Polychronous kinetics with nonstationary rate constants. Effect of a medium

V. I. Gol'danskii,[a] *M. A. Kozhushner,*[a]* *and L. I. Trakhtenberg*[b]

[a]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: 007 (095) 938 2156. E-mail: kozhush@center.chph.ras.ru
[b]*State Research Center of the Russian Federation, L. Ya. Karpov Institute of Physical Chemistry,*
10 ul. Vorontzovo Pole, 103064 Moscow, Russian Federation.
Fax: 007 (095) 975 2450

Characteristic features of the kinetics of solid-state cage reactions with distributed parameters of the relaxing matrix were considered. Depending on the ratio of the constants of the reaction rate and relaxation of environment, the kinetics of chemical conversions can be either exponential or nonexponential. Plausible reasons for the unsteady-state character of the kinetics of the processes of two types, *viz.*, the reactions of alkyl radicals in amorphous alcohol matrices and conversions in biological systems, were discussed. The main reason for the unsteady-state character of the reactions of the first type is a dispersion of the equilibrium distances between the reagents. Kinetics of the reactions of the second type, such as rebinding of the ligands in the heme-containing proteins (*e.g.*, in myoglobin), is determined by the distances in the pairs of reagents and the relaxation transitions.

Key words: biological systems, intermolecular vibrations, nonstationary kinetics, relaxation of matrix, tunneling of atom.

The kinetics of many solid-state chemical processes are inconsistent with conventional laws that the first- or second-order reactions obey. These include such radiochemical and photochemical processes as a stepwise recombination of radicals,[1,2] diffusion-controlled reactions,[3,4] the exothermic reactions of abstraction of the atoms from the molecules by radicals,[5,6] recombination of the ligands with the skeleton and relaxation of heme-containing proteins,[7—10] as well as electron transfer.[11,12] Certain stages of the processes mentioned above can be identical. Thus, for instance, diffusion of free valences is one of the stages of the stepwise recombination of radicals, while a diffusion-controlled reaction involves a chemical act, *etc.* Because of the multistage character of the complex reaction, the limiting stage responsible for the unsteady-state character of the kinetics (*i.e.*, for the change in the rate constants with time) can hardly be distinguished. We restrict our attention to consideration of only one class of processes, the cage reactions with the atom transfer, in which only one stage plays a determining role.

The kinetic curves of the hydrogen atom transfer from matrix molecules to a radical were found to differ from conventional kinetic curves.[13,14] This was explained by diffusion of radicals and superposition of the first- and second-order processes. In Ref. 15, an assumption was made on the basis of analysis of experimental data[16—18] that values of the rate constant in such processes can be dispersed due to various configurations in the pairs of reagents.*

Nonstationary kinetics also were observed in studies of the low-temperature limit of the rate of the reactions of abstraction of the hydrogen atom in the methanol and ethanol matrices,[21,22] where the nonexponential character of kinetics was explained by inhomogeneity of the matrix. To calculate the rate constant, the initial segment of the kinetic curve was used under the assumption that the kinetics of the reaction can be described by the first-order law.

The kinetics of the reactions with the intermolecular transfer of the hydrogen atom were studied in most detail in Refs. 23—26. The kinetic curves of chemical reactions in solid matrices were shown[6,25—27] to be of the form:

$$C(t) = C(0)\exp[-At^{\beta(T)}],\ 0 < \beta \leq 1, \tag{1}$$

where $C(t)$ is the concentration of chemically active species at time t. The values of parameters β and A are determined by the matrix properties and temperature.

In particular, the dependence of the concentration of alkyl radicals on time in glassy alcohol matrices[6,25—27] is

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* The role of the energetic and spatial inhomogeneity resulting in a dispersion of the rates of different processes was discussed in Refs. 19 and 20.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 469—476, March, 1997.

also well described by formula (1). The β values for the reactions of methyl radicals with methanol vary within the limits from $\beta \cong 0.32$ (at 30 K) to $\beta = 0.8$ (at 105 K). According to the data from Refs. 23 and 24, β is equal to 0.5 in the temperature range from 77 to 87 K.

