Hydrogen Halide-Catalyzed Thermal Decomposition of Poly(vinyl Chloride)

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ABSTRACT

The thermal decomposition of solid PVC was studied in the presence of added hydrogen chloride and hydrogen bromide over the temperature range 170-210°C. Under certain conditions the decomposition was shown to be dependent in a first-order manner on the hydrogen halide pressure. These gases acted as catalysts, increasing the rate of HCl evolution and the degree of discoloration but not producing longer polyene sequences. Activation energy for the HCl-catalyzed process was found to be similar to that of the uncatalyzed decomposition of PVC. A unified mechanism is presented for an overall process consisting of three steps: random generation of a single carbon-carbon double bond in the cis configuration; 1,4-elimination of HCl via a six-centered transition state yielding a polyene; HCl- or HBr-catalyzed isomerization of the polyene formed by HCl elimination to regenerate the initial structure. Hydrogen chloride catalysis is seen as an integral part of the overall process.

INTRODUCTION

Considering the large number of investigations reported on the thermal degradation of poly(vinyl chloride), PVC, it is remarkable that even at the present time no coherent mechanism has emerged.

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This polymer cannot be fabricated commercially at high temperatures (i. e., > 150°C) unless it is stabilized. Stabilizers are believed to act in several ways [1], one of which involves absorbing the evolved hydrogen chloride to arrest an autocatalytic reaction. However, little is known about the nature of the autocatalytic process in solid PVC and whether it occurs during the "normal" degradation of PVC, i. e., in the absence of large amounts of added hydrogen chloride. Degradation in the presence of added hydrogen chloride, although demonstrated qualitatively [2-10] has not been subjected to a quantitative test because of the difficulty in determining accurately the small difference, due to evolved HCl, between the initially added pressure and the total pressure after a given time.

In the present study we wish to report on the HCl- and HBr-catalyzed thermal decomposition of PVC. In addition, we wish to propose a new mechanism for PVC degradation which will be based upon our results and on several new developments reported in the PVC literature.

EXPERIMENTAL

Materials

Poly(vinyl chloride), Geon 101EP resin was kindly donated by Goodrich Chemical Co.; $\overline{M_w}$ = 240,000, $\overline{M_n}$ = 70,000.

This polymer was free of stabilizers, plasticizers, and other additives.

Tetrahydrofuran (THF), Merck Reagent Grade, was purified by refluxing with stannous chloride followed by distillation. Only peroxide-free solvent was used.

Hydrogen chloride and hydrogen bromide (Matheson Research Grade) were stored under vacuum in darkened bulbs and were outgassed prior to use.

APPARATUS

Degradation experiments were carried out on PVC powder in a specially designed reaction vessel. The vessel consisted of a cylindrical Pyrex tube (20 cm long, 1.5 cm diameter) connected via narrow tubing to a cylindrical quartz tube (20 cm long, 2.0 cm diameter), which was placed within the optical path of an infrared spectrometer (perkin-Elmer, model 580). The entire assembly could be attached to a vacuum line. Degradation experiments were performed by placing the reaction vessel in an electrically heated furnace controlled to within 1°C by a West Gardian temperature controller. Progress of the reaction was monitored by measuring the absorbance

due to gaseous HCl at 2963 cm^{-1}. A linear calibration plot of known HCl pressures versus absorbance at the various temperatures justified the quantitative measurement.

In a typical run the PVC powder, 0.500 g, was placed in the reaction vessel and was outgassed by pumping to 5×10^{-3} torr for 30 min or longer. A measured pressure of hydrogen halide was admitted into the reaction system, which was then removed from the vacuum line and placed simultaneously into the oven and into the optical path of the spectrometer. At the end of each run the HCl was pumped off from the reaction system, and the degraded polymer was then collected for polyene analysis.

Polymer solutions were prepared by dissolving PVC in the THF (0.1 g/100 cm^3). Polyene spectra were then examined on a Varian Techtron UV-VIS spectrophotometer, model 635A. A reference cell loaded with the THF eliminated any signals due to the solvent itself. Only samples degraded to 1% or less of available HCl were examined by UV spectroscopy, since those with more extensive degradation were only partially soluble in THF. The latter included all samples degraded with more than 2 cm Hg of hydrogen halide.

