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## Review

### Mechanistic Aspects of the Behavior of Molybdenum(VI) Oxide as a Fire-Retardant Additive for Poly(vinyl chloride). An Interpretive Review

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ABSTRACT: The smoke-suppressant and fire-retardant action of molybdenum(VI) oxide during poly(vinyl chloride) combustion is shown to involve a condensed-phase mechanism that limits the formation of benzene. Benzene is proposed to result from the intramolecular cyclization of conjugated polyene segments into 1,3-cyclohexadiene moieties, followed by the removal of polymeric ring substituents through sequential C–C homolyses. Molybdenum(VI) oxide is suggested to interfere with these processes by functioning as a Lewis acid. In this capacity, it may (a) cause the dehydrochlorination of meso dyads to yield trans polyene segments that cannot undergo intramolecular cyclization, (b) induce stereochemical isomerization of meso dyads into racemic dyads whose dehydrochlorination yields trans polyenes preferentially, (c) catalyze the isomerization of cis polyenes into trans polyenes, or (d) facilitate the destruction of cis polyenes and 1,3-cyclohexadienes by catalyzing cross-linking processes. The thermal conversion of poly(vinyl chloride) into a conjugated polyene structure is shown not to involve a radical-chain mechanism in fluid media, and other aspects of the fire-retardant behavior of molybdenum(VI) oxide are briefly discussed.

Poly(vinyl chloride) (PVC) has high inherent fire resistance. This property has permitted the extensive use of PVC in applications such as insulation for electrical and communications cables where the possibility of flame spread by burning plastics must be minimized. The combustibility of the polymer is enhanced, however, by the presence of certain agents, such as plasticizers, which must be incorporated into commercial PVC formulations in order to achieve the mechanical (and other) properties desired. Nevertheless, the fire resistance can be restored by introducing other additives,[1] and antimony trioxide ($Sb_2O_3$) has been widely used in this regard.[1] Its mode of action has been studied by several investigators,[2] who have provided evidence for its operation via a gas-phase mechanism involving the scavenging of chain-carrying radicals (H·, HO·, etc.) by volatile metallic species formed in situ.[2] However, a deleterious consequence of this process is the enhancement of smoke formation, presumably the alternative fate of the organic radicals through polymerization, dehydrogenation, and agglomeration into carbonaceous aerosols.

Many other metal oxides have been tested as fire retardants for PVC,[1] and some recent work has been concerned with the possibility of using molybdenum trioxide ($MoO_3$) for this purpose.[3] In small-scale laboratory tests, $MoO_3$ showed promise as a flame retardant and smoke suppressant,[3] but further work showed that the flame retardance did not occur in large-scale tests involving higher enthalpy inputs.[3d,e] Mechanistic investigations of these phenomena revealed profound effects of $MoO_3$ on the precombustion pyrolysis chemistry of PVC.[3d,e] In particular, the oxide was found to be a potent catalyst for the dehydrochlorination of the polymer,[3d,e] and it also caused a dramatic reduction in the amount of benzene produced.[3d,e] Futhermore, the possibility of a gas-phase mechanism for $MoO_3$ was ruled out by the finding that the compound yielded no volatile metallic species during the process of combustion.[3b,d,e] Parallel work with $Sb_2O_3$ showed that this substance did not catalyze dehydrochlorination appreciably or reduce the yield of benzene;[3d,e,4] thus it was clear that $MoO_3$ and $Sb_2O_3$ were functioning in entirely different ways.[3b,d,e] The present paper explores the effects of $MoO_3$ in depth and offers a detailed hypothesis to account for the remarkable behavior of this additive.

## Mechanism of Benzene Formation

Benzene is the principal volatile organic substance formed during the early stages of the pyrolysis of PVC.[5] Since abundant evidence now exists to show that benzene

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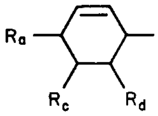
combustion is also the major source of smoke during the burning of the polymer,[3d,e,6] the smoke-suppressant action of MoO$_3$ must be related to the ability of this oxide to reduce the benzene yield. Therefore, in order to understand how MoO$_3$ functions, it will first be necessary to consider the mechanism by which benzene is formed.

