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Mechanism of Autocatalysis in the Thermal Dehydrochlorination of Poly(vinyl chloride)

William H. Starnes, Jr.* and Xianlong Ge†

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

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ABSTRACT: Autocatalysis during the thermal dehydrochlorination of poly(vinyl chloride) (PVC) is shown to be a free-radical process that converts the ordinary monomer units of the polymer into chloroallylic structures that have low thermal stabilities. In the first stage of dehydrochlorination, conjugated polyene sequences are created by a nonfree-radical route. They react with HCl to give cation monoradicals and/or excited cation diradicals. One or both of these species, or other radicals formed from them, can then abstract methylene hydrogen in order to produce new radicals that are also carbon-centered. These are converted by chlorine-atom β scission into the chloroallylic segments, which start the growth of new polyenes in the usual (nonradical) way. At 180 °C in solid PVC, autocatalysis was inhibited by free-radical scavengers (a hindered phenol, triphenylmethane, and metallic mercury) but greatly enhanced by an increased concentration of HCl when all-trans-β-carotene, a model for PVC polyene sequences, was introduced simultaneously. When they were subjected to autocatalytic conditions, other model compounds gave products that apparently resulted from the abstraction of hydrogen by free-radical intermediates.

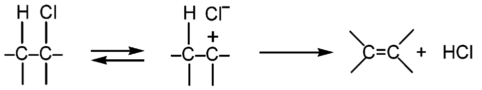
Introduction

Poly(vinyl chloride) (PVC) continues to be an extremely important commercial polymer, despite its relatively low thermal stability, which fortunately can be enhanced considerably by the use of protective additives. Technological advances in the stabilization of PVC obviously should be expedited by the availability of information about the molecular mechanism by which the polymer degrades. For that reason, the mechanism of PVC thermolysis has been subjected to an enormous amount of detailed study (and speculation) for more than 50 years. Nevertheless, there are significant aspects of the mechanism that still have not been clarified. Here we propose solutions to some of the remaining major problems.

Background. In its initial phase, the thermal degradation of PVC is primarily a process of sequential dehydrochlorination that forms conjugated polyene sequences (eq 1).[1] This process is now well-recognized

$$-(CH_2CHCl)_n- \xrightarrow{\Delta} -(CH{=}CH)_n- + n\mathrm{HCl} \qquad (1)$$

to be a chain reaction in which initiation, propagation, and termination steps occur.[1] During initiation, various structural segments of the polymer lose HCl and thereby are converted into allylic chloride groups. During propagation, these groups elongate very rapidly into polyenes as dehydrochlorination progresses. At the outset of degradation, the principal initiating species are highly reactive “structural defects”.[2] They are believed by most researchers to be tertiary chloride moieties or allylic chloride structures that are not at the ends of polymer chains.[2] Both initiation and propagation occur exclusively either via ion pairs (eq 2) or by way of concerted steps whose transition states are highly polarized, as shown in eq 3.[2] Termination refers to the cessation of polyene growth, which occurs when the polyene sequences still are rather short. In fact, all thermal degradations of PVC engender a polyene sequence length distribution wherein the average number of double bonds per sequence typically ranges from only about 3 to 20, depending on conditions.[1] The termination reactions have not been identified. However, several possibilities are apparent, including various intra- or intermolecular cyclizations of the polyenes themselves.[2−4]



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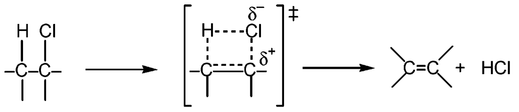

(3)

Other facets of thermal degradation that are, if anything, even more subtle will concern us here. One of these has to do with initiation from the ordinary (head-to-tail) monomer units. Such units are generally believed to be much more stable than the structural defects mentioned above.[2,5,6] Hence, in the absence of perturbing factors, loss of labile defects in the initial stage of degradation should lead to autodeceleration in the rate of evolution of HCl. This behavior is, indeed, observed under some conditions.[5,6] Yet, in other cases, when most or all of the original defects have reacted, dehydrochlorination does not slow appreciably and may even autoaccelerate, sometimes drastically.[5,6] The reason for these kinetic effects has been the subject of much debate, and they have been said by some researchers[7,8] to result from the presence of α,β-unsaturated ketone groups in the polymer. Supposedly formed by adventi-

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* Corresponding author. E-mail: whstar@wm.edu.

† E-mail: gex@nsula.edu.

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tious air oxidation, the cisoid forms of such structures were suggested to serve as true catalysts for the dehydrochlorination of ordinary monomer units, a process that would continually create thermally labile allylic sites and thereby prevent deceleration.[7,8] On the other hand, there is no conclusive evidence for the presence of enone groups in commercial PVC,[2,3] and their proposed catalytic proficiency could not be confirmed by other workers in model-compound studies.[2,9,10]

An alternative explanation for the absence of deceleration is that the dehydrochlorination of ordinary units is catalyzed by the evolving HCl. The presence of this substance does indeed tend to increase the rate dramatically.[1−3,5,6,11] However, the reasons for such behavior are complex, in that HCl is potentially able to alter the rates of propagation and termination as well as that of initiation. The effects of HCl on the degradation of PVC have been discussed in several reviews,[1,3,11] which show that much still remains to be understood about the mechanisms through which these effects occur.

