Factors that Influence the Kinetics of the Degradation of Poly(vinyl Chloride)

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ABSTRACT

The degradation of five samples of PVC having different degrees of polymerization has been studied by a technique that permits a precise measurement of the rate of hydrogen chloride elimination as % HCl/min. All samples followed acceleratory kinetics at both low and high conversions. The conversion rate, which changed from the beginning to the end of a degradation, depended primarily upon the fraction of chains producing hydrogen chloride. The fraction of producing chains and the kinetic pattern were influenced by the presence of hydrogen chloride, the physical state of the sample, the previous degradation history, and the presence of intentionally added substances. Zipper kinetics permit the reproduction of kinetic data in terms of three parameters: k_1, the fraction of chains initiating per second, k_2, the fraction of a zip chain that zips per second, and k_3, an arbitrary parameter that accounts for residual hydrogen chloride after degradation has ceased.

INTRODUCTION

The kinetics of the incipient degradation of PVC at temperatures below 200°C have been extensively studied because of a presumed

relationship to the discoloring and aging characteristics of commer-
cial products containing, or composed of, PVC. Degradations at
higher conversions and at temperatures above 200°C are pertinent for
the better understanding of the performance of PVC under conditions
of overheating and burning.

It is generally agreed that incipient degradation occurs when
irregular chain structures lead to the formation of allylic structures
which form polyene sequences due to hydrogen chloride elimination
by the zip reaction [1]. It is customary that mechanisms and kinetic
schemes are limted to low conversions [2] with the implication that
there is a change in the kinetics and mechanism as the degradation
occurs at higher temperatures and higher conversions. Degradations
at both low conversions [1, 2] and high conversions [3, 4] exhibit
acceleratory behavior in the presence of hydrogen chloride. It will
be shown that the kinetics developed on the basis of the zipper mech-
anism apply with equal effectiveness to both high and low conversions
and that degradation rates change in an acceleratory pattern from
the beginning to the end of a degradation. The rate at any time depends
primarily upon the moles of chains that are unzipping.

EXPERIMENTAL

The apparatus for the precise measurement of degradation rates
has been described [5]. In the present work a 14 in. length of 1/8
in. stainless steel tubing packed with 80-100 mesh Porapak Q (Waters
Associates) was used as the chromatographic column. Rates were
measured over 1-min intervals using crucible reactors which per-
mitted the atmosphere of hydrogen chloride created by the sample
to remain above the sample during the degradation. A thin glass rod
extending from within the sample to the top of the chamber was used
for the easy removal of the sample and crucible at the completion of
a run.

The available characteristics of five PVC samples are summarized
in Table 1. The average degree of polymerization (DP) has been used
to identify the samples throughout this report.

After completion of a run the loss in weight of the sample was
determined and the residual hydrogen chloride was calculated. Peak
areas including the residual area were summed and divided into the
cumulative peak areas to give the values of alpha, the fraction de-
composed, as a function of time. A computer program [6] then
obtained best fit values of the kinetic parameters and printed out α
and $\Delta\alpha$/min as a function of time for the data and calculated points.
An error statistic, Δ, which represented the average percentage
difference per point, indicated the efficiency of the fitting process.

The principal parameters influencing the kinetic pattern were
k_1, the fraction of chains starting per second, and k_2, the frac-
tion of a started chain unzipping per second. During the accel-
eratory period the fraction of started chains increased. Beyond

TABLE 1. Characterization of PVC Samples

Source	M_w	M_n	DP	Powder density[b]
SP² [a]	122,300	57,300	917	0.64
SP²	77,300	39,600	634	0.50
SP²	193,600	86,300	1,381	0.42
B.F. Goodrich	-	79,500	1,272	0.52
B.F. Goodrich	-	42,700	684	0.60

[a]Scientific Polymer Products, Inc.
[b]g/cc of powder.

the maximum rate more chains were terminating than were starting, and terminated chains were taken out of production. When degradation was essentially complete ($\alpha = 1.0$ at $t = \infty$), the ideal equation for the acceleratory period was

$$\alpha = k_2 t + k_2/k_1 e^{-k_1 t} - k_2/k_1$$

The equation for the deceleratory period which began at $t = 1/k_2$ was

$$\alpha = 1 - k_2/k_1 e^{-k_1 t}(1 - e^{k_1/k_2})$$

There is no discontinuity at $t = 1/k_2$.

When significant residual hydrogen chloride remained in the sample after complete degradation, it was assumed that some started chains were prematurely terminated never to start again. With the assumption of premature chain termination it was possible to duplicate observed data in which values of α were less than 1.0 after complete degradation. The parameter, k_3, was a measure of the premature chain termination. It reduced the value of α without significantly altering the kinetic pattern. The kinetic model with the correction for premature chain termination [4] is more complicated than the ideal equations.

In addition to a computer program for obtaining best fit parameters, a program was available for simulating runs for mixtures of as many as 10 different samples [6]. For each component the values of α and $\Delta\alpha$/min were calculated, multiplied by their mole fraction, and these products added at each time to give α, and $\Delta\alpha$/min, as a function of time for the mixture. Values of $\Delta\alpha$/min were directly proportional to the peak areas which would be expected for the mixture and were

entered as peak areas in the preparation of a simulated run. Simulated runs were then fit by the kinetic model to establish how effectively that model fit in situations of variable chain lengths. Computer simulation with single values of parameters was also used to predict the kinetic behavior for standard tests in which hydrogen chloride was swept away.

