliphatics | 2.3 |
| $C_4$–$C_6$ aliphatics | 1.5 |
| Methyl and ethyl chlorides | 2.9 |
| Benzene | 0.20 |
| Toluene | 0.91 |
| Dimethyl- and ethylbenzene | 0.78 |
| Naphthalene | 0.14 |
| Methylnapthalenes | 0.35 |
| Biphenyl | 0.37 |
| | |
| Total aliphatics[b] | 2.1 |
| Total aromatics[c] | 0.60 |
| Total chloro[d] | ~3. |

B. Computer Area per mg Sample (Arbitrary Units)

| | Total aliphatics[b] | Total aromatics[c] | Total chloro[d] |
|---|---|---|---|
| Control | 6,900 | 25,600 | 14 |
| MoO$_3$–PVC | 14,200 | 15,400 | 42 |

[a] Ratio of FID–GC peak area of MoO$_3$–PVC compound to the control compound (average of multiple runs).

[b] Sum of $C_1$–$C_6$ aliphatic hydrocarbons.

[c] Sum of all aromatic compounds detected.

[d] Mostly methyl chloride and ethyl chloride.

amount of chlorine-containing compounds is always very small and is rather unimportant in the overall picture.

A reduction in all aromatic hydrocarbons was observed in the smoke-retarded compound. A closer inspection of the data in Table II reveals two separate categories with respect to the relative amounts of aromatic pyrolyzate reduction. Namely, the "pure" conjugated aromatics (particularly benzene and naphthalene) are reduced considerably more than the nonconjugated "mixed" aromatics containing aliphatic side groups (particularly toluene and the $C_2$-benzenes). This suggests that different mechanisms are involved in the formation of the "pure" versus the "mixed" aromatics. We have already shown this for non smoke-retarded PVC.[11] "Pure" aromatics are formed intramolecularly, while "mixed" aromatics form at least partially via intermolecular reactions.[11]

Our experiments with several other transition metal smoke retarders (data not presented here) have shown that this reduction in aromatic pyrolyzates is a general phenomenon. The reduction is 60–70% for the more effective smoke retarder systems. Reductions of "pure" aromatics of 75–95% are common for the better smoke retarders. "Mixed" aliphatic–aromatic pyrolyzates, however, are generally reduced by only 10–65%.

Although results using dry air as the pyrolysis environment are not reported here, we found that the same general effects noted above are also valid for experiments conducted in air. Comparing "air" versus "helium" experiments for

the unretarded model compound, we found that total aromatic production is suppressed somewhat by air, while total aliphatic production is enhanced. Smoke-retarded PVC samples show the same order of aromatic pyrolyzate reduction (and increase of aliphatics) in air as compared to helium.

## Yields of Benzene and Toluene Pyrolyzates

PY–FID–GC experiments were also carried out (as described in the experimental section) with the following simple compounds: (1) PVC (103EP-F76), (2) syndiotactic PVC (SYN), (3) 100 parts PVC + 10 parts $MoO_3$, and (4) 100 parts SYN + 10 parts $MoO_3$.

Pyrolyses were carried out in a helium atmosphere at 550°C for 20 sec. Quantitative determinations for benzene and toluene pyrolyzates were made on each sample. Response factors were determined (external standard method) by injection of standard solutions of benzene and toluene ($n$-pentane solvent; Porapak PS GC column). The syndiotactic PVC sample was prepared by a urea complexation method[18] and was reported to be nearly 100% syndiotactic. Samples 3 and 4 were mixed with an agate mortar and pestle. The results are presented Table III.

Several literature references have presented evidence that syndiotactic PVC gives a predominance of long trans polyene sequences upon dehydrochlorination.[8,19,20] Trans polyenes cannot cyclize (without isomerization) to produce benzene.[7,8,16] Thus, one would expect syndiotactic PVC to yield less benzene than "normal" PVC. The data in Table III do show that the syndiotactic polymer gives about 25% less benzene than does 103EP-F76; this reduction of benzene with increasing syndiotacticity has been reported previously.[16,21] The addition of $MoO_3$ reduces benzene evolution considerably in either 103EP-F76 or the syndiotactic PVC. The reduction is ~57% in 103EP-F76 and ~72% in syndiotactic PVC (Table III). The quantitative results for toluene show somewhat less variation than the benzene results, which is consistent with the model compound data in Table II. The $MoO_3$ smoke retarder is effective in reducing toluene formation, but the percentage reduction (~40–50%) is smaller than for benzene. The consequences of these data with respect to the mechanism of smoke retarder action will be considered in a later section.

TABLE III
Quantitative Determination of Benzene and Toluene Produced from PVC Pyrolysis

| Sample[a] | Pyrolyzate yield, mg/g PVC | |
| | Benzene | Toluene |
| --- | --- | --- |
| 1. PVC | $40.9 \pm 2.4$[b] | $5.7 \pm 0.4$ |
| 2. SYN | $30.7 \pm 2.9$ | $6.5 \pm 0.2$ |
| 3. PVC/$MoO_3$ | $17.6 \pm 2.1$ | $3.6 \pm 0.6$ |
| 4. SYN/$MoO_3$ | $8.5 \pm 0.7$ | $3.1 \pm 1.3$ |

[a] See text for more complete description.
[b] Standard deviations were determined from triplicate pyrolysis runs.