Several mechanisms have been suggested. One of them[7] involves the thermal cleavage of ring substituents (R$_a$–R$_d$) from cyclic structures (1) that are produced by intermolecular Diels-Alder reactions of dehydrochlorinated polymer segments.[8] The presence of 1 seems to be supported by the ability of maleic anhydride to destroy a major fraction of the cross-links in degraded PVC,[9] an observation which can be attributed to entrapment, by the dienophile, of diene moieties formed from 1 in a retro-Diels-Alder process.[9] Nevertheless, all intermolecular routes to benzene now seem to be excluded by the labeling experiment of O'Mara,[7] who found that the thermolysis of an intimate mixture of PVC-$h_3$ and PVC-$d_3$ gave large amounts of benzene-$h_6$ and benzene-$d_6$ but only traces of other labeled benzenes (this result has been verified independently in our laboratories[10]).



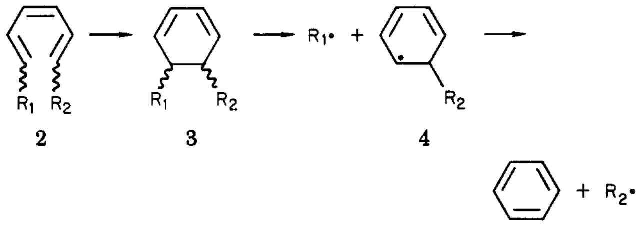
1, R$_a$-R$_d$ = $-CH_2\sim$, $-CHCl\sim$, $-CH{=}CH\sim$

Intramolecular pathways to benzene have been suggested by several workers. Many of these schemes involve the occurrence of cyclization at the ends of polymer chains,[7,11] with subsequent[7,11a] or concomitant[11b,c] scission of a polymeric residue from the ring. However, the vinyl radical intermediates proposed in some of these mechanisms[7,11c] are very unlikely to be formed by hydrogen abstraction or simple main-chain scission at the temperatures where benzene evolution is first observed (~ 150–160 °C[10]), owing to the very high energies required for the homolysis of vinyl-hydrogen and vinyl-(alkyl carbon) bonds (the C–H bond strength of ethylene is about 108 kcal mol$^{-1}$, while ca. 96 kcal mol$^{-1}$ of energy is needed to cleave the C$_2$–C$_3$ bond of 1-butene).[12] Furthermore, the concerted transition state[11b] that one must invoke in order to avoid the intervention of vinyl radicals in such schemes involves very unfavorable orbital overlap and has no literature precedent.

Another suggested intramolecular mechanism involves thermal excitation of a conjugated triene segment into its triplet state, followed by cyclization with concurrent homolytic ejection of one of the ring substituents.[11c] Benzene then results from homolysis of a second C–C bond.[11c] The last step of this mechanism is quite reasonable (see below), but the first two steps have no experimental support and are completely lacking in prior analogy.

However, there is another intramolecular route to benzene which is supported by a large body of data. This route (Scheme I) involves the intramolecular Diels-Alder cyclization of a triene moiety (2) into a cyclohexadiene structure (3) which is converted into benzene by two successive C–C homolyses.[13] The cyclization step of this mechanism is analogous to the well-known thermal cyclization of *cis*-1,3,5-hexatriene,[14] and rate calculations based on the activation parameters of the latter reaction ($A = 7 \times 10^{11}$ s$^{-1}$; $E_a = 29.9$ kcal mol$^{-1}$)[14] suggest that the conversion of 2 into 3 is not unlikely at the temperatures where benzene is formed from PVC.[13] Resonance stabilization would provide a strong driving force for both of the C–C scissions. For example, when R$_1$ = $-CH_2\sim$, $E_a$ for the conversion of 3 into 4 can be estimated to be only about 59 kcal mol$^{-1}$ by subtracting the stabilization energy of the cyclohexadienyl radical (21 ± 4 kcal mol$^{-1}$)[15] from the dissociation energy of the C$_2$–C$_3$ bond of 2-methylpentane (80 kcal mol$^{-1}$).[12] The activation energy for the conversion of 4 into benzene would undoubtedly be lower still. We estimate its value to be ≈22 kcal mol$^{-1}$ (when R$_2$ = $-CH_2\sim$) from the reported[16] $E_a$ of ca. 26 kcal mol$^{-1}$ for the case where R$_2$ = $-CH_3$ and a probable decrease of 4 kcal mol$^{-1}$ upon going from $-CH_3$ to $-CH_2\sim$.[12] Since carbon radicals are stabilized to some extent by an $\alpha$-chloro substituent,[17] the activation energies for cleavage of 3 and 4, with R$_1$ (or R$_2$) = $-CHCl\sim$, should be even less than those computed for the cases where R$_1$ (or R$_2$) = $-CH_2\sim$. On the other hand, bond-energy data[12] suggest that the replacement of $-CH_2\sim$ by $-CH{=}CH\sim$ will cause these $E_a$'s to increase by some 14 kcal mol$^{-1}$. For this reason, side reactions of 3 and 4 may intervene when R$_1$ and/or R$_2$ = $-CH{=}CH\sim$. Bond energies[12] suggest, in fact, that the C–H bonds of tertiary carbons in the ring may cleave competitively in such situations. [If R$_1$ or R$_2$ is a $-(CH{=}CH)_3\sim$ moiety in which the central double bond is cis, the vinyl radical intermediate resulting from scission of such a group (Scheme I) might act as a secondary source of benzene via the mechanism suggested by O'Mara.[7]]

