Kinetics of dehydrochlorination of poly(vinyl chloride)
I. Step-by-step model of hydrogen chloride elimination

L. VALKO, P. KOVAŘÍK, and V. KELLÖ

*Department of Physical Chemistry, Slovak Technical University,
812 37 Bratislava*

Dedicated to Professor Ing. RNDr. A. Tkáč, DrSc., in honour of his 60th birthday

The kinetics of dehydrochlorination of poly(vinyl chloride) from the viewpoint of the step-by-step model of elimination of the molecules of hydrogen chloride from the macromolecules of polymer is discussed. A differential equation was put forward for the step-by-step model under defined conditions. This equation makes possible to obtain a differential equation which is formally identical with a rate equation of the first-order reactions of dehydrochlorination of the model substances containing only one chlorine atom. The correlation of the solutions of the system of differential equations for individual kinetic steps with the experimental kinetic curve enables us to find out the discrete distribution function of rate constants by means of which the mean values of rate constants may be determined for different samples of PVC.

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В работе обсуждается кинетика дегидрохлорирования поливинилхлорида с точки зрения ступенчатой модели отщепления молекул хлористого водорода от макромолекул полимера. Было сформулировано разностное уравнение для ступенчатой модели при определенных условиях и полученное из нее дифференциальное уравнение формально тождественно с уравнением скорости первого порядка дегидрохлорирования модельных веществ, содержащих по одному атому хлора в молекуле. Корреляция решения системы разностных уравнений для отдельных кинетических шагов с экспериментальной кинетической кривой позволяет найти дискретную функцию распределения констант скорости и, при помощи последней, средние значения констант скоростей для различных образцов ПВХ.
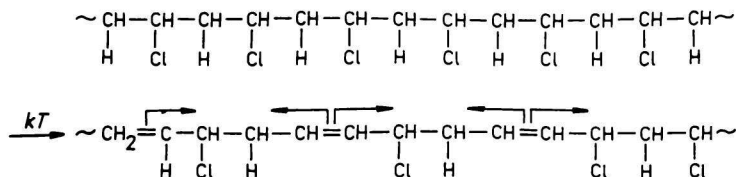
The elimination of small molecules from macrochains of polymer substances represents an important class of chemical reactions not only from the view-point of development of the theory of chemical kinetics but also from the view-point of chemical technology. The kinetics of elimination reactions of macromolecular substances principally differs from the kinetics of elimination reactions of

low-molecular substances the molecules of which possess only one reactive group, irrespective of the fact that these reactions are monomolecular in either case. The principal difference consists in that the elimination reactions of low-molecular substances show single rate constant whereas the elimination of small molecules from macrochains of polymer systems must be characterized by a set of rate constants because, from the theoretical stand-point, a macromolecule of reactant after elimination of each new molecule always possesses other intrinsic structure. It means from the chemical view-point that another molecule of reactant enters into reaction after elimination of each molecule because the reactivity of the not yet eliminated groups depends on the state of their nearest neighbours. For instance, the reactivity of a particular group of polymer chain remarkably depends on the circumstances whether the right-side and left-side vicinal groups or only the groups in one direction in relation to this group have already reacted and whether only one or a greater number of these vicinal groups has been subjected to the reaction.

Examples of the influence of state of the nearest neighbours on reactivity of a group which has not reacted yet are: activation of solvolysis of esters by vicinal ionized carboxyl [1, 2] or vicinal hydroxyl [3] formed by hydrolysis of polyacryl esters or poly(vinyl acetate), activation of amides by nonionized vicinal carboxyls formed during acidic hydrolysis of poly(acryl amide) [4] or polyanilides [5], and activation by vicinal carboxyl in pyrolytic degradation of poly(*tert*-butyl acrylate) [6]. Other examples are represented by the elimination reactions involving elimination of water from poly(vinyl alcohol) [7], hydrogen bromide from poly-(vinyl bromide), and hydrogen chloride from poly(vinyl chloride) [8]. The kinetic analysis of each of these systems requires special approach and information about the mechanism which may be radical, ionic or monomolecular. In subsequent considerations, we shall concentrate our attention on a special case, *i.e.* thermal dehydrochlorination of poly(vinyl chloride) in inert atmosphere.