## Perdeutero-PVC Pyrolysis Results

The PY–GC–FI–MS experiments were carried out as described previously.[11] Deuterium enrichment experiments were conducted with the following simple compounds: (1) PVC/DPVC (coprecipitate) and (2) 100 parts PVC/DPVC + 10 parts $MoO_3$.

Pyrolyses were carried out in helium atmosphere at 550°C for 20 sec, and deuterium enrichments for selected pyrolyzates were calculated from the field ionization mass spectral data. In each experiment the polymer sample used was an equal weight coprecipitate of PVC (103EP-F76) and perdeutero-PVC (DPVC, 97.3% D), prepared as described previously.[11] The PVC/DPVC coprecipitate and $MoO_3$ were mixed with an agate mortar and pestle. About 2 mg of sample was pyrolyzed in each run; duplicate runs were made on both Dexsil 300 and Porapak PS GC columns.

The isotopic distributions for selected pyrolyzates are listed in Table IV. Corrections have been made for the natural abundance of $^{13}C$. No corrections for molecular ion fragmentation were necessary, since pure molecular ion spectra were obtained by field ionization.[11] All pyrolyzates listed, except for benzene, showed very extensive H/D mixing in the $MoO_3$ compound. Benzene gave relatively little H/D mixing, indicating that benzene is mostly formed intramolecularly even with the smoke retarder present. The total amount of benzene formed with the smoke retarder present was of course greatly reduced (see Tables II and III).

With $MoO_3$ present, naphthalene showed considerably more H/D mixing than benzene, indicating that its formation has involved intermolecular reactions. Without smoke retarder present, naphthalene is formed predominately via intramolecular cyclization in a manner analogous to benzene.[11] The other aromatic pyrolyzates listed in Table IV all contain alkyl groups (toluene, indene, 1-methylnaphthalene). These "mixed" aromatics showed considerable H/D mixing even without smoke retarder present; this is due to pyrolyzate formation via scission reactions of crosslinked polymers and/or to intermolecular hydrogen transfer reactions.[11] The H/D scrambling for the "mixed" aromatics is much more pronounced in the smoke retarded compound, however. The mixed aromatics in the $MoO_3$ retarded compounds show H/D mixing of a nearly random nature (Table IV). This very extensive scrambling indicates that the smoke retarder has greatly altered the normal mechanisms by which the volatile pyrolyzates form. We believe that the $MoO_3$ causes the PVC chains to become extensively crosslinked very early in the degradation process. Therefore, volatile pyrolyzate formation has to occur via multiple cleavages of crosslinked chains rather than by intramolecular or simple intermolecular reactions. Thus, a smaller amount of volatile pyrolyzate is formed, char formation is enhanced, and less smoke is produced upon combustion.

One further point should be made regarding the data of Table IV. We cannot rule out the possibility that the extensive H/D scrambling observed for the PVC pyrolyzates is primarily due to metal-catalyzed intermolecular hydrogen transfer reactions rather than to crosslinking reactions. If this were the case, however, we would expect more H/D scrambling for benzene and naphthalene than was observed experimentally. Experiments with $^{13}C$-enriched PVC are planned. They should help to differentiate the roles of crosslinking (intermolecular C—C bond formation) and intermolecular hydrogen transfer reactions. Finally, it

TABLE IV
Isotopic Distribution of Selected PVC Pyrolyzates[a]

| $d_x$-MW[b] | Control[c] | $MoO_3$[d] | $d_x$-MW | Control | $MoO_3$ |
|---|---|---|---|---|---|
| $C_2H_4$ Ethylene | | | $C_7H_8$ Toluene | | |
| $d_0$-28 | 12. | 3.6 | $d_0$-92 | 5.1 | 5.7 |
| $d_1$-29 | 16. | 22. | $d_1$-93 | 14. | 8.6 |
| $d_2$-30 | 31. | 32. | $d_2$-94 | 15. | 13. |
| $d_3$-31 | 27. | 24. | $d_3$-95 | 11. | 14. |
| $d_4$-32 | 14. | 19. | $d_4$-96 | 11. | 17. |
| | | | $d_5$-97 | 13. | 15. |
| | | | $d_6$-98 | 16. | 13. |
| | | | $d_7$-99 | 11. | 10. |
| | | | $d_8$-100 | 3.3 | 4.0 |
| $C_6H_6$ Benzene | | | $C_9H_8$ Indene | | |
| $d_0$-78 | 52. | 43. | $d_0$-116 | 23. | 0. |
| $d_1$-79 | 4.7 | 10. | $d_1$-117 | 11. | 3.3 |
| $d_2$-80 | 1.3 | 3.7 | $d_2$-118 | 9.6 | 8.5 |
| $d_3$-81 | 0.6 | 3.6 | $d_3$-119 | 9.2 | 15. |
| $d_4$-82 | 1.9 | 4.5 | $d_4$-120 | 6.9 | 17. |
| $d_5$-83 | 8.1 | 9.4 | $d_5$-121 | 8.3 | 24. |
| $d_6$-84 | 31. | 26. | $d_6$-122 | 11. | 15. |
| | | | $d_7$-123 | 11. | 12. |
| | | | $d_8$-124 | 10. | 5.3 |
| $C_{10}H_8$ Naphthalene | | | $C_{11}H_{10}$ Methylnaphthalene | | |
| $d_0$-128 | 45. | 23. | $d_0$-142 | 10. | 2.3 |
| $d_1$-129 | 8.7 | 10. | $d_1$-143 | 15. | 4.3 |
| $d_2$-130 | 4.4 | 10. | $d_2$-144 | 14. | 8.7 |
| $d_3$-131 | 2.2 | 7.5 | $d_3$-145 | 9.6 | 9.4 |
| $d_4$-132 | 1.4 | 7.1 | $d_4$-146 | 7.0 | 17. |
| $d_5$-133 | 1.6 | 9.9 | $d_5$-147 | 5.4 | 18. |
| $d_6$-134 | 3.5 | 8.7 | $d_6$-148 | 6.7 | 15. |
| $d_7$-135 | 11. | 9.5 | $d_7$-149 | 8.9 | 11. |
| $d_8$-136 | 22. | 14. | $d_8$-150 | 11. | 11. |
| | | | $d_9$-151 | 8.3 | 2.5 |
| | | | $d_{10}$-152 | 3.0 | 1.7 |