RESULTS AND DISCUSSION

The thermal degradation of PVC can be summarized by the phenomena listed below and by the following stoichiometric (1).

$$-(CH_2CHCl)_m\!-\!CH_2\!-\!CHCl- \longrightarrow$$

$$-(CH_2CHCl)_{m-n}\!-\!(CH\!=\!CH)_n\!-\!CH_2\!-\!CHCl- + nHCl \qquad (1)$$
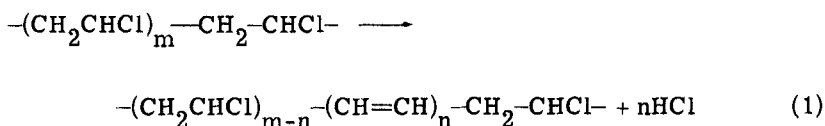
This reaction is generally followed by measuring the rate of HCl evolution and is often accompanied by the determination for the value of n in Eq. (1), usually by UV absorption spectroscopy, and recently by resonance Raman spectroscopy [10]. Typical values of m are of the order of 10^3 and of n between 2 to 15 [11-13]. It is the long polyene sequences which absorb in the visible regions that are responsible for the undesirable discoloration that would develop during processing of PVC, if it is left unstabilized. Development of long sequences ($\geq$ 5) even when as little as 0.1% of the available HCl is lost, has led some workers to consider that the polyene propagation mechanism must involve a radical chain process [2]. In some studies certain free-radical inhibitors have reduced the HCl evolution rate [14], but the polyenes sequences were still long, as demonstrated by the color. However, in the presence of certain stabilizers, the number of conjugated double bonds decreases sharply, yielding only dienes and trienes [11]. The value of n also decreases when the

temperature of degradation is increased [2, 12] but is higher for films than for powdered PVC [2, 13]. When PVC powder of different particle sizes was studied, an enhancement of HCl evolution was observed and this was attributed to the slow diffusion of HCl trapped within the large particles [7]. While PVC is now considered to be a partially crystalline polymer [15], high syndiotactic content has been correlated with enhanced reactivity and long polyene sequences [16-18]. There is also evidence that the polyenes formed in radiation induced degradation are in the all-trans form [18], while it is suggested that those formed in thermal degradation in solution are the cis-polyenes [19]. However, evidence for the latter appears to be rather tentative.

Yet, the following features of this complex reaction still remain unresolved: (a) Does the degradation proceed by molecular or free radical process? (b) Is the HCl catalysis a separate reaction or a part of the overall process involved in the formation of polyenes? (c) Why does the unzippering process that leads to the formation of polyenes terminate when n is 3-15 in PVC, but when n is 5-40 in the case of PVBr [12]? It is because of (c) that we have decided to examine the effect of HBr as well as that of HCl on PVC degradation.

The results shown in Fig. 1 demonstrate that HCl does indeed accelerate the evolution of HCl from PVC. With pressures up to about 5 cm Hg of added HCl, the rate of evolution of HCl appears to behave in a first-order manner with respect to added HCl, though at higher pressures the acceleration is diminished while at the very pressure of 25 cm Hg this acceleration becomes retarded. At other temperatures, similar behavior has been observed although the effect of HCl is much smaller below 190°C. The effect of HBr, demonstrated in Fig. 2 for 190°C, is similar to that of HCl, except that the acceleration is more marked. ·

THF solutions of samples of PVC degraded to approximately the same extent (i. e., loss of 1% of available HCl) were examined by UV spectroscopy. These included the following samples of PVC: without added hydrogen halide; in the presence of 1 cm of hydrogen halide; and without added hydrogen halide and in which the evolved HCl was pumped away as soon as it was formed. (This was accomplished by degrading the sample while it was connected to the vacuum line). As demonstrated in Fig. 3, a single spectrum is found for all of these samples, indicating little difference in the polyene distribution. Thus, although HX catalysis increases the rate of evolution of HCl and the production rate of polyenes, judged by discoloration, the sequences themselves are not lengthened.

The rate constants for the degradations can be derived from the two expressions (2, 3):