A similar dependence was found [28] when studying the reaction of abstraction of the hydrogen atom from the methanol molecules by the methyl radical in an amorphous methanol matrix at 77 K. The dependence of the concentration of methyl radicals on time was found to be mainly determined by the time of accumulation of the radicals. In the case of short accumulation times this dependence is well described by the formula (1) with $\beta = 0.5$. If the accumulation time increases by three orders of magnitude, one should introduce a preexponential multiplier $ct^{1/2} + 1$ (c is a constant) into formula (1) to describe the experimental dependence of the concentration of the radicals on time:

$$C(t) = C(0)(ct^{1/2} + 1)\exp(-ct^{1/2}). \qquad (2)$$

The temperature dependence of parameter β was also studied in Ref. 29 using the reaction of ethyl radicals with triethylamine in the temperature range from 77 to 107 K as an example. The parameter β was changed in this case from 0.5 to 0.75, respectively.

The kinetics of intramolecular processes usually are exponential. However, the kinetics of the reaction of transfer of the hydrogen atom within the 2-(2'-hydroxyphenyl)benzoxazole molecule (HBO) in solid solutions were found[30] to be nonexponential. This can be explained by the effect of the environment on the potential barrier to the reaction. In addition, a conformational rearrangement of the molecules occurs in the course of chemical reaction, which also requires a reorganization of the environment. Because of the inhomogeneity of the matrix, the energy of reorganization varies from one molecule to another. This can be a reason for the unsteady-state character of the process.

The polychronous kinetics also are observed in processes with the transfer of heavier particles. Rebinding of the ligands with the iron atom of the heme group of myoglobin is such a reaction.[7,8] This bond breaks under the action of a microsecond laser pulse, after which rebinding occurs. The process under study likely consists in the iron atom regaining its original position in the plane of the heme group of myoglobin. These investigations were carried out in a wide temperature range (from 2 to 320 K). The polychronous kinetics typical of low-temperature reactions in glasses were observed below 200 K.

The decay of the 1,3-cyclopentadiyl biradical in the cyclohexane matrix[31] is one more example of reactions with nonexponential kinetics. It is believed that here the reason for deviations of kinetic curves from the exponential ones, characteristic of the first-order reactions, lies in the effect of the environment on the probability of the elementary act, as well as in the process studied in Ref. 30.

Theoretical considerations of the effect of dispersion and the change in the rate constant on the kinetics of chemical reactions in the solid state were carried out in Refs. 32 and 33. In the present work, plausible reasons for the polychronous character of kinetics of the processes discussed above and the published experimental data were analyzed.

Polychronous chemical reactions with mixing over the rate constants

The need to use distributed kinetic parameters instead of their unique effective values commonly used is associated with dispersion in the properties of a medium in which the reagents are (for instance, in the energetic depth of the traps in which positively charged ions and recombining electrons are trapped, and in the distances between these traps).

In contrast to the usual monomolecular decay obeying the exponential law $N = N_0\exp(-kt)$ (k is the rate constant), the nonexponential kinetics are characteristic of polychronous reactions: particles that are in more shallow traps with larger k values react first, followed by those in deeper traps with smaller k values, and linear dependences of N (or $\ln N$) on $\ln t$ arise instead of a linear dependence of $\ln N$ on time t.

The internal motion corresponding to continuous transformation of the traps of one type into those of the other types (*i.e.*, mixing over the rate constants) occurs in the medium. With relatively fast mixing (as compared to the consumption rate of the reagents), distributed kinetic parameters (polychronous character of the kinetics), as such, will no more result in the nonexponential dependence.

Let us consider in a general way the kinetics of the reactions with mixing exemplified by a monomolecular reaction. As a rule, the polychronous kinetics are characteristic of bimolecular reactions. However, if the concentration of one reagent is much higher than that of another, the bimolecular reactions are known to be reduced to the monomolecular ones. Let us assume, for instance, that we deal with a capture of an active center located in the trap by an acceptor that is in large excess over the entire sample; then the polychronous character of the kinetics will be determined by the dispersion in the values of the activation energy of leaving the trap.