Another perplexing aspect of PVC thermolysis is how and to what extent free radicals are involved in the process. As noted above, radical species do not intervene in initiation or polyene elongation. Nevertheless, the evidence for their presence in degrading PVC is extensive, and it has been summarized and/or analyzed in some recent publications.[2,5,6,12,13]

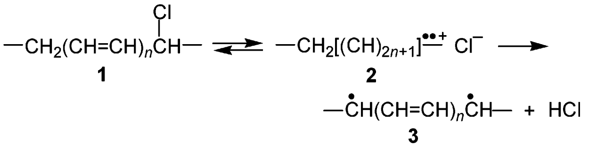
Autocatalysis Retrospective: Previous Studies and Rationales. A principal thesis of this paper is that several features of PVC degradation, identified above, that have not been explained heretofore can now be understood easily in terms of a novel mechanism for autocatalysis during thermal dehydrochlorination. This mechanism requires the simultaneous presence of polyenes and HCl, and it involves cation radicals as essential intermediates. The evidence for its operation will be considered here in detail, beginning with an assessment of work by previous investigators.

More than 30 years ago, Rasuvaev et al.[14] reported the results of experiments in which PVC was first degraded thermally under vacuum for various lengths of time while the HCl formed was removed by freezing. The degraded specimens then were placed under an HCl pressure of 150 mm and subjected to further thermolysis while the HCl formed was allowed to accumulate in the system. This sequential treatment led to huge accelerations in the rate of dehydrochlorination whose magnitudes increased with increasing time of predegradation. The autoaccelerations were attributed to an interaction between HCl and polyene segments to form free radicals that stimulated dehydrochlorination by a radical route, and this proposal was supported by (a) the complete inhibition of autocatalysis by maleic anhydride, which was thought to destroy the polyenes by Diels−Alder cycloaddition, and (b) the retardation of autocatalysis by metallic mercury, toluene, and triphenylmethane, which were believed to serve as radical scavengers. Curiously, at the time when it was suggested, this autoacceleration scenario does not seem to have attracted much support from other researchers, perhaps because the specific chemical mechanism proposed to explain it[14] was unprecedented and highly speculative. The same fate seems to have befallen some additional arguments for a radical pathway that were made later by Troitskii and co-workers,[15] who reported that silver and glass, as well as mercury, retarded dehydrochlorination in the presence of HCl, though not in its absence, and that mercury was thereby converted, to some extent, into mercurous chloride.

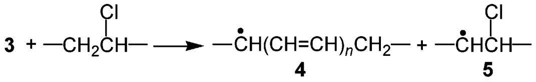
Other relevant observations were reported by Hjertberg and Sörvik,[16] who found that thermal degradation in an atmosphere containing 10 vol % of HCl caused the average polyene length to increase significantly. This result was reasonably attributed to the catalysis of propagation by HCl, although it was pointed out later[3] that HCl inhibition of polyene shortening through cyclization might have been involved. At higher atmospheric HCl contents (up to 40 vol %), the polyene distribution underwent no further change, but the autoacceleration of dehydrochlorination occurred to an extent that increased with increasing concentrations of polyenes and HCl.[16] The autoacceleration was ascribed to enhanced initiation that was caused by polyene−HCl complexes whose formation somehow improved the ability of HCl to promote the dehydrochlorination of ordinary monomer units.[16] Direct evidence for this increased initiation (but not for its mechanistic rationale) was provided later by measurements which showed convincingly that autoacceleration was accompanied by an increase in the number of polyene sequences.[17]

Recent studies in this area by Troitskii et al. are of particular interest. One of these investigations involved the use of literature kinetic data in order to develop mathematical models of several schemes for thermal dehydrochlorination. The results strongly supported a mechanism for autocatalysis in which the interaction of HCl with polyenes forms a chemical species whose reaction with ordinary monomer units gives new sites for initiation.[18] That the autocatalysis involves free radicals was indicated by other findings, one of which was that fullerene C_{60}, an effective radical trap[19,20] that does not react with HCl,[21] retarded thermal dehydrochlorination when HCl was present but not when it was removed by freezing.[21] Also, an ESR study of thermally degraded PVC showed that the number of stable spins was much greater in samples that had experienced autocatalysis caused by exposure to HCl.[22] This result was considered to be indicative of higher spin concentrations in these specimens during the degradation process itself.

New detailed mechanisms for autocatalysis have now been proposed by Troitskii and Troitskaya.[5,6,13] These mechanisms are heavily based on theoretical and experimental evidence in the literature which shows that the energies needed for the conversion of conjugated polyenyl cations into their first excited singlet and triplet states are much less than those required for the analogous excitations of the corresponding neutral polyenes. One of the schemes considered[5,6,13] begins with the reversible transformation of labile structure **1** into an ion pair (**2**) whose cationic component is created in an excited diradical state. Discharge of this ion pair by proton transfer produces the excited neutral diradical, **3** (eq 4), which in theory could abstract a methylene hydrogen atom from an ordinary monomer unit to give monoradical **4** and a β-chloroalkyl radical (**5**) (eq 5). A conventional β-cleavage reaction (eq 6) then forms a new allylic chloride unit that can initiate the growth of a new polyene sequence, thereby causing autocatalysis. However, since autocatalysis requires the presence of HCl, reaction 5 was considered to be much less important than reaction 7, which produces a chlorine atom that was said to initiate a homolytic mechanism for degradation.[13] The exact nature of this mechanism was not



