Influence of metal stearates on thermal stability of poly(vinyl chloride)
IV. Lead stearate

P. ŠIMON, J. OREMUSOVÁ, and L. VALKO

Department of Physical Chemistry, Faculty of Chemical Technology,
Slovak Technical University, CS-812 37 Bratislava

Received 7 November 1989

Kinetics of dehydrochlorination of poly(vinyl chloride) stabilized with lead stearate is examined and the kinetic data are completed with viscosimetric determination of relative molecular mass of the samples thermally stressed. The results show that lead stearate is a very efficient scavenger of HCl split off from PVC. The values of effective rate constants of dehydrochlorination decrease hyperbolically with increasing relative mole fraction of lead stearate in the blend. This led to the conclusion that lead stearate exerts a blocking effect on the propagation stage of the zinc reaction. A reaction mechanism of the dehydrochlorination is suggested and the rate constants of individual reaction steps are obtained by comparing the calculated and experimental kinetic runs. Some general aspects of the dehydrochlorination of PVC stabilized with metal stearates are discussed.

Lead compounds belong to the most efficient thermal stabilizers of PVC [1—4]. Both Pb\(^{2+}\) and Pb\(^{4+}\) compounds exert the stabilizing effect [5]. Despite the fact that lead compounds have been employed in practice for years, the mechanism of their action is not fully clear yet.

In our previous papers [6—8] the mechanism of stabilizing effect of Ca, Mg, and Zn stearates has been studied and the rate constants of individual reaction steps have been obtained by comparing experimental and calculated kinetic curves. This study concerned with the stabilizing effect of lead stearate finishes the series of papers devoted to the influence of metal stearates on thermal stability of PVC.

Experimental

Suspension poly(vinyl chloride) Slovinyl S-621, montan wax, and cyclohexanone have been characterized in Refs. [6, 7]. Lead stearate Pb(C\(_{17}\)H\(_{35}\)COO)\(_2\), m.p. = 110—112 °C, purity determined by elemental analysis 99 %, and lead chloride PbCl\(_2\), anal. grade, were used.

Preparation of PVC foils, determination of HCl evolved from PVC samples and viscosimetric determination of relative molecular mass of PVC samples have been described in detail in Refs. [6, 7].
Results and discussion

The kinetic curves for a set of PVC foils with relative mole fraction of lead stearate $0 - 4.27 \times 10^{-3}$ dehydrochlorinated in the atmospheres of nitrogen and air at 180 °C are given in Figs. 1 and 2. Fig. 3 shows the dependence of the time of thermal stability $\tau$ of PVC on the relative mole fraction of lead stearate. The values of $\tau$ are greater for the PVC dehydrochlorination in nitrogen atmosphere.

![Fig. 1. Kinetic curves of thermal dehydrochlorination (conversion $x$) of the PVC stabilized with lead stearate in nitrogen at 180 °C. Relative mole fraction of lead stearate in mixture: 1. 0; 2. $0.41 \times 10^{-3}$; 3. $0.81 \times 10^{-3}$; 4. $1.23 \times 10^{-3}$; 5. $1.66 \times 10^{-3}$; 6. $2.09 \times 10^{-3}$; 7. $2.51 \times 10^{-3}$; 8. $2.94 \times 10^{-3}$; 9. $3.38 \times 10^{-3}$; 10. $3.82 \times 10^{-3}$; 11. $4.27 \times 10^{-3}$ —— experimental kinetic curve, --- calculated kinetic curve.](image1)

![Fig. 2. Kinetic curves of thermal dehydrochlorination (conversion $x$) of the PVC stabilized with lead stearate in air at 180 °C. Denotation as in Fig. 1.](image2)
The effective rate constants of dehydrochlorination are obtained as the slopes of linear parts of the kinetic curves for the time $t > \tau$, their dependence on the relative mole fraction of lead stearate is demonstrated in Fig. 4. The effective rate constants decrease with increasing relative mole fraction of lead stearate, the dependence resembles a hyperbolic function.

In order to complete information on the mechanism of PVC dehydrochlorination in the presence of lead stearate, dependence of the relative mole-

![Fig. 3. Dependence of the time of thermal stability τ of PVC on the relative mole fraction of lead stearate in nitrogen (■) and air (○).](image)

![Fig. 4. Dependence of the effective rate constants of PVC dehydrochlorination on the relative mole fraction of lead stearate in nitrogen (■) and air (○).](image)
cular mass of the polymer on the time of thermal stress has been examined. Fig. 5 shows this dependence for the degradation under nitrogen of the sample with relative mole fraction of lead stearate $x^o = 2.51 \times 10^{-3}$. The relative molecular mass remains unchanged for approximately 80 min, then it increases and after 180 min of thermal stress, a fraction insoluble in cyclohexanone is formed. The time of unchanged relative molecular mass is in correlation with the time of thermal stability which for this sample is $\tau = 77$ min. As hydrogen chloride causes crosslinking and thus the increase of the relative molecular mass [9], it can be concluded that an important task of lead stearate is to scavenge hydrogen chloride split off from PVC.