In the present work, a chemical reaction and a relaxation of the matrix are considered as simultaneous processes "equal in rights". In this connection, the character of relaxation of the matrix and its control parameters can be functions of the local concentration of the reaction products or, in the general case, of the proceeding chemical reaction. However, hereafter, we shall not consider such a nonlinear problem, assuming that the concentration of at least one of the reagents is low.

Let us ascribe index $j = 1, 2, \ldots, N$ to the local states of the reagents and the matrix. The dependence of the concentration of the subsystems in the $j(C_j(t))$th state on time is defined by the following equation

$$\frac{dC_j(t)}{dt} = -\sum_{j' \neq j} w_{jj'} C_j(t) + \sum_{j' \neq j} w_{j'j} C_{j'}(t) - k_j C_j(t) = \\ = -\sum_{j'=1}^{N} T_{jj'} C_{j'}(t). \tag{3}$$

Here $w_{jj'}$ is the probability of transition of the subsystem from the jth state to the j'th state referred to the time unit, k_j is the rate constant of the chemical reaction in the subsystem in the jth state. Two first terms describe relaxation of the matrix, whereas the last term describes chemical conversion of the reagents into the reaction products.

Summing equations (3) over all j states, we get an equation defining the dependence of the local concentration of the reagents on time

$$\frac{dC(t)}{dt} = -\sum_{j=1}^{N} k_j C_j(t), \quad C(t) = \sum_{j=1}^{N} C_j(t) \cdot \tag{4}$$

It follows herefrom that the dependence of the overall rate constant on time is defined by the following relation:

$$k(t) = -\frac{1}{C(t)} \cdot \frac{dC(t)}{dt} = \frac{1}{C(t)} \sum_{j=1}^{N} k_j C_j(t). \tag{5}$$

Rate constant k can be independent of time if all partial rate constants k_j are equal or if relaxation of the matrix is much faster than chemical conversion. In the first case, $K = k_j = \text{const}$. In the second case, the quasistationary concentrations are rapidly reached

$$C_j(t) = p(j)C(t),$$

where $p(j) = C_j(t)/C(t)$ is the time-independent fraction of the subsystems in the jth state. The quantities $p(j)$ are found from the system of equations

$$p(j) \sum_{j' \neq j} w_{jj'} = \sum_{j' \neq j} w_{j'j} p(j'), \quad \sum_{j=1}^{N} p(j) = 1. \tag{6}$$

Then the expression for the rate constant takes the form

$$k = \sum_{j=1}^{N} k_j p(j). \tag{7}$$

Since Eq. (3) is linear, its general solution is described by expression

$$C_j(t) = \sum_{i,j'} S_{ij} e^{-\frac{t}{\tau_i}} (S^{-1})_{ij'} C_{j'}(0). \tag{8}$$

Here S_{ij} is a matrix diagonalizing the T_{ij} matrix with eigenvalues of $1/\tau_i$ introduced in Eq. (3), *i.e.*,

$$(S^{-1}TS)_{ij} = \frac{1}{\tau_i} \delta_{ij}. \tag{9}$$

Summing up partial concentrations (8), we find the dependence of the concentration of reagents on time:

$$C(t) = \sum_{i=1}^{N} \left[\sum_{j=1}^{N} (S^{-1})_{ij} C_j(0) \right] \left[\sum_{j=1}^{N} S_{ji} \right] e^{-\frac{t}{\tau_i}}. \tag{10}$$

This expression can be written as follows

$$C(t) = C(0) \int_0^{\infty} g(k) e^{-kt} dk \cdot$$

$$g(k) = \frac{1}{C(0)} \sum_{i=1}^{N} \left[\sum_{j=1}^{N} (S^{-1})_{ij} C_j(0) \right] \left[\sum_{j=1}^{N} S_{ji} \right] \delta\left(k - \frac{1}{\tau_i}\right). \tag{11}$$

It should be emphasized that the time constants τ_i characterize simultaneously occurring relaxation of the matrix and reaction (3) under study. The values $1/\tau_i$ and k_i are equal only if one can neglect relaxation of the matrix, *i.e.*, if $w_{jj'} = w_{j'j} = 0$. In this case

$$C(t) = \sum_{j=1}^{N} C_j(0) e^{-k_j t}. \tag{12}$$

Note that according to expression (10), the kinetics, in general, depend on the initial distribution $C_j(0)$. This dependence disappears in the case of fast relaxation of the matrix, when the kinetics are one-exponential with the rate constant defined by formula (7).

