Polychronic Kinetics of Chemical Reactions with the Blending of Rate Constants

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The peculiarities of the kinetics of solid-phase cage reactions with distributed parameters for the relaxing matrix are considered in this study. It is shown that the kinetics of chemical conversions can be either exponential or nonexponential depending on the ratio of the rate constants and relaxation constant. The different cases of the effect of the reaction system on the relaxation constant are considered. The possibility of the analysis of experimental data for reactions of alkyl radicals in amorphous alcohol matrixes and conversions in biological systems within the framework of the treatment developed is discussed.

Introduction

As is well-known, kinetic curves of many solid-phase chemical processes do not obey the ordinary rules of reactions, first or second order. Among such processes one can refer to several radiation-induced or photochemical conversions, such as the stepwise recombination of radicals,[1,2] diffusion-controlled reactions,[3,4] exothermic abstraction of atoms from molecules by free radicals,[5,6] ligand−heme rebinding and relaxation of heme-containing proteins,[7−10] and transfer of electrons.[11,12] Due to the multistage nature of the processes, it is difficult, sometimes even impossible, to extract the limiting stage of the complex process, i.e., the stage responsible for nonstationarity of kinetics, for the change of rate constants with time. We shall restrict ourselves to the treatment of only one class of processes, namely, to reactions in a cage with the transfer of atoms, when one certain stage plays the decisive role.

The deviation of kinetic curves of the transfer of hydrogen atoms from matrix molecules to radicals from ordinary kinetic laws was shown already in earlier works.[3,14] Initially, such a deviation was explained by the diffusion of radicals and superposition of first and second-order kinetics. Such a deviation was explained in ref 15, where, on the basis of experimental data,[16−18] it was supposed the possible spread of rate constants in such reactions is due to the variety of configurations of reactant pairs.

The role of energetic and spatial nonhomogeneity as a possible source of dispersion of the rates of various processes was discussed in many papers since 1955−60.[19,20] The chemical reactions in which the probability of the elementary act depends on the relative position of reagents and is operated by their rotation belong to this type of process. The theory of such processes is considered in ref 21. The intramolecular reaction with the rate constant depending on some coordinate in the many-dimensional space of the considered system was studied in ref 22, where it was supposed that the motion along this coordinate is diffusional.

The observed nonstationarity of the kinetics of atom transfer can be explained by two causes: dispersion of rate constants and the relaxation of the matrix, which leads to a change in the mutual orientation of reactants.[21,22] The aim of this paper is to analyze the role and mutual influence of these two factors.

States Mixing in Chemical Conversion and Relaxation: General Remarks

Instead of the usually assumed single effective values, the distributed kinetic parameters show up in the dispersion of properties to the medium where the reactant species exist. For example, the energy depths of the traps in which positive ions and electrons recombining with these ions are captured and the distances between these traps have different values in the glasses; therefore, corresponding rate constants have different values.

In contrast to ordinary monomolecular decomposition, proceeding exponentially in accordance with the equation $N = N_0 \exp(-kt)$, where k is the rate constant, in the case of polychronic reactions the kinetics are nonexponential. The particles in the shallower traps are consumed first and then those in the deeper traps with smaller values of k. Instead of the linear dependence of $\ln(N)$ on time t, we find a linear dependence of N or $\ln(N)$ on $\ln(t)$.

It is obvious, however, that if internal motion takes place in the medium, corresponding to continuous conversion of one type of trap into another, i.e., rate constant mixing takes place, then, if such mixing is sufficiently fast (in comparison with the rate of consumpsion of the reactants), the presence of distributed kinetic parameters and polychromaticity of the kinetics will no longer lead, by themselves, to nonexponential kinetic relationships.

Such motion is often considered as the matrix relaxation since the variety of parameters of elementary acts of chemical reactions in the sample gives evidence for a nonequilibrium state of the matrix.

Below we will give a general analysis of the kinetics of reactions with mixing, using the example of a quasi monomolecular reaction. As a rule, polychronic kinetics are characteristic for bimolecular reactions, but if the concentration of one of the reactants is far greater than that of the other, it is known that bimolecular reactions reduce to monomolecular reactions. For example, let us consider the capture in a trap of some acceptor present in large excess in the entire sample; then the polychronicity of the kinetics will be determined by the dispersion of the values of activation energy for the escape from the trap.