RESULTS AND DISCUSSION

Zipper Kinetics Properly Represent the Degradation of PVC over the Entire Range of a Degradation at Temperatures Above and Below 200°C

Most kinetic studies have been primarily concerned with incipient degradation of PVC at temperatures below 200°C. It is not uncommon that kinetics and mechanisms suggested are limited to conversions below 2-3% with the implication that different mechanisms and kinetics would be observed at higher conversions [2]. The present work supports the concept that the same kinetics and presumably the same mechanism function over the entire range of conversions at temperatures above and below 200°C.

In order to establish that the acceleratory kinetics observed at 220°C and above also apply at 190°C, it will be shown that a sample which has been partially degraded at 220°C continues to show acceleratory kinetics when that degradation is continued at 190°C, that data in the literature clearly show acceleratory kinetics at 190°C when the degradation occurs in the presence of hydrogen chloride, and that the constant degradation rates reported when hydrogen chloride is swept away in a stream of nitrogen represent a predictable pattern for zipper kinetics.

Figure 1 shows a typical acceleratory degradation for Sample DP684 at 220°C. The line represents the theoretical curve calculated from best fit parameters and the symbols represent actual data points. This run pattern is representative of all degradations. Rates expressed as % HCl/min increase, pass through a maximum, and then decrease. Best fit values of the parameters were: k_1 = 0.00115, k_2 = 0.00050, k_3 = 0.64, t_s = 133, Δ = 0.40%. A second sample of DP684 was then degraded until its rate was 1.25% HCl/min which represents approximately half of the maximum rate that would be expected from the complete degradation shown in Fig. 1. This sample was removed, allowed to stand in air, and reintroduced to the reaction chamber at 190°C. The acceleratory pattern of the partially degraded sample is shown in Fig. 2. The initial degradation rate at 190°C was 0.16%/min. The rate increased to 0.22% HCl/min in 4000 s and then decreased in a pattern typical of acceleratory degradations. Similar behavior was observed when the partially degraded sample
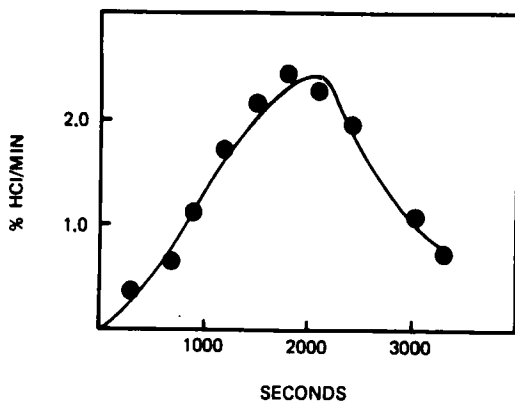
FIG. 1. Typical acceleratory degradation of 71.4 mg DP684 at 220°C. Symbols are data. Line is theory calculated from best fit parameters.
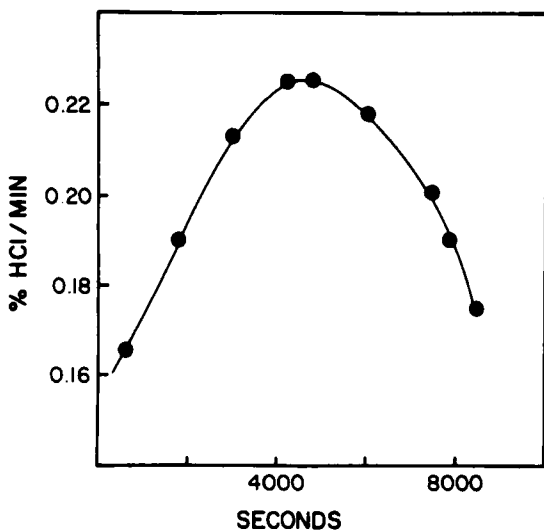

FIG. 2. Degradation rates as a function of time at 190°C for a sample partially degraded at 220°C.

was exposed to air for 14 h before degrading at 190°C, and also when it was cooled to 190°C in flowing helium. When predegradation conversions were extended to or beyond the point of maximum rate shown in Fig. 1, subsequent degradations at 190°C showed only deceleratory behavior. The acceleratory behavior shown in Fig. 2 is evidence that the moles of zipping chains are increasing during the acceleratory period even at 190°C. The increase in the number of zip chains leading to an increase in the rate of hydrogen chloride evolution would be expected for zipper kinetics.

The work reported by Hjertberg and Sorvik [1] and Amer and Shapiro [2] for the degradation of PVC under an atmosphere of hydrogen chloride similarly shows rate acceleration even at low conversions.

When hydrogen chloride was swept away in nitrogen in standard stability tests at 180°C [7] and 190°C [8], a constant rate of hydrogen chloride evolution gave a straight line relationships between percent conversion and time. It is important to understand how zipper kinetics accounts for a constant rate of hydrogen chloride evolution. Hydrogen chloride causes the rate of hydrogen chloride evolution to accelerate by increasing the rate at which chains are started. When hydrogen chloride is swept away, the value of k_1, the fraction of chains starting per second, remains very small. The zip rate of started chains, however, proceeds at a significant rate even at 190° C.

