

Dehydrochlorination Rate in Thermal Degradation of PVC

Yoshiki Tanaka, Toshiro Tsuji*, Toshiharu Shibata,

Osamu Uemaki, and Hironori Itoh

Graduate School of Engineering, Hokkaido University

N13W8, kita-ku, Sapporo, Japan 060-8628

E-mail: ttsuji@eng.hokudai.ac.jp Fax: +81-11-706-6552

Dehydrochlorination rates of PVC have been measured using an isothermal pyrolyzer and a thermobalance. The isothermal pyrolysis data were obtained at temperatures ranged from 502 K to 635 K. The non-isothermal pyrolysis experiments using a thermobalance were carried out at heating rates of 5, 10, 20 and 50 K min⁻¹ up to the final temperature of 673 K. A reaction model for the dehydrochlorination was developed on the basis of the isothermal pyrolysis data. From the Arrhenius plots for the reaction rate constants in this model, the kinetic parameters (the apparent activation energies and the frequency factors) were obtained. The calculated conversions of the dehydrochlorination using these parameters were compared with the experimental values. The experimental results of both isothermal and non-isothermal reactions can be predicted by the present model using some accommodative parameters according to the reaction conditions.

Chlorinated compounds in the produced oil were determined by GC-MS. Though the amount of them increased with the heating period, it was very small (1.4-5.0 mg per gram of PVC). The main components were benzyl chloride and alpha-chloroethylbenzene. The amounts of evolved HCl from PVC degradation were nearly equal at the final temperature higher than 623 K.

Introduction

Many studies have been carried out on the pyrolysis kinetics of PVC [1,2]. However most of these studies are based on the analysis using non-isothermal reactor such as a thermobalance. Although HCl is the main compounds in the pyrolysis of PVC at the temperature lower than 635 K, it is recognized that some hydrocarbons with or without chlorine are also produced accompanying with HCl. Therefore it is questionable that the thermogravimetric analysis can measure the true dehydrochlorination rate.

In this study, the pyrolysis of PVC has been carried out using isothermal reactor. Dehydrochlorination rate was measured by the pH change in the water trap in which evolved HCl is absorbed. And the chlorinated hydrocarbons after dehydrochlorination were analyzed by GC-MS.

Experimental

Commercial PVC powder from Chisso Co. (Grade SH) was used in this study.

Isothermal pyrolysis.

Fig.1 shows a schematic diagram of the experimental apparatus for the isothermal pyrolysis. The experimental data of isothermal pyrolysis was obtained over certain temperatures ranged from 502 K to 635 K. N₂ stream (500 cm³ min⁻¹) was used as a carrier

gas. PVC samples (30 mg) were transported by the entrain gas (N₂) into the preheated reactor, then were subjected to pyrolysis. The produced HCl was collected through the 1000 cm³ water trap, and the pH change of the water was measured continuously. Dehydrochlorination ratio (Conversion) was defined as follows:

$$\text{Conversion [wt\%]} = \frac{W_{\text{HCl},t}}{W_{\text{HCl},0}} \times 100 \quad (1)$$

where $W_{\text{HCl},t}$ and $W_{\text{HCl},0}$ mean the weight of produced HCl at reaction time t and the weight of HCl in original PVC powder, respectively. After the pyrolysis, the residue was analyzed by elemental analysis.

Non-isothermal pyrolysis.

The non-isothermal pyrolysis was conducted using a thermobalance (Shimadzu DTG-50). PVC samples (10 mg) were placed into an alumina cell and heated in N₂ stream (100 cm³ min⁻¹) from room temperature up to 673 K at the heating rates of 5, 10, 20, 50 K min⁻¹. As well as the isothermal pyrolysis, the produced HCl was collected through the 1000 cm³ water trap, and pH change of water was measured continuously. Remaining ratio was calculated with the following equation:

$$\text{Remaining ratio [wt\%]} = \left(1 - \frac{W_{\text{HCl},t}}{W_{\text{PVC},0}}\right) \times 100 \quad (2)$$