$$\text{Rate}_{\text{uncat}} = k_1 [\text{PVC}] \tag{2}$$

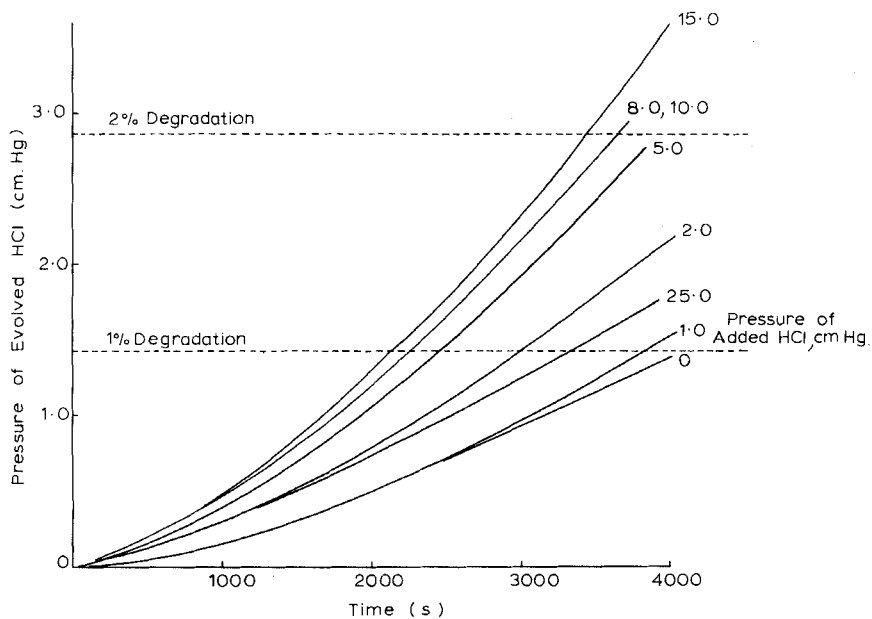$$\text{Rate}_{\text{cat}} = k_{\text{cat}} [\text{PVC}][\text{HCl}] \tag{3}$$

FIG. 1. Pressure of evolved HCl vs. time in the presence of added HCl; degradation at 190°C.
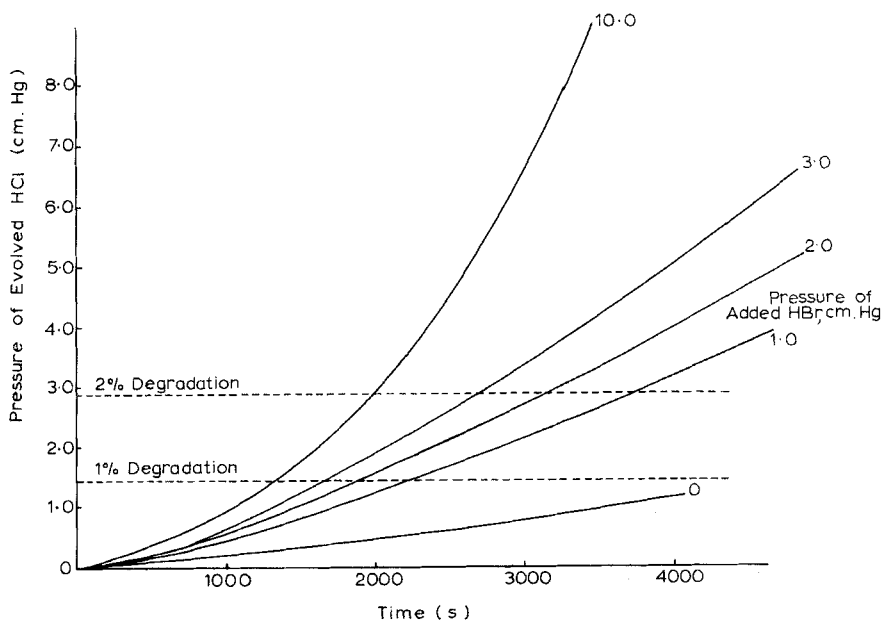

FIG. 2. Pressure of evolved HCl versus time in the presence of added HBr; degradation at 190°C.
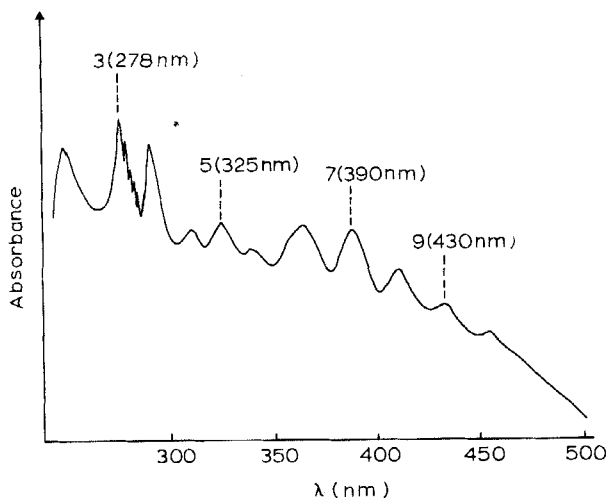
FIG. 3. Absorption spectra of PVC Samples degraded at 190°C to extent of 1%; 1 mg PVC/ml THF.

