Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Östensson, Bengt and Flodin, Per(1978) 'Kinetics of the Alkaline Dehydrochlorination of Polyvinyl Chloride)', Journal of Macromolecular Science, Part A, 12: 2, 249 — 260
To link to this Article: DOI: 10.1080/00222337808061373
URL: http://dx.doi.org/10.1080/00222337808061373

J. MACROMOL. SCI.–CHEM., A12(2), pp. 249-260 (1978)

Kinetics of the Alkaline Dehydrochlorination of Poly(vinyl Chloride)

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ABSTRACT

From previous investigations of the alkaline dehydrochlorination of PVC it is well known that polyene sequences are formed. In this paper the true overall kinetics of the dehydrochlorination reaction between PVC and alcoholic KOH in tetrahydrofuran solution was studied at 9.5°C by measuring the rate of disappearance of KOH. Titrations of the hydroxide ions consumed and the chloride ions evolved showed close agreement. IR spectra of the samples did not show any evidence of substitution by hydroxide ions. Small amounts of DMSO present in the solvent were found to increase the reaction rate markedly. The kinetic scheme was discussed and the first rate constant was determined. Preliminary results of reactions of the polyene sequences with various reagents are presented. These reactions were made in order to introduce new functional groups into the PVC chains.

INTRODUCTION

The thermal dehydrochlorination of poly(vinyl chloride) (PVC) has been the subject of numerous studies, and the kinetics and mechanism now seem fairly well established [1-3]. Also radiation-induced and

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in particular photochemical dehydrochlorination has been studied in detail [3]. On the other hand, the removal of HCl under the influence of alkali has been much less studied, and although some features are known, much remains to be clarified in order to completely understand the reactions involved.

The first reports on base-induced dehydrochlorination dealt with the preparation of essentially completely dehydrochlorinated PVC [4-6]. Bengough and Varma [7] were the first to dehydrochlorinate a PVC solution in tetrahydrofuran (THF) with alcoholic potassium hydroxide (KOH). They found the UV spectrum of partially dehydrochlorinated PVC to be very similar to that obtained by thermal dehydrochlorination in solution. Shindo and Hirai [8] followed the course of the reaction by UV spectrophotometry and on the basis of their results suggested a mechanism. Schwenk [9] discussed the various reactions which might be involved. Wirsén and Flodin [10] studied the structure of the polymers obtained and found that it was possible to dehydrochlorinate PVC partially, essentially without chain scission or crosslinking. They also found that the polyene sequences were randomly distributed along the polymer chains.

In this paper it is our purpose to present the results of a kinetic study in which the dehydrochlorination was measured by determination of the alkali consumed. Furthermore the influence on the dehydrochlorination reactions of small amounts of dimethyl sulfoxide (DMSO) in the solvent will be reported. Finally preliminary results will be given of some reactions of the dehydrochlorinated polymers with various reagents.

EXPERIMENTAL

Potassium hydroxide (KOH), analytical grade (EKA Bohus), and 95% ethanol (Kemetyl) were used without further treatment. Analytical grade THF (Merck) was refluxed over sodium borohydride and calcium hydride under oxygen-free nitrogen and distilled directly into the reaction vessel. Analytical grade DMSO (Fisher) was stored under dry nitrogen and used without further treatment. PVC (Pevikon S-655, KemaNord AB) with K number 65 was dissolved in THF and precipitated with ethanol (EtOH) under such conditions that a fine powder was obtained directly. The purified PVC was dried in vacuo at elevated temperature for one week.

A carefully weighed amount of PVC (20 g) was dissolved in THF (580 ml) under a stream of oxygen-free nitrogen. The KOH/EtOH solution was standardized and 100 ml of it added to the reaction vessel, which was thermostatted at 9.5°C. Then 10-ml samples were withdrawn at certain time intervals and added to a well defined excess of acetic acid dissolved in THF. The PVC was precipitated with EtOH to a fine powder and the samples were titrated with KOH by using a Radiometer TTT60 automatic titrator.

Some samples were titrated for chloride ion content by use of an Aminco-Cotlove automatic chloride titrator.

