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STUDIES ON THE KINETICS OF DEHYDROCHLORINATION OF POLY(VINYL CHLORIDE) IN SOLUTION INDUCED BY A WEAK BASE

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Abstract—Kinetics of dehydrochlorination of poly(vinyl chloride) (PVC), induced by a weak base such as ammonium hydroxide or *n*-butylamine (*n*.BA) in cyclohexanone solution, were studied by following the disappearance of NH_4OH or *n*.BA on reacting with the HCl liberated. An overall kinetic scheme was considered and the rate constants of dehydrochlorination under various sets of conditions determined. The initial rate constants (k_1) of dehydrochlorination at 40°C induced by NH_4OH or *n*.BA are very close ($3.10 \times 10^{-3}\,l\,mol^{-1}\,min^{-1}$) indicating that NH_4OH and *n*.BA are comparable in their capacity to induce dehydrochlorination of PVC in solution.

INTRODUCTION

Among the thermoplastic materials, poly(vinyl chloride) (PVC) probably has the widest range of applications. Its main advantages are relatively low cost and low flamability but its main disadvantage is its thermal degradation at moderate temperatures.

The two most immediate effects of the degradation of PVC are the liberation of hydrogen chloride, i.e. "dehydrochlorination", and the noticeable discolouration of the polymer which contains conjugated double bond sequences introduced as a consequence of dehydrochlorination [1]. A completely or highly dehydrochlorinated product closely resembles the structures of polyacetylene, +CH=CH+_n.

Marvel *et al.* and others [2–8] reported base-induced dehydrochlorination of PVC; some of the studies referred to a strong alkali such as KOH as the dehydrochlorinating agent. Flodin *et al.* [9] made detailed kinetic studies on the dehydrochlorination of PVC in solution using KOH as the dehydrochlorinating agent. However, very little is known about the dehydrochlorination of PVC induced by a weak base, such as ammonia or an amine.

We now report kinetic investigations on dehydrochlorination of PVC in solution induced by ammonium hydroxide (NH_4OH) or *n*-butylamine (*n*.BA). The activation energy for dehydrochlorination induced by NH_4OH has also been determined.

EXPERIMENTAL

Ammonia was prepared in the laboratory by heating NH_4Cl and $Ca(OH)_2$; the evolved gas was dissolved in 95% ethanol, which was subsequently standardized using standard HCl solution. Hydrochloric acid (12N) was of analytical grade. L.R. grade cyclohexanone was dried over anhydrous sodium sulphate and then distilled; the middle fractions were collected and used. *n*-Butylamine (E. Merck) was kept over KOH pellets and finally purified by distillation. Suspension grade PVC resin of *K*-value 70 (NOCIL, Bombay) was used in all experiments. The dehydrochlorination in cyclohexanone solution was studied using alcoholic ammonia or *n*-butylamine (*n*.BA) as the dehydrochlorinating agent. A weighed amount of PVC (2 g) was dissolved in cyclohexanone (50 ml). Alcoholic ammonia of known strength was then added to the solution of PVC in known volume proportions. The ratio of alcohol to cyclohexanone was 1:3 (v/v) and this mixture kept the PVC in solution. The dehydrochlorination studies were done at 40 ± 0.5°C using three molar ratios of PVC/NH_4OH. An additional experiment was done to study the kinetics of dehydrochlorination of PVC using *n*.BA as the dehydrochlorinating agent at 40 ± 0.5°C.

It was found that, on addition of the alcoholic NH_4OH (or *n*.BA) to the PVC solution in cyclohexanone, there was progressive lowering of NH_4OH (or *n*.BA) content with time, evidently as a consequence of its instantaneous reaction with the HCl liberated from the polymer. The progress of dehydrochlorination, given by the progressive consumption of NH_4OH or *n*.BA with time, was followed by titration with standard HCl.

RESULTS

Solution dehydrochlorination of PVC induced by NH_4OH and n.*BA at 40°C*

The dehydrochlorination of PVC in cyclohexanone was studied using three molar ratios for PVC/NH_4OH and one molar ratio for PVC/*n*.BA at 40 ± 0.5°C. The reactions were followed, particularly in the early stages when the consumption of base added was less than 20%. The PVC solution gradually changed from colourless through yellow to brown with progress of reaction. Additional analysis showed gradual appearance and accumulation of chloride ions in the medium.

