Degradation of Poly(vinyl Chloride). I. Kinetics of Thermal and Radiation-Induced Dehydrochlorination Reactions at Low Temperatures*

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Synopsis

The dehydrochlorination reaction arising thermally and from exposure to γ-radiation has been followed, under vacuum, in the temperature range from 80° to 130°C by measuring the pressure of the evolved volatiles. The catalytic action of HCl, which was recently established, has been observed also at these low temperatures. In agreement with previous data, a free-radical mechanism has been accepted to be operating in the radiation-induced reaction, which has been found to be linearly dependent on dose rate and essentially independent of temperature. Assuming the thermal dehydrochlorination to proceed according to the same mechanism, its activation energy, lying within the range of values reported in the literature, represents the activation energy for the thermal process of radical formation by dissociation of normal and anomalous structures in PVC macromolecular chains. Since this value appears to be substantially constant in the temperature range from 90° to 240°C, it can be established whether the dissociation reactions of all the PVC structures are regulated by the same activation energy or, more simply, only one of these structures is concerned.

INTRODUCTION

In thermal, ultraviolet-induced, and high energy radiation-induced degradation of poly(vinyl chloride) (PVC), the macromolecules mainly undergo crosslinking, chain scission, and formation of polyene sequences by dehydrochlorination, the relative extent of these reactions depending on the experimental conditions.

Although in the past twenty years a great amount of work has been devoted to this subject to the purpose of elucidating the reaction mechanism, this is still the object of much controversy.

Undoubtely the discrepancies in the experimental results, found by various authors, can be numbered among the causes for their difference of views. Not always adequate account was taken of the degree of purity of the polymers, whose bearing upon the dehydrochlorination reaction has

been pointed out by the comparison of PVC polymers from different sources and by the changes produced by purification treatments.[1-10]

With regard to experiments carried out with bulk PVC samples, the results are susceptible to be affected by HCl catalysis also in the case of the volatile reaction products being continuously removed from the system. Indeed, an accelerated dehydrochlorination could be observed not only when HCl was present in the atmosphere,[3,9,11-15] but also when an impeded diffusion determined a certain amount of accumulation of HCl in the sample.[5,9,16-18]

A point of general agreement in PVC degradation is the early appearance of rather long polyene sequences, explainable by a reaction mechanism in which the splitting off of HCl proceeds rapidly through a macromolecule chain, once the latter has lost a first HCl molecule. Accordingly, the prevailing kinetic scheme for the dehydrochlorination, occurring in the absence of secondary reactions with reactive species such as oxygen, should be formulated as (1) an initiation step, by which active centers are formed, (2) a propagation step corresponding to the loss of HCl produced by such centers, and (3) a termination step, where their deactivation takes place.

Only for the dehydrochlorination induced by ultraviolet and high energy radiations the active centers have been generally recognized as free radicals and hence the propagation has been accepted to proceed via a free-radical mechanism. For the thermal dehydrochlorination, on the contrary, neither direct evidence has been gathered about the nature of the active centers nor have the kinetic data succeeded in establishing whether the propagation is a free-radical process or consists in a splitting off of HCl molecules in succession along a PVC macromolecule, favored by allylic activation.[19] As to the latter point, also recent results can be seen to fit partly the free-radical[20-23] and partly the unimolecolar mechanism.[9,13,24,25]

To further investigate bulk thermal degradation, in this work the thermal dehydrochlorination has been studied using powder samples at comparatively low temperatures where, to our knowledge, no systematic study exists. Furthermore, by combining thermal degradation with exposure to γ-rays, an attempt has been made to compare the thermal dehydrochlorination with the better understood radiation-induced dehydrochlorination.

EXPERIMENTAL

Material

A commercial PVC, Sicron 548, was used throughout this work: number-average molecular weight, 52,000; weight-average molecular weight, 130,000; intrinsic viscosity in cyclohexanone at 25°C, 0.105 l./g.

Apparatus and Procedure

The dehydrochlorination reaction was followed by measuring the pressure of the volatile products evolved in the course of PVC degradation, using
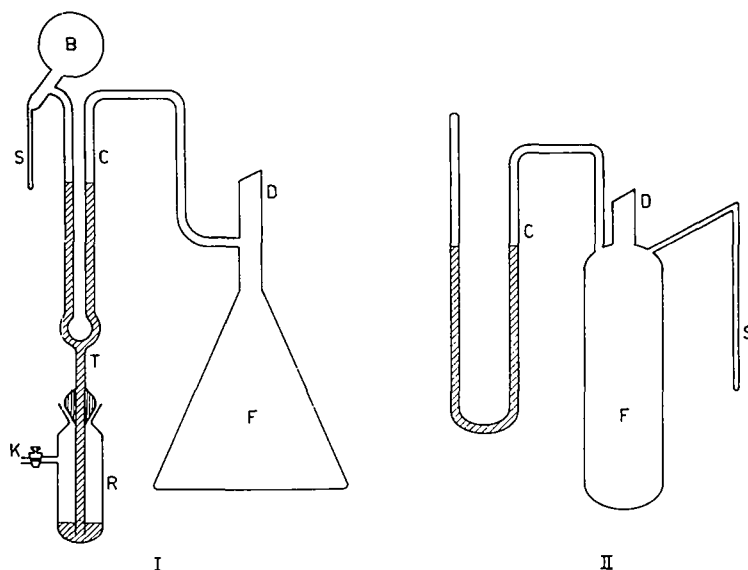
Fig. 1. Glass apparatus for following dehydrochlorination. For explanation see text.

apparatus I and II, entirely made of Pyrex glass, shown in Figure 1. In apparatus I, the mercury contained in reservoir R could be made to rise into the 3-mm i.d. U-shaped capillary C, both to cut off bulb B from flask F and to act as a manometric fluid. The flat bottom of flask F has a diameter of about 60 mm, so that a layer a few millimeters thick could be obtained with the relatively large amount of polymer resin (3–7 g) necessary to have convenient pressures in bulb B and side tube S, whose volumes added up to about 50 ml. The 3-mm i.d. branch T of capillary C is fitted by means of a ground joint into the reservoir R, charged with the required amount of mercury.