In the course of thermal stress, stearic acid and PbCl$_2$ are formed as the products of the reaction of lead stearate with hydrogen chloride. It has been shown that stearic acid slightly accelerates PVC dehydrochlorination [6]. In order to examine the influence of PbCl$_2$ on the dehydrochlorination, we prepared blends of PVC with PbCl$_2$. Fig. 6 shows that PbCl$_2$ decelerates the dehydrochlorination; again, a hyperbolic dependence of the effective rate constants on the relative mole fraction is observed. The decelerating effect of lead stearate prevails over the accelerating effect of stearic acid.

The knowledge gained from our results and papers published led to the suggestion of the following reaction mechanism for the thermal dehydrochlorination of PVC stabilized with lead stearate:

1. Thermal dehydrochlorination of PVC

$$\text{PVC} \xrightarrow{k_1} \text{dePVC} + \text{HCl}$$

where dePVC means dehydrochlorinated PVC.

![Fig. 5. Dependence of relative molecular mass of PVC on the time of thermal stress in nitrogen atmosphere. 1. PVC; 2. PVC stabilized with lead stearate, relative mole fraction $2.51 \times 10^{-3}$.

Chem. Papers 45 (3) 389—399 (1991)
Thermal Stability of PVC. IV

Fig. 6. Effect of PbCl₂ and stearic acid on the dehydrochlorination of PVC under nitrogen at 180 °C. 1. PVC with stearic acid, relative mole fraction 4.51 x 10⁻³; 2. PVC without additives; PVC with PbCl₂ (relative mole fraction 3.228 x 10⁻³; 4. 4.61 x 10⁻³; 5. 6.99 x 10⁻³).

2. Reaction of lead stearate with HCl split off from PVC which assumingly occurs in two reaction steps

\[
PbSt₂ + HCl \xrightarrow{k₂} PbClSt + HSt
\]

\[
PbClSt + HCl \xrightarrow{k₃} PbCl₂ + HSt
\]

where St is the stearate anion and HSt is stearic acid. As the decelerating effect of PbCl₂ prevails over the accelerating effect of stearic acid, the latter is neglected. Also, the accelerating effect of HCl on PVC dehydrochlorination is neglected since the thickness of PVC films is less than the critical value [10]. From infrared spectra we have not obtained any evidence for the reaction of lead stearate with HCl in two steps, but, similarly as in Ref. [8], we assume that trimolecular reaction

\[
PbSt₂ + 2HCl \rightarrow PbCl₂ + 2HSt
\]

is less probable.

The reaction scheme can be described by four independent kinetic equations where the relative mole fractions of individual components are denoted as follows: \(x_1\) — HCl registered by the apparatus, \(x_2\) — HCl in the polymer, \(x_3\) — double bonds in PVC, \(x_4\) — PbSt₂, \(x_5\) — HSt, \(x_6\) — PbClSt. As mentioned in Refs. [6—8], we again assume that HCl is evolved from the polymer sample after the relative mole fraction has reached its critical value \(x_c\). The kinetic equations have then the form
For $x_2 < x_c$

\[
\frac{dx_1}{dt} = 0
\]
\[
\frac{dx_2}{dt} = k_1(1 - x_3) - k_2x_2x_4 - k_3x_2x_6
\]

For $x_2 = x_c$

\[
\frac{dx_1}{dt} = k_1(1 - x_3) - k_2x_2x_4 - k_3x_2x_6
\]
\[
\frac{dx_2}{dt} = 0
\]

The other kinetic equations are

\[
\frac{dx_3}{dt} = k_1(1 - x_3)
\]
\[
\frac{dx_4}{dt} = -k_2x_2x_4
\]

The relative mole fractions $x_5$ and $x_6$ can be expressed by the material balances

\[
x_5 = x_3 - x_2 - x_1 - a
\]
\[
x_6 = 2(x_4^0 - x_4) - x_5
\]

where $a$ means the HCl escaped from the sample after calendering.