Figure 3 shows simulated plots of α vs t for $k_1 = 2 \times 10^{-6}$, $k_2 = 4 \times 10^{-4}$; $k_2/k_1 = 200$, designation ($\bullet$); $k_1 = 1 \times 10^{-5}$, $k_2 = 4 \times 10^{-4}$, $k_2/k_1 = 40$, designation ($\blacktriangle$); and $k_1 = 1 \times 10^{-5}$, $k_2 = 5 \times 10^{-5}$, $k_2/k_1 = 5$, designation ($\circ$); At ratios of k_2/k_1 of 200 and 40, the plots of α vs t at low conversions appeared to be linear. As the ratios of k_2/k_1 decreased to 5, the α-t plots became acceleratory even at low conversions. Thus, simulated data based on the zipper mechanism can account for both the linear and the acceleratory α-t relationships reported on the basis of the ratios of k_2/k_1. These ratios would be expected to be high under conditions where hydrogen chloride is swept away in a stream of nitrogen and linear α-t curves would be expected.

Linear α-t curves can be explained more simply if it is assumed that each PVC sample contains a small proportion of zip chains. That proportion will be a function of the previous treatment of the sample and will vary from sample to sample.

If the sample degradation is carried out in a stream of nitrogen, hydrogen chloride will be swept away and only negligible quantities of new zip chains will be initiated. When negligible initiation occurs, k_1 is extremely small and a large k_2/k_1 ratio will lead to a linear α-t relationship, On the other hand, if the hydrogen chloride is not swept away, the fraction of chains initiating per second will be larger, the k_2/k_1 ratio will be less, and acceleratory behavior will be observed.

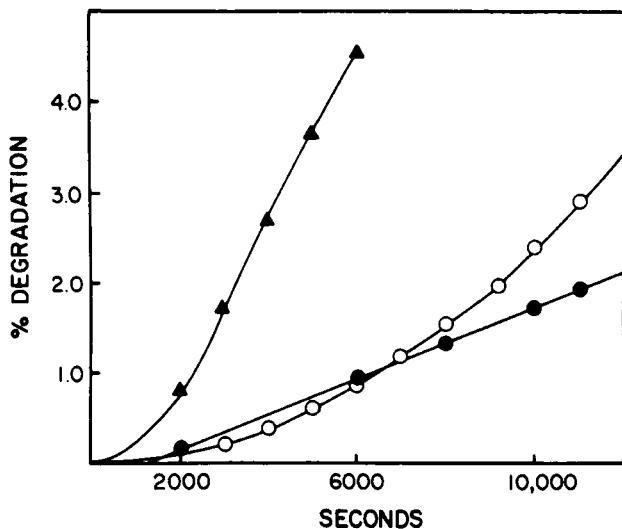On the basis of the acceleratory behavior of previously degraded

FIG. 3. Simulated degradation patterns for designated ratios of
k_2/k_1. (●) 200; (▲) 40; (○) 5.

samples, the acceleration in the presence of hydrogen chloride re-
ported by others, and the simulation of data at low conversions for
assigned k_1s and k_2s, it seems reasonable that the acceleratory re-
action occurs at both high and low conversions and at temperatures
above and below 200°C. Linear α-t curves at low conversions are
expected for high ratios of k_2/k_1.

These observations have significant implications for the way in
which standard tests for the stability of PVC should be carried out
and interpreted. If a stability test is to be related to stability under
conditions of service, it must be decided whether or not the hydrogen
chloride will be efficiently swept away as it forms or whether it will
remain in contact with the sample. The latter seems more probable
and implies that stability evaluations should be carried out under
the atmosphere of hydrogen chloride created by the sample. The
justification for stability tests at low conversions in a stream of
nitrogen was that the data would be directly related to the initiation
process. On the basis of zipper kinetics a conversion of only 0.1%
for a sample of DP1000 would correspond to an average loss of one
hydrogen chloride per chain or more likely about 10 hydrogen
chlorides for 10% of the chains. Thus, even at 0.1% conversion an
estimated 90% of the evolved hydrogen chloride would come from the
zip reaction rather than from the initiation reaction. On the basis
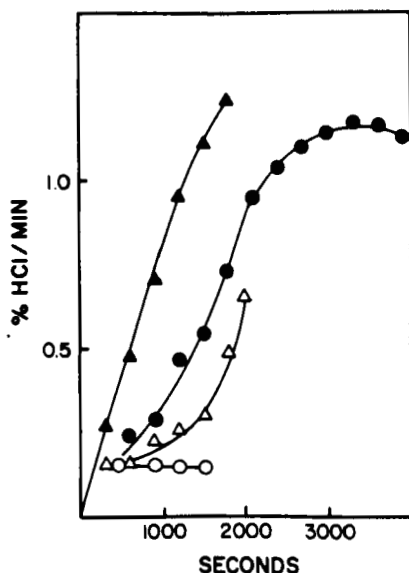of this analysis the direct quantitative observation of initiation

FIG. 4. Rates as a function of time for granules and premelted sample of DP1272. (●) Premelted sample at 220°C. (○) Granules at 220°C. (▲) Premelted sample at 225°C. (△) Granules at 225°C.

hydrogen chloride from "weak linkages" seems unlikely to be achieved by methods that measure evolved hydrogen chloride.

The Physical State of the Sample, Premelted Liquid or Granules, Influences the Degradation Patterns

At 220°C and above, four of the five samples of Table 1 are either molten or melt within a few minutes. Sample DP1272 remains solid at 220°C. As shown in Fig. 4, there is a difference in the degradation pattern that depends upon whether the sample has been premelted for 3 min at 235°C or whether it has been introduced at 220°C as granules. The unmelted granules show a constant degradation rate of 0.15% HCl/min while the premelted granules are acceleratory, rising to a rate of 1.35% HCl/min at the maximum rate. At 225°C a premelted sample shows rapid acceleration and achieves a degradation rate of 0.5% HCl/min in only 700 s. The granules when they are not pre-melted require 1900 s to achieve this same degradation rate, pre-sumably because significant time is required for granules, which are undergoing incipient degradation at 225°C to melt. At temperatures above 230°C, Sample DP1272 melts in a short time and little differ-ence between granules and the premelted sample is observed.

