

The Degradation of Poly(vinyl Chloride). I. Hydrogen Chloride Evolved from Solid Samples and from Solutions

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Synopsis

A technique is described for the accurate and reproducible estimation of hydrogen chloride evolved during the degradation of poly(vinyl chloride). Results of degrading PVC in solvents and in the solid state are reported, and explanations are suggested for the differences in the observed behavior.

INTRODUCTION

Techniques used for studying the degradation of poly(vinyl chloride) (PVC) fall into two groups: (a) the observation of changes in the polymer residue and (b) the measurement of the hydrogen chloride evolved. The former group includes thermogravimetry^{1,2} and infrared, nuclear magnetic resonance, and ultraviolet/visible spectral analysis.³⁻⁵ The measurement of hydrogen chloride produced is the most sensitive quantitative method for following the early stages of degradation, and the simplest technique is acid-base titration of the hydrogen chloride absorbed in water. Measurement of the pressure of volatiles produced during the degradation is a valuable technique which has been used to provide firm evidence for the autocatalytic nature of the reaction in the presence of hydrogen chloride.⁶

The polymer has been studied in a number of forms. Many investigators have used bulk polymer, either as a powder or pressed film; but the effect of gaseous diffusion and catalysis by hydrogen chloride can present major difficulties. Among authors who have taken adequate precautions against these effects there is general agreement that the rate of degradation of PVC is constant at low extents of reaction (up to 5%) and at low temperatures, but at higher temperatures the degradation rate increases with time.⁷⁻⁹

The difficulty in obtaining homogeneous mixtures of solid components has necessitated the use of a solvent when investigating the effects of solid

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additives on PVC degradation. Degradation in solution has been studied in some detail by Bengough^{10,11} and Varma¹² who have reported that the rate of reaction is constant even at relatively high temperatures and high extents of reaction when bulk polymer shows autocatalysis.

In this work, a reproducible technique for studying PVC degradation was developed and used to compare the behavior of PVC degraded in solid form and in a range of solvents.

EXPERIMENTAL

Apparatus

The rate of dehydrochlorination of the polymer sample was measured by continuous titration of hydrogen chloride evolved from the polymer and transferred by carrier gas to the titration cell.

Glass cells of different design were used for studies of polymer in solid form and in solution. Carrier gas was blown through a sinter over the polymer powder surface, but for solutions the gas was bubbled through the liquid.

The cells were heated by a metal-block furnace controlled at a given temperature within $\pm 0.1^\circ\text{C}$ by a platinum resistance thermometer-controlled bridge circuit (Sirect Instruments Ltd.). The temperature was recorded continuously. As there was a slight temperature gradient between polymer sample and the cell block, the apparatus was calibrated before use to determine the polymer temperature accurately.

Hydrogen chloride evolved from the polymer was carried by the carrier gas into the titration cell where it was absorbed in a 1% solution of potassium chloride. The titration cell was a 500-ml flat-bottomed flask with side arms for gas inlet and outlet. A glass electrode, a calomel electrode, and a sodium hydroxide delivery tube passed through a bung fitted in the top of the flask. The solution was stirred vigorously at all times by a PTFE-coated magnetic stirrer resting on the bottom of the cell.

The electrodes and delivery tube were connected to an automatic titration unit (Radiometer Ltd.) which maintained the pH of the solution in the titration cell at a preset value (normally 7.0 to 7.5) by the addition of standard alkali during the degradation. The amount of alkali added was recorded continuously as a function of time by the recorder.

Before commencing a series of degradation runs, carrier gas was bubbled for 3 to 4 hr through a fresh solution in the titration cell until a steady pH value was reached. Known quantities of PVC (and solvent) were introduced into a pyrolysis tube which was fitted in place on the degradation line. Carrier gas was bubbled through the solution or over the solid for at least 15 min to expel carbon dioxide and to change the atmosphere over the sample. The pH meter was set to the required pH-stat value, and sodium hydroxide was automatically metered into the cell to bring the pH up to this value. When the pH reading was steady, the furnace was jacked up around the tube and the recorder chart started.

Materials

The PVC was prepared by suspension polymerization at 50°C using lauroyl peroxide (0.2% by weight on monomer) as initiator. The intrinsic viscosity in tetrahydrofuran at 25°C is 1.12 dl/g, and the number average molecular weight, 51,000.

Nitrobenzene was dried for 24 hr over phosphorus pentoxide and fractionally distilled before use, the fraction boiling at 211°C being taken.

Tricresyl phosphate was shaken over anhydrous calcium sulfate for 24 hr and fractionally distilled under reduced pressure, the fraction distilling at 250°C under a pressure of 20 mm mercury being taken.