Since in uncatalyzed and the catalyzed experiments both [PVC] and [HCl] added were always kept constant and since the measurements were restricted to early stages of the degradation, the rate constants are directly related to the rates by the constant factor of concentrations. Therefore, rates determined from the pressure of evolved HCl versus time (e. g., Fig. 1), rather than rate constants may be used in examining the temperature dependence of the two processes. This procedure is only valid for the estimation of activation energies, and does not apply to the preexponential factors. Arrhenius plots for the two degradations are shown in Fig. 4. For the uncatalyzed reaction an activation energy of 24.5 ± 1.1 kcal/mole (90% confidence limits), which agrees well with the previously reported estimate for this particular resin [14], is found. The HCl-catalyzed process performed with a constant pressure of 2 cm Hg of HCl, displays little difference in activation energy from the uncatalyzed process i. e., 27.2 ± 0.9 kcal/mole. HBr-catalyzed degradations were also not considered to be sufficiently quantitative due to an error arising from ineffective mixing of the evolved hydrogen chloride and the added hydrogen bromide. This was reflected in a small apparent increase in the IR absorbance peak of HBr during the course of reaction.

We now wish to propose a new, unified mechanism for the overall process, of which HX catalysis is but a part. This mechanism is consistent with the data presented above and with the numerous
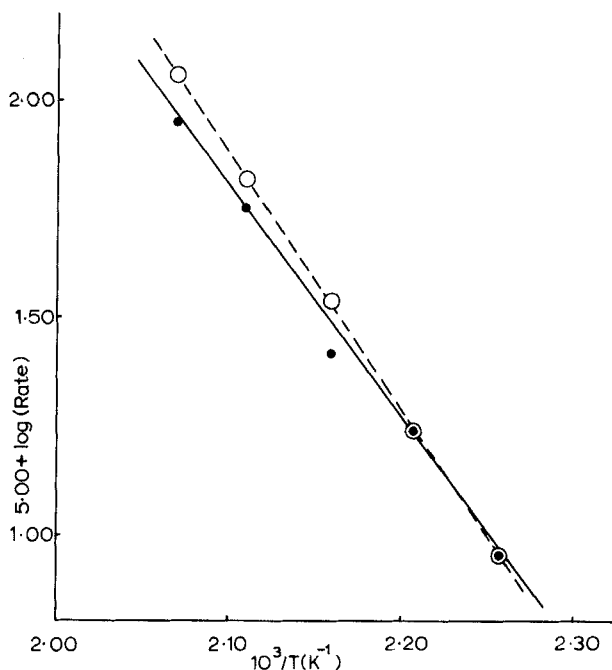
FIG. 4. Arrhenius plots for the degradation of PVC (o) in the presence of 2 cm HCl and (•) without HCl. Each point shown represents an average of 2-3 runs.

experiments previously reported in the literature. This proposal relies heavily on comparisons made between unimolecular gas phase HX elimination reactions, often described as quasi-heterolytic processes [20, 21], and the degradation of solid PVC in the absence of solvent. We believe such a comparison is appropriate and valid. Furthermore, the proposed mechanism is considered to be applicable only for the early stages of the decomposition and comprises three principal steps.

Step 1. Step 1 is formation of a single carbon-carbon double bond randomly along the chain. This may occur via a free radical process, or via a 1,2-unimolecular elimination of HCl, as in isopropyl chloride. Step 1 is considered to be the slow, rate-determining step and is shown in more detail in Fig. 5. "Abnormal" structures are those that have a weak C–Cl bond of an allylic or a tertiary nature. In PVC samples where isolated double bonds are formed prior to degradation, e. g., due to termination by disporportionation during the formation of the resin, high reactivity is expected. Initiator residues may also produce chlorine atoms via a series of reactions,

molecular path   radical chain path

cis or trans double bond
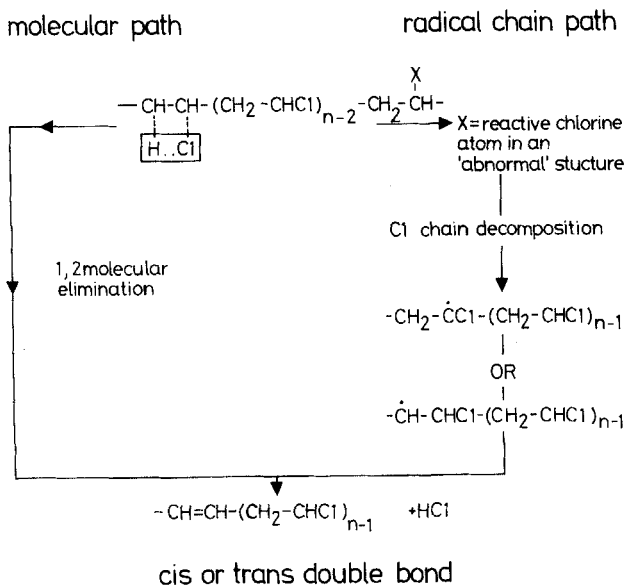
FIG. 5. Step 1: generation of a cis double bond.

starting from hydroperoxides or peroxides and leading to a chlorine atom chain process. Only macromolecular radicals in which the β hydrogen atoms were abstracted are capable of supporting the chain process.