The Prior Degradation of a Sample Influences Subsequent Degradation Rates

It was established by the data of Figs. 1 and 2 that samples which had been partially degraded at high temperatures had significant degradation rates at 190°C. In order to establish how prior degradation influenced degradation rates at 190°C, polymer samples were degraded to various extents at 225°C and their rates of degradation determined at 190°C. Initial degradation rates at 190°C were also determined for samples which had been premelted at 235°C and for samples which had not been premelted. At all temperatures, degradation rates changed with time. The rates that are recorded in Table 2 are best estimates of rates taken after the temperature of the sample had lined out at 190°C. The rates at 225°C were taken as the last value of % HCl/min before the sample was removed.

Every sample that had reached a high degradation rate at 225°C showed much higher than normal rates at 190°C. Thus, Sample DP1272 when degrading at 2.5% HCl/min at 225°C and 45.4% conversion had a degradation rate of 0.28% HCl/min at 190°C. A sample of DP1272 which was degrading at 0.9% HCl/min at 7.7% conversion at 225°C had a degradation rate of only 0.07% HCl/min at 190°C. A premelted sample had a degradation rate of 0.012% HCl/min and the unmelted granules a rate of 0.005% HCl/min at 190°C. Thus the degradation rate at 190°C was a function of the previous degradation of the sample. In terms of the zipper mechanism, samples that had been previously degraded to assure a large fraction of started chains consistently had higher degradation rates at 190°C than samples having a smaller fraction of started chains. The rate of degradation at 190°C depended upon the fraction of chains that had been initiated during previous treatment of the sample. Other samples of PVC recorded in Table 2 followed similar degradation patterns. For comparison with our data, the reported degradation rate of Pervikon 45 was 0.02% HCl/min [8] at 190°C.

The rate of degradation of PVC at any temperature will depend upon the fraction of zip chains that are unzipping. The starting of zip chains at 190°C is a slow process but previously started chains will continue to unzip at surprisingly high rates. Started zip chains can be exposed to the atmosphere for long periods of time and will retain their zip activity [4]. Samples which have been premelted at 235°C for 3 min normally show significantly greater degradation rates at 190°C than samples which have not been premelted. Sample DP634, however, which normally melts at 190°C, shows little difference in rates when granules and premelted granules are compared.

On the basis of these observations it would be expected that zip chains formed in a sample during processing would continue to unzip slowly during the life of the product. The hydrogen chloride formed by the zip reaction would catalyze the initiation of new chains but initiation may be a slow process at low temperatures.

TABLE 2. Degradation Rates at 225 and 190°C, Sample Weights ~80 mg

Sample DP	Run no.	% Conversion at 225°C	%/min at 225°C	%/min at 190°C
1272	81D40	45.4	2.5	0.28
1272	81D47	7.7	0.9	0.07
1272PM[a]	81D42	~0	-	0.012
1272G[b]	81D43	0	-	<0.005
634	81D48	44.0	4.0	0.44
634	81D49	8.7	1.5	0.22
634PM	81D54A	~0	-	0.018
634G	81D54	0	-	0.015
917	81D51	51	4.8	0.43
917	81D52	5.5	1.2	0.10
917PM	81D53A	~0	-	0.02
917G	81D53	0	-	0.003
1381	81D44	38.1	2.0	0.21
1381	81D46	7.5	0.6	0.087

[a]Premelted at 235°C, 3 min.
[b]Granules.

Except for Sample DP917, the rates of hydrogen chloride production shown in Table 2 at similar conversions depend upon the chain length of the sample. Sample DP634 has a degradation rate of 4.0% HCl/min at 44% conversion while Sample DP1272 at 45.4% conversion has a rate of 2.5% HCl/min. Sample DP1381 has a conversion rate of 2.0% HCl/min. An obvious interpretation of these data is that the number of zip chains in a sample depends upon the number of polymer chains. A given weight of a long-chain sample will have fewer chains and fewer degrading chains than an equal weight of a short-chain sample. These data are consistent with a mechanism in which the length of the zip chain is related to the chain length of the polymer. However, Sample DP917 has a much higher zip rate than can be accounted for on the basis of chain length. The behavior of this sample makes it necessary to modify an earlier interpretation of zip kinetics when the length of a zip chain was thought to depend upon the length of the polymer chain [4]. It now appears

that the length of a zip chain must depend upon k_1, the fraction of chains starting per second. For all samples studied, an increase in k_1 has resulted in a larger value of k_2. The reciprocal of k_2 is the time to reach the maximum rate, so samples that have many starts per second have shorter average zip lengths and reach their maximum rates sooner than samples having lower starting rates. The fraction per second of starting chains is significantly influenced by the partial pressure of hydrogen chloride existing throughout the sample. As the fraction of chains starting per second increases, the time required to reach the maximum rate decreases regardless of the chain length of the polymer sample. A decrease in the time to reach the maximum rate corresponds to shorter chains and an increase in k_2, the fraction of a chain degrading per second. When 10 mg of poly(vinylidene chloride) was added above and below and thoroughly mixed with 70 mg of PVC (DP1381), the times to reach the maximum rate at 230°C were: no PVDC added, 2160s; PVDC above PVC, 1620s; PVDC below PVC, 1920s; PVDC thoroughly mixed with PVC, 1260s. The presence of PVDC in 10 mg quantities caused an immediate and copious evolution of hydrogen chloride. The rate of initiation depends upon the activity of hydrogen chloride and in every combination of PVC with PVDC the time to reach the maximum rate was significantly decreased. The intimate mixture of PVDC and PVC was significantly more effective than the unmixed combinations in initiating chains and thereby decreasing the time to achieve the maximum rate. Whether this increased effectiveness of the mixture is attributed only to a greater activity of hydrogen chloride throughout the sample or to the initiation of additional PVC chains by the PVDC cannot be unambiguously established.

