# Temperature Dependence on the Activation Energy of Dechlorination in Thermal Degradation of Polyvinylchloride

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(Received October 26, 2004; CL-041264)

The dechlorination of polyvinylchloride (PVC) powder initially progressed on an apparent zero order reaction, and proceeded in higher dechlorination range by an apparent first order reaction. The apparent activation energies indicate that the rate of the dehydrochlorination is controlled by the chemical reaction at low temperature, but that from 300 to 400 °C is controlled by heat transfer rate.

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Many works have reported the dechlorination behavior of PVC since the late 1930's,[1–4] then some mechanism and many kinetic equations have been proposed.[5–11] The objects of these works were almost stabilization of PVC, and experimental conditions were investigated in the range of low temperatures up to 260 °C and low degrees of dechlorination up to ca. 60%. Therefore, it is important to understand and discuss the dechlorination behavior of PVC in wide range at higher temperatures of 300 to 400 °C, at which pilot plants convert waste plastics into oil by pretreatment.

In this work, PVC powder was held and degraded between 200 to 400 °C with a heating rate of 100 °C/min. under nitrogen flow, and kinetics for high dechlorination degrees were discussed.

PVC powder (Mw = 62500, particle size 0.1 mm) of 30 mg was held and degraded at the required temperature for 5 h after heating with a heating rate of 100 °C/min. under $N_2$ flow of 250 $cm^3$/min. An infrared red reflection type furnace was used in this experiments. The sample placed on a quartz boat was inserted into a quartz reaction tube (27-mm i.d., 610-mm long), which was placed in the furnace, after the reaction temperature was reached. In this analysis, the starting time defines the time of the insertion of the sample into the reactor. Reaction temperature was measured by a thermocouple outside the reaction tube as confirmed to be nearly within ±2 °C equal to the temperature inside the tube. Evolved HCl was collected in 100-$cm^3$ distilled water in a HCl trap. The HCl solution was sampled 2 $cm^3$ every 5 and/or 10 min, and the amount of $Cl^-$ was determined by ion chromatography.

Effect of temperature on the dechlorination is shown in Figure 1. The rate was constant in the range of low dechlorination degree at each temperature, but decreased gradually when the dechlorination degree became higher. Because the dechlorination proceeded as a zero order reaction initially, an apparent initial rate constant $k$ can be defined as Eq 1.

$$\frac{dX}{dt} = k \qquad (1)$$

where $X$ is the degree of dechlorination. The dechlorination could be arranged by the zero order reaction in the range of low degree at all temperatures. Arrhenius plot of the apparent rate constants are shown in Figure 2 including the results of previous thermal dechlorination in inert gases. The plot is a clear straight line independent on experimental conditions between 80 and 280 °C. The activation energy of this temperature range was 116.5 kJ/mol. Although the apparent rate constant in an inert gas is larger than in an oxygen atmosphere or vacuum, the activation energy shows the almost equal value. This result indi-

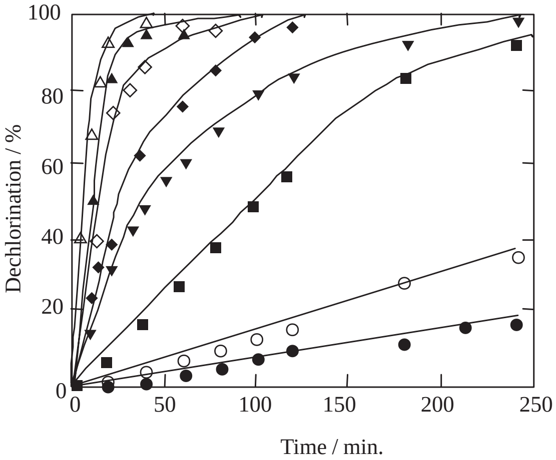

**Figure 1.** The degree of dechlorination of PVC powder in $N_2$ atmosphere. Temperature/°C: ● 200, ○ 220, ■ 240, ▼ 260, ◆ 280, ◇ 300, ▲ 350, △ 400.

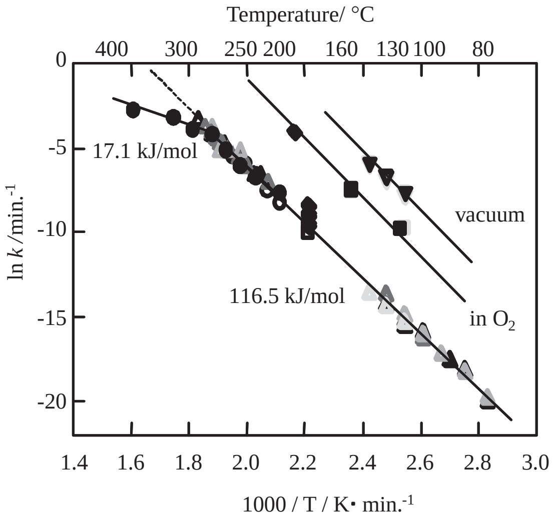

**Figure 2.** Arrhenius plots of the apparent zero order rate constants of dechlorination of PVC. Comparison this of work (●) with previous data.

cates that the dechlorination is controlled by chemical reaction, and the dechlorination mechanism is almost the same.