RESULTS

The reactions were studied only during the early stages, when the consumption of KOH added was less than 30%.

The color of the PVC solution gradually changed from colorless through green, yellow, and red to brown during the reaction. Analysis of the samples withdrawn showed a gradual disappearance of hydroxide ions. Additional analysis in some experiments showed a gradual evolution of chloride ions.

When plotting the values analyzed (calculated as moles per mole of vinyl chloride residue in the polymer) for the hydroxide ion consumption and the chloride ion formation versus time, they were found to fall on the same straight line (Fig. 1). Furthermore no absorption was found in the hydroxyl band region, when films cast from 1,2-dichloroethane were analyzed by IR spectroscopy (Fig. 2). It was concluded that substitution reactions were absent and that the hydroxide ion consumption and the chloride ion formation were due

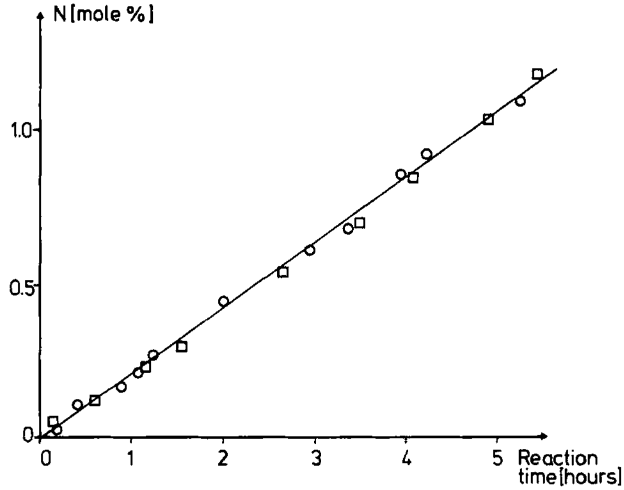

FIG. 1. Degree of dehydrochlorination vs. reaction time: (○) from KOH consumption; (□) from Cl evolution.