To carry out a run, the apparatus was first degassed for at least one day at a pressure of 10^{-5}–10^{-6} mm Hg and then sealed off by flame at D. The resin was brought up to the chosen temperature by partially immersing flask F into an oil thermostat, controlled to within $\pm 0.3°C$. The vacuum was maintained in the apparatus during the run by cooling the side tube S at liquid nitrogen temperature. At suitable intervals, air was introduced through stopcock K for the mercury to rise into the U-shaped capillary C and the side tube S was warmed up to room temperature. The pressure of the reaction products thus vaporized was determined, using a 0.01 mm precision cathetometer. On the average, a measurement required about 15 min, during which the pressure produced in flask F by the volatiles evolving from the resin could be considered negligible.

With the simplified apparatus II, the procedure was not substantially different, only the U-shaped capillary C had to be charged with mercury in such a way that its closed arm was under vacuum during the run. Moreover, when the side tube was warmed up, the volatiles had to expand in the

150-ml flask F (normally filled with 20 g of resin), kept entirely immersed in the oil thermostat. When the side tube S was not cooled down in the runs carried out with apparatus II, the resin remained in contact with the reaction products continuously and not only during pressure measurements.

With apparatus I, the dehydrochlorination was followed also during exposure to the γ-rays of 1000 a Ci ^{60}Co source. With apparatus II, runs were made with PVC preirradiated at liquid nitrogen temperature. The dose rates were determined by means of the Fricke solution being irradiated in flask F, using $G(\text{Fe}^{3+}) = 15.6$.

In all cases the pressure data, followed mostly up to about 150 mm Hg, were transformed into moles of the reaction volatile products by applying the ideal gas law. Assuming HCl as the only component at low temperatures, as can be inferred from the data reported for degradation at similar and higher temperatures,[2,15,16,26,27] the fraction of dehydrochlorination, x, was given by the ratio of moles thus determined to moles of HCl theoretically extractable from the polymer. In this work pressures of 1 mm Hg corresponded to x values of $1-3 \times 10^{-5}$

RESULTS

Though always desirable, the purification treatment of PVC is not too practical when considerable amounts of polymer are needed in degradation experiments. Moreover, some PVC polymers have been found to show no appreciable improvement in stability after purification treatments.[3,5] On this account, Sicron 548 could be used without any previous treatment, since no change was caused by purification consisting in a double dissolution with tetrahydofuran and precipitation with methanol.

Runs of dehydrochlorination were made at temperature ranges from 80° to 130°C. Though the reaction was always confined to the very early stages (x not exceeding 0.005), considerable discoloration was produced in the polymer samples. The kinetic data for HCl evolution are shown in Figures 2 and 3 for two different sets of conditions at each temperature, except at 130°C. The full curves, which are linear for most of the time, were obtained in the absence of HCl, such as resulted from cooling with liquid nitrogen and using a thin layer of resin in apparatus I. On the contrary, the dashed curves, exhibiting important accelerations (and the more important the higher the temperatures), refer to runs carried out with apparatus II filled with a very thick layer of resin and without condensation of the reaction products.

In the above description, the comparatively rapid increase of x occurring at the beginning of each experiment is disregarded. The products responsible for this were condensable, since the pressures were seen to fall to zero during cooling with liquid nitrogen during the experiments with apparatus II. These products can be considered to consist of especially labile HCl or, more probably, of decomposition products from incorporated impurities.[26]
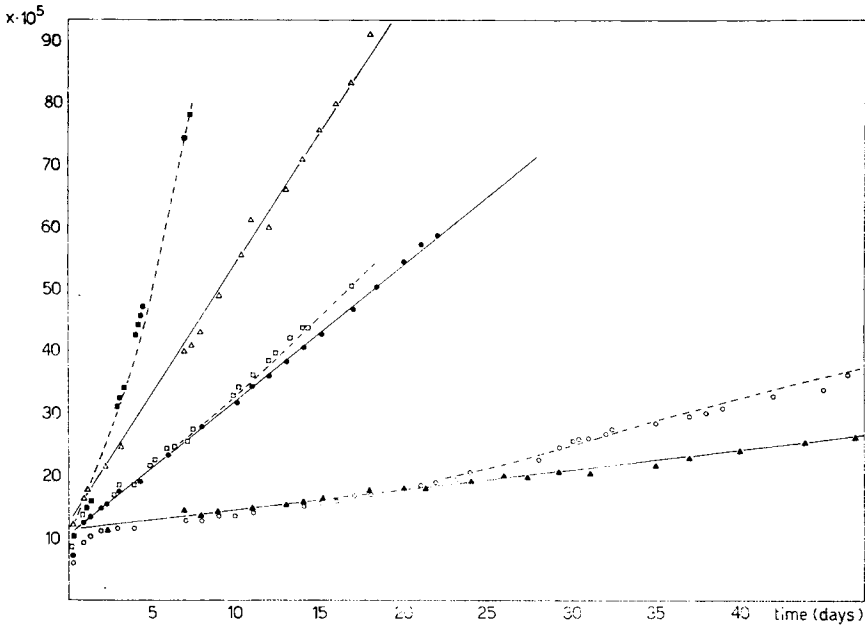
Fig. 2. Kinetics of PVC thermal dehydrochlorination. Thin layer, condensati)n of volatiles: (▲) 80°C; (●) 90°C; (△) 97°C. Thick layer, no condensation: (○) 80°C; (□) 90°C; (■) 101°C.
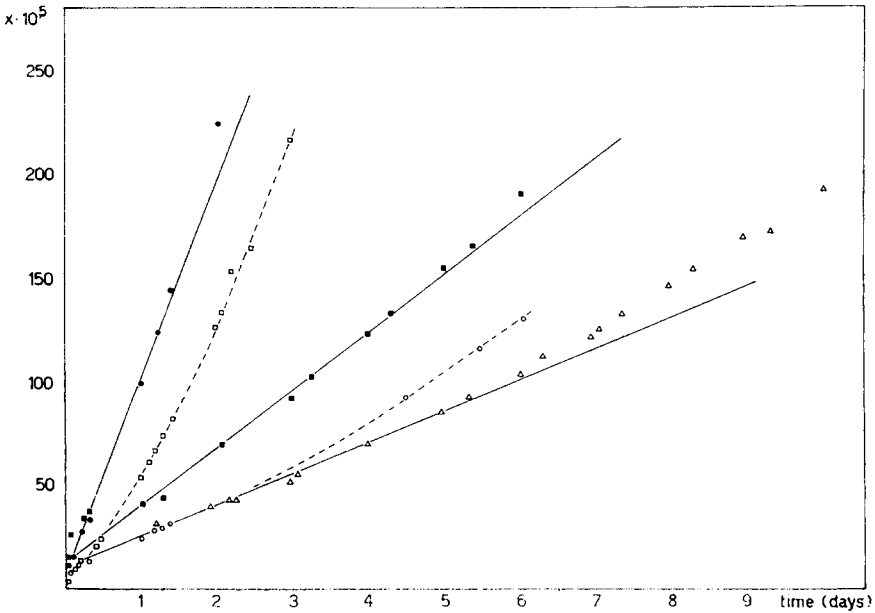