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Matrix relaxation and chemical reactions are considered in this work on an equal basis. Consequently, the character of matrix relaxation and the governing parameters of relaxation can be functions of the local concentration of reaction products or, generally, of the course of the chemical reaction. However, we will not treat below this nonlinear problem since the concentration of at least one of reactants is assumed to be small.

The usual approach to this type of reaction consists of (1) attributing the rate dependence to some subsystem; (2) using the law of motion on this coordinate (more frequently it is diffusion or jumps). Our consideration is based on another introduction of the system motion in one-dimensional space of rate constants k. If we know the coordinate dependence of rate constants and the law of motion on these coordinates, we can find the law of motion in k-space.

Therefore we consider the "projection" of the multidimensional space of real motion of the system on the one-dimensional k-space. From our point of view it gives some advantages in the investigation of chemical kinetics.

We will consider below the general case of a discrete set of rate constants and the particular cases of diffusion and jumps in k-space.

Kinetics of Reactions with Polychronic Rate Constants and Mixing

Due to the mutual influence of microheterogenity (dispersion of rate constants) and polychronic relaxation of the matrix, the manifestation of two types of kinetics—exponential and nonexponential—is possible. The type of kinetics is determined by mixing and depends on the correlation between the rate constants of reactions and relaxation.

Now let us consider the kinetics discussed above. To do this we renumber the local states of reagents and the matrixes with indices $j = 1, 2, ..., N$. The time dependence of the concentration of subsystems $C_j(t)$ in state j is determined by the equation

$$\frac{dC_j(t)}{dt} = -\sum_{j'\neq j} w_{jj'}C_j(t) + \sum_{j'\neq j} w_{j'j}C_j(t) - k_j C_j(t) =$$
$$-\sum_{j'=1}^{N} T_{jj'}C_j(t) \quad (1)$$

Here $w_{jj'}$ is the probability for the subsystem to cross from state j into state j' within unit time; k_j is the chemical reaction rate constant for the subsystem in state j. The first two terms describe matrix relaxation, while the latter term describes the chemical transformation of reagents to reaction products.

It is easy to see that the rate constant does not depend on time in two cases: either all partial rate constants k_j are equal or the matrix relaxation takes place substantially faster than the chemical transformation. In the first case $k = k_j = \text{const}$. In the second case quasistationary partial concentrations are established quickly.

Since eq 1 is linear, its general solution is found easily:

$$C_j(t) = \sum_{i,j'} S_{ji} e^{-t/\tau_i} (S^{-1})_{ij'} C_j(0) \quad (2)$$

Here S_{ij} is the matrix diagonalizing the matrix T_{ij} introduced in eq 1, the proper values of which are equal to $1/\tau_i$ i.e.

$$(S^{-1}TS)_{ij} = (1/\tau_i)\delta_{ij}$$

Summing up the partial concentrations (eq 2), we find the dependence of the reagents' concentration on time:

$$C(t) = \sum_{i=1}^{N}[\sum_{j=1}^{N}(S^{-1})_{ij}C_j(0)][\sum_{j=1}^{N}S_{ji}]e^{-t/\tau_i} \quad (3)$$

The time constants τ_i characterize matrix relaxation and the reaction simultaneously. The values $1/\tau_i$ and k_i are equal only when matrix relaxation can be disregarded, i.e., $w_{jj'} = w_{j'j} = 0$. In this case

$$C(t) = \sum_{j=1}^{N} C_j(0)e^{-k_j t} \quad (4)$$

According to eq 3 the kinetics depends in general on the preparation of the system, i.e., on the initial distribution $C_j(0)$. This dependence disappears with the fast relaxation of the matrix, which occurs when the kinetics is of single-exponential character.

In experimental situations there may be different ratios between the rates of matrix relaxation and chemical transformation itself. The measurement of only $C(t)$ dependencies does not allow one to make a simple conclusion about the processes determining the observed kinetics. To clarify this question it is necessary to conduct special additional experiments.

We consider the common case of the motion of the reaction system in the space of rate constants, without considering what kinds of motions in real space correspond to different models of the motion in the space of the rate constants.