**Scheme I**



R$_1$, R$_2$ = $-CH_2\sim$, $-CHCl\sim$, $-CH{=}CH\sim$

The concerted transformation of *cis*-3 into benzene and a polymeric dimer (R$_1$–R$_2$) is not a likely process, since this is a [$_\sigma 2_s + {}_\sigma 2_s$] reaction which is disallowed by orbital symmetry.[18] The intermediacy of 4 is consistent with the lower yields of benzene obtained in the presence of nitric oxide[11b,19] and $\alpha$-naphthol[19] (radical scavengers), and other workers have noted that benzene production via Scheme I may account for some of the existing evidence for the formation of radicals during the nonoxidative thermolysis of PVC.[13] Scheme I also explains the observation that benzene formation in dilute solution is accompanied by a gradual reduction in polymer molecular weight.[20] This result indicates that an appreciable fraction of the polymeric radicals produced by thermal scission (R$_1$· and R$_2$·) are destroyed by processes (e.g., disproportionation) that do not involve radical coupling.

Intermolecular cross-linking causes the molecular weight of the solid polymer to increase during pyrolysis.[9,20] However, this increase is not relevant to the mechanism of benzene formation, since, as noted above, the mechanism is an intramolecular process whose effect on molecular weight can be studied only in dilute solution where the rate of cross-linking is virtually nil. There is no reason to believe that the mechanism of benzene formation in solution is different from the mechanism in the solid state; thus the molecular weight reduction associated with benzene formation in solution constitutes strong evidence for the operation of Scheme I in the solid state, as well.

Benzene formation from polyene intermediates is supported by several findings. The rate of benzene evolution is enhanced by the presence of hydrogen

**Scheme II**

$$\underset{\mathbf{5}}{\mathrm{Cl\cdot + -(CH{=}CH)_nCH_2CHCl-}} \xrightarrow{-\mathrm{HCl}} \mathrm{-(CH{=}CH)_n\dot{C}HCHCl-} \rightarrow$$

$$\underset{\mathbf{6}}{\mathrm{-(CH{=}CH)_{n+1}CH_2CHCl-}} + \mathrm{Cl\cdot} \xrightarrow{-\mathrm{HCl}}$$

$$\mathrm{-(CH{=}CH)_{n+1}\dot{C}HCHCl-} \rightarrow \text{etc.}$$

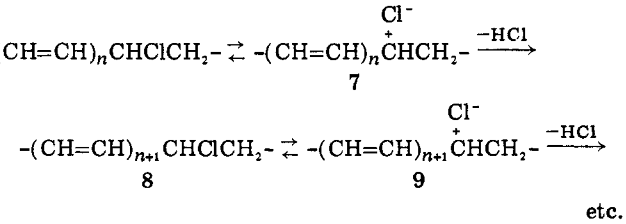
chloride[11b,13] and remains at an abnormally high level for some time after excess HCl is removed.[11b] These observations are consistent with the well-known ability of HCl to catalyze the formation of polyenes from PVC.[21] Furthermore, the rate of benzene evolution at constant temperature is found to be autoaccelerating under conditions that should lead to a constant (steady-state) concentration of HCl.[11b,20,22] The formation of benzene from a metastable progenitor (polyene or cyclohexadiene) would account for this observation.[11b,20,22] It has also been noted that a preliminary thermal dehydrochlorination of PVC will increase the amount of benzene evolved upon subsequent pyrolysis at higher temperatures.[10,23] This result suggests that mild thermolysis gives relatively high yields of intermediate structures that can be converted into benzene by further heating.