Relationships between the rates of relaxation of the matrix and chemical conversion as such can be different under experimental conditions. Determination of only $C(t)$ dependence gives no way of drawing an unambiguous conclusion as to which processes determine the observed kinetics. To elucidate this problem, additional special-purpose experiments are needed.

Let us consider several special cases of kinetics in the space of k constants:

I. A spontaneous transition between two states characterized by constants k_1 and k_2.

II. A diffusion motion in the space of rate constants k within the limits from k_1 to k_2.

III. An equiprobable jump from any state characterized by the rate constant k to any other possible state of the system, $k_1 < k < k_2$ (strong mixing).

I. *For a model of a spontaneous transition between two states characterized by the rate constants* k_1 and k_2, kinetic equations take the form

$$d\rho_1/dt = -\lambda(\rho_1 - \rho_2) - k_1\rho_1,$$

$$d\rho_2/dt = -\lambda(\rho_2 - \rho_1) - k_2\rho_2. \tag{13}$$

Here $\rho_{1,2}$ are populations of the pertinent states; k_1 and k_2 are the rate constants for decay; λ is the mixing constant, $\lambda = \tau^{-1}$, where τ is the lifetime in states 1 or 2 (for simplicity they are considered to be equal). The observed quantity is $\rho(t) = \rho_1(t) + \rho_2(t)$. Assuming that at initial time $\rho_1(0) = \rho_2(0) = 1/2(\rho(0) = 1)$, we get

$$\rho(t) = \frac{1}{2}r^2(\lambda^2 + r^2)^{-1/2}(\mathrm{A} + \mathrm{B}) ,$$

$$\mathrm{A} = \left(\sqrt{\lambda^2 + r^2} - \lambda\right)^{-1} \exp\left[-\left(k + \lambda - \sqrt{\lambda^2 + r^2}\right)t\right] ,$$

$$\mathrm{B} = \left(\sqrt{\lambda^2 + r^2} + \lambda\right)^{-1} \exp\left[-\left(k + \lambda + \sqrt{\lambda^2 + r^2}\right)t\right] , \qquad (14)$$

where $r = 1/2 \cdot (k_2 - k_1)$, $k = 1/2 \cdot (k_1 + k_2)$.

It can easily be seen that at $\lambda >> r$ the decay becomes monochronous with the rate constant $k = (k_1 + k_2)/2$.

More general is the case where the probabilities of transitions 1→2 and 2→1 are not equal. The probability of transition 1→2 and that of transition 2→1 referred to the time unit are denoted a and b, respectively. Here we present no general solution of the problem, but restrict our attention to discussing the most interesting special limiting cases.

1. $k_1 >> a$, $k_2 >> b$, *i.e.*, relaxation is much slower than chemical conversion, and no relaxation of the matrix occurs (it is frozen) during the time of conversion of the reagent. In this case, the dependence of the concentration on time takes the form

$$\rho(t) \cong \rho_1(0)e^{-k_1 t} + \rho_2(0)e^{-k_2 t} . \qquad (15)$$

and the kinetics is dependent on the initial conditions. Formula (15) follows from expression (12) at $N = 2$.

2. a, $b >> k_1$, k_2, *i.e.*, the relaxation rate is high as compared to the reaction rate. In this case, instant relaxation of the matrix to the stationary distribution state occurs. Chemical conversions proceed in the equilibrium matrix, and the kinetic dependence is one-exponential and independent of initial conditions:

$$\rho(t) \cong \rho(0)\exp\left[-\left(k_1\frac{b}{a + b} + k_2\frac{a}{a + b}\right)t\right] . \qquad (16)$$

This formula is obtained after substituting $\rho(1)$ and $p(2)$ from system (6) into expression (7) for the rate constant.