Fig. 3. Kinetics of PVC thermal dehydrochlorination. Thin layer, condensation of volatiles: (△) 110°C; (■) 120°C; (●) 130°C. Thick layer, no condensation: (○) 110°C; (□) 120°C.

Experiments with thick layers of resin have also been performed in which the reaction products were kept condensed. Accelerating curves, not drawn in Figures 2 and 3 for the sake of clarity, were obtained which, though somewhat lower than the dashed curves, indicated that sample thickness was also a factor for dehydrochlorination acceleration. The obvious interpretation of this, already put forward in recent papers,[5,9,16—18] is the catalytic action of the HCl that accumulates in the sample as a result of its diffusion out of the sample being hindered.

In this respect an apparent contradiction should be cleared up. With decreasing temperature the dashed curves approach the others in Figures 2 and 3, and so would intermediate curves, from which it may be inferred that the influence of sample thickness is reduced as the hindrance for HCl to diffuse grows. This unexpected temperature dependence can be accounted for by the changes brought about in the resin's physical state. While appreciable alteration was not observed in the polymer particles by treatments at 80°C, at higher temperatures they were found to stick together in lumps, and the more so the higher the temperature and the longer the treatment. Accordingly, diffusion of HCl out of the polymer particles almost solely has to be considered in the experiments at 80°C, whereas the exit of HCl from the lumps has to be taken increasingly into account as the temperature is raised and the treatment is prolonged. Another fact which can be accounted for in this way is that sometimes the thick samples did not appear uniformly colored, but two colors were discernible, sharply separated by a cross-sectional boundary. Being that the lower layer color shifted toward the violet, as when HCl catalysis is operating,[9,17,28] a sort of diaphragm should be considered to have been formed at the boundary. Furthermore, also the kinetic curves can be seen to fit this picture, since they exhibit progressively increasing slopes, starting from values not significantly different from those in experiments not affected by HCl accumulation or affected only to a minor extent. In this regard it must be recognized that after long treatment times a certain tendency to accelerate is discernible even in the solid curves together with an appearance of double coloration in the samples. This is not unexpected, since the sample sizes necessary to have measurable pressures of volatiles at low x values were not such as to give monoparticle layers.

The approaching to one another of the initial slopes relative to different experimental conditions is clearly deducible from the data in Table I.

In view of the fact that reproducibility of data is usually not too high, the reaction rates in Table I relative to each temperature can be accepted as being equal except for 120° and 130°C, where considerable differences were observed, an obvious explanation for which is that accelerations set in very early.

To determine the temperature dependence of the dehydrochlorination rate, all the values of Table I were plotted in the Arrhenius diagram of Figure 4. Attaching more importance to the values of column A, in agreement with the above considerations, and disregarding the low value at

TABLE I
Initial Dehydrochlorination Rates of PVC at Different Temperatures
Obtained with Experiments Carried out in Different Conditions[a]

Temp, °C	$(\Delta x/\Delta t) \times 10^{10}$, sec^{-1}		
	A	B	C
80	0.38		0.45
90	2.5		2.6
97	4.8		
101			7.2
110	18.9	17.0	19.8
120	32.4	46.3	66.0
130	113	210	

[a] Conditions: A, thin layer, condensation; B, thick layer, condensation; C, thick layer, no condensation.

80°C, the solid straight line was drawn from whose slope an activation energy of 28 kcal/mole is evaluated.

For a comparison of dehydrochlorination rates at temperature ranges usually investigated, Figure 4 also shows the values previously obtained in this labotatory[3,29,30] and now in part repeated, at temperatures upward from 180°C under essentially similar conditions, except for the extent of dehydrochlorination upon which the initial slopes have been determined, in as much as it is impossible to follow the reaction in the very early stages at high temperatures.