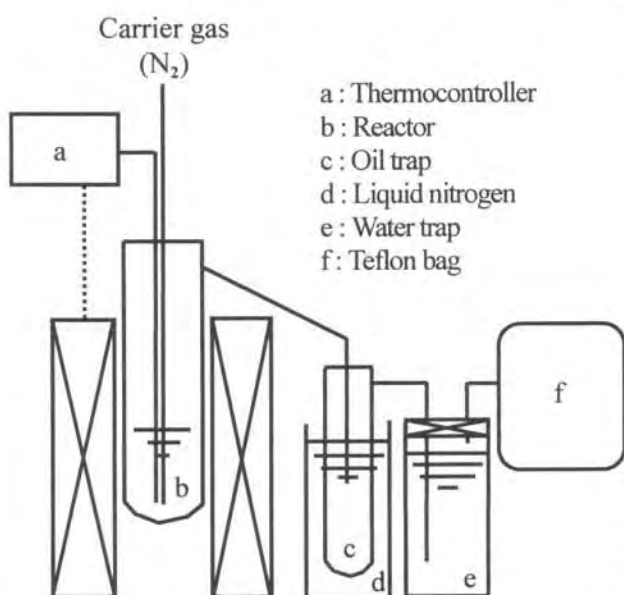


Fig.2 Schematic diagram of the apparatus for the investigation of chlorinated compounds.

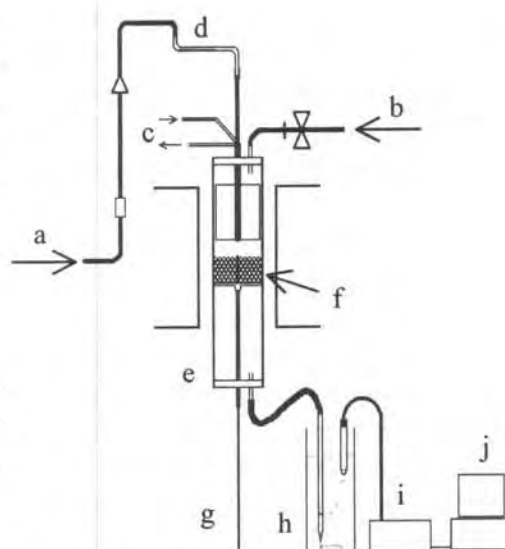


Fig.1 Schematic diagram of the isothermal pyrolyzer.

a : Entrain gas (N₂), b : Carrier gas (N₂),
 c : Cooling water, d : PVC feeder,
 e : Reactor
 (Inside diameter:21 mm , Length:600 mm),
 f : Alumina particle layer, g : Thermocouple,
 h : Water trap, i : pH meter, j : Recorder.

where $W_{\text{PVC},0}$ means the weight of initial PVC powder. After the pyrolysis, the residue was analyzed by FT-IR.

The investigation of chlorinated compounds.

Fig.2 shows a schematic diagram of the apparatus for the investigation of chlorinated compounds. This experiment was conducted using an infrared image furnace (Sinku-Riko Co.). The experiments were carried out PVC samples (5.0 g) were set in the reactor and heated in N₂ stream (20 cm³ min⁻¹) at the heating rate of 30 K min⁻¹ up to the final temperature ranged from 623 K to 773 K, and the holding periods at this temperature were 0 min and 120 min. The products were frozen in the oil trap by liquid nitrogen. After the run, the oil trap was removed from

liquid nitrogen and turned to room temperature, so that the products were melted. The gaseous components flew to the water trap and the Teflon bag, and the oil components which condensed at room temperature remained in the oil trap. The evolved HCl during pyrolysis was collected in the water trap (1000 cm³), and its concentration was determined by titration. Chlorinated compounds in the produced oil were determined by GC-MS.

