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The Kinetics and Mechanism of the Thermal Dehydrochlorination of Poly(vinyl Chloride)

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ABSTRACT

Poly(vinyl chloride) degrades thermally by an acceleratory reaction in which the rate of hydrogen chloride evolution is slow at the beginning, increases with time (passing through a maximum), and then decreases. A kinetic model based on the zipper mechanism shows excellent agreement with observed data from the initial to the final stages of each dehydrochlorination. Hydrogen chloride is shown to be essential for the initiation of zip chains and may or may not be essential for the zip reaction. When hydrogen chloride is removed in a stream of inert gas, as it is in some tests purported to study the kinetics of degradation, the initiation of zip chains is significantly inhibited. The zip reaction, once it has been initiated, is not inhibited or stopped even by long exposure to atmospheric conditions.

INTRODUCTION

Many reviews have included considerations of the thermal dehydrochlorination of PVC [1-9]. Although most workers agree that PVC dehydrochlorinates by a zip mechanism to give a sequence of conjugated double bonds, they have correlated their kinetic data on the basis of conventional kinetics. Most studies have been made at low conversions and at low temperatures, and the implication has been made that a different kinetic pattern would be followed at higher conversions and would not be applicable to the interesting range of low conversions associated with problems of PVC stability.

In the present work five PVC samples from B. F. Goodrich having degrees of polymerization of 546, 684, 845, 1002, and 1272 were dehydrochlorinated at temperatures from 220 to 240°C in an apparatus giving a precise and direct measurement of rate, $\Delta\alpha$ per interval, as a function of time where α is the fraction decomposed. In this temperature range every sample followed a pattern characteristic of acceleratory decompositions. The rate is low at the beginning, increases with time, passes through a maximum, and then decreases [10]. The rate of dehydrochlorination becomes negligible when the conversion reaches 65 to 90%. In the conventional treatment of acceleratory decompositions the incomplete decomposition of samples has been called "retention" and its significance is not well understood [10]. Acceleratory reactions in the solid state are also called "autocatalytic reactions," and the substance undergoing decomposition is presumed to form a catalyst for its own decomposition [11]. It will be shown that hydrogen chloride formed by slow thermal decomposition of polymer or present from other sources is a catalyst for the initiation of the dehydrochlorination of polymer chains. Once initiated, a chain may unzip, forming copious quantities of the initiation catalyst, hydrogen chloride, or it may be prematurely terminated. Because of its volatility, the hydrogen chloride reaches a constant concentration and represents a special case of an autocatalytic reaction.

A kinetic model which assumes first-order initiation of chains in a constant atmosphere of hydrogen chloride followed by premature termination or unzipping at a constant fraction of chain per second correctly represents the data for five PVC samples under a variety of conditions.

The chain initiation process will be shown to be sensitive to termination by inert surface and to the presence of hydrogen chloride while the unzipping reaction, once it is underway, is extremely persistent and insensitive to termination even by long exposure to atmospheric conditions. The kinetic pattern observed at significant dehydrochlorination rates seems applicable to dehydrochlorinations at lower conversions and accounts in a reasonable way for much of the conflicting data in the literature.

EXPERIMENTAL

Five samples of poly(vinyl chloride) were supplied by B. F. Goodrich and have been identified throughout this paper by their degrees of polymerization (DP) which were specified by the supplier.

The apparatus has been previously described [12-15]. The sample (normally in the range of 40 to 100 mg) in a silica tube or silica crucible (a tube closed at the bottom) is introduced into a stainless steel chamber which is held at a constant temperature. Two milligrams of poly(vinylidene chloride) (PVDC) which evolves hydrogen chloride rapidly at the run temperatures was sometimes added to the crucible reactor to provide an immediate supply of thermal hydrogen chloride. Helium carrier gas passes through the chamber for 10 s of each cycle and sweeps out hydrogen chloride which passes through a chromatographic column, then to a detector. The peaks are recorded and their areas measured by an integrator on the recorder.

In the crucible reactor only the hydrogen chloride escaping the top of the crucible is swept out. The sample remains under its own atmosphere of hydrogen chloride. In the tube reactor helium sweeps out hydrogen chloride until the sample melts and obstructs the flow of helium after which the tube reactor behaves as a crucible. In either the tube or crucible the volume of hydrogen chloride retained is negligible compared to the volume of hydrogen chloride formed.

Near the end of a run the peaks become very small. At this time hydrogen chloride retention is measured by one of two methods. In the first method the temperature is raised to ~325°C and the retained hydrogen chloride is evolved and its peak areas recorded. In the second method the sample is removed and its loss in weight determined. From the loss in weight the area of the retained hydrogen chloride can be estimated. All peak areas are recorded. Values of α at any time were the cumulative areas to that time divided by the total area. $\Delta\alpha$ values for each interval were, of course, proportional to the peak area for that interval and are proportional to the average rate of hydrogen chloride production during the interval. $\Delta\alpha$ values have been used to represent rates in this paper. $\Delta\alpha$ divided by the length of the interval would, of course, represent the average rate, $\Delta\alpha/\Delta t$, during each interval. A plot of $\Delta\alpha$ values as a function of time for actual runs and simulated runs reproduces the pattern of an actual run sheet.

CORRELATION OF DATA

An algorithm described by Powell [16], modified for the present work, was used to fit theory with data and thereby obtain best fit values for the following parameters: k_1, the fraction of PVC chains initiated per second; k_2, the fraction of a chain unzipping per second; k_3, a constant that is proportional to the number of chain stopping occurrences when chain stopping is proportional to first order in initiated chains and first order in chain terminators; and t_s, the time shift, which allows the theoretical curve to be moved to the right (+ seconds) or left (- seconds) along the time axis without changing the shape of the observed or calculated curve.