To verify whether there was agreement between the two series of data, the dashed straight line in Figure 4 has been drawn taking into account the data of the high temperature range as a whole. Although the two lines do not coincide, it can be observed that the dashed line, whose slope corresponds to an activation energy of 30–31 kcal/mole, intersects the other in the middle of the lower points. In some respects, it appears to be better aligned with the lower points relative to conditions in which HCl catalysis was operating, and thus a simple explanation can be found in the values at the high temperatures being affected by HCl catalysis to some extent.

Dehydrochlorination experiments under analogous conditions and at the same temperatures of those corresponding to the solid lines of Figures 2 and 3 were carried out with simultaneous exposure to γ-rays at a dose rate of 0.81 rad/sec, and the results can be seen in Figure 5. Since the irradiations had to be interrupted at intervals in order to perform the pressure measurements, allowance was made by subtracting from the experimental x values the contributions due to purely thermal dehydrochlorination during the measuring and plotting the resulting values versus effective irradiation times. These corrections of the x values, practically negligible at lower temperatures, increase in importance as the temperature increases. At 130°C, where the thermal dehydrochlorination rate was found to approach that for the composite dehydrochlorination, this procedure could not be
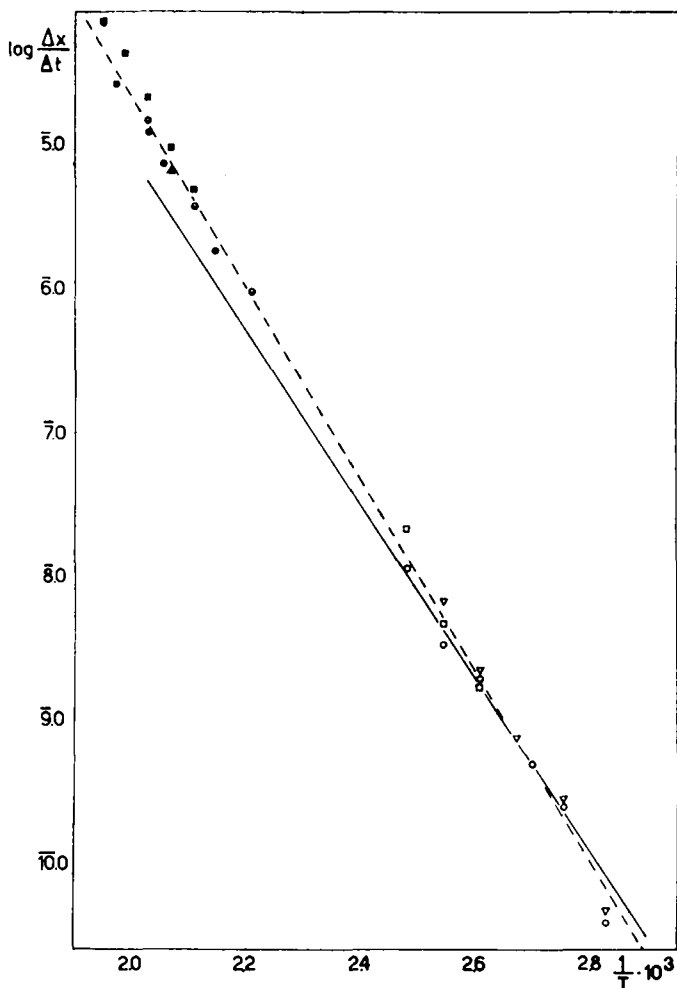
Fig. 4. Arrhenius diagram for thermal dehydrochlorination rate. Data from Table I: (O) column A; (□) column B; (∇) column C. Data at high temperatures: (▲) from ref. 3; (■) from ref. 29; (●) from ref. 30; (◐) now repeated. Solid line refers to point (O) and dashed line takes into account points from references and points (◐) as a whole.

considered completely unobjectionable and the corresponding curve was not reported in Figure 5.

From the x/time plots of Figure 5, which appear to be straight lines in the early stages of the reaction, the slopes, $(\Delta x/\Delta t)_{rad}$, of Table II were determined. For the slope at 130°C, the value in parenthesis has been deduced from a less rigorous kinetic curve.

In order to show the importance of the radiation effect on dehydrochlorination, Table II also reports, for all temperatures, the purely thermal dehydrochlorination rates, $(\Delta x/\Delta t)_{th}$, as derived from the Arrhenius dia-
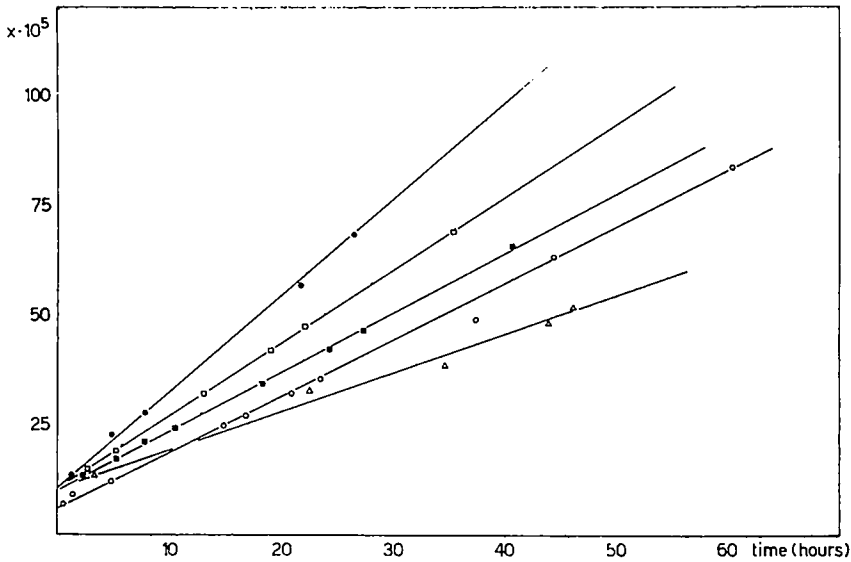
Fig. 5. Kinetics of PVC dehydrochlorination with simultaneous exposure to γ-rays at a dose rate of 0.81 rad/sec: (△) 80°C; (○) 90°C; (■) 97°C; (□) 110°C; (●) 120°C.