3. $k_1 >> a$, $k_2 << b$, *i.e.*, the rate of chemical reaction in the first state is much higher than the relaxation rate, whereas the inverse relation is observed in the second state. Then

$$\rho(t) \cong \left[\rho_1(0) - \rho_2(0)\frac{b}{k_1 - b}\right]e^{-k_1 t} + \rho_2(0)\frac{k_1}{k_1 - b}e^{-bt} . \qquad (17)$$

Here the kinetics are simultaneously affected by both reaction and relaxation. At $k_1 << b$ the system rapidly transforms into the first state and reacts with the rate constant k_1. If $k_1 >> b$, *i.e.*, if the reaction in the first state proceeds faster than transitions from the second state to the first one, it is just the transitions that limit the kinetics. This is a complete analog of the situation in which the kinetics are determined mainly by relaxation of the matrix.

Thus, in all cases considered dependences (15)—(17) are the sums of two exponents* (two states). It is essential that there are no qualitative features, which might point to the mechanism of the phenomenon. Both the dispersion of the rate constants and the relaxation of the matrix result in the same dependences of the concentration of reagents on time. In the general case, the dependence of concentration on time (10) is the sum of N fading exponents (N states) with time constants τ_i. The latter depend on both partial rate constants k_i corresponding to different states of the matrix and probabilities w_{ij} determining its relaxation.

II. *For a model of the diffusion motion of the system in the space of the rate constants for decay*, in the simplest case of a continuous distribution of the rate constants for decay from k_1 to k_2 ($k_2 > k_1$) at a constant coefficient of diffusion in this range, we get an equation for the density of distribution of the system in the interval $\Delta = k_2 - k_1$:

$$\frac{\partial\rho(k,t)}{\partial t} = -k\rho + D\frac{\partial^2\rho(k,t)}{\partial k^2} , \qquad (18)$$

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

Analytical solution of Eq. (18) accessible to a simple analysis is difficult. Therefore, let us use the method of integral relations, which was first applied to the theory of the boundary layer.[34,35] In the case of kinetic problems similar to (18), this method gives good accuracy (about several per cent). Let us write $\rho(k,t)$ as a polynomial of degrees in k:

$$\rho(k,t) = \sum_{S=0}^{n} a_s(t)k^s . \qquad (19)$$

where n determines the accuracy of calculations.

Using boundary conditions of Eq. (18), a relation between coefficients a_s is established; then substituting (19) into (18) we find equations for the first "moments of the function" ρ: $M_r = \int_{k_1}^{k_2} k^r\rho(k,t)\mathrm{d}k$ (r varies from 0 to $n - 2$). Assuming that the initial distribution is uniform, $\rho_0(k) = 1/\Delta$, and using the minimal $n = 3$ in (19), we obtain for $\rho(t) = \int_{k_1}^{k_2} \rho(k,t)\mathrm{d}k$:

$$\rho(t) = \mathrm{FG} + \mathrm{HJ},$$

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* The fact that both exponential functions corresponding to the chemical reactions in both states of the system have equal exponents was taken into account in deriving expression (16).

$$\mathrm{F} = \left(5D + \frac{1}{2}\sqrt{\frac{1}{3}\Delta^6 + 100D^2}\right)\cdot\left(\frac{1}{3}\Delta^6 + 100D^2\right)^{-1/2},$$

$$\mathrm{G} = \exp\left\{\left[-\frac{k_1 + k_2}{2} - \frac{5D}{\Delta^2} + \frac{1}{2\Delta^2}\left(\frac{1}{3}\Delta^6 + 100D^2\right)^{1/2}\right]t\right\},$$

$$\mathrm{H} = \left(\frac{1}{2}\sqrt{\frac{1}{3}\Delta^6 + 100D^2} - 5D\right)\cdot\left(\frac{1}{3}\Delta^6 + 100D^2\right)^{-1/2},$$

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

At $D = 0$ (no mixing), the limiting value of $\rho(t)$ takes the form

$$\rho(t) = \exp\left(-\frac{k_1 + k_2}{2}t\right)\cosh\left(\frac{\Delta}{2\sqrt{3}}t\right) \tag{20}$$

and is a fairly good approximation of a polychronous kinetic curve

$$\rho(t) = \frac{1}{\Delta}\int_{k_1}^{k_2} e^{-kt}\mathrm{d}k = \frac{2}{\Delta t}\exp\left(-\frac{k_1 + k_2}{2}t\right)\sinh\left(\frac{\Delta t}{2}\right). \tag{21}$$

At $D >> \Delta^3/20$, the kinetics of the system becomes exponential with the average rate constant for decay $k = (k_1 + k_2)/2$.