Let us consider several particular cases of kinetics in the space of rate constants:

I. Spontaneous transitions between two states characterized by constants k_1 and k_2.

II. Diffusion motion in space of constants k within limits from k_1 to k_2.

III. A jump from any state (constant k_i) with equal probability to any other possible state of the system that one may choose $\{k_1 < k_i < k_2\}$, the case of strong mixing.

The case of diffusional and jumping modulation in sub-Doppler spectroscopy and in energy-quenching phenomena is studied in refs 25–27.

I. The kinetic equations have the form

$$\frac{d\rho_1}{dt} = -\lambda(\rho_1 - \rho_2) - k_1\rho_1 \quad (5)$$

$$\frac{d\rho_2}{dt} = -\lambda(\rho_2 - \rho_1) - k_2\rho_2$$

Here, $\rho_{1,2}$ are the populations of the corresponding states; k_1 and k_2 are the decomposition rate constants; λ is the mixing constant; $\lambda = \tau^{-1}$, where τ is the lifetime in state 1 or 2 (for simplicity, we will assume that these times are equal). The observed quantity is $\rho(t) = \rho_1(t) + \rho_2(t)$. Assuming that at the initial instant $\rho_1(0) = \rho_2(0) = 1/2$ ($\rho(0) = 1$), we obtain

$$\rho(t) = \frac{1}{2}r^2(\lambda^2 + r^2)^{-1/2}\{[\sqrt{\lambda^2 + r^2} - \lambda]^{-1}\exp[-(k^0 + \lambda - \sqrt{\lambda^2 + r^2})t] + [\sqrt{\lambda^2 + r^2} + \lambda]^{-1}\exp[-(k^0 + \lambda + \sqrt{\lambda^2 + r^2})t]\} \quad (6)$$

where

$$r = \frac{1}{2}(k_2 - k_1), \quad k^0 = \frac{1}{2}(k_1 + k_2)$$

It is not difficult to see that when $\lambda \gg r$, the decomposition becomes monochromatic with a rate constant $k = (k_1 + k_2)/2$. This result was found earlier in ref 22.

A more general case is the case of nonequal probabilities of $1 \rightarrow 2$ and $2 \rightarrow 1$ transitions. Let the probabilities for $1 \rightarrow 2$ and $2 \rightarrow 1$ transitions be a and b respectively. We do not write down here the complete solution of the problem but restrict ourselves to the few most important limiting cases.

1. $k_1 \gg a$, $k_2 \gg b$, i.e., relaxation proceeds essentially slower than the chemical transformation. In this case the time dependence of the concentration has the form

$$\rho(t) \cong \rho_1(0)e^{-k_1 t} + \rho_2(0)e^{-k_2 t} \tag{7}$$

reflecting the case that within the time of the reagents transformation the matrix does not relax (is frozen) and the kinetics depends on the initial conditions. Equation 7 results from eq 4 at $N = 2$.

2. a, $b \gg k_1$, k_2, i.e., the rate of relaxation is high in comparison to the reaction rate. In this case the matrix instantly relaxes to the stationary distribution. Chemical transformations occur in the equilibrium matrix; kinetics is of a single-exponential character and does not depend on the initial conditions:

$$\rho(t) \cong \rho(0) \exp\left[-\left(k_1 \frac{b}{a+b} + k_2 \frac{a}{a+b}\right)t\right] \tag{8}$$

In obtaining the expression 8 it is taken into account that both exponents corresponding to chemical reactions in both states of the system have the same indices.

3. $k_2 \gg a$, $k_2 \ll b$, i.e., in the first state the chemical reaction rate essentially exceeds the rate of relaxation, and in the second state the situation is opposite. Then

$$\rho(t) \cong \left[\rho_1(0) - \rho_2(0)\frac{b}{k_1 - b}\right]e^{-k_1 t} + \rho_2(0)\frac{k_1}{k_1 - b} e^{-bt} \tag{9}$$

Here the reaction and the relaxation equally manifest themselves in the kinetics. At $k_1 \ll b$ the system passes quickly into the first state and reacts with the rate constant k_1. If $k_1 \gg b$, i.e., the reaction in the first state occurs faster than the transitions from the second state into the first one, then just these latter transitions limit the kinetics. This is a complete analogue of the situation when the kinetics is determined by matrix relaxation.