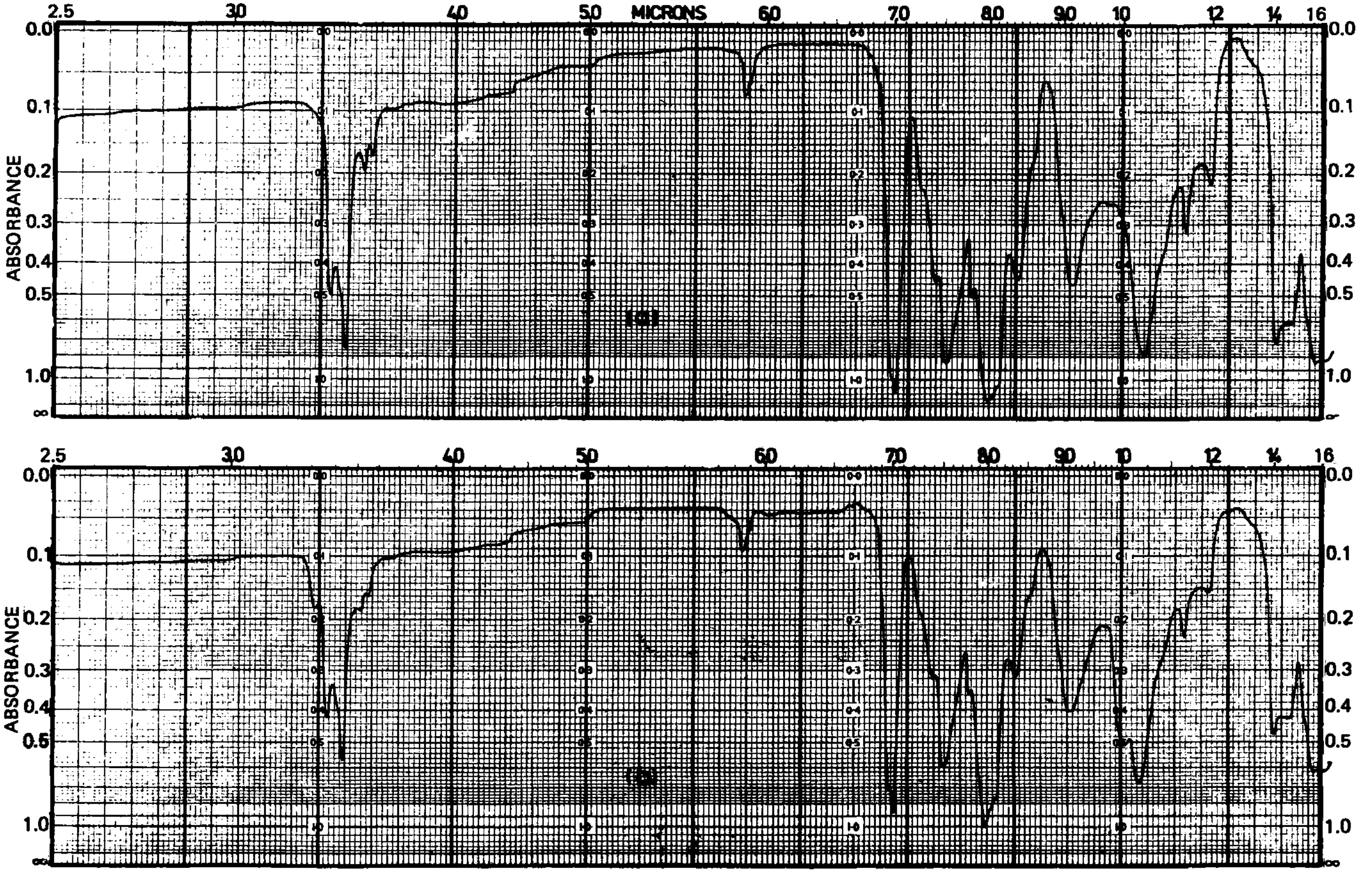

FIG. 2. IR absorption spectra of film cast from 1,2-dichloroethane solution: (a) PVC; (b) PVC dehydrochlorinated to 5 mole %.

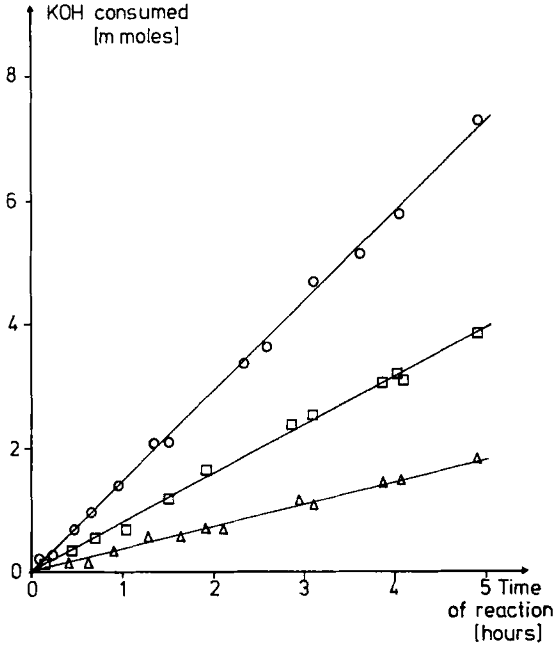

FIG. 3. Conversion of KOH vs. reaction time at 9.5°C for reaction blends of various compositions: (△) 20.20 g PVC, 9.62 mmole KOH; (□) 20.00 g PVC, 29.87 mmole KOH; (○) 40.70 g PVC, 31.14 mmole KOH.

to the elimination reaction leading to dehydrochlorination and formation of polyene sequences. The results thus show that the hydroxide ion titration method gives true values for the degree of dehydrochlorination.

The initial rate of dehydrochlorination was found to depend linearly on both PVC and KOH concentrations (Fig. 3). These results are typical of second-order kinetics.

The presence of DMSO had a strong effect on the reaction rate. The addition of small amounts of DMSO to the solvent increased the reaction rate markedly (Fig. 4).