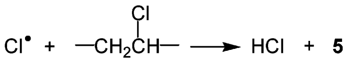
$$\underset{\mathbf{1}}{-\mathrm{CH_2(CH{=}CH)}_n\overset{\mathrm{Cl}}{\mathrm{CH}}-} \rightleftharpoons \underset{\mathbf{2}}{-\mathrm{CH_2[(CH)}_{2n+1}]^{\bullet\bullet+}}\ \mathrm{Cl^-} \longrightarrow \underset{\mathbf{3}}{-\dot{\mathrm{C}}\mathrm{H(CH{=}CH)}_n\dot{\mathrm{C}}\mathrm{H}-} + \mathrm{HCl} \tag{4}$$



$$\mathbf{3} + -\mathrm{CH_2}\overset{\mathrm{Cl}}{\mathrm{CH}}- \longrightarrow \underset{\mathbf{4}}{-\dot{\mathrm{C}}\mathrm{H(CH{=}CH)}_n\mathrm{CH_2}-} + \underset{\mathbf{5}}{-\dot{\mathrm{C}}\mathrm{H}\overset{\mathrm{Cl}}{\mathrm{CH}}-} \tag{5}$$

$$\mathbf{5} \longrightarrow \mathrm{Cl}^\bullet + \mathbf{1}\ (n = 1) \tag{6}$$

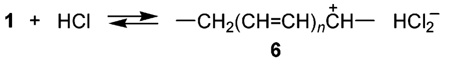
$$\mathbf{3} + \mathrm{HCl} \longrightarrow \mathbf{4} + \mathrm{Cl}^\bullet \tag{7}$$



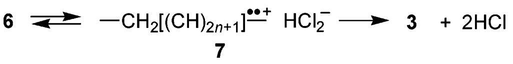
$$\mathrm{Cl}^\bullet + -\mathrm{CH_2}\overset{\mathrm{Cl}}{\mathrm{CH}}- \longrightarrow \mathrm{HCl} + \mathbf{5} \tag{8}$$

explained, but an obvious possibility would involve H atom abstraction by Cl$^\bullet$ from an ordinary monomer unit, as in eq 8.

Another autocatalysis mechanism proposed by Troitskii and Troitskaya[5,6,13] was actually the one that they preferred. It involves new reactions 9−11 and, as presented in one publication,[13] includes reaction 7.



$$\mathbf{1} + \mathrm{HCl} \rightleftharpoons \underset{\mathbf{6}}{-\mathrm{CH_2(CH{=}CH)}_n\overset{+}{\mathrm{C}}\mathrm{H}-}\quad \mathrm{HCl_2^-} \tag{9}$$



$$\mathbf{6} \rightleftharpoons \underset{\mathbf{7}}{-\mathrm{CH_2[(CH)}_{2n+1}]^{\bullet\bullet+}}\ \mathrm{HCl_2^-} \longrightarrow \mathbf{3} + 2\mathrm{HCl} \tag{10}$$

$$\mathbf{6} \longrightarrow \mathbf{4} + \mathrm{Cl}^\bullet + \mathrm{HCl} \tag{11}$$

Formation of **3** via eqs 9 and 10 was thought to be much more facile than its formation by eq 4, owing to the ability of HCl to serve as an electrophilic catalyst for C−Cl heterolysis.

The suggested[5,6,13] formation of cation-diradical-containing ion pairs (**2** and **7**) is intriguing and is considered further below. Difficulties arise, however, with other aspects of the mechanisms just described. First, it is not clear why the suggested pathways leading to **3** would necessarily produce a higher concentration of this intermediate than that resulting from the simple thermal excitation of a conjugated polyene sequence. The overall thermodynamics of all of these routes to **3** are the same, and the thermal formation of diradicals (disolitons) from polyacetylene is documented convincingly.[23] Thermal production of solitons from much shorter polyene sequences, such as that in β-carotene, has also been described.[24,25] Moreover, reaction 7 appears even less likely than the unobserved reaction 5, owing to the bond strength difference between HCl and *sec*-C−H (103 vs ca. 98 kcal/mol)[26] and to the much lower concentration of HCl as compared to that of the ordinary monomer units. Finally, reaction 11 is entirely without precedent.

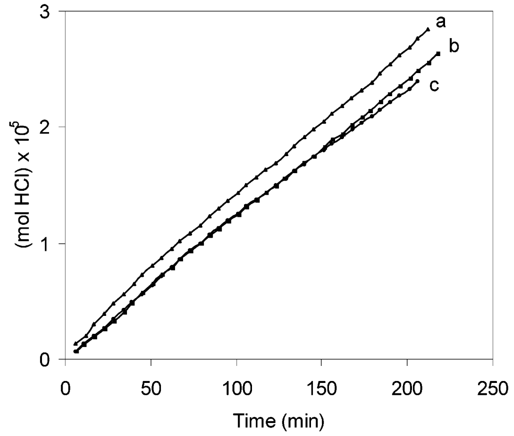


Figure 1. Dehydrochlorination of PVC (100 mg) at 180 °C (mL/min of Ar, mg of BHT): a (10, 0); b (80, 0); c (10, 10).

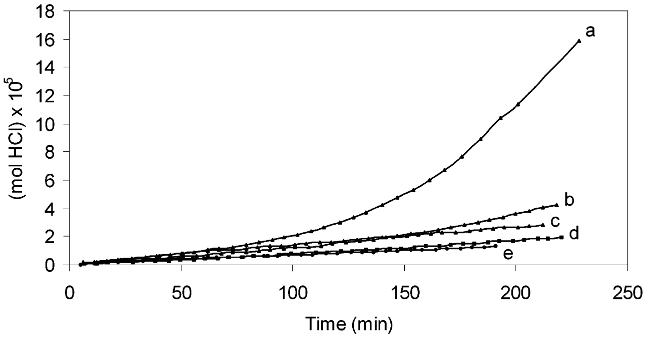


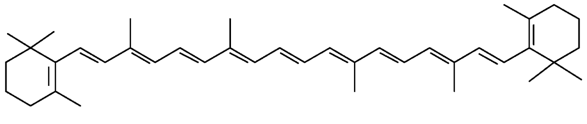
Figure 2. Dehydrochlorination of PVC (100 mg) at 180 °C (mL/min of Ar, mg of **8**, mg of BHT): a (10, 4, 0); b (10, 4, 10); c (10, 0, 0); d (80, 4, 0); e (10, 4, 100).

