Kinetics of Dehydrochlorination of PVC by n-Butylamine, Diethylamine and Triethylamine

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ABSTRACT

Kinetics of dehydrochlorination of poly(vinyl chloride) by n-butylamine, diethylamine and triethylamine in cyclohexanone have been studied by measuring the amount of amine consumed at different time intervals. Initial rate constants for the process of dehydrochlorination were determined to be $3.92 \times 10^{-3}$, $6.93 \times 10^{-3}$ and $6.28 \times 10^{-3}$ mol$^{-1}$ min$^{-1}$ at $50^\circ$C for each amine, respectively. The corresponding activation energies for the same reactions are found to be 52.45, 24.57 and 34.25 kJ mol$^{-1}$. This trend is in agreement with the basic behaviour of these amines. The reaction has been found to be bimolecular and it proceeds by E2 mechanism.

Key Words: PVC, dehydrochlorination, amines, kinetics, activation energy

INTRODUCTION

Thermal degradation of poly(vinyl chloride) (PVC) in solid phase has been extensively investigated [1–5]. The elementary process involved in degradation has been studied using various techniques, e.g., dehydrochlorination, thermogravimetric analysis, infrared, nuclear magnetic resonance and electron spin resonance, and mass spectrometry. Among these techniques dehydrochlorination has been considered to be the most suitable method to study PVC degradation. The degradation of PVC carried out in solid phase may, however, depend on the amount of sample and morphology of the sample. Most of these factors are, however, eliminated if dehydrochlorination tests are carried out in solution.

Relatively less work has been reported on degradation of PVC in solution phase [6–8]. The rate of thermal degradation in solid phase and in organic solvents can be significantly different. Some works on base induced dehydrochlorination of PVC are reported in literature [9–11] which include dehydrochlorination by potassium hydroxide and ammonia.

In the present work dehydrochlorination of PVC induced by n-butylamine, diethylamine and triethylamine in alcoholic cyclohexanone solution has been investigated. The kinetics of dehydrochlorination of PVC by amine is studied at different temperatures using varying concentrations of amines. The activation energies induced by n-butylamine, diethylamine and triethylamine are also determined.
EXPERIMENTAL

Materials
Analytical grade PVC (BDH) of molecular weight 100,000±20 was employed. n-Butylamine (Riedel-de-Haen), diethylamine and triethylamine (Merck) were kept over potassium hydroxide pellets and used after distillation. Cyclohexanone (Fluka) was distilled after being dried over anhydrous sodium sulphite. Absolute ethanol (Fluka) was used as such. The 0.1N HCl solution was obtained by diluting 37% ACS reagent from Aldrich, and it was standardized with sodium carbonate and also with borax as well.

Dehydrochlorination of PVC with Amines
The standard procedure used for dehydrochlorination of PVC with n-butyamine, diethylamine and triethylamine at different temperatures is as follows:
PVC, amine, cyclohexanone and ethanol were weighed in a dry 100 mL round bottom flask. Alcoholic cyclohexanone solvent was used in 1:3 (v/v) ratio for 1:1, 1:1.5 and 1:2 molar ratios of PVC/amine, while for 1:3 molar ratio of PVC/amine, 1:2 (v/v) solvent was used. A magnetic bar was placed in the flask which was suspended in a water bath thermostat operating at a constant temperature with ±0.5 °C. A water condenser with a drying tube attached at the outer end was fixed to the reaction flask and the reaction mixture was stirred at constant temperature for several hours. To measure the extent of dehydrochlorination taking place a small portion of reaction mixture was withdrawn at regular time intervals. The sample was weighed in a dry conical flask and a few drops of methyl orange indicator were added and was finally titrated against standard 0.1N hydrochloric acid to measure the unreacted amine in the sample. The extent of dehydrochlorination taken place was determined from the amount of amine consumed in the reaction.

The effect of varying concentrations of n-butyamine, diethylamine and triethylamine on dehydrochlorination of PVC was studied at 42 ± 0.5 °C using 1:1, 1:2 and 1:3 molar ratios of PVC/amine.

The kinetics of dehydrochlorination of PVC with n-butyamine, diethylamine and triethylamine were studied at different temperatures and the values of the kinetic parameters were determined.

