

Autocatalytic effect of hydrogen chloride on the thermal dehydrochlorination of poly(vinyl chloride)

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The dehydrochlorination of poly(vinyl chloride) under atmospheric pressure of hydrogen chloride has been studied in the temperature range 190—250 °C up to high conversions. Activation energy of the process is found to be (107.3 ± 3.4) kJ mol⁻¹. A new mechanism for the autocatalytic influence of hydrogen chloride based on the reinitiation of allyl catalysis is proposed.

Изучено дегидрохлорирование поливинилхлорида при атмосферном давлении хлористого водорода до высокой степени превращения в интервале температур 190—250 °C. Энергия активации равна $(107,3 \pm 3,4)$ кДж моль⁻¹. Предложен новый механизм автокаталитического влияния хлористого водорода, основан на повторном инициировании аллилового катализа.

It is generally accepted that hydrogen chloride catalyzes the dehydrochlorination of poly(vinyl chloride) (PVC) at high [1—10] and also low [11] temperatures but the dehydrochlorination mechanism has not been satisfactorily explained. This problem is of great importance for the development of efficient heat stabilizers for PVC. Although PVC dehydrochlorination catalyzed by HCl has been already studied, no investigations have been published on the process to high degrees of dehydrochlorination. The present work refers to PVC dehydrochlorination in HCl atmosphere up to high conversions over a wide range of temperatures. Also, a new mechanism describing the autocatalytic influence of HCl is proposed.

Experimental

Employed technique

In the used method, HCl evolved from the PVC sample is used to form the dehydrochlorination atmosphere. A special glass ampoule of diameter 2—3 cm (Fig. 1) is designed and used for this purpose. Bulk PVC (30—100 mg) is introduced to the ampoule through opening 1. Then the ampoule is flushed for 1 h with HCl in order to start the dehydrochlori-

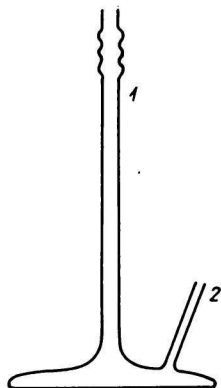


Fig. 1. The ampoule used for the dehydrochlorination of PVC in HCl atmosphere.

nation in HCl atmosphere and to remove the last traces of oxygen. Then, sections 2 and 1 are sealed so that the closed ampoule contains HCl. Immediately before the dehydrochlorination measurement, the sealed end of section 1 is cut off and the ampoule is inserted into the degradation cell of the dehydrochlorination apparatus. HCl evolved from PVC freely escapes out of the ampoule and, at the same time, it forms the dehydrochlorination atmosphere. The escaped HCl is drawn by carrier gas (N_2) into the analysis cell. The used dehydrochlorination apparatus is similar to that described in [12] so that its scheme and details of electrochemical determination of HCl may be omitted. After elimination of systematic errors caused mainly by the original HCl in the ampoule, the measurements are very well reproducible. The elimination of errors is described in [13]. Dehydrochlorination of PVC in inert atmosphere was performed according to [12].

Material

Commercial PVC Vestolit 7055 with viscosimetric molar mass $M = 62\,000\text{ g mol}^{-1}$ (product of West Germany) was used without any purification.

Results and discussion

The measurements of PVC dehydrochlorination in HCl atmosphere were carried out at seven temperatures in the range 190–250 °C. As it can be noted from Fig. 2, the reaction is autocatalytic. The kinetic curves obey the autocatalytic equation up to conversion 0.7, then deviations appear. The maximal rate is 10–20 times the initial rate. The acceleration of PVC dehydrochlorination in HCl atmosphere in contrast to the inert one can be seen from the comparison of Fig. 2 and Fig. 3. Initial rates of both reactions are close.