We attempted to correlate the consumption of KOH used for the dehydrochlorination with the degree of unsaturation of the PVC. Several standard methods [11] were tested for an absolute measurement of the double bond content in the polymer. The methods used were based on addition reactions on the polyene sequences. Peroxybenzoic acid has been used for the preparation of epoxy derivatives

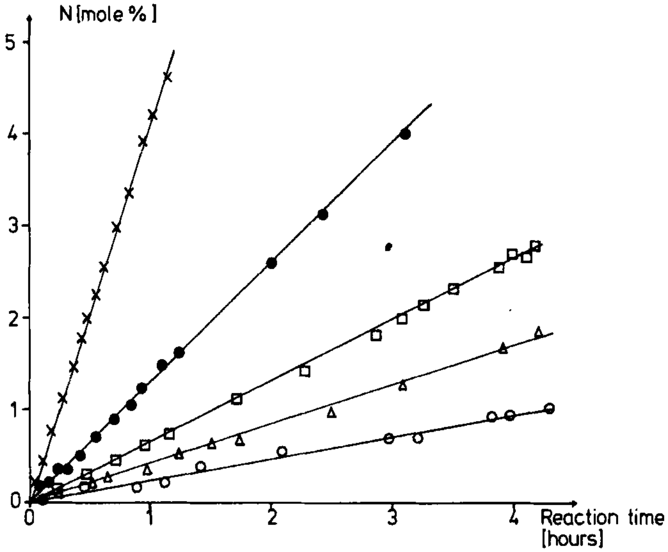

FIG. 4. Degree of dehydrochlorination vs. time of reaction at different DMSO concentrations: (○) [DMSO] = 0; (△) [DMSO] = 0.144 M; (□) [DMSO] = 0.229 M; (●) [DMSO] = 0.549 M; (×) [DMSO] = 1.095 M.

of polyene-containing PVC but calculations of the double bond content based on conversion of peroxybenzoic acid were in poor agreement with calculations based on the chlorine content of the PVC [12].

Several efforts were made to run the reaction between dehydrochlorinated PVC and peroxybenzoic acid to completion. However, the UV spectra of the products showed that polyene sequences still remained in the polymer chains.

Elementary bromine dissolved in methylene chloride added incompletely with dehydrochlorinated PVC. Colored products were always obtained.

Addition of bromine by the bromide-bromate method [11] gave colorless products which seemed to have no unsaturation, but the reproducibility was not satisfactory and the method yielded much lower values than those obtained from the KOH consumption measurements.

The iodine monochloride method [13] was tested for addition of iodine to the double bonds. The reproducibility was poor, and the method was not used further.

In theory, the addition methods and the titration methods based on consumption of hydroxide ions or formation of chloride ions should yield identical results. The poor agreement obtained in our experiments can be explained in two ways. In the first place, Karrer and Jucker [14] have found that iodination and bromination reactions on polyenes do not proceed to completion when the polyene sequences are long. In the second place, in the methods tried, the PVC containing polyene sequences was either insoluble in the reaction medium or was precipitated during the analysis. Thus the availability of the polyene sequences to the reactants was poor, resulting in too low values for the unsaturation. This may also explain the poor reproducibility obtained with some methods.

The dehydrochlorinated samples were completely soluble in THF and 1,2-dichloroethane, even when the degree of dehydrochlorination was as high as 10 mole %. Gel-permeation chromatography showed no change in hydrodynamic volume during the dehydrochlorination reaction, which indicates the absence of chain scission and crosslinking.

We also made preliminary studies of some reactions of polyene-PVC. In all reactions, changes in UV and IR spectra were observed. On the other hand the molecular weight distributions (GPC) were essentially unchanged in the reactions reported below.

Chlorine gas reacted almost instantaneously with polyene-PVC swollen with chlorinated hydrocarbons at room temperature. No UV absorption was observed in the products. Its T_g increased slightly.

Peracids also reacted with polyene-PVC. The aliphatic ones, performic and peracetic acid, reacted completely, as judged from the UV spectra. Aromatic ones, like perbenzoic acid, reacted only partially. The IR spectra of the performic acid-treated samples revealed the presence of hydroxyl and carbonyl groups [15]. Such bands were not observed in the peracetic acid-treated samples.