Results and Discussions

Isothermal pyrolysis

The conversions calculated from pH data in isothermal pyrolysis were shown in Fig.3. From the feature of this plots, it is supposed that dehydrochlorination proceeds via two parallel paths, because dehydrochlorination curves is different from each other in the patterns, and final conversions of dehydrochlorination increase with reaction temperature. From the elemental analysis (Table 1) and FT-IR spectra, it seems that the residue contains little chlorine after the dehydrochlorination. However from measuring the chlorinated compounds in the produced oil, it was found that these compounds were produced during the dehydrochlorination. Thus a reaction model for the dehydrochlorination was proposed as was shown in Fig.4. Each path is supposed as the first-order reaction. Reaction rate constants from k_1 to k_4 were determined by the curve fitting to the plots in Fig.3. Solving the sets of reaction equations from eq.(3) to eq.(6), we can obtain eq.(7), where "X" means the conversion of dehydrochlorination. Calculated curves by eq.(7) are also drawn in Fig.3. The calculated curves explain the experimental results very well.

Table 1. Elemental analysis of isothermal pyrolysis residues (wt%)

Temp/K	C	H	Cl	Total
540	-	-	28.27	-
578	89.60	7.68	0.61	97.89
617	89.55	7.48	<0.2	97.03

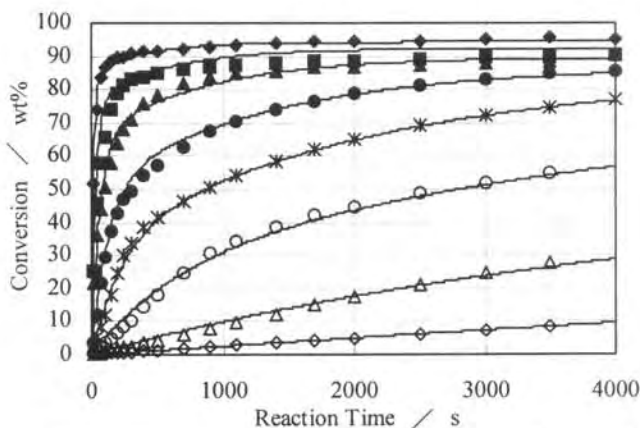
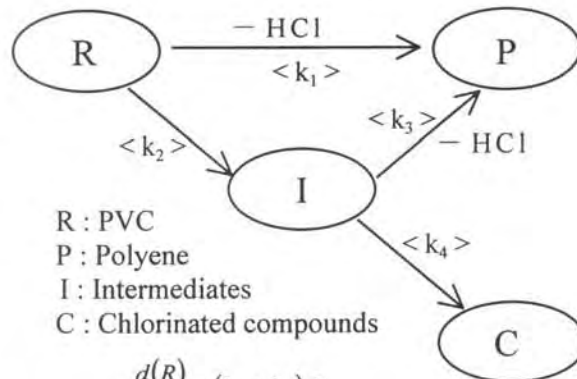


Fig.3 Comparison of calculated conversions with experimental values in the isothermal pyrolyzer.

— : Calculated curve,
 ◆ : 635 K, ■ : 617 K, ▲ : 598 K, ● : 578 K,
 * : 559 K, ○ : 540 K, △ : 520 K, ◇ : 502 K.



$$-\frac{d(R)}{dt} = (k_1 + k_2) R \quad (3)$$

$$\frac{d(I)}{dt} = k_2 \cdot R - (k_3 + k_4) I \quad (4)$$

$$\frac{d(P)}{dt} = k_1 \cdot R + k_3 \cdot I \quad (5)$$

$$\frac{d(C)}{dt} = k_4 \cdot I \quad (6)$$

$$X = \frac{P}{R_0} = C_1 \cdot \exp\{-(k_1 + k_2)t\} + C_2 \cdot \exp\{-(k_3 + k_4)t\} + C_3 \quad (7)$$

$$C_1 = -\frac{k_1}{k_1 + k_2} + \frac{k_2 \cdot k_3}{(k_1 + k_2)(k_1 + k_2 - k_3 - k_4)} \quad (8)$$

$$C_2 = \frac{k_2 \cdot k_3}{(k_3 + k_4)(k_1 + k_2 - k_3 - k_4)} \quad (9)$$

$$C_3 = \frac{k_1 \cdot k_3 + k_1 \cdot k_4 + k_2 \cdot k_3}{(k_1 + k_2)(k_3 + k_4)} \quad (10)$$

Fig.4 Reaction model for the degradation of PVC.