Fig. 4 demonstrates that $k_{\text{eff}}$ hyperbolically decreases with increasing relative mole fraction of lead stearate. Till now, this fact is not involved in the kinetic equations. To do this, it is necessary to take into account that $k_1$ is the rate constant of PVC dehydrochlorination which occurs through the zip reaction. The zip reaction includes initiation, propagation and termination of polyene sequences and $k_1$ is thus expressed as a combination of the rate constants of all these stages [11]

\[
k_1 = k_i \left(1 + \frac{k_p}{k_i}\right) \quad (1)
\]

where $k_i$, $k_p$, and $k_t$ are the rate constants of initiation, propagation, and termination, respectively. Since in the time $t = \tau$ the stabilizer is close to be consumed up, the value of $k_{\text{eff}}$ is determined mainly by $k_1$. Accordingly, the hyperbolical decrease of $k_{\text{eff}}$ should be interpreted through the decrease of $k_1$. We explain it by the blocking of the propagation stage of the zip reaction by lead compounds. For the description of this effect it is necessary to follow the procedure from Ref. [11] where the dehydrochlorination of pure PVC is treated. For this case, formation of the polyene sequences under propagation is expressed as

\[
\frac{dg}{dt} = k_i(1 - x) - k_t g \quad (2)
\]
where $g$ is the concentration of growing zips. Here, $x$ means the conversion of dehydrochlorination. Since in eqn (2) it is assumed that polymer is not stabilized, no HCl reacts with the stabilizer and, therefore, $x = x_1 = x_3$.

If the blocking of the zip propagation by lead compounds is considered, the latter equation takes the form

$$\frac{dg}{dt} = k_i(1 - x) - k_i g - k_{pb} x_{pb} g$$

(3)

where $k_{pb}$ is the rate constant of premature zip termination caused by lead compounds and $x_{pb}$ is the relative mole fraction of lead compounds. After a very short time, dynamic equilibrium is established between the formation and termination of the growing polyene sequences, which is expressed as

$$\frac{dg}{dt} = 0$$

(4)

Combination of eqns (3) and (4) gives

$$g = \frac{k_i(1 - x)}{k_i + k_{pb} x_{pb}}$$

(5)

The rate of dehydrochlorination is given as the sum of terms describing the initiation and propagation of polyene sequences

$$\frac{dx}{dt} = k_i(1 - x) + k_p g$$

(6)

Taking into account eqn (5), eqn (6) gets the form

$$\frac{dx}{dt} = k_i \left(1 + \frac{k_p}{k_i + k_{pb} x_{pb}}\right) (1 - x)$$

(7)

Formally, this is the first-order kinetic equation with the rate constant

$$k_1 = k_i \left(1 + \frac{k_p / k_i}{1 + (k_{pb} / k_i) x_{pb}}\right)$$

(8)

Eqn (8) considers the blocking effect of lead compounds, $k_1$ is a hyperbolic function of $x_{pb}$. This expression of $k_1$ is used when solving the set of kinetic equations for the dehydrochlorination of PVC stabilized with lead stearate. Of course, the kinetic equations involve the reaction of lead stearate with HCl split off from PVC. For this reason, the rate constant $k_1$ refers to the double bond formation in PVC chain, i.e. to the relative mole fraction $x_3$.
The set of kinetic equations is solved by the fourth-order Runge—Kutta method. The values of rate constants are obtained by the nonlinear least-squares method, the sum of deviations between the experimental and theoretical values of conversion ($x_t$) is minimized by the simplex method [12]. The minimization parameters are the ratios $k_p/k_i$ and $k_{pb}/k_t$, the rate constants $k_i$, $k_2$, and $k_3$, and the critical relative mole fraction $x_c$. The parameters corresponding to the minimum sum of deviations are listed in Table 1. Similarly as in Refs. [6—8] the thermal stress during calendering is taken into account in calculation. The least sum of squares is reached when it is assumed that all lead compounds block the zip propagation, i.e. when $x_{pb} = x_2^0$. Figs. 1 and 2 demonstrate the excellent agreement reached between experimental and calculated kinetic runs which documents reasonability of the suggested reaction scheme.

**Table 1**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitrogen</td>
</tr>
<tr>
<td>$k_i$/min$^{-1}$</td>
<td>$1.89 \times 10^{-5}$</td>
</tr>
<tr>
<td>$k_p/k_i$</td>
<td>2.95</td>
</tr>
<tr>
<td>$k_{pb}/k_t$</td>
<td>183</td>
</tr>
<tr>
<td>$k_1$/min$^{-1}$</td>
<td>$7.47 \times 10^{-5}$</td>
</tr>
<tr>
<td>$k_2$/min$^{-1}$</td>
<td>453</td>
</tr>
<tr>
<td>$k_3$/min$^{-1}$</td>
<td>27.4</td>
</tr>
<tr>
<td>$x_c$</td>
<td>$4.13 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

*a) Calculated from eqn (1).