[a] Determined from PY–GC–FI–MS molecular ion intensities; average of duplicate runs. Isotopic abundances have been corrected for the natural abundance of $^{13}C$.

[b] Isotopic species ($d_x$) and molecular weight (MW).

[c] Percent isotopic abundances for the "control" sample are repeated from ref. 11.

[d] Control plus 10 phr $MoO_3$.

can be noted that extensive H/D mixing was observed for ethylene (and other $C_1$–$C_6$ aliphatic hydrocarbons not listed in Table IV), both with and without smoke retarder present. Thus, these experiments do not help to elucidate the mechanisms by which the aliphatics are formed.

We have observed the same general effects shown in Table IV for numerous other smoke retarder systems, including cuprous oxide and other molybdenum compounds. This suggests that most effective metal smoke retarder additives work via similar condensed phase mechanisms.

# MECHANISMS OF SMOKE RETARDER ACTION

## Vapor Phase Mechanisms

The effectiveness of metal oxides (particularly Group VA metals) as *flame* retarders generally increases when used with a halogen source.[22] For $Sb_2O_3$ it is known that the metal oxide–halogen interaction involves reaction with the halogen source and the production of a volatile metal halide species.[23–25] The possibility of a gas-phase mechanism for $MoO_3$ has been eliminated, since this compound yields no volatile metal halide species during combustion.[6,7] Furthermore, it has been shown that $Sb_2O_3$ does not appreciably catalyze PVC dehydrochlorination or reduce the yield of benzene.[6,7] Thus, it is clear that $MoO_3$ and $Sb_2O_3$ function by different mechanisms.

Lawson suggested that ferrocene may also function (at least partially) via a vapor-phase mechanism.[3] Considerable work in our laboratory suggests, however, that ferrocene is not a condensed-phase additive of choice for conducting studies on the functional role of smoke retarders. Ferrocene is first of all not a very effective smoke retarder for PVC (E. D. Dickens, Jr., The BF Goodrich Co., private communication). Since ferrocene is quite volatile at normal processing temperatures, much of the ferrocene compounded into PVC is lost during processing (M. M. O'Mara and E. D. Dickens, Jr., The BF Goodrich Co., private communications). It is clear that ferrocene also can be rapidly vaporized from PVC compounds during burn testing. In addition, ferrocene can be lost from PVC compounds on aging (M. L. Dannis, The BF Goodrich Co., private communication). Thus, we believe that the results of published mechanistic studies using ferrocene as a smoke retarder in PVC[3,4] must not be considered as generally valid for more typical condensed-phase smoke retarders such as $MoO_3$.

## π-Arene Complex Formation

Lum has suggested that $MoO_3$ may reduce the evolution of benzene pyrolyzate from PVC via "heterogeneous reactions" between the metal and aromatic ring.[6] It was proposed that relatively stable π-bonded complexes could be formed which prevent the evolution of benzene (and presumably other aromatics) from the PVC char.[6] This theory was later discounted in other reports from Bell Laboratories.[7,8] It also is inconsistent with our studies. For example, π-arene complex formation could not account for the large H/D scrambling found for the PVC pyrolyzates reported in Table IV. Furthermore, it is unlikely that the π-arene complexes would remain stable at the high temperatures encountered in typical pyrolysis/combustion situations.

## Lewis Acid Mechanism

The "Lewis acid" mechanism has been explained in detail in reports from Bell Laboratories workers.[7,8] Only its main features will be summarized here. The basis of this mechanism in the original Bell disclosure[7] is the well-known isomerization of cis double bonds by Lewis acids. The Bell workers propose that during dehydrochlorination, the $MoO_3$ acts as a Lewis acid isomerization catalyst to favor the formation of trans alkene segments. These trans polyenes, which cannot undergo intramolecular cyclization to form benzene, are stable to higher

temperatures where different mechanisms ensue to give aliphatic (less smoky) products.[7,8]

The Bell reports consider two possibilities for trans polyene formation. One is the straightforward Lewis acid isomerization of cis alkenes into trans alkenes. The other has the $MoO_3$ acting as a Lewis acid which interacts with chain chlorines and induces dehydrochlorination. If a dissociated ion pair forms without retention of the original stereochemistry, trans polyenes can be formed directly during dehydrochlorination.[7,8]

We do not believe the "cis–trans" Lewis acid mechanism as originally proposed by Bell Laboratories workers[7] explains the primary role of $MoO_3$ as a smoke retarder in PVC. It is weak in several respects, both on its own merits and also with regard to the results presented here and in previous work.[1]

A specific objection to the "cis–trans" Lewis acid theory is with regard to its predictions of volatile pyrolyzate formation. Lewis acids can promote the isomerization of *both* cis and trans double bonds; the trans configuration is thermodynamically more stable. Even if trans polyenes are formed initially upon dehydrochlorination, we would expect rapid cis–trans interconversion to occur at the high temperatures and enthalpies encountered in later stages of PVC thermal decomposition. This might lead, for example, to enhanced evolution of benzene at higher temperatures, yet the evidence does not show this. The Lewis acid theory also predicts that aliphatic products will be formed from polyene chains in preference to aromatics. The theory predicts that these aliphatics will burn cleanly (with little smoke). These compounds, however, will in general be unsaturated since they are derived from polyene chains. Thus, they should burn with a smoky flame, similar to benzene and other aromatics.