The Physical State of a Sample Influences the Behavior of a Sample with Respect to Added Gases

When degradations of PVC at 220-230°C showed little variation in degradation behavior in the presence of hydrogen or helium carrier gases, it was assumed that radical reactions were unlikely because hydrogen would be expected to react with radicals [9]. However, degrading films and melts form a tough, cross-linked, and porous mass that slowly evolves hydrogen chloride. Under these conditions gases in the atmosphere above the porous mass would have very little contact with the PVC at the point where degradation occurs. Conflicting reports on the catalytic effect of hydrogen chloride and the influence of oxygen and other gases on degradation rates may result from the physical state of the sample. Granules presumably undergo degradation at their surfaces and added gases would be in contact with the surface and influence the reaction. These same gases would have little access to the degradation sites in films and melts that were slowly evolving hydrogen chloride.

The Density of the Polymer in the Char May Influence the Degradation Behavior

When samples of polymer degrade rapidly during the initial stages, the escape of hydrogen chloride may cause the polymer to froth and the resulting cross-linked char will occupy a volume as much as 30% greater than the original powder. If degradations are started under conditions where frothing does not occur and the temperature is later raised to the conditions where frothing would be expected, expansion of the sample does not occur, presumably because cross-linking has established the volume of the char during the slow degradation.

Samples DP684 and DP917, having the highest bulk densities as powders, had the greatest tendencies to increase their volumes. Presumably, melted polymers have similar densities, and expansion on melting as well as frothing can influence the volume of the char. The influence of char density on the degradation is not known but it seems likely that it should influence degradation kinetics since it is related to the concentration of the polymer.

Substances Which React with Hydrogen Chloride May Cause Significant Differences in Degradation Patterns

Gupta, Kennedy, Nagy, Tüdős, and Kelen recognized the necessity for complete removal of alumina which might react with hydrogen chloride from samples of PVC that had been treated with aluminum alkyls [10]. In any method of measuring degradation rates that involves the determination of evolved hydrogen chloride, substances that react with hydrogen chloride will diminish the apparent rate of reaction in two ways: A significant decrease in rate will occur because the rate of chain initiation is increased by hydrogen chloride and anything that reduces the activity of hydrogen chloride will lower the rate of initiation. A second effect is caused by the actual removal of hydrogen chloride by reaction. Hydrogen chloride that has reacted obviously does not get recorded. Although it is not easy to distinguish the relative contributions of starting inhibition and hydrogen chloride removal, their combined effects can be shown. The data of Fig. 5 were obtained when a straightened paper clip was inserted into the polymer in place of the glass rod that was normally used to aid in the removal of the crucible from the reaction chamber. At 230°C Sample DP1272 in the presence of the paper clip had a constant rate of hydrogen chloride evolution at a peak area of only 20 units over a 30-min period. Apparently the reaction product of the clip and hydrogen chloride remained in the system because immediately following the run with the paper clip a sample of DP1272 with a glass rod showed peak areas of less than 10 units. After baking out the
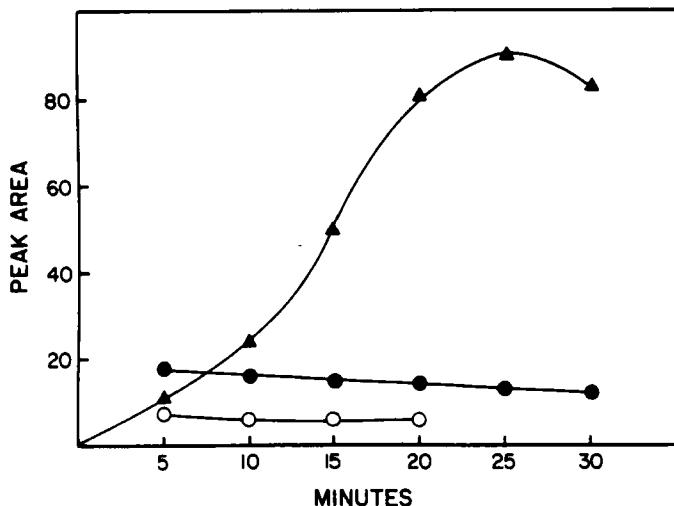
FIG. 5. Effect of metal paper clip on degradation rates at 230°C.
(●) With paper clip. (○) After paper clip. (▲) After baking out.

reaction chamber at 350°C and the chromatographic column at 100°C
in a stream of helium, a similar run with a glass rod returned to the
normal acceleratory pattern.

The need for the exclusion of substances reacting with hydrogen
chloride from the polymer and the reaction line is obvious. Never-
theless, it seemed appropriate to illustrate how drastically the
presence of such substances can influence the kinetic pattern.

The Presence of Sulfur Enhances Both the Initiation and the Zip Reaction

The rates of hydrogen chloride evolution as a function of time are
plotted in Fig. 6 for 50 mg samples of DP634 at 225°C with and without
14 mg of flowers of sulfur. In the absence of sulfur a normal accel-
eratory degradation achieved its maximum rate at about 2000 s and
had the best fit parameters: of $k_1 = 0.0013$, $k_2 = 0.00061$, $k_3 = 0.54$.