In steps 2 and 3, propagation of polyene sequences is visualized as occurring as a series of molecular steps involving: (step 2) 1,4-cis elimination of HCl resulting in a diene or polyene and (step 3) a HCl-catalyzed double bond shift to regenerate the structure that is necessary for step 2 to recur. Repetition of steps 2 and 3 may continue as long as that section of the polymer backbone possesses syndiotactic conformations and is free of other structural defects. These reactions are illustrated in Fig. 6.

A competing reaction is

$$-(CH{=}CH)_{n}- + HCl \longrightarrow -(CH{=}CH)_{a}-CH_{2}-CHCl-(CH{=}CH)_{b}-$$
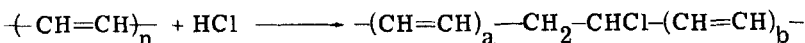
where $(a + b) = (n - 1)$.

Evidence in favor of steps 1-3 and against some previously proposed mechanisms will now be considered.

Allylic activation in radical chain processes has been discussed previously [2, 7, 11, 12, 22]. In such activation, chlorine atoms are postulated to abstract the allylic β-hydrogen atoms, since it is only

$$
\begin{array}{c}
\underset{|}{Cl} \quad \underset{H}{\diagup} \quad \underset{Cl}{\diagdown} \qquad\qquad\qquad \underset{|}{Cl} \\
-CH-CH \qquad CH-CH_2-CH-CH_2-CH \\
\diagdown \quad \diagup \qquad\qquad | \\
CH=CH \qquad\qquad Cl
\end{array}
$$

syndiotactic sequence of length n.

step 2   cis 1,4-elimination

$$
\begin{array}{c}
\underset{|}{Cl} \qquad\qquad\qquad\qquad \underset{|}{Cl} \\
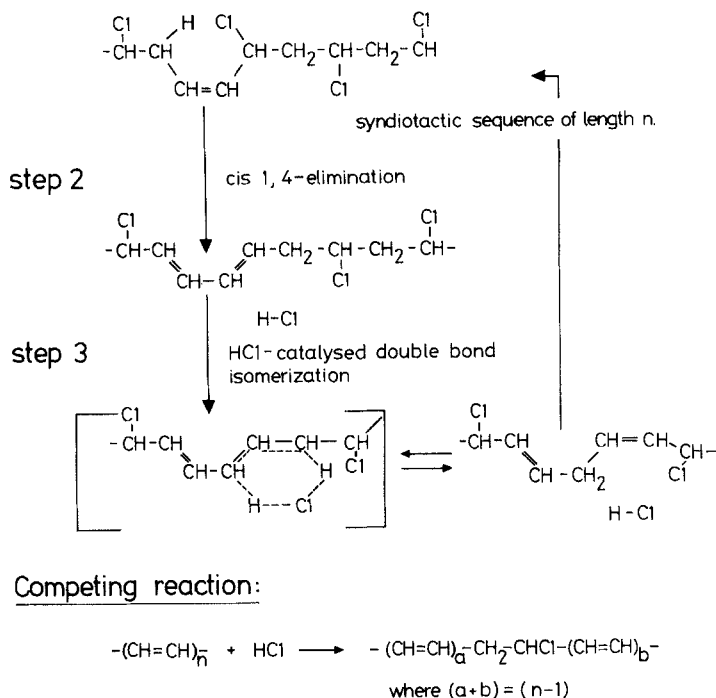-CH-CH \qquad CH-CH_2-CH-CH_2-CH- \\
\diagdown\!\!\!= \quad \diagup \qquad\qquad | \\
CH-CH \qquad\qquad Cl
\end{array}
$$

H-Cl

step 3   HCl-catalysed double bond
                    isomerization

-(CH=CH)$_n$ + HCl $\longrightarrow$ -(CH=CH)$_a$-CH$_2$-CHCl-(CH=CH)$_b$-

Competing reaction:

where (a+b) = (n-1)

FIG. 6. Steps 2 and 3: propagation of polyenes.

the resultant radicals that can lead to a chain process and long poly-
ene sequences. Radicals formed by abstraction of α hydrogens are
incapable of decomposing to yield chlorine atoms and therefore
undergo termination by crosslinking [23, 24]. Chlorination studies
of olefins [25] reveal that: (a) addition of Cl to a double bond is more
highly favored than abstraction of an allylic hydrogen and (b) that Cl
atoms are unselective towards the type of hydrogen they abstract.
These features certainly do not preclude the formation of a single
double bond or even an occasional diene but must exclude the forma-
tion of a long polyene sequence via a radical chain process [26].