Design of the model

Let us consider PVC consisting of M_m macrochains. Each of these macrochains contains m reactive groups —CH_2CHCl—. The basic assumption is the idea that the elimination of a molecule of hydrogen chloride from an arbitrary reactive group occurs incidentally by monomolecular mechanism. The probability that a molecule of hydrogen chloride splits off from a group which has not reacted yet in the time interval $(t, t + \Delta t)$, $\Delta t \rightarrow 0$, is $k_i \Delta t$ where the value of the first-order reaction rate constants k_i for elimination of hydrogen chloride from PVC depends on kinetic state of the nearest neighbours on either side with respect to this group. Some of a great number of situations are represented in Scheme 1.

$$\sim CH-CH-CH-CH-CH-CH-CH-CH-CH-CH-CH-CH-CH\sim$$

$$\xrightarrow{kT} \sim CH_2 = C - CH - CH - CH \equiv CH - CH - CH - CH \equiv CH - CH - CH - CH \sim$$

Scheme 1

The arrows in this scheme indicate further propagation of elimination of the molecules of hydrogen chloride which proceeds always with other rate constant k_i inside the chain as well as at its ends.

If N_x is the number of sequences containing x nonconsumed —CH_2CHCl— groups in the moment of time t, the extent of reaction is to be expressed by the fraction of the eliminated molecules of hydrogen chloride at this time by the following equation

$$\eta(t) = 1 - \sum_{x=1} xN_x/mM_m \qquad (1)$$

Provided $\eta = 1$, all molecules of hydrogen chloride have been eliminated from all chains. Initial conditions $(t = 0)$ are $N_m = M_m$ and $N_x = 0$ for $x \neq m$. In reality, it holds $\eta(t = \infty) = \eta_\infty \neq 1$ because the dehydrochlorination at a given (finite) temperature proceeds to a certain limited degree which depends on the length of macrochains [9].

Let us assume that the molecules of hydrogen chloride are eliminated from M_m original still undisturbed chains. If the reaction takes place on one of the chains, the number N_m decreases by one. In general, the decrease in N_m is proportional to the number of potentially reactive groups, *i.e.* $m - 1$ for each of $N_m m$ sequences

$$\frac{dN_m}{dt} = - k(m - 1) N_m \qquad (2)$$

or

$$N_m = M_m \exp\left[-(m - 1) kt\right] = M_m \exp\left[-k(m) t\right] \qquad (3)$$

where $k(m) \equiv k(m - 1)$. Thus we may get on to find the number of chains without one, two, and so on reactive groups, *i.e.* $N_{m-1}, N_{m-2}, \ldots$, depending on the temporal progress of dehydrochlorination. Thus we may give evidence that the rate constants for hydrogen chloride elimination depend on the number of nonconsumed reactive groups in macrochains of PVC. This idea will be used for designing a discrete step-by-step model of dehydrochlorination of PVC.

Construction of differential equation

The aim is to build up the differential equation for the step-by-step model of the elimination of hydrogen chloride from PVC under the following assumptions:

(i) the macrochains are so long that the end effects on kinetics of the hydrogen chloride elimination may be neglected;

(ii) the elimination of a molecule of hydrogen chloride is an irreversible reaction;

(iii) we do not take into account breaking of the C—C bonds in skeleton;

(iv) the original state of macrochains is of the sort that no molecule of hydrogen chloride has been eliminated even from single reactive group —CH$_2$CHCl—;

(v) the elimination of hydrogen chloride is a monomolecular nonautocatalytic reaction;

(vi) the existence of thermooxidation and reactions giving rise to cross links between chains is not assumed;

(vii) the reactions involving termination of the chain elimination of HCl are not taken into consideration.