Results and Discussion

Autocatalysis Revisited: New Experimental Observations. In an attempt to obtain more insight into the mechanism for autocatalysis, we have measured the rates of HCl evolution from powdered PVC and PVC−additive blends at 180 °C under flowing argon, using a procedure that is described in detail elsewhere.[27] The HCl was swept by the gas stream into a vessel containing water and titrated there automatically with aqueous sodium hydroxide.

Plots a and b of Figure 1 show that the rate of dehydrochlorination (as determined from the slopes) was not affected significantly by an 8-fold increase in the rate of argon flow, which would have reduced the HCl content of the atmosphere surrounding the sample. Since no autoacceleration occurred in these two runs, their observed rates were determined entirely by the rate of initiation and the propagation/termination rate ratio, with the amounts of HCl dissolved in the samples being sufficient to maximize these kinetic factors in both cases. A similar situation was described by Hjertberg et al.[17] Furthermore, at 200 min, the polyene concentrations still were quite low, as the extent of dehydrochlorination at that time was only ~1.5 mol %. This observation tends to support the proposition that autocatalysis arises from an interaction of polyenes with HCl. Last, and very importantly, plot c of Figure 1 shows that the well-known free-radical scavenger “BHT” (2,6-di-*tert*-butyl-4-methylphenol) had no appreciable effect on the rate when autocatalysis was not occurring.

In runs a, b, d, and e of Figure 2, the initial presence of polyene sequences was ensured by incorporating a small amount of β-carotene (**8**, nominally all-trans at the outset) into the starting samples. When the ambient concentration of HCl was minimized (in run d), the addition of **8** did not increase the rate (cf. run c of Figure 2). On the other hand, when **8** was present and the HCl content was maximized by reducing the argon flow, a



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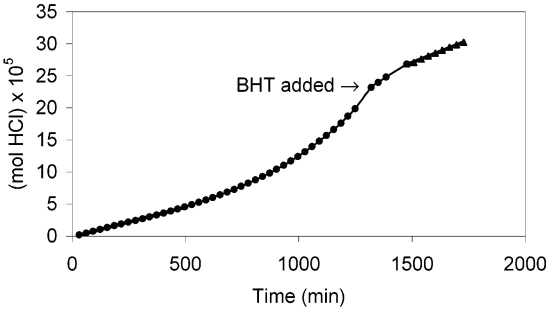


Figure 3. Dehydrochlorination of PVC (100 mg) at 180 °C under Ar (10 mL/min) with addition of BHT (100 mg) at 24 h. See text for discussion.

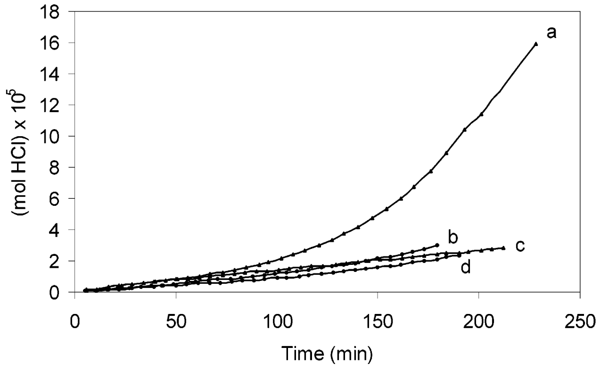


Figure 4. Dehydrochlorination of PVC (100 mg) at 180 °C under Ar (10 mL/min) (mg of **8**, mg of Hg): a (4, 0); b (4, 30); c (0, 0); d (4, 100).

powerful autocatalytic effect was observed. Its temporal profile (run a) closely resembles that reported[24] for the generation of free spins in a similar experiment with **8** and PVC. Moreover, the autocatalysis was greatly reduced (in run b) and eventually obliterated (in run e) by adding increasingly large amounts of the radical scavenger. In the latter run, however, a part of the rate reduction might have resulted from a decrease in the polarity of the medium.

Autocatalysis was also found in the absence of **8** when reaction times were of sufficient length to allow the creation in situ of high polyene concentrations. After 24 h of reaction, the extent of dehydrochlorination was ca. 15 mol %, and the homogeneous blending of BHT with the heavily cross-linked polymer was impossible. Nevertheless, as Figure 3 reveals, the addition of BHT at this point essentially stopped the autoacceleration and thereby provided further evidence for its instigation by free radicals.

As noted above, mercury has been reported to retard the thermal dehydrochlorination of PVC[14,15] and, in so doing, to be converted, in part, into mercurous chloride.[15] In our hands, the preparation of thoroughly homogenized mixtures of PVC and mercury could not be achieved. However, we found that, even so, rather large amounts of mercury effectively thwarted the acceleration of degradation that was caused by **8**. In fact, the rate of dehydrochlorination remained very close to its original (uncatalyzed) level when identical weights of mercury and PVC were used. These effects are illustrated graphically by plots a−d in Figure 4.

The inhibition caused by mercury undoubtedly results, to some extent, from chlorine-atom scavenging involving eqs 12 and 13.[5,6] Reaction 14 is another likely possibility, but the direct scavenging of carbon-centered radicals by mercury is improbable, owing to the very low strength of the C−Hg bond in RHg$^\bullet$ radicals.[28] On the other hand, reaction 15 (where R$^\bullet$ is carbon-centered) seems quite reasonable, and its organometallic product should readily scavenge HCl (eq 16).