III. *For a model with strong mixing*, we have

$$\frac{\partial\rho(k,t)}{\partial t} = -k\rho - \lambda\rho + \frac{\lambda}{\Delta}\int_{k_1}^{k_2}\rho(k,t)\mathrm{d}k, \quad \rho(k,0) = \frac{1}{\Delta}. \tag{22}$$

Here λ is the mixing constant (rate of leaving a $\rho(k)$ state). For the Laplacian transform $R(s)$ of the observed quantity $\rho(t) = \int_{k_1}^{k_2}\rho(k,t)\mathrm{d}k$, we get

$$R(s) = \ln\frac{s + k_2 + \lambda}{s + k_1 + \lambda}\bigg/\left(\Delta - \lambda\ln\frac{s + k_2 + \lambda}{s + k_1 + \lambda}\right), \tag{23}$$

whence

$$\rho(t) = \left(\frac{\Delta}{\lambda}\right)^2\exp\left(\frac{\Delta}{\lambda}\right)\left[\exp\left(\frac{\Delta}{\lambda}\right) - 1\right]^{-2}\cdot\mathrm{Q} + \mathrm{V}\cdot\mathrm{I},$$

$$\mathrm{Q} = \exp\left[\left(\frac{\Delta}{e^{\Delta/\lambda} - 1} - k_1 - \lambda\right)t\right],$$

$$\mathrm{V} = \exp\left[-(k_2 + \lambda)t\right],$$

$$\mathrm{I} = \int_0^1 \exp(z\Delta t)\left[\left(1 - \frac{\lambda}{\Delta}\ln\frac{z}{1 - z}\right)^2 + \frac{\pi^2\lambda^2}{\Delta^2}\right]^{-1}\mathrm{d}z. \tag{24}$$

At $\lambda = 0$ (no mixing), this expression goes into (20); at $\lambda >> 0$

$$\rho(t) = \exp\left(-\frac{k_1 + k_2}{2}t\right).$$

The rates of reaction and mixing have quite different physical natures. Thus, the monomolecular decay depends on intramolecular motions in the molecule, while mixing depends on the motion of the molecule as a whole. Therefore, in particular, the activation energies in the corresponding constants k and λ are quite different. If the energies of activation of the rate of mixing $E_\lambda > E_k$ (E_k is the activation energy for decay), then λ increases faster than k as temperature increases, and one should expect that in this case the kinetics will approach the exponential one. In the case of an inverse relation between the activation energies ($E_\lambda < E_k$), the kinetics will approach the polychronous one with increasing temperature. Therefore, the dependences of the kinetic curves on temperature and time can provide information about the intermolecular motions in the disordered solids.

The effect of matrix inhomogeneity on the kinetics of reactions with the transfer of hydrogen atoms

The kinetics of the solid-state radical reactions in organic matrices were studied in a series of experimental works.[23–26] To explain the regularities of these reactions, a model was proposed[36–38] on the basis of the following assumptions: a) low-temperature chemical reactions with the transfer of the hydrogen atom proceed *via* a tunneling mechanism; b) the main reason for the polychronous character of the kinetics of the reaction of abstraction of the hydrogen atom from the molecule by radicals is dispersion of equilibrium distances between the reagents; c) distances between the reagents in the cage are uncorrelated; and d) the value of the dispersion of equilibrium distances depends on temperature. Specific features of the kinetics of the solid-state reactions of free radicals (CH_3, C_2H_5, and C_4H_9) in the alcohol matrices were explained on the basis of this model.

First of all, the kinetics of the following reaction was explained

$$CH_3OD + {}^{\cdot}CH_3 \rightarrow {}^{\cdot}CH_2OD + CH_4. \tag{25}$$

It was shown[36] that the spatial inhomogeneity of the matrix can result in the nonstationary kinetics of the solid-state cage reactions. The exponential dependence of the rate constant of the tunneling reaction on the intermolecular distance was also taken into account. Thus, the constant of the transition rate increases by an order of magnitude as the distance between reagents decreases by 0.03—0.04 Å.[39] Averaging over the equilibrium intermolecular distances results in kinetics of the reactions between radicals and the molecules of the medium, that deviate from the first-order law. The dependence of the concentration of initial radicals on time at 77 K is well described by Eq. (1) with $\beta = 0.5$ as the extent of conversion varies within the limits of two orders of magnitude.

