

Influence of metal stearates on thermal stability of poly(vinyl chloride) III. Zinc stearate

J. OREMUSOVÁ, P. ŠIMON, L. VALKO, and P. KOVAŘÍK

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

Received 22 September 1989

Influence of zinc stearate on the kinetics of thermal dehydrochlorination of poly(vinyl chloride) (PVC) is studied. The study is completed by viscosimetric determination of the relative molecular mass of the samples thermally stressed. A reaction mechanism of the PVC dehydrochlorination in the presence of zinc stearate is proposed and the rate constants of individual reaction steps are determined by comparing the experimental and theoretical kinetic curves. The results obtained show that zinc stearate is a very efficient scavenger of hydrogen chloride. Considering the accelerating effect of zinc compounds on PVC dehydrochlorination, it is found that only Zn—Cl bonds formed as the product of stabilizer decay exhibit this effect.

In order to prevent degradation in the course of processing, the basic additives in poly(vinyl chloride) (PVC) blends are thermal stabilizers. Among them, the salts of fatty acids form an important group. The salts are mostly used in synergic mixtures which very often contain zinc carboxylates [1—6]. Besides the stabilization, zinc carboxylates also improve colour of the polymer, but, the products of stabilizers decay accelerate dehydrochlorination and the polymer gets dark in the thermal stress [7]. In our previous papers [8, 9] the influence of calcium and magnesium stearates on thermal dehydrochlorination of PVC has been studied and the quantitative analysis of the reaction schemes has been carried out. In the present paper the role of zinc stearate in PVC stabilization is analyzed.

Experimental

Suspension PVC Slovinyl S-621, montan wax, and cyclohexanone have been characterized in Refs. [8, 9]. Zinc stearate, m.p. = 128—130 °C, purity determined by elemental analysis 99 %, and anal. grade ZnCl₂ were used.

Preparation of PVC foils, determination of HCl evolved from PVC samples and viscosimetric determination of relative molecular mass of the polymer have been described in Ref. [8].

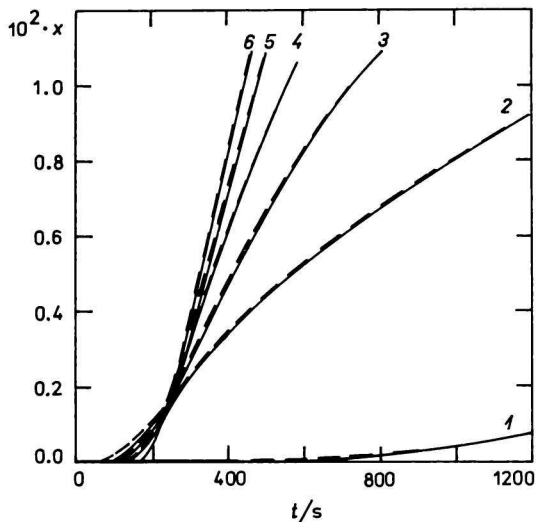


Fig. 1. Kinetic curves of thermal dehydrochlorination (conversion x) of the PVC stabilized with zinc stearate in nitrogen at 180 °C. Relative mole fraction of zinc stearate in mixture: 1. 0; 2. 0.499×10^{-3} ; 3. 1.00×10^{-3} ; 4. 1.51×10^{-3} ; 5. 2.03×10^{-3} ; 6. 2.53×10^{-3} ; — Experimental kinetic curve, ---- calculated kinetic curve.

