

Degradation of Poly(vinyl Chloride). III. Kinetics of Thermal Dehydrochlorination Catalyzed by Slow-Diffusing HCl

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Synopsis

The dehydrochlorination reaction of poly(vinyl chloride) was investigated by subjecting molded polymer discs to thermal treatments at comparatively low temperatures and for low degradation extents, such as to maintain practically unchanged the sample's composition and physical state. The HCl evolution-versus-time curves exhibited accelerating behaviors to be ascribed to the catalytic action of HCl accumulating in the samples owing to a hindered diffusion. By assuming a catalyzed dehydrochlorination reaction occurring independently from the uncatalyzed one and being first order with respect to HCl, a kinetic equation describing satisfactorily the experimental evidence was deduced.

INTRODUCTION

The dehydrochlorination process of poly(vinyl chloride) (PVC) is generally recognized¹ to be catalyzed by HCl present in the atmosphere and/or accumulating in the polymer samples because of a hindered diffusion. Recently,^{2,3} this has been ascertained to occur also at comparatively low temperatures of degradation.

The dehydrochlorination catalyzed by a surrounding atmosphere of HCl was found to occur with a rate increasing with the gas pressure,^{4,5} and quantitative correlations have also been attempted.^{6,7} However, only crude evaluations of the catalytic action could be attained, owing to the lack of the knowledge on the way the repartition of HCl occurred between the polymer phase and the surrounding space. Undoubtedly, a more favorable case is represented by the dehydrochlorination catalysis due to HCl accumulating in the sample, since the extents of this accumulation should be inferable by means of known diffusion laws.⁸

However, at variance with previous investigations carried out on films at 200°C,⁸ a prerequisite for the reliability of the experiments it should be

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considered to operate with PVC samples of well defined dimensions and in such conditions that the sample's composition and physical state can be maintained unaltered during the degradation treatment.

EXPERIMENTAL

Material

The PVC, Lucovyl G B 1210, $\bar{M}_n = 50000$ and $\bar{M}_w = 110000$, was used without purification.

Tetrahydrofuran (THF), a RP C. Erba product, was fractionally distilled under N_2 , after a few hours refluxing over NaOH.

Apparatus and Procedure

Transparent discs of rigid PVC, exhibiting only a slight discoloration, were obtained by molding the PVC powder at $150^\circ C$ under pressure at 250 atm for 5 min with a Buehler Ltd. laboratory press. The constant 3.2-cm-diameter discs were prepared at thicknesses of 0.05, 0.1, 0.2, and 0.4 cm. Dehydrochlorination runs were carried out under vacuum as previously described,² with a slightly modified apparatus to allow the entering of the discs. The number of the discs varied in each run in order to have amounts of polymer similar in all cases and susceptible to give rise to measurable pressure of volatiles. From pressure data, the current² fraction of dehydrochlorination, x , defined as the ratio of the amount of split-off HCl to that theoretically extractable from the polymer, was derived.

The degradation of PVC discs of 0.4-cm thickness was followed through the determination of the ultraviolet and visible light absorption spectra from 270 to 500 nm, adopting the same procedure as in a previous work.³ Regarding the prerequisite of an instantaneous dissolution in THF of the bulk degraded PVC, this could be satisfied by cutting beforehand the discs into very minute pieces (40μ) with a microtome.

For the calculations, use was made of a Digital Computer Corporation PDP-8 computer.

RESULTS AND DISCUSSION

The polymer PVC was used without purification treatments, the latter being found to have produced no improvement in stability. To meet the requirements of well-defined dimensions and a physical state not liable to change, at least in the first degradation stages under concern here, the samples were conveniently prepared in the form of discs by molding. However, by this preparation a certain extent of degradation could not be avoided, although samples rigorously free from HCl were needed, in principle. Beside, another unavoidable source of uncertainty due to molding samples in the air was that the samples entrapped oxygen known¹ to accelerate the degradation course.