When PVC was subjected to thermal dehydrochlorination with argon sweeping in dilute solution at 210 °C, the number of polyene double bonds was found to be less than the total number of moles of HCl evolved during the latter stages of reaction.[22] Under the experimental conditions, the rate of benzene formation was very low, and no increase could be observed in the molecular weight of the polymer.[22] In parallel experiments, the rate of polyene removal relative to dehydrochlorination was slower in the solid state than in solution, even though the solid polymer underwent cross-linking during degradation.[22] These findings point to the destruction of polyenes in solution via a kinetically first-order process (i.e., **2** → **3**) that was facilitated by the ability of the liquid medium to increase the mobility of polymer chains.[22]

One of the most interesting observations to be reported thus far with regard to benzene production is that the yield of benzene is related inversely to the syndiotacticity of the polymer.[5a,24] In order to demonstrate the significance of this finding, we now examine the mechanism of polyene formation in detail.

Various scenarios involving free radicals have been proposed for polyene growth.[25] One of these mechanisms is the radical-chain process depicted in Scheme II.[11a,26] However, we suggest that this mechanism is extremely unlikely to operate in situations where the medium has sufficient fluidity to allow the facile diffusion of chlorine atoms (this condition probably obtains in plasticized PVC at elevated temperatures). Although the allylic hydrogen atoms of structures **5** and **6** may be slightly more reactive toward chlorine atoms than the hydrogens of unactivated $-CH_2CHCl-$ groups, relative rate data for model compounds[27] show that the reactivity difference will certainly not be large enough to compensate for the much higher concentration of the latter moieties in the early stages of reaction. Under these circumstances, freely diffusing chlorine atoms will attack the unactivated $-CH_2CHCl-$'s preferentially, and a chain reaction analogous to Scheme II may ensue if some of the attack is on methylene hydrogen. However, this process will lead to a random distribution of double bonds throughout the entire sample, rather than to the stepwise growth of a conjugated polyene sequence. The mechanism of Scheme II may become more likely at extents of reaction where allylic hydrogen concentrations are relatively high, but this mechanism cannot account for the finding that polyenes are formed in fluid media at very low levels of dehydrochlorination.[22]

**Scheme III**



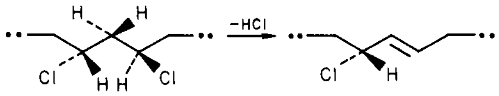
$$\mathrm{-(CH{=}CH)_nCHClCH_2-} \rightleftarrows \underset{\mathbf{7}}{\mathrm{-(CH{=}CH)_n\overset{\overset{Cl^-}{+}}{C}HCH_2-}} \xrightarrow{-\mathrm{HCl}}$$

$$\underset{\mathbf{8}}{\mathrm{-(CH{=}CH)_{n+1}CHClCH_2-}} \rightleftarrows \underset{\mathbf{9}}{\mathrm{-(CH{=}CH)_{n+1}\overset{\overset{Cl^-}{+}}{C}HCH_2-}} \xrightarrow{-\mathrm{HCl}}$$

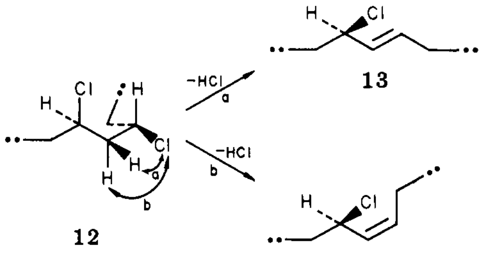
$$\text{etc.}$$

In our opinion, the most plausible mechanism for the growth of polyenes in PVC is the ion-pair process of Scheme III. The case for dehydrochlorination of the polymer via ionic intermediates has been summarized elsewhere[28] and has received further support from a recent theoretical study,[29] which showed that PVC is a suitable medium for the formation of carbenium chloride ion pairs (**7**, **9**, and their homologues), even at very low values of $n$. In relatively nonpolar media, these ion pairs would be expected to retain their original stereochemistry to a large extent.[30] Thus, under these conditions, the chloride ion should abstract the nearest available proton in order to complete the elimination process[30] (e.g., **7** → **8** + HCl). On the other hand, factors that would tend to increase the lifetime of the ion pairs (or allow free ions to be formed) might cause a change in the stereochemistry of elimination,[30b] for under these circumstances the polymer chain would have more time to rotate into its most stable conformation. We suggest that the former situation obtains during the uncatalyzed thermal dehydrochlorination of PVC. An alternative possibility is that the elimination occurs in a concerted manner via a highly polarized transition state,[28] but in either case the original steric arrangement of the polymer chain would be reflected in the configuration of the product double bond. These arguments are strongly supported by experimental results on other systems.[30]