Another specific objection to the "cis–trans" Lewis acid theory is based on our deuterium labeling experiments. The Lewis acid theory apparently does not predict or require crosslinking or intermolecular hydrogen exchange. Therefore, one should not expect the very extensive H/D scrambling which was observed in our pyrolysis experiments with smoke-retarded labeled PVC (Table IV).

Our studies using syndiotactic PVC are also significant (Table III). According to the "cis–trans" Lewis acid mechanism, since syndiotactic PVC will dehydrochlorinate into trans polyene chains, it should pyrolyze like a very effectively smoke-retarded normal rigid PVC compound. Yet instead of the expected 50% or better reduction in benzene relative to the control PVC sample, only a 25% reduction was observed (Table III). Also, if the principal action of the smoke retarder is to induce the formation of trans polyene segments on dehydrochlorination, one would expect the metal additive to have *less* effect in syndiotactic PVC than in "normal" 103EP-F76. In fact, $MoO_3$ reduced benzene by only ~57% in 103EP-F76 compared to ~72% in syndiotactic PVC (Table III).

A general problem with the Lewis acid mechanism is that there seems to be no demonstrated correlation between the Lewis acid character of smoke retarders and their effectiveness in reducing smoke from PVC. We recognize, however, that most metal compounds that either are Lewis acids, or can react with HCl to form Lewis acids, are effective smoke retarders for PVC. A careful study of our work[1] clearly shows that for a given group of Lewis acid smoke retarders, there is no Lewis acid ranking which will correlate well with the effectiveness of the individual smoke retarders. This is not surprising, since the Lewis acid-type compounds used as Friedel–Crafts catalysts can effect an astounding di-

versity of organic reactions—including alkylations, dealkylations, acylations, polymerization, and a wide variety of coupling reactions between different classes of compounds.[26] And for each specific reaction, there will be a unique order of effectiveness for a given group of Lewis acid catalysts.

The lack of correlation between Lewis acidity and smoke retarder effectiveness is clearly illustrated for the case of aluminum and copper smoke retarders. Copper compounds are the single most effective class of smoke retarders for PVC.[1,5] In contrast, only some aluminum compounds are effective, and with a *much* lower level of activity.[1] Based on Lewis acidity, one would predict that aluminum compounds would be very effective smoke retarders, since $AlCl_3$ is about the strongest Lewis acid known. In the same way one would not expect copper compounds to be very effective smoke retarders, since the copper halides are generally very mild Lewis acids compared to $AlCl_3$.

In their detailed discussion of the Lewis acid mechanism, Starnes and Edelson do point out that in addition to cis–trans effects, $MoO_3$ or species derived from it might destroy the olefinic precursors of benzene by catalyzing intermolecular Diels–Alder cyclizations or Friedel–Crafts alkylations. This would lead to crosslinking of the thermally decomposing PVC chain segments. However, they state that completely convincing correlations of char yield with smoke emission or Lewis acid content have not been observed in published combustion studies.[8] And they conclude "that crosslinking catalyzed by metal species has not been established as the principal mechanism for smoke inhibition, although it undoubtedly occurs in many systems."

We believe that crosslinking of the decomposing PVC chain segments *is* the principal mechanism by which $MoO_3$ inhibits smoke formation, reduces aromatic pyrolyzate reduction, and promotes the formation of char during the combustion and pyrolysis of rigid PVC. This belief is consistent with the results of our perdeuterated PVC experiments and the consistently good correlations we find between smoke reduction and char formation.[1]

The lack of convincing smoke/char correlations (as documented by Starnes and Edelson[8]) reported in the literature disagrees with our experimental observations. We find good general correlations between smoke reduction and char formation for a large number of metal-based smoke retarders,[1] including $MoO_3$ (Table I). Our correlations were made using the Goodrich smoke–char test,[1] a small-scale laboratory burn test. It was designed to be a rapid test to be used for the direct measurement of smoke and char from plastic materials. Small samples (~0.3 g) are exposed to a propane flame for 1 min, and char and smoke formation are measured. A general correlation exists between the smoke–char test smoke number and the NBS smoke rating. If the sample recipes are simple, the linear correlation is better. Although it is difficult to accurately measure the char residue from our pyroprobe experiments, the relative char yields compared favorably with the relative char yields as determined in the smoke–char test.