gram of Figure 4 (solid line), the ratios of the latter to the composite reaction rates, $(\Delta x/\Delta t)_{th}/(\Delta x/\Delta t)_{rad}$, and their differences $(\Delta x/\Delta t)_{rad} - (\Delta x/\Delta t)_{th}$. From Table II the increment in dehydrochlorination caused by the radiation appears to be substantially independent of temperature and to account for the composite dehydrochlorination to an extent that increases with decreasing temperature.

If temperature and dose rates were so chosen that thermal reaction rate was much lower than the composite reaction rate, then the latter could be regarded as entirely due to radiation and an investigation of its dose rate dependence could be performed. To this purpose, experiments were car-

TABLE II
Dehydrochlorination Rates of PVC at Different Temperatures[a]

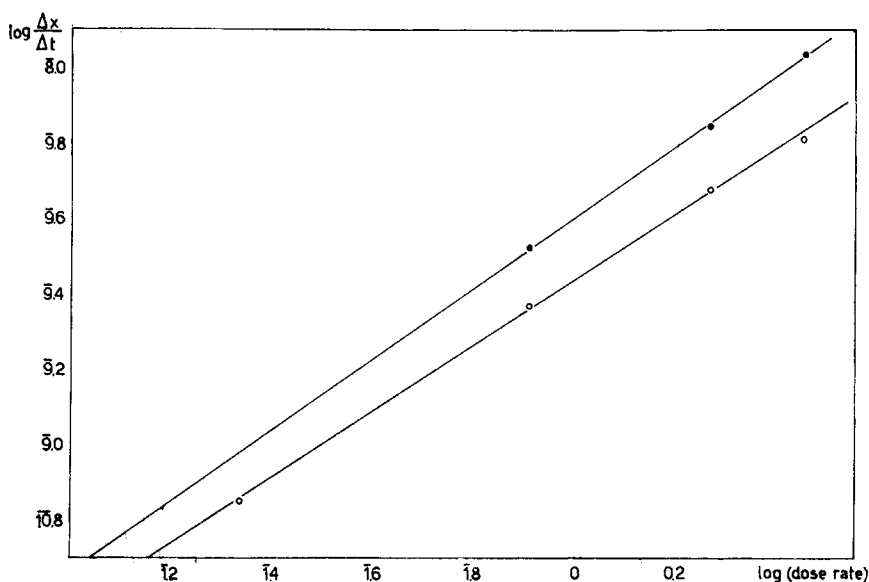| Temp, °C	$\left(\dfrac{\Delta x}{\Delta t}\right)_{th} \times$ 10^{10}, sec^{-1}	$\left(\dfrac{\Delta x}{\Delta t}\right)_{rad} \times$ 10^{10}, sec^{-1}	$\left(\dfrac{\Delta x}{\Delta t}\right)_{th} / \left(\dfrac{\Delta x}{\Delta t}\right)_{rad}$	$\left[\left(\dfrac{\Delta x}{\Delta t}\right)_{rad} - \left(\dfrac{\Delta x}{\Delta t}\right)_{th}\right] \times$ 10^{10}, sec^{-1}	$G(HCl)$
80	0.8	23.2	0.03	22.4	43
90	2.2	35.5	0.06	33.3	63
97	4.8	37.3	0.13	32.5	62
110	17.0	45.4	0.37	28.4	54
120	40.7	67.2	0.60	26.5	50
130	102	(139)	(0.73)	(37)	(70)

[a] For explanation see text.

Fig. 6. Irradiation dose rate dependence of dehydrochlorination rate: (○) 80°C; (●) 90°C.

ried out at temperatures of 80° and 90°C and at the additional radiation dose rates of 0.218, 1.85, and 2.84 rad/sec. The slopes of the x/time plots, which were satisfactorly straight lines, are reported as a function of dose rate in Figure 6, after subtraction of the corresponding small thermal value. Values of 0.86 and 0.93 were derived from the slopes at 80° and 90°C, respectively. As to the radiation yields of HCl, G(HCl) values were deduced ranging from 35 to 50 at 80°C and from 59 to 67 at 90°C, in dependence on dose rate.

Analogous calculations made with the increments in dehydrochlorination rate caused by the radiation reported in Table II lead to the G(HCl) values of the last column of that table.