The experimental data were then treated graphically, showing the plot of mmol of NH_4OH or *n*.BA consumed vs time of dehydrochlorination (Figs 1 and 2). The plots are essentially linear over the time period and extent of dehydrochlorination studied [9]. For a given value of [PVC], higher concentration of a base, say NH_4OH, gives a plot of higher slope i.e. dehydrochlorination is faster with higher concentration of the base.

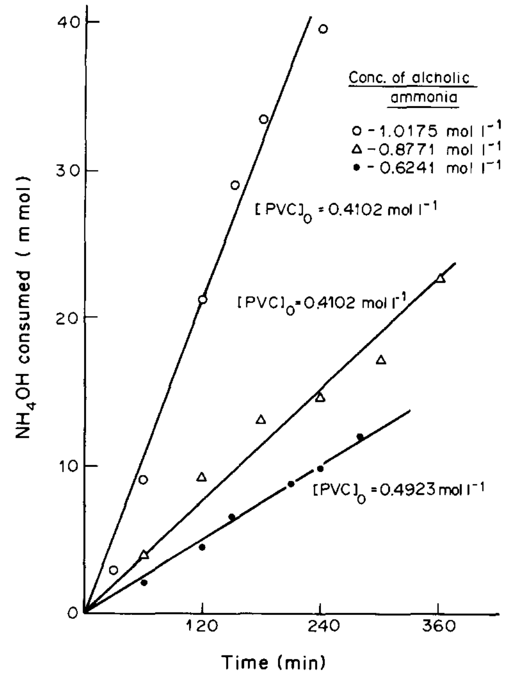

Fig. 1. Dehydrochlorination of PVC in solution by alcoholic ammonia at 40°C. Plot of mmol of NH_4OH consumed vs time.

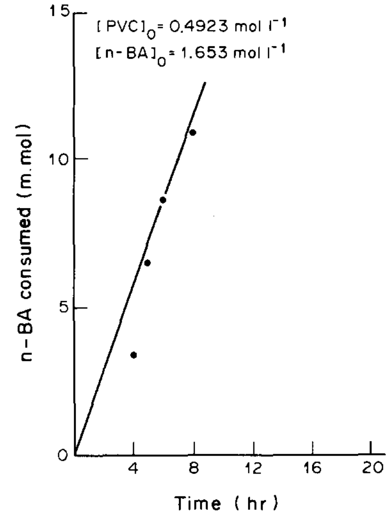

Fig. 2. Dehydrochlorination of PVC in solution by alcoholic *n*.BA at 40°C. Plot of mmole of *n*.BA consumed vs time.

Kinetic analysis and mechanism

From previous reports on extended thermal and alkaline dehydrochlorination of PVC, it is known that long conjugated polyene sequences are introduced into the polymer structure. When alkyl halides are dehydrohalogenated by bases, the reaction is reported [10] to proceed by a bimolecular mechanism. Assuming that the HCl splitting reactions are irreversible, the following reaction scheme may be formulated and considered for NH_4OH induced dehydrochlorination of PVC in solution [9].

$$NH_4OH + PVC \xrightarrow{k_1} P_1 + NH_4Cl + H_2O$$

$$NH_4OH + P_1 \xrightarrow{k_2} P_2 + NH_4Cl + H_2O$$

$$NH_4OH + P_{n-1} \xrightarrow{k_n} P_n + NH_4Cl + H_2O \qquad (1)$$

Here P_n represents a polyene sequence containing n conjugated double bonds and $k_1 \ldots k_n$ are the rate constants. One can then readily construct the following rate equations:

$$d[P_1]/dt = k_1[NH_4OH][PVC] - k_2[NH_4OH][P_1]$$

$$d[P_2]/dt = k_2[NH_4OH][P_1] - k_3[NH_4OH][P_2]$$

$$d[P_n]/dt = k_n[NH_4OH][P_{n-1}] \qquad (2)$$

This reaction scheme was suggested by Shindo and Hirai [11].