RESULTS AND DISCUSSION
Solution phase dehydrochlorination of PVC with various amines cause colour changes in the reaction mixtures. The addition of n-butyamine
Dehydrochlorination of PVC in solution by diethylamine in 1:3 molar ratio at temperatures °C: 30(●), 35(▲), 40(■), 45(○), and 50(▲); plot of DEA consumed vs time.

changes the reaction mixture from colourless through yellow to brown with progress of reaction while diethylamine and triethylamine cause only a change from colourless to yellow. The extent of dehydrochlorination is followed by measuring the amine consumed on reaction with HCl that is liberated as a result of dehydrochlorination of PVC (Scheme I).

The unreacted amine was determined by titration against standard 0.1 N HCl and the percent dehydrochlorination was calculated.

Dehydrochlorination of PVC by n-butylamine, diethylamine and triethylamine is temperature dependent. The increase in reaction temperature increases the rate of dehydrochlorination of PVC (Figure 1). Similarly the increase in concentration of amine also increases the rate of dehydrochlorination (Figure 2).

Kinetics of Dehydrochlorination
Reactions of PVC with diethylamine are expected to produce long chain conjugated polyene sequences according to Scheme II.

Dehydrochlorination of PVC is expected to proceed through bimolecular reaction mechanism [9, 12]. Polyene sequences are formed in stepwise reactions that are supposed to be irreversible.

\[ \text{RNH}_2 + \text{PVC} \xrightarrow{k_1} \text{P}_1-\text{PVC} + \text{RNH}_3\text{Cl} \]
\[ \text{RNH}_2 + \text{P}_1-\text{PVC} \xrightarrow{k_2} \text{P}_2-\text{PVC} + \text{RNH}_3\text{Cl} \]
\[ \text{RNH}_2 + \text{P}_2-\text{PVC} \xrightarrow{k_3} \text{P}_3-\text{PVC} + \text{RNH}_3\text{Cl} \]
\[ \text{RNH}_2 + \text{P}_{n-1}-\text{PVC} \xrightarrow{k_n} \text{P}_n-\text{PVC} + \text{RNH}_3\text{Cl} \]

Scheme III

Where \( k_1, k_2, k_3, \) and \( k_n \) are the rate constants with 1, 2, 3 and \( n \) conjugated double bonds in the polyene sequences. The rate equation for the first step is:

\[
\frac{d[\text{P}_1-\text{PVC}]}{dt} = k_1[\text{RNH}_2][\text{PVC}] 
\]

The overall dehydrochlorination can be expressed as:

\[
\frac{d[A]}{dt} = (d[\text{P}_1-\text{PVC}]/dt) + 2(d[\text{P}_2-\text{PVC}]/dt) + \ldots \ n'(d[\text{P}_n-\text{PVC}]/dt) 
\]

Figure 2. Dehydrochlorination of PVC in solution by diethylamine at 42 °C in molar ratios; 1:1 (●), 1:2 (○), 1:3 (▲); plot of DEA consumed vs time.
Table 1. Rate constant for the reaction of PVC with n-butylamine, diethylamine and triethylamine at various temperatures.

<table>
<thead>
<tr>
<th></th>
<th>PVC/n-butylamine</th>
<th>PVC/diethylamine</th>
<th>PVC/triethylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>k₁ (mol⁻¹min⁻¹)</td>
<td>T (°C)</td>
<td>k₁ (mol⁻¹min⁻¹)</td>
</tr>
<tr>
<td>40</td>
<td>2.98 X 10⁻³</td>
<td>30</td>
<td>3.88 X 10⁻³</td>
</tr>
<tr>
<td>50</td>
<td>3.92 X 10⁻³</td>
<td>35</td>
<td>4.42 X 10⁻³</td>
</tr>
<tr>
<td>60</td>
<td>5.11 X 10⁻³</td>
<td>40</td>
<td>5.00 X 10⁻³</td>
</tr>
<tr>
<td>65</td>
<td>6.15 X 10⁻³</td>
<td>45</td>
<td>6.37 X 10⁻³</td>
</tr>
<tr>
<td>70</td>
<td>8.10 X 10⁻³</td>
<td>50</td>
<td>6.93 X 10⁻³</td>
</tr>
</tbody>
</table>

where A is the concentration of total number of double bonds present in the polyene sequences. The symbol n' gives total number of polyene sequences; P₁, P₂, ...Pₙ are the polyene sequences with 1, 2 and n conjugated double bonds.