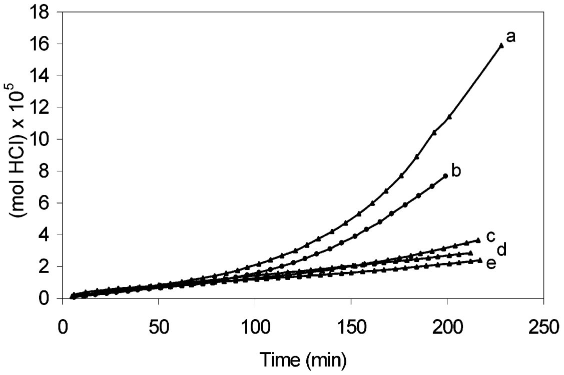


Figure 5. Dehydrochlorination of PVC (100 mg) at 180 °C under Ar (10 mL/min) (mg of **8**, mg of triphenylmethane): a (4, 0); b (4, 20); c (4, 60); d (0, 0); e (4, 100).

$$\mathrm{Cl^\bullet + Hg \rightarrow ClHg^\bullet} \tag{12}$$

$$\mathrm{2\ ClHg^\bullet \rightarrow Hg_2Cl_2} \tag{13}$$

$$\mathrm{Cl^\bullet + ClHg^\bullet \rightarrow HgCl_2} \tag{14}$$

$$\mathrm{R^\bullet + ClHg^\bullet \rightarrow RHgCl} \tag{15}$$

$$\mathrm{RHgCl + HCl \rightarrow RH + HgCl_2} \tag{16}$$

To confirm the expected inability of HCl to react directly with mercury, 0.1 g of the metal was heated in a sealed tube at 180 °C with 2.0 g of 5-chloro-5-methylnonane. After 9 h, analysis by GC/MS showed that 62% (14 mol equiv) of the alkyl chloride had undergone dehydrochlorination. However, visual inspection strongly suggested that the mercury had survived the reaction entirely unscathed.

Various workers have reported the use of triphenylmethane to retard the thermal dehydrochlorination of PVC.[5,6,14,29,30] The retardation mechanism has not been firmly established but is reasonably presumed to involve the abstraction of hydrogen by radicals from the aliphatic C−H bond. Curves a−c and e in Figure 5 show that triphenylmethane was able to reduce the autocatalytic effect of **8**. Though not as efficient in this respect as BHT (cf. the curves in Figure 2), it completely removed the autocatalysis when a sufficient amount of it was present (cf. curves d and e of Figure 5). Significantly, as was the case for BHT and mercury, it had no effect on the rate of dehydrochlorination when autocatalysis was not occurring, apart from a slight decrease in run e that a reduction in medium polarity could have caused.

Does autoacceleration require the presence of HCl at the outset, or will another Brönsted acid suffice? This question was addressed by studying the dehydrochlorination of 4-chloroheptane at 180 °C in the presence of **8** and/or phosphoric acid. The total yield of heptenes was measured, and the data are summarized in Table 1. Runs 1 and 2 listed therein show that, in the absence of H_3PO_4, the extent of dehydrochlorination was insignificant and was not increased by the presence of **8**. The latter observation indicates that neutral diradicals formed from the β-carotene by thermal excitation did not abstract hydrogen from the substrate to form

Table 1. Thermal Dehydrochlorination of 4-Chloroheptane[a]

	additive wt,[b] mg			
run	**8**	H_3PO_4	heptenes, mol %	yield ratio
1	0	0	0.36	1.0
2	40	0	0.34	0.9
3	0	40	4.6 ± 0.9[c]	13
4	40	40	18.4 ± 1.5[d]	51

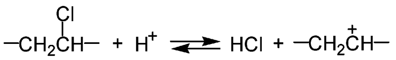
[a] At 180 °C for 8 h in a sealed tube under argon. See Experimental Section for details. [b] Weight of 4-chloroheptane was 400 mg in all runs. [c] Average deviation for five experiments. [d] Average deviation for four experiments.

Table 2. Decarbonylation of 2-Ethylhexanal[a]

	additive wt,[b] mg		
run	**8**	PVC	heptane, mol %
1	0	0	0
2	40	0	0
3	0	160	0.15 ± 0.05[c]
4	40	160	0.28 ± 0.02[c]

[a] At 180 °C for 8 h in a sealed tube under argon. See Experimental Section for details. [b] Weight of 2-ethylhexanal was 400 mg in all runs. [c] Average for two experiments.

β-chloroalkyl radicals (cf. **5**) that were converted by thermolysis into alkenes (cf. eq 6). This finding argues strongly against the occurrence of reaction 5 in degrading PVC. The increased yield of heptenes found in run 3 of Table 1 can be rationalized easily by invoking the acid catalysis of C−Cl heterolysis (eq 17) followed by proton loss (eq 18).[2] However, the strong synergism



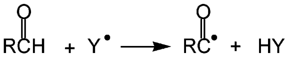
$$-CH_2\overset{Cl}{C}H- + H^+ \rightleftharpoons HCl + -CH_2\overset{+}{C}H- \quad (17)$$

$$-CH_2\overset{+}{C}H- \longrightarrow H^+ + -CH{=}CH- \quad (18)$$

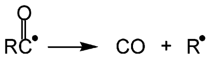
between **8** and phosphoric acid in run 4 seems best explained by an interaction of these two additives to form one or more free-radical intermediates that are not analogous to **3** but can abstract hydrogen from the 3- and 5-positions of the alkyl chloride, nonetheless.