Obviously, some of the inconsistencies in the smoke–char correlations reported in the literature[3-5,7] reflect differences in the burn test conditions and in the configuration of the samples. We believe, however, the principal problem has been the failure to design smoke–char experiments which can yield meaningful results. In searching for mechanistically useful smoke–char relationships under conditions of burning, the important part of the burn cycle is that in which the

smoke is being generated.   The burn time in the smoke–char test was 1 min. This was long enough to ensure that the primary combustion of the sample was complete and that no more smoke was being evolved.   For example, for one commercial PVC compound we found no statistically significant differences in char and smoke yields with burn times between 30 and 90 sec.   In order to eliminate, or minimize, afterglow/incandescence phenomena, all of the smoke– char test residues were immediately quenched in nitrogen at the completion of the test.

If the metal smoke retarders or their combustion residues are good oxidation catalysts for the char, this could lead to systematic errors which would result in low char yields.   This could explain why in unstabilized PVC $MoO_3$ appears to be a better char former than $Cu_2O$, even though $Cu_2O$ is more effective in re- ducing smoke.[1]   In other words, char formation and char combustion can be competing processes which can occur simultaneously during burning.   In a system where the char is being consumed almost as fast as it forms, it would be essentially impossible to make a meaningful correlation between smoke and char.

To summarize our experience based on NBS smoke chamber and smoke–char test data, good smoke retarders are always good char formers.   While we cannot offer any unequivocal explanations for the specific char–smoke inconsistencies in the literature, we can offer some reasonable possibilites.

First, the failure of other workers[3,4] to find strong correlations between smoke reduction and char formation when ferrocene is used is not surprising.   It was pointed out in a previous section that ferrocene is not a typical condensed phase smoke retarder additive.

Second, Edelson et al. reported that $MoO_3$ did not promote the formation of char in large-scale tunnel tests.[7]   Three important differences should be noted between our tests with $MoO_3$ and those reported by Bell researchers:   (1) our experiments were with rigid PVC, while the Bell workers used plasticized for- mulations; (2) our tests were conducted on a small laboratory scale, while the Bell workers reported a char decrease in large-scale testing; and (3) our tests were run on a short time scale (1 min) compared to the Bell tunnel tests.   One likely possibility is that a "mass effect" gave rise to increased combustion temperatures and enhanced the rate of char combustion in the tunnel tests (relative to small- scale tests).   Another possibility is that the longer duration of the tunnel test permitted significant combustion of the char which formed during the early stages of thermal decomposition.

This implies that the metal residues left after burning can act as oxidation (prodegradant) catalysts for the initial char or residue which is formed.   The heat generated by the combustion of the char will assist in the propagation of the flame front down the tunnel.   In fact, this suggestion has been made in the literature for rigid PVC burned in the smoldering mode in a tubular reactor combustion experiment.[5]   Yet another possibility is that during the initial burning and degradation of the PVC, reduced metal species are formed which remain in the char.   Such "metastable" species might combine with oxygen and give rise to hot spots which can initiate the oxidation of the initial char.

Obviously, the last two speculations are closely related and could occur si- multaneously.   Either the catalysis or reoxidation mechanism could give rise to the phenomenon of "afterglow."   This could be significant because afterglow

and reignition phenomena are especially noticeable when the mass of material being tested is large (E. D. Dickens, Jr., The BF Goodrich Co., private communication). Bert, Michel, and Guyot have described the phenomenon of "afterglow" or "incandescence" with respect to smoke-retarded PVC.[5] These workers concluded that "those additives which are the most efficient in smoke reduction are precursors of oxidation catalysts which cause incandescent combustion of the solid residue with low smoke production." The major products produced during the incandescent stage are CO and $CO_2$; a concomitant loss of residue (char reduction) results.[5]

## Reductive Coupling Mechanism

The previous discussion suggests that no satisfactory explanation has been presented to adequately explain the primary role of metal-based smoke retarders for PVC. We propose that transition metal smoke retarders, such as $MoO_3$, promote early crosslinking of the PVC chains during thermal degradation. In effect, the smoke retarders act as coupling agents to join together allylic or alkyl chain segments during PVC thermal decomposition (allylic sites would be more reactive):
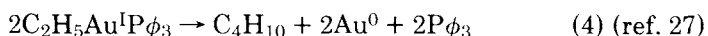
(a) Allylic Site Coupling



$$+ [MCl] \quad (1)$$
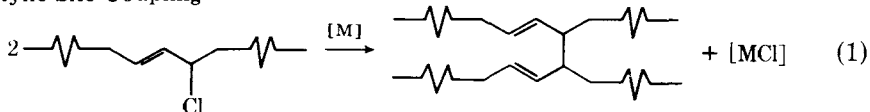
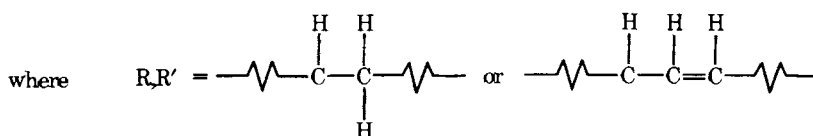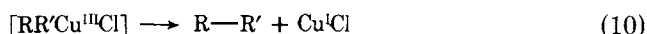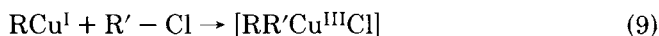(b) Alkyl Site Coupling