Some reactions of polyene-PVC with dienophiles have been reported by Loan [16]. In our experiments the reactions were relatively slow and proceeded to completion (UV spectra) at room temperature with only one dienophile, dimethyl maleate. The product with maleic anhydride had roughly the calculated amount of carboxyl groups (by titrations) after hydrolysis. Further details are given by Wirsén and Flodin [15].

In some cases grafting to polyene-PVC was possible. Thus methacrylic acid and methyl acrylate were introduced in amounts up to 15%, through the action of radical initiators.

In conclusion, it is possible to introduce various groups into PVC via polyene-PVC with small changes in molecular weight distribution, i.e., essentially without chain scission or crosslinking.

DISCUSSION

When alkyl halides are dehydrohalogenated by strong bases like hydroxide ions, the reaction is known to proceed by a bimolecular (E2) mechanism [17]. Since our results showed some features typical for second-order kinetics, we assumed a similar mechanism for the alkaline dehydrochlorination of PVC. Previous results [10] showed a gradual increase in the length of the polyene sequences, indicating a series of consecutive dehydrochlorination reactions and not a zipping type of reaction. On assuming that the reactions are irreversible, the scheme shown in Eqs. (1) can be formulated.

$$
\begin{aligned}
&KOH + PVC \xrightarrow{k_1} P_1 + KCl + H_2O \\
&KOH + P_1 \xrightarrow{k_2} P_2 + KCl + H_2O \\
&\vdots \\
&KOH + P_{n-1} \xrightarrow{k_n} P_n + KCl + H_2O \qquad (1)
\end{aligned}
$$

Here P_n represents a polyene sequence containing n conjugated double bonds and $k_1, \ldots, k_n$ are the rate constants.

The rate equations (2) can then be written:

$$
\begin{aligned}
&d[P_1]/dt = k_1\,[KOH]\,[PVC] - k_2\,[KOH]\,[P_1] \\
&d[P_2]/dt = k_2\,[KOH]\,]P_1] - k_3\,[KOH]\,[P_2] \\
&\vdots \\
&d[P_n]/dt = k_n\,[KOH]\,[P_n] \qquad (2)
\end{aligned}
$$

The reaction scheme (2) was suggested by Shindo and Hirai [8].

We designated the total concentration of double bonds in the polyene sequences by [E] and introduced the rate equation (3) for the overall dehydrochlorination:

$$
\begin{aligned}
d[E]/dt = (d[P_1]/dt + 2(d[P_2]/dt) + 3(d[P_3]/dt) + \ldots\ldots + \\
+ n(d[P_n]/dt) \qquad (3)
\end{aligned}
$$

Substitution of Eqs. (2) in Eq. (3) gives

$$d[E]/dt = k_1[KOH][PVC] + k_2[KOH][P_1] + k_3[KOH][P_2] + \ldots + k_n[KOH][P_{n-1}] \quad (4)$$

Equation (4) is too complicated for evaluation without simplification. Therefore the following assumptions were made. Initially (i.e., at $t = 0$) the concentrations of P_1, P_2, P_3, . . . , P_n are small compared to the PVC concentration. All terms containing these concentrations can thus be neglected, and Eq. (4) reduces to

$$d[E]/dt = k_1 [KOH] [PVC] \quad (5)$$

On introducing $[PVC]_0$ = initial concentration of repeat units in the PVC and $[KOH]_0$ = initial KOH concentration, we obtain at any arbitrary time

$$[PVC] = [PVC]_0 - [E] \quad (6)$$

$$[KOH] = [KOH]_0 - [E] \quad (7)$$

These expressions are substituted in the rate equation, Eq. (5), to give:

$$d[E]/dt = k_1([PVC]_0 - [E])([KOH]_0 - [E]) \quad (8)$$

Integration gives

$$(1/\ln 10)([PVC]_0 - [KOH]_0)k_1 t + \log([PVC]_0/[KOH]_0) = \log\{([PVC]_0 - [E])/([KOH]_0 - [E])\} \quad (9)$$

If $\log\{([PVC]_0 - [E])/([KOH]_0 - [E])\}$ is plotted against t, a curve will be obtained from which the rate constant k_1 can be calculated from the slope in the origin and the initial concentrations of PVC and KOH.

