Kinetics of the poly(vinyl chloride) dehydrochlorination in a stream of oxygen

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Received 14 February 1973

Accepted for publication 4 July 1973

The kinetics of isothermal dehydrochlorination of the non-fractionated powdered poly(vinyl chloride) in a stream of oxygen was investigated experimentally at 183-216°C. In this temperature interval the dehydrochlorination is an autocatalytic process. The degree of dehydrochlorination corresponding to its maximum rate increases with increasing temperature (from 8% at 183°C to 19% at 216°C). This shift of the inflexion point of the kinetic curves brought about by the temperature change corroborates that consecutive reactions occur in poly(vinyl chloride) during the thermal oxidative dehydrochlorination. The effective activation energy of this process is 32 kcal mol⁻¹ in the studied temperature range.

Kinetic studies of the poly(vinyl chloride) dehydrochlorination in the presence of oxygen to high degree of conversion revealed an autocatalytic character of this process [1-6]. The autocatalytic character is mostly assumed to be a consequence of the preferential reaction of oxygen with unsaturated bonds of macromolecular chains and with macromolecular radicals, thus forming peroxides. The peroxides decompose into radicals attacking undegraded parts of the macromolecular chains. *Bersh* and *Harvey* [9, 10] pointed out that oxygen may react also with saturated bonds of a polymer.

The kinetic curves of dehydrochlorination in the presence of oxygen are characterized by the initial and maximum rates. *Talamini* and *Pezzin* [3] showed that the maximum dehydrochlorination rate in the presence of oxygen and at the temperatures $200-250^{\circ}$ C corresponds to the 50% degree of the dehydrochlorination. According to other works [5, 6], in the mentioned temperature interval and in the presence of air, the degree of dehydrochlorination corresponding to its maximum rate decreases with temperature.

A theory of the step by step mechanism of the dehydrochlorination [14] was worked out in which it is important to know a hypothetic amount of hydrochloride eliminated in the isothermal dehydrochlorination at the time $t = \infty$. Since the confidence of measurements of the released hydrochloride decreases with the degree of conversion, only the initial and maximum rates were determined in this work.

Experimental

The kinetics of isothermal dehydrochlorination of poly(vinyl chloride) in a stream of oxygen was studied by a potentiometric method [7] with a counter-flow absorption [8] of the released hydrochloride from the carrier gas (oxygen) into a water-alcoholic solution of silver nitrate.

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The investigated polymer was an industrial product, Pevikon KL-2. Its residual impurities were removed by the multiple water and methanolic extraction, then the polymer was dried in the nitrogen atmosphere at 50°C. The removal of methanol from the polymer was checked by the DTA method. The optimum sample weights of the polymer for the isothermal dehydrochlorination at different temperatures were found by preliminary measurements. The thermostat was filled with a silicon oil and its temperature was kept at a chosen value with the confidence of ± 0.5 °C. Before each measurement, the glass surfaces of the apparatus were saturated with the gaseous hydrogen chloride at a given temperature. The speed of the oxygen stream was always 28 cm³ min⁻¹ at room temperature and atmospheric pressure. Before the measurement, the atmospheric nitrogen was removed from the weighed polymer sample as well as from the apparatus by the oxygen stream of the above-mentioned speed, for *ca* one hour at room temperature.

Results

The results of measurements of the isothermal dehydrochlorination of poly(vinyl chloride) at 210°C are shown in Fig. 1. The dehydrochlorination degree was calculated with respect to the theoretical content of chlorine in poly(vinyl chloride). The points corresponding to the mean rate (they are, in fact, tabular differences of the first order) and the time dependence of the dehydrochlorination rate are also plotted in Fig. 1. The maximum rate was calculated from the dependence of the dehydrochlorination degree, *i.e.* conversion (m), on the time (t) in the neighbourhood of the inflexion point of the conversion curve. This dependence was expressed by an empirical equation in the form

$$m = a t + b t^2 + c t^4.$$
 (1)



Fig. 1. Time dependence of the degree of dehydrochlorination (\bigcirc) and the mean dehydrochlorination rates (\bullet) at 210°C.



Fig. 2. Time dependence of the calculated dehydrochlorination rate at 210°C.

The plotted confidence interval corresponds to standard deviations of the rate values.

 \bigcirc The mean rates of dehydrochlorination.



Fig. 3. Time dependence of the degree of dehydrochlorination (\bigcirc) and the mean dehydrochlorination rates at 183°C.

For the sake of simplicity, only a half of the measured points are plotted.



Fig. 4. Time dependence of the calculated dehydrochlorination rate at 183°C. The plotted confidence interval corresponds to standard deviations of the rate values.

O The mean rates of dehydrochlorination.

Values of the constants a, b, and c were calculated by the rigorous least squares method [11, 12] from the nearest eleven experimental points on both the left and the right hand side of the inflexion point. From eqn (1) we have, for the dehydrochlorination rate r:

$$r = a + 2b t + 4c t^3.$$
 (2)

The known standard deviations of the coefficients a, b, and c enabled to calculate the time dependence of the confidence interval of the rate using the law of errors propagation. In Fig. 2 the time dependence of the dehydrochlorination rate is plotted, together with the confidence interval corresponding to the standard deviation of the rate. It is clearly seen there that the uncertainty of the determination of the dehydrochlorination rate increases sharply in the times exceeding the point of the maximum rate.