The sample containing sulfur achieved its maximum rate in about
half the time and had a higher initiation rate ($k_1 = 0.0027$) and a higher
zip rate as fraction of chain unzipping per second ($k_2 = 0.00098$).
The higher zip rate corresponds to shorter chains which would be
expected when the number of starts per sample increases.

Sulfur is known to form radicals at 225°C due to the opening of S_8
rings. The significant enhancement of starting rates in the presence
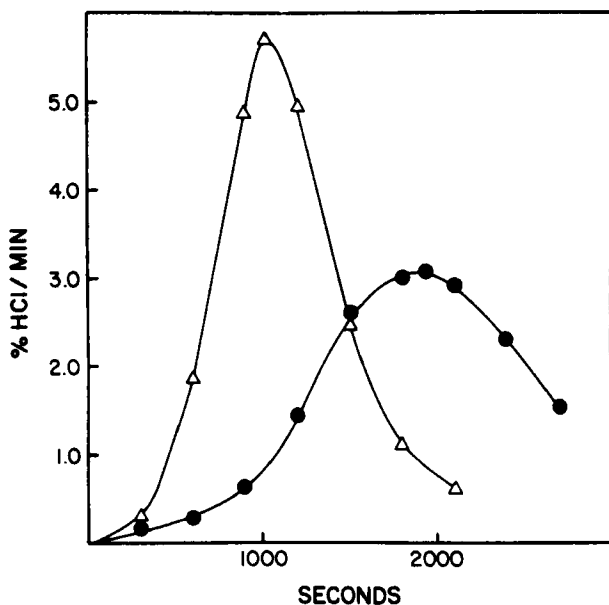of intentionally added sulfur can be interpreted to mean that radicals

FIG. 6. Effect of sulfur on degradation rates at 225°C. (●)
DP634. (△) DP634 with added sulfur.

are involved in chain initiation. The increase in k_2 does not neces-
sarily imply an increase in the intrinsic rate of unzipping because k_2,
the fraction of a chain unzipping per second, must become larger as
the zip chains become shorter.

Does Hydrogen Chloride Catalyze the Zip Reaction?

Our work and the work of others has clearly established that hydro-
gen chloride catalyzes the degradation of PVC. In the zipper model the
degradation is defined in terms of an initiation reaction with a param-
eter, k_1, and a zip reaction with a parameter, k_2. The increased
rate of initiation in the presence of hydrogen chloride has been
clearly established but the influence of hydrogen chloride on the zip
rate was not [4].
     In order to establish the effect of hydrogen chloride on the zip
rate, identical samples of DP684 were degraded under similar condi-
tions until the degradation rate exceeded 3.0% HCl/min. The plots of
rates as a function of time up to the time of removal are shown in
Fig. 7. Hydrogen chloride rates of 3.0% HCl/min are expected only
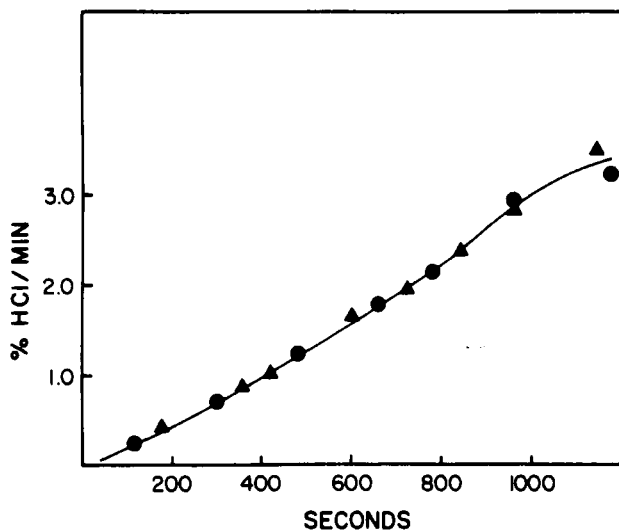if there are large fractions of unzipping chains. The samples were

FIG. 7. Degradation rates of DP684 at 225°C: (●) 86.7 mg, (▲) 84.4 mg.

removed from the chamber and subsequently degraded at 225°C under the atmosphere of hydrogen chloride created by the sample and under a vacuum of 1 torr. After 20 min the samples had lost an additional 22.5 and 22.0 mg, respectively, of hydrogen chloride. Because continued formation of hydrogen chloride during evacuation may not permit complete removal of hydrogen chloride from the char, the catalytic effect of hydrogen chloride at 1 torr cannot be rigorously excluded. However, the insensitivity of the zip reaction to hydrogen chloride pressure is strong evidence that hydrogen chloride does not significantly catalyze the zip reaction.

The Length of a Zip Chain Is Probably Related to k_1, the Number of Starts per Second, Rather than to the Length of a Polymer Chain

In an earlier interpretation of the zip mechanism as it applied to the degradation of PVC, zip chains were assumed to start at or near chain ends and the length of the zip chain depended upon the length of the polymer chain [4]. The alternate interpretation in which the length of a zip chain depended upon the fraction of chains starting per second was also suggested because lower values of k_1 were always associated with longer chains. For the B.F. Goodrich samples used in an earlier study a decision between the two options was not

possible because long chains consistently had lower values of k_1.
Three samples from Scientific Polymer Products Co., which are
characterized in Table 1, clearly demonstrate that k_1, the fraction
of chains starting per second, has a primary influence on the time
required for a degradation to reach its maximum rate. The time to
reach the maximum rate is $1/k_2$, so long times are associated with
small values of k_2. A large value of k_2, the fraction of a chain
unzipping per second, is associated with a short zip chain since the
intrinsic rate of unzipping, $k_2 \cdot$(zip chain length), is assumed to be
constant for all samples.