Thus, in all cases considered the dependencies 7–9 represent the sum of two exponents (two states) and, which is essential, without any qualitative peculiarities that would indicate the mechanism of the phenomena. Both the spread of the rate constants and the matrix relaxation lead to the same time dependencies of the reagents concentration on time. In the general case the time dependence of the reagents concentration (eq 3) is the sum N of damping exponents (N-states) with characteristic times τ_i. These parameters τ_i are the mixture of both partial rate constants k_i corresponding to different states of the matrix and the probability $w_{jj'}$ defining its relaxation.

II. For the model of diffusional motion of a system in a space of decomposition rate constants, for the simplest case of a continuous distribution of decomposition constants from k_1 to k_2 ($k_2 > k_1$) with a constant of the diffusion coefficient in this interval, we obtain the following equation for the system distribution density in the interval $\Delta = K_2 - K_1$:

$$\frac{\partial \rho(k,t)}{\partial t} = -k\rho + D\frac{\partial^2 \rho(k,t)}{\partial k^2} \tag{10}$$

$$\left.\frac{\partial \rho}{\partial k}\right|_{k=k_1} = \left.\frac{\partial \rho}{\partial k}\right|_{k=k_2} = 0 \qquad \rho(k,0) = \rho_0(k)$$

The analytical solution of eq 10, accessible for simple analysis, is difficult. As mentioned above, we do not study the actual connection between motion of reagents in real space and the motion system in the space of the reaction rate constants. But it is apparent that in every case it is necessary to find such a connection. In this case the coefficient of diffusion may depend on k, and this dependence can be very complex. The solution of the corresponding diffusion equation, which permits us to find the analytical dependence on parameters, may be obtained by the method of integral relationships. This method at first was used in boundary layer theory.[28,29] We shall demonstrate the method of solution of such a diffusion equation as an illustration of the process of diffusion with a constant diffusional coefficient (eq 10). For kinetic problems such as eq 10, this method gives good accuracy (on the order of a few percent). We will write $\rho(K, t)$ in the form of a polynomial in k:

$$\rho(k,t) = \sum_{S=0}^{n} a_S(t)k^S \tag{11}$$

By means of boundary conditions in eq 10, we establish relationships among the coefficients a_S and then substitute eq 11 into eq 10 and find equations for the first moments of the function ρ: $M_r = \int_{k1}^{k2} k^r \rho(k,t)\, dk$ (r varies from 0 to $n - 2$). Assuming that the distribution is uniform, $\rho_0(k) = 1/\Delta$, and using in eq 11 the minimal $n = 3$, we obtain for

$$\rho(t) = \left[5D + \frac{1}{2}\sqrt{\frac{1}{3}\Delta^6 + 100D^2}\right]\left[\frac{1}{3}\Delta^6 + 100D^2\right]^{-1/2}$$
$$\exp\left\{\left[-\frac{K_1 + K_2}{2} - \frac{5D}{\Delta^2} + \frac{1}{2\Delta^2}\left(\frac{1}{3}\Delta^6 + 100D^2\right)^{1/2}\right]t\right\} +$$
$$\left[\frac{1}{2}\sqrt{\frac{1}{3}\Delta^6 + 100D^2} - 5D\right]\left[\frac{1}{3}\Delta^6 + 100D^2\right]^{-1/2}\exp\left\{\left[-\right.\right.$$
$$\left.\left.\frac{k_1 + k_2}{2} - \frac{5D}{\Delta^2} - \frac{1}{2\Delta^2}\left(\frac{1}{3}\Delta^6 + 100D^2\right)^{1/2}\right]t\right\}$$

With $D = 0$ (absence of mixing), the limiting value of $\rho(t)$ from

$$\rho(t) = \exp\left(-\frac{k_1 + k_2}{2}t\right)\cosh\left(\frac{\Delta}{2\sqrt{3}}t\right) \tag{12}$$

is a poor approximation of the polychronic kinetic curve

$$\rho(t) = \frac{1}{\Delta}\int_{k1}^{k2} e^{-kt}\, dk = \frac{2}{\Delta t}\exp\left(-\frac{k_1 + k_2}{2}t\right)\sinh\left(\frac{\Delta t}{2}\right) \tag{13}$$

With $D \gg \Delta^3/20$, the kinetics of the system becomes exponential, with a mean decomposition rate constant $K = (K_1 + K_2)/2$.