Bearing in mind that, in addition, the pressures of volatiles to be measured were low, a rather poor reproducibility of the data was not unex-

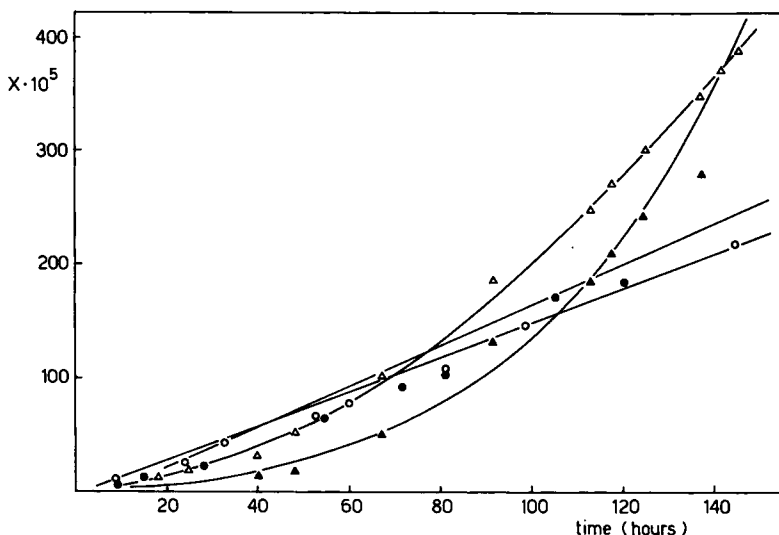


Fig. 1. Kinetics of PVC dehydrochlorination. Data at 120°C for samples of 0.05 (○), 0.1 (●), 0.2 (△), and 0.4 (▲) cm thickness. The fitting curves are theoretically deduced using $D = 3.5 \times 10^{-8}$ cm²/sec and $k = 8 \times 10^{-6}$ sec⁻¹.

pected. In this context, mention should be made that in some runs evolution of volatiles started very rapidly and then proceeded normally as previously found,² but for this initial burst of volatiles, not likely to consist of HCl, allowance was regularly made.

The results, which in view of all the above considerations show a not unexpected scattering and, even more, should be taken as to give only in an approximate fashion the ideal patterns of HCl evolution, are reported in the x versus-time diagrams of Figures 1, 2, and 3 for the earlier stages of degradation at temperatures of 120°, 130°, and 140°C, respectively.

As it could be inferred by a general survey of the figures, a strong influence is exerted on the HCl evolution kinetics by the disc thickness h , which is to be correlated with the catalytic action and the ability to diffuse of HCl.²

For its interpretation, a previous suggestion⁸ was followed, except for the fact that here no consideration was given to the initial burst of volatiles. Accordingly, the dehydrochlorination process is assumed to be made up by two independent contributions and, precisely, by an uncatalyzed reaction of constant rate k_0 and a catalyzed one of rate kc , with k being a constant and c the HCl concentration existing in any given point volume of the PVC sample. Then, with samples in the shape of thin discs, the extent of HCl evolution at time t , in terms of the dehydrochlorination fraction x , is given by the following summation extending to all integers n :

$$x \simeq \frac{4Dk_0}{h^2\mu} \sum_{n=1}^{\infty} \frac{1 - \cos \pi n}{(k - D\pi^2 n^2/h^2)^2} [e^{t(k - D^2\pi n^2/h^2)} - t(k - D\pi^2 n^2/h^2) - 1] \quad (1)$$