Results and discussion

The kinetic curves for a set of PVC foils with relative mole fraction of zinc stearate 0 — 5.23×10^{-3} dehydrochlorinated in the atmospheres of nitrogen and air at 180 °C are shown in Figs. 1—4. Fig. 5 gives the dependences of the times of thermal stability τ of PVC on the content of zinc stearate. As can be seen the values of τ are greater in the atmosphere of nitrogen. The time of thermal

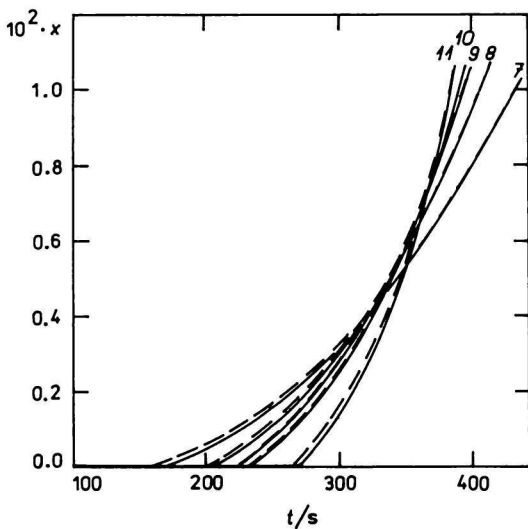
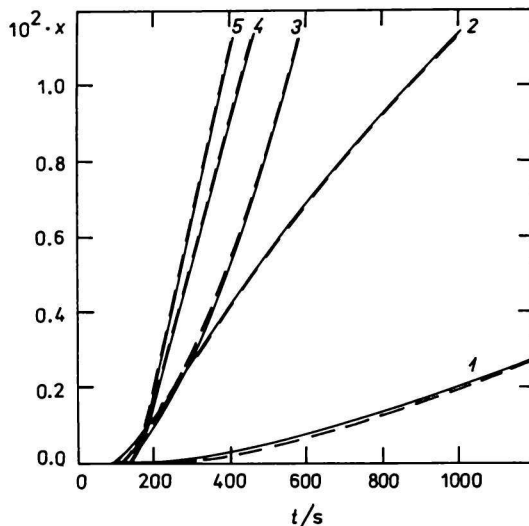


Fig. 2. Kinetic curves of thermal dehydrochlorination (conversion x) of the PVC stabilized with zinc stearate in nitrogen at 180 °C. Relative mole fraction of zinc stearate in mixture: 7. 3.07×10^{-3} ; 8. 3.60×10^{-3} ; 9. 4.14×10^{-3} ; 10. 4.68×10^{-3} ; 11. 5.23×10^{-3} — Experimental kinetic curve, ---- calculated kinetic curve.

Fig. 3. Kinetic curves of thermal dehydrochlorination (conversion x) of the PVC stabilized with zinc stearate in air at 180 °C. Denotation as in Fig. 1.



stability of PVC increases with increasing relative mole fraction of zinc stearate and probably tends to a stationary value or to a maximum. The effective rate constants of dehydrochlorination, which were obtained as the slopes of linear parts of the kinetic curves for the times $t > \tau$, are given in Fig. 6. The constants in both atmospheres are practically identical; for the atmospheres of nitrogen and air their values lie within $(1.2\text{--}54) \times 10^{-4} \text{ min}^{-1}$ and $(1.8\text{--}58) \times 10^{-4} \text{ min}^{-1}$, respectively. The dependence of the effective rate constants on the relative mole fraction of zinc stearate is linear.

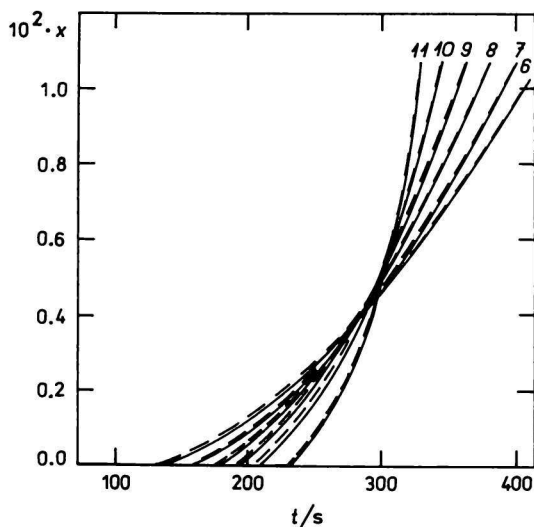


Fig. 4. Kinetic curves of thermal dehydrochlorination (conversion x) of the PVC stabilized with zinc stearate in air at 180 °C. Denotation as in Figs. 1 and 2.

