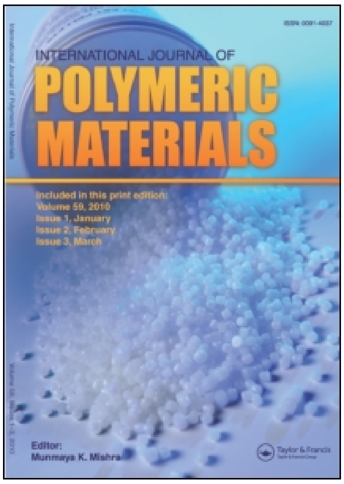

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Kinetic Parameters of PVC Dehydrochlorination in Solutions

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Kinetic parameters of PVC dehydrochlorination in solution are reviewed.

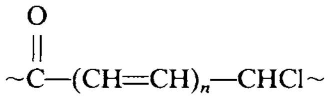
KEY WORDS PVC, dehydrochlorination, kinetics

More than half of the materials and products are obtained from PVC using solvents (fibres, lacquers, plasticates etc.). Meanwhile, the kinetics of HCl elimination during thermal destruction of PVC and PVC in organic solvents and, consequently, ways for PVC stabilization are basically different.

The PVC dehydrochlorination rate is described by the correlation.[1,2]

$$V_{\mathrm{HCl}} = V_{1S} + V_{1P} = K_{1S} \cdot \alpha_0 + K_{1P} \cdot \bar{\gamma}_0,$$

where $V_{1S} = K_{1S} \cdot \alpha_0$ is a fundamental characteristic showing that all macromolecular chains in PVC are equally contributing to the HCl elimination at random: $V_S = \text{const}$, and when $t = 448$ K, $K_{1S} = 0.8 \cdot 10^{-7}\ \mathrm{s}^{-1}$ ($E_a^{1S} = 90 \pm 6.5$ kJ/mol; $1\ gA_{1S} = 3.4 \pm 0.7$). Therefore, V_{HCl} is determined by the content of polyene, mainly carbonylallyl (oxovinylene)



$$\sim\overset{\overset{\Large O}{\|}}{C}—(CH{=}CH)_n—CHCl\sim$$

groups within the macromolecules of the PVC: at $t = 448$ K, $K_{1P} = 7.5 \times 10^{-3}$ $\mathrm{s}^{-1}/E_a^{1P} = 146.5 \pm 6.5$ kJ/mol, $1\ gA_{1P} = 14.9 \pm 0.8$. Here K_{1S} and K_{1P} are the rate constants of the non-catalytic reaction of statistical (at random) HCl elimination and the formation of polyconjugated systems of C=C bonds within the macromolecules when the HCl elimination process is initiated by the HCl-labile carbonylallyl groups, correspondingly; $\alpha_0 = 1$ mol HCl/base mol PVC for the HCl content within the PVC macromolecules before the dehydrochlorination process is started.

Kinetic laws for PVC thermal degradation in the presence of solvents (plasticizers included) are essentially different and depend on the chemical structure of the