If the dehydrochlorination of PVC is pursued to a high degree of conversion under isothermal conditions, the real dehydrochlorination process may be divided into a great number of kinetic steps ($i = 1, 2, ..., N$) and each of them is to be characterized by its proper rate constant ($k_1, k_2, ..., k_N$) as well as by the quasi-equilibrium value of the fraction of eliminated hydrogen chloride ($\eta_{\infty 1}$, $\eta_{\infty 2}, ..., \eta_{\infty N}$). Provided each kinetic step may be described by a differential equation of the first-order reactions of low-molecular substances owing to eqns (2) and (3) by the expression

$$\frac{d\eta_i}{dt} = k_i(\eta_{\infty i} - \eta_i) \quad i \in [1, N] \tag{4}$$

the course of the kinetic curves corresponding to individual steps of elimination is to be described in the following form

$$\eta_i(t_i) = \eta_{\infty i}[1 - \exp(-k_i t_i)] \tag{5}$$

where k_i is the rate constant of the i-th kinetic step and t_i is the time variable determined by effective contribution of the i-th dehydrochlorination step to the overall amount of eliminated hydrogen chloride. It results from these facts that the reaction involving hydrogen chloride elimination gets in each reaction step into a stationary state and the resulting kinetic curve $\eta = \eta(t)$ may be constructed by superimposing the kinetic curves $\eta_i = \eta_i(t_i)$ corresponding to particular kinetic steps of dehydrochlorination.

Let us assume that it is characteristic of the temporal sequence of the kinetic steps that the total time of the dehydrochlorination process may be divided into N equal time intervals, *i.e.* $\Delta t_1 = \Delta t_2 = ... = \Delta t_N = \Delta t$. Individual kinetic steps succeed
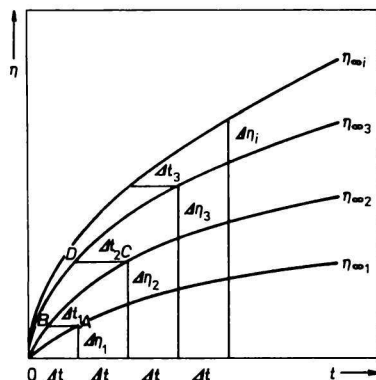
Fig. 1. Schematic representation of the step-by-step model of hydrogen chloride elimination from poly(vinyl chloride).

each other at intervals Δt, as represented in Fig. 1 and each kinetic step is governed by the time dependence $\eta_i = \eta_i(t)$. By combining eqns (4) and (5), we obtain

$$\frac{d\eta_i}{dt} = \dot{\eta}_i = \eta_{\infty i} k_i \exp\left(-k_i t_i\right) \tag{6}$$

Because of eqn (6), the final contribution of a fraction of eliminated hydrogen chloride in the time interval Δt in arbitrary kinetic step $i \in [1, N]$ may be expressed by means of the following equation

$$\frac{\Delta\eta_i}{\Delta t} = \eta_{\infty i} k_i \exp\left[-k_i t_i(\Delta t)\right] \tag{7}$$

Hence, the rate of hydrogen chloride elimination in the first kinetic step $(t_1 = 0)$ obeys the equation

$$\frac{\Delta\eta_1}{\Delta t} = \eta_{\infty 1} k_1 \tag{8}$$

The first kinetic step finished, the amount of eliminated hydrogen chloride has somewhat increased and the functional dependence $\eta = \eta(t)$ in the second kinetic step is represented by the kinetic curve corresponding to $\eta_2 = \eta_2(t_2)$. The increase in the fraction of eliminated hydrogen chloride by $\Delta\eta_2$ in the second kinetic step, however, corresponds to the time interval $\Delta t_2 = \Delta t - \Delta t_1$, as it is shown in Fig. 1. Hence, we may write

$$\frac{\Delta\eta_2}{\Delta t} = \eta_{\infty 2} k_2 \exp\left[-k_2(\Delta t - \Delta t_1)\right] \tag{9}$$

where Δt_1 is the time of retardation of the start of kinetic development of the second kinetic step. Thus by the use of inductive way, we may express a contribution $\Delta\eta_i$ in the time interval Δt for arbitrary i-th kinetic step

$$\frac{\Delta\eta_i}{\Delta t} = \eta_{\infty i}k_i \exp\left[-k_i(i-1)\Delta t + k_i \sum_{j=1}^{i} \Delta t_{j-1}\right] \qquad (10)$$

where $\Delta t_0 = 0$ and

$$\frac{\Delta\eta_1}{\Delta t} > \frac{\Delta\eta_2}{\Delta t} > \ldots > \frac{\Delta\eta_i}{\Delta t} > \ldots > \frac{\Delta\eta_i}{\Delta t}$$