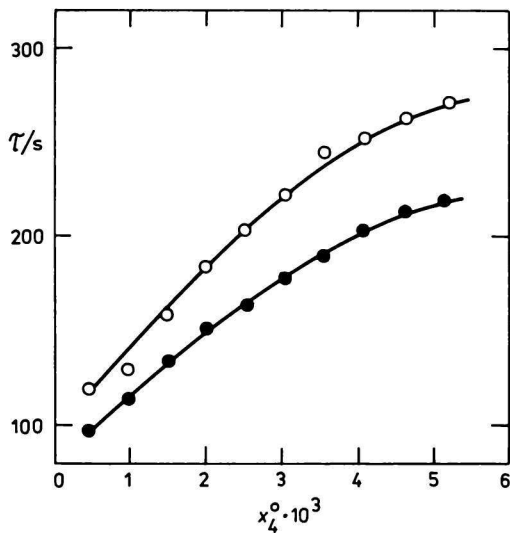


Fig. 5. Dependence of the time of thermal stability τ of PVC on the relative mole fraction of zinc stearate in nitrogen (○) and air (●).

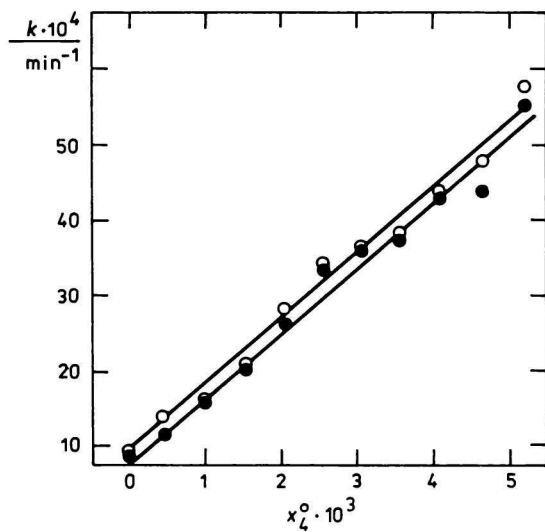
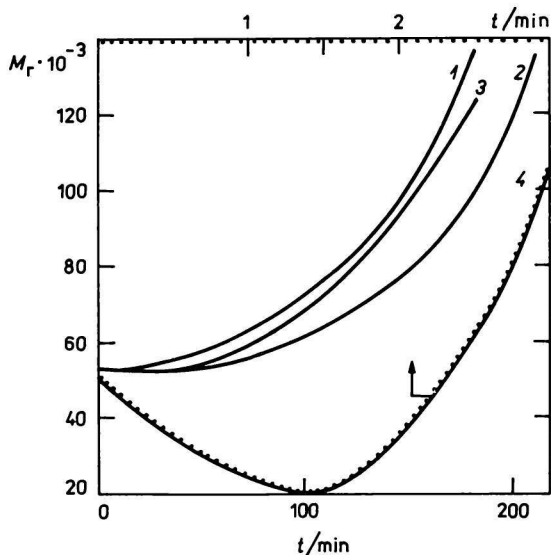


Fig. 6. Dependence of the effective rate constants of PVC dehydrochlorination on the relative mole fraction of zinc stearate in nitrogen (●) and air (○).

Fig. 7. Dependence of relative molecular mass of PVC on the time of thermal stress in nitrogen atmosphere. 1. PVC; 2. PVC stabilized with calcium stearate, relative mole fraction 3.20×10^{-3} ; 3. PVC stabilized with magnesium stearate, relative mole fraction 3.28×10^{-3} ; 4. PVC stabilized with zinc stearate, relative mole fraction 3.07×10^{-3}



The relative molecular mass M_r of the samples thermally stressed, was determined viscosimetrically. The dependence of M_r on the time of thermal stress for the sample with relative mole fraction of zinc stearate $x_4^0 = 3.07 \times 10^{-3}$ is shown in Fig. 7; for comparison, also the curves for non-stabilized PVC as well as for PVC stabilized with calcium and magnesium stearates are drawn. The relative molecular mass of PVC stabilized with zinc stearate steeply decreases at the beginning of thermal stress from 53 000 to 20 000, which points to an intense scission of PVC chains; this finding is in agreement with *Wytych* [10]. After 1.5 min of thermal stress, the increase of relative molecular mass is observed thus indicating crosslinking. The increase is so great that a fraction insoluble in tetrahydrofuran is formed after 3 min of thermal stress.