An algorithm with four parameters and an efficient computer can probably fit almost any set of data. However, the best fit program gives options by which any one of the four parameters can be allowed to vary or can be held constant while the values of the remaining parameters are established. Fortunately, there are certain limitations on the values of k_2 and t_s, and an inspection of the actual run sheet can give reasonable values that would be allowed for these two parameters. When these limitations are introduced, the best fits are primarily dependent upon k_1 and k_3. Even these values have certain limits since α at infinite time, α_∞, can be calculated from theory and must have a value, depending upon how long the run was continued before measuring retention; that is, about 0.02 to 0.06 units above the value of α at the completion of a run, α_E.

THE KINETIC MODEL

The principles underlying the kinetic model and the techniques used in its derivation have been described [17]. For the present work the value of F, the chain termination approximation, was $k_3e^{-k_1t}$. This approximation assumes that chain termination is proportional to first order in started chains and first order in chain terminators, and k_3 is the proportionality constant. The chain-stopping function is at best an approximation which accounts for the retention of hydrogen chloride in the dehydrochlorinated polymer. As the retention becomes larger, the errors of the approximation may become more significant. The observation that the first-order relationship for the chain-stopping function gives somewhat better correlation than other approximations should not necessarily be taken to mean that the mechanism of chain termination is thereby known.

The integrated form of the kinetic equation and the significance of the various terms in that equation when $F = k_3e^{-k_1t}$ are as follows:

A represents the value α would have if all started chains continued to produce forever:

$$A = k_2t + \frac{k_2}{k_1}e^{-k_1t} - \frac{k_2}{k_1}$$

B represents the term to be subtracted from A due to premature chain termination:

$$B = -\frac{k_3k_2}{k_1}e^{-k_1t} + \frac{k_3k_2}{2\,k_1}e^{-2k_1t} + \frac{k_3k_2}{2k_1}$$

Until the first started chains go to completion at $t = 1/k_2$, the value of α is

$$\alpha = A - B$$

There is no discontinuity at $t = 1/k_2$, but at this time chains that originally started go to completion and must be removed from production. In the ideal situation where there has been no premature chain termination, the value of C to be subtracted would be

$$C = k_2 t + \frac{k_2}{k_1} e^{k_1/k_2} e^{-k_1 t} - 1 - \frac{k_2}{k_1}$$

However, some chains have already been taken out of production by term B, so term C is too large and must be corrected by adding a term D representing those chains prematurely terminated:

$$D = \frac{k_2 k_3}{2k_1} e^{k_1/k_2} e^{-2k_1 t} + \frac{k_2 k_3}{k_1} e^{-k_1 t}$$

Beyond $t = 1/k_2$ the value of α becomes

$$\alpha = A - B - C + D$$

Although the integrated equation involves an unusually large arithmetic expression, it is derived on the basis of the zipper mechanism assuming that chain initiation occurs as first order in polymer chains. An initiated chain is prematurely terminated or it unzips at a certain fraction of a chain per second which is dependent on the length of the polymer chain. For any polymer sample the rate of hydrogen chloride production is assumed to be proportional to the fraction of chains that are unzipping times the fraction of a chain unzipping per second. The production of "thermal hydrogen chloride" that is necessary to initiate the chains is considered to be negligible compared to the hydrogen chloride formed by the zip process. The value of α at infinite time can be calculated from the best fit values of the parameters k_1, k_2, and k_3 according to

$$\alpha_\infty = 1 - \frac{k_3 k_2}{2k_1}(1 - e^{-k_1/k_2})$$

THE APPLICATION OF THE COMPUTER TO THE CALCULATION AND EVALUATION OF DATA

Peak areas and the time interval between peaks are entered into the computer under an assigned run number, and any run can be called up for printout or for the curve fitting program. In the fitting program the operator gives a best estimate for each parameter. If no estimate is given, the computer makes its own estimate. The operator can fix the value of any one or all of the parameters. The program then prints out the values of the parameters at best fit and values of α, data; α, calc.; $\Delta\alpha$ per interval, data; and $\Delta\alpha$ per interval, calc. as a function of time. The best fit values are calculated so that the square root of the sum of the squares of (α data - α calc.) is a minimum. When this minimum value is divided by the number of fit points and multiplied by 100, a quantity designated as Δ is obtained. Δ is a measure of how the calculated values of α agree with the observed values and is approximately the absolute difference per point times 100. After the best fit values of the parameters are printed out, the operator has an option of fitting the data to higher precision. Two-digit precision is normally specified for a first fit. When higher precision is requested, the results of two-digit precision are automatically used as best estimates for a fit at three-digit precision and so on to four- and five-digit precision if desired. Three-digit precision was normally used in the present work.

For good runs all parameters could be allowed to vary, and the best fit values of t_s and k_2 would be in the range estimated from the run data. Thus t_s would not normally vary by more than one or two intervals from the estimated starting time. When an induction period preceded the "take-off," a time shift to the approximate "take-off" time was acceptable. When PVDC was added to the sample to furnish extra thermal hydrogen chloride at the start of a run, a negative time shift of a few hundred seconds seemed reasonable and appropriate.

The reciprocal of k_2, the time for a chain to unzip completely, also fell reasonably close to the observed time at which the maximum rate was attained. For occasional runs, unrealistic values of t_s and/or k_2 would be obtained for best fit. When this occurred, the fixing of k_2 and t_s at reasonable values usually gave satisfactory fits of theory and data at slightly higher values of the average error per point.

Only the runs giving reasonable values of all parameters without fixing any parameter have been reported in this work. It seems significant that t_s, k_2, and α_∞ have proper values when the computer is allowed to find best values for all parameters. Thus, even though four parameters are used to obtain best fits, two of those parameters have definite limits placed upon them and all parameters must be properly related to give reasonable values of α_∞.