Syndiotactic segments of PVC contain racemic dyads, which exist primarily in the trans-trans ($tt$) conformation (**10**).[31] According to the hypothesis presented above, a dyad of this type would be expected to undergo preferential cis elimination to generate a trans alkene (**11**). On the other hand, the isotactic portions of the polymer consist of meso dyads, which prefer to exist in the asymmetric trans-gauche ($tg$) array (**12**).[31] One of the chlorine atoms in this conformer is approximately equidistant from the two hydrogen atoms of the central methylene group. Therefore, HCl elimination involving this chlorine atom would be expected to produce a sig-



**10** **11**



**13**

**12**

**14**

nificant amount of cis alkene (**14**, path b) in addition to trans alkene (**13**, path a) if the preceding arguments hold. Since benzene formation via Scheme I requires the presence of a central cis double bond in **2**, it is clear that an increase in the proportion of meso dyads should increase the yield of benzene, in keeping with experimental findings.[5a,24] The same stereochemical arguments also apply, of course, to the heterotactic portions of the polymer, since these segments consist of overlapping meso and racemic dyads.[32]

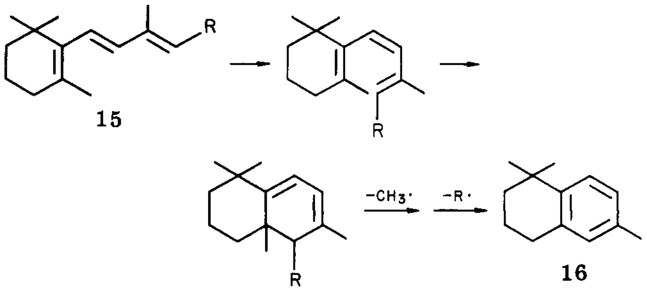
The elimination mechanism we propose should have other observable consequences. Since cyclization (Scheme I) either interrupts the growth of polyenes or destroys them after their growth has been completed, one might suppose that the average polyene length would increase with increasing syndiotacticity of the polymer. Several groups of workers have shown that this is, indeed, the case.[32b,33,34] Cis double bonds will be removed preferentially from polyenes by intramolecular cyclization, and they are probably less likely to be formed from **12** than are trans double bonds, owing to their higher energy content. These considerations suggest that most of the polyene double bonds should be trans, a conclusion that seems to be supported by infrared evidence.[32b,35] Finally, we note that the interruption of polyene growth by cyclization should reduce the rate of dehydrochlorination. Polymers containing relatively high proportions of racemic dyads should therefore dehydrochlorinate faster than those having lower syndiotacticites (assuming a similarity in initiation rates), and this prediction has also received some experimental corroboration.[33,36]

Millân and co-workers[33b-d] have reported that the overall activation energy for dehydrochlorination is independent of polymer tacticity. Since the activation energy probably relates only to a slow initiation step, this result suggests that the more rapid dehydrochlorination observed for polymers of high syndiotacticity must be due to a high rate of polyene growth relative to polyene termination. Slow termination (slow polyene cyclization) would explain the facts, but the possibility that growth occurs more rapidly along *tt* conformational sequences[32b,33,36b] also merits consideration. Furthermore, Ellinghorst and Hummel[36a,b] have obtained kinetic data that disagree with Millân's conclusion regarding activation energies and imply a faster initiation step for the more highly syndiotactic materials. It therefore seems premature to conclude that slow polyene cyclization is the only source of the decreased stability that results when the syndiotacticity of the polymer is enhanced. Nevertheless, kinetic analysis suggests that intramolecular cyclization must be a major contributor to the interruption of polyene growth.[20,22,37]

The complete mechanism of Scheme I has few analogies in the literature. However, Ishiwatari[38] has recently discovered that β-carotene (**15**) yields ionene (**16**) upon heating under vacuum at 150–350 °C. We suggest that this result can be accounted for by a mechanism (Scheme IV) whose resemblance to Scheme I should be obvious.