The rate of degradation as a function of time is shown in Fig. 8 for
Samples DP634, DP917, and DP1381. Samples DP634 and DP1381
followed the pattern of the B.F. Goodrich samples in which the time
to reach the maximum rate depended upon the chain length of the
polymer. The lines are calculated from best fit parameters and the
data are represented by the symbols. Samples DP634 and DP1381
required 1500 and 3300 s, respectively, to achieve their maximum
rates. Sample DP917, however, required only 1100 s to reach the
maximum rate, and this time could not be understood in terms of
the chain length in Table 3. The number of zip chains and the time
to reach the maximum rate appear to be a function of k_1, the fraction
of chains starting per second. Sample DP917 from Scientific Poly-
mer Products is a fully characterized sample for general application
studies, and there is no reason to suspect that its characterization
could be in error. On the basis of these observations, it seems
appropriate that zipper kinetics be interpreted in terms of the aver-
age length of a zip chain rather than on the basis of the length of a
polymer chain.

In this interpretation the polymer chains are initiated and the
average length of the zip chain depends on the fraction of initiation
sites. The zip chain is probably not limited to zips along a single
polymer chain but can move from chain to chain until it is eventually
terminated and ceases to produce hydrogen chloride.

A uniform zip length would not be expected in this interpretation
of zipper kinetics. There should be a most probable value of zip
chain length with a statistical distribution of shorter and longer chains
around this value. Using a computer program, a simulated run for
the situation of constant starting characteristics with variation in k_2,
depending on chain length, gave raw data which were then fit by the
best fit program [6]. Table 4 summarizes the assigned parameters
and the best fit parameters for the situation in which the chain length
of the sample varies evenly around an average value. The best fit
parameters fall within 3% of the average value of the assigned param-
eters and the average error per fit point is 0.62. Thus the kinetic
model derived on the basis of a single length for zip chains also fits
the situation in which there is a significant variation of zip chain
length around some most probable value. Also included in Table 4
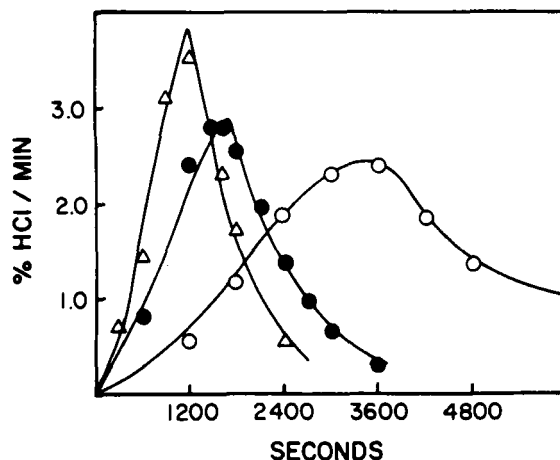is an example of a best fit obtained for a simulated run for single

FIG. 8. Degradation rates as a function of time at 225°C. Symbols are data, lines are theory. (●) DP634. (△) DP917. (○) DP1381.

TABLE 3. Best Fit Parameters at 225°C

DP	k_1	k_2	k_3	t_s	Δ
634	0.0013	0.00062	0.78	115	0.28
917	0.0017	0.00088	0.96	65	0.40
1381	0.00056	0.00031	0.96	198	0.42

valued parameters. As would be expected, the average error per fit point is very low.

The Mechanism of PVC Degradation

On the basis of the excellent agreement of data and theory illustrated in the rate-time plots of Figs. 1 and 8, it seems reasonable that the mechanism of PVC degradation should be consistent with zipper kinetics. In zipper kinetics the rate of initiation and the rate of the zip reaction are the important parameters. The rate of initiation clearly depends upon the activity of hydrogen chloride which is assumed to attain a constant saturation value. The rate of initiation, in addition to being very sensitive to the activity of hydrogen chloride, is probably sensitive to minor impurities and changes in operating conditions on the following basis: One initiation site per chain for a

TABLE 4. Simulated Runs: Assigned and Best Fit Parameters

	k_1	k_2	k_3	t_s	Mol. fraction	Δ[a]
Assigned	0.001	0.0006	0	0	0.2	
	0.001	0.0008	0	0	0.2	
	0.001	0.0010	0	0	0.2	
	0.001	0.0012	0	0	0.2	
	0.001	0.0014	0	0	0.2	
Best fit	0.00097	0.00098	0.01	4.8	-	0.62
Assigned	0.0010	0.0010	0	0	1	
Best fit	0.00099	0.00102	0.007	7	-	0.06

[a]Δ is average percentage difference per fit point.

sample of DP1000 would mean that the initiation reaction represented only 0.1% of the total degradation. Even for greater numbers of initiation sites per chain and for shorter chains, the initiation process must always represent a very small part of the overall degradation. The zip reaction, on the other hand, represents at least 99% of the degradation. Whenever, a single event, initiation, leads to many events, unzipping, minor impurities, or changes in operating conditions that alter the single event can cause profound changes in the overall process.

Based on the behavior of Sample DP917, the fraction of chains starting per second rather than the length of the polymer chain establishes the length of a zip chain. The sensitivity of the initiation reaction causes changes in k_1 which in turn lead to changes in k_2. The overall kinetic patterns of degradations remain acceleratory but the time to reach the maximum rate changes with changes in k_1. The factors which have been shown to influence degradation patterns probably exert their primary influence on the initiation reaction.