In a randomly generated double bond in PVC, there are allylic
hydrogen atoms on one side and an allylic chlorine on the other side
of the double bond. The possibility of a single double bond enhancing
the reactivity of neighboring monomer units in terms of molecular
elimination of HCl has been considered by other workers [7, 11, 12,
22], though no experimental evidence for such a process has ever
been presented in the PVC literature. In gas-phase reactions of alkyl
bromides it has been shown that the presence of an allylic hydrogen
does not enhance the rate of elimination of HBr from 4-bromopentene-1

relative to 2-bromobutane [27]. Unfortunately the corresponding
model of 3-bromopentene-1 was not studied as well. However, an
extensive discussion of gas phase pyrolysis of allylic chlorides which
occur via a molecular pathway by Maccoll and co-workers [28, 29]
highlights the following important features: α-vinyl substitution does
not produce a marked accelerating effect; allylic chlorides with a cis
configuration undergo faster HCl elimination than the corresponding
trans isomer [30] (e. g., cis-α,γ-dimethylallyl chloride versus trans-α,γ-
dimethylallyl chloride); in the gas phase, unlike the situation in solu-
tion, γ,γ-dimethylallyl chloride pyrolyzes faster than its α,α-isomer.
These faster reactions have been attributed to 1,4-eliminations pro-
ceeding via six-membered transition states analogous to those in
pyrolysis of esters [21]. Thus, in summary, we note that the pres-
ence of a double bond does not activate the allylic molecule signifi-
cantly, nor could it activate further 1,2-elimination since the most
likely reaction to occur in 1,4-elimination, as postulated for step 2.
This will be discussed below in greater detail.

Coexistence of molecular and radical chain processes as proposed
for path 1 can resolve the uncertainty often expressed regarding the
nature of the degradation mechanism. In a previous paper [14] it
was suggested that the molecular path predominates at high tempera-
tures, i. e., above 200°C, since a larger activation energy is in-
volved than for an overall activation energy for a chain process.
It is of interest that an activation energy of 40.3 kcal/mole has also
been reported by Figge and Findeiss [31] for PVC stabilized with an
organotin compound, this being about 27 kcal/mole higher than for
the same PVC resin when unstabilized. The action of the stabilizer
is suggested to be due to the elimination of most of the abnormal
structures, leaving the molecular path to be the one possible one.

Step 2.   Perhaps the best available model for step 2 in PVC
is that of cis-α,γ-dimethylallyl chloride to 1,3-pentadiene and HCl.
Although the Arrhenius parameters for this decomposition are not
stated, its rate constant was found to be 5.5 times faster than that of
γ,γ-dimethylallyl chloride at 293.5°C [28]. From the known param-
eters of the latter, and therefore on the assumption of a similar
preexponential factor to that for γ,γ-dimethylallyl chloride pyrolysis
[27], the activation energy for HCl elimination from cis-α,γ-dimethyl-
allyl chloride is estimated to be 36.4 kcal/mole. It is now possible
to make comparisons of relative rates for unimolecular HCl elimi-
nation at a temperature where PVC degrades at a reasonable rate,
e. g., 190°C. This is shown in Table 1.

It is seen that at 190°C, while introduction of a double bond en-
hances reactivity by approximately a factor of 13, 1,4 vs 1,2-elimina-
tion is favored by a factor of about 10^4 and is therefore a much more
probable process.

In step 1, both cis- and trans-double bonds may be formed, but
only the former will lead to step 2. For comparison, in gas-phase
pyrolysis of sec-butyl chloride the proportions of cis and trans

TABLE 1. Rates of Reactions of Allyl and Alkyl Chlorides (T = 190°C)

Chloride	Relative rate of pyrolysis	Reference
Isopropyl chloride	1	[32]
α-Methylallyl chloride	13	[31]
Cis-α,γ-dimethylallyl chloride	1.1×10^5	[28]

butene-2 formed are approximately equal [33]. Similar ratios are expected in PVC.