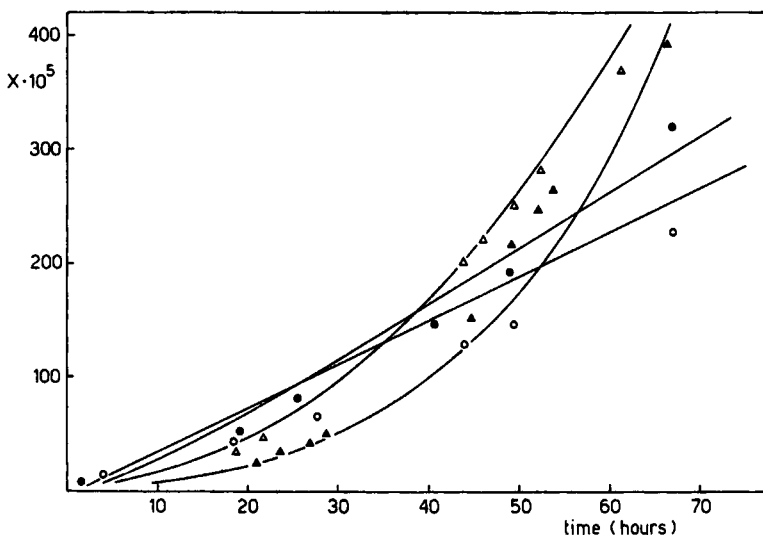


Fig. 2. Kinetics of PVC dehydrochlorination. Data at 130°C for samples of 0.05 (○), 0.1 (●), 0.2 (△), and 0.4 (▲) cm thickness. The fitting curves are theoretically deduced using $D = 6 \times 10^{-8}$ cm²/sec and $k = 17 \times 10^{-6}$ sec⁻¹.

where D is the HCl diffusion coefficient, h is the disc thickness, and μ is the amount of HCl theoretically extractable from a unit volume of polymer (see Appendix A).

A special case arises when the catalyzed reaction occurs to a negligible extent as in conditions such that $k \ll D\pi^2/h^2$. However, the predictable patterns of HCl evolution, as briefly outlined in Appendix B, are by no means in agreement with the plots in Figures 1, 2, and 3.

Consequently, the general case of occurrence of catalysis to a substantial extent had to be taken into consideration, in other words, eq. (1) had to be applied without simplifications. To this end it was necessary to assign the values of the parameters. As to the k_0/μ value, it should be noted that the limiting form of eq. (1), as h approaches zero, is

$$x \simeq \frac{k_0}{\mu} t \quad (2)$$

The agreement of eq. (2) with experimental evidence on the PVC degradation has been established in previous investigations,² where the x -versus- t curves, normally curving upward, were made to approach straight lines by drastically reducing the thickness of the polymer layer. Therefore, the slopes $\Delta x/\Delta t$ obtained there can be identified with the k_0/μ values to be utilized in eq. (1) for the general case of not negligible h values.

The other parameters needed, D and k , on the contrary, were unavailable and were assessed arbitrarily to solve eq. (1) at regularly spaced times, carrying out the calculation of the summation over the first odd integers n

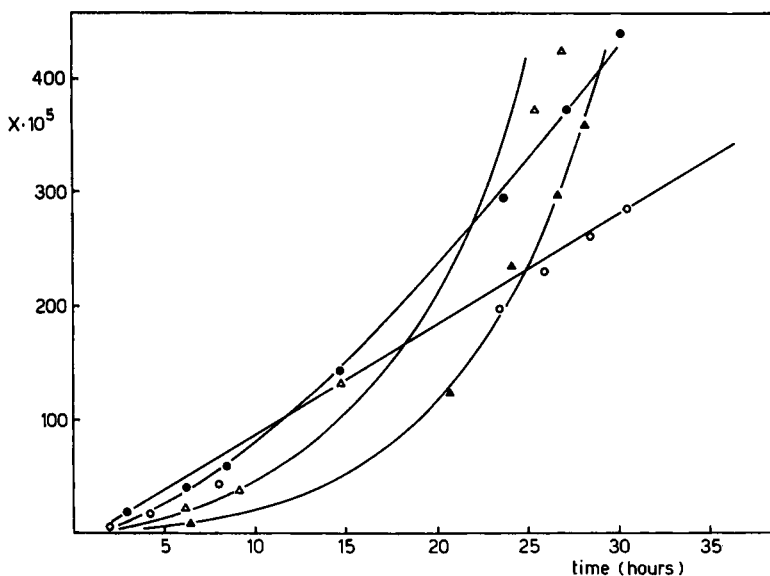


Fig. 3. Kinetics of PVC dehydrochlorination. Data at 140°C for samples of 0.05 (O), 0.1 (●), 0.2 (△), and 0.4 (▲) cm thickness. The fitting curves are theoretically deduced using $D = 7 \times 10^{-8}$ cm²/sec and $k = 45 \times 10^{-6}$ sec⁻¹.