We determined the rate constant for different concentrations of

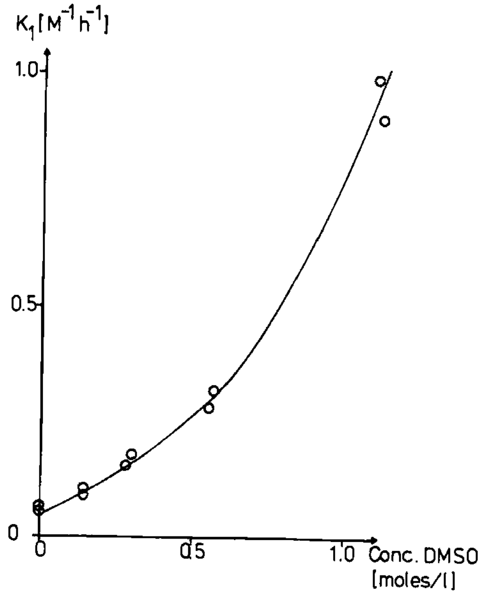

FIG. 5. Rate constant K_1 vs. DMSO concentration at 9.5°C.

DMSO and found that the presence of small amounts of DMSO in the solvent had a very strong influence on the first rate constant (Fig. 5). These results cannot be explained only by the fact that DMSO increases the polarity of the solvent. The amounts of DMSO are much too small to have any dramatic effect on the dielectric constant of the solvent, but the rate of reaction nearly doubles when 1% (v/v) of DMSO is added to the solvent. Thus the conclusion can be made that DMSO has a catalytic effect on the alkaline dehydrochlorination reaction.

Some preliminary results seem to indicate that the same type of effect on the reaction rate is also obtained with other strongly polar aprotic solvents such as dimethylformamide and nitrobenzene.

In earlier studies of the rate of base-induced dehydrochlorination, the degree of dehydrochlorination was determined by elementary analysis of polymers from samples withdrawn at intervals [5, 18] or by UV spectroscopy [8].

Extrapolation of the data of Chang and Salovey [18] to zero reaction time yielded an initial degree of dehydrochlorination of more than 4%. Probably the reason for this lies in the necessity to dry the samples prior to elementary analysis. In similar experiments we have observed two effects which cause similar discrepancies.

In the first place, hydrogen chloride is evolved at a measurable rate from PVC containing polyene sequences, even at temperatures as low as 50°C. The second reason is related to the necessity to dry below 50°C to avoid further dehydrochlorination. As the solvent is removed, the T_g of the sample increases, and when it goes higher than the temperature of the sample the rate of solvent removal decreases drastically. The complete removal of the last few percent of a good solvent thus becomes extremely difficult. In case the solvent is a nonhalogenated one, this results in too high degrees of dehydrochlorination.

The UV spectrophotometric methods used in some investigations [8] yield the total concentration of polyene sequences with three and more conjugated double bonds. Since, at least in the early stages of the reaction, isolated double bonds and diene sequences prevail, the values of the degree of dehydrochlorination are too low. However, there probably exists a correlation between the UV values and the true value of the dehydrochlorination. That such a correlation exists in thermal dehydrochlorination has been shown by Geddes [19].

We conclude that the titration method used in our study gives more representative values for the overall kinetics than has been reported earlier. The close agreement between the result obtained by determination of KOH consumption and chloride ion formation and the fact that no hydroxyl band was observed by infrared spectrophotometry strongly suggests that no substitution reaction occurs. Our results indicate that the initial reaction in the alkaline dehydrochlorination of PVC is an E2 reaction.

The detailed step-by-step kinetics requires access to all the individual rate constants. In our method the first rate constant was obtained from the initial reaction rates. A combination of this method with UV determinations of individual sequences in the manner described by Shindo and Hirai [8] might yield the required individual rate constants.

ACKNOWLEDGEMENTS

This work has been supported by the Swedish Board for Technical Development.

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