The kinetics of reactions of methyl radicals in the mixtures of deuterated and nondeuterated alcohols at the temperature of liquid nitrogen were explained in Ref. 36. In these mixtures, the derivative of concentration of methyl radicals with respect to $\sqrt{t}$ depends linearly on the relative fraction of nondeuterated molecules in the matrix.[23,24] Such a dependence can be obtained if the distances between the methyl radicals and molecules in the cage are considered to be uncorrelated. In this case, they can be treated as independent random variables identically distributed over different cages.

A comparison between the experimental data[23,24] and the theory was performed for the radical reactions in the alcohol matrices (C_2H_5OD and C_2D_5OD) in Ref. 37. The reactions with free radicals of three types, CH_3, C_2H_5, and C_4H_9, were studied. The calculations showed that the growth of the radical is accompanied by an appreciable decrease in the number of molecules in the cage instead of an increase. The reason is that in the course of the "search" for the partner, the radicals can leave the initial cage. At the same time, the mobility of the radical decreases as it grows. This results in a decrease in the "cage size".

The temperature dependence of the kinetics of the solid-state radical reactions proceeding analogously to reaction (25) is well described by relation (1). The parameter β is nearly independent of temperature at $T < 50$ K, and its value linearly increases at higher temperatures from 0.35 at 60 K to 0.8 at $T = 105$ K.[25,26] This can be explained assuming that dispersion of the equilibrium distances between the reagents decreases as temperature increases, since increasing temperature removes spatial limitations in the mutual positions of the molecules.[29,38] Hence, the kinetics of the process will become unhampered, which must result in an increase in the parameter β with increasing temperature. At the limit, the value of this parameter must approach unity.

The validity of this mechanism follows from a simple polychronous model. The kinetics of the reaction will be considered to be characterized by two parameters, the minimum ($k_{\min}$) and the maximum ($k_{\max}$) values of the rate constant. In the case of tunneling, the rate constant depends exponentially on the length of tunneling (l), $k \sim \exp(-\alpha l)$. Then, if the lengths of tunneling (distances between the reagents) are distributed uniformly in the range $l_1 < l < l_2$, we get a uniform distribution of $\ln k$ in the region $k_1 > k > k_2$. According to formula (11), the dependence of the concentration of radicals on time in the framework of this model takes the following form:[29,38]

$$C(t)/C(0) = (\delta \ln \bar{k})^{-1} \int_{k_{\min}}^{k_{\max}} (k)^{-1} \exp(-kt)\mathrm{d}k =$$

$$= \delta(\ln \bar{k})^{-1}\left[Ei(k_{\min}t) - Ei(k_{\max}t)\right], \qquad (26)$$

$$\delta \ln \bar{k} = \ln(k_{\max}/k_{\min}), \quad Ei(x) = \int_x^{\infty} s^{-1} \exp(-s)\mathrm{d}s .$$

Here $Ei(x)$ is the integral exponential function. The dependence of the rate constant of chemical reaction on temperature and the role of intermolecular vibrations that result in the encounter of reagents and thus in a decrease in the potential barrier[40—43] were taken into account in deriving Eq. (26). As a result, the probability of tunneling of an atom increases as temperature increases.

A comparison of the results of the calculation carried out by formula (26) and experimental data[25,26] for the reaction of alkyl radicals with alcohols made it possible to draw the following conclusions: a) the dependence of the concentration of radicals on time and on temperature is well described by Eq. (1); b) the width of distribution of the distances between the reagents becomes more narrow as temperature increases; and c) the center of gravity of distribution of the distances shifts toward shorter distances (*i.e.*, to higher reaction rates) as temperature increases. It follows from the data of Ref. 38 that the results of the experiments are in line with both expressions, (1) and (26). It is obvious that the decrease in the concentration of methyl radicals corresponds to a functional dependence, which decreases more slowly than the exponential one. A logarithmic dependence offers an example of such a dependence.