Designating the total concentration of double bonds in the polyene sequences by $[E]$, the rate Eqn (3) may be used to express the overall dehydrochlorination.

$$d[E]/dt = (d[P_1]/dt) + 2(d[P_2]/dt) + 3(d[P_3]/dt) + \cdots + n(d[P_n]/dt) \qquad (3)$$

Substitution of Eqn (2) in Eqn (3) gives

$$d[E]/dt = k_1[NH_4OH][PVC] + k_2[NH_4OH] \times [P_1] + k_3[NH_4OH][P_2] + \cdots + \times k_n[NH_4OH][P_{n-1}] \qquad (4)$$

Equation (4) is rather complicated. For simplicity it was assumed that at time, $t = 0$ the concentrations of P_1, P_2, $P_3 \ldots P_n$ are small compared to the PVC concentration. All terms containing the concentration of P are then neglected, thus reducing Eqn (4) to

$$d[E]/dt = k_1[NH_4OH][PVC] \qquad (5)$$

On introducing $[PVC]_0$ as the initial concentration of repeat units in the PVC and $[NH_4OH]_0$ as the initial NH_4OH concentration, the following equations were obtained at any arbitrary time (t)

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

$$[NH_4OH] = [NH_4OH]_0 - [E] \qquad (7)$$

Using Eqns (6) and (7) in the rate Eqn (5), one obtains:

$$d[E]/dt = k_1([PVC]_0 - [E])([NH_4OH]_0 - [E]) \qquad (8)$$

Integration of this equation gives:

$$\left(\frac{1}{\ln 10}\right)([PVC]_0 - [NH_4OH]_0)k_1 t + \log([PVC]_0/[NH_4OH]_0) = \log([PVC]_0 - [E])/([NH_4OH]_0 - [E]) \qquad (9)$$

A plot of $\log([PVC]_0 - [E])/([NH_4OH]_0 - [E])$ vs t would give a curve from which the rate constant k_1 could be calculated from the initial slope with knowledge of $[PVC]_0$ and $[NH_4OH]_0$. Using Eqn (9)

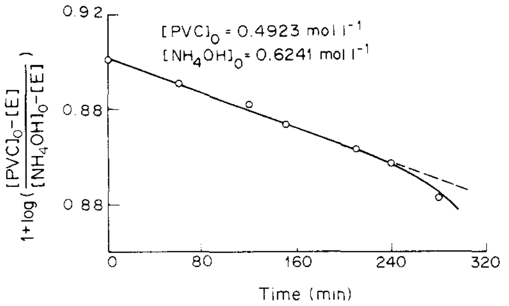

Fig. 3. Dehydrochlorination of PVC in solution at 40°C. Plot of $\log\left(\frac{[PVC]_0-[E]}{[NH_4OH]_0-[E]}\right)$ vs time.

and the experimental data, a plot of $\log [PVC]_0-[E])/([NH_4OH]_0-[E])$ vs t, for each of several dehydrochlorination studies at 40 ± 0.5°C, was made and the rate constant k_1 was evaluated from the initial slope in each case. A typical plot is shown in Fig. 3. Close values of k_1 at 40°C were obtained from plots with different $[PVC]_0/[NH_4OH]_0$, the average value being 3.10×10^{-3} l mol^{-1} min^{-1}.

Dehydrochlorination of PVC by n.*BA*

An additional experiment was done to study the kinetics of dehydrochlorination of PVC using *n*.BA. The related first step dehydrochlorination reaction may be represented by the equation:

$$RNH_2 + PVC \xrightarrow{k_1} P_1 + RNH_2 \cdot HCl \qquad (10)$$

where RNH_2 stands for *n*.BA. Equation (5) then

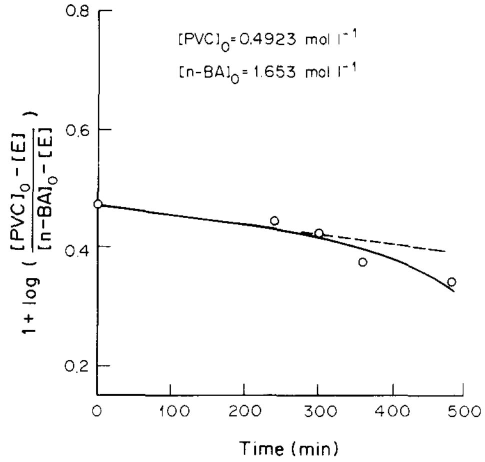

Fig. 4. Dehydrochlorination of PVC in solution at 40°C. Plot of $\log\left(\frac{[PVC]_0-[E]}{[n.BA]_0-[E]}\right)$ vs time.