Ethyl benzoate was dried in the same manner and fractionally distilled, the fraction boiling at 212°C being collected.

Di-2-ethylhexyl phthalate was used as supplied. By gas-liquid chromatography this material was found to have a purity of greater than 98%.

Triphenyl phosphate and benzophenone were used as supplied. Preliminary experiments showed that degradation behavior in these solvents was unchanged after purification by fractional distillation under reduced pressure.

RESULTS

Experimental Conditions

The PVC sample did not reach its equilibrium temperature until 6 min after immersion in the furnace. Rates measured within this time were not used.

An increase in the flow rate of carrier gas from 60 ml/min to 200 ml/min caused the temperature of a solution of PVC to fall by only 0.4°C. The change in flow rate had virtually no effect on the measured rate of degradation in solution. More cooling of solid samples occurred using nitrogen at high flow rate, so nitrogen was always preheated when using solid polymer samples.

The absorption of hydrogen chloride in the potassium chloride solution was quantitative, as shown by control tests with a further connected cell.

Degradation in Solution

The result of degrading PVC in di-2-ethylhexyl phthalate at 207.0°C is shown graphically in Figure 1. There is a fall in the rate of reaction with time, and this is shown quantitatively in Table I. To investigate the curvature of the degradation rate plot, a number of changes in the experimental conditions were made.

Extraction of Polymer. One sample of PVC was extracted with cold acetone, and another was dissolved in tetrahydrofuran and precipitated with methanol. PVC precipitated from tetrahydrofuran degraded in solution at the same rate as that of the unextracted sample material (Fig. 1, curve 2), while the acetone-extracted sample degraded at a slower rate

TABLE I
Variation in Rate of Degradation of PVC in Di-2-ethylhexyl
Phthalate with Extent of Reaction^a

Loss of available hydrogen chloride, %	Rate of PVC degradation, micromole HCl/g min
2.0	5.0
5.0	2.4
8.0	1.8

^a Temperature of degradation: 207.0°C.

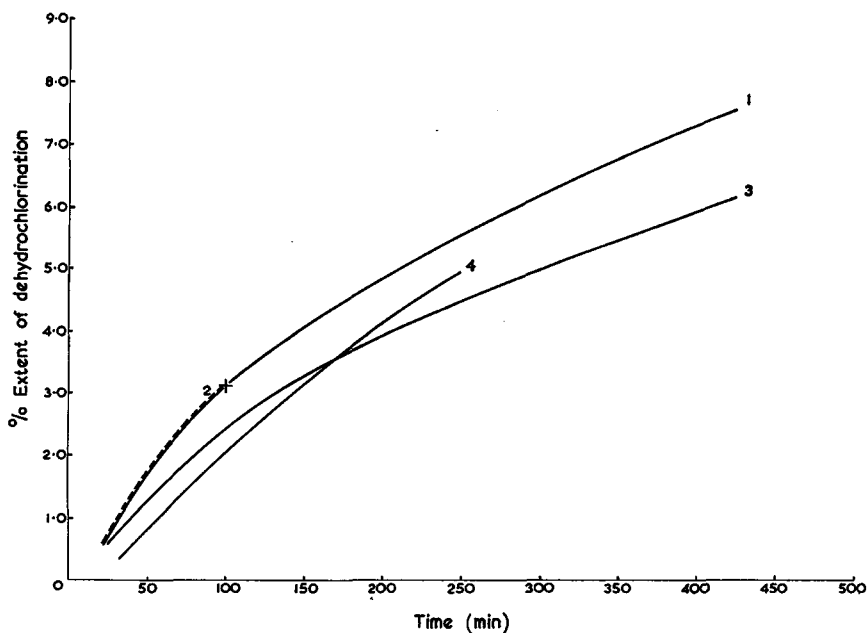


Fig. 1. The degradation of PVC in di-2-ethylhexyl phthalate at 207°C: (1) at concentration of 20 g PVC/l.; (2) after precipitation from tetrahydrofuran; (3) after extraction by acetone; (4) when nitrogen passes over instead of through the solution.

(Fig. 1, curve 3). The overall shape of the degradation graphs was unchanged.

Modification of Apparatus. A pyrolysis vessel was modified to allow carrier gas to pass over the solution rather than bubble through it, and the result is shown in Figure 1, curve 4. The rate is lower at first, but the degradation continued at a slightly higher rate compared to that obtained using the standard conditions. Curvature of the trace is still apparent although less marked.

Variation of Polymer Concentration in Solvent. Rates of degradation of PVC at different concentrations in di-2-ethylhexyl phthalate were measured, and the results are summarized in Table II.