$$+ [MCl] \quad (2)$$
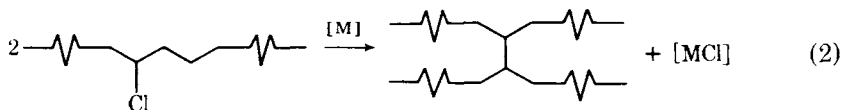
The results presented here along with previous results[1] suggest to us that corsslinking via "reductive coupling" mechanisms may be principally responsible for the action of $MoO_3$ and other transition metal smoke retarders. This general mechanism provides a means to "couple" (or crosslink) R groups containing halogens. Organometallic intermediates are involved which lead to the reduction of the metal cation(s) during the coupling step. Reductive coupling is well documented in the literature and is commonly promoted by Group IB metals (Cu, Ag, Au).[27] Typical examples from the literature are shown below[27-29]:

$$C_2H_5Au^{III}(CH_3)_2P\phi_3 \rightarrow C_3H_8 + CH_3Au^IP\phi_3 \quad (3) \text{ (ref. 27)}$$

$$2C_2H_5Au^IP\phi_3 \rightarrow C_4H_{10} + 2Au^0 + 2P\phi_3 \quad (4) \text{ (ref. 27)}$$



$$2\phi-CH_2-Cl \xrightarrow[\text{CH}_3\text{CN, en}]{\text{Cu}^I\text{OAc}} \phi-CH_2-CH_2-\phi \quad (6) \\ \text{(ref. 29)}$$

$$2 CH_2=CH-CH_2Cl \xrightarrow[\text{CH}_3\text{CN, en}]{\text{Cu}^I\text{OAc}} CH_2=CH-CH_2-CH_2-CH=CH_2 \quad (7) \\ \text{(ref. 29)}$$
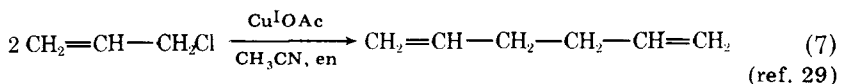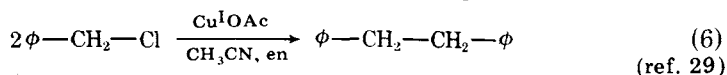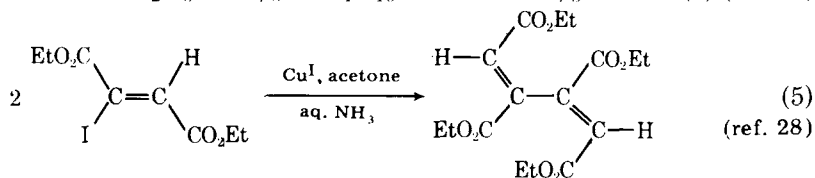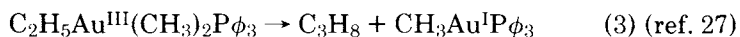
where en: ethylenediamine.

Generalized schemes have been proposed to explain reductive coupling reactions.[27,30] The reaction sequences seem best established for copper compounds. This is fortuitous, since copper compounds form the most effective class of smoke retarders for PVC.[1,5] Therefore, we will use copper compounds to illustrate how smoke retarders can promote crosslinking of PVC chain segments via a reductive coupling mechanism.

With copper as the metal, 1,1 elimination[30] (or "cross-coupling"[27]) may be a feasible pathway to effect reductive coupling. This involves a single cation and can be formalized as follows:

$$R\cdot + Cu^0 \rightarrow R-Cu^I \qquad (8)$$

$$RCu^I + R' - Cl \rightarrow [RR'Cu^{III}Cl] \qquad (9)$$

$$[RR'Cu^{III}Cl] \longrightarrow R-R' + Cu^ICl \qquad (10)$$

where     R,R′ =



This pathway involves two oxidative additions, reactions (8) and (9), followed by the reductive elimination, reaction (10), to give the coupled product (R—R'). An alternate means of forming the $Cu^{III}$ intermediate would be the oxidative addition of two radicals (R· and R'·) to $Cu^ICl$. The initiating radical can be formed via PVC chain scission reactions[8,11] or else via chlorine extraction by the metal additive:

$$R - Cl + Cu^0 \rightarrow R\cdot + Cu^ICl \qquad (11)$$
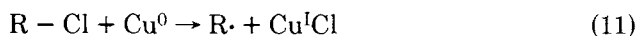
The initiating steps in the above reaction sequences begin with the metal in a low oxidation state ($Cu^0$ or $Cu^I$). $Cu^{II}$ salts, for example, in general need to be reduced before the coupling sequences can proceed. The reduction to $Cu^I$ might be accomplished by reaction with a diene chain segment with accompanying rechlorination of the chain segment (L represents an unspecified ligand):



$$2\,Cu^{II}LCl + \cdots \longrightarrow 2\,Cu^IL + HCl + \cdots \qquad (12)$$
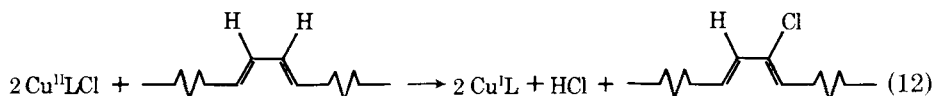
It is known that 1,3-butadiene will reduce $Cu^{II}Cl_2$ to $Cu^ICl$, so this type of reaction seems reasonable (A. J. Magistro, The BF Goodrich Co., private communication).

Our experience indicates that $Cu^{II}$ is readily reduced to $Cu^I$ and $Cu^0$ during PVC thermal decomposition. For example, when PVC containing copper(II) sulfide was burned in an Oxygen Index Test environment, significant quantities of copper metal and copper(I) oxide were found in the char residues.