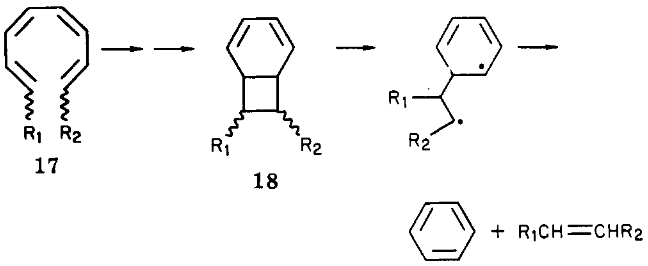
In light of the preceding arguments, Scheme I now seems to be established with reasonable certainty, but there is a closely related mechanism that should also be taken into account. This mechanism (Scheme V) involves the cyclization of a tetraene segment containing two central cis double bonds (**17**) into a bicyclo[4.2.0]octadiene moiety (**18**, cf. **3**) which is probably derived from a conjugated cyclooctatriene intermediate.[39] Structure **18** then produces benzene via homolyses analogous to those depicted in Scheme I. Although Scheme V has ample precedent,[39] it does not require polymer backbone scission and thus does not explain the molecular weight reduction associated with benzene formation in dilute solution[20] (as noted above, this reduction is accounted for by Scheme I). Nevertheless, we cannot rule out the possibility that Scheme V operates to some extent. Schemes I and V are both consistent with the principal thesis of the discussion presented thus far, viz., that benzene probably results from cyclohexadiene intermediates that are formed by the intramolecular cyclization of conjugated polyene segments in the polymer.

Scheme IV



R = conjugated alkenyl

Scheme V

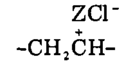


$R_1, R_2$ = $-CH_2\sim$, $-CHCl\sim$, $-CH{=}CH\sim$

Cyclohexadienes have apparently not been observed directly in degraded PVC. However, their presence has been inferred from spectral data,[40] and the degraded polymer has been said to yield phthalic acid upon oxidation with alkaline permanganate.[41] Although the latter observation was originally taken as evidence for the formation of **1**,[41] it would seem to be more nearly consistent with the presence of **18** and/or **3**.

## Inhibition of Benzene Formation by Molybdenum Trioxide

Acceptance of Scheme I (or Scheme V) allows one to consider several possibilities for the action of $MoO_3$. Since $MoO_3$ is a Lewis acid,[42] it would be expected to accelerate the heterolysis of a C–Cl bond by coordinating with the chloride anion, as in structure **19**. The electrophilic attack of $MoO_3$ upon halogen could occur either before ionization or after the formation of a carbenium chloride ion pair,[29] but in either case the rate of HCl elimination would be likely to be enhanced, since the equilibrium constant for ionization would be increased by coordination, owing to the low basicity of the complex Mo(VI) anion. The observation that $MoO_3$ does, indeed, catalyze the dehydrochlorination of the polymer[3d,e] is consistent with this explanation, and any $MoO_2Cl_2$ (or other molybdenum-containing species?) formed in situ[3d] might act in a similar way. Now the decreased basicity of its anion will cause ion-pair **19** to undergo elimination more slowly than the ion pairs of Scheme III. Thus the increased lifetime of **19**



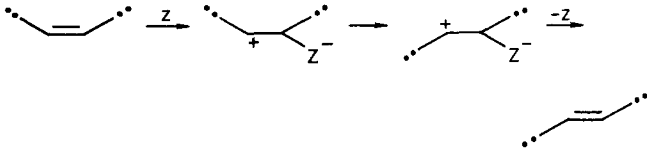
$$\overset{ZCl^-}{-CH_2\overset{+}{C}H-}$$

**19**, Z = $MoO_3$, etc.

will tend to allow its cationic member to rotate into the conformation of lowest energy. For an ion pair formed from a meso dyad (or, for that matter, from a racemic dyad), the low-energy conformer will undoubtedly be the *tt* form, since the removal of a chlorine atom from the polymer chain will also remove the steric interactions that caused the dyad to exist preferentially in the *tg* arrangement before ionization occurred. Discharge of **19** by proton transfer will thus tend to yield an alkene linkage whose configuration is exclusively trans (cf. **10** → **11**), and continual elimination down the chain in this way will tend to produce an all-trans polyene sequence that cannot be a precursor of benzene. This general argument agrees with many literature observations on related systems,[30b–d] which have shown that ion-pair eliminations tend to involve more extensive conformational (or skeletal) reorganization when the lifetimes of the ion pairs are increased by factors such as decreased anion basicity and enhanced ion-solvating power of the medium.