In the same temperature range dehydrochlorination has been followed in polymer samples preirradiated at liquid nitrogen temperature at a dose rate of 0.81 rad/sec for different times, using apparatus II with large amounts of resin and no condensation of volatiles. With preirradiation, dehydrochlorination started very rapidly as the chosen experimental temperature was approached and then proceeded at a progressively decreasing rate, attaining eventually an almost constant value. Some of the x/time curves so obtained are shown in Figure 7. The large initial increments of x, in which the evolution of decomposition products is not included, since in this case the samples were kept at 100°C under pumping for a suitable time prior to irradiation, should be considered a result of preirradiation, whereas the subsequent linear increase can conceivably be ascribed to purely thermal dehydrochlorination, bearing in mind that the high slopes are to be expected
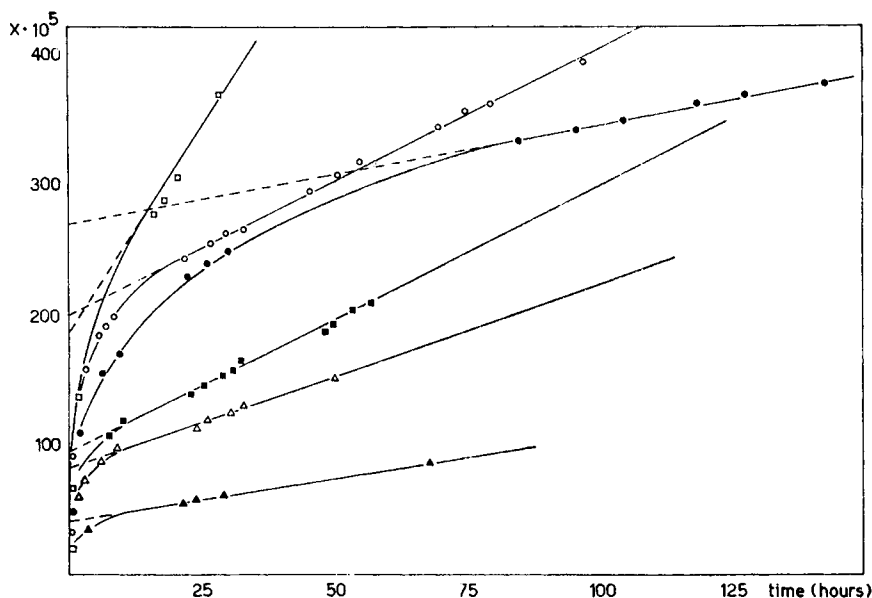
Fig. 7. Kinetics of PVC dehydrochlorination at certain temperatures with preir-radiation: (▲) 110°C, 0.2 Mrad; (△) 110°C, 0.4 Mrad; (■) 110°C, 0.6 Mrad; (●) 80°C, 1 Mrad; (○) 100°C, 1 Mrad; (□) 120°C, 1 Mrad.

under the given experimental conditions. The beginning of the linear part of the curves occurs at times varying with temperature, the radiolysis effects lasting the longer the lower the temperature. An evaluation of the extent of dehydrochlorination due to preirradiation is approximatively given by the extrapolation to zero time of the linear part of the curves. The considerably higher intercept at 80°C with respect to the others, as it appears from the examples of Figure 7 for a preirradiation dose of 1 Mrad, can possibly be associated with the longer survival of the radiolysis inter-mediates in that a higher rate of splitting of HCl than in thermal treatment results in a higher concentration of HCl in the sample. Therefore, the intercept includes also the dehydrochlorination fraction due to the incre-ment of HCl catalysis for all the time over which the radiolysis intermediates last. This time being reduced and thus the intercepts being less affected as the temperature increases, values obtained at higher temperatures were plotted against preirradiation time in Figure 8. From the satisfactory alignment of the points, the extent of dehydrochlorination caused by pre-irradiation appears to be proportional to the absorbed energy, and the G(HCl) value obtained from the slope is about 31.

DISCUSSION

The measurement of thermal dehydrochlorination rate has proved to be feasible down to the temperature of 80°C. For still lower temperatures,
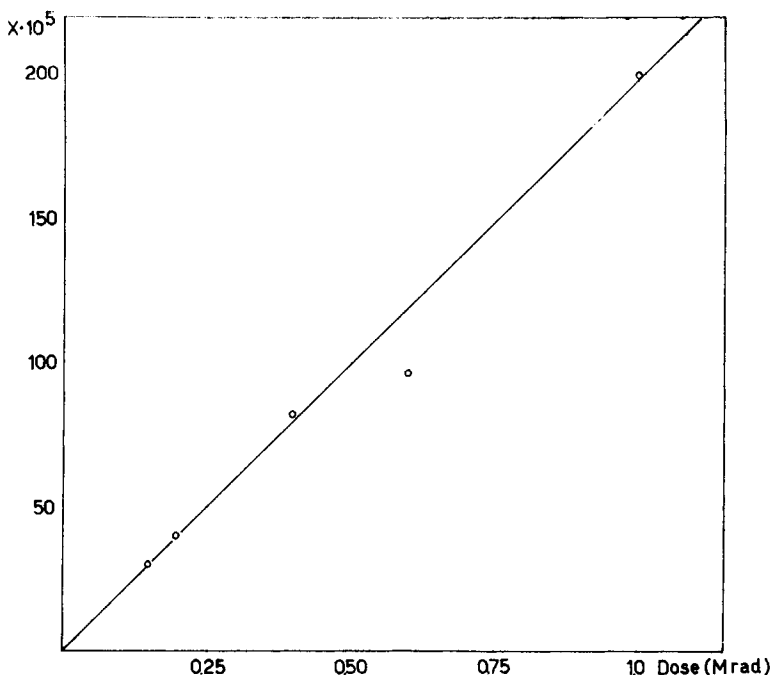
Fig. 8. Dependence on preirradiation dose of extrapolated dehydrochlorination extent obtained from the curves of dehydrochlorination with preirradiation.

however, the time required to follow the reaction would have become prohibitive even in the very early stages with which this kinetic study is concerned.

Also, at the low temperatures used in this work an accelerating influence on dehydrochlorination due to HCl, present in the atmosphere or accumulating in the polymer samples, has been recognized.
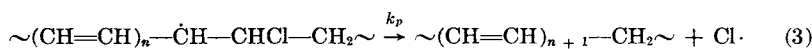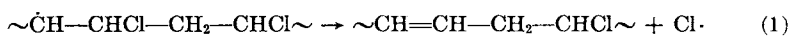
The interpretation of the acceleration only in terms of HCl catalysis seems to be justified by the attainment or, more precisely, by the approach to linearity of the dehydrochlorination–time plots, when HCl concentration is reduced as effectively as possible. Moreover, other reaction products likely to cause autoacceleration, such as crosslinks,[31] cannot conceivably amount to any major role in the mild degradation conditions of this work. In this regard it should be mentioned that no change in molecular weight has been revealed by intrinsic viscosity measurements (in tetrahydrofuran at 25°C) of the thermally degraded polymer samples.