reduces to the following form for the *n*.BA induced dehydrochlorination:

$$d[E]/dt = k_1[RNH_2][PVC] \qquad (11)$$

The final equation, on the basis of the deductions given earlier, may be written thus:

$$(1/\ln 10)([PVC]_0-[RNH_2]_0)k_1t + \log([PVC]_0/[RNH_2]_0) = \log([PVC]_0-[E])/([RNH_2]_0-[E]) \qquad (12)$$

The rate constant, k_1 was determined from the

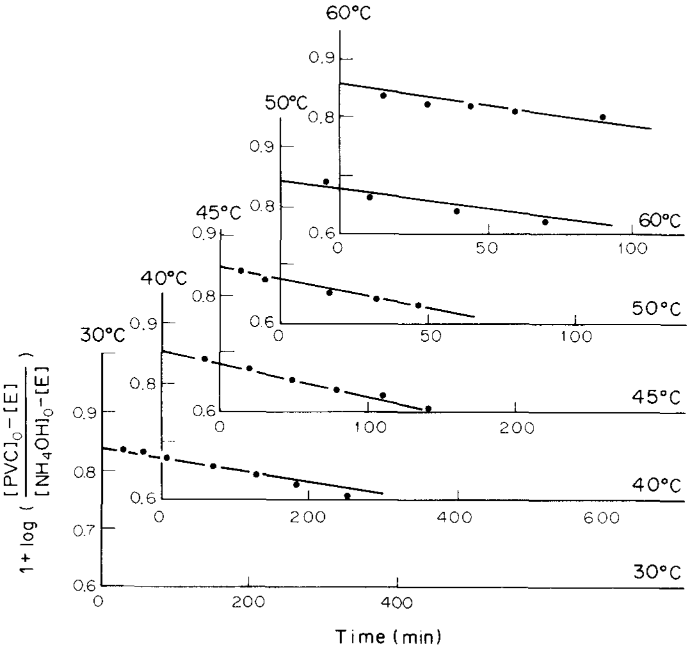

Fig. 5. Dehydrochlorination of PVC in solution by alcoholic ammonia. Plot of $\log\left(\frac{[PVC]_0-[E]}{[NH_4OH]_0-[E]}\right)$ vs time.

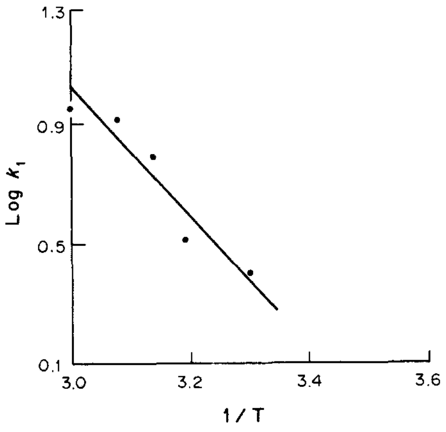

Fig. 6. Dehydrochlorination of PVC in solution by alcoholic ammonia. Plot of log k_1 vs $1/T$.

initial slope of the plot of log([PVC]$_0$ − [E])/([RNH$_2$]$_0$ − [E]) vs time. k_1 For n.BA induced dehydrochlorination at 40°C is 3.09×10^{-3} l mol^{-1} min^{-1} (Fig. 4). This value is close to that obtained for NH$_4$OH induced dehydrochlorination at the same temperature.

Activation energy of the dehydrochlorination induced by NH_4OH

The dehydrochlorination of PVC in cyclohexanone solution using NH$_4$OH as the dehydrochlorinating agent was also studied at five temperatures in the range 30°–60°C under otherwise comparable conditions. In each case, a plot of log ([PVC]$_0$ − [E])/([NH$_4$OH]$_0$ − [E]) vs time (Fig. 5) was made and the slope of the plot was used to evaluate k_1. A plot of log k_1 vs $1/T$, is shown in Fig. 6; the activation energy of the dehydrochlorination is 42.0 kJ/mol. The activation energy of dehydrochlorination of PVC in bulk under heat and light was reported [12] to be nearly 151 kJ/mol. It is thus clear that solution dehydrochlorination of PVC, in this case by a weak base such as ammonia, is a process with a significantly lower activation energy than thermal or photo dehydrochlorination in bulk.

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