Non-isothermal pyrolysis

TGA curves were calculated using the apparent activation energies and the frequency factors calculated from the isothermal pyrolysis data. However, this calculated curves were out of accordance with experimental data. The apparent activation energies and the frequency factors may vary with the reaction condition. By adjusting these parameters and re-calculating the remaining ratio according to this model, the calculated curves agreed well with the experimental results (Fig.5).

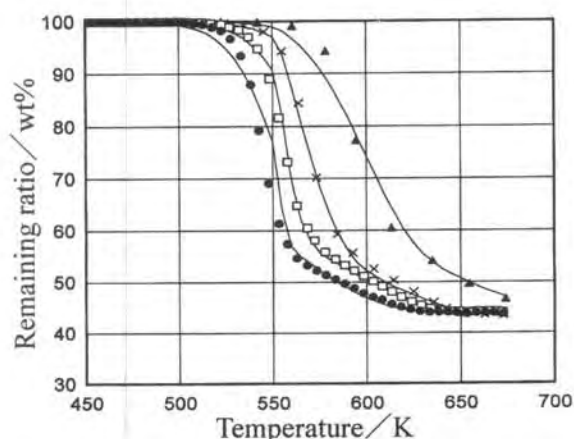


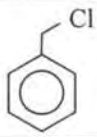
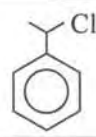
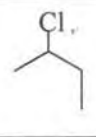

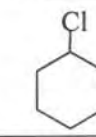
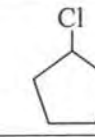
Fig.5 Comparison of calculated remaining ratio with experimental values in the thermobalance.

— : Calculated curve,
 ● : 5 K min⁻¹, □ : 10 K min⁻¹,
 × : 20 K min⁻¹, ▲ : 50 K min⁻¹.

The investigation of chlorinated compounds.

As is stated above, chlorine in produced residue at 617 K is under the detection limit by elemental analysis and FT-IR. A small amount of chlorinated compounds was detected in the produced oil, and increased with heating period of pyrolysis. From this, it is suggested that a mere trace of chlorine remains in the residues and evolves as the chlorinated compounds in longer heating period. Main chlorinated compounds in the produced oil are tabulated in Table 2. With respect to identifiable chlorinated compounds, the sums of chlorine in these compounds are small amounts, 0.5-3.0 mg per gram of chlorine in PVC. Most of the chlorinated compounds are chlorinated alkenes and aromatics such as benzyl chloride and alpha-chloroethylbenzene etc.

Table 2 Main chlorinated compounds in the produced oil

						
723 K, 0 min	0.117	0.097	0.053	0.083	0.000	0.043
723K, 120 min	0.184	0.312	0.861	0.119	0.097	0.228

$$\text{value} = \frac{\text{weight of chlorine in compound [g]}}{\text{weight of chloride in PVC [g]}} \times 1000$$

Conclusions

From the isothermal pyrolysis data, it was suggested that dehydrochlorinations proceed via two parallel paths.

The apparent activation energies and the frequency factors vary in the dehydrochlorinating conditions. By adjusting parameters, both isothermal and non-isothermal dehydrochlorination curves are well explained with the same model proposed in the present study.

After dehydrochlorination has proceeded almost perfectly, a mere trace of chlorine still exists in the residue and a small amount of chlorine evolves as the chlorinated compounds.

References

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- Knümann, R.; Bockhorn, H. *Combust. Sci. Tech.* 1994, **101**, 285-299