But the slope of the straight line decreased rapidly at higher temperature than ca. 280 °C and the obtained activation energy was 17.1 kJ/mol. According to this value, it is considered that the dechlorination is controlled by the mass transfer and heat transfer, as well.

It is well known that the dechlorination proceeds as a zipper reaction and HCl is released by a radical reaction mechanism. In this case, the apparent rate seems to be a zero order reaction due to the high concentration of vinyl chloride units during the lower state of dechlorination. On the other hand, dechlorination proceeds as a apparent first order reaction mechanism (Eq 2) due to the reduced chlorine concentration at the end of the dechlorination process.

$$-\frac{dX'}{dt} = -k(1 - X') \tag{2}$$

where X′ is defined as the degree of dechlorination over the plot which can be arranged by the zero order reaction, *t* is the reaction time. The first order plot was approximately straight, and the activation energy was 58.9 kJ/mol between 200 and 300 °C (Figure 3). On the other hand, the activation energy between 300 and 400 °C was 15.0 kJ/mol. These results indicate that the dechlorination is controlled by the heat conduction rate at temperatures over 300 °C in the same manner as in the temperature range of the lower degree of dechlorination.

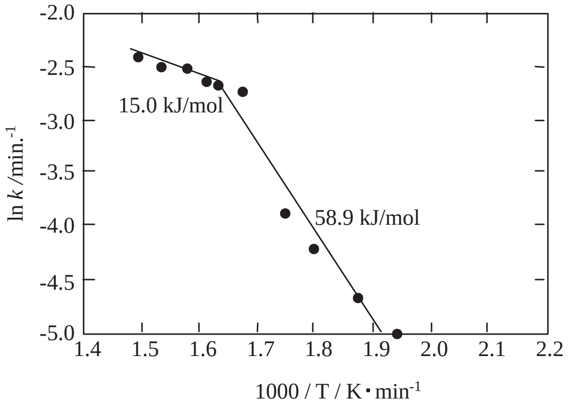

**Figure 3.** Arrhenius plots of apparent rate constants for the high degree of dechlorination of PVC.

This means that dechlorination processing is conducted in the heat transfer-controlled range in many plastic recycling plants.

Therefore, it is thought to increase the rate constant by addition of a high heat conductor materials such as graphite. Figure 4 shows the effect of the graphite addition on the apparent rate constant of dechlorination at 350 °C. Two types of graphite powder were mixed with PVC powder, the first one had a heat conductivity of 116 W/m/K (MF), and other of 140 W/m/K (GE). The rate constant increased 1.35 times for PVC powder in case of MF, and increased 1.45 times in case of GE. It is clear that the apparent rate constant increases by addition of high heat conductors. However, over a graphite/PVC ratio of 5, the rate constant is constant. This means that contacting surface between PVC powder and graphite powder is saturated at this graphite/PVC ratio. Therefore, if the particle size of PVC and graphite powder is smaller, the ratio of the rate constant and the graphite/PVC ratio is approximated to shift to higher values.

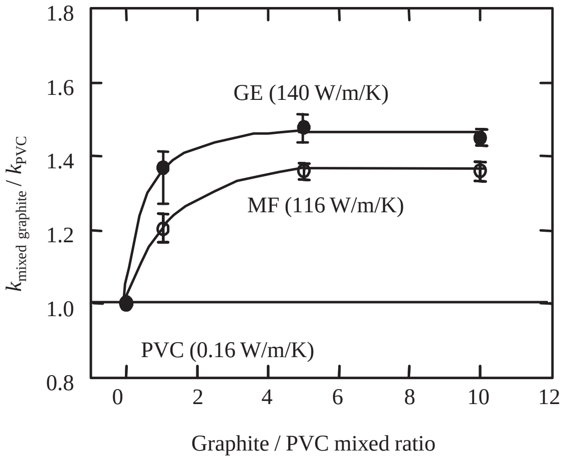

**Figure 4.** Effect of the graphite addition on the apparent rate constants of dechlorination of PVC.

Thus, it is clear that dechlorination is controlled by the heat transfer rate at temperatures over 280 °C. Also, the addition of high heat conductor materials, such as graphite, has an effect of increasing the dechlorination rate. When the dechlorination is performed in a dry process as a pretreatment of waste plastics recycling, it is necessary to consider the heat transfer.

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Published on the web (Advance View) December 11, 2004; DOI 10.1246/cl.2005.70