Then, in principle, PVC bulk dehydrochlorination can be said to be always affected by HCl catalysis to some extent, since accumulation of HCl in the polymer can never be avoided completely, bearing in mind that also from very thin layers of resin in unmodified physical state the removal of HCl implies its diffusion out of the resin granules.[16] Obviously, the disturbing effect of HCl can be better avoided when the dehydrochlorination

reaction is studied either with PVC solutions from which HCl diffusion is considerably facilitated, or with bulk PVC to which substances capable of deactivating HCl by combining with it are added. However, in the first case the solvent influence has to be taken into account,[4,13,25,32,33] and in the other case it is doubtful whether actions other than suppression of HCl catalysis would also take place.[12] Therefore, it follows that the catalysis-free dehydrochlorination data can be most conveniently taken as the limiting values which the bulk dehydrochlorination data approach when HCl diffusion is progressively improved.

Once the main features of the purely thermal dehydrochlorination reaction are established, the additional effects due to irradiation can be better differentiated. They are in line with the interpretation of radiation effects given by previous authors.

Exposure to ionizing radiations of PVC at liquid nitrogen temperature under vacuum gives rise to frozen free radicals in amounts proportional to the dose, when the latter is not too high. If the irradiated polymer is brought up to room temperature, a rapid decay takes place for most radicals, while those of the type $\sim$CHCl—$\dot{C}$H—CHCl $\sim$undergo, at least in part, dissociation with formation of chlorine atoms which, by attacking adjacent methylene groups, regenerate the polymer radicals. Since with the latter the cycle can be repeated, a chain reaction occurs involving long-living polyene radicals[34-38]:

$$\sim\dot{C}H—CHCl—CH_2—CHCl\sim \rightarrow \sim CH{=}CH—CH_2—CHCl\sim + Cl\cdot \quad (1)$$

$$Cl\cdot +\sim CH{=}CH—CH_2—CHCl\sim \rightarrow HCl + \sim CH{=}CH—\dot{C}H—CHCl\sim \quad (2)$$

$$\sim(CH{=}CH)_n—\dot{C}H—CHCl—CH_2\sim \xrightarrow{k_p} \sim(CH{=}CH)_{n+1}—CH_2\sim + Cl\cdot \quad (3)$$

$$Cl\cdot + \sim(CH{=}CH)_{n+1}—CH_2\sim \xrightarrow{k_a} HCl + \sim(CH{=}CH)_{n+1}—\dot{C}H\sim \quad (4)$$

Though in the abstraction of the hydrogen atom the adjacent methylene groups are preferentially concerned, other methylene groups cannot be excluded, i.e., reaction (4) can be replaced by

$$Cl\cdot + \sim CHCl—CH_2—CHCl{-}CH_2\sim \xrightarrow{k_{tr}} HCl + CHCl—\dot{C}H—CHCl—CH_2\sim \quad (5)$$
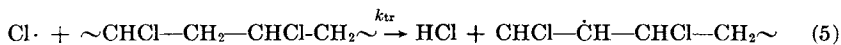
Since by this event a sequence of conjugated double bonds ceases to grow and a new one is started, it can be assimilated to a chain transfer in free-radical addition polymerizations.

If the irradiation is performed directly at room temperature, the free radicals are liable to react as soon as they are generated. By employing high dose rates for short times, the same free radicals as those obtained in the frozen state are present in large amounts at the irradiation end,[37,39] while long irradiations at low dose rates give rise only to accumulation of polyene radicals.[36,40-43] Thus, the difference of irradiation conditions is to be considered one of the causes for the lack of concordance of the free-radical yields G_R so far reported, most of which lie in the range 0.5–2.5[34,35,39,40,43-45] excepting $G_R = 17$[41] and $G_R = 7$.[36]

When the temperature is raised also the polyene radicals, which do not disappear appreciably at room temperature, undergo decay at an increasing rate, so that at temperatures above 80°C their complete removal takes place rapidly.[37-39,43,45,46] The rate of the chain reaction leading to formation and growth of polyenes also increases with temperature, passing from a low value at room temperature to considerably high values above 80°C.[34,36-39,46]

On the assumption of the polyene radicals decaying by a first-order reaction, which is generally accepted[34,35,38,39,45,46] although a second order[41,44,47] and a complex order[43] are also suggested, the kinetic scheme for radiation-induced dehydrochlorination can be formulated as follows:

(1) Initiation, whose rate R_i given by $d[R\cdot]/dt$, with $[R\cdot] = \sum\limits_{n=0}^{\infty} [\sim CH{=}CH)_n{-}\dot{C}H{-}CHCl\sim]$, is proportional to dose rate.

(2) Propagation (given by the sequence of the two-step cycles: reaction (3) followed either by reaction (4) or by reaction (5), with n being any integral number including zero) whose rate R_p may be expressed, under the simplifying hypothesis of reactivity being independent of polyene length, by

$$R_p = k_p [R\cdot] \tag{6}$$

where k_p contains concentration terms of reacting species other than polymer radicals. Evidently R_p represents the dehydrochlorination rate.