An alternative explanation for the benzene-inhibiting action of $MoO_3$ is that the meso dyads are isomerized into racemic dyads via the intermediacy of **19**. This factor alone seems insufficient to account for the great effect of the oxide on benzene production,[3d,e] since the meso-to-racemic dyad ratio at stereochemical equilibrium will still be rather large (calculated value of ca. 28:72 at 20 °C[43] vs. ca. 45:55 for commercial polymers[44]).

A further possibility is that $MoO_3$ (and/or its derivative species) can isomerize cis alkenes into trans alkenes via Lewis acid catalysis:



Z = $MoO_3$, etc.

In addition, the metal compounds might destroy the olefinic precursors of benzene by catalyzing intermolecular Diels-Alder cyclizations[45] or Friedel-Crafts alkylations.[6,28b] Such reactions would lead, of course, to cross-linking of the polymer. Recent publications have focused on catalyzed cross-linking as a possible mechanism for the smoke-suppressant action of metallic additives in PVC;[6,46] moreover, cross-linking has been invoked to account for the ability of zinc stearate to inhibit benzene production upon thermolysis.[47] However, completely convincing correlations of char yield with smoke emission or Lewis acid content were not obtained in the combustion work,[6,46] and $MoO_3$ was found to cause very drastic reductions in the yield of char under large-scale testing conditions.[3e] We therefore conclude that cross-linking catalyzed by metal species has not been established as the principal mechanism for smoke inhibition, although it undoubtedly occurs in many systems.

Finally, there is the possibility that Mo(VI) compounds can inhibit benzene evolution by forming stable coordination complexes with benzene or its olefinic precursors. Brief consideration suggests that this mechanism is highly unreasonable: Mo(VI) possesses a rare-gas (krypton) electronic configuration and is thus unlikely to complex readily with $\pi$ electron donors. Furthermore, such a mechanism fails to account for the finding that benzene formation is also decreased by other metallic compounds that do not form stable $\pi$ complexes with organic ligands.[6,23,47,48] Nevertheless, some evidence has been obtained for a weak interaction between benzene and $MoO_3$ that may be due to adsorption or chemisorption.[3d]

## Concluding Remarks

In brief, we suggest that the smoke-suppressant action of $MoO_3$ in PVC results from the ability of this additive to reduce the yield of benzene and is likely to be connected with the ability of molybdenum species to function as Lewis acids. Several factors may be important in the latter regard; they include changes in the stereochemistry of elimination, stereochemical isomerization of the starting polymer, stereochemical isomerization of alkene linkages, and catalyzed cross-linking via alkene groups. The relative importance of these factors is unknown, but there are strong indications for their operation in other systems, since a large number of acidic metal oxides and chlorides are now known to be able to reduce the amount of benzene formed upon pyrolysis of the polymer.[6,23,48] On the other hand, it would perhaps be naive to assume that these effects are the only ones produced by metallic oxides in the extremely complex chemical systems that are created by the combustion of PVC. Physical properties also undoubtedly have a major influence on the behavior of fire-retardant additives, in general, and an observation that tends to exemplify their importance has been provided by Abu-Isa,[49] who found that the thermal dehydrochlorination of chlorinated polyethylene at 150 and 180 °C was strongly catalyzed by a substance (apparently $SbCl_3$) that was generated in situ from $Sb_2O_3$. In contrast, no significant dehydrochlorination catalysis was observed with $Sb_2O_3$ during combustion studies on PVC,[3d,e] presumably because the $SbCl_3$ formed (bp[50] 223 °C) was volatilized very rapidly at the high temperatures that were reached.

In addition to its smoke-suppressant property, $MoO_3$ has the ability to limit flame spread in PVC under laboratory testing conditions.[3] The latter result has been attributed to a decreased rate of production of a volatile fuel (benzene),[3e] and it could also be connected with the accelerated liberation rate of HCl, a potential radical scavenger. However, $MoO_3$ does not reduce the spread of flame when the enthalpy input is very high.[3e] This anomaly has been discussed elsewhere,[3e] and we have little else to contribute to its rationalization at the present time, except to speculate that the catalysis of high-temperature combustion by $MoO_3$ (as suggested for $\alpha$-$Fe_2O_3$)[6] may be a contributing factor.[51] Further work is needed to confirm or disprove this hypothesis and to elucidate the details of the mechanism by which $MoO_3$ suppresses smoke evolution from the burning polymer.

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