III. Let us discuss the case where the reacting particle may jump in the different places in the glass structure with the same probability but where these places are characterized by different rate constants. For the model with strong mixing, we have the integro-differential equation

$$\lambda\frac{\partial \rho(k,t)}{\partial t} = -k\rho - \lambda\rho + \frac{\lambda}{\Delta}\int_{k1}^{k2}\rho(k,t)\, dk, \quad \rho(k,0) = \frac{1}{\Delta} \tag{14}$$

Here, λ is the mixing constant, i.e., the rate of departure from

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the state $\rho(K)$. For the Laplace transform $R(s)$ of the observed quantity $R(s) = \int_{k1}^{k2}\rho(k,t)\,dk$, one obtains

$$R(s) = \ln\frac{s + k_2 + \lambda}{s + k_1 + \lambda}\Big/\left[\Delta - \lambda \ln\frac{s + k_2 + \lambda}{s + k_1 + \lambda}\right] \quad (15)$$

whence

$$\rho(t) = (\Delta/\lambda)^2 \exp(\Delta/\lambda)\left[\exp\left(\frac{\Delta}{\lambda}\right) - 1\right]^{-2} \exp\left[\left(\frac{\Delta}{e^{\Delta/\lambda} - 1} - \right.\right.$$

$$\left.\left. k_1 - \lambda\right)t\right] + \exp[-(k_2 + \lambda)t]\int_0^1 \exp(z\Delta t)\left[\left(1 + \right.\right.$$

$$\left.\left.\frac{\lambda}{\Delta}\ln\frac{z}{1-z}\right)^2 + \frac{\pi^2\lambda^2}{\Delta^2}\right]^{-1} dz \quad (16)$$

At $\lambda = 0$ (absence of mixing), this equation is converted to eq 13, and at $\lambda \gg 0$, it is converted to $\rho(t) = \exp[-\{(K_1 + K_2)/2\}/t]$.

The rates of reaction and mixing are determined by entirely different physical factors. For example, monomolecular decomposition depends on intramolecular motion in the molecule, and mixing depends on the motion of the molecules as a whole. Therefore, in particular, the activation energies in the corresponding constants are entirely different.

If the activation energy of the constant λ is greater than the activation energy of decomposition, i.e., if $E_\lambda > E_K$, then, as the temperature increases, λ will rise more rapidly than k, and we should expect that the kinetics will approach an exponential form. With the reverse relationship of activation energies, $E_\lambda < E_K$, as the temperature is increased, the kinetics will become closer to nonexponential polychromaticity. Therefore, the temperature and the course of the kinetics curves can yield information on intermolecular motions in disordered solids.

Conclusion

The treatment presented allows us to describe the kinetics of chemical processes accounting for the dispersion of equilibrium distances and matrix relaxation. Earlier experiments were conducted on the kinetics of low-temperature solid-phase reactions of the methyl radicals with hydrogen-containing alcohol molecules.[6,30−32] The kinetics of these reactions was explained[33−35] by dispersion of equilibrium distances between reagents. Of course, in these low-temperature processes there is no motion in the space of rate constants. There is a large set of experimental works in which the nonstationarity of the kinetics of the ligand rebinding with heme iron of myoglobin was studied.[7,9,36,37] This process was interpreted in a set of theoretical papers (see, for example, refs 8 and 10). These kinetics may apparently be explained by motion in constant rate space with exponential dependence of a jump's probability on length. But this question demands separate consideration.

One has to emphasize that the regularity of kinetics of various solid-phase chemical conversions are determined not only by the nature of reactants but also by the conditions of the performance of the reaction. An important part is played by the temperature, pressure, and viscosity of the medium. In particular the reaction kinetics is quite different in crystalline and amorphous substances. Along with the peculiarities of reactions in amorphous phase described in this article there exist also various distinctions connected to the energy stored in the medium.[38]

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