(3) Termination, given by disappearance or deactivation of polymer radicals involving undefined processes, whose rate R_t may be expressed, with the same considerations for k_t as above for k_p, by

$$R_t = k_t [R\cdot] \tag{7}$$

According to eqs. (6) and (7), the ratio R_p/R_t, representing the number of HCl molecules being split off per radical being deactivated, is independent of radical concentration. Accordingly it remains constant throughout the radical decay in preirradiated polymers, as directly determined previously,[38,39,46] and can be evaluated by dividing the amount of HCl corresponding to the increment in x due to preirradiation by the initial radical concentration. Thus, the former value should be proportional to the latter and therefore to the preirradiation dose when various preirradiation doses are used, as has been the case in the present work. Moreover, the proportionality constant $G(HCl)$ from preirradiation effects has been found to be only slightly-dependent on temperature above 80°C, and the same should be said for the ratio k_p/k_t.

Another indication deducible from these preirradiation effects is that the time of radical survival decreases rapidly with increasing temperature, in agreement with previously reported radical lifetimes.[38,39,43,45] Then, irradiating the polymer at temperatures above 80°C, an equilibrium can presumably be attained between the rates of radical production and of deactivation after a comparatively short time, and the higher the tempera-

ture the shorter the time. Under the steady-state conditions of R_i equal to R_t, the dehydrochlorination rate may be written as

$$R_p = k_p R_i / k_t \tag{8}$$

thus presenting a first-order dependence on radical production rate and therefore on dose rate. Though this is not verified satisfactorily by the irradiation at 80°C, owing probably to steady-state requirements not being fulfilled, a better agreement has been observed at 90°C, as is to be expected, indicative of the validity of eq. (8) at higher temperatures.

The radiation-induced dehydrochlorination rate being a linear function of radical production rate, its contribution and the thermal contribution to the composite dehydrochlorination rate should be additive, whether the same free-radical mechanism or another mechanism is operating in thermal dehydrochlorination. Indeed, in the former case radiolysis radicals and thermal radicals give rise to dehydrochlorination independently of one another because of the first-order termination and in the other case the independence of the active centers arises from their different nature. Thus, it is justified to regard the increments in dehydrochlorination rate caused by radiation (Table II) as the rates of radiation-induced dehydrochlorination. Then, with these rates eq. (8) holds and their survey indicates that, the dose rate and therefore R_i being unchanged, the change with temperature of the ratio k_p/k_t is not systematic and rather small if the 80°C value is excluded. In view of the imprecision by which the determinations are affected, the ratio k_p/k_t can be accepted, in a first approximation, as temperature independent above 80°C.

Regarding the substantially lower dehydrochlorination rate at 80°C, it can be considered to arise from the appreciable increase of the temperature coefficient below 80°–90°C, in accordance with the fact that at lower temperatures both k_p and k_t should decrease drastically.

These conclusions are consistent with the preirradiation findings. From a quantitative standpoint, furthermore, the discrepancy of the $G(\text{HCl})$ determined in direct irradiation from those resulting from preirradiation can be associated with the decrease of k_p/k_t below 80°–90°C, bearing in mind that a not inappreciable part of the dehydrochlorination following preirradiation occurs below the chosen temperatures during the heating of the samples. Taking the value of 55 as average $G(\text{HCl})$ at temperatures above 80°C, which cannot be profitably compared with the previous determinations, widely different from one another,[10,36–38] the average dehydrochlorination chain length per propagating radical results in a value of about 36 using the middle point of the range of the more reliable $G(R\cdot)$ values. This chain length is remarkably greater than the average length of the sequences of conjugated double bonds produced,[28] implying thus a frequent occurrence of transfer reaction (7).

In this connection, it is worth noting that this reaction scheme adequately accounts for the constancy of polyene distribution during the early stages of radiation-induced dehydrochlorination.[28]

In view of the resemblance shown by the kinetic data of polyene formation observed in thermal dehydrochlorination,[28] the same reaction mechanism can be plausibly accepted also for the latter. Evidently thermally generated free radicals, which recent evidence supports,[21,22] are involved in this case.

Sources of free radicals might be foreign substances present in the polymer, liable to dissociate into radicals. In particular, if these substances decompose very rapidly, such as the ordinary polymerization initiators at high temperatures, the kinetic dehydrochlorination behavior which can be observed[11,20,48,49] is similar to that with preirradiated polymers, as is to be expected from rapidly exhaustible radical sources. With slowly decomposing impurities, there result dehydrochlorination rates not so high but exhibiting no decrease for long times.

Removal of these impurities will leave in the polymer sources of free radicals represented by the normal and anomalous structures present in the PVC macromolecules, and in such a case the rate of radical production, R_i, can be regarded as characteristic of the polymer. A constancy of R_i, which can safely be assumed for low extents of reaction, implies a constant dehydrochlorination rate R_p according to eq. (8).

For this, however, the polymer must be free also from the type of impurities responsible for the dehydrochlorination acceleration in the course of the treatment, whose actions are to be explained by their interaction with dehydrochlorination products and/or intermediates. Examples of these substances are provided by nitrogen oxide and nitrogen dioxide. An investigation on the influence of inorganic gases on dehydrochlorination, under progress in this laboratory, has revealed them to be capable of promoting enormous accelerations at pressures as low as a few mm Hg. Assuming that these conditions are fulfilled by the adopted polymer, the activation energy found for the thermal dehydrochlorination reaction represents the activation energy for the reaction of dissociation into radicals of normal and anomalous structures of PVC, bearing in mind the low temperature dependence of the ratio k_p/k_t of eq. (8). Though two lines have been drawn in the Arrhenius diagram of Figure 4, their not too relevant divergence can be attributed more plausibly to differences in experimental conditions and to imprecisions affecting the determinations rather than to a decomposition reaction which changes its activation energy with temperature. Therefore, the results appear to be in favor of the various PVC structures dissociating into radicals by reactions regulated by a single activation energy for the whole range of temperatures investigated or, more simply, of only one structure producing the free radicals.

For the low point at 80°C, again a decrease in the ratio k_p/k_t in this temperature region is the explanation.

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