Abstraction from the other positions of 4-chloroheptane may have occurred as well. In that event, the resulting radicals could not have formed heptenes but probably were scavenged by **8** instead.

As a further test for the presence of radicals, the radical-induced decarbonylation of an aldehyde was explored. Such reactions are known to proceed by the mechanism shown in eqs 19−21,[31] where for our system,



$$R\overset{O}{C}H + Y^\bullet \longrightarrow R\overset{O}{C}^\bullet + HY \quad (19)$$



$$R\overset{O}{C}^\bullet \longrightarrow CO + R^\bullet \quad (20)$$

$$R^\bullet + [H^\bullet] \longrightarrow RH \quad (21)$$

R is 3-heptyl; $Y^\bullet$ represents the radical(s) formed from polyenes and HCl; and $[H^\bullet]$ is an abstractable hydrogen atom in the reaction matrix. Runs 1 and 2 of Table 2 show that, under our conditions, the aldehyde failed to decarbonylate thermally or in the presence of **8**. However, a small but reproducible yield of heptane was produced when PVC was added (run 3), and the yield was higher when **8** was present as well (run 4). We regard these results as prima facie evidence for radical intermediates.

The product mixtures formed in runs 3 and 4 of Table 2 were complex and could not be analyzed fully. Possible chemical complications were, inter alia, (a) loss of the $O{=}C^\bullet R$ and $R^\bullet$ radicals via their rapid addition to polyenes[31] and (b) aldol condensation of the aldehyde, which would have been promoted by HCl. In similar experiments, our use of an aldehyde stable to acid, 2,2-dimethyloctanal, afforded intractable mixtures containing none of the 2-methyloctane that would have resulted from reactions 19−21.

Mechanism of Autocatalysis: A New Proposal. When considered within the context of credible earlier findings that were discussed above, our new experimental observations conclusively show that autocatalysis during the thermal dehydrochlorination of PVC involves the reaction of HCl with polyenes in order to form free radicals that attack the ordinary monomer units of the polymer. These units are thereby converted into thermally labile structures that initiate the growth of additional polyene sequences. The attack on the ordinary units is logically formulated as a hydrogen abstraction process that creates radical **5**, which then produces the unstable moiety **1** ($n = 1$) by chlorine-atom β scission (eq 6). What still remains to be addressed is the nature of the initial reactive radical species.

A defensible possibility was previously discussed by one of us.[2] This is the excited cation diradical component of ion pair **7**, which is shown in eq 10. Its potential intermediacy follows by analogy from a speculated[32] thermal equilibration of β-carotene with an orthogonal neutral diradical formed by twisting about the central double bond. Energy comparisons summarized elsewhere[13] and calculated energy barriers for rotation[33] show that the formation of analogous diradicals from conjugated polyenyl cations should be much more facile.[13] As a result, in PVC, the equilibrium concentrations of these cation diradicals might be higher than those of the corresponding neutral diradicals (**3**) formed from neutral polyenes by thermal excitation. Moreover, owing to electrophilicity conferred by the positive charge, the cation diradicals could well be more reactive than **3** in the abstraction of methylene hydrogen from the polymer.

Cation diradicals conceivably could arise from growing polyenes containing a chloroallylic terminus, as shown in eqs 9 and 10. However, polyenes, once initiated, grow and terminate very rapidly.[1,2,4] Hence, even at rather low levels of dehydrochlorination, the concentration of “dead” polyenes (those that no longer have a reactive chloroallylic group) should be much greater than that of **1**. For this reason, the protonation of dead polyenes, P (eq 22), followed by thermal excitation (eq 23) would seem to be a more likely route to cation diradicals than reactions 9 and 10. The diradicals could exist primarily as triplets, but they might be formed from excited singlet diradical intermediates.

$$P + H^+ \rightleftarrows PH^+ \quad (22)$$

$$PH^+ \rightleftarrows PH^{\bullet\bullet +} \quad (23)$$

Cation monoradicals comprise another type of reactive radical species that could result from the interaction of polyenes with HCl. Ample precedent for their formation in similar systems exists. For example, in a seminal study of the protonic acid doping of conjugated polymers, Han and Elsenbaumer[34] showed that, in such situations, cation radical production is a general phenomenon that apparently is effected by reactions 24 and 25. Reactions analogous to the latter one have also been reported by Kispert and co-workers,[35−38] who generated dications from various carotenoids by electrochemical oxidation and provided strong evidence for their subsequent comproportionation with their neutral precursors, C, as in eq 26. In the case of carotenoid **8**, the equilibrium constant for comproportionation (K_{com}) was found to

$$P + 2H^+ \rightleftarrows PH_2^{++} \tag{24}$$

$$PH_2^{++} + P \rightleftarrows PH_2^{\bullet +} + P^{\bullet +} \tag{25}$$

$$C^{++} + C \xrightleftharpoons{K_{com}} 2C^{\bullet +} \tag{26}$$

have a value of 1.22 at ambient temperature in dichloromethane solution.[38] Moreover, Kispert et al.[39] demonstrated that various carotenoids, including **8**, were converted into polyenyl cation monoradicals when they were simply exposed to an excess of HCl (concentration, ∼1 M) in dichloromethane solution. This result also strongly supports the occurrence of reactions 24 and 25 in thermally degrading PVC.