Table 1 reveals that the initiation step of the zip reaction proceeds more quickly in air. The ratios $k_p/k_i$ show that also the propagation kinetic chain is longer in air. Both these facts result in the higher value of $k_1$ for the air dehydrochlorination atmosphere. From the value of $k_{pb}/k_t$ it can be deduced that the blocking effect of lead compounds on the zip propagation can reach up to 50 %. The values of $k_2$ and $k_3$ show that lead stearate is an efficient scavenger of HCl, the first step of the reaction is much more rapid than the other one. The kinetic parameters obtained make it possible to calculate the consumption of lead stearate during calendering which is 3—13 %, the consumption in the time $t = \tau$ (95—98 %, calculated as the decrease of Pb—St bonds), time dependences of relative mole fractions of individual components in PVC blend (Fig. 7), etc.

This is the closing paper of our series devoted to the study of influence of
metal stearates on PVC dehydrochlorination. Thus we would like to present some general remarks. The first one is concerned with the expression of the reaction rate which has been done via the relative mole fractions. The reaction rate \( v \) is defined \([13]\) as

\[
    v = \frac{1}{v_i} \frac{dn_i}{dt}
\]

where \( v_i \) is the stoichiometric coefficient and \( n_i \) means the amount of substance of the \( i \)-th component. For the conditions of constant volume, eqn (9) can be expressed as

\[
    v = \frac{V}{v_i} \frac{dc_i}{dt}
\]

where \( V \) is volume and \( c_i \) is concentration of the \( i \)-th component. Dividing eqn (10) by volume one obtains the reaction rate in a volume unit \( v_1 \)

\[
    v_1 = \frac{1}{v_i} \frac{dc_i}{dt}
\]

This rate is usually called the reaction rate. In the course of dehydrochlorination, the volume of the polymer changes, it is not constant. Therefore, we cannot use eqn (11) for the expression of the reaction rate. The relative mole fraction is defined as
\[ x_i = \frac{n_i}{n_0} \quad (12) \]

where \( n_0 \) stands for the amount of substance of vinyl chloride monomeric units. For the polymers degrading via splitting-off of small molecules, the number of links in the polymer chain does not change in the course of degradation. Combination of eqns (9) and (12) gives

\[ v = \frac{n_0}{v_i} \frac{dx_i}{dt} \quad (13) \]

Dividing eqn (13) by \( n_0 \), we obtain

\[ v_0 = \frac{1}{v_i} \frac{dx_i}{dt} \quad (14) \]

The rate \( v_0 \) is the reaction rate per mole of monomeric units of the polymer. This is the expression of reaction rate we have used. It seems to us to be the most appropriate for the polymers splitting-off of small molecules in their degradation.

The rate constant \( k_1 \) describes the splitting-off of HCl from PVC. It is rather surprising that the values of \( k_1 \) are for all stabilizers studied in this series of papers lower than the rate constants of the dehydrochlorination of non-stabilized PVC which are \( k_1 = 1.31 \times 10^{-4} \text{ min}^{-1} \) in the nitrogen atmosphere and \( k_1 = 1.93 \times 10^{-4} \text{ min}^{-1} \) for the dehydrochlorination under air. This general decrease in \( k_1 \) seems to us to be convincing enough to conclude that the stabilizers affect elimination of HCl from PVC also in another way than we have considered. It could be the Frye—Horst mechanism of esterification of labile chlorines [14], or the reversible blocking mechanism [15]. However, for calcium stearate, Vymazal et al. have shown that the esterification takes place to a low extent only [16]. Also, chemistry of the reversible blocking mechanism is not satisfactorily understood. These are the reasons why we did not include these mechanisms to our reaction schemes. The values of \( k_1 \) unequivocally show that the stabilizers exert an additional stabilizing effect which affects the rate of HCl elimination from PVC.

The values of \( k_2 \) and \( k_3 \) show that metal stearates are efficient scavengers of HCl. From the calculations it follows that the parameters \( k_2, k_3, \) and \( x_c \) are not linearly independent in the region of the minimum sum of squares. As a consequence, fairly broad intervals of these parameters correspond to the minimum so that their values carry great errors (about 30 %).

In this series of papers we have presented the quantitative kinetic description of thermal dehydrochlorination of PVC stabilized with metal stearates. The method is far from being perfect, it should be understood only as a first attempt.
It has been demonstrated that the kinetic parameters make possible to calculate such characteristics as the consumption of stabilizer in the time of thermal stability, etc. We believe that, despite the imperfection, the kinetic parameters can be used for further consideration on the mechanisms of stabilization and for the estimation of the durability of PVC blends.

References


Translated by P. Šimon