SIMULATED COMPUTER RUNS

Simulated computer runs are prepared by calculating and properly combining $\Delta\alpha$ values for data obtained by fixing all parameters. In our earlier work [17] simulation was used to establish that the kinetic model gives first-order kinetics for $k_2 \gg k_1$, zero-order kinetics for $k_1 \gg k_2$, and acceleratory kinetics (S-shaped α-t curves) for $k_1 \cong k_2$. As would be expected, simulated runs with and without induction periods can be fit by our computer program and give values of the four parameters that agree with those assigned.

Simulated runs representing mixtures of different chain lengths (varying k_2) give the assigned value of k_1 and a weighted average of k_2. The weighting of k_2 is on a mole basis rather than on a weight basis. Thus the k_2's reported in our work represent an average k_2 for samples that would normally be expected to have a distribution of chain lengths around an average value.

A significant simulated run assumed that one-fifth of a sample became saturated evenly with hydrogen chloride and started acceleratory decomposition immediately, while the remaining sample did not start decomposition until 480 s had elapsed. This simulation represents in a crude way what may occur when hydrogen chloride saturation does not occur simultaneously throughout a sample. The simulated run was fit by the program but, as would be expected, gave values of k_1 and k_2 that were significantly lower than those assigned in preparing the simulated run. It is believed that uneven saturation of actual samples with hydrogen chloride is at least partly responsible for the difficulty of obtaining exactly reproducible data.

RESULTS

Figures 1, 2, and 3 are reproductions of actual run sheets for the designated samples and are representative of the raw data for all runs. Table 1 represents the raw data as stored in the computer for the run of Fig. 1. Every run has its own record of peak areas for a specified time interval. From these data, computer printouts of t_{sec}, α data, α calc., $\Delta\alpha$ data, $\Delta\alpha$ calc., and the value of the parameters at best fit are calculated. Table 2 records values at selected times for the data of Fig. 1 to illustrate the kinds of data that are available for every run.

Figure 4 is a plot of α, the fraction decomposed, vs t for the run of Fig. 1. The line represents the theoretical values calculated from best fit parameters and the points are actual data. These same data are shown in Fig. 5 in which rates, $\Delta\alpha$ per interval, are shown as a

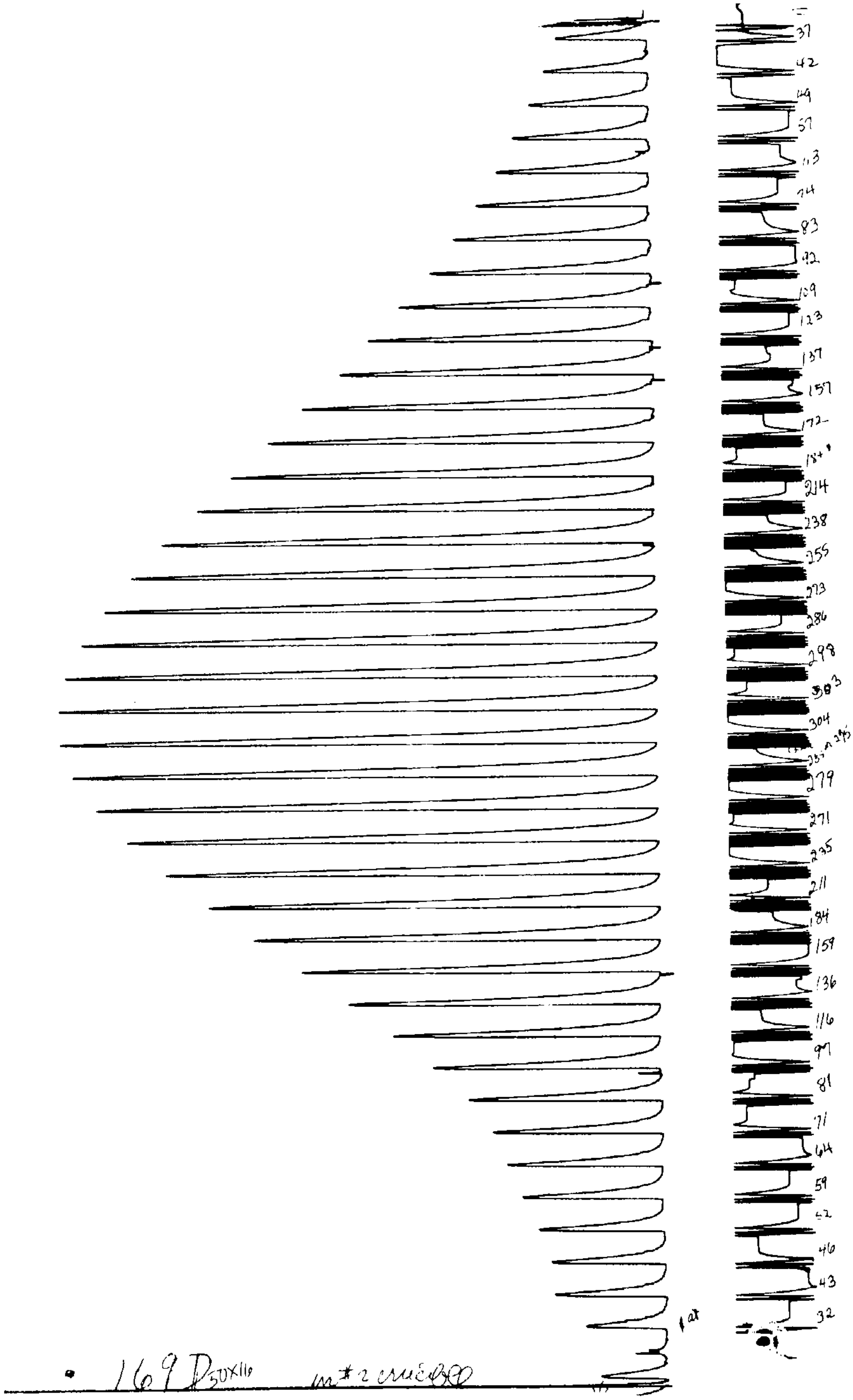

FIG. 1. Reproduction of run sheet for Run 180D.RAW. 97.8 mg DP 684, 2.2 mg PVDC, 225° C, 90 sec cycle, crucible reactor, retention by weight loss.