Now, let us consider the discrete model of hydrogen chloride elimination from PVC from other point of view. As shown in Fig. 1, the coordinates of the point B are $[\Delta\eta_1, \Delta t - \Delta t_1]$. Since the point B is situated on dehydrochlorination curve 2, the increase in the fraction of eliminated hydrogen chloride during the first elimination step may be expressed in accord with eqn (5) in the form

$$\Delta\eta_1 = \eta_{\infty 2}\{1 - \exp[-k_2(\Delta t - \Delta t_1)]\} \qquad (11)$$

Similarly, if we take into consideration the position of the point D on the third curve with the coordinates $[\Delta\eta_2, 2\Delta t - \Delta t_1 - \Delta t_2]$, we obtain for the sum of the fractions of eliminated hydrogen chloride

$$\Delta\eta_1 + \Delta\eta_2 = \eta_{\infty 3}\{1 - \exp[-k_3(2\Delta t - \Delta t_1 - \Delta t_2)]\} \qquad (12)$$

By generalizing this procedure for the sum of the fractions of eliminated hydrogen chloride for individual elimination steps, we obtain

$$\Delta\eta_1 + \Delta\eta_2 + \ldots + \Delta\eta_{i-1} = \eta_{\infty i}\left\{1 - \exp\left[-k_i(i-1)\Delta t + k_i \sum_{j=1}^{i} \Delta t_{j-1}\right]\right\} \quad (13)$$

This equation is fulfilled for $i \geq 2$ and $\Delta t_0 = 0$. By combining eqns (10) and (13), we may write a system of kinetic equations of the first order in the difference form

$$\frac{\Delta\eta_i}{\Delta t} = k_i\left(\eta_{\infty i} - \sum_{j=1}^{i-1} \Delta\eta_j\right) \qquad i = 1, 2, \ldots, N \qquad (14)$$

As $\sum_{j=1}^{i-1} \Delta\eta_j = \eta_i(\Delta t)$ for $i \gg 1$, the quasi-stationary fraction of eliminated hydrogen chloride, too, explicitly depends on the magnitude of the used time step Δt, i.e. $\eta_{\infty i} = \eta_{\infty i}(\Delta t)$, which enables us to write difference equation (14) in the form

$$\frac{\Delta\eta_i}{\Delta t} = k_i[\eta_{\infty i}(\Delta t) - \eta_i(\Delta t)] \qquad (15)$$

This linear difference equation may be solved by means of numerical methods. This solution requires a convenient choice of the number of steps N, magnitude of the time interval Δt, and system of rate constants, e.g. k_1 for fortuitous elimination of hydrogen chloride from undisturbed chains of PVC and k_2, k_3, k_4, ..., k_j for elimination of hydrogen chloride from chains having one, two, three, etc. double bonds with respect to the noneliminated Cl atom occurring in β position with

regard to double bond. Besides, the rate constants characterizing the elimination of hydrogen chloride from structures with a tertiary Cl atom (k_{j+1}) or a tertiary H atom (k_{j+2}), *etc.* may be respected. By using the input data thus chosen and numerical method of solving the linear difference equations of the first order, we may achieve the agreement of the experimental curve with the curve obtained by numerical procedure.

Another method of solving this problem consists in the replacement of difference differential equation by the differential equation describing the continuous process of hydrogen chloride elimination from PVC. For this reason, we define the mean value of rate constant characterizing the overall process of hydrogen chloride elimination

$$\sum_{i=1}^{N} k_i \eta_{\infty i}(\Delta t) = \langle k \rangle \, \eta_{\infty}(\Delta t)$$
$$\sum_{i=1}^{N} k_i \eta_i(\Delta t) \; = \langle k \rangle \, \eta(\Delta t) \tag{16}$$

where $\eta_{\infty}(\Delta t)$ is the quasi-stationary fraction of eliminated hydrogen chloride for which it always holds $\eta_{\infty}(\Delta t) < 1$ and $\eta(\Delta t)$ is the fraction of eliminated hydrogen chloride for a certain selected multiple of the time interval Δt.