How do the cation di- and/or monoradicals transform the ordinary monomer units into thermally labile sites? As noted above, the simplest and by far the most probable explanation involves the abstraction of methylene hydrogen to form **5**, which then undergoes reaction 6. Potential abstracting species are $PH^{\bullet\bullet +}$, $PH_2^{\bullet +}$, $P^{\bullet +}$, and neutral polyenyl monoradicals resulting from the deprotonation of cation monoradicals. However, the concentrations of these neutral radicals are likely to be insignificant, in view of the very low Brönsted acidity of the cation monoradical formed from **8**.[38] Moreover, the abstraction reactivity of the neutral monoradicals may be much less than those of the related charged species, a suggestion that is consistent with our failure to detect any reaction of PVC, 4-chloroheptane, or 2-ethylhexanal with excited neutral diradicals (cf. **3**) formed from **8** by heating. In any case, it now is apparent that the thermal degradation of PVC will produce many different cation radicals whose specific structures are determined by factors such as the lengths of the precursory neutral polyenes, the position(s) of polyene protonation,[33] cis−trans isomerism,[32,33,39−41] and various reactions of the polyenes and cation radicals that change their sequence lengths.[33,40,42−44] All of the cationic radical species are potentially able to abstract a hydrogen atom from the polymer.

Conventional wisdom holds that phenols such as BHT are ineffective traps for carbon-centered radicals.[45] However, this belief is based primarily on the behavior of phenols as antioxidants. In autoxidations that are not oxygen-starved, carbon-centered radicals are not efficiently trapped by most phenols, because they are converted very rapidly into peroxy radicals, highly electrophilic species that are quickly scavenged instead.[45−47] Reactions of carbon-centered radicals with phenols can actually be quite fast,[46,48] and they may be even faster when the radicals are made electrophilic by the presence of a positive charge. Thus, the inhibition of autocatalysis by large amounts of BHT, as revealed in Figure 2, is by no means inconsistent with the abstraction of hydrogen from the polymer by carbon-centered cation radicals.

If such intermediates were indeed the only initial H abstracters, autocatalysis would not be avoided by chlorine-atom entrapment per se, because chlorine atoms and labile defects are generated simultaneously (eq 6). Chlorine-atom scavenging would, however, tend to prevent the formation of additional labile sites in a chain reaction consisting of eqs 6 and 8. Reaction 15 (where $R^\bullet = \mathbf{5}$, $PH^{\bullet\bullet +}$, $PH_2^{\bullet +}$, $P^{\bullet +}$) and reaction 16 could also contribute to the inhibition caused by mercury, but even so, the ability of this additive to prevent all of the autocatalysis (see Figure 4) compels one to address the possibility that the initial H abstracters are actually chlorine atoms. These are unlikely to be formed directly from HCl by hydrogen transfer, owing to the high dissociation energy of the H−Cl bond,[26] but an alternative possibility is the β scission (eq 6) of allylic C−Cl bonds in cation radicals. On the other hand, the presence of such bonds in the cation radicals formed from dead polyenes is uncertain, and even though the readdition of HCl to dead polyenes can occur to some extent,[49] it may form carbenium chloride ion pairs[50] instead of covalently bonded chlorine when it takes place at the temperatures that degradation requires.

Summarizing the discussion in this section, we conclude that cation radical intermediates are intimately involved in autocatalysis and that this process involves the abstraction of methylene hydrogen atoms from ordinary monomer units. However, the identity of the abstracting radicals remains to be established. The literature contains conclusive evidence for the formation of cation monoradicals from polyenes and HCl, and the presence of excited cation diradicals in such systems is still a reasonable possibility.

Related Studies. Zuoyun et al.[51] have argued emphatically that free radicals are not involved in the thermal dehydrochlorination of PVC. This conclusion was based primarily on (a) the failure of a hindered phenol and a polymeric nitroxyl radical to affect the rate, (b) a lack of ESR evidence for consumption of the nitroxyl during degradation, and (c) the failure of an arylnitroso spin trap to scavenge any radicals while the reaction was in progress. However, all of these results were obtained in experiments where autocatalysis did not occur, apparently because it was prevented by the use of very dilute solutions of PVC, very low extents of conversion, and low concentrations of HCl caused by rapid bubbling with nitrogen. For this reason, the authors' findings[51] do not relate in any way to the mechanism for autocatalysis, though they do confirm the absence of radicals from the earlier stages of degradation.

In a study reported by van Hoang and Guyot,[49] small amounts of **8** decreased the rate of HCl evolution from heated solutions of PVC in 1,2,4-trichlorobenzene. This effect apparently resulted from the reversible addition of HCl to the carotenoid polyene system. At 195 °C, increasing amounts of **8** caused further rate reductions until the initial concentration of the additive had reached a certain level. Surprisingly, the use of additional **8** at this point then caused a rate enhancement. Apparently inexplicable when it was first obtained, this result now seems consistent (qualitatively) with the occurrence of autocatalysis by the mechanism we propose, the importance of which would increase, of course, with increasing amounts of additive **8**.

Tran et al.[12,24,25,52] have suggested a polaron (cation radical) mechanism for the thermal degradation of PVC and have argued for its operation in several publications that were recently reviewed in detail.[12] As formulated by its originators, the polaron scheme is strictly a mechanism for normal chain propagation. It does not address the question of autocatalysis, and it suffers from several deficiencies that have been discussed elsewhere.[2,3] Nevertheless, its postulation has had heuristic value, for it apparently was the first mechanism (and, for several years, the only one) to consider the possibility that cation radicals are involved in the thermolysis of PVC.

Conclusions

The new mechanism for PVC degradation that has been presented here accounts for several features of the process that have been puzzling heretofore. These relate not only to catalysis by HCl but also to the evidence for the involvement of free radicals and to the initiation of polyene growth from ordinary monomer units.