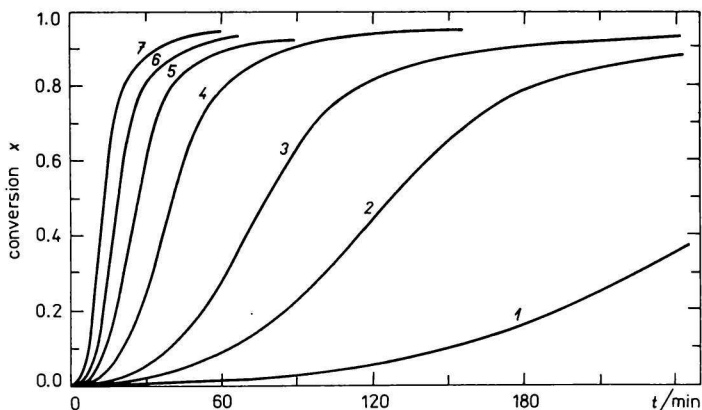


Fig. 2. Kinetics of PVC dehydrochlorination in HCl atmosphere. Temperatures ($\theta/^\circ\text{C}$): 1. 191.3; 2. 201.7; 3. 209.9; 4. 222.0; 5. 230.6; 6. 240.5; 7. 248.8.

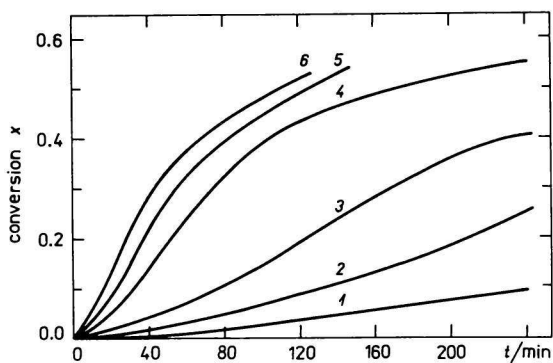


Fig. 3. Kinetics of PVC dehydrochlorination in inert atmosphere. Temperatures ($\theta/^\circ\text{C}$): 1. 201.7; 2. 209.9; 3. 222.0; 4. 230.6; 5. 240.5; 6. 248.8.

Maximal rates shift towards lower conversions with increasing temperature (Fig. 4). Since conversion at the maximal rate is not constant, the rate constants k of the reaction were obtained using the equation

$$r_m = kx_m(1 - x_m) \quad (1)$$

where r_m is the maximal rate of the dehydrochlorination and x_m is the conversion at

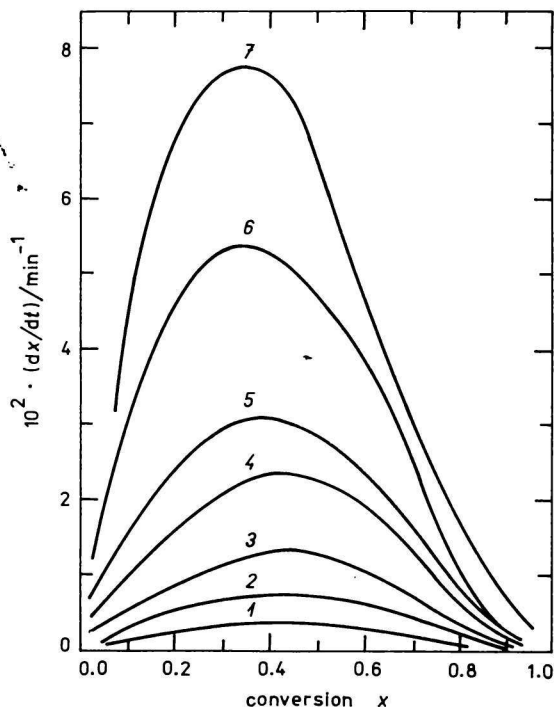


Fig. 4. Derived kinetic curves of PVC dehydrochlorination in HCl atmosphere. Temperatures as in Fig. 2.

the maximal rate. Rate constants are listed in Table 1 and their related Arrhenius plot is shown in Fig. 5. Activation energy E_a and pre-exponential factor A were found by the rigorous least-square method to be $E_a = (107.3 \pm 3.4) \text{ kJ mol}^{-1}$, $\log (A/\text{s}^{-1}) = 8.5 \pm 0.4$. From early stages of PVC dehydrochlorination in inert atmosphere following values were obtained: $E_a = 132.2 \text{ kJ mol}^{-1}$, $\log (A/\text{s}^{-1}) = 9.3$. It can be seen that the magnitude of the activation energy of PVC dehydrochlorination is less by 25 kJ mol^{-1} in HCl atmosphere than in inert one.