In conformity with kinetic arguments, we assume that neither the rate constants k_i, $i \in [1, N]$ nor the mean value of rate constants $\langle k \rangle$ are functions of time, *i.e.* $k_i \neq k_i(t)$, $\langle k \rangle \neq \langle k \rangle(t)$. In the limit case $\Delta t \rightarrow 0$, $N \rightarrow \infty$, *i.e.* $i \in [1, N] \rightarrow i \in [1, \infty]$, we obtain the following differential equation from eqn (*15*)

$$\lim_{\Delta t \rightarrow 0} \sum_i \Delta \eta_i / \Delta t = \lim_{\Delta t \rightarrow 0} \langle k \rangle [\eta_{\infty}(\Delta t) - \eta(\Delta t)] \tag{17}$$

or

$$\frac{d\eta}{dt} = \langle k \rangle [\eta_{\infty}(t) - \eta(t)] \tag{18}$$

This equation is formally identical with the rate equation of the first-order reaction valid for dehydrochlorination of the model substances containing only one chlorine atom on condition that $\eta_{\infty}(t) = \text{const.}$

Discussion

By integrating differential equation (*18*) on assumption that the explicit form of the function $\eta_{\infty}(t)$ is known, it is possible to find out the kinetic curves for dehydrochlorination in inert atmosphere as well as in an atmosphere catalyzing hydrogen chloride elimination. On the basis of solution of this equation, the

elimination of hydrogen chloride in the atmosphere catalyzing by oxygen at a certain partial pressure of oxygen and varying temperature as well as at a given temperature and varying partial pressure of oxygen has been described [10—12]. The autocatalytic influence of hydrogen chloride on dehydrochlorination of PVC may be also described by this differential equation [13]. It is worth noticing that this differential equation is related with the idea of the interchain mechanism of initiation of the elimination of hydrogen chloride from PVC, as it is treated in papers [14, 15].

In conclusion, we must remark that this step-by-step model constitutes a time-discrete or time-continuous Markov process with very well defined rates of transition probability. The most logical analytical means for the description of such process is a master differential difference equation for the probability of finding different populations of molecular states in different time moments [16]. This step-by-step model of PVC dehydrochlorination exhibits the character which is in very close connection with the description of hydrogen chloride elimination from PVC by means of master equation. Nevertheless, the integral character of the variables of molecular population in the master equation is not suited for many purposes so that the analysis is usually carried out by means of the Fokker—Planck partial differential equation in which the populations of molecular states are described directly by means of real variables [17]. This procedure will be the topic of one of our subsequent papers.

References

1. Morawetz, H. and Zimmering, P. E., *J. Phys. Chem. 58*, 753 (1954).
2. De Loecker, W. and Smets, G., *J. Polym. Sci. 40*, 203 (1959).
3. Nagai, E. and Sagane, N., *Chem. High Polym.* (Japan) *12*, 195 (1955).
4. Smets, G. and Hosbain, A. M., *J. Polym. Sci. 40*, 217 (1959).
5. Westhead, E. W. and Morawetz, H., *J. Amer. Chem. Soc. 80*, 237 (1958).
6. Schaefgen, J. R. and Sarasohn, I. M., *J. Polym. Sci. 1963*, 1962.
7. Aoki, H., Uehara, M., Suzuki, T., and Yoshida, A., *Eur. Polym. J. 16*, 571 (1980).
8. Braun, D. and Thallmaier, H., *Makromol. Chem. 29*, 59 (1966).
9. Flory, P. J., *J. Amer. Chem. Soc. 61*, 3241 (1939).
10. Valko, L., *J. Polym. Sci., Part C 16*, 545 (1967).
11. Valko, L., *J. Polym. Sci., Part C 16*, 1979 (1967).
12. Valko, L., *DrSc. Thesis.* Slovak Technical University, Bratislava, 1979.
13. Šimon, P. and Valko, L., *Eur. Polym. J.,* in press.
14. Valko, L., Šimon, P., and Kellö, V., *Makromol. Chem.,* submitted for publication.
15. Světlý, J., Lukáš, R., and Kolínský, M., *Makromol. Chem. 180*, 1363 (1979).
16. van Kampen, N. G., *Can. J. Phys. 39*, 551 (1961).
17. Nitzan, A., Ortoleva, P., Deutch, J., and Ross, J., *J. Chem. Phys. 61*, 1056 (1974).