The dependence of the concentration of radicals on time (see Refs. 23 and 24) differs from that predicted by formula (1) at short accumulation times. To explain this, a function of distribution of the reagents over the rate constants is introduced in Ref. 28. The shape of this distribution depends on the time required for accumulation of the initial concentration of radicals. Averaging time over the short and long accumulation time (<10 s and >10^4 s, respectively) gives formulas (1) (with $\beta = 0.5$) and (2), respectively.

Mechanisms of polychronous kinetics of reactions in myoglobin

Studies of the kinetics of rebinding ligands with the iron atom of heme began in Ref. 7. On the basis of numerous subsequent experiments a model was designed, the basic principles of which are outlined in review.[8] According to this model, the rate constant for rebinding of the ligand to the iron atom depends on the mutual positions of reagents. In this case, there are three groups of conformational substates separated by high barriers. It appeared to be possible to perform the studies of the kinetics of the Fe—ligand rebinding separately for each group. It was found that not only the overall dependence of the concentration of separated pairs on time is nonexponential. In each group, the process of rebinding proceeds at its own rate and has an unsteady-state character. It is essential for this model that each conformational substate splits into a number of new substates separated by lower barriers, and the system moves over all these conformational substates thanks to the relaxation transitions.

Later on, the dependence of the shape of absorption band of the porphyrine molecule on the degree of the influence of the environment was used in designing a more detailed picture.[9,10,44] This influence is mainly determined by the geometry of the environment. The dependence of the shift of the optical absorption band of porphyrine for each of three groups of conformational substates on the rate of the transitions between different conformational substates of the protein was taken into account. The observed inhomogeneous broadening of the absorption band is caused by the interaction of the porphyrine molecule with protein environment and dispersion of the parameters of conformational transitions of protein in the vicinity of the porphyrine molecule. The conformational transitions result in a spectral diffusion in the inhomogeneously broadened absorption band of porphyrine.

The studies of spectral diffusion at the temperatures lower than 8.1 K showed[9,44] that the change in the width of the absorption line logarithmically depends on time. This is associated with the specific character of conformational transitions in protein*. The mechanism of transitions is unclear. In the case of conventional diffusion, the increase in the resonance frequency of the absorption band would be proportional to $\sqrt{t}$. It should likely be assumed that this is a one-jump relaxation of the matrix, and the energy of activation of this process should be related to the length of the jump (which apparently varies in parallel with the length of the "spectral jump"), *i.e.*, with the change in the resonance absorption frequency.

It is essential that the energy of activation of the jump is approximately proportional to the value of the "spectral jump." This means that the probability of the transition decreases exponentially as the length of the jump decreases. It is easy to show that the averaging of this probability (an exponent with a time-dependent rate constant) can result in the experimentally observed logarithmic dependence.

Thus, the results of Refs. 9 and 44 bring out clearly that the unsteady-state character of the kinetics of rebinding of the ligand is due to two reasons, *viz.*, a different configuration of the iron atom—ligand pair and relaxation of the matrix. It is just such an approach based on these mechanisms that was suggested previously.[32,33]

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The regularities of the kinetics of various solid-state chemical conversions are determined not only by the nature of the reagents, but also by the conditions under which the reaction proceeds. Temperature, pressure, and viscosity of the medium play an important role. In particular, the kinetics of reaction appreciably differ for crystalline and amorphous substances.

In the present work, we describe specific features of the reactions in amorphous phase caused by a dispersion in the values of parameters of the potential barrier, which the particle needs to overcome in the course of the chemical reaction, and those of the relaxation processes in the medium. Along with them, there are a number of distinctions associated, for instance, with the energy stored in the medium.[46] Thus, rebinding CO in a heme-containing protein has been considered in the framework of the model with a variable rate constant.[47]

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* The effect of temperature on the kinetics of the reactions in protein is likely due to the changes in the viscosity of the medium. Thus, it was shown in Ref. 45 that the kinetics of rebinding the ligands in myoglobin holds its nonexponential character as the viscosity of the medium increases even at room temperature.

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Received August 23, 1996