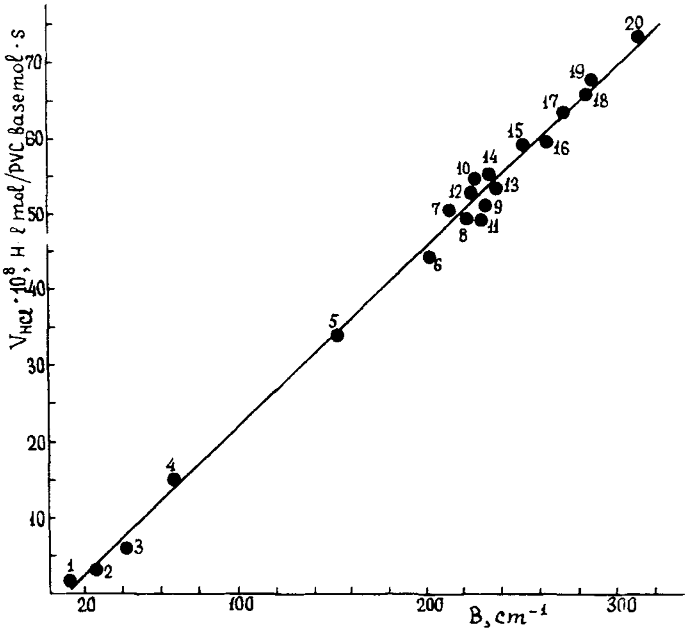


FIGURE 1 The effect of the solvent basicity on the PVC thermal dehydrochlorination (423 K, N_2) in the solution: (1) *n*-dichlorbenzene; (2) *o*-dichlorbenzene; (3) naphthalene; (4) nitrobenzene; (5) acetophenone; (6) acetophenone; (7) di-*n*-(chlorphenyl-chlorpropyl)phosphate; (8) triphenylphosphate; (9) phenyl-bis-(β-chlorethyl)phosphate; (10) tri-(*n*-chlorphenylphosphate); (11) 2-ethylhexylphenylphosphate; (12) tricresylphosphate; (13) cyclohexanone; (14) phenyl-bis-(β-chlorpropyl)phosphate; (15) tri-β-chlorethylphosphate; (16) tri-β-chlorpropylphosphate; (17) di(2-ethylhexyl)phosphate; (18) 2-ethylhexyldinonylphosphate; (19) tri-(2-ethylhexyl)phosphate; (20) tributylphosphate.

solvent applied.[2-4] There exists a distinct linear dependence of the HCl elimination rate from the PVC in solution on the basicity of the solvent "B" (Figure 1). When the values of "B" are less than 50 cm^{-1} (except the ester plasticizers which are an abnormality[2]) we can observe the inhibition of the PVC dehydrochlorination. This increases as the value of B decreases, i.e., when the case of "solvation" stabilization of the PVC is evident.[3] This effect is of great significance in the selection of effective ways of PVC stabilization in solutions (concentrated ones included). It determines, under real conditions of PVC degradation in solutions, i.e., in the presence of the air oxygen, the possibility for realization of a new fundamental effect, PVC "echo"-stabilization, which occurrs in the presence of stabilizers (antioxidants).[5]

In the solvents with $B > 50$ cm^{-1} HCl elimination during PVC thermal degradation is accelerated. This fact is determined by the specific solvation interaction between the polymer and the solvent.[6]

Thus, the kinetics of PVC thermal degradation in the presence of solvents with other conditions the same, depends on the solvent basicity, the kinetic parameters of the process being governed by the interaction of the functional groups of the molecules of the solvent and the polymer, i.e., by the specific solvation of the polymer by the solvent. For PVC degradation in solutions with solvent basicity $B > 50$ cm^{-1} a marked acceleration of PVC degradation is observed. This can be seen, in particular, in the example of benzonitrile, acetophenone, cyclohexanone etc. (Figure 1).

Ethers of *o*-phosphoric acid due to their high nucleophilic nature ($B > 200\ \text{cm}^{-1}$) markedly increase PVC dehydrochlorination as well, with experimental points having a high correlation coefficient ($z = 0.986$) being situated at the same linear dependence as $V_{\text{HCl}} = f(B)$ (Figure 1). It should be stressed that the rates V_{1P} both in PVC degradation and PVC in the presence of phosphates and other solvents with $B > 50\ \text{cm}^{-1}$ are nearly the same. At the same time the HCl elimination rate from PVC at random (V_{1S}) increases considerably in direct correspondence with the numerical values of B, and chemical interaction both with normal vinyl chloride units and carbonylallyl groups does not occur.

During PVC degradation with $B < 50\ \text{cm}^{-1}$, when the PVC solvation stabilization effect is evident, the rate of polyene sequence growth V_{1P}, initiated by the carbonylallyl groups, decreases, with V_{1S} remaining constant.[7]

Judging by the above, the HCl elimination rate during PVC thermal degradation in solutions is generally described by the equation:

$$V_{\text{HCl}} = (V_{1S} + V_{1P}) + V_3 = (V_{1S} + V_{1P}) + K_{\text{ef}}(B - 50)m,$$

where m is the proportionality coefficient (cm mol HCl/mol PVC).

Calculated from the experimental data the values of the effective constants of HCl elimination rate from PVC in solution are the following: $K_{\text{ef}} = (0.20 \mp 0.03) \times 10^{-8}\ \text{s}^{-1}$, ester plasicizers excluded.[2]

Hence, the dependence of the kinetic parameters of HCl elimination on solvent basicity during thermal degradation of PVC in solutions proves to be a fundamental property, determined mainly by the interaction of the PVC macromolecules with the solvent. All the facts discussed above should be taken into account while working with PVC in solutions.

In our work we used suspension made PVC C-7059 M ($K_F = 70$, $[\eta]_0 = 1.300\ \text{m}^3/\text{kg}$; $\bar{M}_\eta = 137{,}500$; $\bar{\gamma}_0 = 1.2 \cdot 10^{-4}$ mol HCl/base mol PVC). PVC degradation in solutions was investigated according to the procedure given in Reference 8. The parameters of the self basicity "B" of the solvents were estimated according to Reference 9. The solvent basicity was determined on the basis of the characteristic band shift of the phenol OH-group in the infrared spectra in the CCl_4 medium, the above shift being caused by hydrogen bond formation of the phenol OH-group and the respective functional group contained within the solvent molecule.

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