In the case of copper, reductive coupling of PVC chain segments by means of a dinuclear transition state seems less likely:

$$[2\,R - Cu^{III}LCl] \rightarrow R - R + 2Cu^{II}LCl \tag{13}$$
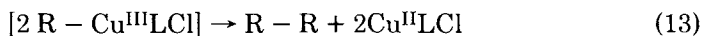
The unspecified dinuclear intermediate would have to involve the formation of copper–copper bonds and/or metal–hydrocarbon bridges.[30] The [R—$Cu^{III}LCl$] precursor to the dinuclear intermediate could readily form by the oxidative addition of a PVC chain segment or radical to an appropriate copper complex:

$$R - Cl + Cu^{I}L \rightarrow [R - Cu^{III}LCl] \tag{14}$$

$$R\cdot + Cu^{II}LCl \rightarrow [R - Cu^{III}LCl] \tag{15}$$

Because of the lability of $Cu^{III}$ complexes, however, $\beta$-elimination to form an alkene chain segment should be favored over the formation of a dinuclear $Cu^{III}$ transition state:

$$[R - Cu^{III} - LCl] \rightarrow \underset{\text{alkene}}{R(-H)} + HCl + Cu^{I}L \tag{16}$$
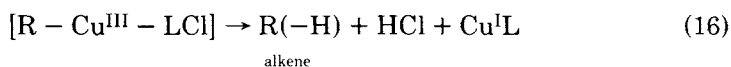
Molybdenum also should be able to promote crosslinking of PVC chain segments via reductive coupling reactions. For example, the following coupling reactions have been described in the literature[31]:

$$2\phi_2CCl_2 \xrightarrow[\text{DME}]{Mo(CO)_6} \phi_2C{=}C\phi_2 \tag{17}$$
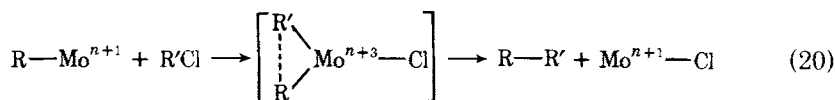


$$\tag{18}$$
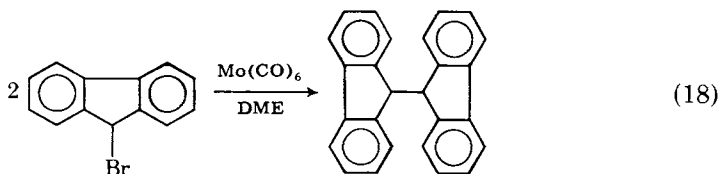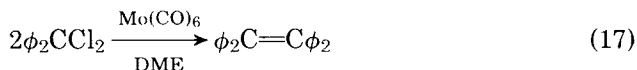
where DME = 1,2-dimethoxyethane.

Furthermore, $Mo(CO)_6$ and/or $ArMo(CO)_3$ can promote dehydrohalogenation, alkylation, and polymerization reactions involving organic chlorides.[32] The Mo(I) complex $[(\pi\text{-PhMe})Mo(\pi\text{-}C_3H_5)Cl]_2$ homogeneously catalyzed the oxidatve dimerization of propene to 2,4-hexadiene and the polymerization of the diene.[33] Finally, $MoO_3$ supported on $Al_2O_3$ has been claimed to promote the conversion of ethylene to butenes and minor amounts of other alkenes such as propene and pentene when combined with an appropriate cocatalyst.[34]
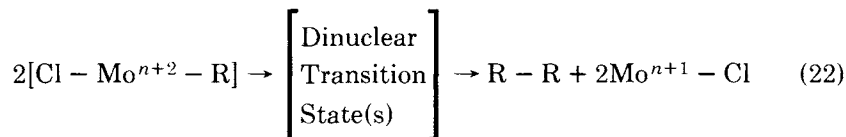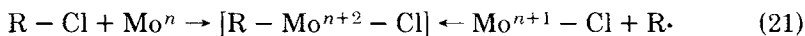
Molybdenum(VI) oxide, $MoO_3$, should be readily reduced to lower-valent molybdenum species during the thermal degradation of PVC. For example, $MoO_3$ is easily reduced by $H_2$ or $NH_3$ to either $Mo^{IV}O_2$ (<470°C) or $Mo^0$ (>470°C).[35] Carbon, carbon monoxide, and unsaturated organic compounds also should be able to reduce $MoO_3$ at elevated temperatures. In fact, under the conditions of the smoke–char test, we found that Mo exists in the char residue as $MoO_2$ and $Mo_2C$.

Low-valent molybdenum species could react with free radicals formed on PVC chain segments during thermal decomposition as shown for copper in reaction
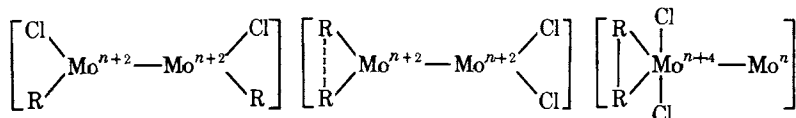
(8). This leads to an oxidative addition, 1,1-elimination reductive coupling mechanism similar to reactions (9) and (10) (for clarity, other necessary ligands are omitted):

$$R\cdot + Mo^n \rightarrow R - Mo^{n+1} \tag{19}$$

$$R—Mo^{n+1} + R'Cl \rightarrow \begin{bmatrix} R' \\ \diagdown \\ \diagup Mo^{n+3}—Cl \\ R \end{bmatrix} \rightarrow R—R' + Mo^{n+1}—Cl \tag{20}$$