The products of the reaction of HCl with the stabilizer are stearic acid and zinc chloride; both compounds are known to accelerate PVC dehydrochlorination. Fig. 8 shows the comparison of the catalytic effects of stearic acid and zinc chloride. As can be seen, stearic acid slightly accelerates the PVC dehydrochlorination, but, its effect is negligible in comparison with that of zinc chloride.

Our results as well as the published information lead us to the suggestion of the following reaction scheme of thermal dehydrochlorination of PVC stabilized with zinc stearate:

1. Dehydrochlorination of PVC



where dePVC means dehydrochlorinated PVC.

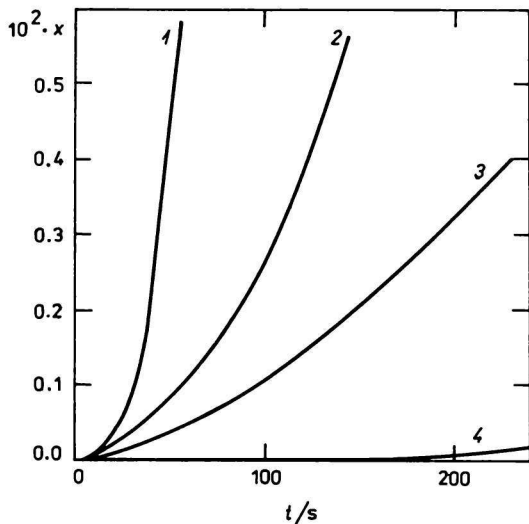
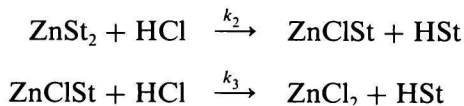


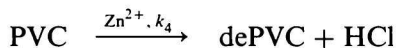
Fig. 8. Catalytic effect of ZnCl_2 and stearic acid on the dehydrochlorination of PVC. Relative mole fractions of ZnCl_2 in PVC: 1. 14.2×10^{-3} ; 2. 9.50×10^{-3} ; 3. 4.75×10^{-3} ; 4. PVC with stearic acid, relative mole fraction 6.83×10^{-3}

2. Two-step reaction of zinc stearate with HCl split off from PVC



where ZnSt_2 , ZnClSt , and HSt mean zinc stearate, $\text{ZnCl}(\text{C}_{17}\text{H}_{35}\text{COO})$, and stearic acid, respectively.

3. Catalytic influence of zinc compounds on PVC dehydrochlorination



Seemingly, the reaction scheme does not comprise the strong interaction between PVC chains and zinc stearate (or the products of its decay), which is documented in Fig. 7. We do not know anything about the nature of this interaction. However, if it affects PVC dehydrochlorination and if the effect is constant, it should be implicitly involved in the rate constant k_1 ; if the effect depends on the relative mole fraction of zinc compounds, it should be involved in the rate constant k_4 . The rate constants k_2 and k_3 correspond to the two-step reaction of zinc stearate with HCl split off from PVC. Infrared spectra do not provide any evidence for the two-step decay of zinc stearate. Nonetheless, the two-step reaction of zinc stearate with HCl seems to be more probable than the trimolecular reaction $\text{ZnSt}_2 + 2\text{HCl} \rightarrow \text{ZnCl}_2 + 2\text{HSt}$. In the reaction scheme only the dominant catalytic effect of zinc compounds is included, the minor effects of stearic acid and HCl are neglected.