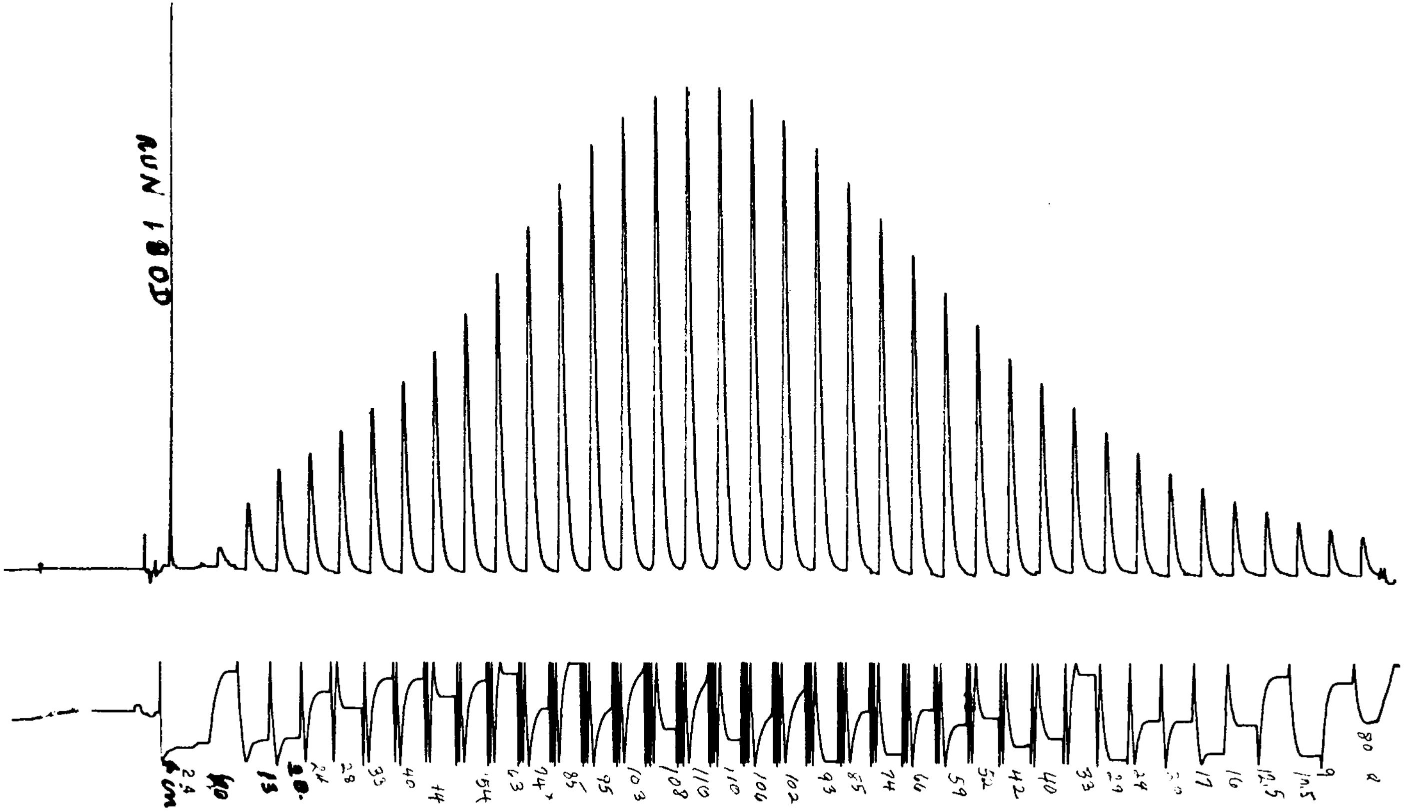

FIG. 2. Reproduction of run sheet for Run 169D.RAW. 60.2 mg DP 1002, 2.0 mg PVDC, 225°C, 120 sec cycle, crucible reactor, retention by weight loss.

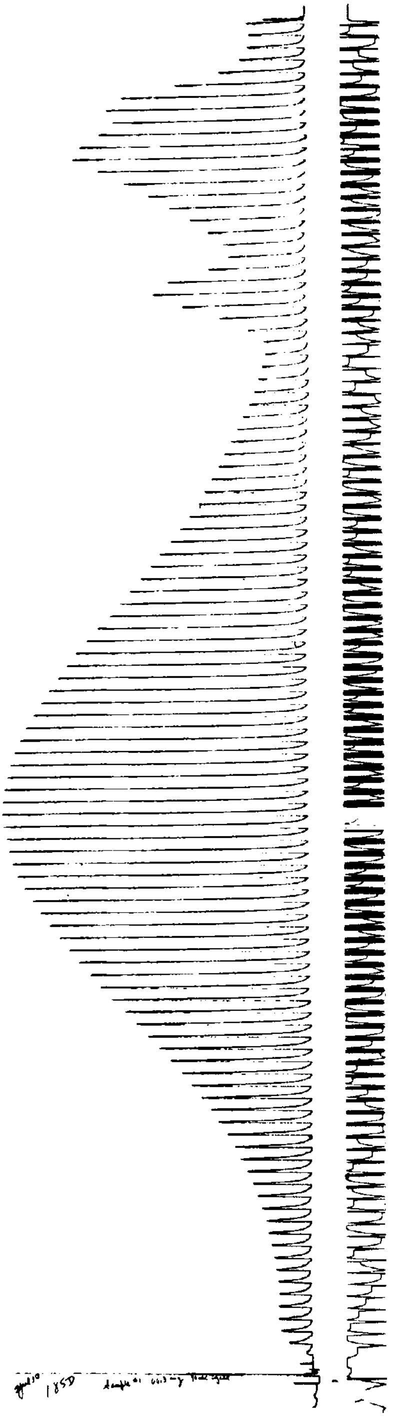

FIG. 3. Reproduction of run sheet for Run 185D.RAW. 66.3 mg DP 1272, 225°C, 90 sec cycle, crucible reactor, retention by driving off HCl at 325°C.