The results of measurements at other temperatures were processed in the same way. The time dependence of the degree of the isothermal dehydrochlorination at 183°C is outlined in Fig. 3. Fig. 4 shows the time dependence of the dehydrochlorination rate at this temperature, calculated from an equation similar to eqn (2), together with the confidence interval.

For the purpose of the calculation of the initial rate, the time (t) dependence of the dehydrochlorination degree (m) was expressed by another empirical equation

$$m = a' + b' t + c' t^2.$$
 (3)

The dehydrochlorination rate derived from eqn (3) is

$$\boldsymbol{r} = \boldsymbol{b}' + 2\boldsymbol{c}'\,\boldsymbol{t},\tag{4}$$

and the initial rate r_0 is defined as follows

$$r_0 = \lim_{t = 0} r = b'. \tag{5}$$

The constants a', b', and c' from eqn (4) were calculated analogously to the previous case, by the rigorous least squares method. Five experimental points corresponding to the lowest values of time were taken into calculation of these constants. The points measured at the times t < 10 min were omitted.

The sample weights of poly(vinyl chloride) used at different temperatures, the found values of the maximum and initial rates and the dehydrochlorination degrees corresponding to the maximum rates are summarized in Table 1.

Table 1

Characteristic parameters of the poly(vinyl chloride) dehydrochlorination

Т [°С]	Sample weights [mg]	71 _{max} [%]	fmax [% min ⁻¹]	r 0 [% min ⁻¹]
183.0	40.41	7.996 ± 0.072	0.0543 ± 0.0065	0.0389 ± 0.0062
190.0	16.62	11.70 ± 0.090	0.0768 ± 0.0017	0.0516 ± 0.0071
197.0	18.05	14.89 ± 0.147	0.1394 ± 0.0060	0.1082 ± 0.0025
204.2 .	15.93	14.976 ± 0.264	0.2449 ± 0.0121	0.1489 ± 0.00079
210.0	14.79	18.68 ± 0.516	0.3755 ± 0.022	0.2192 ± 0.00464
215.7	17.57	20.14 ± 0.202	0.4707 ± 0.107	0.4158 ± 0.00374

 m_{max} — degree of dehydrochlorination corresponding to its maximum rate, r_{max} — maximum rate of dehydrochlorination, r_0 — the initial rate of dehydrochlorination.

Discussion

The effective activation energy was calculated by means of the Arrhenius equation

$$k = A \exp(-E/RT). \tag{6}$$

Because of the unknown mechanism of the dehydrochlorination, values of the maximum or initial rates listed in Table 1, were inserted into eqn (β) instead of the rate constants (Fig. 5).

The effective activation energy resulting from the initial rates is (32.3 ± 0.7) kcal mol⁻¹, and from the maximum rates (31.6 ± 0.7) kcal mol⁻¹.

Uncertainties in the activation energy values are expressed by standard deviations. With respect to the confidence of the measurements, these two values of the activation energy of the thermal oxidative dehydrochlorination may be considered as being undistinguishable and equal to 32 kcal mol⁻¹. Talamini and Pezzin [3] studied the poly(vinvl chloride) dehydrochlorination in the oxygen atmosphere in the temperature interval $200-250^{\circ}$ C and assumed the effective activation energy of 24 kcal mol⁻¹. Valko [14, 15] revalued results of their measurements [3] on the basis of his step by step mechanism hypothesis and calculated the value 17 kcal mol⁻¹. Imoto and Otsu [4] investigated the dehydrochlorination in the oxygen atmosphere at temperatures $160-260^{\circ}$ C. From the initial rates they calculated the value 11.5 kcal mol⁻¹.

Fig. 5. Dependence of the maximum (\bigcirc) and initial (\bullet) rates on the inversed value of the absolute temperature.



Values of the effective activation energy of the dehydrochlorination of poly(vinyl chloride) in an inert atmosphere reported by several investigators [1-3, 13, 16, 17] lies in an interval from 26 to 34 kcal mol⁻¹. However, equality of the effective activation energies of dehydrochlorination in both the inert and the oxidizing atmosphere which follows from the results of the present work, may occur at random. We cannot therefore unambiguously assume the formation of hydrochloride from identical or very similar intermediates in both these cases.

The process of the thermal oxidative dehydrochlorination of poly(vinyl chloride) consists of the series of elementary consecutive and parallel reactions. The course of the found S-shaped kinetic curves as well as the shift of their inflexion point on the change of temperature, is characteristic also of the consecutive reactions of low molecular substances:

$$A \rightarrow B \rightarrow \qquad \rightarrow D \xrightarrow{1} E \xrightarrow{2} \text{HCl.}$$
 (7)

On the basis of a similarity of the kinetics of the poly(vinyl chloride) dehydrochlorination to scheme (7), we can postulate

$$\frac{\mathrm{d}r_1}{\mathrm{d}T} > \frac{\mathrm{d}r_2}{\mathrm{d}T},\tag{8}$$

where T is temperature, r_1 the rate of formation of the last intermediate E, and r_2 the rate of formation of hydrochloride. When assuming the zipper-like dehydrochlorination accompanied by the formation of polyenes, the rate-determining step of the hydrochloride formation is then the initiation rate of the zipper-like dehydrochlorination and the average length of one zip, *i.e.* the rate of termination. The values of the dehydrochlorination degrees corresponding to the maximum rates (see Table 1) justify another postulate

$$r_1 > r_2, \qquad (9)$$

where r_1 is the rate of formation of the intermediate E expressed in the same units as the dehydrochlorination rate r_2 .

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Translated by F. Kopecký