TABLE II
Rates of Degradation of Various Concentrations of PVC
in Di-2-ethylhexyl Phthalate at 207.0°C.

Concentration of PVC, g/l.	Rate of degradation at 2% loss of available HCl, micromoles HCl/g min	Rate of degradation at 8% loss of available HCl, micromoles HCl/g min
20	4.9	1.9
40	5.1	2.0
80	5.0	1.9
160	5.0	1.8
320	7.7	— ^a

^a Solution gelled.

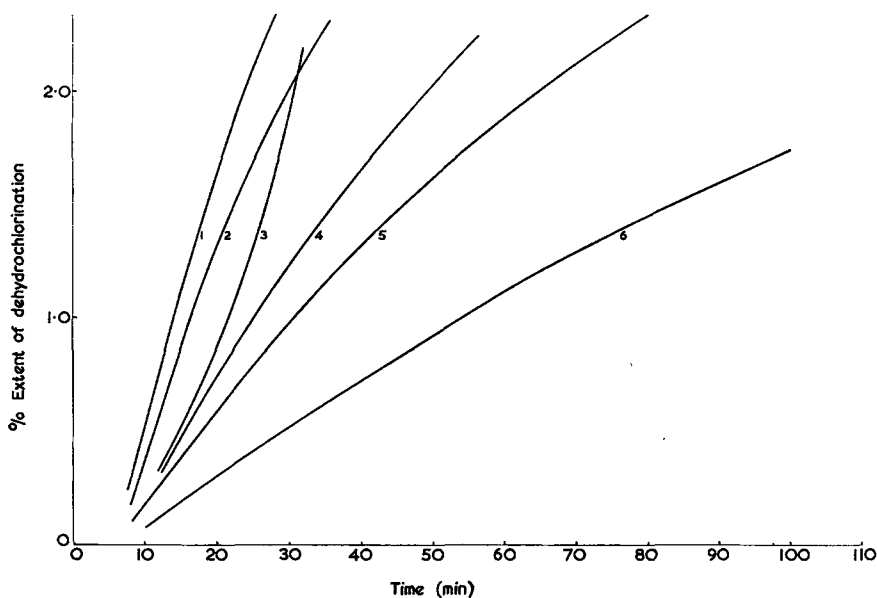


Fig. 2. The degradation of PVC in various solvents at 207°C: (1) triphenyl phosphate; (2) tricresyl phosphate; (3) nitrobenzene; (4) benzophenone; (5) di-2-ethylhexyl phthalate; (6) ethyl benzoate.

The rate of degradation is directly proportional to concentration up to at least 160 g/l. At concentrations greater than about 320 g/l., the decomposition is no longer in solution but heterogeneous. A plot of log rate against log concentration is linear, with a slope of unity, showing a first-order dependence of rate of degradation upon PVC concentration. The rate values in Table II are quoted at two different extents of reaction to demonstrate that the curve slope is unaltered by polymer concentration.

Degradation in Different Solvents. PVC was degraded in a range of solvents, and the results are shown graphically in Figure 2. The rate of reaction falls with time in all solvents, with the exception of nitrobenzene which induces a rapid acceleration.

TABLE III
Rate Constants, Activation Energies, and Entropies of Activation for
Degradation of PVC in Various Solvents

Solvents	First-order rate constant k, sec^{-1}				$E_A, \text{kcal/mole}$	$\Delta S^\ddagger, \text{e.u.}$
	170°C	181°C	191°C	207°C		
Di-2-ethylhexyl phthalate	0.52	1.06	2.45	7.21	29.8	-22.8
Ethyl benzoate	0.33	0.66	1.43	3.63	27.8	-28.9
Tricresyl phosphate	1.26	2.97	5.84	15.40	28.2	-24.3
Triphenyl phosphate	1.70	4.00	8.04	20.00	28.5	-23.0
Benzophenone	0.72	1.79	3.44	9.57	28.5	-24.6
Nitrobenzene	0.89	2.01	3.45	8.14	24.0	-34.3

The degradation was found to be first order with respect to polymer concentration in all of the solvents studied, and first-order rate constants were calculated from the "initial rates" which were measured at 0.2% loss of available hydrogen chloride. Using these results, the activation energy E_A and the entropy of activation ΔS^\ddagger were calculated; the values are tabulated in Table III.

Degradation in Solid Form

It has been established⁷ that the rate of degradation of PVC is strongly influenced by the thickness of the powder layer. The linear relation between sample weight and rate of degradation (Table IV) shows that weights of up to 0.1 g of PVC formed suitably thin layers in the cell such that diffusion-controlled effects did not become rate determining.