TABLE 1. Raw Data Stored in Computer for Run of Fig. 1. (Run 180D.RAW, 97.8 mg DP 684 + 2.2 mg PVDC at 225°C, crucible reactor, 90-s cycle)[a]

Peak areas						
0.0	10.0	13.0	20.0	24.0	28.0	33.0
40.0	44.0	54.0	63.0	74.0	85.0	94.0
103.0	108.0	110.0	110.0	106.0	102.0	93.0
85.0	74.0	66.0	59.0	52.0	42.0	40.0
33.0	29.0	24.0	20.0	17.0	16.0	12.5
10.5	9.0	8.0				

[a] Retention peak area by weight loss of sample: 586.

function of time. Even in this more critical comparison there is close agreement between theory and data.

Figure 6 shows the α-t curves obtained when 0, 5, and 20 mg Chromosorb W (Johns Manville Co.), an inert diatomaceous earth, was mixed with 43 mg DP684 and the mixture dehydrochlorinated in a crucible reactor at 230°C. The behavior of DP684 in the presence of Chromosorb was characteristic of that observed with other samples. The sharp drop in conversion associated with the increase in Chromosorb is attributed to premature chain termination.

Figure 7 illustrates the critical nature of hydrogen chloride in starting reaction chains. Sample DP1272, which gives no evidence of decomposition in a tube reactor at 225°C, shows slow initiation even at 235°C where the sample slowly melts, obstructs the sweepout of hydrogen chloride, and eventually undergoes an acceleratory decomposition. In the crucible reactor which retains the thermal hydrogen chloride, the same sample takes off more rapidly, but time is required for the build-up of hydrogen chloride. In the crucible reactor to which 2 mg PVDC was added to furnish hydrogen chloride, the sample took off immediately in an acceleratory decomposition. PVDC evolves hydrogen chloride at 160°C and would be expected to supply immediate hydrogen chloride when present at higher temperature.

Figure 8 illustrates that a sample, DP684, at its maximum rate of dehydrochlorination can be removed from the reaction chamber, allowed to stand for 15 h, and will immediately resume a high rate of dehydrochlorination when reintroduced to the heated chamber. Other samples behaved similarly.

Figure 9 shows plots of rate $\Delta\alpha$ per interval as a function of time for runs of Figs. 1, 2, and 3. Even though the exact reproduction of the time of the maximum for duplicate runs is sometimes difficult, there is a clear and definite trend for the time to reach the maximum

TABLE 2. Computer Printout for Best Fit of 180D.RAW, 97.8 mg DP684 + 2.2 mg PVDC 225°, 90-s Cycle, Crucible Reactor[a]

Time (s)	Alpha, data	Alpha, calculated	Rate, data, $\Delta\alpha$/ interval	Rate, calculated, $\Delta\alpha$/ interval
0	0	-0.204E-06	0	0.204E-06
180	0.907E-02	0.253E-02	0.520E-02	0.211E-02
360	0.268E-01	0.152E-01	0.961E-02	0.794E-02
540	0.512E-01	0.417E-01	0.132E-01	0.151E-01
720	0.849E-01	0.825E-01	0.176E-01	0.221E-01
900	0.132	0.136	0.252E-01	0.286E-01
1080	0.195	0.202	0.340E-01	0.341E-01
1260	0.275	0.277	0.412E-01	0.387E-01
1440	0.362	0.360	0.440E-01	0.425E-01
1620	0.448	0.449	0.424E-01	0.449E-01
1800	0.526	0.527	0.372E-01	0.366E-01
1980	0.590	0.589	0.296E-01	0.289E-01
-	-	-	-	-
3150	0.759	0.765	0.42E-02	0.57E-02
3330	0.765	0.775	0.32E-02	0.45E-02
	$\alpha_{\text{End}} = 0.765$	$\alpha_{\infty\text{calc.}} = 0.806$		

[a] Best fit values:
k_1, 0.0014224
k_2, 0.0006304
k_3, 0.9701898
Time shift, -3.708 s
Error per fit point, 0.498%
Three digit precision

to increase as the degree of polymerization increases. Thus Samples DP684, DP1002, and DP1272 required 1500, 2300, and 4000 s, respectively, to attain their maximum rates.

Table 3 summarizes run conditions and the values of the parameters for representative runs at 225°C. The trends of both k_1 and k_2 are to decrease with increasing molecular weight although occasionally values

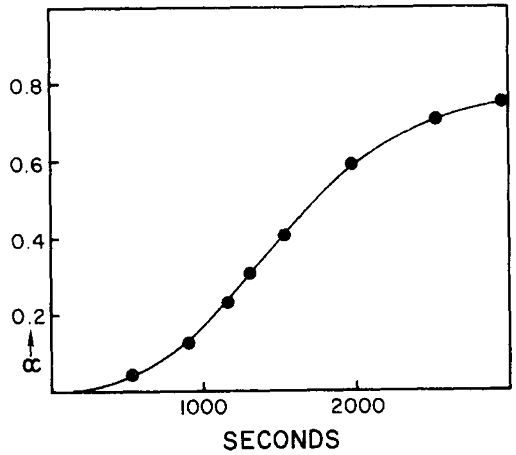

FIG. 4. Alpha-time plot for Run 180D.RAW. Line represents theory; points are actual data.