Previous work has shown that dehydrochlorination begins primarily at thermally labile defect sites. They start the growth of conjugated polyenes in a process that is either ionic or quasiionic but certainly does not involve free radicals. When the concentrations of HCl and polyenes have reached a certain level, these products react to form polyenyl cation radicals that lead to autocatalysis. The cation radicals are either monoradicals or excited diradicals, and the autocatalysis involves the abstraction of methylene hydrogen from ordinary monomer units in order to form new radicals that are also carbon-centered. However, the identity of the abstracting species is not entirely clear. The new radicals are converted by chlorine-atom β scission into allylic chloride structures that can start the growth of new polyene sequences in the conventional way.

Experimental Section

Materials. Poly(vinyl chloride) with $M_n = 1.96 \times 10^4$ and $M_w = 3.88 \times 10^4$, 2,6-di-*tert*-butyl-4-methylphenol (BHT, nominal purity, 99+%), triphenylmethane (nominal purity, 99%), all-trans-β-carotene (**8**, nominal purity, 95%), mercury (nominal purity, 99.9995%), and phosphoric acid (nominal purity, 99.999%) were obtained from Aldrich. The other chemicals were purchased from various suppliers and had the highest available purities. Purities of organic materials were confirmed by NMR and/or (gas chromatography)/(mass spectrometry) (GC/MS) measurements.

Instrumental Analysis. A Varian Mercury VX-400 spectrometer was used to record ^{1}H NMR spectra at 400.128 MHz and proton-decoupled ^{13}C NMR spectra at 100.623 MHz. The spectra were obtained at ambient temperature from chloroform-*d* solutions containing Me_4Si ($\delta = 0.00$ ppm) for internal standardization.

The GC/MS measurements were made with a Hewlett-Packard HP 5890*A*/5988A apparatus that was equipped with a fused-silica HP-1 capillary column [cross-linked methylsilicone, 12 m × 0.2 mm (i.d.), 0.33 mm film thickness]. Helium was used as the carrier gas, and the column temperature was increased from 50 to 300 °C at the rate of 20 °C/min.

Preparation of 4-Chloroheptane. A solution of sodium borohydride (7.13 g, 189 mmol) and sodium hydroxide (1.5 g) in water (300 mL) was added dropwise to a stirred solution of 4-heptanone (10.0 g, 87.6 mmol) in ethanol (400 mL) while the temperature was kept at ca. 10 °C by external cooling. The resulting mixture was stirred for 12 h at room temperature and then acidified with dilute aqueous HCl and extracted with ether (3 × 300 mL). The combined extracts were washed with brine (3 × 300 mL), dried over anhydrous $MgSO_4$, and freed of solvent by rotary evaporation under vacuum, to obtain 10.0 g (yield, 98%) of residual 4-heptanol that was used without purification in the following step.

Under an argon atmosphere, thionyl chloride (20.5 g, 172 mmol) was added dropwise with stirring to a mixture of pyridine (3 mL, 37 mmol) and 4-heptanol (10.0 g, 86.1 mmol) while the temperature was kept at 0−5 °C with an ice bath. When the addition was complete, the mixture was stirred and heated at 85−90 °C for 3 h, cooled to room temperature, treated with ice water (100 mL), and extracted with ether (3 × 200 mL). The combined extracts were washed in succession with 3% aqueous $NaHCO_3$ (2 × 150 mL) and water (2 × 100 mL), dried over anhydrous $MgSO_4$, and concentrated in a rotary evaporator under aspirator vacuum. Short-path distillation of the residue afforded 6.0 g (yield based on starting ketone, 51%) of 4-chloroheptane (bp 78−80 °C at 60 Torr) in a purity of ~100%, according to GC/MS analysis: *m*/*e* 98 ($M^+ - HCl$). ^{1}H NMR: δ 0.93 (t, 6H, $2CH_3$), 1.4−1.6 (m, 4H, $2CH_2$-CH_3), 1.6−1.7 (m, 4H, $2CH_2CHCl$), and 3.91 ppm (qnt, 1H, $CHCl$). ^{13}C NMR: δ 13.91 (C-1, −7), 20.04 (C-2, −6), 40.94 (C-3, −5), and 63.87 ppm (C-4).

PVC Dehydrochlorination Kinetics. Dehydrochlorinations were carried out under flowing argon in a glass vessel thermostated at 180 ± 1 °C, using a Metrohm 702 SM Titrino apparatus for automatic titration by a procedure that was previously described.[27] The evolving HCl was swept by argon into water and titrated periodically with 0.01 N NaOH in order to maintain a solution pH of 7.10. Each sample, including those with additives, contained 0.100 g of PVC. The PVC−additive mixtures were prepared by grinding with a mortar and pestle, and they afforded aliquots whose titration curves were highly reproducible in the replicate experiments (at least 2−3) that were performed for each composition. Compound **8** was stored in the dark under argon at 0−5 °C. Blends containing this additive were made in a drybox under argon and kept under argon protection before being used in kinetic runs. Deterioration of **8** with time was ruled out by the excellent reproducibility of the results obtained in control runs that were performed at frequent intervals with mixtures of **8** and PVC.

Dehydrochlorination of 4-Chloroheptane. The reactants were thoroughly degassed on a vacuum manifold, sealed in a heavy-walled glass tube in a drybox under argon, and heated for 8 h at 180 ± 1 °C. The percentage conversion into heptene isomers was then determined by GC/MS analysis. Details of these experiments are summarized in Table 1.

Decarbonylation of 2-Ethylhexanal. The procedure used was identical to that for the experiments with 4-chloroheptane. After 8 h of heating under argon at 180 ± 1 °C, GC/MS analysis gave the results in Table 2.

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