Table 1

Values of rate constants at various temperatures

$\theta/^\circ\text{C}$	191.3	201.7	209.9	222.0	230.6	240.5	248.8
$k \cdot 10^3/\text{s}^{-1}$	0.25	0.52	0.90	1.6	2.2	3.7	6.1

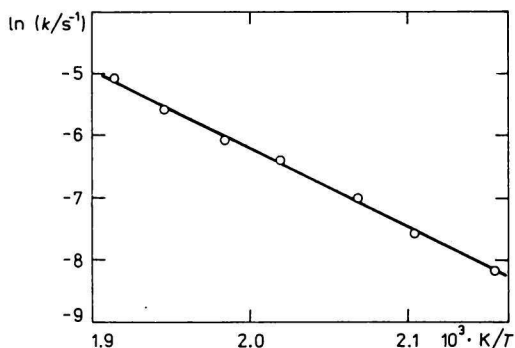


Fig. 5. Arrhenius plot of PVC dehydrochlorination in HCl atmosphere.

From Fig. 3 it is obvious that kinetic runs of PVC dehydrochlorination in inert atmosphere also exhibit an autocatalytic character. We did not succeed in removal of this effect although the amount of PVC sample was so low that different PVC granules were separated.

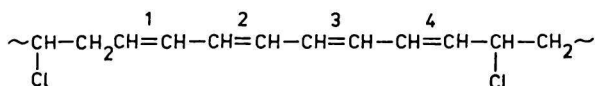
The mechanism of HCl influence on the PVC dehydrochlorination is not yet fully clear. There are two points of view on this mechanism which differ in the proposed site of HCl attack on PVC. According to the first alternative the HCl molecule interacts with a nondehydrochlorinated unit in PVC chain [14]. The elimination of HCl occurs via six-membered cyclic transition state. In this way an increase in the dehydrochlorination rate should be obtained but no autocatalysis should occur so far as the pressure of HCl is constant [1].

The second alternative is explanation of the autocatalytic influence of HCl by its interaction with the double bonds of the dehydrochlorinated parts of polymer chain. Radical [9] and ionic [9, 15–17] mechanisms were suggested. Here an autocatalytic effect is expected, but most of these mechanisms include such reaction steps which require high energy content of interproducts and, therefore, they seem to be improbable. Another very interesting explanation suggested Amer and Shapiro [18]. In their mechanism HCl has a role of H-transferer and dehydrochlorination occurs via six-centred transition state yielding a polyene.

In this work we wish to propose a new mechanism accounting for the autocatalytic influence of HCl and exploiting the fact that the dehydrochlorination of PVC is a partly reversible reaction [8, 19, 20]. The outline of the mechanism is following:

It is known that the monomer unit of PVC chain in the vicinity of polyene system dehydrochlorinates more easily than the monomer unit of ideal PVC chain as a consequence of the conjugation between the polyene system and rising π -orbitals in the transition state of dehydrochlorination. This is called the allyl catalysis. The longer polyene system the less gain in conjugation energy and, therefore, if polyene sequence in PVC chain attains some length, the influence of allyl catalysis is over and the growth of the polyene system stops [21]. Allyl catalysis can be reinitiated if long and highly stable polyene sequence is broken.

Let us consider the following segment of the dehydrochlorinated PVC chain



If HCl was absent in the course of PVC dehydrochlorination the growth of polyene sequence would have stopped, for example, at the fourth C=C bond. If HCl is present, it can add to C=C bonds. Addition of HCl molecule to the second or third C=C bond shortens the polyene sequence and the reinitiated allyl catalysis initiates splitting-off not only of added HCl molecule but also the dehydrochlorination of monomer unit in the vicinity of arisen shorter polyene sequence. If HCl molecule adds to the first or fourth C=C bond the reinitiated allyl catalysis will preserve the length of polyene sequence. In average, every added HCl molecule causes the splitting-off of more than one HCl molecule. In our opinion, this would be an explanation of the autocatalytic influence of HCl on the PVC dehydrochlorination.

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