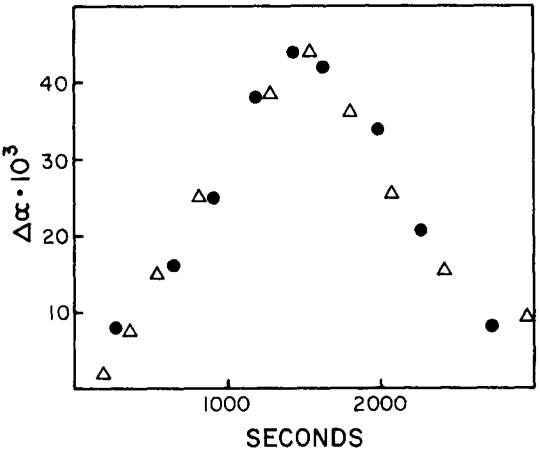

FIG. 5. Rate as a function of time for Run 180D.RAW: (●) data, (△) theory.

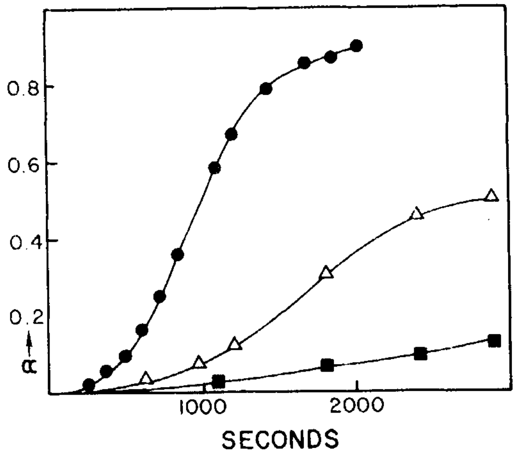

FIG. 6. The effect of Chromosorb W on the decomposition of 43 mg DP 684 at 230°C: (●) 0.0 mg, (△) 5.0 mg, (■) 20 mg.

fall completely out of line for reasons which may be related to the uneven saturation with hydrogen chloride.

Table 4 summarizes representative values of the parameters for DP684 at different temperatures. All samples were run at different temperatures and show similar behaviors. The trend clearly shows that both k_1 and k_2 increase with temperature as would be expected, and the kinetic model continues to give good fits of data with an average error per point of less than 0.72%.

DISCUSSION

The acceleratory dehydrochlorinations of PVC shown in Figs. 1, 2, and 3 and hundreds of other similar dehydrochlorinations have been consistent in a qualitative way with the zipper mechanism. The small peaks at the start of a run represent hydrogen chloride from the first started zip chains. These chains continue to produce and are joined by other starting chains during the acceleratory period. When the first started chains have completely unzipped and cease production, there will be more chains stopping production than are starting and the deceleratory period begins. The time from the beginning of the run to the maximum peak is the time required for a chain to unzip completely, and the reciprocal of that time will be k_2, the fraction of a chain unzipping per second. When hydrogen chloride production practically ceases, significant hydrogen chloride is retained in the

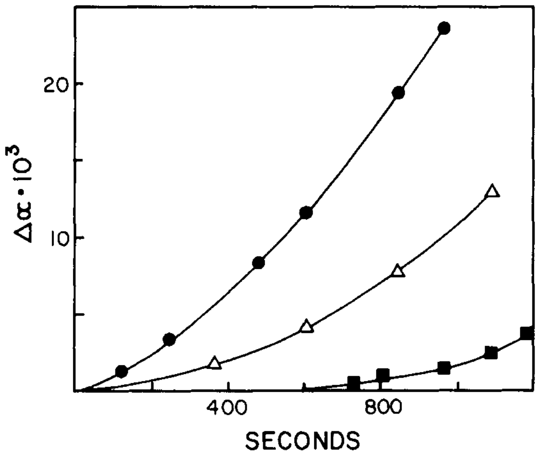

FIG. 7. Initial rates of DP 1272 at 235°C: (■) tube reactor, (△) crucible reactor, (●) crucible reactor with PVDC.

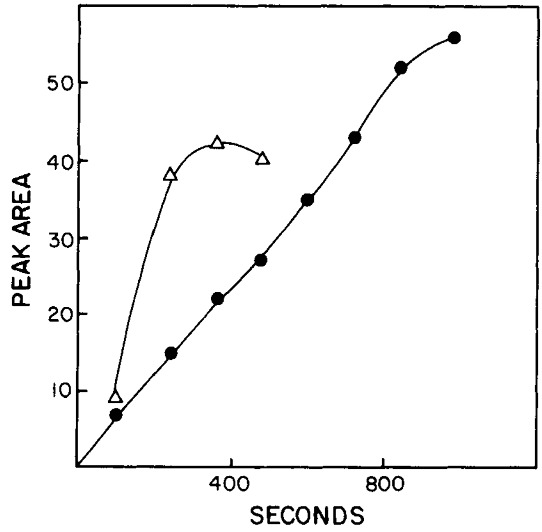

FIG. 8. Stability of a producing chain (●) original sample DP 684; (△) after removal from the chamber and standing in the atmosphere for 15 h.