Substitution of Equation 1 in Equation 2 and assuming that concentrations of polyene sequences are small at t=t₁ as compared to PVC concentration, then:

\[
\frac{d[A]}{dt} = k₁[PVC][RNH₂]
\]

and at particular time:

\[
[PVC] = [PVC]₀ - [A]
\]

\[
[RNH₂] = [RNH₂]₀ - [A]
\]

Substituting [PVC] and [RNH₂] in Equation 3:

\[
\frac{d[A]}{dt} = k₁([PVC]₀ - [A])([RNH₂]₀ - [A])
\]

Figure 3 shows a typical plot of \(\log([PVC]₀ - [A])/(RNH₂)₀ - [A])\) vs time (t). The initial slope of this curve was used to calculate \(k₁\) for each amine. The rate constants for reaction of PVC with n-butylamine, diethylamine and triethylamine are given in Table 1. It is observed that rate constants increase with the increase in temperature. As the kinetic plot obtained using second order rate expression gives a straight line, the overall reaction is of second order. However, beyond four hour reaction time there is a deviation from straight line due to increase in by-products and complexity of further reactions.

The activation energies for the reaction of PVC with n-butylamine, diethylamine and triethylamine have been determined from the slopes of the plots of \(\log k₁ vs 1/T\) (Figure 4), and are 52.45, 24.67 and 34.25 kJ mol⁻¹ for each, respectively. The order of reactivity on the basis of activation energy.
energy is DEA > TEA > n-BA. This trend is in agreement with the basic behaviour \( (k_b) \) of these amines. The \( k_b \) values are \( 4.8 \times 10^{-4}, 10.0 \times 10^{-4} \) and \( 5.6 \times 10^{-4} \), respectively [13]. This reflects that the increase in the basic character of amines lowers the activation energy of the reaction and thus increases the dehydrochlorination process in PVC. Activation energy of dehydrochlorination of PVC under heat or light is about 151 kJ mole\(^{-1}\) [14]. It means that the solution phase dehydrochlorination of amines are processes with significantly lower activation energy as compared to thermal and photo-dehydrochlorination of PVC in bulk.

**Mechanism of Dehydrochlorination**

When PVC reacts with amine, the HCl is produced and polyene sequences are formed with conjugated double bonds. Removal of HCl from alkylhalides may take place by \( E_1 \) or \( E_2 \) elimination reaction. If \( E_1 \) elimination reaction occurs then the mechanism of dehydrochlorination would be followed according to Scheme IV. The rate of reaction in this case is dependent only on the concentration of PVC and expressed as:

\[
\frac{d[A]}{dt} = k_1 [\text{PVC}].
\]

\( E_2 \) elimination of HCl from PVC will be followed as in Scheme V, which is a one step reaction and the rate of reaction is dependent on the concentration of PVC and RNH\(_2\).

\[
\frac{d[A]}{dt} = k_1 [\text{PVC}]_t [\text{RNH}_2].
\]

In the present work it is observed that the rate of dehydrochlorination is dependent on the concentration of amine. The rate increases with rising concentration of amine (Figure 2).

Dehydrochlorination of alkylhalides is also reported to be dependent on the concentration of a base [12]. Thus dehydrochlorination reaction of PVC by n-BA, DEA and TEA is expected to be bimolecular and it proceeds by \( E_2 \) mechanism.

**CONCLUSION**

Kinetics of dehydrochlorination of PVC by n-butylamine, diethylamine, and triethylamine in a solvent such as cyclohexanone was studied. Initial rate constants for the process of dehydrochlorination were \( 3.92 \times 10^{-3}, 6.93 \times 10^{-3} \) and \( 6.28 \times 10^{-3} \) mol\(^{-1}\) at 50 °C for n-BA, DEA and TEA, respectively.

The activation energies for the same reactions are, 52.45, 24.67 and 34.25 kJ mol\(^{-1}\). This trend is in agreement with the basic behaviour of these amines. The kinetic studies show that reactions proceed by \( E_2 \) mechanism.
REFERENCES