up to 29, the contribution of higher n values being negligible. Then, by systematically changing D and k , a large number of curves could be traced, among which those best describing the experimental data could be chosen. Some indications on the order of magnitude of these parameters could be inferred by observing that eq. (1) allows to distinguish two cases. For $k \geq D\pi^2/h^2$, the increase of x proceeds always in an accelerated fashion, while if $k < D\pi^2/h^2$, acceleration ceases and a maximum rate is attained at sufficiently high times, i.e., when the exponential terms become negligibly small. Incidentally, this reflects the attainment of a stationary HCl concentration profile along the cylinder altitude, as can be inferred by $\delta c/\delta t$ depending on analogous exponential terms, derivative of eq. (A-2).

With reference to the parameter h , the two cases above occur for $h \geq D^{1/2}\pi/k^{1/2}$ and $h < D^{1/2}\pi/k^{1/2}$, respectively, so that the h value equal to $D^{1/2}\pi/k^{1/2}$ can be looked upon as a critical thickness. Now, an inspection of the experimental data permitted the conclusion that the range of thicknesses investigated comprised the critical value; and, therefore, the k/D ratios had to be chosen around the π^2/h^2 values. On the other hand, there is to say for D that, regardless of k , very high values would have had the same consequence as the very low values of h in reducing eq. (1) to eq. (2) (see Appendix B). Since this is by no means in agreement with the results, resort had to be made only to D values from a certain order of magnitude downward. Furthermore, the latter could not be too low such as to prevent the x -versus- t curves relative to $h = 0.05$ cm to approximate to straight lines at the higher times.

TABLE I
Values Relative to the PVC Dehydrochlorination Process
at Different Temperatures

	$D \times 10^8, \text{cm}^2/\text{sec}$	$k \times 10^6, \text{sec}^{-1}$	$(\Delta x/\Delta t) \times 10^{10},^a$ sec ⁻¹
120°C	3-4	7-8	41
130°C	5-6	17-20	102
140°C	7-8	42-46	235
$E, \text{kcal/mole}$	10-15	26-30	28

^a Data from ref. 2.

Choosing D and k within the thus delimited ranges, the calculated curves showing the best fit are traced in Figures 1, 2, and 3. As can be seen, the extent to which they are capable describing the complex kinetic patterns appears undoubtedly remarkable. Also of relevance is that a discrimination satisfactory enough was possible among the various combinations of D and k . Indeed, the ranges within which they could allow a still acceptable fit are reasonably narrow, taking into account the uncertainty affecting the experimental data. These ranges, together with the utilized k_0/u values, i.e., the previously² found $\Delta x/\Delta t$ values, are reported in Table I. From the parameters D and k , approximate values of the activation energy E were also drawn.

The values of D and k at 200°C could be roughly derived therefrom by means of extrapolation. In comparison with the values of $D = 5.5 \times 10^{-9} \text{cm}^2/\text{sec}$ and $k = 1.7 \times 10^{-4} \text{sec}^{-1}$, obtained in a previous work⁸ at this temperature, they appear higher by two and one order of magnitude, respectively. This discrepancy may be ascribed to the inadequacy of the assumption of an unchanged physical state with respect to samples treated at 200°C up to not very low extents of degradation, as was the case in that work.

On the other hand, the present data relative to HCl diffusion in PVC can be given some acceptability by the comparison with recent direct measurements⁹ with several biatomic gases in a range of temperature just above the PVC glass point. The activation energy appears to be similar, while the D values of Table I lie, by about a factor of 5, below those obtained by extrapolating the literature data.⁹

Regarding the rate constant of the reaction catalyzed by HCl, its activation energy is in fair agreement with the value of 21 kcal/mole, found with a different type of experiments.⁶

Further insight on the HCl catalysis is undoubtedly provided by following the formation of sequences of conjugated double bonds by means of spectroscopic analysis.³ The results, reported as absorbance-versus-time curves in analogy with a previous work,³ are shown in Figure 4 for the degradation of 0.4-cm-thick discs at 120°C. In contrast with the previous findings³ of a lengthening of the unsaturation sequences by HCl action,

Figure 4 shows that the acceleration is the larger the shorter the wavelength, or, in other words, the shorter the unsaturation sequences under concern. Moreover, a subsequent deceleration appears to take place starting the earlier the longer the wavelength. It should be mentioned that the latter phenomenon sets in still earlier at the higher temperatures, and at 140°C, almost no acceleration is discernible any more in the curves relative to the long wavelengths.