Molybdenum, unlike copper, favors the formation of lower valent complexes which exhibit metal–metal bonding. Therefore, in analogy to reactions (13)–(15), low-valent molybdenum complexes should be able to promote the coupling of PVC chain segments by a dinuclear elimination from a transition state which contains Mo—Mo bonds.

$$R - Cl + Mo^n \rightarrow [R - Mo^{n+2} - Cl] \leftarrow Mo^{n+1} - Cl + R\cdot \tag{21}$$

$$2[Cl - Mo^{n+2} - R] \rightarrow \begin{bmatrix} \text{Dinuclear} \\ \text{Transition} \\ \text{State(s)} \end{bmatrix} \rightarrow R - R + 2Mo^{n+1} - Cl \tag{22}$$

Several possible configurations for the transition state are

$$\begin{bmatrix} Cl \\ \diagdown \\ \diagup Mo^{n+2}—Mo^{n+2} \diagdown \\ R' \quad\quad\quad R \end{bmatrix} \begin{bmatrix} R \\ \diagdown \\ \diagup Mo^{n+2}—Mo^{n+2} \diagdown \\ R' \quad\quad\quad\quad Cl \end{bmatrix} \begin{bmatrix} R \quad Cl \\ \diagdown \; | \\ \diagup Mo^{n+4}—Mo^n \\ R' \quad | \\ \quad Cl \end{bmatrix}$$

Low-valent molybdenum compounds are also effective catalysts for promoting olefin metathesis reactions.[36] This provides a potential route for molybdenum to promote rearrangement of decomposing PVC chains. Olefin metathesis certainly would explain the extensive H/D scrambling we observed in our PVC/DPVC experiments (Table IV). Unfortunately, normal olefin metathesis would not lead to a net increase in crosslinks between the thermally degrading PVC chain segments (which would favor the formation of char).

If molybdenum-catalyzed metathesis of polyene segments took place early in the thermal degradation process, it could significantly interfere with the intramolecular polyene cyclization reactions which give rise to benzene and other conjugated aromatic hydrocarbons. However, it is unclear how olefin metathesis by itself would reduce the number of double bonds in the decomposing PVC chain segments and give a pyrolyzate pattern essentially identical to that we obtained when cuprous oxide was substituted for molybdenum trioxide.

Several features of a reductive coupling mechanism make it attractive as a smoke retarder mechanism. First, it predicts early chlorine removal from PVC chains, which could help to explain the catalyzed dehydrochlorination at lower temperatures and increased rates for $MoO_3$–PVC.[6] Second, it would promote

the extensive crosslinking of PVC chains. This would explain the H/D scrambling in the PVC/DPVC experiments (Table IV). This extensive early crosslinking would lead to volatile pyrolyzate (and smoke) reduction and to enhanced char formation (Tables I and II). Third, the coupling reactions can occur very early in the degradation process. For example, an allylic chlorine dehydrochlorination site can be attacked directly. The removal of an allylic chlorine provides a shortstop for polyene chain propagation. Fourth, it is significant to note that all copper compounds yet tested are effective smoke retarders for PVC.[1,5] This includes both $Cu^I$ and $Cu^{II}$ compounds. Fifth, reductive coupling should be at least as effective for syndiotactic PVC as for "normal" PVC (Table III).

A reductive coupling mechanism leads to other predictions that may be observable. For example, an increase of chlorine in char might be expected from rechlorination of polyene chains, reaction (12). This is consistent with preliminary char analysis studies that show an increase of chlorine in the char formed with a molybdenum/copper smoke retarded PVC as compared to char formed in the unretarded compound (G. F. Smith, The BF Goodrich Co., private communication).

In addition, it has been previously reported that some combinations of smoke retarders are synergistic in reducing smoke relative to the individual components.[1] $MoO_3$–$Cu_2O$ is one such system. We suggest that the copper and molybdenum interact in this case (as a redox couple) to give a more effective redox catalyst system for promoting the reductive coupling of PVC chains. Perhaps molybdenum is better at catalyzing certain types of coupling reactions, while copper is more effective at catalyzing other crosslinking reactions.

## CONCLUSIONS

In this report we have shown that $MoO_3$, when added to a rigid PVC compound, shows three general effects:

(1) Smoke formation is reduced dramatically as measured either by the NBS smoke chamber or Goodrich smoke–char tests.

(2) Aromatic pyrolyzate formation is reduced dramatically (the "pure conjugated" aromatics are reduced the most).

(3) Char formation is effectively promoted.

We believe that these effects are all manifestations of the same basic mechanism by which the smoke retarder functions in PVC. Our results from studying $MoO_3$ (and several other metal-based additives) in regular, perdeuterated, and syndiotactic PVC have led us to propose a "reductive coupling" mechanism to explain the primary action of the smoke retarder. In this mechanism the metal additive promotes extensive crosslinking of the PVC polymer chains very early in the thermal degradation process. Specifically, the metal additive acts as a redox catalyst to promote intermolecular crosslinking of adjacent polymer chains to form char, rather than the conventional degradation process which gives rise to volatile aromatics and smoke.

The "reductive coupling" mechanism best explains the experimental data relating to the primary action of additive metal-based smoke retarders for PVC. Other mechanisms proposed in the literature are deficient in their abilities to predict a number of effects reported here and elsewhere. Further work is

planned in this area to help elucidate the role of additive smoke retarders in greater detail.

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