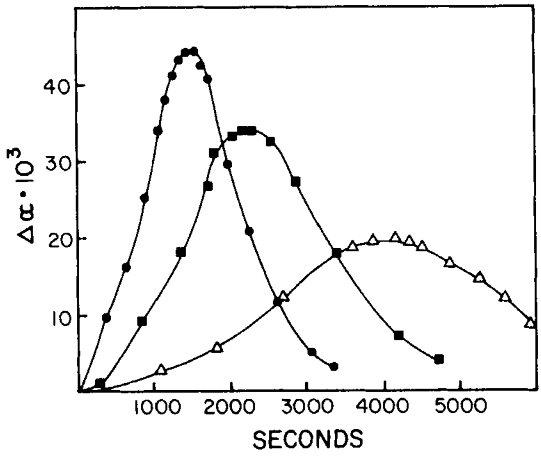

FIG. 9. Dependence of time to reach the maximum rate on degree of polymerization at 225°C in the crucible reactor: (●) DP 684, (■) DP 1002, (△) DP 1272.

sample. Retention has been explained on the basis of premature termination of starting chains by contact with the container surface and impurities in the sample. An approximation to account for chain termination is included in the kinetic model. Hydrogen chloride is an essential catalyst for the initiation of zip chains and may or may not catalyze the unzipping reaction. The kinetic model assumes a constant atmosphere of hydrogen chloride which is difficult to reproduce from one run to another. Thus individual runs display regular and even hydrogen chloride peaks and can be fit efficiently by the kinetic model. When the hydrogen chloride saturation is uniform, the runs should be reproducible. Variations in the values of k_1 and k_2 for runs on the same sample at the same temperature may be attributed to unavoidable differences in the saturation of the sample by hydrogen chloride.

The quantitative agreement of theory and data is illustrated in Figs. 4 and 5 which show, respectively, plots of α and $\Delta\alpha$ per interval as a function of time. The average error per fit point was 0.5%. For each run reported in Table 3 the average error per fit point was less than 0.65%.

Since the kinetic model so effectively predicts dehydrochlorination patterns of PVC, it seems appropriate to describe that model and summarize the evidence supporting it. The kinetic model can be represented as

TABLE 3. Best Fit Parameters at 225°C, 120-s Cycle

Run[a]	DP[b]	mg sample	$k_1 \times 10^3$	$k_2 \times 10^3$	k_3	t_s	Δ(%)	α_E	α_∞
7724-T	546	50	1.54	0.72	0.97	-35	0.44	0.78	0.80
7750-T	684	50	1.50	0.74	0.84	-82	0.34	0.80	0.82
7751-T	684	50	1.47	0.62	0.99	-177	0.49	0.78	0.81
7752-T	684	50	1.54	0.78	0.96	-88	0.40	0.77	0.79
794S-C	684	43	1.03	0.69	0.84	-50	0.21	0.77	0.78
7981S-C	684+	43	1.16	0.63	0.51	-202	0.38	0.87	0.88
170D-C	845+		1.30	0.50	0.97	64	0.58	0.77	0.83
7721-T	845	50	1.01	0.49	1.16	-142	0.35	0.70	0.76
7967S-C	1002+	62	0.95	0.53	0.63	-82	0.35	0.83	0.85
7920S-C	1002	62	2.13	0.71	0.71	617[c]	0.47	0.87	0.89
171D-C	1272+	77	0.72	0.29	0.57	327	0.63	0.84	0.90
7924S-C	1272	80	0.66	0.28	0.52	316	0.44	0.87	.90
7975S-C	1272+	80	0.66	0.28	1.01	-317	0.35	0.78	.81

[a] Appended letter designates tube (T) or crucible (C) reactor.

[b] Degree of polymerization. An appended + means 2 mg PVDC.

[c] Run started slowly and first real peak was near 600 s but after start accelerated rapidly. Occasionally high k_1 values encountered with this sample.

TABLE 4. Best Fit Parameters for Representative Runs of DP684 at Various Temperatures

Temperature (°C)	220T[a]	222.5T	225.5T	227.5T	230T	235C	240C
$k_1 \times 10^3$	1.17	1.32	1.48	1.60	1.62	2.29	2.04
$k_2 \times 10^3$	0.47	0.62	0.62	0.83	0.96	1.09	1.45
k_3	1.02	1.05	0.99	1.06	.82	0.76	0.57
t_s	-163	-16	-177	-58	-58	121	7
Δ (%)	0.26	0.30	0.49	0.29	0.49	0.72	0.46

[a] T is tube reactor, C is crucible.

$$\begin{tikzcd} \mathrm{PVC} + \mathrm{HCl} \arrow[r, shift left] & \mathrm{PVC{\cdot}HCl^*} + \mathrm{S} \arrow[l, shift left] \arrow[r] \arrow[d] & \mathrm{PVC{\cdot}S} \text{ (retention)} \\ & \text{Unzipping chain at intrinsic rate, } k_2{\cdot}\mathrm{DP} \arrow[d] & \\ & \text{Amorphous coke} + \mathrm{HCl} & \end{tikzcd}$$

Hydrogen chloride is assumed to saturate the polymer and because of its volatility remains at a constant activity. The hydrogen chloride may be added to initiate the reaction or it may be formed by slow thermal decomposition of PVC. Thermal hydrogen chloride has been postulated to form from tertiary chloride or allyl chloride moieties presumed to be present in PVC [18]. These chlorides, if present, could certainly be sources of thermal hydrogen chloride. In the temperature range of our work the amount of thermal hydrogen chloride, while negligible in comparison with the unzipping hydrogen chloride, is nevertheless greater than that which would be expected from these special chlorides. Regardless of its source, hydrogen chloride is assumed in the kinetic model to have a constant activity. Because of the slow formation of thermal hydrogen chloride and its possible uneven distribution throughout the polymer sample, even when artificially introduced, the actual decomposition does not always attain an even saturation with hydrogen chloride until the run is well under way. It is believed that the difficulty of reproducing data and the occasional spurious run is the result of the variations in saturation with hydrogen chloride in the early stages of a run and in the actual saturation pressure maintained during the run. Evidence for the critical nature of hydrogen chloride for the initiation reaction is presented in Fig. 7 in which Sample DP1272 shows extreme variation in the initial dehydrochlorination patterns depending on the efficiency of saturation with hydrogen chloride.