This difference in behavior may be attributed to the oxygen entrapped during molding since spectra exhibiting a decrease in absorbance with increasing wavelengths, such as are inferable from curves of Figure 4, are

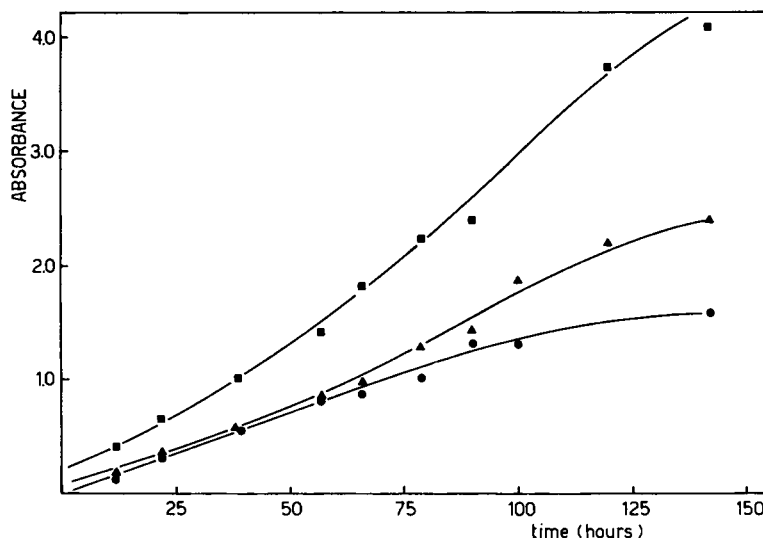


Fig. 4. Absorbance vs. time for degradation at 120°C at wavelengths of 273 (■), 335 (▲), and 468 (●) nm.

typical³ of degradation carried out in the presence of oxygen. Indeed, similar spectra have been found with samples molded without exclusion of air by other workers recently.¹⁰ Among the causes for this discrepancy, mention should be made of a rather rapid crosslinking process occurring in the present experimental conditions, as argued by the insolubility in THF of the PVC discs corresponding to comparatively early stages of degradation. This is in line with the evidence for a crosslinking process enhanced by HCl reported¹¹ in the bulk degradation of PVC at high temperatures.

In conclusion, the results seem to support all the proposed formulations for the HCl-catalyzed dehydrochlorination reaction, although further investigations would be desirable with samples in which entrapping of oxygen is accurately avoided.

Appendix A

On the assumption of a production of HCl with the composite rate $k_0 + k \cdot c(z,t)$ in a cylindrical sample, the change with time t of the HCl concentration $c(z,t)$ at any point of the coordinate z taken in the direction of the cylinder altitude h can be written

$$\frac{\delta c(z,t)}{\delta t} = D \left[\frac{\delta^2 c(z,t)}{\delta z^2} \right] + k_0 + k \cdot c(z,t) \quad (\text{A-1})$$

where D is the diffusion coefficient, if samples with the shape of a right cylinder with the radius of the base r , far larger than the altitude h , are concerned and if the sample portion near the curved surface is excepted. For simplicity's sake, k_0 and k comprise the concentration terms of the reactants remaining constant during treatment, as is the case for all chemical species other than HCl in the very early stages of degradation.

Integration of eq. (A-1), with fulfillment of the $c(z,0) = c(0,t) = c(h,t) = 0$ conditions for any z and t , gives

$$c(z,t) = -\frac{2k_0}{\pi} \sum_{n=1}^{\infty} \frac{1 - \cos \pi n}{n(k - D\pi^2 n^2/h^2)} [1 - e^{t(k - D\pi^2 n^2/h^2)}] \sin \frac{\pi n z}{h} \quad (\text{A-2})$$

with the summation extending over all integers n .