On the basis of our data and the data of others, an acceptable mechanism for PVC degradation must be consistent with zipper kinetics and must account for 1) the critical nature of hydrogen chloride in the initiation of zip chains, 2) the source of the initial hydrogen chloride, 3) the nature of the zip reaction and its unusual persistence, and 4) the extensive cross-linking during the early stages of a degradation that has been reported by Kelen [11].

It is generally agreed that the nominal PVC structure is stable toward thermal degradation [12]. Many structures have been suggested as points of initiation and sources of hydrogen chloride [13]. There seems to be an additional source of hydrogen chloride that

should be considered. That source would be zip chains that were introduced during the polymerization. Hydrogen chloride is present during polymerization [14] and trace formation of zip chains would seem possible. A single started zip chain in a sample should be more efficient in producing initial hydrogen chloride than hundreds of "weak linkages."

In an earlier paper [4] the initiation site was suggested to be a 2,2,4-trichloro moiety formed by the addition, elimination, and re-addition of hydrogen chloride at an allylic double bond. The reported proton exchange of hydrogen chloride and PVC [15] and the slow initiation of the acceleratory reaction even in the presence of hydrogen chloride [2] are consistent with a rate-controlling initiation mechanism that requires the reaction of hydrogen chloride with the PVC.

The 2,2,4-trichloro moiety has not been evaluated for stability in the extensive work on the stability of model compounds [16]. Its presumed instability and chain initiating ability are based on the observation that poly(vinylidene chloride), containing a somewhat analogous 2,2,4,4-tetrachloro moiety, readily loses hydrogen chloride at 180°C and the initiation of the zip reaction for PVDC apparently does not require the presence of hydrogen chloride [17]. The amount of hydrogen chloride involved in initiation is so small compared to the amount of hydrogen chloride from the zip reaction that direct evidence supporting any specific initiation mechanism is not available from degradation studies. However, the apparent insensitivity of the zip reaction to hydrogen chloride pressure, the increase in degradation rates in the presence of sulfur (and oxygen and peroxides), and the extensive cross-linking at low conversions [11] seem to support the radical nature of the initiation and zip reactions.

The concept of a radical mechanism is not new. Ayrey, Head, and Poller [16] regard free radical chain dehydrochlorination as the preponderant mechanism for PVC degradation. Arlman [18] and Winkler [19] depicted radical mechanisms in great detail. Arlman envisioned a radical,
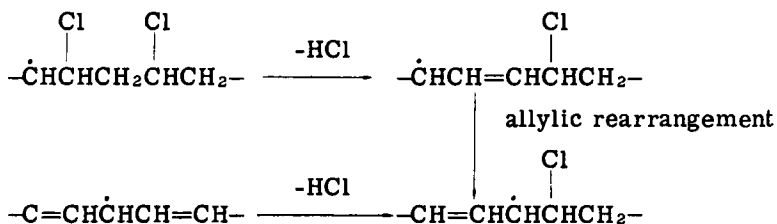
which split out hydrogen chloride from the 2 and 3 positions, then rearranged to form a similar radical which continued the process. The breaking of a carbon-carbon bond at the 2 position instead of the carbon-chlorine bond would result in the zip elimination of monomer. The zip elimination of monomer has been observed for poly(methyl

methacrylate) [20]. The zip elimination proposed by Arlman still seems to be a reasonable and logical pattern for zip elimination of hydrogen chloride. It seems appropriate to suggest how a radical reaction might be initiated and the reaction paths that could account for the extensive cross-linking at very low conversions reported by Kelen [11].

The presumed initiator, 2,2,4-trichloro sequence, or a similar polychlorinated sequence can lose hydrogen chloride in three ways. ' Loss of hydrogen chloride by intrachain molecular elimination is a reversible process that does not necessarily start a radical zip chain. Interchain elimination of hydrogen chloride with cross-linking would result in the reported increasing molecular weight at low conversions [11] but would not start a radical chain. Interchain elimination of hydrogen chloride without cross-linking of the radical fragments would start two radical chains. Once radicals have been created by intermolecular dehydrochlorination, which may represent a very minor amount of the hydrogen chloride eliminated, the radical reaction described by Arlman can follow. An unzipping radical chain may add across a double bond or transfer the radical to an adjacent chain. In either case the radical zip would continue. Radical addition to a double bond in the same chain can occur and would be most likely to form a six carbon ring which would be a precursor of benzene that is eliminated at higher degradation temperatures. The mechanism of Arlman with interchain and intrachain additions seems to represent satisfactorily a radical zip reaction. The interchain elimination of hydrogen chloride with cross-linking seems essential to account for the increase in molecular weight at very low conversions reported by Kelen [11]. Our own data neither refutes nor supports interchain elimination of hydrogen chloride as a source of radical initiation.

The persistence of the chain zip in partially degraded samples that have been exposed to the atmosphere seemed at first to be incompatible with a radical mechanism [4]. However, oxygen is known to react with polyene sequences, destroying their color [21]. It appears that the product with oxygen would be stable at room temperature but would decompose at 180°C and higher to regenerate radicals that would continue the zip reaction.

On the basis of these kinetic studies it seems clear that the degradation behavior of PVC can be characterized in terms of a starting reaction and a zip reaction. The degradation rate at any time will depend upon the fraction of chains unzipping and the rate of the zip. The fraction of chains starting per second is difficult to control and is significantly influenced by some of the factors described in this paper.

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