Once hydrogen chloride has reacted with the PVC to form a site active for initiation of the zip reaction, that site may presumably revert to hydrogen chloride and polymer, it may react with surface or impurities to deactivate, or it may start the unzipping reaction. The effect of the inert substance, Chromosorb, on the retention of hydrogen chloride is considered to be good evidence for the occurrence of chain termination although random initiation of chains unzipping in one direction and chain branching could also contribute to retention.

Once the unzipping reaction is under way, it seems to be especially persistent. As illustrated in Fig. 8, decomposing chains retain their activity even after standing for 15 h exposed to the atmosphere.

Hydrogen chloride is essential for chain initiation. Whether it also catalyzes the unzipping reaction cannot be easily established since the unzipping chain must always be in contact with hydrogen chloride while it is unzipping.

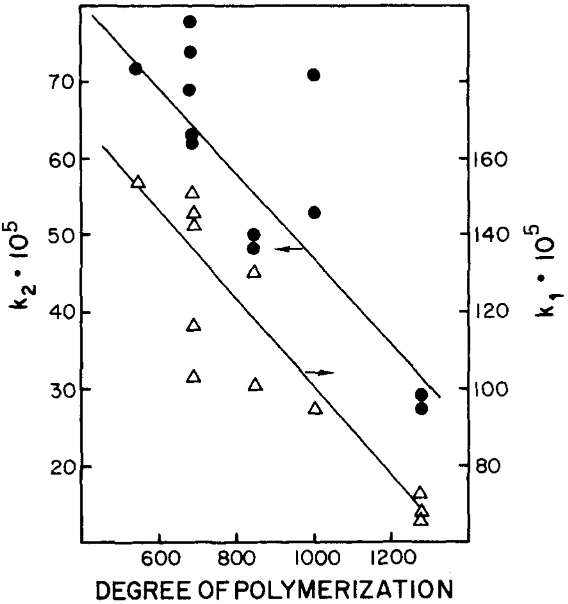

FIG. 10. Variations of k_1 and k_2 as a function of degree of polymerization for representative runs of Table 3: (●) k_2, left axis; (△) k_1, right axis.

The kinetic model was based on chain activation at or near a chain end followed by complete unzipping of nonterminated chains at an intrinsic rate, $k_2 \cdot DP$ molecules hydrogen chloride per chain per second. The dependence of zip time and k_2 on the degree of polymerization illustrated in Figs. 9 and 10 is consistent with the concept of chain-end initiation but does not prove it. Since k_1, the fraction of chains initiated per second, as shown in Fig. 10, decreases with increasing chain length, it might be possible to develop a model in which chain unzipping occurred throughout the sample without regard for individual chains. In this model the fewer the chain initiations the longer on the average would be the zip chain.

The concept of chain initiation catalyzed by hydrogen chloride followed by unzipping at a constant intrinsic rate seems strongly favored by the data. The initiation at a double bond at or near chain ends as assumed in the model is entirely consistent with the data. Unfortunately, chain starting at selective sites within the polymer cannot be ruled out.

If it is assumed that the kinetics observed in our work persist at lower temperatures, and there seems to be no compelling reason not to make this assumption, then many conflicting reports concerning the dehydrochlorination of PVC can be reasonably explained. Many studies have been made at low conversions on samples of powdered PVC below their melting points under vacuum or in a stream of nitrogen. Under these conditions the hydrogen chloride necessary for initiation of the chain is swept away and only slow and constant thermal dehydrochlorination would be observed. If the sample agglomerated and/or the hydrogen chloride was not efficiently removed, there would be some initiation of zip chains which would in turn evolve hydrogen chloride to start more zip chains, and an increase in the rate of hydrogen chloride production as the conversion increased would be observed. The observed rate would, of course, be a function of the efficiency with which the hydrogen chloride was removed. Preliminary studies of thermal dehydrochlorination have shown a first-order dependence of rate on the remaining polymer, $(1 - \alpha)$. This first-order dependence and decreasing rate is also approximated during a substantial portion of the deceleratory portion of a normal acceleratory dehydrochlorination. Thus it is not surprising that the rate of hydrogen chloride production has been reported to increase, remain constant, or decrease with time [19].

Catalysis by hydrogen chloride has also been controversial [20]. According to the present scheme, hydrogen chloride would be an effective catalyst only under conditions where saturation with hydrogen chloride had not already occurred.

Even though kinetic studies do not define a specific chemical mechanism, it is not inappropriate to suggest a possible mechanism. The addition of hydrogen chloride to a double bond, $-CH{=}CCl-$, would form $-CH_2-CCl_2-$ which is the structural unit in PVDC which readily decomposes at temperatures of 160°C [21]. The entity $-CH{=}CCl-$ can easily be formed at a double bond in the PVC chain by several additions and eliminations of hydrogen chloride according to known reactions. On the basis of these considerations it seems possible that the function of hydrogen chloride in initiating reaction chains is to react with double bonds to form the entity $-CH_2-CCl_2-$ which is known to degrade at low temperatures in PVDC.

The observation that hydrogen bromide is a more effective catalyst than hydrogen chloride [22] may imply that the rate-controlling step in a constant atmosphere of hydrogen halide is the elimination of the hydrogen halide. Certainly hydrogen bromide would be eliminated more readily than hydrogen chloride and would therefore appear to be a better catalyst.

How the presence of chromosorb or surface can prevent the initiation of the zip reaction is not clear, but the concept of a molecular elimination for the zip reaction seems more consistent with the observed stability of the unzipping chain than either a carbonium ion or radical mechanism.

In addition to the theoretical implications of the kinetic model, there are practical implications as well. Thus, once a chain decomposition has been initiated during processing, that chain may remain in the zip state for the life of the product. The zip reaction would presumably continue at a very slow rate even at room temperature.

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