The reaction scheme can be described by a set of four differential equations where the relative mole fractions of individual components are denoted as follows: x_1 — conversion of dehydrochlorination, x_2 — HCl in the polymer, x_3 — double bonds in the polymer, x_4 — ZnSt₂, x_5 — HSt, x_6 — ZnClSt, x_7 — ZnCl₂. As previously [8, 9], we assume that HCl is evolved from the polymer after the relative mole fraction x_2 has reached the critical value x_c . The first couple of kinetic equations has the form

If $x_2 < x_c$

$$dx_1/dt = (k_1 + k_4x_{zn})(1 - x_3) - k_2x_2x_4 - k_3x_2x_6$$

$$dx_2/dt = 0$$

If $x_2 = x_c$

$$dx_1/dt = 0$$

$$dx_2/dt = (k_1 + k_4x_{zn})(1 - x_3) - k_2x_2x_4 - k_3x_2x_6$$

where x_{zn} is the relative mole fraction of zinc compounds.

The kinetic equations for the components x_3 and x_4 are

$$dx_3/dt = (k_1 + k_4x_{zn})(1 - x_3)$$

$$dx_4/dt = -k_2x_2x_4$$

The relative mole fractions x_5 , x_6 , and x_7 can be expressed by the material balances

$$x_5 = x_3 - x_1 - x_2 - a$$

$$x_6 = 2(x_4^0 - x_4) - x_5$$

$$x_7 = x_4^0 - x_4 - x_6$$

where x_4^0 is the initial relative mole fraction of zinc stearate in the PVC blend and a is the amount of HCl which escapes from the sample after calendaring.

The system of differential kinetic equations has been solved by the fourth-order Runge—Kutta method, the sum of squares of deviations between theoretical and experimental kinetic runs has been minimized by the simplex method [11] simultaneously for the whole set of eleven runs. Minimization parameters were the rate constants of the process and the critical relative mole fraction x_c . The calculation procedure is described more in detail in Refs. [8, 9]. In the course of calculation we have found that the least sum of squares is reached if it is assumed that solely the Zn—Cl bonds accelerate the elimination of HCl from PVC. In this case the relative mole fraction x_{zn} is expressed as

$$x_{zn} = x_6 + 2x_7$$

Using this expression, the minimized sum of squares is more than by an order less than as when taking into consideration all zinc compounds. The kinetic parameters corresponding to the minimum sum of squares are listed in Table 1. Reasonability of the proposed reaction scheme is documented in Figs. 1—4 where comparison of the experimental and calculated kinetic runs is shown. As can be seen the agreement between theory and experiment is excellent.

Table 1

Kinetic parameters of thermal dehydrochlorination of PVC stabilized with zinc stearate

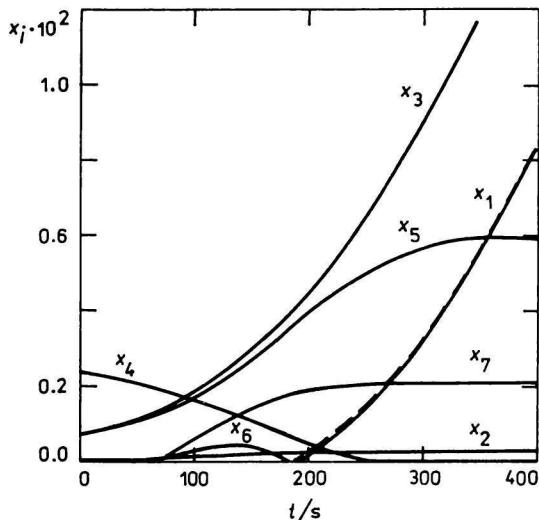
Parameter	Atmosphere	
	Nitrogen	Air
k_1/min^{-1}	1.0×10^{-4}	1.56×10^{-4}
k_2/min^{-1}	3.36×10^3	5.34×10^3
k_3/min^{-1}	6.06×10^3	5.70×10^3
k_4/min^{-1}	0.26	0.27
x_c	$4.0 \times 10^{-}$	$3.2 \times 10^{-}$

Table 1 reveals that the rate constant k_1 is greater for the dehydrochlorination in air than in nitrogen, which is documented by the well-known fact that dehydrochlorination proceeds more rapidly in the presence of oxygen. The rate constants for both dehydrochlorination atmospheres are greater than their counterparts describing the dehydrochlorination of PVC stabilized with calcium and magnesium stearates [8, 9]. These greater values are probably due to the above-mentioned strong interaction of PVC chains with zinc stearate documented in Fig. 7.