It is proposed that the mechanism for the HCl or HBr catalyzed isomerization of the double bond in PVC is akin to one proposed by Ross and Maccoll [34] for HBr-catalyzed butene-1 isomerization. The superiority of HBr over HCl in PVC degradation is consistent with its behavior as a molecular gas phase catalyst [35]. Conversion of a conjugated double bond system to two isolated double bonds merits careful consideration, since at first it would appear to be thermodynamically untenable. However, it is the allylic chlorine substituent that makes the process more likely. In the absence of suitable model compounds we can first compare cis- or trans-1,3 pentadiene with 1,4-pentadiene at 450°K, where differences in the ΔG_f° of about 5 kcal/mole are reported [36] - a rather large amount.

Now, comparing allyl chloride with propylene, ΔG_f° for the former is about 4.5 kcal/mole less than for the latter. Thus the double-bond-isomerization step is feasible, since only a small difference exists between the standard free energy of formation of the reactants and products of step 3. Nevertheless, it is not expected to occur extensively. Slow diffusion of HCl away from its evolution site could be expected to increase the probability of step 3. The HX-catalyzed isomerization step is consistent with the observation of first-order dependence on HCl, if the concentration of HCl "dissolved" within the polymer is directly proportional to its gas phase concentration. Reaction order with respect to PVC must necessarily be unity.

Complete unzipping of a syndiotactic sequence of length n to the corresponding polyene will depend on a number of factors, such as concentration of HCl "dissolved" in the polymer matrix, presence of branching, thermal history, and degradation temperature.

In two recent publications [9, 37] it was stated that the proportion of longer polyene sequences increases relative to the shorter ones as the degradation proceeds, that situation applying to very low extents of dehydrochlorination, i. e., 0.1%. At more extensive levels, the polyene ratios tend towards a constant value. In one study [9],

the catalytic effect of HCl on the relative polyene sequences was re-
ported for a flow system. Here at low levels of added HCl longer
polyenes were found than when pure nitrogen was used as carrier,
however at higher added HCl levels the polyene distribution became
invariant, irrespective of conversion or HCl level. Both these situa-
tions can be explained in terms of step 3, when the concentration of
"dissolved" HCl is insufficient both at low conversions and at low
HCl pressures to allow the unzippering of the syndiotactic segments
of the chain to develop fully.

Not only is it necessary for the polymer chain to possess a
significant length of tactic perfection, but it is also important for
other structural imperfections to be absent. Abnormal structural
units [16] containing methyl, chloromethyl [38], or allyllic C-Cl
groups are expected to exercise a dual effect on the stability of the
resin in the manner described below. Recent estimates [39, 40] of
short-chain branching (2-6/1000C) and long-chain branching
($\sim$0.5/1000C) show these to be sufficiently infrequent to interfere
with step 3.

Ability of hydrogen ions from trifluoroacetic acid to lengthen
polyene sequences in degraded PVC resins dissolved in dichloro-
methane is discussed in a recent paper [41]. However, this cannot
be compared with the present thermal decomposition of solid PVC.

The thermal history of PVC is known to influence its physical
properties, hence it is likely to affect is thermal stability [42].
PVC films prepared under pressure at 160°C are expected to have
undergone a certain amount of annealing, this resulting in a higher
level of crystallinity than for untreated samples. Experimental
observation [13] of longer polyenes in degraded films than in powders
suggests that the alignment and orientation of some of the macro-
molecular chains during the preparation of the films is favorable
in achieving the maximum development of the polyene sequences
from the syndiotactic sections of the chain via steps 2 and 3. An
interesting example further supporting this idea is provided by the
highly syndiotactic and crystalline PVC synthesized by the urea
clathrate method [43]. This resin tends to darken at temperatures
as low as 150°C.

Back addition of HCl to polyenes appears to become an important
process only at high HCl pressures at a given temperature. For the
solvolytic degradation, HCl inhibition has even been reported [44];
however, the full spectrum ranging from catalysis to inhibition, as
demonstrated in Fig. 1, has not been reported in previous studies.
From a thermodynamic viewpoint, the addition of HCl to polyenes
could be expected to be less favored by high temperatures (by
analogy to HCl addition of olefins [36]). Actual observation of
shorter rather than longer polyenes with increasing temperature
[13] supports the proposal of crosslinking and other secondary
processes [12, 23, 24] occurring extensively at the higher tem-
peratures.