The amount of HCl diffusing out of the cylinder base at $z = h$ in the time interval dt per unit area is

$$dm = -D \left[\frac{\delta c(z,t)}{\delta z} \right]_{z=h} dt. \quad (\text{A-3})$$

The derivative of eq. (A-2) with respect to z , solved for $z = h$, is then introduced in eq. (A-3) to give

$$dm = \frac{2Dk_0}{h} dt \sum_{n=1}^{\infty} \frac{(1 - \cos \pi n) \cos \pi n}{(k - D\pi^2 n^2/h^2)} [1 - e^{t(k - D\pi^2 n^2/h^2)}]. \quad (\text{A-4})$$

In this equation it can be observed that $1 - \cos \pi n$ is equal to 2 for all odd n 's and equal to zero for all even n 's, while in the former case $\cos \pi n$ is equal to -1 . Therefore $\cos \pi n$ can be omitted provided the sign of the summation is changed. By integration of eq. (A-4) from time zero to time t , the amount of HCl diffused out per unit area results to be

$$m = \frac{2Dk_0}{h} \sum_{n=1}^{\infty} \frac{1 - \cos \pi n}{(k - D\pi^2 n^2/h^2)^2} \times [e^{t(k - D\pi^2 n^2/h^2)} - t(k - D\pi^2 n^2/h^2) - 1]. \quad (\text{A-5})$$

If the portion of the cylindrical sample affected by the perturbations due to the curved surface is comparatively small with respect to the rest, to a good approximation the amount of HCl diffused out of the whole surface of the cylinder base under concern is given by $\pi r^2 \cdot m$. Moreover, since on symmetry grounds the same reasoning holds for the other base of the

cylinder, $2\pi r^2 \cdot m$ can be taken as the total amount of HCl evolved from the sample at the time t . To convert it into the commonly used fraction of dehydrochlorination, x , the above value should be divided by the amount of HCl theoretically extractable from the sample, i.e., $\pi r^2 h \mu$, denoting μ as the theoretical amount relative to a unit volume of polymer. Thus, eq. (1) is obtained.

Appendix B

A special case arises when no catalyzed reaction occurs, i.e., when the kc term vanishes in eq. (A-1). Proceeding along the same lines as above, it can be readily recognized that the relative equations are those obtainable from eqs. (A-2), (A-4), (A-5), and (1), respectively, simply by putting $k = 0$. Incidentally, since not dissimilar results should be expected when $k \ll D\pi^2/h^2$, any noticeable catalytic effect can be ruled out if this disequilibrium holds.

Examining the last of this new series of equations, which can be written

$$x \simeq \frac{k_0}{\mu} \left[t - \frac{h^2}{12D} + \frac{4h^2}{D\pi^4} \sum_{n=n}^{\infty} \frac{1 - \cos \pi n}{n^4} e^{-D\pi^2 n^2 t/h^2} \right] \quad (\text{B-1})$$

it can be predicted for a dehydrochlorination reaction unaffected by HCl catalysis that kinetic curves would approximate closely to the straight lines of k_0/μ slope and of $h^2/12D$ intercept with the time axis, after the comparatively short times required for the exponential terms to become negligibly small are elapsed. As a consequence, runs carried out with samples of different h values would give rise to x -versus- t curves which, after an initial period of acceleration, all run parallel to one another and intersect the time axis at a varying distance proportional to h^2 .

A point also worth noting is that the end of the period of acceleration marks the acquisition of a stationary profile along the z -axis by the HCl concentration, as can be argued by the exponential terms in eq. (B-1) being analogous to those characterizing the time dependence of the $\delta c(z,t)/\delta t$ term (see derivative of eq. (A-2) with $k = 0$).

Of interest is that the limiting form of eq. (B-1), as the intercept $h^2/12D$ approaches zero, is eq. (2), implying that the stationary profile is attained almost instantaneously and that the stationary concentration, too, approaches zero; in other words, the $\delta c/\delta t$ and kc terms vanish in eq. (A-1). Indeed, it can be seen that eq. (2) is readily obtainable from eq. (A-1) thus modified in the cases of very small thickness and/or very high diffusion rate. Moreover, it makes no difference in these circumstances if HCl has or does not have catalytic action.

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