The degradation rate plots for various weights of PVC are shown in Figure 3. In each case at the temperature of these experiments (207°C), the rate of degradation is not constant. There is an initial period of acceleration followed by a period of constant rate and finally a falloff in rate starting at about 30% loss of available hydrogen chloride.

TABLE IV
Rates of Degradation of Various Weights of PVC^a

Sample weight, g	Rate of degradation at 5% loss of available hydrogen chloride, micro-moles HCl/min
0.0125	0.11
0.025	0.20
0.050	0.45
0.100	0.81

^a Temperature of degradation: 207.0°C.

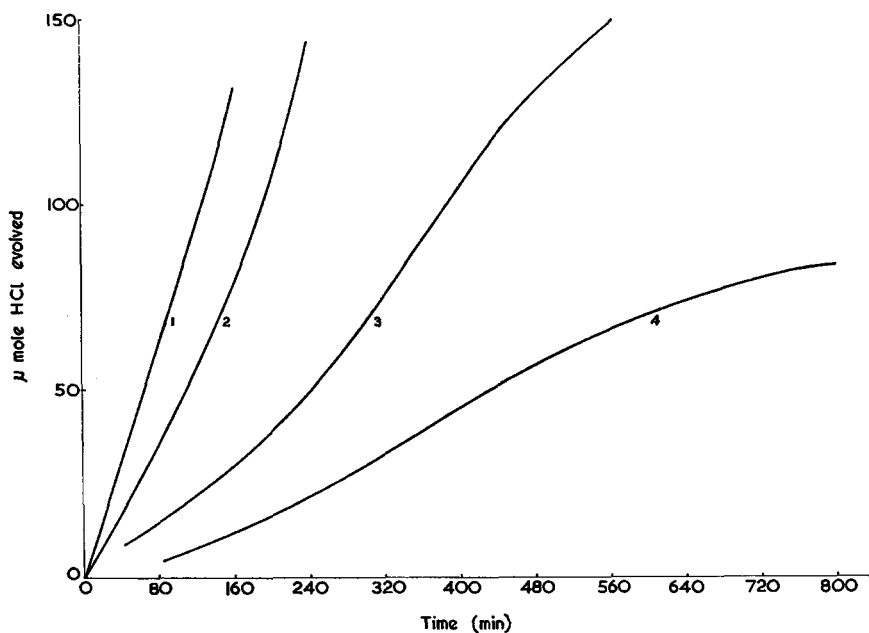


Fig. 3. Rate of degradation of various weights of solid PVC at 207°C: (1) 0.100 g; (2) 0.050 g; (3) 0.025 g; (4) 0.0125 g.

DISCUSSION

The rate of loss of hydrogen chloride at 207°C from PVC in all of the solvents except nitrobenzene is not constant but decreases with time (Fig. 2). This effect is not caused by the formation of a heterogeneous mixture or by gelation, which occurs at a much later stage in the reaction. It has been suggested¹¹ that high initial rates of degradation may be due to residual catalyst, but purification of the polymer by the methods described above did not affect the shape of the degradation graph.

The almost linear rate plots obtained when the carrier gas is passed over the solutions are consistent with the results of Bengough et al.^{10,11} Figure 1, curve 4 does show slight curvature; but since Bengough's technique probably involved intermittent titration rather than the continuous method used in this work, it would be easy for this to go unnoticed. The different rate plot obtained when carrier gas is passed over the solution does not represent the true degradation behavior but is almost certainly due to inefficient removal of hydrogen chloride at the start of the reaction which made the initial rate of degradation appear slower. Catalysis by the relatively high concentration of hydrogen chloride in the solution then made the reaction continue at a faster rate than when the hydrogen chloride was efficiently removed by carrier gas bubbling through the solution. Braun¹² did bubble carrier gas through the solution when studying the degradation

of PVC in ethyl benzoate; but since his reactions were taken to only about 0.3% loss of available hydrogen chloride, a falloff in rate of degradation with time was not apparent.