The rate constants k_2 and k_3 are related with the two-step reaction of zinc stearate with HCl split off from PVC. Their values are very high, which indicates that zinc stearate is a very efficient scavenger of HCl. Similarly as in the case of magnesium stearate [9], in the region of minimum, conjugation of parameters k_2 , k_3 , and x_c was observed in calculations so that the error of these parameters is about 30 %. The rate constant k_4 is more than by three orders greater than k_1 . From this it follows that the dehydrochlorination rate accelerated by zinc compounds is about 20 times greater than the "normal" rate. Obviously, this acceleration is responsible for the short times of thermal stability as is demonstrated in Fig. 5.

The catalytic influence of Zn^{2+} ions on PVC dehydrochlorination can be explained by the fact that they possess unsaturated *d*-orbitals. The orbitals can

Fig. 9. Calculated dependences of the relative mole fractions in mixture on the time of dehydrochlorination in nitrogen ($x_4^0 = 3.07 \times 10^{-3}$). x_1 — conversion of dehydrochlorination; x_2 — HCl in polymer; x_3 — double bonds in polymer; x_4 — ZnSt_2 ; x_5 — HSt ; x_6 — ZnClSt ; x_7 — ZnCl_2 . — Experimental kinetic curve, ---- calculated kinetic curve.



form a bond with a nonbonding electron pair of Cl atom from the PVC chain; this brings about the weakening or scission of C—Cl bond. It is more difficult to answer the question why only Zn—Cl bonds exert the catalytic influence. The most probable reason is that stearate anions form the chelate bonds with d -orbitals of Zn^{2+} ion and thus the catalytic influence of d -orbitals is inhibited [12].

When knowing the values of the rate constants, it is possible to calculate the time dependences of the components in PVC blends (Fig. 9). Also, it is possible to find out the consumption of stabilizer during calendering which is 12—58 %, and the consumption of stabilizer in the time $t = \tau$ which is 90—97 % (evaluated as the ratio of Zn—St bonds consumed). These examples demonstrate that the kinetic parameters obtained can be used for further considerations on the stabilization of PVC with zinc stearate.

References

1. Ayrey, G., Head, B. C., and Poller, R. C., *J. Polym. Sci., Macromol. Rev.* 8, 1 (1974).
2. Naqui, M. K., Unnikirshnan, P. A., Sharma, Y. N., and Bhardwaj, I. S., *Eur. Polym. J.* 20, 95 (1984).
3. Onozuka, M., *J. Polym. Sci., A1*, 2229 (1967).
4. Onozuka, M. and Asahina, M., *J. Macromol. Sci., Rev. Macromol. Chem.* C3, 235 (1969).
5. Anderson, D. F. and McKenzie, D. A., *J. Polym. Sci., A1*, 2905 (1970).
6. Klemchuk, P. P., *Adv. Chem. Eng.* 85, 1 (1968).

7. Popova, Z. V. and Yanovskii, D. M., *Zh. Prikl. Khim.* (Leningrad) **34**, 1324 (1961).
8. Oremusová, J., Šimon, P., Valko, L., and Kovařík, P., *Chem. Papers* **43**, 721 (1989).
9. Šimon, P., Oremusová, J., Valko, L., and Kovařík, P., *Chem. Papers* **45**, 127 (1991).
10. Wypych, J., *J. Appl. Polym. Sci.* **23**, 39 (1979).
11. Nelder, J. A. and Mead, R., *Comput. J.* **7**, 308 (1965).
12. Troitskii, B. B. and Troitskaya, L. S., *Usp. Khim.* **54**, 1287 (1985).

Translated by P. Šimon