While polyene propagation via steps 2 and 3 is consistent with enhanced reactivity due to added HBr relative to HCl, the superiority of HBr as a gas phase catalyst cannot by itself account for the longer polyene sequences observed in PVBr degradation [12]. It is also significant that, even in the thermal decomposition of PVC, added HBr does not lead to longer polyene sequences than HCl. Hence it is suggested that the factor controlling the length of polyene sequences is the existence of rather long syndiotactic sequences up to about 13 in PVC, and much longer ones in PVBr.

No more than four or five consecutive syndiotactic sequences can be resolved even via the use of high resolution ^{13}C-NMR spectroscopy [45]. Furthermore, several workers have indicated that the observed levels of crystallinity in PVC [46, 47], and its gels [48] are consistent with about 10-13 consecutive syndiotactic units in the chain. Very recently, the first direct experimental evidence for the existence of long tactic segments in commercial PVC resins was presented [49]. This involved x-ray diffraction studies of highly oriented PVC filaments. Assuming the applicability of Bernoullian statistics [50] and a value of $P_r = 0.55$ for a commercial resin prepared at 50°C, the calculated probability of finding a sequence of 13 syndiotactic units is about 0.08%. For a molecule of M_n of 70,000, i. e., one possessing about 1100 monomer units, this amounts to about one long sequence per macromolecule. This is not an unreasonable estimate and is consistent with the data observed at low levels of dehydrochlorination [16].

Existence of even longer polyene sequences in PVBr than in PVC would be accountable on this basis if much longer tactic segments are to be found in the former. Such an expectation is likely to be supported by the larger atomic size of bromine relative to the chlorine substituent. Although the global sequence composition of PVBr is reported [48, 51] to be similar to that of PVC, it has not been established whether vinyl bromide polymerization follows Bernoullian or other statistics, and therefore probability calculations of the kind performed on PVC cannot be made at present.

A comment is warranted about the relationship between the polymerization temperature and the reactivity of the resultant PVC resin. It is now well established that, as polymerization temperature is lowered, a more highly syndiotactic but more linear resin of enhanced crystallizability is produced [52]. Chain linearity, i. e., absence of branches and other reactive sites, would tend to reduce the rate of step 1 via the radical chain process, and higher temperatures would be required to generate random double bonds by 1,2-dehydrochlorination. Nevertheless, once sufficient numbers of double bonds can be generated, steps 2 and 3 would occur more readily and lead more completely to the maximum possible polyene sequences. Two examples are worth citing to illustrate these opposite influences. The first involves the resins reported by Gupta and St. Pierre [23]: the -43°C resin was more stable to much higher temperatues than that

prepared at 50°C, but once the former started to degrade, it yielded the longest "kinetic chain length." A second example is a series of resins described by Millan and co-workers [53], in which a minimum in reactivity was observed for resin prepared at temperatures of 0-25°C, while those prepared at lower and higher temperatures were considerably less stable. On the basis of comments made above, it is tempting to ascribe the minimum reactivity in the resins to a balancing situation where the reduction in rate of step 1 is just offset by the acceleration in rate of step 3. While in the relatively highly syndiotactic resin (-50°C) degradation is very fast due to unzippering of long segments to yield very long polyene sequences, the more branched resin (40°C) experiences step 1 more frequently than the -50°C resin, resulting in more frequent but shorter polyene sequences. A further study of fractionated resins reported recently [54] eliminated molecular weight as an important factor responsible for minimum reactivity region.

Another issue concerns the relative rates of steps 1-3. Intuitively, step 1, whether proceeding by molecular or chain process, would be expected to be the slow step and step 3 would be expected to be the fastest one. Step 3 could be at least as fast as step 2 if it occurred homogeneously, i. e., in a single phase as does the latter. Step 3 is a heterogeneous reaction; hence diffusion to and away from the surface probably plays an important role and could be expected to increase the rate of step 3 significantly. Because of the slow diffusion of HCl away from its evolution site, highly concentrated pockets of trapped HCl could exist in the bulk, and these could be responsible for the enhanced reactivity observed in large PVC particles [7]. A high value was found for the activation energy for diffusion of krypton in PVC films above T_g, i. e., ca. 30 kcal/mole [55]. Values of similar magnitude may well apply to diffusion of HCl and HBr within the solid polymer. The similar values for the activation energy of the catalyzed and uncatalyzed decompositions confirm that step 3 is not the rate-determining step. At the temperatures examined in the present study the observed activation energy is expected to consist of contributions from the initiation and the propagation steps. However, at the current level of understanding of the complex overall process further consideration of the relative contributions by steps 1 and 2 to the overall activation energy would be purely speculative.

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