The rate of degradation varied with the solvent used; but in all cases, with the exception of nitrobenzene, the overall pattern of a falling rate of degradation with extent of reaction was observed. According to Ben-

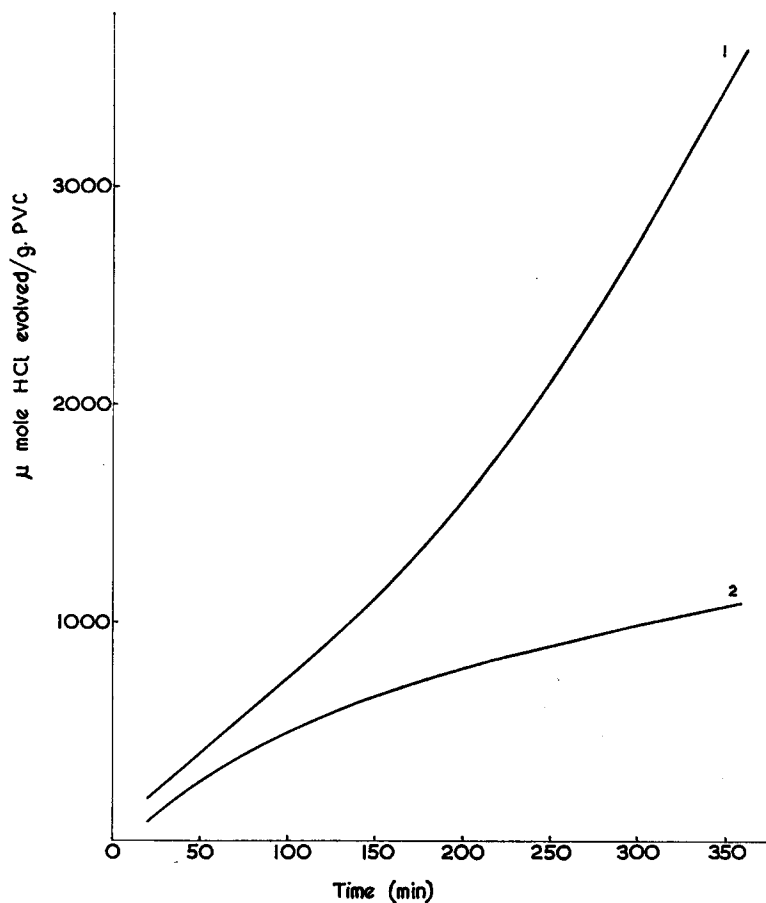


Fig. 4. Rates of degradation of (1) solid PVC, and (2) PVC in di-2-ethylhexyl phthalate at 207°C.

gough,¹¹ the solvents can be divided into three groups on the basis of their activation energies. In this work, the activation energy of degradation was found to be constant in all solvents (28.8 ± 1 kcal/mole), except nitrobenzene which gave a significantly lower value. The behavior of nitrobenzene is clearly different from that of all of the other solvents studied and will not be discussed further.

The entropies of activation in all of the solvents were fairly large and negative, and it is reasonable to relate the entropy decrease in going from reactants to activated complex to the "freezing" of solvent molecules around the macromolecules (or possibly incipient ions). Although the solvents affect the rate of degradation in this way, it is unlikely that they are responsible for the fall in rate of degradation with time, since the change in rate is constant for all of the solvents and independent of polymer concentration. The decreasing rate is probably caused by exhaustion of structural irregularities within the macromolecule which initiate loss of hydrogen chloride.

The results presented in Table III confirm that conduction of heat through the polymer is not controlling the rate of the reaction and that the powder layers are not sufficiently thick for hydrogen chloride trapped between the granules to cause autocatalysis. The results do not, however, eliminate the possibility of hydrogen chloride catalysis brought about by gas trapped within individual granules. Figure 3 shows that the rate of degradation of PVC increased with time even for very small sample weights (0.0125 g), corresponding to a monoparticle layer, and it is probable that hydrogen chloride trapped within the granules is responsible for this autocatalysis. The importance of particle size was shown by Luther,¹² who demonstrated that the smaller the particle size of a PVC sample, the greater was its stability.

In the main, reports in the literature show that at lower temperatures (below about 190°C), the rate of dehydrochlorination is virtually constant at the start of the reaction and tends to fall as the reaction progresses. The slower generation of hydrogen chloride at lower temperatures probably means that a high concentration of gas does not build up within the granules and catalysis of the degradation is reduced. At higher temperatures, the rate of degradation increases with time since the hydrogen chloride, which is liberated at a faster rate, cannot escape sufficiently quickly from the polymer granules.

A comparison of the rates of degradation of PVC in the solid state and in solution are shown in Figure 4. When reactions are carried out in solution, with efficient removal of hydrogen chloride, the curve produced represents the true pattern of behavior in the absence of catalysis by the hydrogen chloride.

The ideas discussed above are supported by our observation that the rate of change of degradation of solid PVC at a very low temperature (140°C) is fairly close to that of PVC degraded in di-2-ethylhexyl phthalate at that temperature.

It is concluded that solid-state studies may be unreliable for information concerning the basic dehydrochlorination reaction at higher temperatures since catalysis by hydrogen chloride invariably occurs. It is possible to resort to solution studies although these may be complicated by polymer-solvent interactions.

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